"STOPPED-FLOW STUDIES OF REACTIONS OF CHROMIUM(VI) AND IRON(III)"

by

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TABLE OF CONTENTS

SUMMARY

Stopped-flow devices have been constructed and are described. Using this technique reactions of iron(III) and chromium(VI) with organic substrates in aqueous perchlorate media have been investigated.

Iron(III) has been found to react in the form of $Fe^{3+}(aq)$ and $FeOH^{2+}(aq)$ with both salicylaldehyde and salicylamide. The results obtained in this study not only confirm that $Fe(H_2O)_5OH^{2+}$ reacts by an I_d mechanism but also indicate that a similar mechanism operates in the case of $Fe(H_2O)_6^{3+}$. This latter finding is of some particular interest in view of the current controversy regarding the mode of anation of this latter ion.

$HCrO_4^-$ has been found to oxidise L-cysteine via the formation of intermediate sulphur-bonded esters which have been identified spectrophotometrically. The rate constant for the acid-catalysed formation pathway has been found to be markedly smaller than has been measured previously for other ligands with this metal-ion. The significance of this phenomenon is discussed, as also is the interpretation of the second-order substrate dependence of the redox rate.

Chromate(VI) esters have also been shown to form in the course of the reduction of $HCrO_4^-$ by both malic and thiomalic acids. Absorbance-time profiles have been simulated in order to aid the analysis of the kinetics of this latter reaction.

As has been found for other metal-ions, the most significant common factor in the reactions of these two substrates with chromium(VI) is the participation of intermediate complexes. The influence of the disimilar chemical natures of oxygen and sulphur is discussed with particular reference to the relative kinetic complexities of these systems.

GENERAL INTRODUCTION

Fast Reaction Techniques

During the last decade, fast reaction techniques for the study of chemical reaction mechanisms have passed from the stage of being research subjects in themselves to that of being almost routine research tools. In that period have been published some monographs,[1-4] a number of reviews,[5-8] and the proceedings of several symposia,[9-11] all devoted exclusively to the latest developments in this area of chemistry.

The problems associated with the study of fast chemical reactions are twofold. The first is the requirement of rapid initiation of reaction; the other is that of detecting the processes occurring during the course of reaction. It is obvious that to overcome the first difficulty the reactants must be brought together as quickly as possible. This has led to the development of what are termed "rapid flow" methods.

As far as is known, Ernest Rutherford, in a study in 1897 of the lifetime of an excited state of a gas was the first person to use a flow apparatus[12] to measure a phenomenon occurring in less than one second. No mixing, however, was involved in this work. Hartridge and Roughton were the first scientists to apply this principle to the study of chemical reactions in solution.[13] They introduced the continuous-flow method, in which the two reagent solutions flow towards a junction from which the mixed solution emerges to pass along an observation tube at a constant velocity (u). The distance along this tube from the mixing chamber (d) can be easily converted to a time-scale for the reaction i.e. $t = \frac{d}{u}$.

For monitoring very fast reactions, especially those with half-lives less than 10 milliseconds, a T-junction mixer is inadequate and for this reason Hartridge and Roughton introduced their multiple-jet mixer in 1923.[13] The various mixer designs in use today are all variations of the basic concept which they pioneered.

The reliability of the continuous-flow method depends not only on fast efficient mixing, but also on the existence of a uniform composition of solution at any cross-section of the observation-tube. This in theory necessitates the maintenance of mass flow of the mixed solution. Retardation of liquid at the walls of the tube makes it impossible for mass flow to be obtained but turbulent flow, as opposed to laminar stream-line flow, has been experimentally shown to be a statisfactory approximation. An additional advantage of turbulence is that the eddying which accompanies it leads to more thorough mixing of the solution. Flow of a liquid in a tube becomes turbulent if its associated Reynolds number is sufficiently high.[14] This number is given by the following relationship,

$$R = \frac{uD\rho}{\eta} \qquad (1)$$

where u is the flow velocity (cm/sec), D is the diameter of the tube (cm), ρ is the density of the liquid (g/ml) and η is the viscosity of the liquid (poise). For fairly short tubes with a streamline entry R is about 2000.[15] This gives a value of 2 metres/second as the critical velocity, u_c, for the achievement of turbulent flow by water at 20^o in a tube of 1 mm. diameter. This flow velocity is in practice achieved quite readily. In a rapid flow apparatus the mixing process imparts a violent motion to the solution as it enters the observation tube and consequently the critical velocity will be somewhat less than this.[15] As a consequence of the existence of a necessary minimum operating solution velocity, the maximum half-life measurable by a continuous-flow apparatus is limited mainly by what is the maximum practical length of the observation tube. Thus it is rare for this method to be used for the measurement of half-lives greater than one second. The lowest half-life measurable by a continuous-flow apparatus is approximately 0.5 milliseconds.[16] This limitation is imposed by the difficulty of achieving complete mixing of reagent solutions in less than that time without employing fluid velocities requiring prohibitively high drive system pressures.

In view of the fact that before 1922 the smallest half-life measurable by the currently available conventional techniques was of the order of 10 seconds, the introduction of rapid-flow methods nevertheless constituted a major breakthrough in the study of chemical kinetics in solution. Although historically the first of the flow methods, continuous flow has not been bettered in its lower limit in timescale of detection by any other flow methods since introduced. It has, however, largely been supplanted for most purposes by more sophisticated developments of this technique mainly as a result of their greater economy of materials, an extremely important factor particularly in the study of enzyme kinetics.

These other variations are the accelerated-flow and stopped-flow techniques. The first of these is a straightforward alternative to the continuous-flow method in that whereas the latter entails measurements at various points along the observation tube while employing a constant velocity of solution, in the accelerated-flow technique there is during a single push continuous variation of the velocity of solution flowing past one fixed observation point. This method is capable of measuring half-lives down to the order of 0.3 milliseconds.[17(a)]

The stopped-flow method is, in concept, simpler than either of the rapid-flow methods so far discussed since the rapid flow serves only to bring the mixture of reagents to the observation point as quickly as possible. The flow of solution is rapidly stopped to enable almost the entire course of reaction to be monitored at one point. The first recorded instance of the use of the stopped-flow principle is that by

Stewart and Edlund[18] in 1922 in their study of the gas phase reaction of ethylene with bromine. There is, in theory, no upper limit to the half-lives it can be used to measure and its lower limit is of the same order of magnitude as those of the two other methods discussed above.[19] This technique is sufficiently similar to accelerated flow that a stopped-flow apparatus can fairly readily be converted to operate in the latter mode.[17] The apparatus, however, then requires much more sophisticated electronic circuitry and for this reason, and to a lesser extent because of its relative inflexibility in timescale, this method is not nearly as generally used as stopped flow for reactions where the physical properties of the reagents and/or products are such that a fast-response detector can be used. In the case of reactions which can only be monitored by thermal or other methods for which a slow response is unavoidable, the "time-clamp" properties of the continuous-flow technique make it much more suitable than the other two methods.[20]

The stopped-flow technique has two further advantages over methods where measurements are made on a flowing solution. There are (a) the character of flow down the observation tube does not affect it and (b) it is largely free from the distorting effect of mechanical disturbances.[21] The other commonly used flow method, capacity flow, has not been included in this discussion since its mode of operation limits it to the measurement of half-lives upwards of one second.[22] It is particularly useful, however, for detailed study of intermediates.

For very fast reversible reactions in solution, relaxation methods such as temperature-jump have recently been developed.[23,24] By employing solutions where the reactants are already mixed these methods are obviously not subject to the limitations of flow techniques and provide a means of following the progress of reactions which are so fast that the rate-determining process is the diffusion together of reagents.[25] These diffusion-controlled reactions almost invariably have second-order rate constants in the range 10^{10}-10^{11} $\mathrm{l\,mol^{-1}s^{-1}}$.[25] Although relaxation methods have been used in conjunction with the continuous flow technique in the study of irreversible reactions,[26,27] the considerable difficulties associated with this application make it desirable to use stopped-flow wherever it is a viable alternative. Reversible reactions in the stopped flow time-scale range are better suited to that technique in view of the much greater reproducibility afforded by it.

Photoelectric spectrophotometry is the most widely used technique for monitoring reactions in fast-reaction devices[28] owing to the availability of fast response electronic detectors, the output of which is usually displayed on a cathode ray oscilloscope. Solution reactions are commonly accompanied by changes in the electronic spectrum of the solution. The linear relationship between optical density and concentration, in addition to the possible precision of measurement with photoelectric spectrophotometers is a factor which accounts for its popularity. Where necessary, however, other physical properties have been monitored [4] and it is desirable for the same reaction to be followed, if possible, by two or more independent means.

Hartridge and Roughton were biochemists, and it was for investigations of biological systems that stopped-flow was originally developed. With the exception of some preliminary results given in a paper by Britton Chance in 1940,[17c] it was not until the 1960's that results were published of systematic investigations by the stopped-flow technique of the reactions of metal-ions in solution.[29,30]

Such reactions generally involve ligand-substitution or electron-transfer or both, for it has often been found in studies of redox reactions between metal-ions and non-metallic species, and sometimes other metal-ions, that ligand-substitution is a prerequisite for electron-transfer.[31,32,33] Thus ligand-substitution is involved in the majority of reactions of metal-ion species in solution.

Ligand Substitution Processes

The most general form of ligand-substitution reaction is as given in equation (2).

$$MX_n + Y \rightleftharpoons MX_{n-1}Y + X \qquad (2)$$

In 1952, Taube introduced the concept of inert and labile metal-ion complexes.[34] This is a purely artificial division based on whether or not the rates of ligand-substitution in a complex are measurable by so-called "conventional" techniques. The relatively recent application of rapid-reaction techniques to the study of labile complexes has made accessible the complete range of time-scales appropriate to molecular rearrangement.[35] Hence they have been, and still are, playing an important role in providing an overall picture of ligand-substitution processes at metal-ions centres.[36-38]

Most studies in this field are of complexation reactions of metal-ions in view of the biological interest which is often present in a knowledge of their mechanism.[36,37]

It is evident that interpretation of the results of such studies requires knowledge of the structure of the solvated metal-ion and the lability of its associated solvent molecules. These data are available for a substantial number of ions,[37] but the nature of many is still far from certain.

Metal-ion complexes are of two general types, outer-sphere and inner-sphere. This dichotomy was recognised in principle by Werner as long ago as 1912.[39] In an outer-sphere complex in solution the primary co-ordination sphere of the metal-ion is intact but that of the ligand is generally considered to be penetrated. In an inner-sphere complex, the primary co-ordination sphere of the metal-ion is penetrated by the ligand, providing direct contact between the interacting species in the form of a bond which generally possesses some covalent character.

The existence of outer-sphere complexes in solution was first recognised in 1926 by Bjerrum,[40] who called them "ion-pairs". These have been characterised for several substitution-inert complex ions, particularly cobalt(III) ammine complexes.[38] It has been found possible to monitor directly outer-sphere complex formation of $Co(NH_3)_6^{3+}$ and $Co(en)_3^{3+}$ with sulphate.[41]

The interconversion of $Co(NH_3)_5H_2O^{3+}$, SO_4^{2-} to the inner-sphere complex has been directly observed.[42]

Such a process obviously involves both breaking and making of metal-ion ligand bonds. In favourable circumstances, analysis of the rate-law and products of a chemical reaction allows not only identification of the individual steps involved but also determination of their chronological order. This has been termed the stoicheiometric reaction mechanism.[43] For outer-sphere to inner-sphere interconversion three distinct stoicheiometric mechanisms can be envisaged.[43] (M = solvated metal-ion of reduced co-ordination number.)

$$MX \underset{+X}{\overset{-X}{\rightleftharpoons}} M \underset{-Y}{\overset{+Y}{\rightleftharpoons}} MY \qquad (3)$$

$$MX \underset{-Y}{\overset{+Y}{\rightleftharpoons}} X\text{-}M\text{-}Y \underset{+X}{\overset{-X}{\rightleftharpoons}} MY \qquad (4)$$

$$MX + Y \rightleftharpoons MY + X \qquad (5)$$

The first of these involves the formation of a kinetically detectable intermediate of reduced co-ordination number and is described as dissociative, D, or often SN_1.[43]

The second represents the other extreme, i.e. formation of a kinetically detectable intermediate of increased coordination number, and is called associative, A, or often SN_2(lim).[43] The third possible process is that in which no intermediate is detectable kinetically and is described as ligand interchange, I, or SN_2.[43] In view of the somewhat greater suitability of the former nomenclature to a full description of ligand-substitution processes it will be used exclusively in this discussion.

It is possible to subdivide I processes by using the criterion of whether their so-called "intimate" mechanisms have dissociative or associative modes of activation.[43] A ligand interchange is said to have a dissociative mode of activation if bond-breaking provides a greater contribution to the activation energy than does bond-making in which case it is termed I_d. The converse is designated I_a.

Operational discrimination between dissociative and associative modes of activation is simple in principle.[43] Invariance of the rate constants for reactions of a complex with a series of ligands, by demonstrating entering group insensitivity, provides the basis of designation of the intimate mechanism as dissociative.[43] Conversely, the existence of entering-group sensitivity is taken as evidence for an associative process.[43]

A semi-quantitative estimate of the extent to which a mechanism is dissociative is provided by the slopes of plots of linear free-energy relationships such as $\Delta G^{\ddagger}$ versus ΔG^{o} or $\Delta S^{\ddagger}$ versus ΔS^{o}.[43] A slope of unity indicates that the activated complex closely resembles the products. Such a result is found for plots of log k versus log K for the acid hydrolysis of a series of $Co(NH_3)_5X^{2+}$ ions.[44] Additional evidence regarding the intimate mechanism is provided by $\Delta S^{\ddagger}$ itself, which when large and negative indicates an associative process and, when large and positive, a dissociative process. Volumes of activation are particularly useful, although data for reactions with charged ligands are not straightforward in interpretation owing to contributions from the solvent. For reactions with uncharged ligands the effects of solvent can be safely neglected and $\Delta V^{\ddagger}$ is positive for dissociative and negative for associative processes. The limiting values are +18 and -18 ml mol^{-1}, representing D and A water-exchange processes respectively. For a series of $Co(NH_3)_5X^{2+}$ species, $\Delta V^{\ddagger}$ for their aquation has in fact been found[45] to equal the overall molar volume change, indicating that the transition state is virtually identical with the products.

For substitution at octahedral species such as these of Co(III), a dissociative process would be expected to be favoured over an associative one on both electronic and steric grounds. Not only are there no low-lying empty d-or p-orbitals available to accept electrons from an entering group, but also such small metal-ions have little space for more than six inner-sphere ligands.

It is clear that there is a spectrum of possible mechanisms ranging from D to I_d through I_a to A. It is generally more difficult to distinguish between D and I_d, and between A and I_a, than it is to distinguish between I_d and I_a. This latter distinction is somewhat more meaningful than the former, where the necessary discrimination between intermediates and activated complexes is based entirely on their respective life-times.

Two main methods are available for the detection of an intermediate of increased co-ordination number formed in an A process. These are either direct observation, e.g. spectrophotometric, or evidence from deviations from a second-order rate law that the formation equilibrium is tending towards saturation. Two such intermediates have so far been found in substitution processes.[46,47] These are both five-co-ordinate species which derive from square planar rhodium(I) and platinum(II) complexes respectively. As expected, an A mechanism has yet to be unequivocally demonstrated for substitution at an octahedral species.

Rate laws resulting from D and I_d mechanisms differ only in detail and consequently it is rare for unambiguous assignment to be made on the basis of rate law alone. It has been possible, however, to show in this way that $Co(CN)_5^{2-}$ (ref. 48) and $Co(NH_3)_4SO_3^+$ (ref. 49) are intermediates in some substitution reactions of cobalt(III). Confirmation of their existence as discrete species has been achieved by showing that not only do they both exhibit selective reactivity towards a variety of ligands[48,49] but that this selectivity is similar in trend for both species.[49]

No intermediates of reduced co-ordination number have been observed directly, but evidence has been presented for the existence of such entities by showing that the product distribution arising from induced aquations of related complexes which have a large variety of leaving groups is strictly independent of the leaving group.[50,51] The existence of the presumably 5-co-ordinate $Co(CN)_4SO_3^{3-}$ has been demonstrated[52] by the observation of its discrimination towards nucleophiles. $Cr(H_2O)_5^{2+}$ in aqueous methanol has been identified in a similar manner.[53] Tobe showed that the radiochloride exchange of $Co(en)_2Cl_2^+$ in methanol proceeds <u>via</u> a D mechanism. He synthesised the complex which would be the intermediate in the alternative mechanism and showed that it reacted too slowly to account for the overall reaction rate.[54]

For ligand substitution processes which are mainly dissociative, the rate constant for ligand incorporation is expected to be of the same order of magnitude as that for independently measured solvent exchange. For a number of $Co(NH_3)_5(H_2O)^{3+}$, X species such rate constants have been found to be somewhat smaller than the known water exchange rate of $Co(NH_3)_5H_2O^{3+}$.[55] This has been attributed to the statistical discrimination in favour of water-capture rather than ligand-capture from the outer co-ordination sphere.[55] Although in principle it should be possible to show that a reaction has a D mechanism by proving that its ligand incorporation rate constant is in fact equal to that for solvent exchange, this has rarely been presented as proof in itself of the existence of such a mechanism.

It is to be noted that the examples quoted here regarding D mechanisms have all involved inert complex ions. No indisputable instance of the reaction of a labile metal-ion by this route has so far been found.

The Complexation of Labile Metal-Ions

A classification of labile metal-ions exists which is based largely but not entirely on the magnitude of their first-order substitution rate-constants. Into the first category, group A, fall the alkali and alkaline earth metal-ions, except Be^{2+} and Mg^{2+}, and also the d^{10} transition-metal triad.

For all of these the life-time of an individual aquo entity is less than 10^{-7} seconds.[56] This is almost certainly a consequence of the low charge/radius ratio of these ions, and the resulting low charge density on their surface. The complexation reactions of many of these with ligands of biological interest have been studied as models for cell membrane transport and metallo-enzyme behaviour.[57]

In each of the three individual sub-groups of this category, rates of complexation of the metal-ions by a particular ligand are proportional to the radius of the ion.[58] This would seem to indicate the measure of ease with which water is lost by the respective metal-ions. It also is considered to reflect the presence of a large degree of ionic character in the metal-ligand bonds. The absence of partially-filled d-orbitals in these ions precludes the complications which are often created by crystal field effects. Because most complexes of these ions are weak it was necessary to use multidentate chelating ligands in kinetic studies of their formation. The modest variations in rates of anation of group A metal-ions by different ligands have been attributed to differences in the number of water molecules which are replaced.[56]

These is some lack of coincidence of views as to whether the above findings are indicative of a dissociative or an associative general mechanism. The latter alternative finds more favour generally,[24,58] although the case for the former is strong. In the light of what has been stated earlier regarding the principles behind this problem, the correlation of the rates of the reverse reaction, i.e. aquation with the stability constants of the complexes would be interpreted as evidence for at least an I_d mechanism. There is, however, a widely held opinion that the rates of the processes involved are sufficiently close to the diffusion-controlled limit for it to be difficult, if not meaningless, to distinguish between such classes of mechanism.[38,59]

Group B contains the divalent metal-ions of the first transition series, in addition to Mg^{2+} and the lanthanides. All of these have intermediate surface charge densities, while the third group, group C, represents ions of high charge to radius ratio, such as the tervalent ions of the first transition series, along with Be^{2+}, the members of group IIIb of the periodic table, and most tetravalent ions. Although the plus-three lanthanide ions would be expected to be in class C, their kinetic behaviour resembles more closely that of the class B metal-ions. Their anomalously high lability has been attributed to their having co-ordination numbers greater than six.[60] Ligand field effects are unimportant owing to the deep penetration of the 4f electrons into the core of the ion.

Much evidence has been obtained to support the proposal that most ions of group B react by the Eigen Mechanism, which involves formation of an outer sphere complex at rates in the region of diffusion-controlled processes, followed by a dissociative ligand interchange:-

$$MS + Y \underset{k_{-o}}{\overset{k_o}{\rightleftharpoons}} MS,Y \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} MY,S \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} MY + S \qquad (6)$$

where S represents a solvent molecule and Y is the entering ligand. This is of course merely an extension of Langford and Gray's I_d mechanism.

The role of precursor outer-sphere complexes in substitution processes at inert metal-ion centres has been extensively reviewed.[38,42,43,55]

In his sound-absorption studies of the inner-sphere complex formation of some divalent metal ions with sulphate, Eigen with his co-workers observed[61] two relaxations, the slower of which yielded a rate constant of the same order of magnitude as that for water exchange. The other relaxation, which was several orders of magnitude faster, was attributed to outer-sphere complex formation.

Other workers who have subsequently studied these reactions are not in agreement as to whether or not there is only one fast relaxation;[24] some workers believe that two fast relaxations occur, corresponding to a two-stage outer-sphere complex formation, equation (7)

$$M_{aq} + X_{aq} \rightleftharpoons M,H_2O,H_2O,X \rightleftharpoons M,H_2O,X \qquad (7)$$

The overall picture is not much affected by this controversy. In an electron-pair donor solvent, such as water, it is to be expected that loss of a solvent molecule from the primary co-ordination sphere will be more facile for a ligand than for a metal-ion.

Eigen and Wilkins also noted[59] that k_1, equation (6) for divalent metal ions with a variety of ligands was mostly independent of the nature of the ligand after allowance had been made for the effect of $K_o (= \frac{k_o}{k_{-o}})$ on the overall rate-constant. (K_o is not accessible experimentally and is calculated by the theoretically derived Fuoss relationship.[62]) This is obviously indicative of a dissociative process.

In addition, k_1 was also found to be of the same order of magnitude as the corresponding rate of water exchange for a particular metal-ion. Thus it appears that the same process is rate-determining in each case. This can only be water-loss, which is in agreement with the conclusion arrived at above concerning the intimate mechanism of such reactions.

In the intervening years since Eigen first proposed this mechanism, no convincing evidence has yet been presented for the existence of an alternative mechanism for group B metal-ions. In fact there is now a virtually universal acceptance of its validity in the light of the volume of data which now supports it.[36,37,38,63]

The issue concerning whether the general intimate mechanism of ligand substitution at group C metal-ions is primarily dissociative or associative is far from resolution.

Calculations of expected activation energies for the reactions of some group C metal-ions[64] yield values of about 100 kcal mol^{-1} for the complete removal of a water molecule from the inner co-ordination sphere which would take place to form the intermediate of reduced co-ordination number characteristic of a D process. Even the Eigen mechanism would be expected[64] to give rise to activation energies of about 20 kcal mol^{-1} whereas values of about 11 kcal mol^{-1} are found experimentally.

Metal-ions of groups A and B lose water much more quickly than they undergo hydrolysis; the converse is true of group C metal-ions. As a result, these are often able to react through their hydrolysis products, usually the mono-hydroxy complex. Kinetic evidence of such parallel reactions is often obtained for complexation by anions of strong acids with the observed rate constant, k_{obs}, being of the form $k_{obs} = k_1 + \frac{k_2}{[H+]}$ with the latter term being interpreted as resulting from reaction of $MOH^{(n-1)+}$.[65] The consequent reduction in charge upon hydrolysis leads to a more facile loss of water by such species with the result that they exhibit kinetic behaviour similar to that of group B metal-ions.

Evidence for some degree of associative character exists for the largest ions of group C, such as $Rh(NH_3)_5H_2O^{3+}$,[66] and also for ions in this group which are of moderate size with fewer than three d-electrons, such as V^{3+}.[67,68] The ferric ion, which is small and possesses five d-electrons, is however the only group C metal-ion whose anation reactions have been extensively studied.

The Mechanism of Formation of Iron(III) Complexes

Ka for reaction (8)

$$Fe(H_2O)_6^{3+} \xrightleftharpoons{Ka} Fe(H_2O)_5OH^{2+} + H^+ \qquad (8)$$

at 25°C and unit ionic strength is[69] 1.64×10^{-3} mol l^{-1}. Since the forward reaction has so far proved too rapid to be monitored,[70] it is to be expected that $Fe(H_2O)_5OH^{2+}$

should play an important role in reactions of iron(III) in aqueous solution, especially since it reacts approximately a hundred times faster than does Fe^{3+} (ref. 71).

The anation reaction rates of Fe^{3+} (and of Al^{3+}

$$Fe^{3+}_{(aq)} + L^{n-} \rightleftharpoons FeL^{(3-n)+}_{(aq)} \qquad (9)$$

and Be^{2+}) show a pronounced dependence on the basicity of the reacting anion. This could of course be interpreted as indicating some associative character in the intimate mechanism. Eigen, however, proposed[61] an alternative explanation wherein a water-molecule separating Fe^{3+} from L^-, while the latter is in the outer co-ordination sphere, dissociates under the influence of Fe^{3+} and the anion to give $FeOH^{2+}$ and HL, which then react in a dissociative manner. Thus the overall substitution rate is governed by the extent of hydrolysis. This mechanism is consistent with the correlation of anation rates with ligand basicity and does not contradict the observed pH independence of this pathway. Criticism of the validity of this mechanism has been made[43] owing to the lack of sensitivity of $Cr(H_2O)_6{}^{3+}$ anation rates constants to ligand basicity, since this species also undergoes hydrolysis much more rapidly than it loses water.

Seewald and Sutin drew attention[72] to the fact that the proton ambiguity associated with this acid-independent path does not allow an a priori distinction to be made between routes (10) and (11).

$$Fe(H_2O)_6{}^{3+} + L^- \rightleftharpoons Fe(H_2O)_6{}^{3+},L^- \rightleftharpoons Fe(H_2O)_5L^{2+} + H_2O \qquad (10)$$

$$Fe(H_2O)_5OH^{2+} + HL \rightleftharpoons Fe(H_2O)_5OH^{2+},HL \rightleftharpoons Fe(H_2O)_5L^{2+} + H_2O \qquad (11)$$

Interpretation of the available kinetic data in terms of reaction (11) reduced the range of anation rate constants associated with Fe^{3+} and $FeOH^{2+}$ to between 4 and 127 $l\ mol^{-1}s^{-1}$ for the former species and 3×10^3 to 3×10^5 $l\ mol^{-1}s^{-1}$ for the latter. The first-order rate constant for water exchange[73] for Fe^{3+} is 150 s^{-1}, while that for $FeOH^{2+}$ has been estimated[73] as 10^4 s^{-1}. These relatively small trends in rate constants with varying ligands have been attributed to the variations in the magnitudes of the outer-sphere complex formation-constants.[74] If this interpretation is valid, it would appear that bond-breaking is the dominant feature of ligand incorporation into the inner co-ordination sphere of both iron(III) species.

Attempts to resolve the proton ambiguity between (10) and (11) are currently centred on studies[75] of the reactions of iron(III) with ligands of the form HL which have dissociation constants sufficiently high for rate constants, determined on the assumption that only path (10) is operating, to be greater than the commonly accepted diffusion-controlled limit. It is then hoped that when the alternative, route (11), has been adequately identified and characterised it will prove possible in cases where the above approach is not appropriate to resolve the dilemma associated with this kinetic ambiguity.

Other Rate-Limiting Processes in Ligand Substitution Reactions

It should be noted that making and breaking of bonds between metal-ions and ligands are not the only molecular processes which have been found to be rate-determining in complexations of labile metal-ions. Loss of a proton from an otherwise fully-formed complex [76] and also ring-closure [37] in complexation reactions where ring-strain and entropy effects dominate, have both been shown to be rate-determining in some instances.

Electron-Transfer Reactions

The stability of a particular oxidation state of a metal is the result of redox involving either an unfavourable free energy change or too large a free energy of activation.[31] It is well known that the presence of co-ordinating ligands can influence both these factors.[32,77-79]

The electron-transfer step itself is subject to the restrictions of the Franck-Condon principle.[80] Electrons are much lighter than nuclei and move so rapidly in comparison with them that the latter can be regarded as stationary during the time taken for electron-transfer. Before the electron can pass in solution from one reactant centre to another, the redox partners and their co-ordination spheres must adopt the unique configuration which minimises the energy charge on electron-transfer. Thus, for most redox reactions, molecular processes play a very important part in determining the energetics of the reaction and hence its rate. Spin-inversion, when it occurs, is found to inhibit the overall redox rate because such transitions are quantum-mechanically forbidden.[77]

Electron-transfer reactions in solution are generally classified according to whether they proceed by way of an inner-sphere or outer-sphere activated complex.[81] The primary co-ordination spheres of the reaction partners remain intact in an outer-sphere activated complex. In an inner-sphere activated complex for redox between two metal-ions, a ligand is shared directly between the ions. The equivalent transition state involving a metal-ion and a reducing ligand corresponds <u>in structure</u> to the stable inner-sphere complexes discussed earlier.[32] Both types of inner-sphere activated complex may in some instances lead to the formation of detectable intermediates of similar constitution.[31-33]

The reduction of $Co(NH_3)_6^{3+}$ by $Cr(H_2O)_6^{2+}$ is forced to proceed by an outer-sphere mechanism as a result of the inert nature of the cobalt(III) species with respect to substitution.[78] However, Taube, in the first conclusive demonstration of an inner-sphere mechanism for a redox reaction involving two metal ion complexes, showed[82] that the transfer of Cl^- in the reduction of $Co(NH_3)_5Cl^{2+}$ by $Cr(H_2O)_6^{2+}$, equation (12),

$$Cr(H_2O)_6^{2+} + Co(NH_3)_5Cl^{2+} \xrightarrow{H^+} Cr(H_2O)_5Cl^{2+} + Co(H_2O)_6^{2+} + 5NH_4^+ \qquad (12)$$

occurs in the transition state, since, although the cobalt(III) and chromium(III) complexes involved are inert to substitution, $t_{\frac{1}{2}} \gg 1$ hr.,[78] the overall reaction is rapid. Confirmation of this mechanism was obtained by the discovery that, when the reaction was run in the presence of free radioactive chloride ions, the resultant $Cr(H_2O)_5Cl^{2+}$ had little radioactivity.

Extensive study of the oxidations of ligands by metal-ions has established that these reactions generally proceed by an inner-sphere mechanism with the involvement in some cases of well-characterised intermediates.[31-33] The stopped-flow technique has been especially useful in studying these transient complexes.[31]

The formation of such inner-sphere complexes

$$MX_n^{a+} + L \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} MX_{n-1}L^{a+} \xrightarrow{k_2} M^{(a-1)+} + P \qquad (13)$$

is more likely to take place where negatively-charged or neutral substrates are involved than with cationic reductants. There are three possible rate-controlling factors in the overall formation of products.

(i) the rate of formation of the intermediate;

(ii) the rate of transfer of the electron;

(iii) the rate of breakdown of the complex. The factors important if (i) holds have already been discussed. If the electron-transfer itself is rate-determining, reaction rate constants for a particular oxidant should correlate with the electron affinities of the ligands in the absence of spin-inversion effects.[83] The molecular re-arrangement necessary to satisfy the requirements of the Franck-Condon principle would not be expected to dominate in the case of electron-transfer within an inner-sphere complex. If breakdown of the complex is rate-determining, the strength of the metal-ligand bond will clearly be critical.

Whether or not the intermediate itself is observed depends on the relative magnitudes of the rate constants k_1, k_{-1}, and k_2. Four possibilities will be considered.

(a) If k_1 and k_{-1} are both much greater than k_2, with $k_1 > k_{-1}$, complex formation will be completed instantaneously as judged on the time-scale of the redox reaction. For systems studied by the stopped-flow method this often means that the complex formation step is generally not observed since it often occurs within the dead-time of the instrument.

(b) If $k_1 < k_{-1} > k_2$, complex formation and disappearance will both be observed.

(c) If $MX_{n-1}L$ is maintained at a small steady state concentration the observed rate constant will be a function of k_1, k_{-1} and k_2.

(d) If $k_2 >> k_1$, then k_{obs} equals k_1.

This corresponds to case (a) in the considerations of the possible rate-determining processes i.e. substitution-controlled redox reactions. Many metal-ion oxidations of ligands are believed to be of this type.[84]

The detection of complex formation between oxidant and reductant does not in itself prove that this entity plays a direct role in the redox process.[85] There is a kinetic ambiguity which does not allow distinction to be made, solely on the basis of the observed rate law, between whether or not the complex is a true intermediate. If such a complex is formed in measurable concentrations, however, the establishment of the existence of a sequential process may be made spectrophotometrically, especially by the observation of induction periods and and isosbestic points.

Reactions of Oxyanions

It has been known for a long time that oxyanion reaction rates are markedly dependent on hydrogen-ion concentration.[32] This is true for both ligand-substitution and redox processes.[32] The role of the proton is almost certainly the labilisation of the co-ordinated oxide and hydroxide anions by converting them to water.[32] There is generally a close correlation between the rates of ligand-exchange and electron-transfer reactions of such compounds.[32]

In any horizontal row of the periodic table, the rate of oxygen exchange in water decreases with an increase in oxidation state of the central atom :[32]

$$H_2SiO_4^{2-} > HPO_4^{2-} > SO_4^{2-} > ClO_4^-$$

A similar oxidation state effect is observed for oxyanions of a single element :[32]

$$ClO > ClO_2^- > ClO_3^- > ClO_4^-$$

The size of the central atom also plays an important role :[32]

$$IO_3^- > BrO_3^- > ClO_3^-$$

The two trends given above for the oxyhalides are also the trends for the rates of oxidation by these species.[32] This correlation has been discussed.[86]

Thus replacement in the co-ordination sphere of the oxyanion seems an important prerequisite to redox between reductant and oxidant, presumably because the formation of a bond for the mediation of electron-transfer is such a low energy-path compared with alternative outer-sphere routes.

Perchlorate is an interesting example of a complex ion whose redox reactions are substitution-controlled. When boiled in 9 M acid, the half-life of oxygen exchange with water is more than a century;[87] even the hydrated electron will not reduce it readily.[78] There is, however, a substantial thermodynamic driving force for the reduction of this species which has caused many spectacular explosions, often with tragic consequences.[88] Its kinetic inertness in aqueous solution renders it a very useful inert constituent of the background electrolyte in studies of reactions in this medium, especially in view of its very poor co-ordinating properties.[89]

CHAPTER I

THE CONSTRUCTION OF THE STOPPED-FLOW DEVICES

The Theory of the Stopped-Flow Method

By 1934 Hartridge and Roughton had used the stopped-flow method to study reactions in solution, the half-lives which they measured being of the order of ten seconds.[90] By 1940, however, Chance had developed a stopped-flow apparatus capable of measuring reaction times down to thirty milliseconds.[17]

Although it utilises technology which is mostly derived from continuous-flow and accelerated-flow, both of which are rapid flow methods, the essential aspect of the stopped-flow method is based on rapid mixing techniques. Thus whereas in rapid flow both mixing efficiency and the character of flow down the observation tube are of paramount importance, only the former consideration applies to stopped-flow because the mixed solution is stationary when measurements are made. It is especially true that flow characteristics beyond the observation point are of no importance at all.

There are five factors which govern the reliability of a stopped-flow apparatus in its measurement of reaction rates and the value of the shortest reaction time accessible to it.

(a) Flow velocity.

(b) Cavitation.

(c) Mixing efficiency.

(d) Distance between mixing chamber and observation point.

(e) Time taken to initiate and terminate flow of solution.

It is desirable to use the highest possible push rate because it has been established that mixing efficiency increases when higher solution velocities are employed.[91] In addition, the time taken for solution to travel from the mixing chamber to the point of observation is minimised thus reducing the portion of reaction which can not be observed owing to its having taken place before flow is stopped. The turbulence associated with flow rates in excess of the critical velocity is also advantageous in that it allows the elements of solution of equal age to arrive simultaneously at the observation point.[92] Also, when flow is stopped, the disturbance of the solution continues for a short time and helps keep the solutions mixed while stationary.[93]

The upper limit to solution velocities employed in flow devices is expected to be governed only by the technical difficulties involved in achievement of the necessarily very high push rates. In fact, however, a frequent limiting factor is the onset of cavitation,[94] which is the formation of visible bubbles in solution. In most cases this imposes a limit of the order of 15-20 Ms^{-1} on flow rates.[95]

Cavitation results when the external pressure on a solution falls below the vapour pressure of water.[96] The bubbles formed are in fact localised pockets of water vapour. Total internal reflection by these bubbles causes anomalous light transmission effects in solution. Local pressure drops within a stopped-flow apparatus arise from fluid flow through restrictions and past sharp edges.[94]

Although the 'degassing' of solutions and the application of a positive back pressure while reactants are discharged have both been used successfully as methods of reducing or eliminating cavitation, consideration of this phenomenon nevertheless limits the scope of designs of mixing devices which provide optimum efficiency because mixers are often the principal sources of cavitation.[94] They must be constructed in such a way that they provide the means for maximum dissipation of energy by the reactant solutions in the mixing process.[97]

It is therefore necessary to have the mixer jets impinge directly upon one another with the maximum possible velocity.[98] The kinetic energy is lost mainly in the form of work done in breaking up the solution into sufficiently small elementary volumes that an artificial diffusion control is not imposed upon the reaction rate.[98] To satisfy these requirements, and also the need for observation as near as possible to the mixer, the jets are generally arranged approximately radial to the axis of the observation tube. A strictly radial array has been found to give maximum mixing efficiency but it also gives rise to cavitation at the intersection of the jets with the axis of the observation tube.[17a] A tangential array leads to vortex cavitation as a result of the additional contribution to pressure drop from the angular velocity.[17a] A compromise configuration, with the jets normal to the observation tube axis but displaced from each other by a distance equal to their diameter, was found to give vortex cavitation at moderate flow velocities of about 10 Ms^{-1}.[99] Using similar compromise arrangements, no visible cavitation was found at flow velocities as high as 25 Ms^{-1}.[17a] This configuration imparts a rotary motion to the solution leading to faster and more efficient mixing and improving the character of flow down the observation tube.[100] This swirling motion has been found to continue for some time after flow has stopped and helps maintain a homogeneous mixture while observations are being made.[20]

Since mixing efficiency increases with the number of jets incorporated in the mixer[91] it is obviously desirable to have a very large number of them. However, to minimise the pressure drop across the mixing chamber it is necessary to have an arrangement where the total cross-sectional area of the jets is approximately equal to that of the observation tube.[93] In view of the generally small bore of the latter, engineering problems limit the number of jets which is practical. Also, the presence of a large number leads to such a great resistance to flow that high push rates become difficult to achieve.[91] Most mixers in general use do not incorporate more than eight jets. Gibson's pioneering stopped-flow apparatus utilised two four-jet mixers in series.[101]

Swirlers and meshes are some of the devices which have been used to promote turbulence in flow devices.[102]

Increased mixing efficiency is achieved, but a compromise must be arrived at between this factor and the consequent increase in cavitation.[95]

It is obviously desirable to minimise the extent of reaction which has taken place before observation by reducing the "dead space" between the mixing chamber and the observation point. Nevertheless the distance between these two points must not be so small that the solution has not yet been thoroughly mixed when observed.

Rapid starting and stopping of the solution, especially the latter, is of great importance in the operation of a stopped-flow apparatus. The former is clearly necessary to achieve the highest possible push rate in the short time available. The rapidity of stopping can govern whether or not a very fast reaction will be detected. Also, if stopping is slow the mixing efficiency will drop during the deceleration and the portion of solution observed will not be adequately mixed.[101] In addition, the rapid starting and stopping again promotes turbulence in solution. Gibson has developed a means of rapid stopping where the solution is driven against the plunger of a syringe. The plunger is halted abruptly when it encounters a block.[101] This method has the added advantage of providing a back pressure which helps prevent cavitation.

The so-called "slit-width" error,[17b] which arises in the monitoring of segments of solution as a result of it being necessary to scan a finite length of the observation tube, causes a "blurring" of time-scale in continuous- and accelerated-flow methods. This effect is, however, quite negligible.[17b] Similarly, slit-width error has not been found to make a significant contribution to the overall uncertainty in stopped-flow measurements.[103]

Objections have been made to the use of square or rectangular cross-sectional observation tubes, which would allow more precise optical measurement, on the grounds that flow characteristics would be uncertain and that elements of solution of equal age would not arrive together at the point of observation.[104] However, in a stopped-flow device not only is a solution stationary when observed but also the generally turbulent nature of flow imparts a character which is a reasonable approximation to that of mass flow. Finally, any error present as a consequence of this factor would have a similar magnitude to the slit-width error, which, as stated above, is usually found to be negligible.

Description of the Stopped-Flow Devices

Two types of stopped-flow apparatus were used, one for reactions having half-lives less than ten seconds, the other for all reactions slower than this. A diagram of the first type is provided in Figure 1.1.

The reactant solutions were delivered from two horizontal "Zippette" pyrex glass syringes of 2 ml capacity (Jencons, Hemel Hempstead). Specially constructed teflon plungers were used. These were fitted with flat

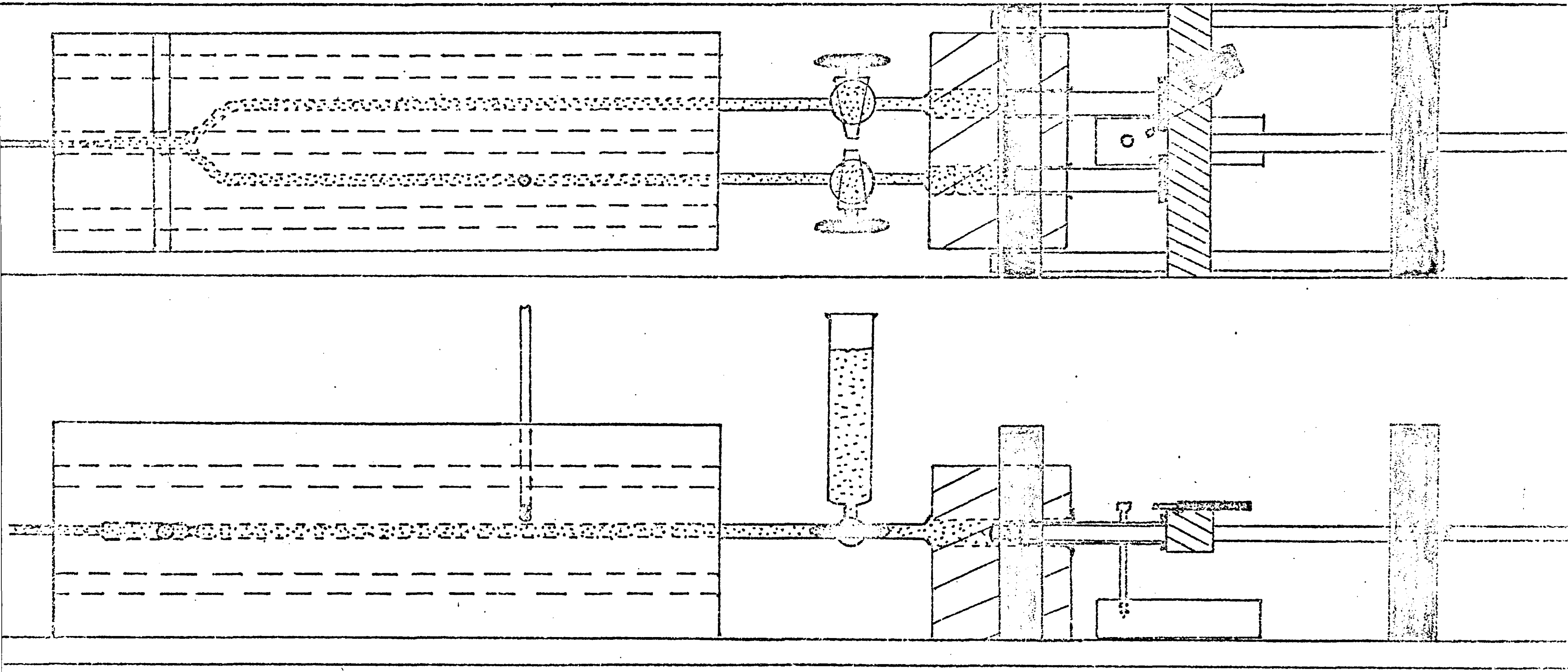


Fig. 1.1.

"Fast" Stopped-Flow Apparatus

1 cm = 1 inch

Top :- Plan View; Bottom :- Side View

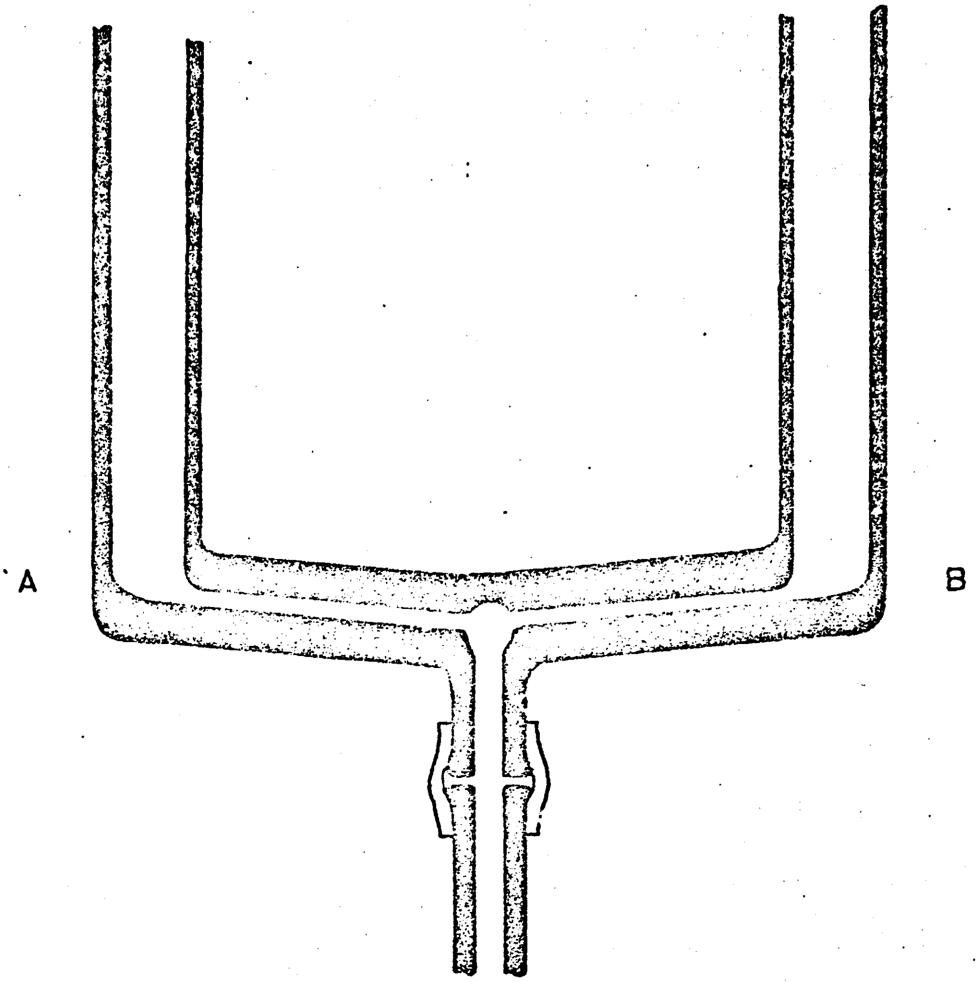
brass screw-in heads which were fitted vertically into brass collars tapped into an aluminium pushing-block. In order to achieve an effective seal within the drive-syringes, neoprene 'o'-rings (Edwards Vacuum Components Ltd., Crawley) were fitted to the plungers near their tips. Each of these syringes was connected to a three-way T-bore glass-barrelled stop-cock (Springham, Harlow) either by glass-blowing or by the use of short lengths of plastic tubing(Portex Surgical Tubing, Hythe, Kent) secured by windings of copper wire and embedded in plaster of Paris to prevent their expansion during pushes and the consequent relaxation of solution when flow was stopped. The vertical reservoir-syringes were glass pyrex with a capacity of 10 ml. Connection of these to the three-way taps was achieved by the use of short lengths of "Portex" plastic tubing. The nozzles of these syringes were lapped with glass to increase their external diameter and hence facilitate the connection. Solution was transferred to the mixing device by way of glass tubing of 5 mm internal diameter. The feed tubes were connected to the mixer by short lengths of "Portex" plastic tubing which were secured by windings of copper wire. In instances where copper wire was used in this way it was totally impossible for solutions to be contaminated by contact with it. In order to prevent expansion and relaxation of this tubing, the ends of the feed tubes were situated almost flush with the extruded inputs to the mixer. Also, plaster of Paris was used, not only to help alleviate this problem, but also to secure the mixing chamber to prevent movement of the flow system while the plungers were being driven.

The mixing chamber was a teflon one-stage eight-jet device modified from the original design of Dulz and Sutin.[105] A cylindrical quartz observation tube was secured at one end within the exit of the mixer by two neoprene 'o'-rings. The optical path-length was determined as 2.2 mm by comparison of absorbance as measured by this arrangement with that obtained using an S.P.500 spectrophotometer with a 10 mm path-length cell.

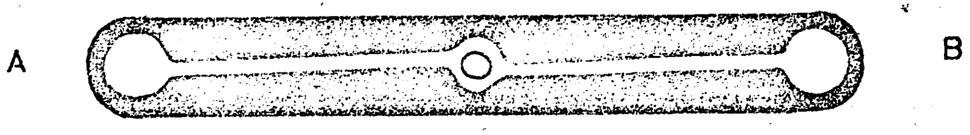
This apparatus was later modified by fusing a 'spectrosil' type 134QS flow-through spectrophotometer cell (Hellma Instruments, Southend-on-Sea) to the observation tube very close to its exit from the mixer. This cell had a rectangular cross-section and 5 mm path-length. In addition, another stopped-flow apparatus was constructed. It was virtually identical in design but for the material of the mixer, which was perspex.

Some minor leakage at the mixing chambers was encountered with both these devices and, as a result, one mixer was replaced by an all-glass two-jet mixer of the design shown in Fig. 1.2. Reaction rates were found to be identical on both flow devices well within experimental error, indicating that the mixing efficiency of the two-jet device was not measurably inferior to that of the eight-jet one. This result was anticipated from similar

Fig. 1.2.



PLAN



SECTION

ALL GLASS TWO JET TANGENTIAL MIXER

findings for reactions of $t_{\frac{1}{2}}$ greater than 10 ms. The other mixing chamber was then similarly replaced.

A metal rod projected horizontally from the rear of the pushing-block, which itself ran on iron rods. When compressed gas was released into a 50 ml 'Atlas' nylon syringe (Thackray Ltd., Leeds) by quickly turning a three-way tap (Fison Glassware, Loughborough), the plunger was driven out within the syringe and drove the pushing-block via the metal rod. Flow was stopped when the pushing block encountered a vertical iron pin which was placed in one of several available holes in a brass block. This front-stopping method was used in preference to the conventional back-stopping system as it was found to lessen the recoil which occurred when flow was stopped. Also, it provided greater operational flexibility in that by having a number of holes in series in the stopping-pin holder, it was possible to obtain several pushes without refilling the drive-syringes. The solution finally travelled upwards into an inverted Dreschel-head fitted with a round-bottom flask.

Thermostatting of solutions was achieved by incorporation of the feed-tubes, mixing chamber and observation cell all within a two-piece aluminium block through which water was circulated lengthwise via copper tubes, three in the top section, three in the bottom. A thermometer was placed in a cavity in the top block, providing contact of the bulb with one of the feed-tubes. Thermal contact between the flow system and both the thermometer and the aluminium block was achieved by packing brass filings into any air-spaces which existed. The thermostatting water was heated and circulated from a tank by means of a Circotherm Mk. II Thermomix Series 769 (Shandon Southern, Camberley) which incorporated a 27559/E contact thermometer (Braun, Melsungen). Cooling was achieved using a "Tecam" dip-cooler refrigeration unit (Techne Ltd., Cambridge).

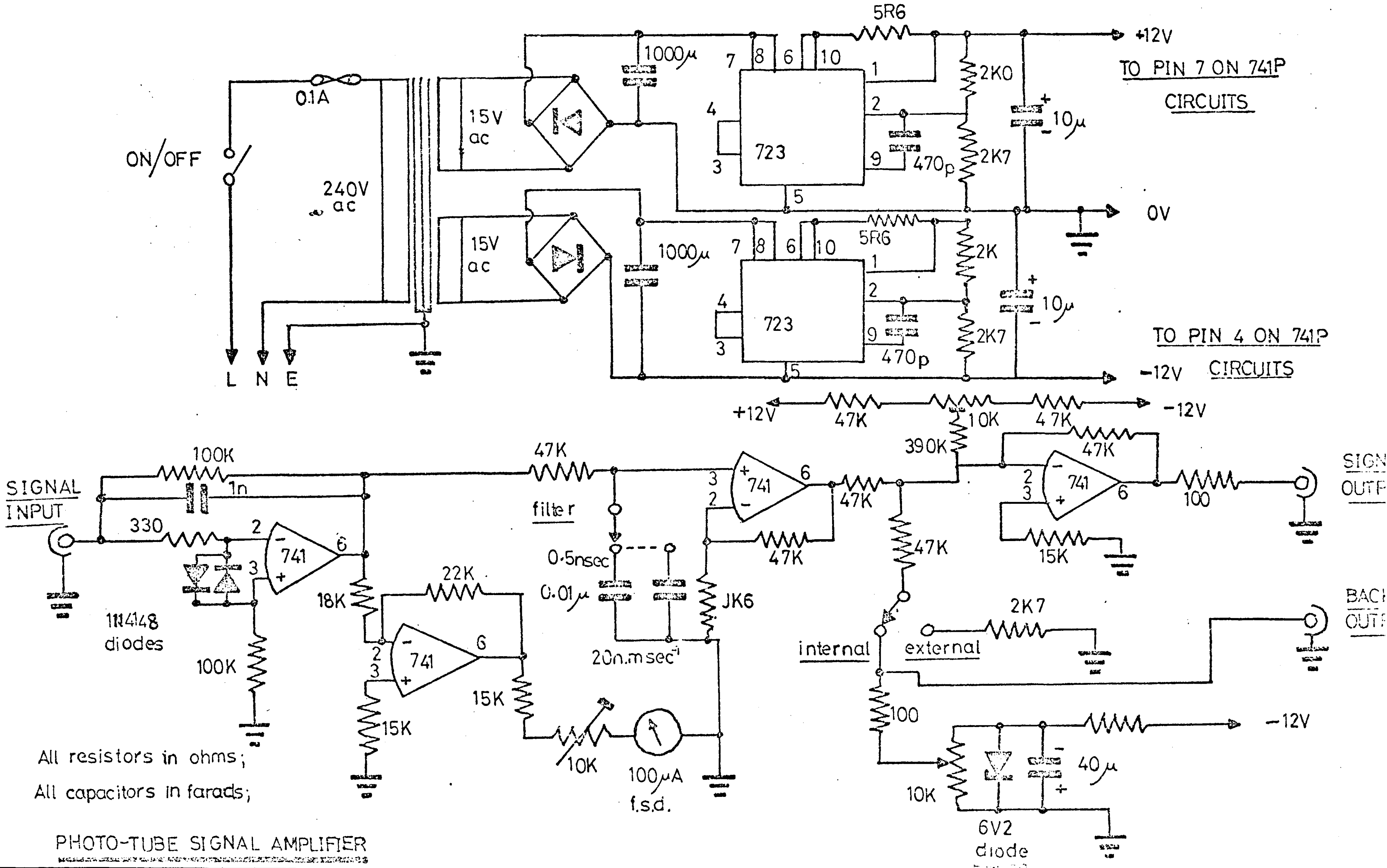
The power supplies and ancillary electronic equipment were operated from the mains via a type BTR-5 A.C. automatic voltage stabiliser (Claude Lyons Ltd.) with an output of 240 volts at 50 Hz.

One of the stopped-flow devices of the type described above used a S.P.500 monochromator (Pye Unicam Ltd., Cambridge) as its light source. Visible radiation was provided by a tungsten lamp which was operated at 36 watts (6 volts, 6 amps) from a Unicam 115D power pack. Ultraviolet radiation was supplied by a deuterium lamp which utilised the standard Unicam power unit. The intensity of light leaving the spectrophotometer cell, which was masked with black tape to create an aperture approximately one millimetre in diameter, was monitored using an E.M.I. 6256S photomultiplier tube. Its operating voltage was supplied by an A.E.I. type R1184 power unit. The output of the photomultiplier tube was fed by way of a D.C. amplifier into one input of a Tektronix 2A63 differential amplifier which was incorporated in a Tektronix 564 storage oscilloscope. The D.C. amplifier circuit contained a number of resistor-capacitor filters. The decision regarding which one was used for a particular run was governed by a consideration of the magnitude of the time-constant of the filter compared with the half-life of the reaction. The other D.C. input signal to the oscilloscope differential amplifier was also provided by the D.C. amplifier circuit. This current could be varied by means of a calibrated helipot and enabled partial cancellation of the signal from the photomultiplier tube.

Current in the triggering circuit was drawn from the calibration voltage output of the oscilloscope to one terminal of a roller miniature microswitch (R.S. Components Ltd., London) which was mounted on top of the pushing-block. The other terminal was connected to the external trigger input of the 2B67 Tektronix time base. Triggering of the oscilloscope sweep took place when the microswitch was closed as it past the stopping-pin shortly before flow stopped. Oscilloscope traces were photographed using a Shackman Super Seven Mk. II oscilloscope camera fitted with a Polaroid CB-40 Land back. Type 47 Polaroid Land film was used.

The other stopped-flow apparatus of similar design used as its light source a modified Hilger "Uvispec" monochromator containing a 100 watt Osram tungsten lamp (6.6 amps, 15 volts). Its power pack was a Farnell stabilised voltage/current S-series type 15/106L unit. A glass lens was used to concentrate light on the cell. This limited this apparatus to operation in only the visible

Fig. 1.3.



All resistors in ohms;

All capacitors in farads;

PHOTO-TUBE SIGNAL AMPLIFIER

region of the electromagnetic spectrum. It used a Tektronix 5103N single-beam storage oscilloscope in conjunction with a Tektronix 5A20N differential amplifier and Tektronix BB10N time-base. Traces were photographed with a Tetronix C-5 oscilloscope camera using type 107 Polaroid film.

The stopped-flow apparatus which was used for slow reactions ($t_{\frac{1}{2}} > 10s$) is shown schematically in Fig. 1.4.

The drive- and reservoir-syringes, as well as the mixing device, were all thermostatted within a one-foot plexiglass tank through which was circulated water from another larger tank by means of a B.T.L. Circon heater-pump. Temperature control within this tank was provided by a Circotherm unit as described above, fitted with the same type of contact thermometer. Cooling was again provided by a "Tecam" dip-cooler. Each of the two 10 ml capacity pyrex glass drive syringes (Chance Bros., Malvern Link), (fitted with specially constructed teflon plungers sealed with neoprene 'o'-rings) was connected to a three-way teflon-barrelled stop-cock by short lengths of "Portex" surgical tubing. The three-way taps were situated as shown and supported by perspex pillars. The glass reservoirs were specially blown, as was the mixer, which was of the type shown in Fig. 1.2. A fused glass multibore network was placed downstream from this device in order to aid the efficiency of mixing. The plexiglass tank was situated above a Unicam S.P.800D spectrophotometer which was fitted with an S.P.820 Series 2

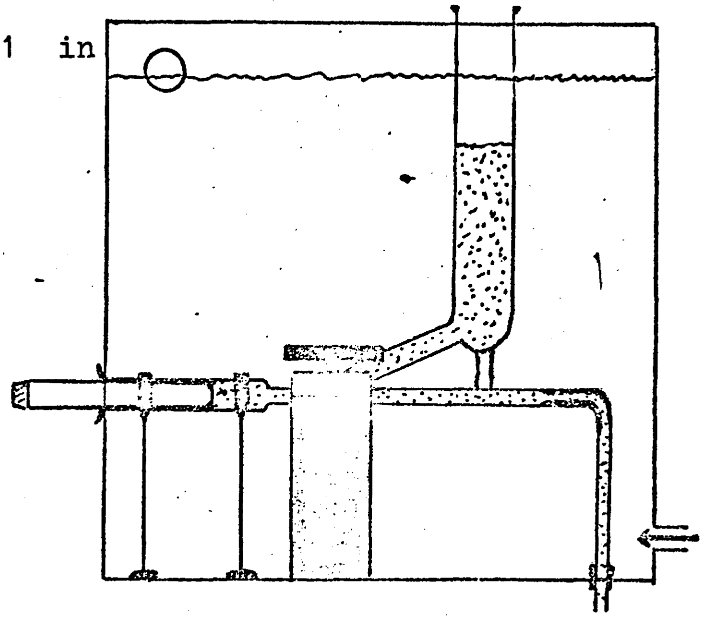
Fig. 1.4.

"Slow" Stopped-Flow Apparatus

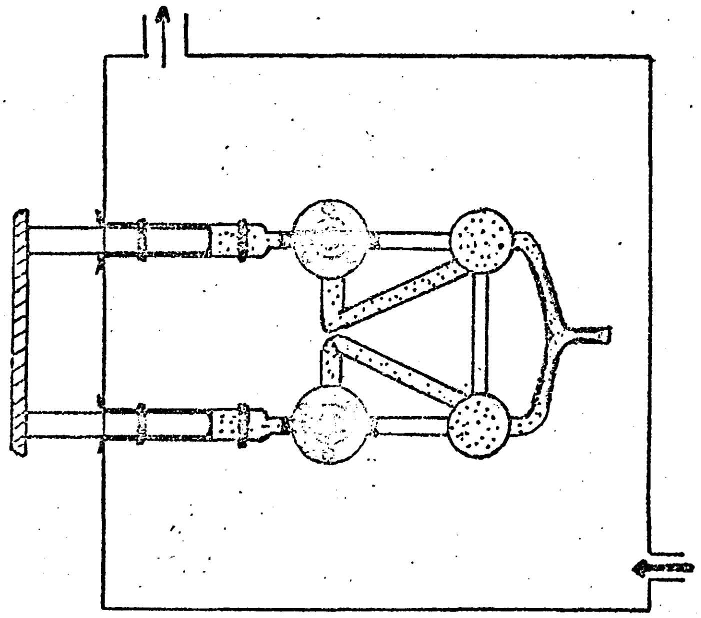
I Side View

II Plan View

1 cm = 1 in



I



II

constant wavenumber scan control and S.P.850 scale expansion unit linked to a Servoscribe chart recorder. The mixed solution entered the cell compartment of the spectrometer which contained a 10 mm path-length quartz flow-through cell (Hellma QS130).

Thermostatting was achieved by passage of water through the hollow cell-holder using the Circotherm heater-pump. Thermometers were used to monitor the temperatures of the water in both tanks in addition to that of the cell-holder effluent. Overall temperature control was to within 0.2^{o}C.

Calculation of Results

In order that a thorough kinetic analysis could be obtained with the two "fast" stopped-flow devices, it was necessary to convert the oscilloscope displays of voltage as a function of time to the equivalent absorbance data which could be used, with knowledge of the appropriate molar extinction coefficients, as a direct measure of the way in which component concentrations varied during the course of reaction.

Optical density, O.D., can be expressed as in equation (1)

$$O.D._t = \log_{10} \frac{I_o}{I_t} \qquad (1)$$

where I_o is the intensity of light transmitted by an optically clear solution and I_t is the intensity of light transmitted by a solution of absorbance $O.D._t$, or A_t. For a calibrated photomultiplier tube where the output current, i, is linearly proportional to the intensity of incident light,

$$O.D._t = \log_{10} \frac{i_o}{i_t} \qquad (2)$$

The impedance of the system obviously does not change with absorbance. Hence.

$$O.D._t = \log_{10} \frac{V_o}{V_t} \qquad (3)$$

where V_o and V_i are as displayed on the oscilloscope screen.

Calibration of the helipot control entailed plotting its voltage output, as measured on the oscilloscope screen, against the corresponding readings on the control knob, see Fig. 1.5. When the photomultiplier tube signal was exactly balanced by the signal from this back-off source, as illustrated in Fig. 1.6., the horizontal line on the oscilloscope screen which represented zero volts of P.M.T. signal when no backing-off was applied, clearly then represented the voltage of P.M.T. output equal to that of the oppositely applied signal, with zero volts of light signal being as shown. V_t, the P.M.T. voltage corresponding to any other horizontal line on the screen, could be computed simply by adding or subtracting the appropriate voltage, ΔV, with respect to this reference voltage $V_{B.O.}$. ΔV could be calculated simply by multiplying the vertical distance of separation, ΔR, by the oscilloscope gain setting.

Fig. 1.5.

Calibration of Helipot Control

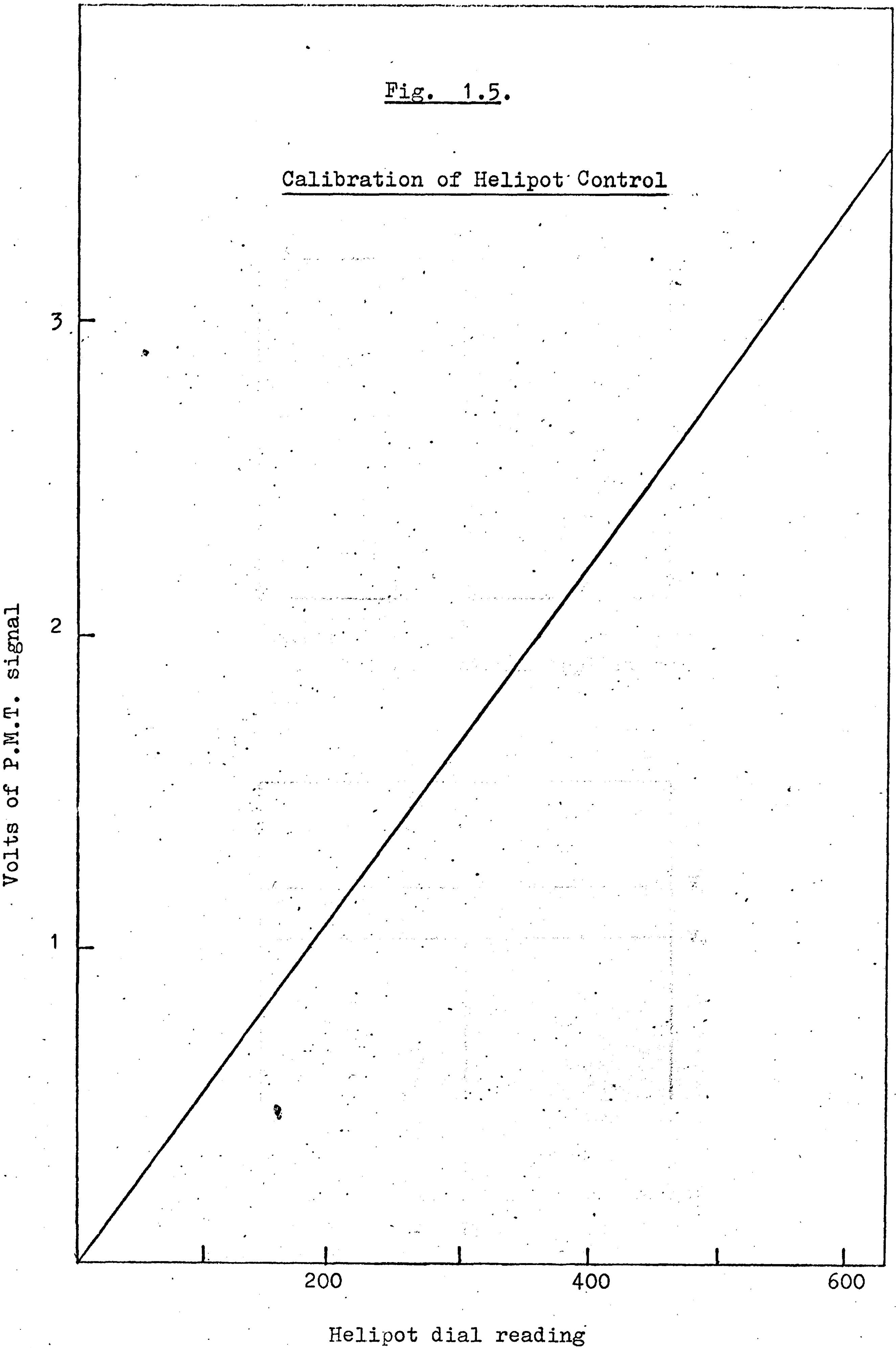
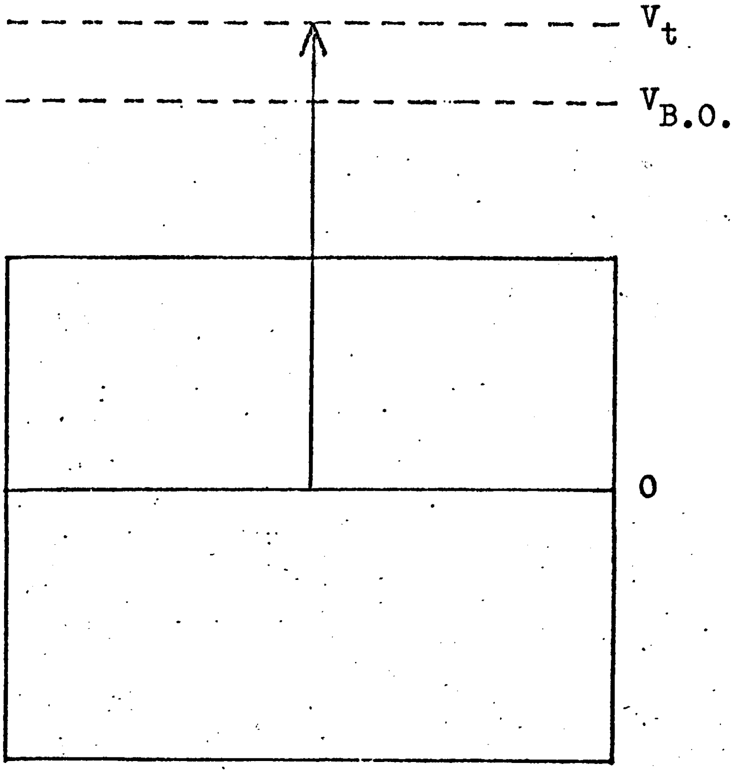


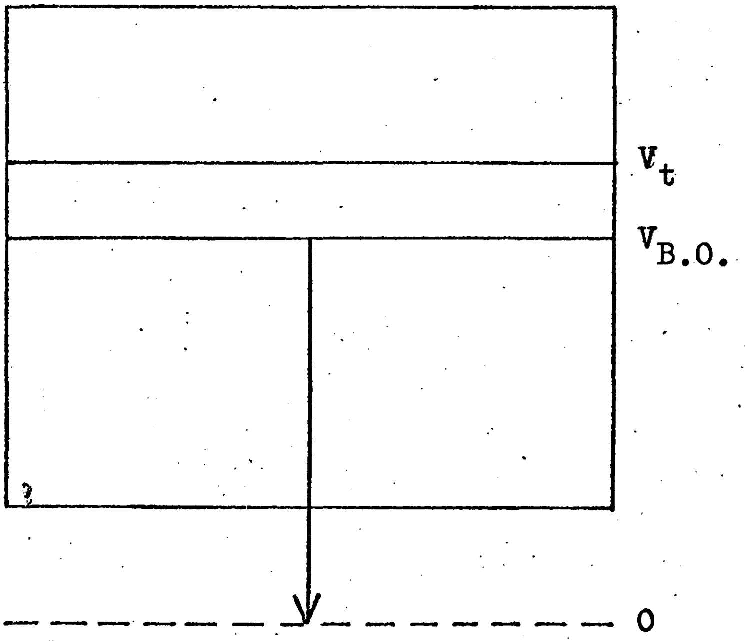
Fig. 1.6.

The Use of the "Back-Off" Helipot



I

V_t volts of P.M.T. signal applied



II

$V_{B.O.}$ volts of helipot signal applied in opposite direction to "back-off" most of P.M.T. signal.

The most common form of information collected was the exponential increase in optical density resulting from pseudo-first-order formation of a complex metal-ion which absorbed more strongly than the starting materials.

It can readily be shown that for such a situation

$$\log_e \left(\frac{A_\Omega - A_o}{A_\Omega - A_t}\right) = k_{obs}.t \tag{4}$$

where A_Ω is the absorbance of the solution when equilibrium has been attained, A_o is the absorbance of the mixed solution at zero extent of reaction and A_t is that of the reaction mixture at any time, t.

Thus the pseudo-first-order rate constant, k_{obs}, can be obtained simply by evaluating the slope of a plot of $\log_e(A_\Omega - A_t)$ against time.

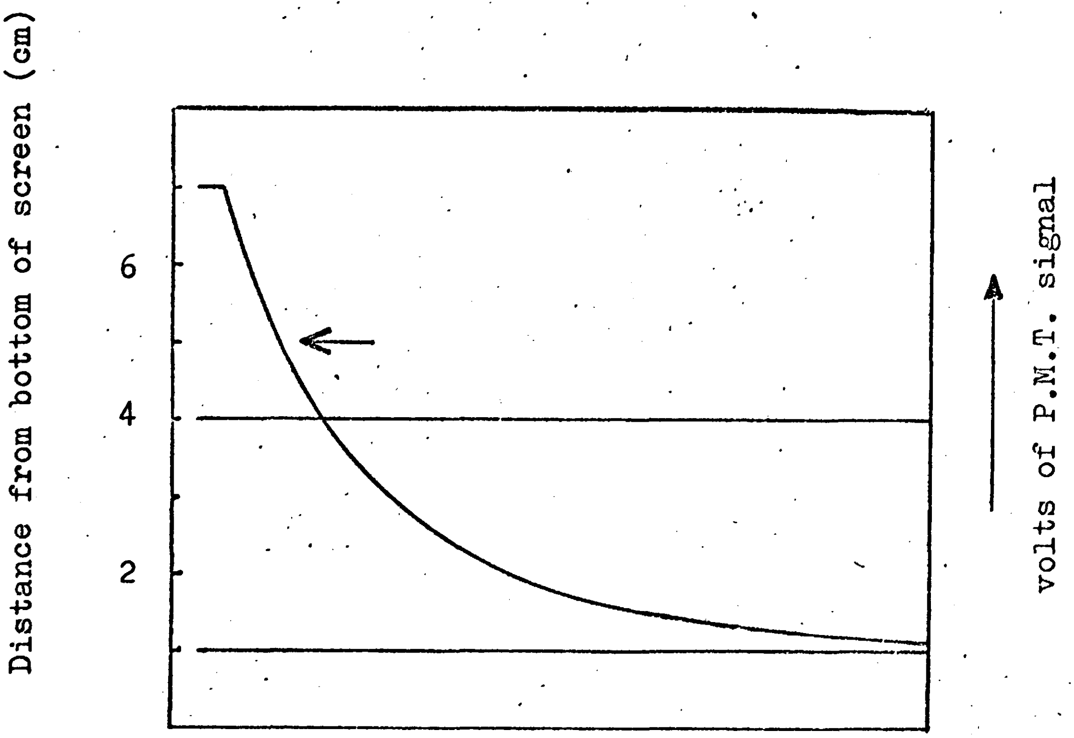
$$\begin{aligned} A_\Omega - A_t &= \log_{10}\frac{I_o}{I_\Omega} - \log_{10}\frac{I_o}{I_t} \\ &= \log_{10}\frac{I_t}{I_\Omega} \\ &= \log_{10}\frac{V_t}{V_\Omega} \\ &= \log_{10} V_t - \log_{10} V_\Omega \end{aligned} \tag{5}$$

An illustration of this procedure is provided by calculation of $\log_e(A_\Omega - A_t)$ for the point marked with an arrow in the hypothetical trace in Fig. 1.7.

$$\begin{aligned} V_{B.O.} &= B.O. \times 0.005575 \\ &= 540 \times 0.005575 \\ &= 3.00 \text{ volts} \end{aligned}$$

Fig. 1.7.

Hypothetical Oscilloscope Trace Representing an Absorbance Increase.



Helipot dial reading = 540

The horizontal line at 4 cm represents the zero setting of the oscilloscope i.e. the display obtained in the absence of any applied signal.

The voltage corresponding to the bottom of the oscilloscope screen i.e. zero cm, V_Z, is calculated by equation (6)

$$V_Z = V_{B.O.} - \Delta V_{B.O.} \tag{6}$$

$$\Delta V_{B.O.} = R_{B.O.} \text{ x GAIN} \tag{7}$$

$$= 4.00 \text{ x } 0.1$$

$$= 0.40 \text{ volts}$$

$$V_Z = 2.60 \text{ volts}$$

$$\Delta V_\Omega = R_\Omega \text{ x GAIN} \tag{8}$$

$$= 1.00 \text{ x } 0.1$$

$$= 0.10 \text{ volts}$$

$$V_\Omega = V_Z + \Delta V_\Omega \tag{9}$$

$$= 2.70 \text{ volts}$$

$$\Delta V_t = R_t \text{ x GAIN} \tag{10}$$

$$= 5.00 \text{ x } 0.1$$

$$= 0.50 \text{ volts}$$

$$V_t = 3.10 \text{ volts}$$

$$\log_{10} V_t - \log_{10} V_o = 0.06$$

$$\log_e (A_\Omega - A_t) = -2.81$$

When using the Tektronix 564 oscilloscope, account was taken of the parallax error which arose from the graticule being fractionally closer to the lens of the camera than was the screen. Thus distances as measured from photographs of traces were somewhat smaller than they actually were. This phenomenon is illustrated in Fig. 1.8. It can easily be shown by the theorem of similar triangles that the necessary correction factor is y/x. This was not, however, directly evaluated in this way. Instead a plot was made of distances between horizontal lines as measured by eye as a function of the corresponding apparent distances as measured from photographs. y/x was found to be 1.032 ± 0.006.

Operational Characteristics of the "Fast" Stopped-Flow Apparatus

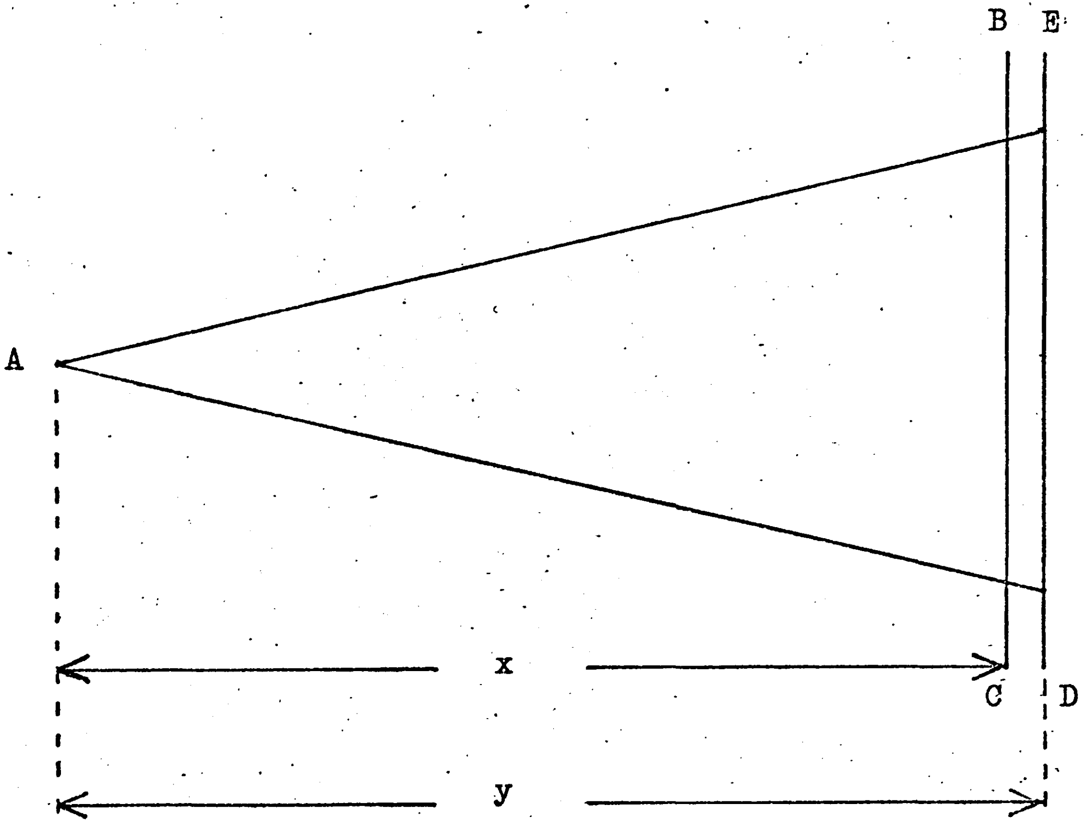
Although it would clearly have been preferable to employ greater gas pressures to drive the pushing-block, it was found that when more than 20 p.s.i. was used the shock caused by the stopping-pin being struck brought about undesirable optical effects in the initial portion of oscilloscope traces. (It is unlikely that these were the result of cavitation since they were also observed when degassed solutions were used.)

In order to observe absorbance changes occurring during a push, and also to measure the flow rate, it was necessary to trigger the oscilloscpe at the start of a push. This was achieved by keeping the microwitch closed while earthing the negative terminal of the switch using a short length of wire which was placed sufficiently precariously that current could flow to the trigger input of the oscilloscope time-base as soon as the pushing-block started to move.

The flow rate at 20 p.s.i. was measured in this

Fig. 1.8.

Illustration of the manner in which error can arise as a result of the graticule not being in the same plane as the oscilloscope display.



A :- Camera aperture
BC :- Graticule
ED :- Oscilloscope screen

manner, using the Fe^{III}/SCN^- reaction to indicate the end of a push. The volume discharged could easily be measured quite accurately from the calibration markings on the reservoir syringes. It was possible to observe the flushing-out of the dead-space. A push-length equivalent to three times the distance between adjacent stopping-pin holes was 4-5 times longer than was necessary for this process and was adopted as standard. The duration of such a push was found to be 200 ms, yielding a flow rate of 15 ± 1.5 ml s^{-1}. To create turbulent flow in a fairly short tube of diameter d cm, the fluid velocity, u, should be greater than (3.2 d) ml s^{-1}. Thus, as indicated by equation (11)

$$d < \frac{u}{3.2} < 5 \text{ cm} \qquad (11)$$

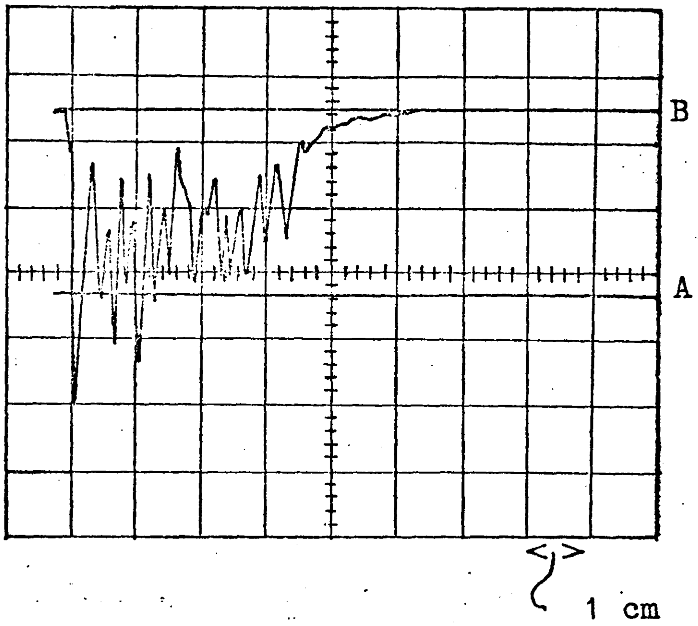
turbulent flow should be present in the "fast" stopped-flow devices used in this work.

Mixing efficiency was tested by the Schlieren method using water and ~8M $NaClO_4$. Fig. 1.9. illustrates the absorbance charges during and after a typical push; a line indicating the transmittance of water is superimposed. It is evident that the multiple refractions which are found for incomplete mixing of liquids of differing refractive index, such as these, were, within 30 ms after stopping, too small to be measurable.

Mixing ratios were determined by pushing a dilute solution of ferroin, $Fe(phen)_3^{2+}$, against water. The resultant optical density was compared with that obtained

Fig. 1.9.

Oscilloscope display of the transmittance changes which occur in the course of a Schlieren test.



Standard three-hole push: duration 200 ms.

Back-off voltage = 2.84

Gain = 0.2 volts/cm

Sweep = 50 msec/cm

Drive pressure = 20 p.s.i.

A = $R_{B.O.}$, the display obtained with no input

B = the transmittance of water

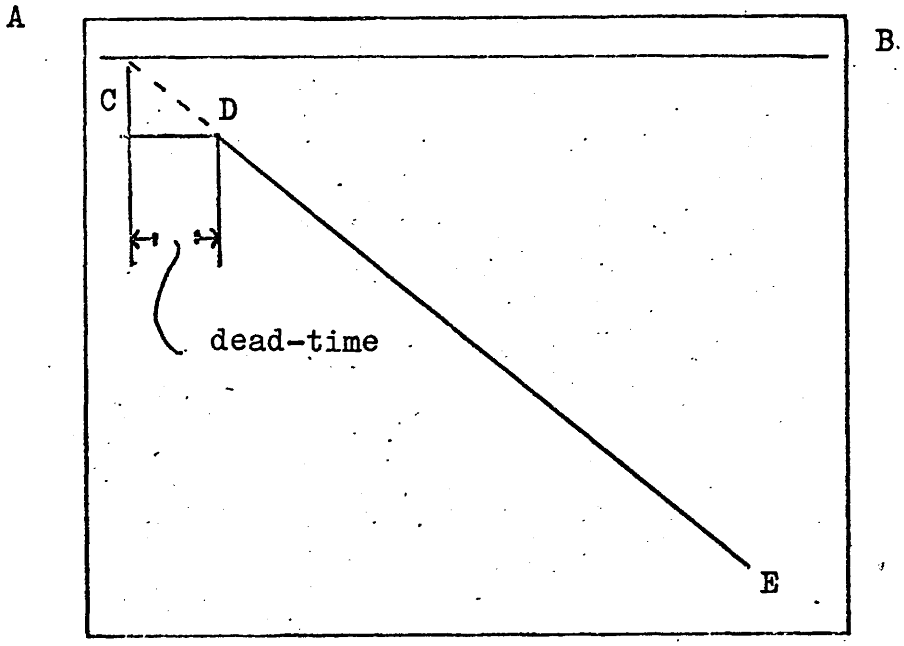
using the alternative mixing configuration and also with that obtained when the same concentration of ferroin was driven from both syringes. Absorbances were measured by evaluating the logarithm of the ratio of the voltage necessary to completely back-off the P.M.T. signal for water to that necessary to do likewise for ferroin. The results, within experimental error, indicated a ratio of 1:1.

The dead-times were measured as indicated schematically in Fig. 1.10. Both Fe^{3+} and NH_4NCS do not absorb at 465 nm when dissolved in 0.2M $HClO_4$. The formation of $FeNCS^{2+}$ was monitored, using excess iron(III) to give a pseudo-first-order absorbance increase.[65] The dead-time is the time through which it was necessary to extrapolate a plot of $\log(A_\Omega - A_t)$ vs. time to reach the value corresponding to $\log A_o$, which was derived from a superimposed water-line corresponding to the zero absorbance of a newly-formed mixture of reactants. The stopped-flow apparatus using the Unicam S.P.500 monochromator was found to have a dead-time of 15 ms, while that of the other was 35 ms.

The mixing ratio of the "slow" stopped-flow apparatus was determined as 1:1 by the method described above. Its dead-time was derived experimentally as 300 ms.

Fig. 1.10

The calculation of the dead-time of a stopped-flow apparatus.



AB represents the transmittance of water

CD represents the transmittance observed at the start of the trace.

DE represents a plot of $\log(A_{\Omega} - A_t)$ versus time.

CHAPTER II

THE COMPLEXATION OF IRON(III) BY SALICYLALDEHYDE AND SALICYLAMIDE

Introduction

Although chelate ring-closure has been found to be rate-determining in a number of complexations of metal-ions by multidentate organic ligands,[37] it nevertheless seems that replacement of the first co-ordinated water molecule is generally slower than subsequent substitution by the remaining donor atoms of the ligand.

Bauer and Smith[106] found a rate constant of 1.44×10^3 $l\ mol^{-1}\ s^{-1}$ for the reaction of Fe^{3+} with $HC_2O_4^-$ to form a chelated monocomplex. They did not detect a hydrogen-ion-independent pathway. After allowance for the outer-sphere association constant, the rate of outer-sphere to inner-sphere interconversion was calculated as $\sim 100\ s^{-1}$. Since this is considerably lower than values of the water-exchange rate constants then available, $(2.4 - 110) \times 10^4\ s^{-1}$, it was concluded that this reaction has some associative character.

Moorhead and Sutin obtained[107] 8.6×10^2 $l\ mol^{-1}\ s^{-1}$ as the rate constant for this same process. In addition, these workers observed a hydrogen-ion-independent rate term which they attributed to reaction of $FeOH^{2+}$ with $HC_2O_4^-$ with a specific rate of 2.0×10^4 $l\ mol^{-1}\ s^{-1}$. Their data were interpreted as supporting the hypothesis that loss of the first bound water molecule is rate-determining in such reactions.

Further evidence in favour of the idea that this dissociative character is common to anation reactions of iron(III) came from results of Gilmour and McAuley[108] concerning the formation of the monocomplex of the bidentate chelating agent, mandelic acid, which yielded rate constants of 2.56 x 10^3 and 5 l mol^{-1} s^{-1} for the reaction of the undissociated ligand with $FeOH^{2+}$ and Fe^{3+} respectively.

Cavasino and Di Dio tested the possibility of rate-determining ring-closure in the formation of six-membered chelate rings formed by malonic acid and various substituted derivatives with iron(III).[109] Employing estimates of the "reasonableness" of possible rate constants in the process of deciding whether the acid-independent term in their experimentally derived rate-law arose from reaction of $FeOH^{2+}$ and H_2A or from that of Fe^{3+} and HA^-, they concluded that interactions of $FeOH^{2+}$ with both H_2A and HA^- were the two important pathways in the overall reaction. The similarity of the rate constants for these processes to those found for other, monodentate, ligands of like charge was used as an argument against the operation of steric control, the rate-determining process being considered to be the loss of the first co-ordinated water molecule.

Sutin and co-workers extended earlier work on the formation of the six-membered chelate rings formed by acetylacetone and thenoyltrifluoroacetone with iron(III).[110] The rate constants for reaction of Fe^{3+} and $FeOH^{2+}$ with the undissociated enol form of the former ligand are 5.2 l mol^{-1} s^{-1} and 4.4 x 10^3 l mol^{-1} s^{-1}. The equivalent parameters for the reaction with the latter ligand are 1.4 l mol^{-1} s^{-1} and 1.3 x 10^3 l mol^{-1} s^{-1}. In both cases the proton ambiguity of the acid-independent path was resolved by consideration of the lack of "reasonableness" of the rate constants ascribed to the hypothetical reaction of Fe^{3+} with the monodissociated ligand. For both systems these were higher than is usual for such reactions, especially in the case of acetylacetone. The rate constants quoted above are not atypical for such reactions, but the values of 0.29 and 5.4 l mol^{-1} s^{-1} for the reaction of Fe^{3+} and $FeOH^{2+}$ respectively with the keto form of acetylacetone are anomalously low. This has been taken to show that in this case water-loss is not rate-determining. Instead, the mechanism was believed to be one analogous to that postulated for the corresponding reaction involving Cu(II) which was mentioned in the General Introduction viz. protonation of an otherwise fully formed complex.[76]

In order to extend the range of basicities of anionic ligands used in kinetic studies of anations of iron(III), Cavasino and Di Dio investigated rates of its complexation by various monosubstituted phenols.[111] They found that the sole pathway in these reactions involves $FeOH^{2+}$ and the undissociated ligand. The alternative interpretation of the observed hydrogen-ion-independence of the rate, that reaction takes place to at least some extent by way of interaction of Fe^{3+} with the monodissociated phenol, led to the unlikely result for phenol and m-cresol that this latter process is diffusion-controlled with a specific rate of the order of 10^{10} l mol^{-1} s^{-1}.

Tsuchida and co-workers, extending the acidity range of this last study, confirmed[112] the absence of any hydrogen-ion dependence of rates of reaction of iron(III) with phenols, (HL). At 25° and I = 1.0M, the rate constants for reaction of HL with $FeOH^{2+}$ were all very close to 10^3 l mol^{-1} s^{-1}.

The reaction of iron(III) with p-nitrophenol was reinvestigated by Tamura.[113] He recalculated earlier data on the kinetics of formation of iron(III) complexes of monosubstituted phenols and confirmed that the only operative reaction pathway involves substitution of the undissociated ligand at $FeOH^{2+}$. He also drew attention to the seemingly anomalously low values of rate constants for such processes at 25° ($\sim 10^3$ l mol^{-1} s^{-1}) compared with those for corresponding reactions involving other uncharged organic ligands ($2.56 - 7.4 \times 10^3$) l mol^{-1} s^{-1} at 20-25°C.

A stopped-flow kinetic study has been made of the complexations of iron(III) by phenol and o-aminophenol.[75] Acid-independent pathways were unambiguously attributable to the reaction of $FeOH^{2+}$ with the undissociated ligand; in both cases the alternative formulation required that reaction of $Fe(H_2O)_6^{3+}$ with L^- proceeds with a specific rate in excess of the diffusion-controlled limit for a bimolecular reaction by between one and two orders of magnitude. Fe^{3+} was observed to react with undissociated phenol with a rate constant of 25 l mol^{-1} s^{-1}. The rate constant for the reaction of $FeOH^{2+}$ with this species was determined as 720 l mol^{-1} s^{-1}. $FeOH^{2+}$ and undissociated neutral aminophenol were found to react with a specific rate of 1.1×10^5 l mol^{-1} s^{-1}. These authors also drew attention to the fact that rates of outer-sphere to inner-sphere interconversion in reactions of Fe^{3+} with L^- are generally of the order of 10^1 s^{-1} and that this route will hence be negligible with ligands which are mostly protonated in acid solutions.

In their investigations of iron(III) complexation kinetics, Mentasti and co-workers have used a number of bidentate substituted phenols.[114-116].

Iron(III) and o-dihydroxybenzene form a bidentate chelate complex which has a five-membered ring. These authors concluded from a study of this system[114] that formation of this species takes place exclusively by way of reaction of $FeOH^{2+}$ with the undissociated ligand, H_2L, with a specific rate of 3.1×10^3 l mol^{-1} s^{-1} at 25°C. This was interpreted as indicative of an I_d mechanism with ring-closure playing no part in limiting the rate.

The monosalicylato chelate complex of iron(III) has been studied kinetically by both Mentasti and co-workers[115] and Fogg and Hall.[117] The former group observed a minimum in a plot of their rate parameters as a function of $[H^+]^{-1}$. This enabled them to derive the rate constants for three pathways. Those for reaction of Fe^{3+} and $FeOH^{2+}$ with the undissociated ligand, H_2Sal, at 25°C were determined as 3.0 and 5.5×10^3 l mol^{-1} s^{-1}

respectively. Reaction of $FeOH^{2+}$ with $HSal^-$ was found to proceed with a specific rate of 1.4×10^4 l mol^{-1} s^{-1}. The corresponding parameters with sulphosalicylic acid, where H_2Sal is equivalent to H_2SS^- and $HSal^-$ to HSS^{2-}, were found to be extremely close to these values. This was taken to indicate that charge effects arising from the non-interacting ionised sulphonate group are not important in determining the magnitude of the outer-sphere association constant. Consequently, no correction was made for this parameter but it was agreed that the results of this work were consistent with dissociative character in the substitution mechanism.

Fogg and Hall found[117] $FeOH^{2+}$ to react with undissociated salicylic acid with a specific rate of 2.9×10^3 l mol^{-1} s^{-1}. The corresponding value for sulphosalicylic acid, H_2SS^-, was 5.7×10^3 l mol^{-1} s^{-1}. This latter figure is in good agreement with that obtained by Saini and Mentasti for the same process.[116] The reaction of $FeOH^{2+}$ with either $HSal^-$ or HSS^{2-} was not detected[117] in the acidity range employed in this investigation, nor was reaction of Fe^{3+} with either H_2Sal or H_2SS^-.

However, with salicylaldehyde which, like both these compounds, is a possible bidentate chelating ligand, reaction of Fe^{3+} with the undissociated molecule was observed[117] to occur with a rate constant of 24.6 l mol^{-1} s^{-1} at 25°C. The rate constant for the reaction of $FeOH^{2+}$ with the same ligand was found to be 6.5×10^2 l mol^{-1} s^{-1}.

In this chapter, data will be presented on the reactions of iron(III) with salicylaldehyde and salicylamide in aqueous perchloric acid media. This latter ligand is also believed to form a bidentate monochelate with iron(III) in the conditions employed in this work, with the amide group bonding through oxygen rather than nitrogen.[118]

In some experiments concerning the reaction of iron(III) with salicylamide, lithium perchlorate was used instead of sodium perchlorate as the background electrolyte. It is known that many "hydrogen-ion dependences" are in fact a direct consequence of a lack of constancy in the ionic strength when Na^+ is substituted by H^+ at appreciable concentrations of H^+.[119-121] This is a result of a significant difference in the activity coefficients of both these species. Li^+ appears to have an activity coefficient much closer to H^+ than does Na^+.

Experimental

Iron(III) perchlorate was prepared as follows :- Ferric nitrate (Hopkin and Williams, General Purpose Reagent), dissolved in water, was brought to pH7 by dropwise addition of aqueous ammonia (B.D.H., AnalaR). After the resultant precipitate of iron(III) hydroxide had settled, the supernatant liquid was siphoned off with the aid of a water suction-pump. This precipitate was then washed with water which was in turn siphoned off. This last process was repeated until the supernatant liquid was found to be of neutral pH whereupon siphoning was followed by dissolution of the hydroxide in concentrated perchloric acid (Hopkin and Williams, AnalaR). The solution was then heated until crystallisation began. The iron(III) perchlorate filtered from the cooled solution was recrystallised from concentrated AnalaR perchloric acid. The final crystals were sucked dry in a glass sintered filter to remove as much perchloric acid as possible.

The iron(III) content of stock solutions was determined by reduction to iron(II) and titration with $KMnO_4$ solution which was prepared and standardised as described previously.[122a] Reduction was achieved using tin(II) chloride or a Jones reductor.[122b,c]

The acid content of stock solutions of iron(III) perchlorate was determined by titration of hot solutions with freshly prepared 0.1M sodium hydroxide (Hopkin and Williams, Convol) which had been standardised using potassium hydrogen phthalate,[122d] (Hopkin and Williams, AnalaR). Once coagulation of iron(III) hydroxide occurred, phenolphthalein was added and the titration continued. In the calculation of the hydrogen-ion concentration, allowance was made for the quantity of NaOH necessary to form $Fe(OH)_3$.

Stock solutions of perchloric acid were standardised by titration against disodium tetraborate (Hopkin and Williams, AnalaR). Stock solutions of sodium perchlorate (Fluka, puriss p.a.), which were used to adjust the ionic strength to 1.00M, were standardised by evaporation of known volumes and weighing the resultant anhydrous solid.

Lithium perchlorate was prepared by slow addition of anhydrous $LiCO_3$ (Hopkins and Williams, Reagent Grade) to AnalaR concentrated perchloric acid at 80°C. The pH was then adjusted to pH 5.5 by addition of the necessary quantity of either of these reagents. The hot solution was filtered and cooled slowly to 0°C. The isolated solid was recrystallised three times from distilled water. Appropriate chemical spot tests demonstrated the absence of significant concentrations of chloride or sulphate. Stock solutions of $LiClO_4$ were standardised either by the same procedure as that used for $NaClO_4$ or by titration, with standard base, of the eluent of a cation exchange column in the hydrogen-ion form which had been charged with a known volume of a stock solution. Both methods yielded identical results.

Salicylaldehyde was purified by distillation at reduced pressure.

Some experiments were attempted using as ligands Schiff bases derived from salicylaldehyde and either 1,2-diaminoethane or 1,3-diaminopropane. These compounds were prepared in ethanol, recrystallised from that solvent, and dissolved initially in sodium hydroxide before being adjusted to the required hydrogen-ion concentration. Spectrophotometric and kinetic results with these ligands were identical to those obtained with salicylaldehyde. Thus it would appear that hydrolysis of the Schiff bases was occurring rapidly, as has been observed previously for similar species.[123,124] The presence of appreciable quantities of amine did not appear to lead to any measurable reaction with iron(III).

Salicylamide was recrystallised from ethanol. Hydrolysis of this ligand could be justifiably neglected at the temperatures and perchloric acid concentrations employed in this work.[125]

The gas-driven stopped-flow devices described in the previous chapter were used to study the complexations of iron(III) by salicylaldehyde and salicylamide. In the former case 540 nm was chosen as the wavelength at which to monitor the reaction; in the latter case 550 nm was used. Neither the metal-ion nor these ligands absorb to any measurable extent at these wavelengths, both of which are very close to the absorption maxima of the purple complexes, 550 and 525 nm respectively; see Fig. 2.1.

An excess of iron(III) was used to minimise formation of higher complexes; no evidence has been found for the existence of such species[126] under the conditions used in this work. Log $(A_{\Omega}-A_{t})$ was found to be a linear function of time to greater than 90% reaction. Reactant solutions were allowed to equilibrate at the required temperature for at least thirty minutes.

Results and Discussion

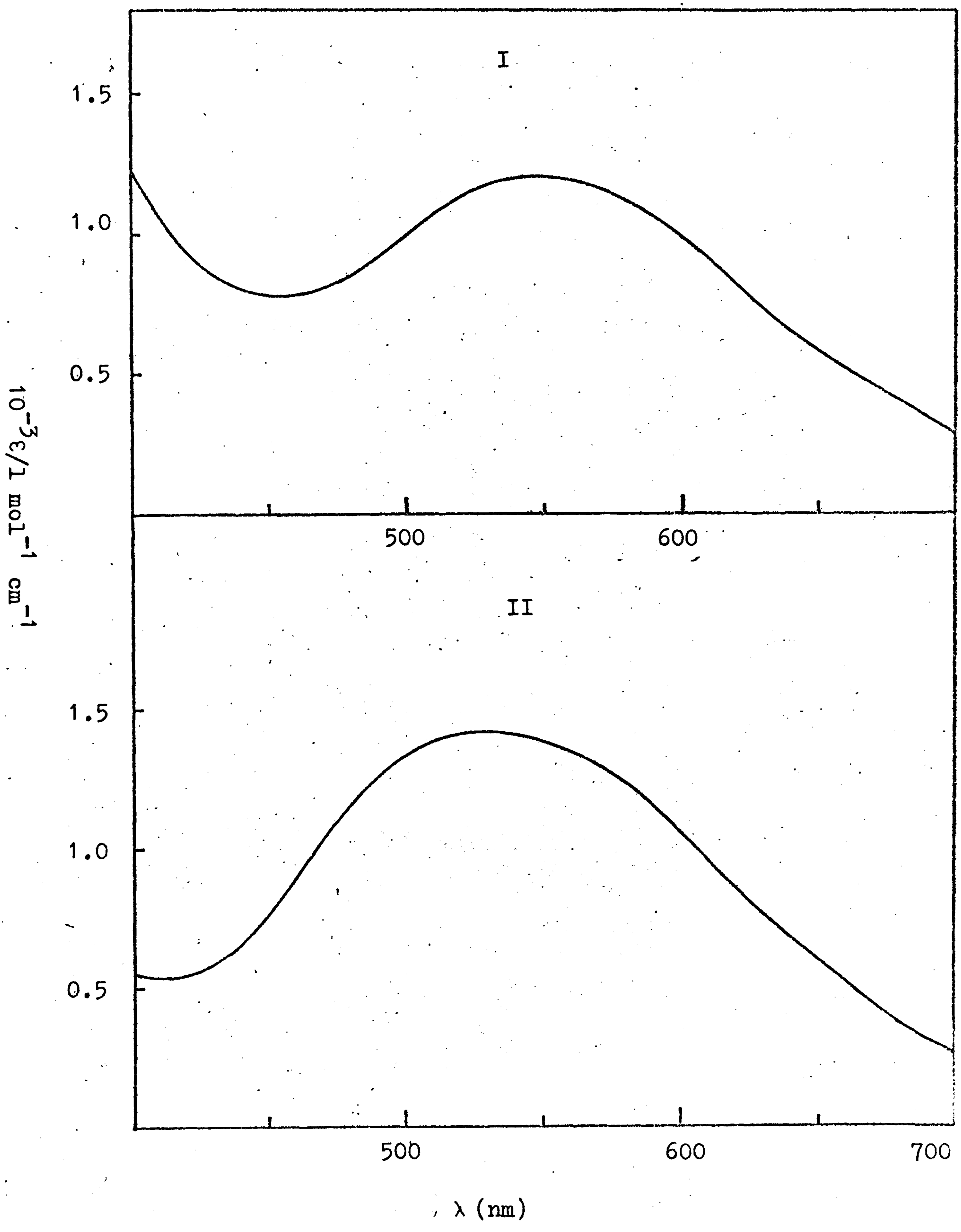
(a) Iron(III) and Salicylaldehyde

Previous studies[69,126] have shown that under the

Fig. 2.1.

Spectra of FeL^{2+} complexes

I : L = Salicylaldehyde; II : L = salicylamide



conditions employed in this investigation the important equilibria in this system are given by equations (1)-(3).

$$Fe^{3+} \rightleftharpoons FeOH^{2+} + H^{+} \qquad K_h \qquad (1)$$

$$HL \rightleftharpoons H^{+} + L^{-} \qquad K_a \qquad (2)$$

$$Fe^{3+} + HL \rightleftharpoons FeL^{2+} + H^{+} \qquad K \qquad (3)$$

Co-ordinated water molecules are not indicated since their inclusion in the text is unnecessary and because of the greater clarity obtained by omitting them.

Four possible routes to FeL^{2+} can be envisaged,

$$Fe^{3+} + L^{-} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} FeL^{2+} \qquad (4)$$

$$FeOH^{2+} + HL \underset{k_{46}}{\overset{k_{64}}{\rightleftharpoons}} Fe(OH)HL^{2+} \qquad (5)$$

$$Fe^{3+} + HL \underset{k_{25}}{\overset{k_{52}}{\rightleftharpoons}} FeHL^{3+} \qquad (6)$$

$$FeOH^{2+} + L^{-} \underset{k_{43}}{\overset{k_{34}}{\rightleftharpoons}} Fe(OH)L^{+} \qquad (7)$$

with protolytic equilibria interrelating the various immediate products as defined in equations (8)-(11).

$$K'_h = \frac{[H^{+}][Fe(OH)L^{+}]}{[FeL^{2+}]} \qquad (8)$$

$$K'_a = \frac{[H^+][FeL^{2+}]}{[FeHL^{3+}]} \qquad (9)$$

$$K''_h = \frac{[H^+][Fe(OH)HL^{2+}]}{[FeHL^{3+}]} \qquad (10)$$

$$K''_a = \frac{[H^+][Fe(OH)L^+]}{[Fe(OH)HL^{2+}]} \qquad (11)$$

Assuming that establishment of these equilibria is much faster than the substitution processes involved, the rate of complex formation is given by equation (12)

$$\frac{d(FeL^{2+})}{dt} = k_{12}(Fe^{3+})(L^-) - k_{21}(FeL^{2+}) + k_{64}(FeOH^{2+})(HL) - k_{46}(Fe(OH)HL^{2+}) + k_{52}(Fe^{3+})(HL) - k_{25}(FeHL^{3+}) + k_{34}(FeOH^{2+})(L^-) - k_{43}(Fe(OH)L^+) \qquad (12)$$

Curved brackets indicate instantaneous concentrations, whereas square brackets denote equilibrium concentrations. At equilibrium

$$\frac{d[FeL^{2+}]}{dt} = 0 \qquad (13)$$

Hence,

$$k_{21}[FeL^{2+}] = k_{12}[Fe^{3+}][L^-] + k_{64}[FeOH^{2+}][HL] - k_{46}[Fe(OH)HL^{2+}] + k_{52}[Fe^{3+}][HL] - k_{25}[FeHL^{3+}] + k_{34}[FeOH^{2+}][L^-] - k_{43}[Fe(OH)L^+] \qquad (14)$$

Also, under the conditions employed in this work,

$(H^+) = [H^+]$, $(Fe^{3+}) = [Fe^{3+}]$ and $(FeOH^{2+}) = [FeOH^{2+}]$

Thus, substituting for k_{21} in equation (12)

$$\begin{aligned}
\text{Rate} = {} & k_{12}[\mathrm{Fe}^{3+}](\mathrm{L}^-) - k_{12}\frac{(\mathrm{FeL}^{2+})}{[\mathrm{FeL}^{2+}]}[\mathrm{Fe}^{3+}][\mathrm{L}^-] - \\
& k_{64}\frac{(\mathrm{FeL}^{2+})}{[\mathrm{FeL}^{2+}]}[\mathrm{FeOH}^{2+}][\mathrm{HL}] + k_{46}\frac{(\mathrm{FeL}^{2+})}{[\mathrm{FeL}^{2+}]}[\mathrm{Fe(OH)HL}^{2+}] - \\
& k_{52}\frac{(\mathrm{FeL}^{2+})}{[\mathrm{FeL}^{2+}]}[\mathrm{Fe}^{3+}][\mathrm{HL}] + k_{25}\frac{(\mathrm{FeL}^{2+})}{[\mathrm{FeL}^{2+}]}[\mathrm{FeHL}^{3+}] - k_{34}\frac{(\mathrm{FeL}^{2+})}{[\mathrm{FeL}^{2+}]} \\
& [\mathrm{FeOH}^{2+}][\mathrm{L}^-] + k_{43}\frac{(\mathrm{FeL}^{2+})}{[\mathrm{FeL}^{2+}]}[\mathrm{Fe(OH)L}^+] + k_{64}[\mathrm{FeOH}^{2+}](\mathrm{HL}) - \\
& k_{46}(\mathrm{Fe(OH)HL}^{2+}) + k_{52}[\mathrm{Fe}^{3+}](\mathrm{HL}) - k_{25}(\mathrm{FeHL}^{3+}) + k_{34}[\mathrm{FeOH}^{2+}](\mathrm{L}^-) - \\
& k_{43}(\mathrm{Fe(OH)L}^+) \qquad (15)
\end{aligned}$$

Using the equilibrium constants implicit in equations (1)-(3), and also equations (8)-(10), equation (16) can be derived.

$$\begin{aligned}
\frac{d(\mathrm{FeL}^{2+})}{dt} = {} & \frac{k_{12}K_a}{[\mathrm{H}^+]}[\mathrm{Fe}^{3+}](\mathrm{HL}) - k_{12}\frac{K_a}{K}(\mathrm{FeL}^{2+}) - \\
& k_{64}\frac{K_h}{K}(\mathrm{FeL}^{2+}) + k_{46}\frac{K''_h}{K'_a}(\mathrm{FeL}^{2+}) - k_{52}\frac{[\mathrm{H}^+]}{K}(\mathrm{FeL}^{2+}) + k_{25}\frac{[\mathrm{H}^+]}{K'_a}(\mathrm{FeL}^{2+}) - \\
& k_{34}\frac{K_aK_h}{[\mathrm{H}^+]^2}\frac{[\mathrm{Fe}^{3+}][\mathrm{HL}]}{[\mathrm{FeL}^{2+}]}(\mathrm{FeL}^{2+}) + k_{43}\frac{K'_h}{[\mathrm{H}^+]}(\mathrm{FeL}^{2+}) + k_{64}\frac{K_h}{[\mathrm{H}^+]}[\mathrm{Fe}^{3+}](\mathrm{HL}) - \\
& k_{46}\frac{K''_h}{K'_a}(\mathrm{FeL}^{2+}) + k_{52}[\mathrm{Fe}^{3+}](\mathrm{HL}) - k_{25}\frac{[\mathrm{H}^+]}{K'_a}(\mathrm{FeL}^{2+}) + \\
& k_{34}\frac{K_hK_a}{[\mathrm{H}^+]^2}[\mathrm{Fe}^{3+}](\mathrm{HL}) - k_{43}\frac{K'_h}{[\mathrm{H}^+]}(\mathrm{FeL}^{2+}) \qquad (16)
\end{aligned}$$

It can readily be seen by inspection that terms involving K'_h, K'_a, K''_h cancel each other. Assuming that $L^- \ll HL$, which is valid in the $[H^+]$ range 0.25 - 0.60M for an acid such as salicylaldehyde having a $pK > 8$,[127] and that the other protolytic isomers of FeL^{2+} are maintained at a negligibly low steady state concentration compared with FeL^{2+} itself, the mass balance relationship (17) holds.

$$(HL) = [HL] + [FeL] - (FeL) \qquad (17)$$

It should be noted that the existence of a great excess of HL over L^- does not directly eliminate the possibility of L^- being kinetically significant since it is conceivable, though unlikely , that HL could in fact react much faster than L^-.

Thus
$$\frac{d(FeL^{2+})}{dt} = k_{12}\frac{K_a\,[Fe^{3+}][HL]}{[H^+]} + \frac{k_{12}K_a[Fe^{3+}][FeL^{2+}]}{[H^+]} -$$

$$\frac{k_{12}K_a[Fe^{3+}](FeL^{2+})}{[H^+]} - k_{12}\frac{K_a}{K}(FeL^{2+}) + \frac{k_{64}K_h[Fe^{3+}][HL]}{[H^+]} +$$

$$\frac{k_{64}K_h[Fe^{3+}][FeL^{2+}]}{[H^+]} + \frac{k_{64}K_h[Fe^{3+}](FeL^{2+})}{[H^+]} - k_{64}\frac{K_h}{K}(FeL^{2+}) +$$

$$k_{52}[Fe^{3+}][HL] + k_{52}[Fe^{3+}][FeL^{2+}] - k_{52}[Fe^{3+}](FeL^{2+}) -$$

$$\frac{k_{52}[H^+](FeL^{2+})}{K} + \frac{k_{34}K_hK_a[Fe^{3+}][HL]}{[H^+]^2} + \frac{k_{34}K_hK_a[Fe^{3+}][FeL^{2+}]}{[H^+]^2} -$$

$$\frac{k_{34}K_hK_a[Fe^{3+}](FeL^{2+})}{[H^+]^2} - \frac{k_{34}K_hK_a[Fe^{3+}][HL](FeL^{2+})}{[H^+]^2[FeL^{2+}]} \qquad (18)$$

i.e.

$$\frac{d(\mathrm{FeL}^{2+})}{dt} = \left\{\left(\frac{k_{12}K_a}{[H^+]} + \frac{k_{64}K_h}{[H^+]} + k_{52} + \frac{k_{34}K_hK_a}{[H^+]^2}\right)[\mathrm{Fe}^{3+}] + \right.$$

$$\left.\left(k_{12}K_a + k_{64}K_h + k_{52}[H^+] + k_{34}\frac{K_hK_a}{[H^+]}\right)\left(\frac{1}{K}\right)\right\}\left\{[\mathrm{FeL}^{2+}] - (\mathrm{FeL}^{2+})\right\} \qquad (19)$$

Equation (19) can be expressed in the form shown in equation (20).

$$\frac{d(\mathrm{FeL}^{2+})}{dt} = k_{obs}\left\{[\mathrm{FeL}^{2+}] - (\mathrm{FeL}^{2+})\right\} \qquad (20)$$

Integration of (20) leads to (21).

$$\log_e\left\{[\mathrm{FeL}^{2+}] - (\mathrm{FeL}^{2+})\right\} = k_{obs.}t \qquad (21)$$

In the situation which holds in this study, whereby only FeL^{2+} absorbs to any measurable extent at the monitoring wavelength employed, (21) can readily be equated to (22).

$$\log_e(A_{\Omega}-A_t) = k_{obs.}t \qquad (22)$$

Plots of the L.H.S. of equation (22) as a function of time yield a slope of k_{obs} which can be expressed as in equation (23), assuming all pathways (4)-(7) to be operative.

$$k_{obs} = \left(\frac{k_{12}K_a}{[H^+]} + \frac{k_{64}K_h}{[H^+]} + k_{52} + \frac{k_{34}K_hK_a}{[H^+]^2}\right)[Fe^{3+}] +$$

$$\left(k_{12}K_a + k_{64}K_h + k_{52}[H^+] + \frac{k_{34}K_hK_a}{[H^+]}\right)\left(\frac{1}{K}\right) \quad (23)$$

Plots of k_{obs} against $[Fe^{3+}]$ are thus expected to be linear, with slopes and intercepts being given by equations (24) and (25).

$$\text{Slope} = \frac{k_{12}K_a}{[H^+]} + \frac{k_{64}K_h}{[H^+]} + k_{52} + \frac{k_{34}K_hK_a}{[H^+]^2} \quad (24)$$

$$\text{Int} = \frac{1}{K}\left(k_{12}K_a + k_{64}K_h + k_{52}[H^+] + \frac{k_{34}K_hK_a}{[H^+]}\right) \quad (25)$$

The variation of k_{obs} with reagent concentrations is given in Table 2.1. While such kinetic behaviour was indeed found for this system, the low value of K resulted in the slopes of these latter plots being negligible. It was possible to determine the intercepts quite precisely but since these were expected to be similar in general form to equation (25), it was desirable to obtain accurate values of K at the temperatures and ionic strength used in this study. The only values available were for an ionic strength of 3M.[126]

Examination of spectrophotometric data collected in the course of the kinetic experiments showed that A_Ω was directly proportional to [Fe(III)], the reagent in excess. Graphical methods of the type used by Benesi and Hildebrand[128] were, as a consequence, unsuitable for

Table 2.1.

Kinetic, Spectrophotometric and Equilibrium Data Concerning the Reaction of Iron(III) with Salicylaldehyde at Unit Ionic Strength and λ = 540 nm.

$T = 12.3^{o}C$

$[H^+]$/M	10^3[Fe(III)]/M	10^3[Scde*]/M	k_{obs}/s^{-1}	$A_{\Omega}{}^{a}$	K^b
0.200^c	2.821	1.814	0.758	0.0139	0.925
0.200^c	4.937	1.814	0.738	0.0247	0.948
0.200^c	7.053	1.814	0.723	0.0349	0.948
0.200^c	8.463	1.814	0.743	0.0416	0.947
0.200^c	11.28	1.814	0.788	0.0551	0.952
0.200^c	14.11	1.814	0.794	0.0665	0.930
0.200	2.821	1.794	0.763	0.0138	0.929
0.200	4.937	1.794	0.715	0.0249	0.967
0.200	7.053	1.794	0.718	0.0358	0.984
0.200	8.463	1.794	0.746	0.0412	0.949
0.200	11.28	1.794	0.735	0.0545	0.952
0.200	14.11	1.794	0.770	0.0622	0.876
0.300	2.821	2.245	0.833	0.0117	0.941
0.300	4.937	2.245	0.835	0.0201	0.925
0.300	7.053	2.245	0.770	0.0297	0.962
0.300	8.463	2.245	0.766	0.0357	0.972
0.300	11.28	2.245	0.813	0.0454	0.932
0.300	14.11	2.245	0.920	0.0588	0.977
0.300	2.821	2.966	0.732	0.0167	0.982
0.300	4.937	2.966	0.793	0.0308	1.08
0.300	11.28	2.966	0.764	0.0710	1.11
0.300	14.11	2.966	0.760	0.0929	1.18
0.400	2.821	2.681	0.880	0.0105	0.936
0.400	4.937	2.681	0.778	0.0179	0.915
0.400	7.053	2.681	0.900	0.0252	0.907
0.400	8.463	2.681	0.940	0.0298	0.897
0.400	11.28	2.681	0.903	0.0401	0.909
0.400	14.11	2.681	0.868	0.0498	0.911

$T = 12.3^{o}C$

$[H^+]/M$	$10^3[Fe(III)]/M$	$10^3[Scde\ ]/M$	k_{obs}/s^{-1}	A_{Ω}	K^b
0.450^c	2.821	3.005	0.905	0.0096	0.859
0.450^c	4.937	3.005	0.888	0.0171	0.877
0.450^c	7.053	3.005	0.839	0.0248	0.895
0.450^c	8.463	3.005	0.876	0.0297	0.896
0.450^c	11.28	3.005	0.855	0.0385	0.874
0.450^c	14.11	3.005	0.941	0.0478	0.874
0.500	2.821	3.621	0.879	0.0096	0.788
0.500	4.937	3.621	1.06	0.0171	0.806
0.500	7.053	3.621	0.969	0.0267	0.888
0.500	8.463	3.621	0.888	0.0320	0.889
0.500	11.28	3.621	0.920	0.0425	0.888
0.500	14.11	3.621	0.929	0.0522	0.878
0.500^d	2.821	3.210	0.915	0.0093	0.859
0.500^d	4.937	3.210	0.903	0.0164	0.873
0.500^d	7.053	3.210	0.890	0.0233	0.875
0.500^d	8.463	3.210	0.908	0.0286	0.897
0.500^d	11.28	3.210	0.955	0.0372	0.877
0.500^d	14.11	3.210	0.895	0.0457	0.867
0.600	2.821	2.842	0.980	0.0064	0.810
0.600	4.937	2.842	0.938	0.0123	0.886
0.600	7.053	2.842	0.900	0.0180	0.912
0.600	8.463	2.842	1.05	0.0197	0.832
0.600	11.28	2.842	0.921	0.0279	0.887
0.600	14.11	2.842	0.984	0.0314	0.801
0.600	2.821	3.186	0.900	0.0080	0.902
0.600	4.937	3.186	0.910	0.0140	0.903
0.600	11.28	3.186	0.940	0.0326	0.925
0.600	14.10	3.186	0.925	0.0397	0.906

T = 25.0°C

$[H^+]$/M	10^3[Fe(III)]/M	10^3[Scde]/M	k_{obs}/s^{-1}	A_Ω	K^b
0.300	2.821	2.828	2.76	0.0191	1.22
0.300	4.937	2.828	2.83	0.0336	1.24
0.300	7.053	2.828	2.80	0.0491	1.28
0.300	8.463	2.828	2.79	0.0575	1.26
0.300	11.28	2.828	2.61	0.0719	1.19
0.300	14.11	2.828	2.87	0.0996	1.34
0.300	4.576	2.922	2.71	0.0319	1.23
0.300	9.152	2.922	2.67	0.0627	1.23
0.300	13.73	2.922	2.89	0.0938	1.25
0.300	18.30	2.922	2.99	0.1216	1.24
0.300	22.88	2.922	2.93	0.153	1.26
0.300	27.46	2.922	3.01	0.179	1.26
0.300	4.576	3.322	2.69	0.0308	1.04
0.300	9.152	3.322	2.89	0.0612	1.05
0.300	13.73	3.322	2.79	0.0943	1.10
0.300	18.30	3.322	2.99	0.122	1.09
0.300	22.88	3.322	2.88	0.152	1.10
0.300	27.46	3.322	3.12	0.179	1.09
0.350	2.821	2.970	2.89	0.0152	1.08
0.350	4.937	2.970	2.85	0.0266	1.08
0.350	7.053	2.970	2.83	0.0371	1.06
0.350	8.463	2.970	2.89	0.0459	1.10
0.350	11.28	2.970	2.96	0.0587	1.06
0.350	14.11	2.970	2.93	0.0687	1.00
0.400	2.288	6.234	2.94	0.0249	1.19
0.400	9.152	6.234	3.08	0.0980	1.20
0.400	18.30	6.234	3.18	0.196	1.23
0.400	27.46	6.234	3.19	0.296	1.28
0.400	45.76	6.234	3.31	0.475	1.29
0.400	4.576	4.880	3.00	0.0349	1.07
0.400	9.152	4.880	2.94	0.0713	1.11
0.400	13.73	4.880	3.06	0.106	1.11
0.400	18.30	4.880	3.12	0.142	1.12
0.400	22.88	4.880	3.00	0.171	1.11
0.400	27.46	4.880	3.23	0.209	1.13

T = 25.0°C

$[H^+]$/M	10^3[Fe(III)]/M	10^3[Scde]/M	k_{obs}/s^{-1}	A_Ω	K^b
0.500	2.821	2.994	3.19	0.0112	1.11
0.500	4.937	2.994	3.14	0.0190	1.09
0.500	7.053	2.994	3.46	0.0266	1.07
0.500	8.463	2.994	3.23	0.0333	1.12
0.500	11.28	2.994	3.25	0.0439	1.12
0.500	14.11	2.994	3.32	0.0541	1.11
0.500	2.288	4.934	2.94	0.0154	1.16
0.500	4.576	4.934	2.96	0.0294	1.11
0.500	6.865	4.934	3.24	0.0433	1.10
0.500	9.152	4.934	3.22	0.0574	1.09
0.500	11.44	4.934	3.22	0.0724	1.12
0.500	13.73	4.934	3.12	0.0911	1.16
0.600	4.576	5.564	3.49	0.0221	0.882
0.600	9.152	5.564	3.28	0.0454	0.910
0.600	13.73	5.564	3.53	0.0678	0.914
0.600	16.02	5.564	3.40	0.0774	0.896
0.600	22.88	5.564	3.47	0.110	0.901
0.600	2.288	4.934	2.68	0.0132	1.19
0.600	4.576	4.934	3.39	0.0494	1.12
0.600	13.73	4.934	3.45	0.0704	1.08
0.600	22.88	4.934	3.53	0.121	1.13

$T = 30.5^{o}C$

$[H^+]/M$	$10^3[Fe(III)]/M$	$10^3[Scde\ ]/M$	k_{obs}/s^{-1}	A_Ω	K^b
0.200	2.821	2.832	3.83	0.0286	1.24
0.200	4.937	2.832	3.80	0.0484	1.21
0.200	7.053	2.832	3.94	0.0732	1.30
0.200	14.11	2.832	4.34	0.149	1.39
0.300	2.821	2.804	3.84	0.0186	1.20
0.300	4.937	2.804	4.35	0.0307	1.14
0.300	7.053	2.804	4.66	0.0442	1.16
0.300	8.463	2.804	4.74	0.0527	1.16
0.300	11.28	2.804	4.45	0.0631	1.04
0.300	14.11	2.804	4.68	0.0801	1.07
0.300	14.11	3.262	4.45	0.1023	1.19
0.400	2.821	2.859	4.24	0.0135	1.13
0.400	4.937	2.859	4.03	0.0234	1.13
0.400	7.053	2.859	4.50	0.0308	1.04
0.400	8.463	2.859	4.51	0.0391	1.11
0.400	11.28	2.859	4.30	0.0444	0.946
0.400	14.11	2.859	4.38	0.0535	0.920
0.400	11.28	3.078	4.58	0.0580	1.16
0.400	14.11	3.078	4.50	0.0727	1.17
0.500	2.821	2.954	4.97	0.0111	1.12
0.500	4.937	2.954	5.04	0.0185	1.07
0.500	7.053	2.954	5.18	0.0254	1.04
0.500	8.463	2.954	4.59	0.0322	1.10
0.500	11.28	2.954	4.58	0.0402	1.03
0.500	14.11	2.954	4.91	0.0480	0.994
0.600	2.821	2.968	4.15	0.0087	1.05
0.600	4.937	2.968	4.62	0.0156	1.08
0.600	7.053	2.968	4.61	0.0212	1.03
0.600	8.463	2.968	4.89	0.0236	0.956
0.600	11.28	2.968	4.75	0.0349	1.07
0.600	14.11	2.968	5.12	0.0410	1.01

*Scde = Salicylaldehyde

(a) A_{Ω} = absorbance of reactant solution at equilibrium; optical path length = 0.5 cm.

(b) $K = \frac{[FeL^{2+}][H^+]}{[Fe^{3+}][HL]}$ with $[FeL^{2+}]$ evaluated as

$$\frac{A_{\Omega}}{1200 \times 0.5}$$

(c) $T = 12.0^\circ C$.

(d) $T = 12.1^\circ C$.

evaluation of K from these results.

It was noted, however, that Agren obtained good agreement between spectrophotometric and kinetic determinations of K using an extinction coefficient of 1200 l mol^{-1} cm^{-1}.[126] Although this value was derived for 550 nm, λ_{max}, the spectrum is sufficiently broad that its use at 540 nm is reasonable. K, as defined in equation (3), was evaluated with $[FeL^{2+}]$ being calculated by use of equation (26).

$$[FeL^{2+}] = \frac{A_{\Omega}}{\varepsilon . l} \qquad (26)$$

with ε = 1200 l mol^{-1} cm^{-1} and l = 0.5 cm. The results are listed in Table 2.1.

K at 25°C was found to be $1.13 \pm .06$, where the quoted limit of uncertainty is twice the standard error of the mean. This is very close to the values of 0.9 and 1.0 which Agren obtained.[126] It would appear that K is not markedly dependent on ionic strength. (The absence of a trend in the variation of K with temperature, as shown in Table 2.2, indicates that ΔH is negligible, and since ΔG is approximately zero, so also is ΔS.)

The intercepts of plots of equation (23) were found to be a linear function of $[H^+]$ with a finite intercept being observed, see Fig. 2.2. No indications of a $[H^+]^{-1}$ dependence were noted. It was concluded from this that pathway (7) does not contribute significantly to the formation of FeL^{2+}.

Table 2.2

The Variation with Temperature of K for the Fe^{3+}-Salicylaldehyde Monocomplex at $I = 1.00M$

temp/°C	K
12.3	0.92 ± 0.02
25.0	1.13 ± 0.03
30.5	1.11 ± 0.04

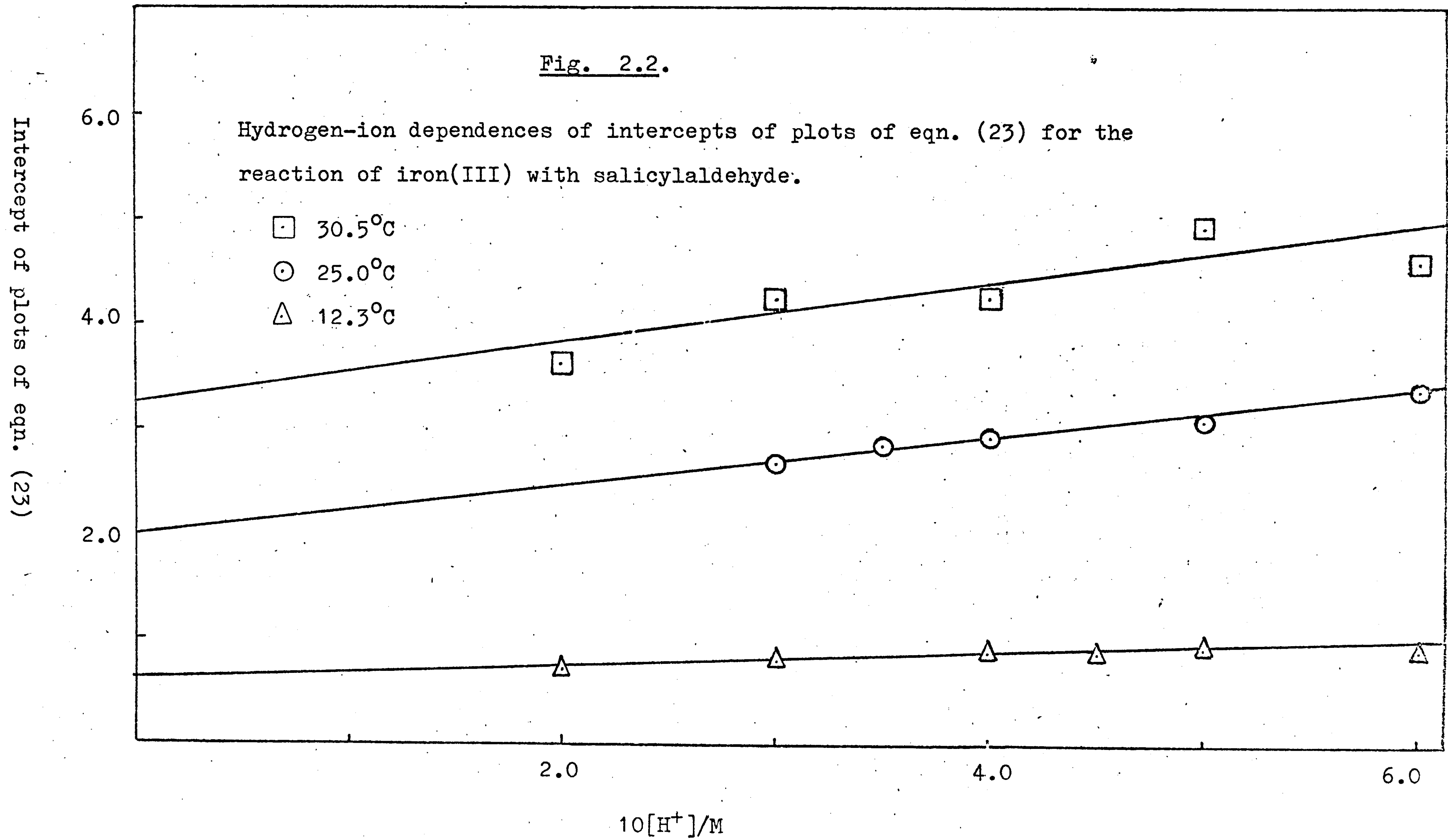


Fig. 2.2.

Hydrogen-ion dependences of intercepts of plots of eqn. (23) for the reaction of iron(III) with salicylaldehyde.

k_{52} for Fe^{3+} + HL was obtained unambiguously from the slope of plots of equation (25). The calculated values at the appropriate temperatures are listed in Table 2.3.

The acid-independent portion, k', of intercepts of plots of k_{obs} as a function of [Fe(III)] is given by equation (27).

$$k' = \frac{1}{K}(k_{12}K_a + k_{64}K_h) \qquad (27)$$

K_a is considerably less than 10^{-8}M.[127] Thus for pathway (4) to contribute to any measurable extent to the formation of FeL^{2+}, k_{12} would require to be at least of the order of 10^8 l mol^{-1} s^{-1}. It is, however, generally assumed that $FeOH^{2+}$ reacts several orders of magnitude faster than Fe^{3+} and substitution rates of $FeOH^{2+}$ are rarely found to exceed 10^5 l mol^{-1} s^{-1}.

By attributing k' solely to $k_{64}K_h$ and using extrapolated values of K_h from Milburn's data[69] relating to the hydrolysis of Fe^{3+}, equation (1), k_{64} was evaluated to yield the results tabulated in Table 2.3. 1.37 x 10^3 l mol^{-1} s^{-1} is very close to values of k_{64} obtained for comparable substitution reactions of $FeOH^{2+}$, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for this pathway were found to be 6.6 ± 0.8 k cal mol^{1} and -22 ± 3 cal K^{-1} mol^{-1}.

The significance of these results will be examined along with those from a similar study of the reaction of iron(III) with salicylamide in section (c) later in this chapter.

Table 2.3

Variation with temperature of k_{52} and k_{64} for the Reaction of Iron(III) with Salicylaldehyde at Unit Ionic Strength.

temp/°C	k_{52}/l mol^{-1} s^{-1}	$10^{-3}k_{64}$/l mol^{-1} s^{-1}
12.3	0.5 ± 0.1	0.76 ± 0.05
25.0	2.6 ± 0.3	1.37 ± 0.08
30.5	3 ± 1	1.63 ± 0.16

$$\Delta H^{\ddagger}_{64} = 7 \pm 1 \text{ kcal mol}^{-1}$$

$$\Delta S^{\ddagger}_{64} = -22 \pm 3 \text{ cal K}^{-1} \text{ mol}^{-1}$$

(b) Iron(III) and Salicylamide

The kinetic scheme used to describe the processes involved in the formation of the mono-complex of salicylamide with iron(III) is exactly analogous to that used in the preceding section for the corresponding reaction of iron(III) with salicylaldehyde. The individual observed pseudo-first-order rate constants are listed in Table 2.4.

The rather larger equilibrium constant, K, facilitated measurement of the slopes of plots of equation (23), page (63); see Fig. 2.3. Plots of these slopes as a function of $[H^+]$ showed that they were of the form shown in equation (28).

$$\text{Slope} = a + \frac{b}{[H^+]} \qquad (28)$$

This is illustrated in Fig. 2.4. The constant, a, which was clearly the limiting value observed at high acid concentrations, is simply k_{52}. Values of this parameter so obtained are listed in Table 2.5. The slopes of plots of equation (23) were not sufficiently reproducible for accurate measurement of b to be made. It is again evident that pathway (7) is of minimal importance in the overall anation reaction. This was confirmed by the variation of intercept of plots of equation (23) with $[H^+]$; see Fig. 2.5. Not only was there an absence of a significant $[H^+]^{-1}$ term but also the linearly hydrogen-ion-dependent term was too small to be precisely measurable.

Table 2.4

Kinetic, Spectrophotometric and Equilibrium Data Concerning the Reaction of Iron(III) with Salicylamide at Unit Ionic Strength and $\lambda = 550$ nm.

$T = 15.4^{\circ}C$

$[H^+]$/M	10^3[Fe(III)]/M	10^3[Salicylamide]/M	k_{obs}/s^{-1}	A_{Ω}^{a}	K^{b}
0.250	5.491	0.893	0.188		
0.250	7.320	0.893	0.204		
0.250	10.98	0.893	0.231		
0.250	14.64	0.893	0.273		
0.250	18.30	0.893	0.294		
0.250	21.96	0.893	0.308		
0.350	5.491	1.062	0.197		
0.350	7.320	1.062	0.199		
0.350	10.98	1.062	0.229		
0.350	14.64	1.062	0.249		
0.350	18.30	1.062	0.254		
0.350	21.96	1.062	0.284		
0.400	5.491	1.426	0.206		
0.400	7.320	1.426	0.198		
0.400	10.98	1.426	0.234		
0.400	14.64	1.426	0.264		
0.400	18.30	1.426	0.291		
0.450	6.864	1.471	0.212	0.175	14.3
0.450	9.152	1.471	0.212	0.229	15.0
0.450	13.73	1.471	0.233	0.308	14.9
0.450	18.30	1.471	0.255	0.378	15.2
0.450	22.88	1.471	0.290	0.412	14.0
0.450	27.46	1.471	0.319	0.483	15.5
0.550	5.491	1.235	0.208	0.0964	13.2
0.550	7.32	1.235	0.210	0.126	13.5
0.550	10.98	1.235	0.239	0.171	13.0
0.550	14.64	1.235	0.252	0.214	13.0
0.550	18.30	1.235	0.255	0.247	12.6
0.550	21.96	1.235	0.291	0.286	13.0

$T = 20.4^{\circ}C$

$[H^+]$/M	10^3[Fe(III)]/M	10^3[Salicylamide]/M	k_{obs}/s^{-1}	A_{Ω}	K^b
0.250	5.491	0.893	0.302		
0.250	7.320	0.893	0.345		
0.250	10.98	0.893	0.412		
0.250	18.30	0.893	0.429		
0.250	21.96	0.893	0.530		
0.350	5.491	1.062	0.366		
0.350	7.320	1.062	0.335		
0.350	10.98	1.062	0.377		
0.350	14.64	1.062	0.414		
0.350	18.30	1.062	0.434		
0.350	21.96	1.062	0.482		
0.400	5.491	1.426	0.354		
0.400	7.320	1.426	0.334		
0.400	10.98	1.426	0.413		
0.400	14.64	1.426	0.447		
0.400	18.30	1.426	0.470		
0.400	21.96	1.426	0.538		
0.450	6.864	1.469	0.358	0.186	15.5
0.450	9.152	1.469	0.360	0.238	15.8
0.450	13.73	1.469	0.407	0.322	16.0
0.450	18.30	1.469	0.443	0.392	16.2
0.450	22.88	1.469	0.490	0.443	15.9
0.450	27.46	1.469	0.522	0.490	16.0
0.550	5.491	1.225	0.322	0.103	14.4
0.550	7.320	1.225	0.376	0.130	14.1
0.550	10.98	1.225	0.373	0.186	14.6
0.550	14.64	1.225	0.428	0.232	14.7
0.550	18.30	1.225	0.450	0.272	14.7
0.550	21.96	1.225	0.491	0.290	13.5

$T = 24.9^{\circ}C$ ($NaClO_4$)

$[H^+]$/M	10^3[Fe(III)]/M	10^3[Salicylamide]/M	k_{obs}/s^{-1}	A_{Ω}	K^b
0.250	5.491	0.893	0.527	0.140	14.0
0.250	7.320	0.893	0.534	0.166	13.2
0.250	10.98	0.893	0.628	0.225	13.7
0.250	14.64	0.893	0.728	0.261	13.0
0.250	18.30	0.893	0.794	0.297	13.2
0.250	21.96	0.893	0.868	0.317	12.5
0.350	5.491	1.062	0.520	0.128	14.1
0.350	7.320	1.062	0.551	0.159	13.8
0.350	10.98	1.062	0.624	0.203	12.7
0.350	14.64	1.062	0.682	0.258	13.5
0.350	18.30	1.062	0.731	0.301	13.8
0.350	21.96	1.062	0.805	0.328	13.4
0.400	5.491	1.426	0.529	0.151	13.9
0.400	7.320	1.426	0.572	0.190	13.7
0.400	10.98	1.426	0.611	0.268	14.3
0.400	14.64	1.426	0.671	0.318	13.6
0.400	18.30	1.426	0.710	0.372	13.9
0.400	21.96	1.426	0.774	0.417	14.0
0.450	6.864	1.469	0.591	0.197	16.7
0.450	9.152	1.469	0.666	0.242	16.2
0.450	13.73	1.469	0.610	0.331	16.7
0.450	18.30	1.469	0.712	0.398	16.6
0.450	22.88	1.469	0.829	0.438	15.6
0.450	27.46	1.469	0.868	0.490	16.0
0.550	5.491	1.234	0.577	0.0935	12.8
0.550	7.320	1.234	0.532	0.120	12.7
0.550	10.98	1.234	0.606	0.166	12.5
0.550	14.64	1.234	0.691	0.208	12.5
0.550	18.30	1.234	0.711	0.246	12.6
0.550	21.96	1.234	0.768	0.269	11.9

$T = 35.3^{o}C$

$[H^+]/M$	$10^3[Fe(III)]/M$	$10^3[Salicylamide]/M$	k_{obs}/s^{-1}	A_{Ω}	K^b
0.250	5.491	0.893	1.45	0.155	16.1
0.250	7.320	0.893	1.57	0.181	14.9
0.250	10.98	0.893	1.85	0.247	16.0
0.250	14.64	0.893	2.11	0.289	15.7
0.250	18.30	0.893	2.19	0.331	16.5
0.250	21.96	0.893	2.55	0.351	15.7
0.350	5.491	1.062	1.47	0.140	15.8
0.350	7.320	1.062	1.59	0.177	15.9
0.350	10.98	1.062	1.79	0.236	15.8
0.350	14.64	1.062	2.00	0.283	15.7
0.350	18.30	1.062	2.09	0.318	15.2
0.350	21.96	1.062	2.42	0.355	15.6
0.400	5.491	1.426	1.35	0.173	16.4
0.400	7.32	1.426	1.50	0.231	17.7
0.400	10.98	1.426	1.72	0.297	16.6
0.400	14.64	1.426	1.82	0.360	16.5
0.400	18.30	1.426	2.01	0.407	16.1
0.400	21.96	1.426	2.16	0.458	16.6
0.450	6.864	1.466	1.64	0.198	16.8
0.450	9.152	1.466	1.34	0.256	17.5
0.450	13.73	1.466	1.90	0.333	16.9
0.450	18.30	1.466	2.04	0.402	17.0
0.450	22.88	1.466	2.12	0.452	16.6
0.450	27.46	1.466	2.59	0.472	14.9
0.550	7.320	1.231	1.52	0.135	14.7
0.550	10.98	1.231	1.75	0.180	13.9
0.550	14.64	1.231	1.86	0.230	14.4
0.550	18.30	1.231	2.06	0.259	13.6
0.550	21.96	1.231	2.22	0.328	16.3

T = 24.9°C ($LiClO_4$)

$[H^+]$/M	10^3[Fe(III)]/M	10^3[Salicylamide]/M	k_{obs}/s^{-1}	A_Ω	K^b
0.250	6.864	0.881	0.528		
0.250	11.44	0.881	0.642		
0.250	16.02	0.881	0.752		
0.250	22.88	0.881	0.901		
0.350	6.864	1.065	0.503	0.152	13.9
0.350	11.44	1.065	0.584	0.220	13.6
0.350	16.02	1.065	0.686	0.280	14.0
0.350	22.88	1.065	0.808	0.335	13.3
0.450	6.864	1.464	0.552		
0.450	11.44	1.464	0.658		
0.450	16.02	1.464	0.727		
0.450	22.88	1.464	0.820		
0.550	6.864	1.175	0.568	0.108	12.7
0.550	11.44	1.175	0.617	0.170	13.2
0.550	16.02	1.175	0.662	0.232	14.2
0.550	22.88	1.175	0.772	0.285	13.4

(a) A_Ω = absorbance of reactant solution at equilibrium; optical path length = 0.5 cm.

(b) $K = \frac{[FeL^{2+}][H^+]}{[Fe^{3+}][HL]}$ with $[FeL^{3+}]$

evaluated as $\frac{A_\Omega}{1370 \times 0.5}$

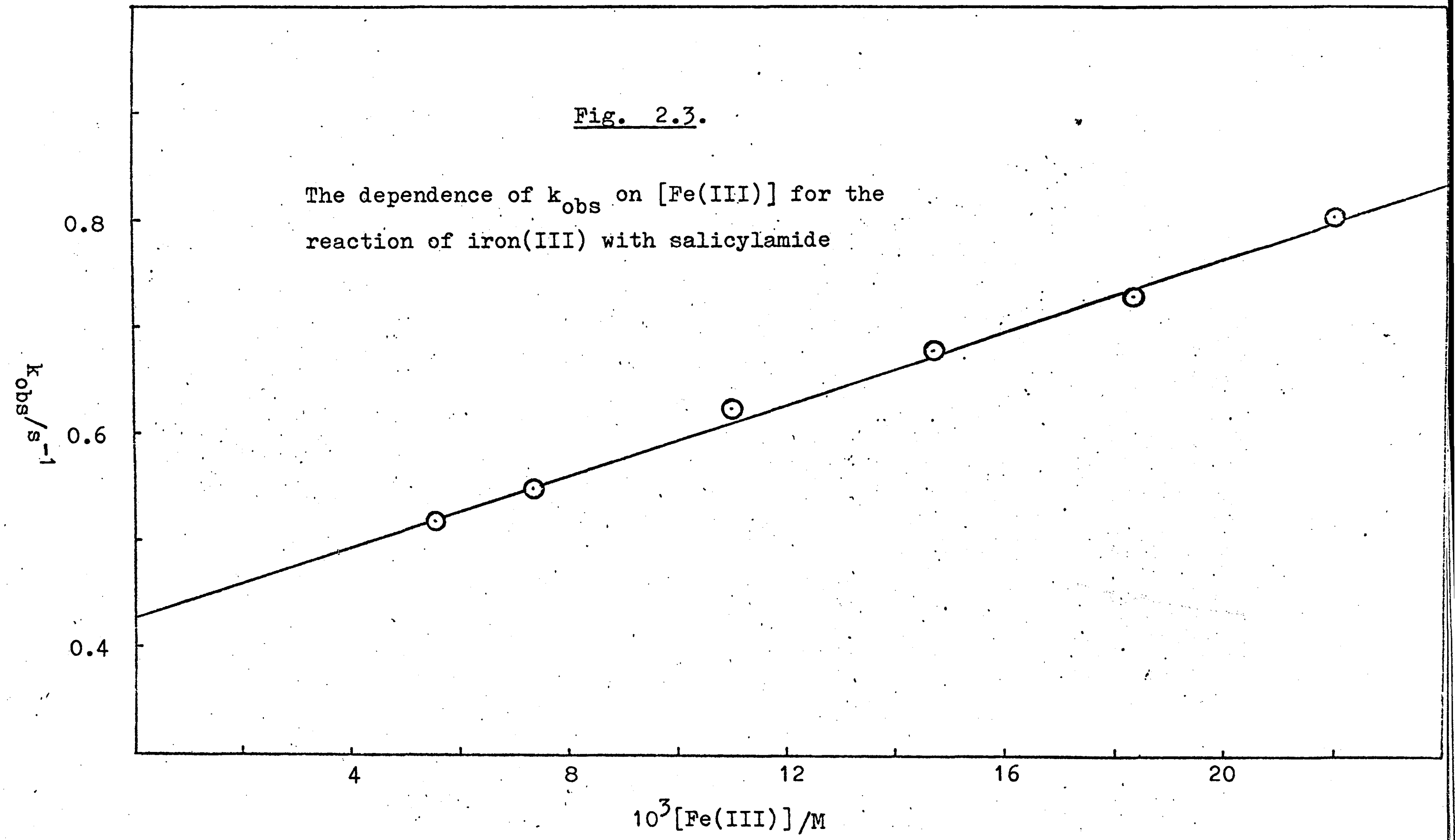


Fig. 2.3.

The dependence of k_{obs} on [Fe(III)] for the reaction of iron(III) with salicylamide

[SMDE] = 1.06×10^{-3}M; [H^+] = 0.350M; I = 1.00M ($NaClO_4$); temp = 24.9°C.

Fig. 2.4.

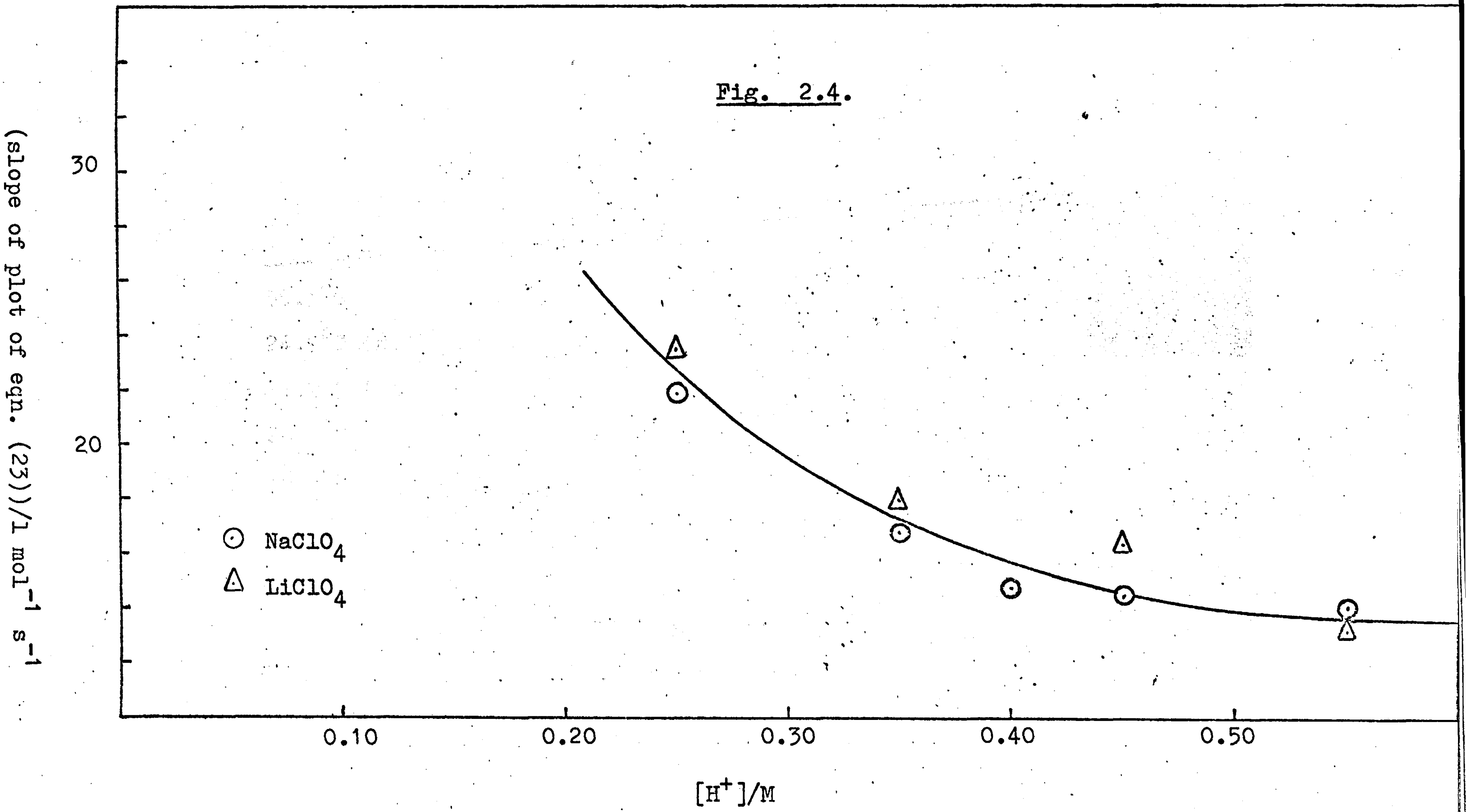
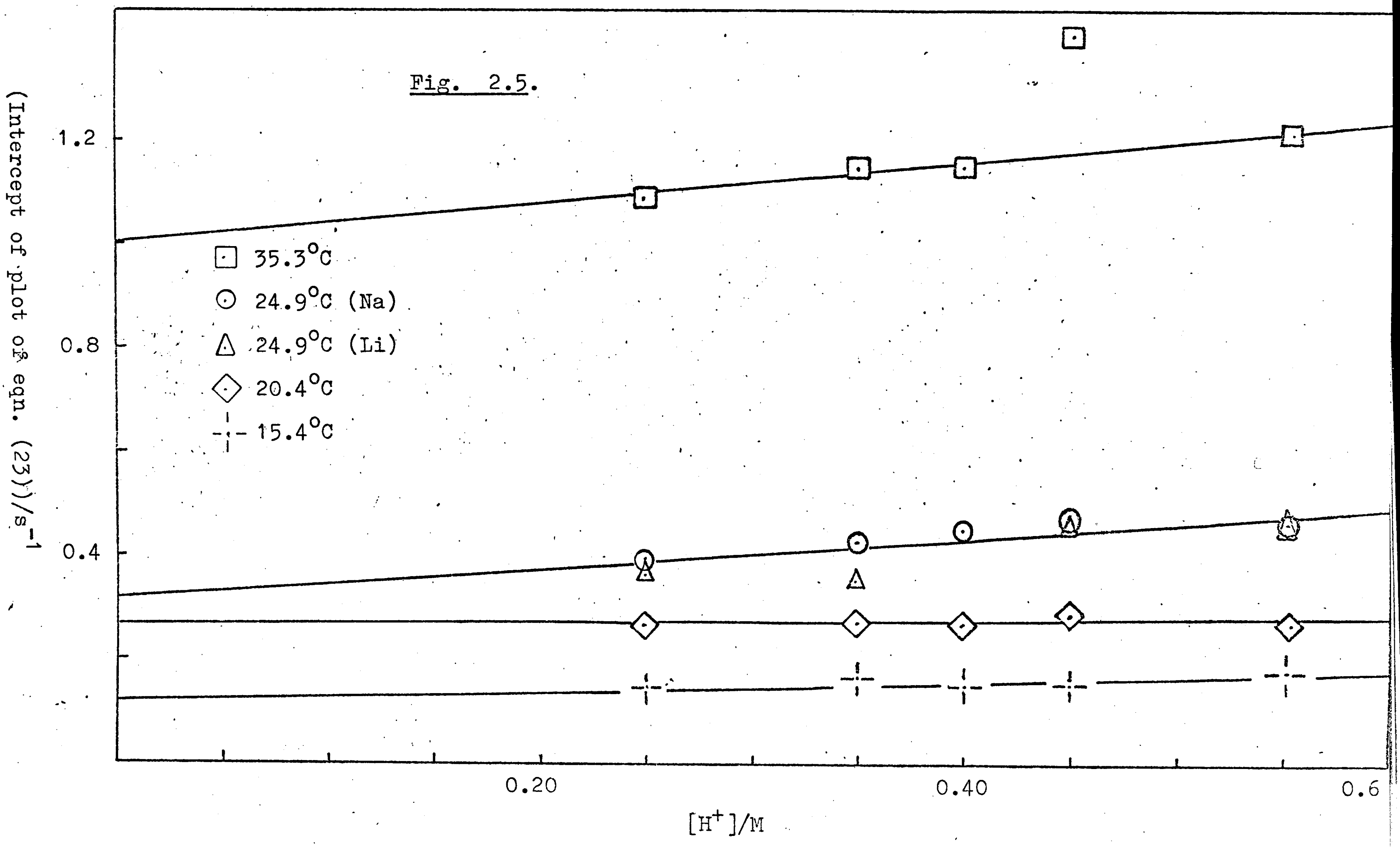

(slope of plot of eqn. (23))/l mol^{-1} s^{-1}
30
20
⊙ NaClO$_4$
△ LiClO$_4$
0.10
0.20
0.30
0.40
0.50
[H$^+$]/M

Fig. 2.5.



Variation of intercepts of plots of eqn. (23) with [H$^+$] for the reaction of iron(III) with salicylamide

The acid-independent term is again as shown in equation (27).

The spectrophotometric data collected in the course of the kinetic experiments were in this case more suitable for the use of a graphical method to evaluate K and ε.

If K is formulated as in equation (29).

$$K = \frac{x(c+x)}{(a-x)(b-x)} \qquad (29)$$

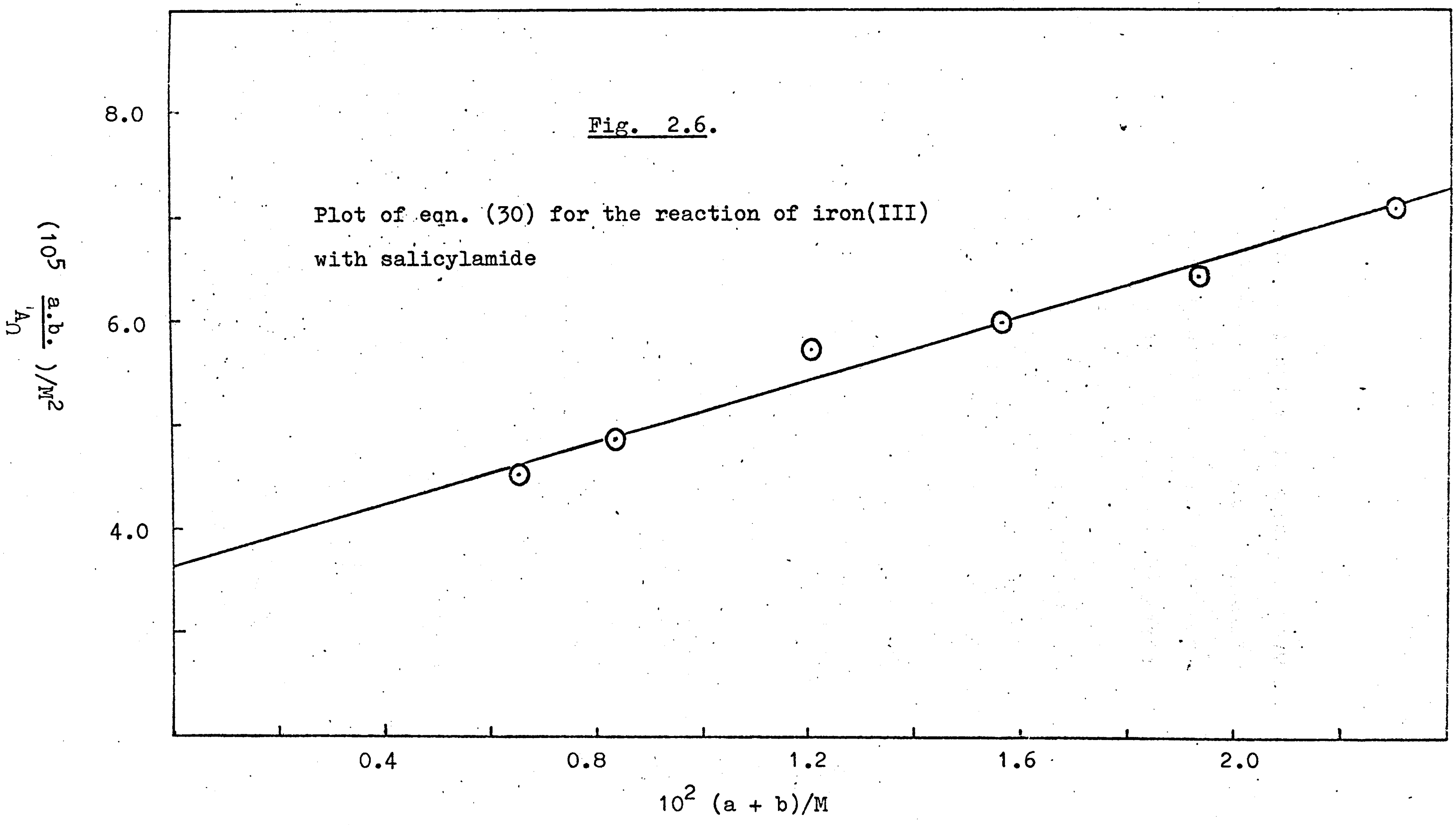
with $x = [FeL^{2+}]$, $(c+x) = [H^+]$, $(a-x) = [Fe^{3+}]$ and $(b-x) =$ [Salicylamide] , it can readily be shown, using equation (26) and neglecting terms in x^2 when expanding the right-hand side, that, if FeL^{2+} is the only absorbing species at a particular wavelength, as is the case in this study,

$$\frac{a.b}{A_\Omega} = \frac{c}{\varepsilon.1.K} + \frac{1}{\varepsilon.1}(a+b) \qquad (30)$$

Plots of the left-hand side of equation (30) against (a+b) were linear, as shown in Fig. 2.6. Each individual plot at a particular temperature and hydrogen-ion concentration should yield the same value of ε. It was found in practice, however, that the extinction coefficients derived from plots of data collected using the apparatus, which utilised the Hilger monochromator, exhibited much greater scatter than those derived <u>via</u> the apparatus which was equipped with the Unicam spectrometer. Only these latter data were used in a direct evaluation of

Fig. 2.6.

Plot of eqn. (30) for the reaction of iron(III) with salicylamide



$[H^+]$ = 0.350M; I = 1.00M(Na); temp = 24.9°C; λ = 550 nm.

K using equations (26) and (29), with $\varepsilon = 1370$ l mol^{-1} cm^{-1} derived from the mean of all the "Unicam" values obtained with $NaClO_4$, with the exception of one which was clearly anomalous. All the spectrophotometric data in Table 2.4. were derived using the Unicam. Since no trend of the mean equilibrium constants with temperature was observed, K was taken as 15 ± 1 at all temperatures. This is in good agreement with the values of 13.5 and 15.5 obtained by Agren.[126] This again appears to illustrate a lack of dependence of K on ionic strength.

Using this value of K, values of $(k_{64}K_h + k_{12}K_a)$ were derived. As with salicylaldehyde, it can be seen that k_{12} would have to be of the order of 10^7-10^8 l mol^{-1} s^{-1} to be of any importance. Again, invoking the lack of "reasonableness" of this value to show that the intercept of plots of equation (23) is entirely $k_{64}K_h$, k_{64} was derived using the appropriate value of K_h calculated as described in the previous section. The results are shown in Table 2.5. The slopes of plots of equation (25) were not sufficiently well-defined to allow k_{52} to be obtained in the manner used for salicylaldehyde.

It was found evident from kinetic, equilibrium and spectrophotometric data that no significant effect was caused by the use of $LiClO_4$ instead of $NaClO_4$. This is not entirely surprising in view of the apparent independence of the equilibrium constant, K, for this reaction, of ionic strength.

Table 2.5

Variation with temperature of k_{52} and k_{64} for the Reaction of Iron(III) with Salicylamide at Unit Ionic Strength.

temp/^{o}C	k_{52}/l mol^{-1} s^{-1}	$10^{-3}k_{64}$/l mol^{-1} s^{-1}
15.4	6 ± 1	2.1 ± 0.3
20.4	9 ±	3.2 ± 0.3
24.9[a]	14.5 ± 0.5	2.9 ± 0.3
24.9[b]	16 ± 3	2.3 ± 0.5
35.3	40 ± 10	5 ± 0.5

a = $NaClO_4$
b = $LiClO_4$

$\Delta H^{\ddagger}_{52}$ = 17 ± 2 k cal mol^{-1}
$\Delta S^{\ddagger}_{52}$ = 3 ± 7 cal K^{-1} mol^{-1}
$\Delta H^{\ddagger}_{64}$ = 7 ± 2 k cal mol^{-1}
$\Delta S^{\ddagger}_{64}$ = −19 ± 7 cal K^{-1} mol^{-1}

(c) General Discussion

One of the main points of interest common to both reactions described in this chapter is the proton ambiguity relating routes (4) and (5). From purely chemical considerations both are equally valid possibilities; there is no direct chemical reason why both could not play a part in complex formation. In order to help resolve this dilemma it is necessary to invoke indirect criteria concerning the "reasonableness" of the rate constants which would exist if a given hypothetical situation existed.

In virtually every instance where this problem has arisen it has been concluded that pathway (5) is the sole contributor to the formally composite term, k', in the rate-law. A recent paper has discussed the main reasons for this decision.[75]

It has already been seen in the General Introduction that substitution reactions of the majority of labile metal-ions proceed by a dissociative interchange mechanism. When pathway (4) is excluded from consideration the derived values of k_{64}, regardless of ligand basicity and denticity, all lie in a narrow range the limits of which depend on the ligand charge. Such values are invariably within an order of magnitude of those for reaction of $FeOH^{2+}$ with negatively charged ligands of low basicity where no proton ambiguity arises, such as NCS^-, Cl^-, Br^- etc. The fact that k_{64} is generally somewhat less for neutral ligands can be rationalised on a simple electrostatic basis.

It therefore appears that $FeOH^{2+}$ reacts in a similar manner to most other labile metal-ions. It has been argued[75] that consideration of pathway (4) introduces an artificial variation of k_{12} with ligand basicity because of incorporation of the appropriate acid dissociation constant.

Also, since at high ligand basicities it is necessary to exclude route (4), because otherwise it would be necessary for k_{12} to possess a value in excess of the diffusion-controlled limit, the operation of this pathway for ligands of lower basicity is unlikely as this would demand that a switch of mechanism took place at an arbitrary ligand basicity.[75]

In addition, although the range of values obtained unambiguously for k_{64} is several orders of magnitude greater than that for unambiguously determined k_{12} values, it is necessary to postulate for ligands with pK_a's greater than 5 that, if pathway (4) is of any importance, k_{12} would be in fact significantly greater than k_{64}. It would also have a value considerably in excess of the water exchange rate.[73]

It therefore seems reasonable to ascribe k' entirely to $\frac{k_{64}K_h}{K}$ in all cases, and indeed it can be seen from Table 2.6 that values of k_{64} obtained for these two ligands are fairly typical. They appear to be at the low end of the range but this is presumably due to the close chemical similarity to monosubstituted phenols which have

Table 2.6

Some Rate Constants for the Reactions of Neutral Ligands with Fe^{3+} and $FeOH^{2+}$ at 25°C.

Ligand	I^a	$k_{34}(Fe^{3+})$/ l mol^{-1} s^{-1}	$10^{-3}k_{64}(FeOH^{2+})$/ l mol^{-1} s^{-1}	ref.
salicylaldehyde	1.0	2.6	1.37	c
salicylaldehyde	0.2	24.6	0.65	d
salicylamide	1.0	15	2.6	c
salicylic acid	0.1	-	2.9	d
salicylic acid	1.0	3.0	5.5	e
phenol	0.1	~25	0.72	f
"	0.1	-	1.5	g
"	0.1	-	1.1	h
o-hydroxy- "	1.0	-	3.1	i
m-Me- "	0.1	-	1.6	g
m-Me- "	0.1	-	0.9	h
o-Cl- "	0.1	-	1.2(0.35)[j]	g
o-Cl- "	0.1	-	1.0	h
m-Cl- "	0.1	-	3.2(1.3)	g
p-Cl- "	0.1	-	1.6(0.66)	g
p-Cl- "	0.1	-	1.2	h
o-Br- "	0.1	-	1.9	h
p-Br- "	0.1	-	0.7	h
$m-NO_2-$ "	0.1	-	1.2(0.8)	g
$m-NO_2-$ "	0.1	-	0.7	h
$m-NO_2-$ "	0.1	-	0.59	k
mandelic acid	0.35	5	2.56	l

Ligand	I^a	$k_{34}(Fe^{3+})/$ $l\ mol^{-1}\ s^{-1}$	$10^{-3}k_{64}(FeOH^{2+})/$ $l\ mol^{-1}\ s^{-1}$	ref.
acetic acid[b]	1.0	4.8	5.3	m
monochloro " "[b]	1.0	2.2	6.8	m
iminodi- " "	1.0	-	2.5	n
nitrilotri- " "	1.0	-	15.0	n
propionic "[b]	1.0	5.7	5.1	m
malonic "	0.5	-	6.2	o
methyl- " "	0.5	-	4.3	o
n-butyl- " "	0.5	-	2.6	o
benzyl- " "	0.5	-	5.4	o
cyclobutane-1,1-dicarboxylic "	0.5	-	3.3	o
acetylacetone	1.0	5.2	4.4	p
thenoyltrifluoroacetone	1.0	1.4	1.3	p
H_3PO_2	1.0	13.0	21.0	q
HF	0.5	11.4	3.1	r
HN_3	1.0	4.0	6.8	s
HN_3	1.0	2.6	6.1	t
HN_3	0.1	-	7.4	u

(a) Ionic strength.

(b) Temp = $20^{\circ}C$.

(c) This work.

(d) P.G.T. Fogg and R.J. Hall, J. Chem. Soc. (A), 1971, 1365.

(e) G. Saini and E. Mentasti, Inorg. Chim. Acta, 1970, 4, 585.

(f) S. Gouger and J. Stuehr, Inorg. Chem., 1974, 13, 379.

(g) F.P. Cavasino and E. Di Dio, J. Chem. Soc. (A), 1970, 1151.

(h) K. Nakamura, T. Tsuchida, A. Yamagishi and M. Fujimoto, Bull. Chem. Soc. Japan, 1973, 46, 456.

(i) E. Mentasti and E. Pelizzetti, J. Chem. Soc. Dalton, 1973, 2605.

(j) Figures in brackets were recalculated from the data presented in ref. (g) by K. Tamura in ref. (k).

(k) K. Tamura, Bull. Chem. Soc. Japan, 1973, 46, 1581.

(l) A.D. Gilmour and A. McAuley, J. Chem. Soc. (A), 1969, 2345.

(m) F. Accascina, F.P. Cavasino and E. Di Dio, Trans. Faraday Soc., 1968, 65, 489.

(n) E. Mentasti, E. Pelizzetti and G. Saini, Gazzetta, 1974, 104, 201.

(o) F.P. Cavasino and E. Di Dio, J. Chem. Soc. (A), 1971, 3176.

(p) M.R. Jaffe, D. Fay, M. Cefola and N. Sutin, J. Amer. Chem. Soc., 1971, 93, 2878.

(q) J.H. Espenson and D.F. Dustin, Inorg. Chem., 1969, 8, 1760.

(r) D. Pouli and W. MacF. Smith, Canad. J. Chem., 1960, 38, 567.

(s) D. Seewald and N. Sutin, Inorg. Chem., 1963, 2, 643.

(t) D.W. Carlyle and J.H. Espenson, Inorg. Chem., 1967, 6, 1370.

(u) F. Accascina, F.P. Cavasino and S. D'Alessandro, J. Phys. Chem., 1967, 71, 2474.

values of k_{64} which are anomalously low, but only slightly so.

Comparison of activation parameters related to route (5) is made in Table 2.7. The spread of $\Delta S^{\ddagger}$ values precludes meaningful interpretation but the $\Delta H^{\ddagger}$ values for these two systems, while being perhaps at the low end of the range, are not significantly different from the remainder.

Thus consideration of the values of k_{64}, and to a lesser extent its activation parameters, lends weight to the hypothesis that substitution at $FeOH^{2+}$ proceeds by dissociative interchange.

The activation parameters listed in Table 2.8, relating to anation reactions of $Fe(H_2O)_6{}^{3+}$, are significantly different from those for similar processes involving $FeOH^{2+}$. $\Delta H^{\ddagger}$ is consistently larger, possibly reflecting the greater energy necessary to weaken the Fe^{3+}-OH_2 bond in going to the transition state.

The spread of values of $\Delta S^{\ddagger}_{64}$ precludes meaningful comparison with $\Delta S^{\ddagger}_{52}$.

The chelate ring is six-membered in each of the iron(III) complexes. It is expected that ring-closure is more likely to be rate-limiting in formation of a six-membered ring than a five-membered ring because of the greater strain in the former entity. It is, however, evident that, as has been found[109,110,115-117] in other investigations of formation of six-membered chelate rings incorporating iron(III), such factors are unimportant in the case of both salicylaldehyde and salicylamide.

Table 2.7.

Some Activation Parameters for the Reactions of Various Ligands with $FeOH^{2+}$.

Ligand	I^a	$\Delta H^{\ddagger}$/kcalmol^{-1}	$\Delta S^{\ddagger}$/calK^{-1}mol^{-1}	ref.
salicylaldehyde	1.0	7	-22	e
salicylamide	1.0	7	-19	e
H_2Sal^b	1.0	12	-2	f
$HSal^-$	1.0	11	-3	f
o-hydroxyphenol	1.0	9.6	-11.1	g
mandelic acid	0.35	16	+10	h
H_2IDA^c	1.0	6.1	-23	i
$HIDA^-$	1.0	4.9	-22	i
H_3NTA^d	1.0	9.9	-5	i
H_2NTA^-	1.0	6.3	-16	i
HF	0.5	10	-8	j
HN_3	0.1	9	-10	k
NCS^-	0.4	10	-7.6	l
Cl^-	1.0	13	+4	m
HSO_4^-	0.5	5	-18	n
SO_4^{2-}	0.5	11.3	+4	o

(a) I = ionic strength.

(b) H_2Sal = salicylic acid.

(c) H_2IDA = iminodiacetic acid.

(d) H_3NTA = nitrilotriacetic acid.

(e) This work.

(f) G. Saini and E. Mentasti, Inorg. Chim. Acta, 1970, 4, 585.

(g) E. Mentasti and E. Pelizzetti, J. Chem. Soc. Dalton, 1973, 2605.

(h) A.D. Gilmour and A. McAuley, J. Chem. Soc. (A), 1969, 2345.

(i) E. Mentasti, E. Pelizzetti, and G. Saini, Gazzetta, 1974, 104, 201.

(j) D. Pouli and W. MacF. Smith, Canad. J. Chem., 1960, 38, 567.

(k) F. Accascina, F.P. Cavasino and S.D 'Alessandro, J. Phys. Chem., 1967, 71, 2474.

(l) J.F. Below, R.E. Connick, and C.P. Coppel, J. Amer. Chem. Soc., 1958, 80, 2961.

(m) R.E. Connick and C.P. Coppel, J. Amer. Chem. Soc., 1959, 81, 6389.

(n) G.G. Davis and W. MacF. Smith, Canad. J. Chem., 1962, 40, 1836.

(o) F.P. Cavasino, J. Phys. Chem., 1968, 72, 1378.

Table 2.8.

Some Activation Parameters for the Reactions of Some Ligands with Fe^{3+}

Ligand	I^{a}	$\Delta H^{\ddagger}$/kcalmol^{-1}	$\Delta S^{\ddagger}$/calK^{-1}mol^{-1}	ref.
Salicylamide	1.0	17	3	b
HF	0.5	8.7	-24	c
NCS^-	0.4	13	-5	d
Cl^-	1.0	16.6	2	e
SO_4^{2-}	0.5	14.3-16.6	6-14	f

(a) I = ionic strength.

(b) This work.

(c) D. Pouli and W. MacF. Smith, Canad. J. Chem., 1960, 38, 567.

(d) J.F. Below, R.E. Connick, and C.P. Coppel, J. Amer. Chem. Soc., 1958, 80, 2961.

(e) R.E. Connick and C.P. Coppel, J. Amer. Chem. Soc., 1959, 81, 6389.

(f) F.P. Cavasino, J. Phys. Chem., 1968, 72, 1378.

Table 2.6. shows that values obtained for k_{52} are also fairly typical. As the range of values for this parameter is no greater than for k_{64} it seems logical to conclude that Fe^{3+} reacts by a similar mechanism to $FeOH^{2+}$.

The most recent value for the water exchange-rate constant for Fe^{3+} is 150 s^{-1}.[73] The second order rate constant for this process is calculated[77] as $\sim$16 l mol^{-1} s^{-1}. Of the two values of k_{52} in Table 2.6. which are in excess of this value, one is admitted as being approximate[75] while the other,[117] being dependent on accurate knowledge of the acid dissociation constant of salicylaldehyde, is subject to error arising from this inherent uncertainty.

The rate constant for water-exchange of $FeOH^{2+}$, like its anation rate parameters, is generally considered[71] to be $\sim 10^2$ times greater than the equivalent parameter relating to Fe^{3+}. This leads to a value of $\sim 1.6 \times 10^3$ l mol^{-1} s^{-1} for the rate constant for water exchange at $FeOH^{2+}$. This is clearly quite close to the rate constants, k_{64}, for substitution of other neutral ligands; see Table 2.6.

It is necessary to point out that while the values of water exchange rate constants appear to reinforce the conclusions reached concerning the dissociative nature of substitution at Fe^{3+} and $FeOH^{2+}$ by neutral ligands, such values are presumably, as in the past, subject to change and hence possibly misleading if too fine a point is made of their magnitude. Nevertheless, the overall evidence in favour of this mechanism is too striking to be ignored completely.

Outer-sphere association constants have not been considered so far but, because all the ligands whose reactions are being compared are neutral, such comparisons are not greatly affected by their values as these appear to be invariably of the order of 0.2-0.3 l mol^{-1}.[75,117] (These constants are the result of calculations on the basis of ion-dipole interactions.) It is thus apparent that the true rate constant for the ligand interchange process will not differ dramatically from those derived neglecting the phenomenon of outer-sphere complexation.

CHAPTER III

THE REACTION OF CHROMIUM(VI) WITH L-CYSTEINE

INTRODUCTION

I Some Features of the Chemistry of Chromium(VI)

Attention has been focussed for a large number of years on the chemistry of chromium(VI). One of the papers in the first issue of the Journal of the Chemical Society described[129] "the analysis of Bichromate of Ammonia and some double Salts of Chromic Acid". The oxidative properties of this metal-ion have proved of considerable value in both volumetric analysis and synthetic organic chemistry; it is used in the form of potassium dichromate in the former and chromic acid in the latter. The diversity and complexity of its reactions have been revealed by detailed kinetic studies in addition to a wide variety of mechanistic investigations.[130-133]

Most metal-ion oxidants require only a one-electron transfer to attain a lower stable oxidation state; chromium(VI), however, requires three electrons for this purpose. Almost all known redox reactions involve transfer of no more than a pair of electrons in one step. The reduction of chromium(VI) to the stable +3 state usually proceeds in a similar manner, with chromium(V) and chromium(IV) being formed as intermediates. A small number of cases have, however, been reported[134] where chromium(VI) appears to accept three electrons simultaneously.

In aqueous solution chromium(VI) exists in several oxyanionic forms and, as a consequence of this, usually requires the participation of hydrogen-ions in its transformation to the product chromium(III) complexes which are invariably of the general formula, in acid media, $[Cr(H_2O)_nX_{6-n}]^{(n-3)+}$. Because of the poor co-ordinating ability of ClO_4^-,[89] the most frequently employed source of hydrogen-ions in studies of such reactions is perchloric acid.

In dilute solutions of this acid, the predominant form of chromium(VI) is $HCrO_4^-$ when $[Cr(VI)] < \sim 10^{-2}M$.[135,136]

As was discussed in the General Introduction, oxidation of non-metallic substrates by both metal-ions and oxyanions is often accomplished by way of inner-sphere complexes, presumably because these provide a low-energy pathway for electron-transfer. The ability of $HCrO_4^-$ to form esters with electron-pair donors, particularly those with -OH groups, is already well established.[133] A list of some complexes of this type which have been characterised to date is given in Table 3.1. The co-ordination of reductants to the chromium centre in a step preceding the redox process has been observed for a number of reactions of this oxidant.[133]

Knowledge of the elementary steps leading to the redox transition state can be derived from characterisation of intermediates and establishment by means of the rate-law of the composition of the activated complexes. Identification of the final products, which usually include various inert chromium(III) complexes as described above, yields information concerning the elementary steps which take place after the transition state.

Table 3.1.

Chromate(VI) Ester Formation Constants at 25.0°C.

Complex	I/M	K/M^{-1}	ref.
$HOCrO_3^- + HOCrO_3^- \rightleftharpoons [O_3CrOCrO_3]^{2-} + H_2O$	1.0	98	a
$HOCrO_3^- + HOSO_2^- \rightleftharpoons [O_3CrOSO_2]^{2-} + H_2O$	0.5	36	b
$HOCrO_3^- + HOSO_3^- \rightleftharpoons [O_3CrOSO_3]^{2-} + H_2O$	3.0	4.1	c
$HOCrO_3^- + HSSO_3^- \rightleftharpoons [O_3CrSSO_3]^{2-} + H_2O$	0.17	1.24×10^4	d
	0.11	1.1×10^4	e
$HOCrO_3^- + HOP(=O)H_2 \rightleftharpoons [O_3CrOP(=O)H_2]^- + H_2O$		11	f
$HOCrO_3^- + HOP(=O)(OH)H \rightleftharpoons [O_3CrOP(=O)(OH)H]^- + H_2O$		16	f
$HOCrO_3^- + HOP(O)_2H^- \rightleftharpoons [O_3CrOP(O)_2H]^{2-} + H_2O$		7	f
	3.0	8	g
$HOCrO_3^- + HOP(=O)(OH)_2 \rightleftharpoons [O_3CrOP(=O)(OH)_2]^- + H_2O$	0.25	9.4	h
$HOCrO_3^- + HOP(O)_2OH^- \rightleftharpoons [O_3CrOP(O_2)OH]^{2-} + H_2O$	0.25	2.9	h
	3.0	6	i
$HOCrO_3^- + HOAs(OH)O^- \rightleftharpoons [O_3CrOAs(OH)O]^{2-} + H_2O$		22	j
$HOCrO_3^- + HOC(=O)CH_3 \rightleftharpoons [O_3CrOC(=O)CH_3]^- + H_2O$	1.0	1.5	k
$HOCrO_3^- + HONH_2 \rightleftharpoons [O_3CrONH_2]^- + H_2O$	1.0	1.2×10^3	k
$HOCrO_3^- + HNHNH_3^+ \rightleftharpoons [O_3CrNHNH_3] + H_2O$	1.0	3.2	l
$H^+ + HOCrO_3^- + Cl^- \rightleftharpoons [O_3CrCl]^- + H_2O$	1.0	17*	c
	1.0	11*	m
$H^+ + HOCrO_3^- + SCN^- \rightleftharpoons [O_3CrSCN]^- + H_2O$	0.3	220*	n

* Units are M^{-2}

(a) J.Y. Tong and E.L. King, J. Amer. Chem. Soc., 1953, 75, 6180.

(b) G.P. Haight, E. Perchonock, F. Emmenegger, and G. Gordon, J. Amer. Chem. Soc., 1965, 87, 3835.

(c) G.P. Haight, D.C. Richardson and N.H. Coburn, Inorg. Chem., 1974, 3, 1777.

(d) I. Baldea and G. Niac, Inorg. Chem., 1968, 7, 1232.

(e) K.A. Muirhead, G.P. Haight, and J.K. Beattie, J. Amer. Chem. Soc., 1972, 94, 3006.

(f) G.P. Haight, M. Rose, and J. Preer, J. Amer. Chem. Soc., 1968, 90, 4812.

(g) S.A. Frennesson, J.K. Beattie, and G.P. Haight, Acta. Chem. Scand., 1969, 23, 3277.

(h) F. Holloway, J. Amer. Chem. Soc., 1952, 74, 224.

(i) S.A. Frennesson, J.K. Beattie and G.P. Haight, J. Amer. Chem. Soc., 1968, 90, 6018.

(j) J.G. Mason and A.D. Kolowak, Inorg. Chem., 1964, 3, 1248.

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(l) G.P. Haight, T.J. Huang, and H. Platt, J. Amer. Chem. Soc., 1974, 96, 3137.

(m) J.Y. Tong and R.L. Johnson, Inorg. Chem., 1966, 5, 1902.

(n) C.T. Lin and J.K. Beattie, J. Amer. Chem. Soc., 1972, 94, 3011.

(a) The role of chromium(VI) esters in the oxidation of some organic molecules by $HCrO_4^-$

Early mechanistic data relating to redox reactions of chromate(VI) were reviewed[130] in 1949 by Westheimer in an important paper dealing mainly with the oxidation of secondary alcohols in aqueous solution. The conversion of isopropyl alcohol to acetone by chromic acid, the reaction he discussed most extensively, was postulated to involve the formation of chromate esters which underwent internal oxidation-reduction. Stable complexes of this type had previously been known for tertiary alcohols.[137,138]

Although Rocek at first challenged this mechanism, proposing[139] as an alternative that the reaction proceeded by way of hydride-ion abstraction, substantiation of the Westheimer theory was provided by the observation that ester formation could become rate-determining if an alcohol were sufficiently hindered.[140]

Spectrophotometric measurements have since confirmed the involvement of such esters in the oxidation of isopropyl alcohol in aqueous solution.[141,142] These complexes have been found to form to a lesser extent in dilute aqueous perchloric acid than in glacial acetic acid.[141]

Although there is general agreement that the first step in the decomposition of such esters formed in the chromate(VI) oxidations of alcohols and aldehydes (the latter react as the hydrate $RH(OH)_2$) is formation of chromium(IV), much effort has been expended in attempts to ascertain the fate of this intermediate.[142–144] The mechanism which currently finds most favour is given below.

$$\mathrm{Cr(IV)} + \mathrm{R,R'CH - OH} \rightleftharpoons \mathrm{R,R'\dot{C} = O} + \mathrm{Cr(III)} \qquad (1)$$

$$\mathrm{Cr(VI)} + \mathrm{R,R'\dot{C} = O} \rightleftharpoons \mathrm{R,R'C = O} + \mathrm{Cr(V)} \qquad (2)$$

$$\mathrm{Cr(V)} + \mathrm{R,R'CH - OH} \rightleftharpoons \mathrm{R,R'C = O} + \mathrm{Cr(III)} \qquad (3)$$

(b) The roles of chromium(V) and chromium(IV) in chromate(VI) oxidations

A number of salts of chromium(V) have been both isolated and identified.[145] Only a few complexes of chromium(IV) have been isolated;[146,147] this scarcity has been attributed to the high oxidative power of this ion.[147] Much information regarding the behaviour of complexes of both these ions has been obtained from studies of the chromate(VI) oxidation of organic materials.[142]

The formation of these ions in such circumstances was at first detected purely by indirect methods, particularly by noting that some added substrates which were oxidised could not reduce chromium(VI) under the conditions being employed.[130]

Chromium(V), which has a d' electronic configuration, has been monitored by the use of both E.P.R. spectrometry,[141,148,149] and U.V./visible spectrophotometry.[141,142,148,149] Its chemical behaviour has been found to be quite similar to that of chromium(VI).[142,149,150]

The presence of water in a mixture of potassium dichromate and ethylene glycol is known[151,152] to bring about the disproportionation of chromium(V), equation (4)

$$3CrV \rightleftharpoons 2CrVI + CrIII \qquad (4)$$

and exclusion of moisture has enabled a full investigation of this system using E.P.R.[153]

Although no direct observation of intermediate chromium(IV) complexes has been reported, sufficient evidence has accumulated to establish without doubt that such an intermediate does participate in reactions of chromate(VI) with two-equivalent reductants, particularly aldehydes and secondary alcohols.[142-144] Its oxidising power is greater than that of either of the +6 and +5 chromium species.

(c) Reactions of chromate(VI) with one-equivalent reductants

Most metal-ion reductants are one-equivalent reagents. A comprehensive review by Espenson of the reactions of chromate(VI) with such substrates has recently been published.[132] The mechanism is generally found to be as below, with (6) being the rate-determining step.

$$Cr(VI) + M^{n+} \rightleftharpoons Cr(V) + M^{(n+1)+} \qquad (5)$$

$$Cr(V) + M^{n+} \rightleftharpoons Cr(IV) + M^{(n+1)+} \qquad (6)$$

$$Cr(IV) + M^{n+} \rightleftharpoons Cr(III) + M^{(n+1)+} \qquad (7)$$

(5) is, however, rate-determining for a small number of metal-ions. King, who first proposed the above mechanism, has postulated[154] that (6) is commonly rate-determining because

the necessary change from four- to six-co-ordination occurs at this stage.

(d) The interaction of $HCrO_4^-$ with sulphur-containing reductants

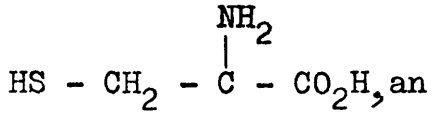
There is currently much interest in the reactions of chromate(VI) with sulphur-containing reducing agents. Formation constants for transient sulphur-bonded esters have been found to be significantly larger than those of the corresponding oxygen-bonded species.[133]

Acid sulphite,[155] HSO_3^-, and acid sulphate,[156] HSO_4^-, both form 1:1 chromate esters with formation constants of 36 and 4 $l\ mol^{-1}$ respectively. Reference to Table 3.1. shows that these values can be seen to be of the order of magnitude found for esters in which the substrate is linked to the chromium centre by oxygen. Acid thiosulphate, however, forms with $HCrO_4^-$ a complex which has a formation constant of $\sim 10^4\ l\ mol^{-1}$.[157] A red-shift of the charge-transfer band in the near U.V. range of the electronic spectrum of the oxidant has been interpreted as evidence for a sulphur linkage.[157] The high value of the formation constant was taken as additional evidence for such a bond.[158]

Similar behaviour was found in this laboratory for a number of organic molecules which contained sulphydryl groups; one of these substrates was L-cysteine.

II The Chemistry of L-cysteine

(a) Co-ordination to metal-ions



Although L-cysteine, $HS - CH_2 - \overset{NH_2}{\overset{|}{C}} - CO_2H$, an amino acid, is of considerable biological importance, its chief attraction to co-ordination chemists is that for such a small, otherwise simple, molecule it affords a wide variety of potential bonding modes, having three different atoms, O, N and S, available for attachment to metal-ions.

Because this ligand possesses both class a donors, O and N, and a class b donor, S, it is of some potential value in the assessment of whether a metal-ion is a class a or class b acceptor. Platinum(II) and palladium(II) both form bis-chelate complexes with cysteine[159] in which carboxyl and sulphydryl groups provide the co-ordination sites. In acidic solution Hg^{2+} and Ag^+ both form cysteine complexes in which the metal-ion is exclusively sulphur-bonded.[160,161] A sulphur-bonded complex is also formed between copper(I) and cysteine.[162]

A rhodium cysteine complex which has been isolated is believed[163] to be dimeric with both amino and sulphydryl groups being co-ordinated.

Potentiometric evidence has been obtained for an O, N-bonded chelate cysteinate complex of calcium(II).[164] A solution infra-red study[165] of alkaline solutions of the 1:2 complexes formed by cysteine with lead(II), cadmium(II) mercury(II) and zinc(II) indicated that both amino and sulphydryl groups are bonded to the metal-ion. It had previously been proposed[166] that cysteine behaves as a tridentate chelate with the first two of these ions. A novel complex was reported[165] to form at low pH with cadmium(II) and zinc(II), the formula being $[M_3L_4][MX_4^{2-}]$, where L = cysteine and X^- = halide. Bonding was postulated to exist through only $-CO_2H$ and -SH.

For the reactions of both zinc(II) and nickel(II) with cysteine, Perrin and Sayce found[167] a variety of complexes having a wide range of stoicheiometries and differing degrees of protonation. It has been suggested[166,168] that nickel(II) is chelated by cysteine via N, S co-ordination.

The reactions of cobalt ions with cysteine have been studied extensively. Cobalt(II) forms a monocomplex in which the ligand has been proposed to use all three of its available binding sites.[166] In alkaline media the blue-green cobalt(II) bis-cysteinate complex is believed to possess nitrogen and sulphur linkages,[169] as is the blue-violet tris-cysteinate.[170] The brown cobalt(III) bis-cysteinate and the green cobalt(III) tris-cysteinate species are, in alkaline solution, believed[170] to be similarly bonded. However, the red cobalt(III) tris-cysteinate complex found in mildly acidic solutions is thought[170] to possess nitrogen and oxygen linkages.

(b) Reduction of metal-ions by L-cysteine

The most reactive functional groups present in biological systems are thiols. These can be oxidised readily to disulphides which are resistant, under mild conditions, to further oxidation. The RSH/RSSR redox couple plays an important role in electron-transport enzymes which very often incorporate metal-ions associated with readily oxidisable sulphydryl groups.

In perchloric acid solution, $Co(H_2O)_6^{3+}$ oxidises cysteine to its disulphide, cystine, by way of a spectrophotometrically identifiable transient intermediate which is believed to incorporate a metal-sulphur bond.[171]

Iron ions catalyse the oxidation by molecular oxygen of cysteine to cystine. In acidic media oxidation by iron(III), in excess metal-ion, is accomplished by the participation of a blue bidentate monocomplex which contains oxygen and sulphur linkages.[172] In alkaline media a violet tris cysteinate complex, in which the ligand is similarly bonded, appears to perform the same function.[172]

Copper ions, like iron ions, are very important biologically. Although their catalysis of the aerial oxidation of cysteine has been widely reported, no copper(II) complex of this ligand has been characterised and the overall reaction is still far from being understood.[163]

Of the large number of systems involving this ligand with metal-ions, that which is currently attracting most attention is its reaction with molybdenum(V) and (VI). This interest is largely the result of a desire to find satisfactory models for the molybdenum-containing enzymes, xanthine oxidase and nitrogen reductase, in which interaction of a cysteine residue with the metal has been proposed to exist.[173,174]

Both oxidation states of this ion form complexes with cysteine. That of molybdenum(V) is a binuclear doubly-oxygen-bridged diamagnetic species[175] which, in alkaline medium, is in equilibrium with a small proportion of paramagnetic monomer.[176] This complex, in which cysteine is terdentate, has been stated[176] to be a fairly good model for xanthine oxidase. The corresponding entity with sulphur bridges has also been proposed as a model for xanthine oxidase.[177]

The reduction of molybdenum(VI) by cysteine yields cystine and the +5 ion. The redox rate is second order in ligand and a 1:2 metal to ligand stoicheiometry has been measured[178] for the final solution. The only solid complex which could be isolated for such mixtures, however, was the 1:1 oxygen-bridged species described above.

III The Reaction of Chromate(VI) with Cysteine

In view of the chemical similarity expected between high oxidation states of chromium and molybdenum as a result of their being in the same group of the periodic table, it was considered of interest to investigate the chromate(VI) L-cysteine system which also, in the light of data discussed in Part I, appeared to offer much of interest concerning the chemistry of the metal-ion.

The reaction of chromium(VI) with cysteine has previously been studied,[179] but that work was carried out at pH 7. No detailed mechanism was given but 1:3 chromium(III) cysteinate complexes were found upon reduction of chromate(VI) by this ligand. In addition, an account was given[179] of the medical significance of this system.

EXPERIMENTAL

L-cysteine (pure, Koch-Light) was used without further purification. Potassium dichromate (B.D.H. AnalaR grade) was used for kinetic runs. Sodium dichromate (B.D.H. Reagent) was used in some of the studies of the stoicheiometry and final products where concentrations of chromium(VI) were such as would have caused precipitation of potassium perchlorate had the potassium salt been used. Mixtures of sodium perchlorate (Fluka puriss p.a.) and perchloric acid (A.R.) were used to maintain a constant ionic strength of 1.00 M at varying hydrogen ion concentrations. Concentrations of stock solutions of perchloric acid were determined by titration against weighed quantities of sodium tetraborate.

Kinetics

The complex-formation reaction was studied using the "fast" stopped-flow apparatus, described in Chapter I, which had a Unicam S.P.500 monochromator as its light source. The optical path-length was either 2.20 or 5.00 mm. Pseudo-first-order rate constants were derived from transmission curves, using a Nova 1200 computer, by the method given in Chapter I.

The slower redox reaction was monitored using the hand-driven stopped-flow system which is also described in Chapter I. Since all the processes studied with this apparatus had half-lives greater than one minute the fraction occurring before observation was considered negligible.

Stoicheiometry

Attempts were made to determine the stoicheiometry of the overall redox reaction by spectrophotometric titration using [L-cysteine] = 4×10^{-2} M and varying [Cr(VI)] in the range $(0.4 - 2.6) \times 10^{-2}$ M at $[H^+] = 0.10$ M and I = 1.00 M. This method indicated a variable stoicheiometry as has been observed for the corresponding reaction with thiosulphate.[180] For this reason, and because it was considered desirable to measure the stoicheiometry under conditions related directly to the kinetic data, acidimetric titration of the sulphydryl group[181] was used. This involved mixing 50 ml. of a solution of ~0.2 M L-cysteine, of known concentration, with 20 ml. of approximately 6×10^{-2}M Cr(VI) and the requisite volumes of stock sodium perchlorate and perchloric acid to give $[H^+] = 0.10$ M and I = 1.00 when the mixture was diluted to 100 ml. When reaction was complete, a 25 ml. sample of this mixture was used to charge a Dowex 50W X8 100/200 mesh cation-exchange resin. The column was rinsed first with water and then with a solution having $[H^+] = 0.10$ M and I = 1.00 M. Successive column fractions were titrated until no L-cysteine could be detected.

Products

Separation of the Cr(III) final products present in the reaction mixture was achieved using nitric acid solutions of varying concentrations. Use of this eluent showed no differences in the products from those obtained using $HClO_4$.

Solutions containing 8 x 10^{-4}M Cr(VI), 3.7 x 10^{-2}M L-cysteine and 9.5 x 10^{-2}M $HClO_4$, having been allowed to react to completion, were used to charge columns of the same resin as was used in the stoicheiometry experiments.

In order to minise any aquation of the chromium(III) products the ion-exchange column was maintained at 0°C during the separation procedure in which use was made of suction at a water pump.

The chromium content of the product complexes was determined using bromine oxidation in basic media with spectroscopic measurement of the resultant CrO_4^{2-}, (ε = 4810 M^{-1} cm^{-1}).[182]

RESULTS AND DISCUSSION

Nature of Reactant Species

A detailed knowledge of the form of the reactants is necessary for interpretation of the data.

It is possible to calculate, using the known values of K_d at unit ionic strength for the dimerisation of $HCrO_4^-$,[135,136]

$$2HCrO_4^- \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} Cr_2O_7^{2-} + H_2O \qquad (8)$$

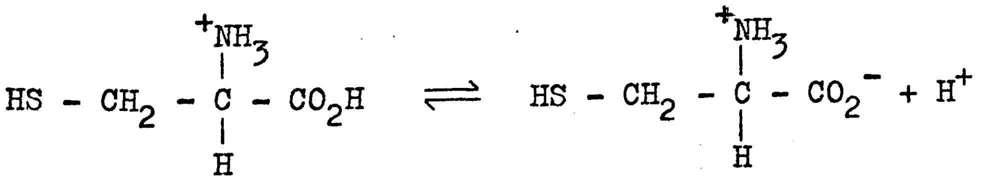
$$K_d = \frac{[Cr_2O_7^{2-}]}{[HCrO_4^-]^2} \qquad (9)$$

that when the initial chromium(VI) concentration, $[Cr(VI)]_o$, is 4×10^{-4}M, as is the case in most of this work, ~91% Cr(VI) exists as $HCrO_4^-$ at 35°C; this percentage increases with decreasing temperature. The maximum value of $[Cr(VI)]_o$ was 8×10^{-4}M. At 30°C, the highest temperature where this concentration was employed, $HCrO_4^-$ is 87% of total Cr(VI). At the highest acid-concentration used in this study, 0.10 M,

$$[H_2CrO_4] / [HCrO_4^-] = 0.02^{183} \qquad (10)$$

Protonation of $HCrO_4^-$ was therefore neglected, as was its dissociation since the acid dissociation constant is about 10^{-6} l mol^{-1}.[127] Thus, as in previous studies where similar concentrations of chromium(VI) and H^+ were used,[158,184-186] the results are interpreted in terms of $HCrO_4^-$ being the sole reactant species, with no account being taken of parallel reactions of $Cr_2O_7^{2-}$. The lability of the oxygen atoms of $HCrO_4^-$ compared with the relative inertness of CrO_4^{2-} adds weight to this assumption.[187] $HCr_2O_7^{2-}$ is generally considered to be insignificant in concentration.[183]

For the dissociation of monoprotonated L-cysteine, equation (11)



$$HS - CH_2 - \overset{\overset{+}{N}H_3}{\underset{H}{C}} - CO_2H \rightleftharpoons HS - CH_2 - \overset{\overset{+}{N}H_3}{\underset{H}{C}} - CO_2^- + H^+ \qquad (11)$$

K_a, as given by equation (12)

$$K_a = \frac{[H_2RCO_2^-][H^+]}{[H_2RCO_2H]} \qquad (12)$$

has a value of about 10^{-2} mol l^{-1}.[188] pK_a values corresponding to loss of a proton by -SH or $^+NH_3$ of RCO_2^- are > 8. Hence although under the conditions used in this study the zwitterion is the dominant species, there is usually a significant proportion of mono-protonated L-cysteine present.

I Formation of the Intermediate Species

1. Characterisation

(a) Spectrum

No absorbance change could be detected when solutions of chromium(VI) were mixed under typical reaction conditions with 'blank' solutions containing no L-cysteine. Superimposition of an oscilloscope trace from such an experiment on one obtained from a normal run showed the initial absorbance, OD_o, of the latter trace to correspond to that of chromium(VI).

If OD_{max} is defined as the absorbance value corresponding to maximum concentration of intermediate species, and $(OD_{max} - OD_o)$ defined as ΔOD, then ΔOD is given by equation (13).

$$\Delta OD = \log_{10} \frac{I_{H_2O}}{I_{max}} - \log_{10} \frac{I_{H_2O}}{I_o} = \log_{10} \frac{I_o}{I_{max}} \qquad (13)$$

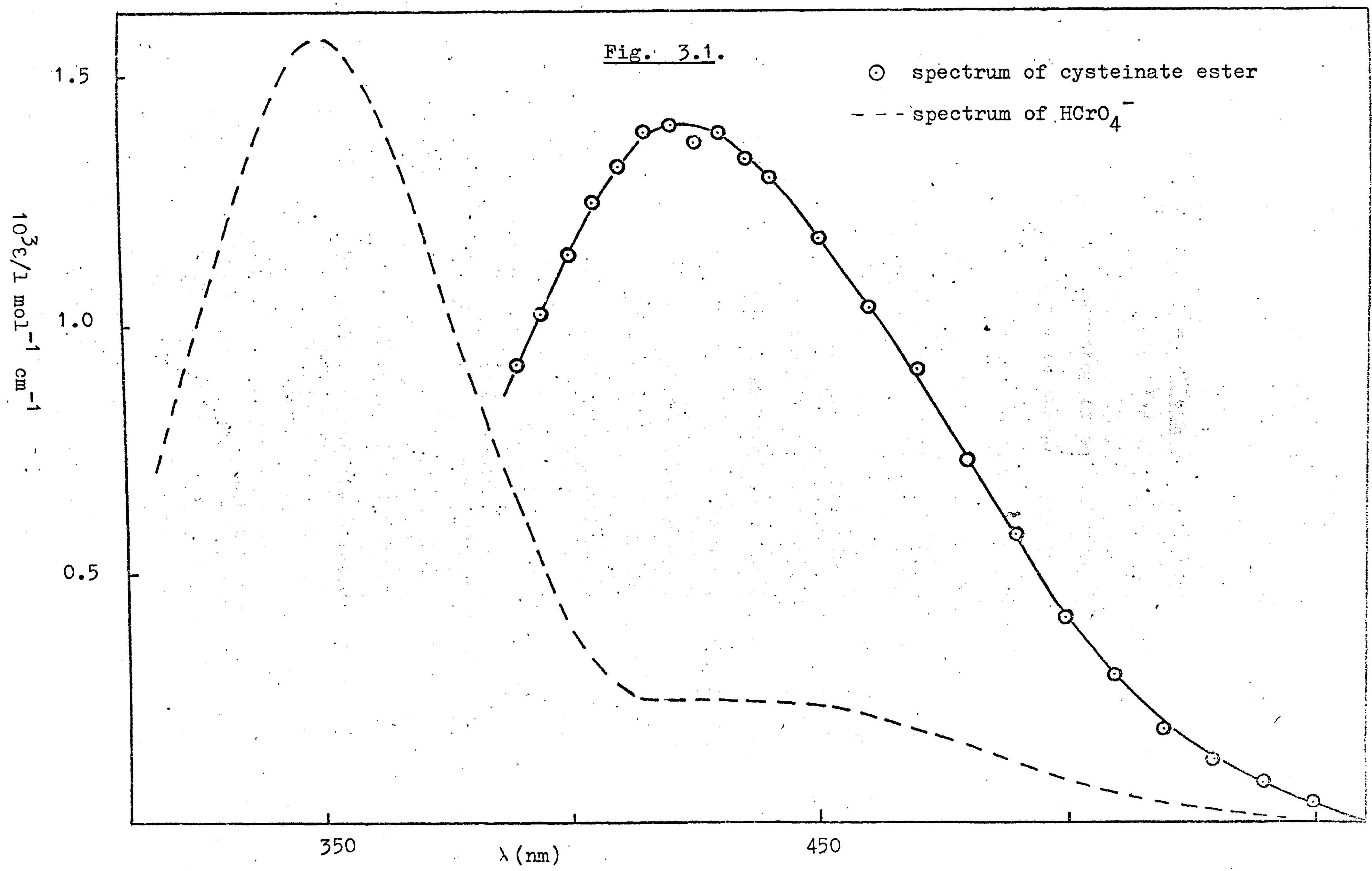
where I_i is the intensity of light corresponding to OD_i. ΔOD can thus be easily calculated from stopped-flow traces. By measuring ΔOD at suitable wavelengths under normal reaction conditions it was possible to compile the spectrum of the orange species. λ_{max} was found to be 420 nm as is shown in Fig. 3.1. Kinetic and equilibrium measurements were therefore carried out at this wavelength.

(b) Extinction coefficients and equilibrium constants

In the acid concentration range 0.01 - 0.10 M, formation of the intermediate species was sufficiently fast with respect to the subsequent decay for the assumption to be reasonably made that the absorbance maximum observed in traces obtained at 420 nm corresponded to a state of equilibrium between reactants and intermediates.

It was found that, when $[\text{L-cysteine}]_o$ was increased with $[Cr(VI)]_o$ and $[H^+]_o$ held constant, $O.D._{max}$ did not increase beyond a limiting value which was directly proportional to $[Cr(VI)]_o$. This is consistent with all the chromium(VI) being present as intermediate at equilibrium. Under such conditions, as in the kinetic studies of the decay, a value for an apparent extinction coefficient, ε_{APP}, could be obtained using equation (14).

Fig. 3.1.


⊙ spectrum of cysteinate ester
- - - spectrum of $HCrO_4^-$
1.5
1.0
0.5
$10^3\varepsilon$/l mol^{-1} cm^{-1}
350
450
λ (nm)

$$\varepsilon_{APP} = \frac{OD_{eqm}}{x.l} \qquad (14)$$

where OD_{eqm} is the absorbance at equilibrium, l is the optical path-length and x is the concentration of complex present which is itself equal to the concentration of chromium(VI) initially present. Calculation of the molar absorbitivity using this method yielded a value of 1375 ± 25 l mol^{-1} cm^{-1}.

Under conditions where uncomplexed chromium(VI) was present at equilibrium, i.e. in the kinetic studies of the intermediate formation, the measured value of OD_{eqm} was found to be independent of $[H^+]_o$. Since $HCrO_4^-$ is generally considered to form only 1:1 complexes under the conditions employed in this work, the equilibrium constant was assumed to be as formulated in equation (15).

$$K = \frac{x}{(a-x)(b-x)} \qquad (15)$$

where x is the concentration of metal complex, a = $[Cr(VI)]_o$, and b = $[L\text{-cysteine}]_o$. Assuming only that (b-x) = b, it is possible to derive the relationship (16)

$$\frac{a.b.}{\Delta O.D.} = b\frac{1}{\Delta\varepsilon.l} + \frac{1}{\Delta\varepsilon.K.l} \qquad (16)$$

Plots of $\frac{a.b.}{\Delta O.D.}$ against b gave excellent linearity; see Fig. 3.2. The absence of any variation of intercept with differing acid concentrations confirms that little or no net

Table 3.2

Primary Kinetic and Spectrophotometric Data Concerning the Complex-Formation Reaction between Chromate(VI) and L-Cysteine at Unit Ionic Strength and λ = 420 nm

temp. = 15.0°C; path-length = 0.50 cm

$10^2[H^+]_o$/M	$10^4[Cr(VI)]_o$/M	10^3[L-cysteine]$_o$/M	$10^2k_{obs}/s^{-1}$	A_Ω
4.00	8.00	2.374	1.32	0.325
4.00	8.00	3.562	1.67	0.379
4.00	8.00	4.749	2.10	0.402
4.00	8.00	7.123	2.88	0.428
4.00	8.00	9.498	3.62	0.439
4.00	8.00	11.87	4.42	0.447
6.00	4.00	1.049	1.20	0.127
6.00	4.00	1.573	1.45	0.154
6.00	4.00	2.097	1.71	0.174
6.00	4.00	3.146	2.25	0.195
6.00	4.00	4.194	2.84	0.204
6.00	4.00	5.243	3.38	0.212
7.00	4.00	1.183	1.44	0.137
7.00	4.00	1.774	1.75	0.163
7.00	4.00	2.366	2.09	0.181
7.00	4.00	3.549	2.75	0.201
7.00	4.00	4.732	3.56	0.209
7.00	4.00	5.915	4.30	0.215

$10^2[H^+]_o$/M	10^4[Cr(VI)]/M	10^3[L-cysteine]$_o$/M	$10^2k_{obs}/s^{-1}$	A_Ω
8.00	4.00	1.235	1.69	0.145
8.00	4.00	1.853	2.08	0.171
8.00	4.00	2.471	2.44	0.183
8.00	4.00	3.706	3.30	0.203
8.00	4.00	4.942	4.12	0.212
8.00	4.00	6.172	5.04	0.217
9.00	4.00	1.179	1.79	0.136
9.00	4.00	1.768	2.21	0.160
9.00	4.00	2.357	2.64	0.180
9.00	4.00	3.536	3.89	0.186
9.00	4.00	4.714	4.46	0.209
9.00	4.00	5.893	5.34	0.212

temp. = 25.0°C; path-length = 0.50 cm

$10^2[H^+]_o$/M	$10^4[Cr(VI)]_o$/M	10^3[L-cysteine]$_o$/M	$10^2k_{obs}/s^{-1}$	A_Ω
4.00	4.00	1.214	1.70	0.123
4.00	4.00	1.821	1.98	0.146
4.00	4.00	2.427	2.36	0.166
4.00	4.00	3.641	3.17	0.186
4.00	4.00	4.855	3.83	0.195
4.00	4.00	6.069	4.60	0.203
5.00	4.00	1.157	2.08	0.117
5.00	4.00	1.736	2.48	0.146
5.00	4.00	2.314	2.84	0.164
5.00	4.00	3.472	3.70	0.184
5.00	4.00	4.629	4.55	0.195
5.00	4.00	5.786	5.34	0.199
5.00	4.00	1.058	2.08	0.114
5.00	4.00	1.587	2.38	0.138
5.00	4.00	2.116	2.75	0.153
5.00	4.00	3.175	3.58	0.178
5.00	4.00	4.233	4.40	0.188
5.00	4.00	4.762	4.98	0.190
5.00	4.00	5.291	5.29	0.194
6.00	4.00	1.182	2.37	0.119
6.00	4.00	1.773	2.86	0.148
6.00	4.00	2.364	3.42	0.165
6.00	4.00	3.546	4.41	0.186
6.00	4.00	4.729	5.49	0.195
6.00	4.00	5.911	6.56	0.203

$10^2[H^+]_o$/M	10^4[Cr(VI)]/M	10^3[L-cysteine]$_o$/M	$10^2k_{obs}/s^{-1}$	A_Ω
7.00	4.00	1.186	2.81	0.121
7.00	4.00	1.779	3.34	0.150
7.00	4.00	2.372	3.89	0.168
7.00	4.00	3.559	5.05	0.183
7.00	4.00	4.745	6.35	0.198
7.00	4.00	5.931	7.43	0.205
8.00	4.00	1.232	3.16	0.119
8.00	4.00	1.847	3.77	0.146
8.00	4.00	2.463	4.42	0.164
8.00	4.00	3.695	5.82	0.185
8.00	4.00	4.926	7.18	0.198
8.00	4.00	6.158	8.35	0.207
9.00	4.00	1.064	3.33	0.107
9.00	4.00	1.596	3.96	0.134
9.00	4.00	2.126	4.72	0.146
9.00	4.00	3.192	6.11	0.170
9.00	4.00	3.724	6.67	0.180
9.00	4.00	4.256	7.14	0.186
9.00	4.00	5.320	8.47	0.194

temp. = 30.0^{o}C; path-length = 0.22 cm.

$10^2[H^+]_o/M$	$10^4[Cr(VI)]_o/M$	10^3[L-cysteine]$_o$/M	$10^2k_{obs}/s^{-1}$	A_Ω
4.00	8.00	2.661	3.65	0.136
4.00	8.00	3.990	4.58	0.155
4.00	8.00	5.322	5.47	0.168
4.00	8.00	7.983	7.50	0.178
4.00	8.00	10.64	8.69	0.182
4.00	8.00	13.30	10.2	0.187
5.00	8.00	2.133	3.82	0.115
5.00	8.00	3.200	4.69	0.139
5.00	8.00	4.266	5.71	0.152
5.00	8.00	6.399	7.43	0.169
5.00	8.00	8.532	9.30	0.176
5.00	8.00	10.67	10.9	0.178
5.00	4.00	1.117	2.80	0.105$^{(a)}$
5.00	4.00	1.675	3.28	0.134$^{(a)}$
5.00	4.00	2.234	3.83	0.151$^{(a)}$
5.00	4.00	3.351	4.93	0.171$^{(a)}$
5.00	4.00	4.468	6.05	0.185$^{(a)}$
5.00	4.00	5.585	6.96	0.193$^{(a)}$
6.00	8.00	2.125	4.80	0.115
6.00	8.00	3.188	5.82	0.136
6.00	8.00	4.251	6.86	0.151
6.00	8.00	6.376	9.01	0.167
6.00	8.00	8.502	11.2	0.174
6.00	8.00	10.63	13.2	0.178

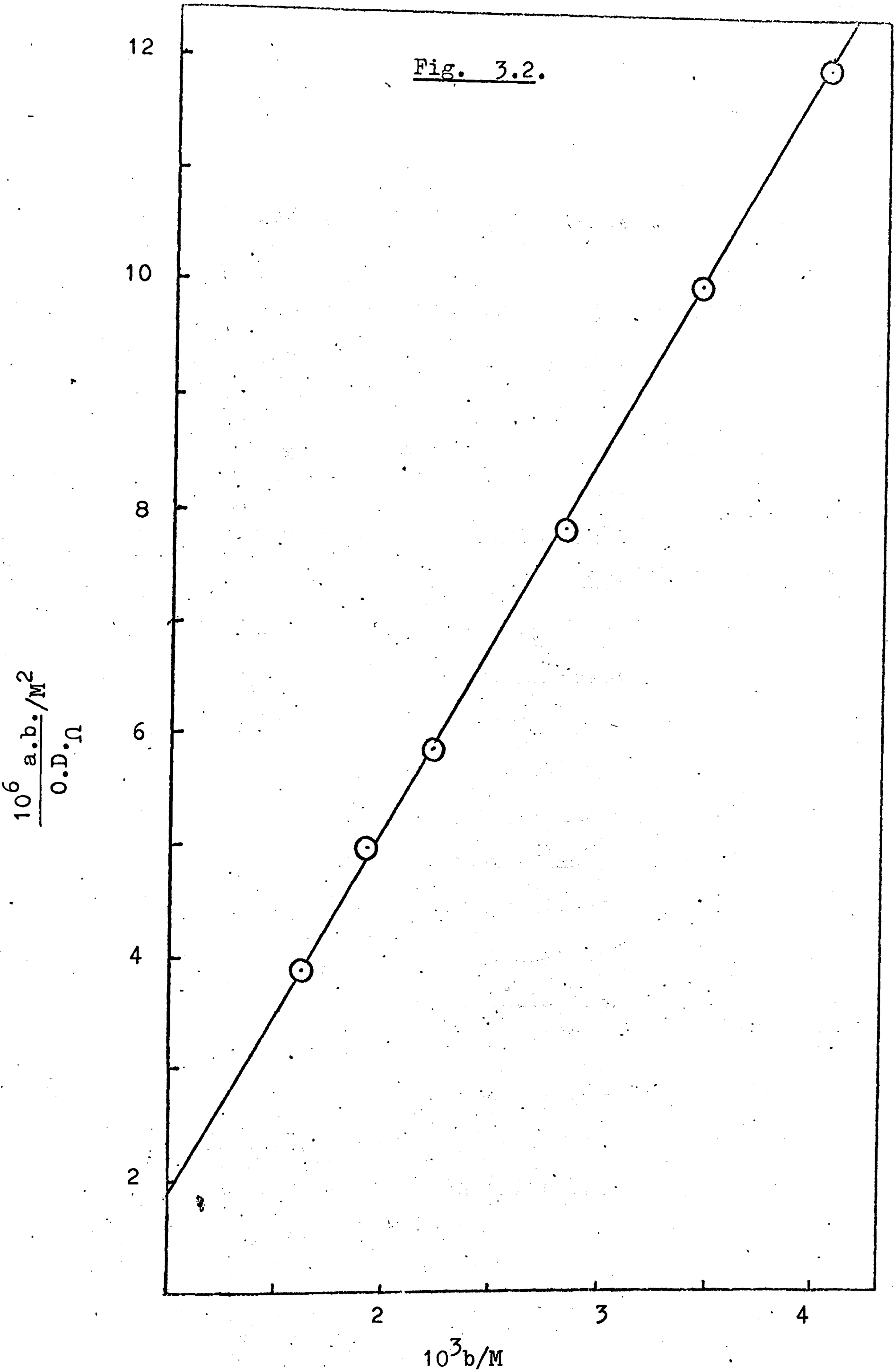
$10^2[H^+]_o/M$	$10^4[Cr(VI)]_o/M$	10^3[L-cysteine]$_o/M$	$10^2k_{obs}/s^{-1}$	A_Ω
7.00	4.00	0.5315	3.29	0.272
7.00	4.00	1.063	3.76	0.438
7.00	4.00	1.595	4.23	0.549
7.00	4.00	2.126	4.85	0.616
7.00	4.00	3.189	6.34	0.723
7.00	4.00	4.252	7.71	0.779
7.00	4.00	5.315	9.08	0.818
8.00	8.00	2.217	6.27	0.115
8.00	8.00	3.326	7.85	0.138
8.00	8.00	4.434	9.47	0.154
8.00	8.00	6.652	13.1	0.157
8.00	8.00	8.868	14.8	0.177
8.00	8.00	11.09	18.1	0.179

(a) path-length = 0.50 cm.

temp. = 35.0°C; path-length = 0.50 cm.

$10^2[H^+]_o$/M	$10^4[Cr(VI)]_o$/M	10^3[L-cysteine]$_o$/M	$10^2k_{obs}/s^{-1}$	A_Ω
4.00	4.00	1.236	3.37	0.106
4.00	4.00	1.854	3.82	0.130
4.00	4.00	2.473	4.43	0.146
4.00	4.00	3.709	5.59	0.167
4.00	4.00	4.945	6.83	0.181
4.00	4.00	6.182	8.01	0.190
5.00	4.00	1.092	3.76	0.099
5.00	4.00	1.638	4.16	0.118
5.00	4.00	2.184	5.02	0.141
5.00	4.00	3.276	6.39	0.164
5.00	4.00	4.368	7.51	0.177
5.00	4.00	5.460	8.80	0.188
6.00	4.00	1.070	4.62	0.096
6.00	4.00	1.605	5.22	0.117
6.00	4.00	2.140	5.70	0.136
6.00	4.00	3.210	7.20	0.160
6.00	4.00	4.280	8.72	0.174
6.00	4.00	5.350	10.2	0.186
7.00	4.00	1.108	5.42	0.098
7.00	4.00	1.662	6.09	0.122
7.00	4.00	2.215	6.88	0.143
7.00	4.00	3.323	8.67	0.164
7.00	4.00	4.431	10.4	0.180
7.00	4.00	5.539	12.2	0.187

Fig. 3.2.



Typical Benesi-Hildebrand Plot for the $HCrO_4^-$/L-cysteine Complex.

uptake or loss of protons is involved in complex formation.[189]

Values of K and $\Delta\varepsilon$ were obtained more directly by evaluating equation (16) using the relationship (17).

$$x = \frac{\Delta O.D.}{\Delta\varepsilon . l} \qquad (17)$$

$\Delta\varepsilon$ was varied at intervals of 20 l^{-1} mol^{-1} cm^{-1} in order to minimise variations in the value of K thus obtained. Such values were higher than those yielded by the Benesi-Hildebrand plot. It has previously been noted[190] that when the concentration of complex is not negligible compared with that of the reagent in excess an equilibrium constant derived from such a plot is always lower than the true constant. Consequently the values of K and $\Delta\varepsilon$ quoted in this chapter are those obtained by this latter direct evaluation method since it involves no approximations.

Values of K and $\Delta\varepsilon$ are shown in Table 3.3. The good agreement between the two values of ε ($\varepsilon^{420}_{HCrO_4^-}$ = 228 $l^{-1}mol^{-1}$ cm^{-1}),[157] in addition to the linearity of the Benesi-Hildebrand plot, suggests that the assumption of solely monocomplex formation is justified.

The red shift of the charge-transfer band in the electronic spectrum of the chromium species is almost twice as large as that found[157] for $CrS_2O_6^{2-}$ where the shift of λ_{max} to 390 nm has been interpreted as evidence for a chromium-sulphur linkage.[157] The values of ε_{max} for these species are very similar (ε_{max} for $CrS_2O_6^{2-}$ is 1400 l^{-1} mol^{-1} cm^{-1}).

Table 3.3

K_1 and $\Delta\epsilon$ for $HLCrO_3^-$ at λ = 420 nm and I = 1.00M

temperature/°C	K_1/mol l^{-1}	$\Delta\varepsilon$/l mol^{-1} cm^{-1} (a)
15	1280 ± 160	1230 ± 10
25	1030 ± 110	1180 ± 40
30	830 ± 200	1160 ± 20
35	760 ± 60	1160 ± 20

(a) $\varepsilon^{420}_{HCrO_4^-}$ = 228 l mol^{-1} cm^{-1} [157]

ΔG = -4.1 ± 0.1 kcal mol^{-1};

ΔH = -5.0 ± 0.5 kcal mol^{-1};

ΔS = -3 ± 2 cal mol^{-1} K^{-1}.

The magnitude of the equilibrium constant provides further indirect evidence for such a bond on the basis of arguments reported elsewhere[158] where comparison is made of equilibrium constants for various chromate esters.

Although this leaves little doubt that chromium-sulphur bonding is present in the intermediate species it has to be decided whether or not there is chelation.

No complexes higher than 1:2 have been reported for chromate(VI), presumably because of the poor lability of the two chromyl oxygens. As a consequence of this, no more than bidentate chelation would be expected.

However, the invariance of measured values of K, equation (15), with differing hydrogen-ion concentrations would not be found if either an O,S or N,S bonding configuration were present within the chromate(VI) cysteinate species. It can readily be shown that in each case at least one proton would be consumed in the overall complex formation.

A less substantial piece of evidence against chelation is provided by the low value of the entropy of complex formation; see Table 3.3.

According to the HSAB theory of metal-ligand bonding it would be anticipated that sulphur would be the least likely of the three potential donor atoms to co-ordinate to chromium(VI), since the latter would generally be considered a "hard acid". Jorgensen has stated,[191] however, that on going to its highest oxidation states a metal-ion may behave as a soft acid.

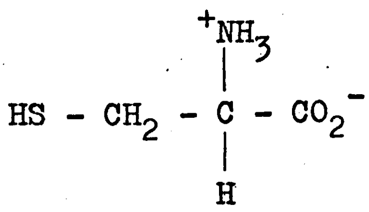
Sulphydryl-containing ligands which are structurally related to cysteine have been found[192] to form chromate(VI) esters with similar characteristics to that of this complex Penicillamine, 2-mercaptoethylamine and glutathione (γ-L-glutamyl-L-cysteinyl glycine) all form complexes with $HCrO_4^-$ which have λ_{max} in the range 420-430 nm, ε1250-1300 l mol^{-1} cm^{-1} and K of between 700 and 1200 l mol^{-1}.

Thus it would appear likely that only equilibria (18) and (19) are involved in intermediate formation.

$$HCrO_4^- + H_2L \underset{}{\overset{K_1}{\rightleftharpoons}} HLCrO_3^- + H_2O \qquad (18)$$

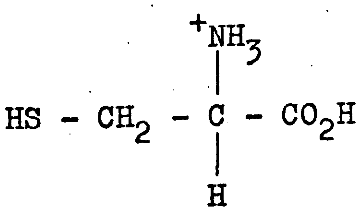
$$HCrO_4^- + H_3L^+ \underset{}{\overset{K_2}{\rightleftharpoons}} H_2LCrO_3 + H_2O \qquad (19)$$

where H_2L, H_3L^+, $HLCrO_3^-$ and H_2LCrO_3 are, I, II, III, and IV respectively.



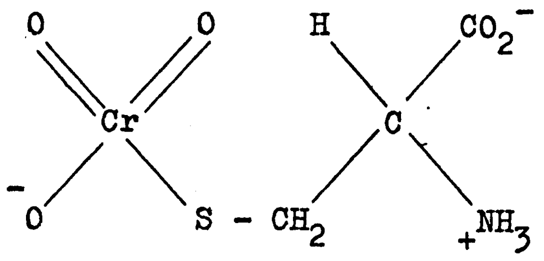
$HS - CH_2 - \overset{\overset{+}{N}H_3}{\underset{H}{C}} - CO_2^-$

(I)

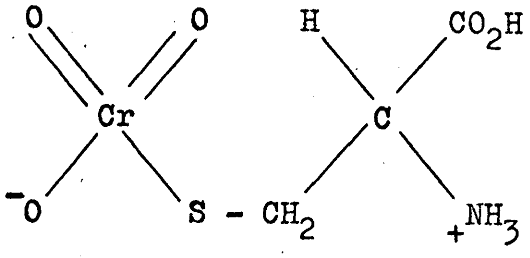


$HS - CH_2 - \overset{\overset{+}{N}H_3}{\underset{H}{C}} - CO_2H$

(II)



(III)



(IV)

If K_a and K_b are as defined in equations (20) and (21)

$$K_a = \frac{[H^+][H_2L]}{[H_3L^+]} \tag{20}$$

$$K_b = \frac{[H^+][HLCrO_3^-]}{[H_2LCrO_3]} \tag{21}$$

then $\Delta\varepsilon$ and K are given by equations (22) and (23) respectively.

$$\Delta\varepsilon = \frac{K_b\Delta\varepsilon_{HLCrO_3^-} + [H^+]\Delta\varepsilon_{H_2LCrO_3}}{K_b + [H^+]} \tag{22}$$

$$K = \frac{K_aK_1 + [H^+]K_2}{K_a + [H^+]} \tag{23}$$

Since the measured values of $\Delta\varepsilon$ and K are independent of acid concentration, it would appear that within the errors of experiment equations (24) and (25) hold for this system,

$$\Delta\varepsilon_{HLCrO_3^-} = \Delta\varepsilon_{H_2LCrO_3} \tag{24}$$

$$K_1 = K_2 \tag{25}$$

hence making differentiation between the overall complex-formation reactions involving the two species of L-cysteine, I and II, impossible.

Equation (26) can readily be derived

$$K_1/K_2 = K_b/K_a \tag{26}$$

Thus it seems that the acid dissociation constant of the carboxyl group of L-cysteine is not radically changed by co-ordination of this ligand to $HCrO_4^-$, equation (27),

$$K_a = K_b \tag{27}$$

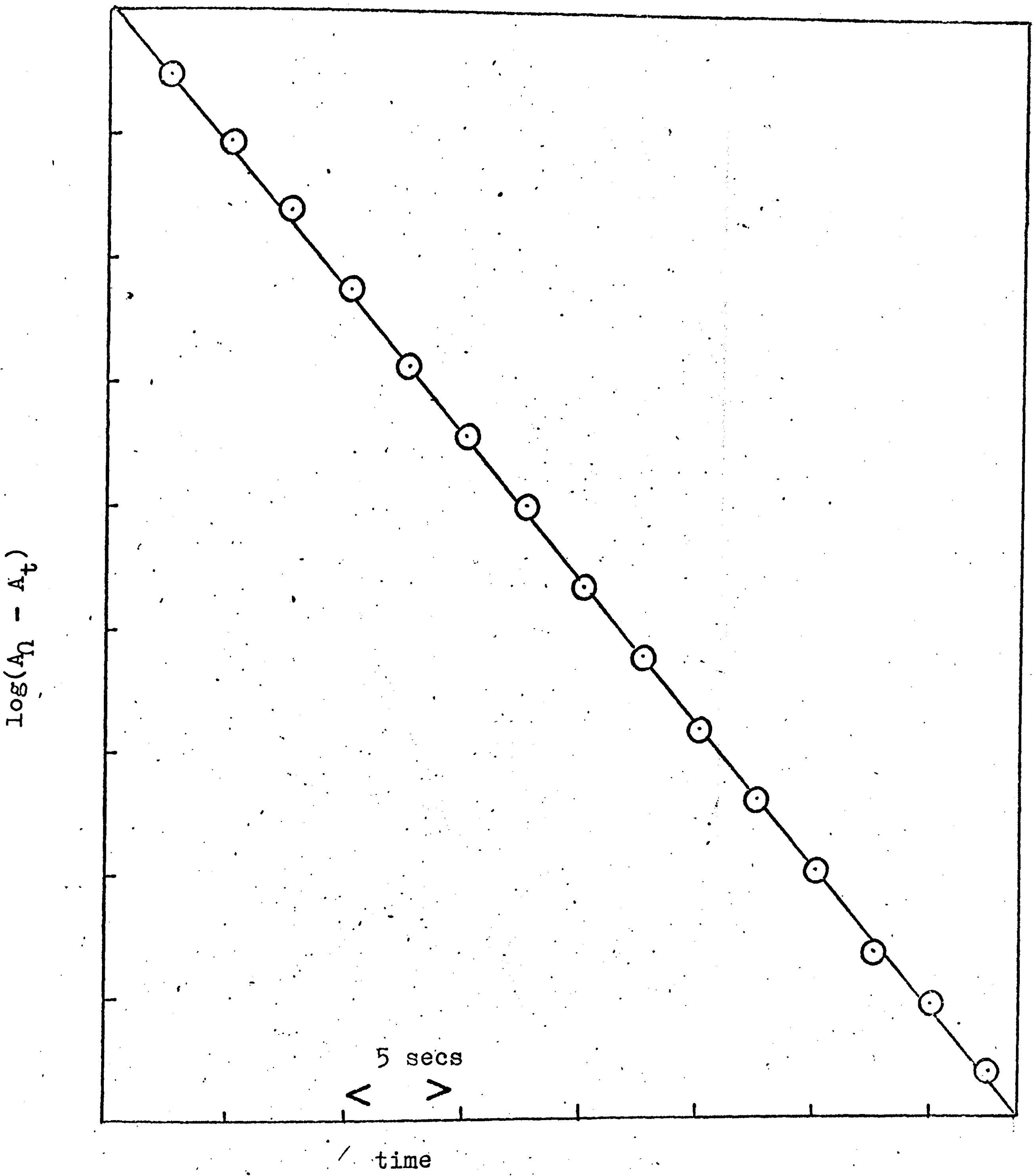
which can most reasonably be explained in terms of metal-ligand bonding being exclusively through sulphur.

2. Formation Kinetics

All the kinetic data were obtained using an excess of L-cysteine. Plots of $\ln(OD_\Omega - OD_t)$ as a function of time were linear to at least 80% reaction, usually more; Fig. 3.3. Evaluation of the slopes of these lines gave pseudo-first-order rate constants, k_{obs}. These were found to be independent of the wavelength used to monitor the reaction. Degassing reactant solutions had no effect on reaction rates.

Plots of k_{obs} against $[\text{L-cysteine}]_o$ at constant $[H^+]_o$ yielded good straight lines with positive intercepts; Fig. 3.4. Since $[\text{L-cysteine}]_o$ was usually comparable in magnitude with $[H^+]_o$, the concentrations of free hydrogen ion, $[H^+]_o^f$, were obtained by calculating the concentration

Fig. 3.3.

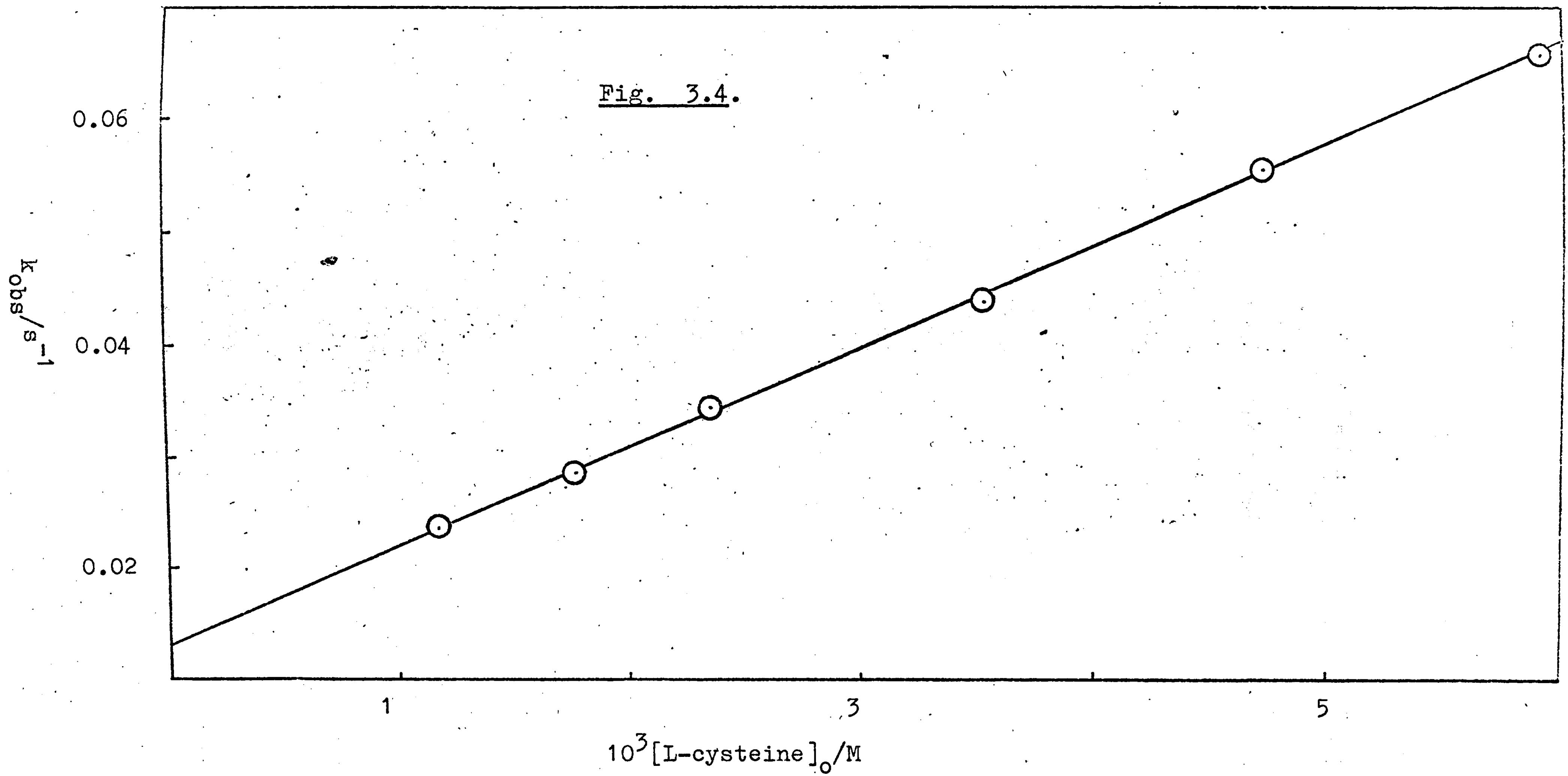


Linearisation of Pseudo-First-Order Complex Formation in the Reaction of $HCrO_4^-$ with L-cysteine.

[Cr(VI)] = 4.00×10^{-4}M; [L-cysteine] = 2.43×10^{-3}M;

[H^+] = 0.040M; I = 1.0M; temp = 25°C; λ = 420 nm.

Fig. 3.4.



The Dependence of k_{obs} on Initial Ligand Concentration for the Chromate(VI) Ester Formation.

$[Cr(VI)]_o = 4 \times 10^{-4}M$; $[H^+] = 0.0600M$; $I = 1.0M$; temp = 25°C; λ = 420 nm.

Table 3.4.

Rate Constants for the formation of the Cr(VI) - L-cysteine complex

$[\mathrm{Cr(VI)}] = 4 \times 10^{-4}\mathrm{M}$; $I = 1.00\mathrm{M}$; $\lambda = 420$ nm; temp. = $15.0^{\circ}\mathrm{C}$.

$10^2[\mathrm{H}^+]_o{}^f/\mathrm{M}$	$10^3k_{obs}/\mathrm{s}^{-1}$	$10^2[\mathrm{H}^+]_o{}^f/\mathrm{M}$	$10^3k_{obs}/\mathrm{s}^{-1}$
$10^3[\text{L-cysteine}]_o = 1.0\mathrm{M}$		$10^3[\text{L-cysteine}]_o = 4.0\mathrm{M}$	
3.92	0.85	3.69	1.85
5.91	1.14	5.66	2.73
6.91	1.26	6.65	3.11
7.91	1.40	7.65	3.51
8.91	1.67	8.64	3.93
$10^3[\text{L-cysteine}]_o = 2.0\mathrm{M}$		$10^3[\text{L-cysteine}]_o = 5.0\mathrm{M}$	
3.84	1.19	3.61	2.17
5.83	1.67	5.58	3.27
6.83	1.88	6.57	3.73
7.82	2.10	7.56	4.17
8.82	2.43	8.55	4.69
$10^3[\text{L-cysteine}]_o = 3.0\mathrm{M}$		$10^3[\text{L-cysteine}]_o = 6.0\mathrm{M}$	
3.76	1.51	3.53	2.51
5.74	2.20	5.49	3.80
6.74	2.50	6.48	4.33
7.73	2.80	7.47	4.87
8.73	3.19	8.46	5.43

Temp. 25.0°C

10^3[L-cysteine]$_o$= 1.0M

3.92	1.52
4.92	1.92 1.89
5.91	2.19
6.91	2.57
7.91	2.94
8.91	3.34

10^3[L-cysteine]$_o$= 2.0M

3.84	2.15
4.83	2.71 2.66
5.83	3.09
6.83	3.58
7.82	4.00
8.82	4.54

10^3[L-cysteine]$_o$= 3.0M

3.76	2.76
4.75	3.50 3.36
5.74	3.98
6.74	4.57
7.73	5.08
8.73	5.74

10^3[L-cysteine]$_o$= 4.0M

3.69	3.38
4.67	4.29 4.08
5.66	4.87
6.65	5.56
7.65	6.15
8.64	6.94

10^3[L-cysteine]$_o$= 5.0M

3.61	4.00
4.59	5.07 4.79
5.58	5.76
6.57	6.56
7.56	7.22
8.55	8.14

10^3[L-cysteine]$_o$= 6.0M

3.53	4.62
4.51	5.86 5.50
5.49	6.66
6.48	7.56
7.47	8.29
8.46	9.34

Temp. 30.0°C

10^3[L-cysteine]$_o$= 1.0M

3.92	2.83
4.92	2.93
4.92	2.68
5.91	3.80
6.91	3.33
7.91	4.77
7.91	3.77

10^3[L-cysteine]$_o$= 2.0M

3.84	3.45
4.83	3.78
4.83	3.64
5.83	4.79
6.83	4.77
7.82	6.10
7.82	5.20

10^3[L-cysteine]$_o$= 3.0M

3.76	4.07
4.75	4.61
4.75	4.60
5.74	5.77
6.74	6.10
7.73	7.43
7.73	6.65

10^3[L-cysteine]$_o$= 4.0M

3.69	4.69
4.67	5.47
4.67	5.55
5.66	6.73
6.65	7.42
7.65	8.78
7.65	8.10

10^3[L-cysteine]$_o$= 5.0M

3.61	5.32
4.59	6.29
4.59	6.51
5.58	7.73
6.57	8.72
7.56	10.12
7.56	9.53

10^3[L-cysteine]$_o$= 6.0M

3.53	5.93
4.51	7.11
4.51	7.47
5.49	8.72
6.48	10.07
7.47	11.47
7.47	11.00

Temp. 35.0°C

10^3[L-cysteine]$_o$ = 1.0M

3.92	3.02
4.92	3.66
5.91	4.24
6.91	4.98

10^3[L-cysteine]$_o$= 2.0M

3.84	3.99
4.83	4.77
5.83	5.61
6.83	6.58

10^3[L-cysteine]$_o$= 3.0M

3.76	4.94
4.75	5.94
5.74	6.97
6.74	8.17

10^3[L-cysteine]$_o$ = 4.0M

3.69	5.91
4.67	7.10
5.66	8.33
6.65	9.73

10^3[L-cysteine]$_o$= 5.0M

3.61	6.87
4.59	8.26
5.58	9.69
6.57	11.32

10^3[L-cysteine]$_o$= 6.0M

3.53	7.83
4.51	9.42
5.49	11.07
6.48	12.92

Dependence of k_{obs} on [Cr(VI)]

$[H^+]$ = 0.08M; I = 1.00M; temp. = 30.0°C;

λ = 420 nm

$10^4[Cr(VI)]_o/M$	10^3[L-cysteine]$_o/M$	$10^2k_{obs}/s^{-1}$
2	2.307	5.60
4	"	5.89
6	"	6.12
2	4.614	9.08
4	"	9.07
6	"	9.33
2	6.921	1.22
4	"	1.22
6	"	1.25
2	9.228	1.58
4	"	1.56
6	"	1.57

of H_3L^+ at known total concentrations of L-cysteine and hydrogen ion using $K_a = 0.01 \text{ mol.l}^{-1}$. Considerable variation in the value of K_a used ($\pm$ 50%) was found to have a negligible effect on the calculated values of $[H^+]_o^f$.

From the known dependence of k_{obs} on $[\text{L-cysteine}]_o$ it was possible to plot k_{obs} against $[H^+]_o^f$ at constant $[\text{L-cysteine}]_o$ using the data presented in Table 3.4. Such plots were linear with positive intercepts; see Fig. 3.5. (Similar behaviour was exhibited by a plot (Fig. 3.6.) of initial rate against $[H^+]_o^f$.) The slopes of these graphs were found to plot linearly as a function of $[\text{L-cysteine}]_o$, yielding positive intercepts.

In interpreting these kinetic data H_2L and H_3L^+ are both considered to be kinetically important species. Thus these data, taken together with conclusions drawn in the previous section concerning the overall reaction, indicate that the four reactions contributing to complex formation are as given by equations (28) - (31)

$$HCrO_4^- + H_2L \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HLCrO_3^- + H_2O \tag{28}$$

$$HCrO_4^- + H_3L^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} H_2LCrO_3 + H_2O \tag{29}$$

$$H^+ + HCrO_4^- + H_2L \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} HLCrO_3^- + H_2O + H^+ \tag{30}$$

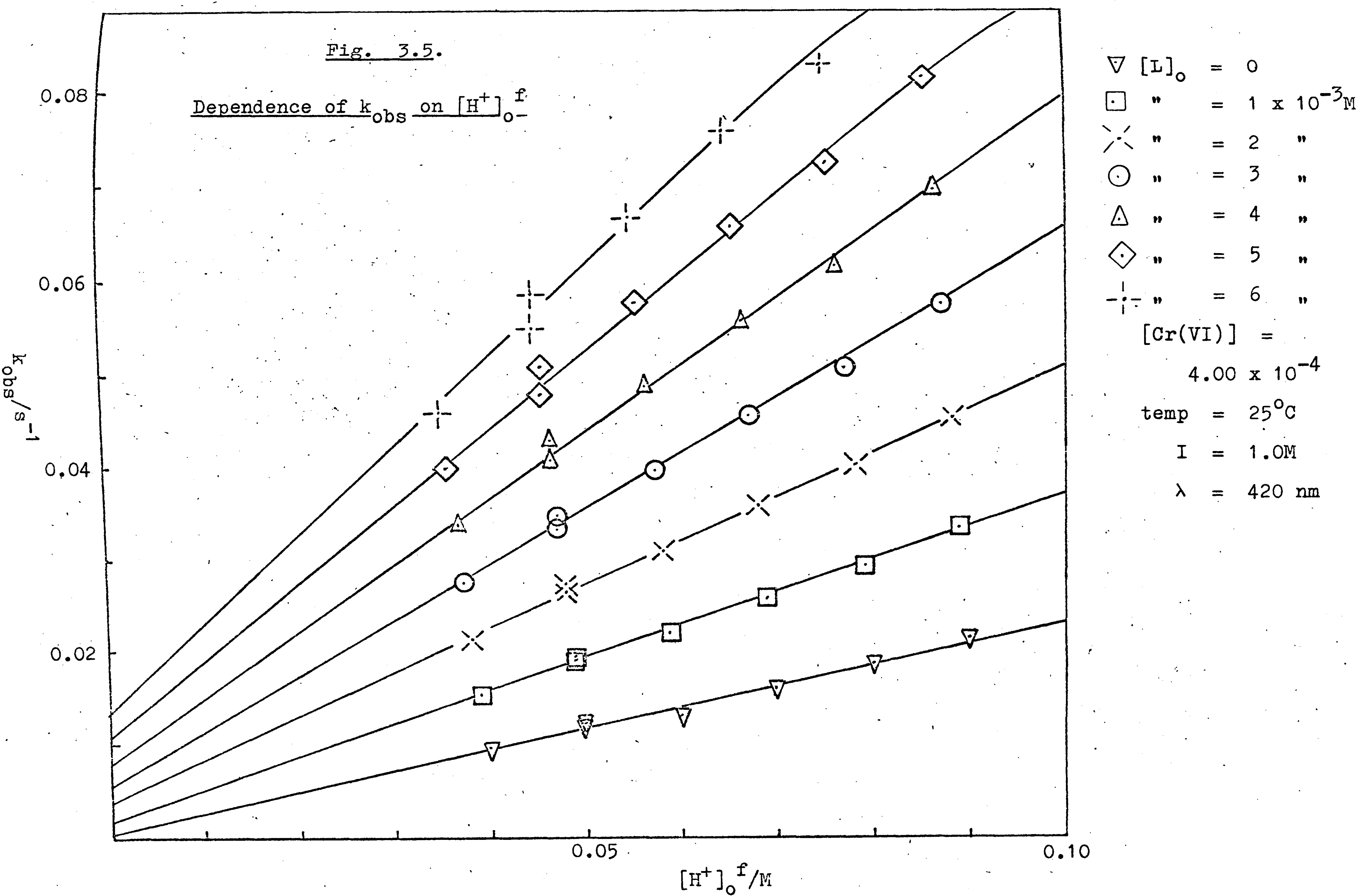


Fig. 3.5.

Dependence of k_{obs} on $[H^+]_o^f$

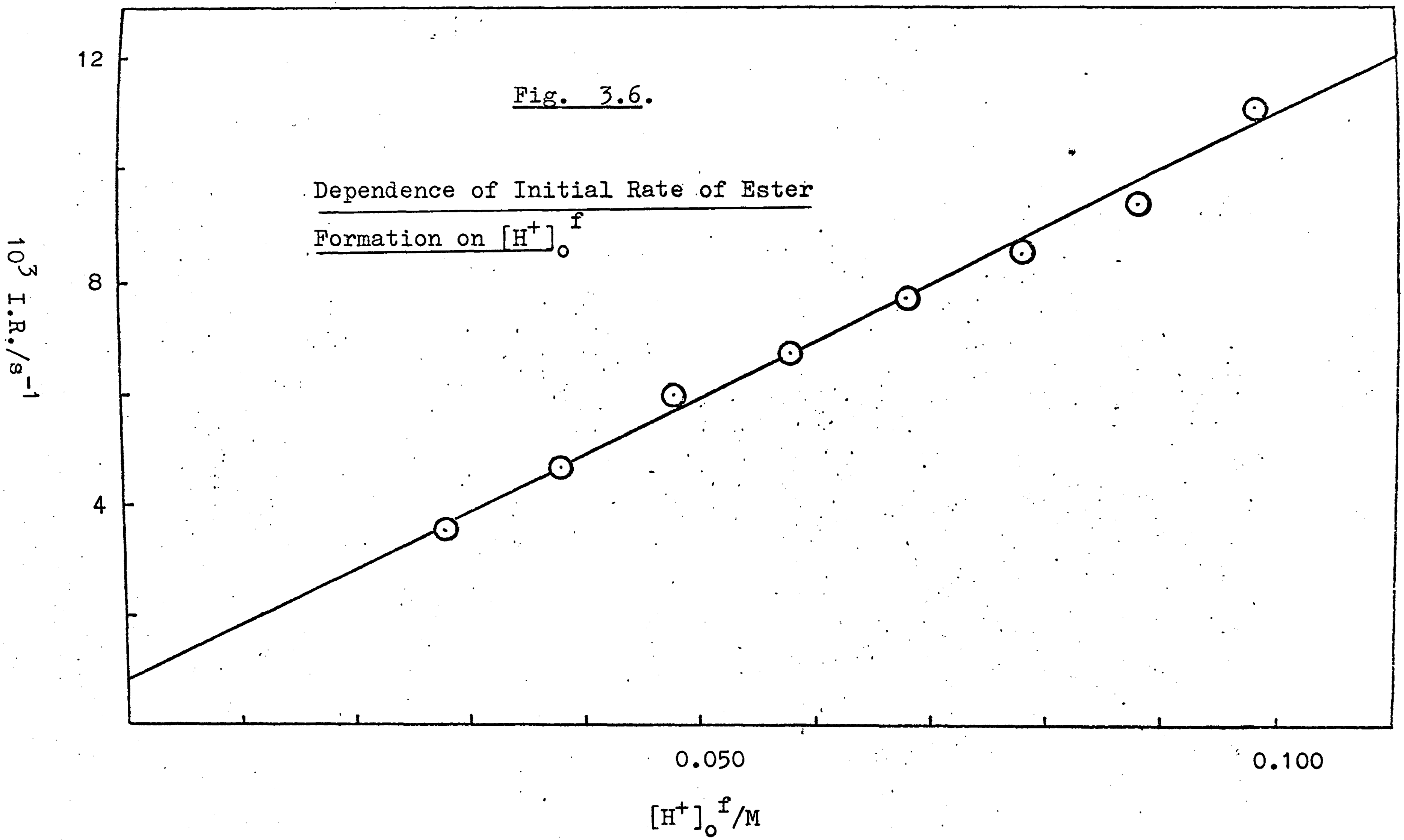


Fig. 3.6.

Dependence of Initial Rate of Ester Formation on $[H^+]_o^f$

$[Cr(VI)]_o = 5.00 \times 10^{-4}M$; $[\text{L-cysteine}]_o = 2.304 \times 10^{-3}M$; temp = 25°C

λ = 420 nm; path-length = 0.5 cm.

$$H^+ + HCrO_4^- + H_3L^+ \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} H_2LCrO_3 + H_2O + H^+ \qquad (31)$$

It can be shown that, under conditions of a sufficient excess of L-cysteine, this reaction scheme would give rise to the relationship, equation (32)

$$\frac{d\,[\mathrm{COMPLEX}]}{dt} = \left\{\left(\frac{k_1K_a+(k_2+k_3K_a)[H^+]_o{}^f+k_4([H^+]_o{}^f)^2}{K_a + [H^+]_o{}^f}\right)[\text{L-cysteine}]_o + \left(\frac{k_{-1}K_b+(k_{-2}+k_{-3}K_b)[H^+]_o{}^f+k_{-4}([H^+]_o{}^f)^2}{K_b + [H^+]_o{}^f}\right)\right\}\left\{[\mathrm{COMPLEX}]_\Omega - [\mathrm{COMPLEX}]_t\right\} \qquad (32)$$

Assuming (27) to hold, (33) derives from (32).

$$k_{obs} = \left(\frac{k_1K_a + (k_2+k_3K_a)[H^+]_o{}^f + k_4([H^+]_o{}^f)^2}{K_a + [H^+]_o{}^f}\right)[\text{L-cysteine}]_o + \left(\frac{k_{-1}K_a + (k_{-2}+k_{-3}K_a)[H^+]_o{}^f + k_{-4}([H^+]_o{}^f)^2}{K_a + [H^+]_o{}^f}\right) \qquad (33)$$

If the kinetic data conformed to the above relationship, (33), plots of k_{obs} as a function of $[H^+]_o{}^f$ should show curvature in the region of $[H^+]_o{}^f$ corresponding in magnitude to the value of K_a of L-cysteine. In the present study it was found that a plot of initial rate as a function of $[H^+]_o{}^f$, varying from 0.026 M to 0.096 M was linear with a positive intercept (Fig. 3.6.). Baldea and Niac in a separate study of this reaction confirm linearity of plots of k_{obs} against $[H^+]_o{}^f$ in the range $[H^+]_o{}^f = 0.005$ -

0.100 M.[193] We have attributed this to there being no difference in the rates of complex formation of the two predominant L-cysteine species, thus rendering it unnecessary, as in the overall equilibrium study, to distinguish between them.

Previous reports[115,194] have been made of absences of effects on observed substitution rates resulting from variations in charge at a part of a substrate molecule which is fairly remote from the reaction centre, That such a rate invariance is encountered with this reaction strengthens the case for exclusively sulphur-linkage between metal-ion and ligand.

Representing the total L-cysteine as the predominant form, H_3L^+, the reaction scheme can be simplified to equations (34) and (35)

$$HCrO_4^- + H_3L^+ \underset{k_b}{\overset{k_f}{\rightleftharpoons}} H_2LCrO_3 + H_2O \qquad (34)$$

$$H^+ + HCrO_4^- + H_3L^+ \underset{k_b^{H^+}}{\overset{k_f^{H^+}}{\rightleftharpoons}} H_2LCrO_3 + H_2O + H^+ \qquad (35)$$

where $k_f = k_1 = k_2$; $k_b = k_{-1} = k_{-2}$;

$k_f^{H^+} = k_3 = k_4$; $k_b^{H^+} = k_{-3} = k_{-4}$.

On the basis of this scheme equation (36) can readily be derived.

$$k_{obs} = (k_f + k_f^{H^+}[H^+]_o^f)[\text{L-cysteine}]_o + (k_b + k_b^{H^+}[H^+]_o^f) \quad (36)$$

Rearrangement of (36) yields (37)

$$k_{obs} = \left(k_f^{H^+}[\text{L-cysteine}]_o + k_b^{H^+}\right)[H^+]_o^f + \left(k_f[\text{L-cysteine}]_o + k_b\right)$$
$$= \alpha[H^+]_o^f + \beta \quad (37)$$

Plots of α against $[\text{L-cysteine}]_o$ were linear (Fig. 3.7.) with slope $k_f^{H^+}$ and intercept $k_b^{H^+}$. Similarly the hydrogen-ion independent rate constants were derived from linear variations of β with ligand concentration. Values of both these constants at various temperatures are presented in Table 3.5.

Any thought that the orange intermediate species involve chromium in the +5 oxidation state rather than +6 is dispelled not only by the finding that the form of the formation rate law is that generally found for equilibria but also the fact that the ratio of $k_f^{H^+}$ to $k_b^{H^+}$ is of the same order of magnitude as the spectrophotometrically measured equilibrium constant.

The Hydrogen-Ion-Dependent Pathway

As can be seen by inspection of Table 3.6, where data are presented on kinetic parameters relating to complex formation with $HCrO_4^-$ by ligands structurally related to cysteine, $k_f^{H^+}$ is in each case less than

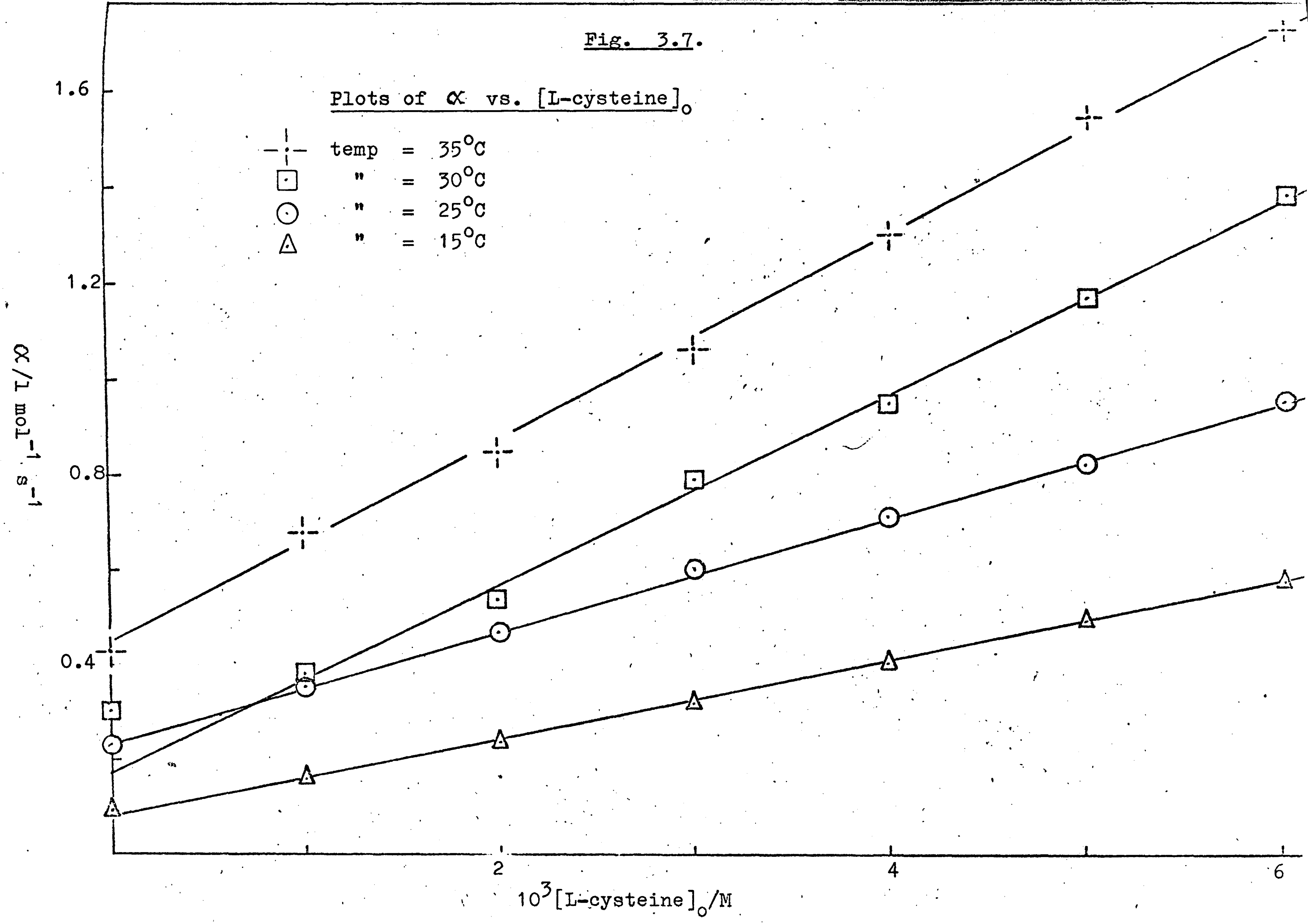


Fig. 3.7.

Plots of α vs. $[\text{L-cysteine}]_o$

Table 3.5.

Dependence of $k_f^{H^+}$ and k_f on temperature

temperature/^{o}C	$k_f^{H^+}/l^2\ mol^{-2}\ s^{-1}$ (a)	$k_f/l\ mol^{-1}\ s^{-1}$
15.0	84 ± 15	0.5 ± 0.5
25.0	130 ± 20	2 ± 1
30.0	204 ± 20	-
35.0	216 ± 20	2 ± 1

(a) $\Delta H^{\ddagger} = 7 \pm 3$ kcal mol^{-1};

$\Delta S^{\ddagger} = -24 \pm 11$ cal mol^{-1} K^{-1}

Table 3.6.

Parameters Relating to Intermediate Chromate(VI) Esters Formed in the Course of the Reduction of $HCrO_4^-$ by some Sulphydryl-Containing Substrates at Unit Ionic Strength and 25.0°C in Aqueous Perchloric Acid Media.

	ε_{max}	$\lambda_{max}^{(a)}$	$K^{(b)}$	$k_f^{H^+ (c)}$	$k_f^{(d)}$	ref.
mercaptoethylamine	430 nm	1300	1200	380	1.7	e
cysteine	420 nm	1410	1030	130	2	f
penicillamine	420 nm	1250	680	34	2.0	e
glutathione	430 nm	1280	1260	700	-	e

(a) Units of $l\ mol^{-1}\ cm^{-1}$.

(b) Units of $l\ mol^{-1}$.

(c) Units of $l^2\ mol^{-2}\ s^{-1}$

(d) Units of $l\ mol^{-1}\ s^{-1}$

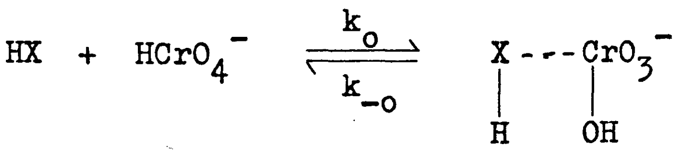
(e) A. McAuley and M.A. Olatunji, to be published.

(f) This work.

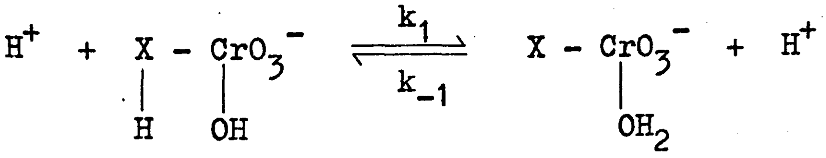
$10^3\ l^2\ m^{-2}\ s^{-1}$.

There has been some recent controversy concerning the nature of the general mechanism of acid-catalysed substitution of -OH in the hydrogen chromate anion.[186,195] All rate constants so far determined for such reactions have values in the range (1-7) x $10^5\ l^2\ mol^{-2}\ s^{-1}$ (Table 3.7.).

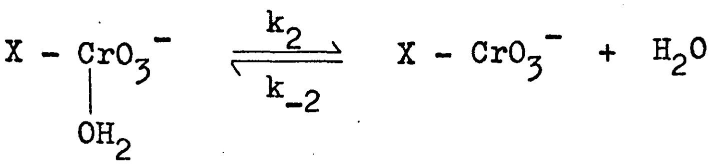
To explain the independence of the magnitude of this parameter of the nature of the ligand involved, Lin and Beattie[186] postulated that this phenomenon was a result of the rate-determining step being diffusion-controlled protonation of co-ordinated hydroxyl ion. The mechanism suggested involves three stages :



$$\mathrm{HX} + \mathrm{HCrO_4^-} \underset{k_{-o}}{\overset{k_o}{\rightleftharpoons}} \underset{\mathrm{H}}{\overset{}{\mathrm{X}}}\text{- - -}\underset{\mathrm{OH}}{\mathrm{CrO_3^-}} \qquad K_o = \frac{k_o}{k_{-o}} \qquad (38)$$



$$\mathrm{H^+} + \underset{\mathrm{H}}{\mathrm{X}} - \underset{\mathrm{OH}}{\mathrm{CrO_3^-}} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{X} - \underset{\mathrm{OH_2}}{\mathrm{CrO_3^-}} + \mathrm{H^+} \qquad (39)$$



$$\mathrm{X} - \underset{\mathrm{OH_2}}{\mathrm{CrO_3^-}} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{X - CrO_3^-} + \mathrm{H_2O} \qquad (40)$$

The first stage, (38), is the diffusion-controlled formation of a weak complex and the second, (39), involves diffusion-controlled protonation of -OH co-ordinated to the chromium centre, with subsequent loss of a proton from the substrate resulting in the formation of a fully 5-co-ordinate intermediate.

Knowing that the rate of this pathway is proton-

Table 3.7.

Chromate(VI) Ester Formation Rate Constants at 25.0°C as Measured in Other Laboratories

($k_f^{H^+}$ is the specific rate for the hydrogen-ion-dependent pathway.

k_f is the specific rate for the hydrogen-ion-independent pathway.)

Substrate	I/M	$k_f^{H^+}/l^2mol^{-2}s^{-1}$	$k_f/lmol^{-1}s^{-1}$	ref.
$HCrO_4^-$	1.0	6.2×10^5	-	(a)
	0.1	-	2	(b)
$H_2PO_4^-$	3.0	1.2×10^5	-	(c)
$H_2PO_3^-$	3.0	5.0×10^5	-	(d)
$HS_2O_3^-$	0.11	-	2×10^4	(e)
$S_2O_3^-$	0.11	$(3.7 \times 10^5)^*$	-	(e)
SCN^-	0.3	5.4×10^5	-	(f)
$(NH_3)_5CoOH^{2+}$	0.25	4.0×10^5	-	(g,h)
$(NH_3)_4Co(OH_2)OH^{2+}$	0.25	4.0×10^5	-	(g,h)

* Calculated on the basis of the alternative interpretation of the rate data by A. Haim, Inorg. Chem., 1972, 12, 3147.

(a) J.R. Pladziewicz and J.H. Espenson, Inorg. Chem., 1971, 10, 634.

(b) J.H. Swinehart and G.W. Castellan, Inorg. Chem., 1964, 3, 278.

(c) S.A. Frennesson, J.K. Beattie, and G.P. Haight, J. Amer. Chem. Soc., 1968, 90, 6018.

(d) S.A. Frennesson, J.K. Beattie, and G.P. Haight, Acta Chem. Scand., 1969, 23, 3277.

(e) K.A. Muirhead, G.P. Haight, and J.K. Beattie, J. Amer. Chem. Soc., 1972, 94, 3006.

(f) C.T. Lin and J.K. Beattie, J. Amer. Chem. Soc., 1972, 94, 3011.

(g) M. Woods and J.C. Sullivan, Inorg. Chem., 1973, 12, 1459.

(h) G.P. Haight, Inorg. Chem., 1973, 12, 1461.

dependent, the authors reasoned that the rate-determining step occurred at either (39) or (40).

Since the acid-catalysed rate constants for the anation reaction, $k_f^{H^+}$, are independent of the acid strength of the substrate, it was necessary to assume that loss of the proton from the substrate took place after the transition state, thus leading to the conclusion that the rate-determining step is (39). On the basis of this reaction scheme, equation (41) holds.

$$K_f^{H^+} = K_o k_1 \qquad (41)$$

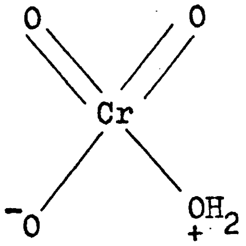
To explain the fact that K_o is independent of the chemical nature of HX it was proposed[158] that K_o was determined mainly by electrostatic factors.

It has been shown by Haim,[195] however that for k_{-o} to have a physically possible value, k_o must be less than $\sim 5 \times 10^4$ l mol^{-1} s^{-1}. He also expressed doubt that K_o would in reality be as invariant as would be required by this scheme and concluded that the more likely mechanism is one involving protonation of $HCrO_4^-$ as the first step with loss of water being rate-determining.

Moreover, the formation of the first intermediate, assuming that release of the proton and the water molecule occur faster, would in fact be the rate-determing step. This, however, would not give rise to the observed dependence of the rate on hydrogen ion concentration.

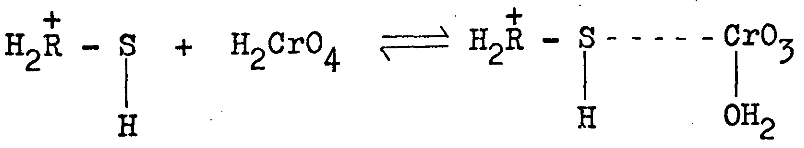
Since $k_f^{H^+}$ for substitution of L-cysteine on $HCrO_4^-$ is $\sim 10^3$ times smaller than for all other similar reactions previously studied,[196] it seems reasonable to conclude that in this present reaction either formation of the Cr-S bond or dissociation of the -S-H bond is rate-determining.

Protonation occurs before the rate-determining step, and co-ordination of sulphur either is the rate-determining step or occurs before it. Assuming the general mechanism preferred by Haim[195] to hold, water loss, which is not rate-determining in this reaction, takes place with a specific rate probably greater than 10^5 s^{-1} as the equilibrium constant for formation of



is almost certainly less than 1.

$$HCrO_4^- + H^+ \rightleftharpoons H_2CrO_4 \qquad (42)$$



$$H_2\overset{+}{R}-\underset{\substack{|\\ H}}{S} + H_2CrO_4 \rightleftharpoons H_2\overset{+}{R}-\underset{\substack{|\\ H}}{S}\text{-----}\underset{\substack{|\\ OH_2}}{CrO_3} \qquad (43)$$

If the rate of protonation of $H_2\overset{+-}{RS}$ is diffusion-controlled[197] and the strength of the S-H bond is unaffected by a weak S...Cr linkage, the rate of deprotonation of $H_2\overset{+}{R}SH$ can be estimated from the known dissociation constants, K_a', for the two species of L-cysteine.

$$H_2\overset{+}{R}SH \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} H_2\overset{+-}{RS} + H^+ \qquad (44)$$

$$K_a' = {}^{k_d}/_{k_{-d}} \qquad (45)$$

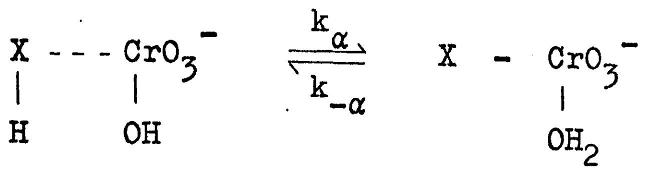
$$k_d \cong 10^{10}K_a' \qquad (46)$$

Values of k_d obtained in this way are less than $10^2\ s^{-1}$. Thus one might expect water loss to be faster than deprotonation, which would then be the final step. If deprotonation were rate-determining, however, then by the principle of microscopic reversibility the rate-determining step for aquation of the complex would be protonation, which is usually diffusion-controlled. Such a situation is unlikely, not only because it is highly unusual for a diffusion-controlled step to be rate-determining, but also because the rate constant for acid-catalysed aquation of the complex would be expected to be $\sim 10^{10}\ l\ mol^{-1}\ s^{-1}$ as opposed to the observed value of $\sim 0.15\ l\ mol^{-1}\ s^{-1}$.

We conclude, therefore, that formation of the Cr-S bond is the rate-determining process.

The Hydrogen-Ion Independent Pathway

A general mechanism has been proposed[186] for acid-independent substitutions on $HCrO_4^-$ where it is necessary to postulate internal proton-transfer to form the departing water molecule, equation (47), assuming that general acid catalysis is not occurring.



$$\underset{\mathrm{H}}{\mathrm{X}}\cdots\underset{\mathrm{OH}}{\mathrm{CrO_3^-}} \underset{k_{-\alpha}}{\overset{k_\alpha}{\rightleftharpoons}} \mathrm{X} - \underset{\mathrm{OH_2}}{\mathrm{CrO_3^-}} \qquad (47)$$

The approximate proportionality of k_f to the acid strength of HX has led to the proposal[186] that loss of a proton from the loosely co-ordinated acidic substrate is rate-determining. Values of k_α have been estimated, assuming that this is equal to the proton dissociation rate constant, k_d, of non-bonded HX, using equation (45). By ascribing to K_o the estimated value of 10^{-5} l mol^{-1},[158,186] k_f can be calculated from equations (46) and (48).

$$k_f \quad = \quad K_o k_d \qquad (48)$$

Using the maximum possible values of K_o, K_a', and k_{-d}, this procedure yields a value of k_f two orders of magnitude less than that obtained experimentally in this study.

Table 3.6. illustrates that values of k_f found for 2-mercaptoethylamine and penicillamine with $HCrO_4^-$ are very close to that measured for the corresponding process with L-cysteine.

II The Electron-Transfer Reaction

1. Stoicheiometry and Final Products

Results obtained by the acidimetric titration method[181] indicate a value for the L-cysteine : Cr(VI) ratio of 3.05 ± 0.06 suggesting the overall reaction to be given by equation (49)

$$x\,H^+ + 2HCrO_4^- + 6HS\text{-}RH_2^+ \rightarrow 2Cr(III) + 3H_2\overset{+}{R}S\text{-}S\overset{+}{R}H_2 \qquad (49)$$

with L-cysteine acting as a one-equivalent reductant under conditions of excess ligand.

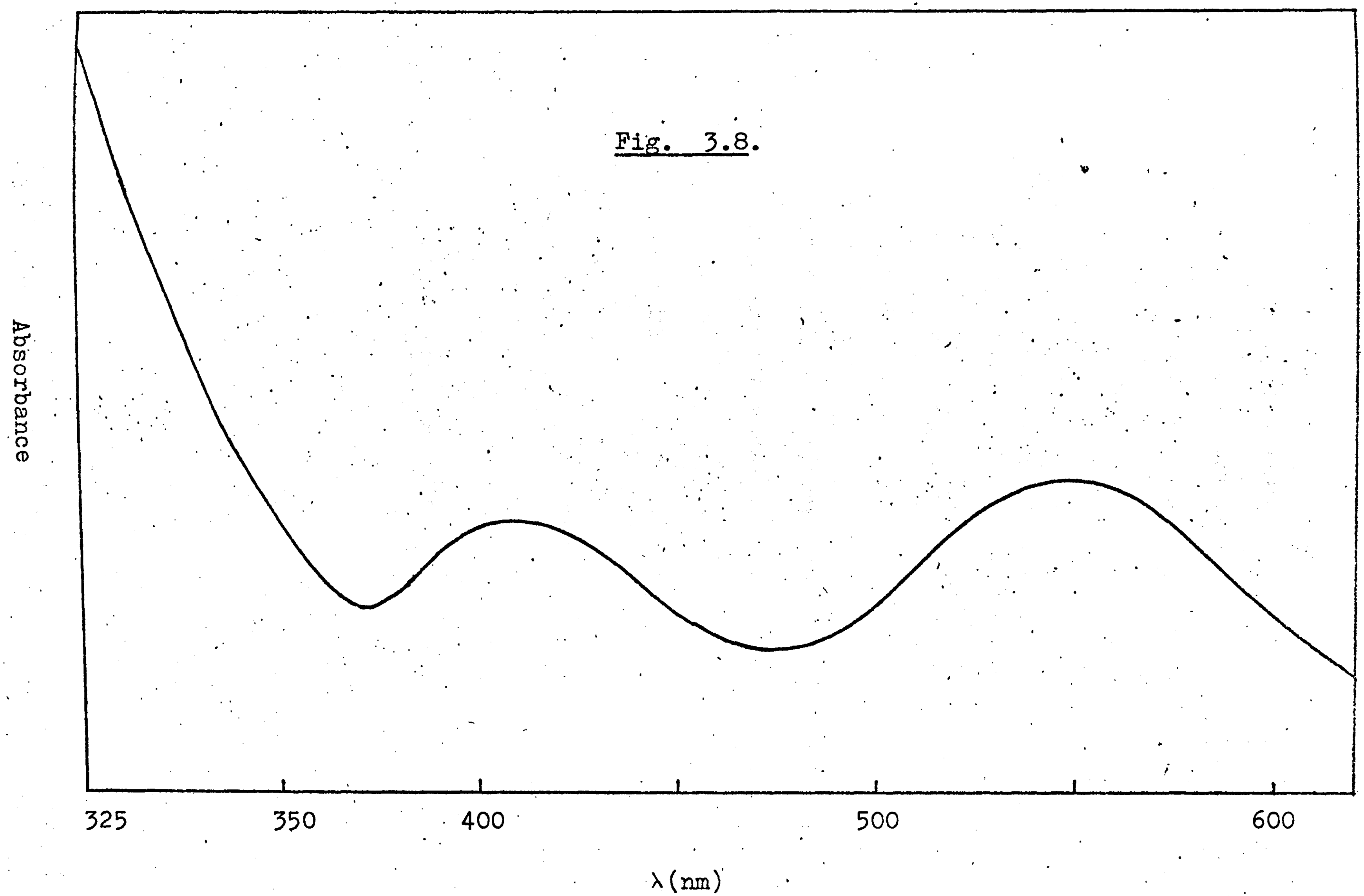
In the spectrophotometric titration, solutions having chromium(VI) in excess were found to undergo further reaction, presumably overoxidation of L-cysteine.

Under conditions described in the experimental section the chromium(III) products were coloured complexes; see Fig. 3.8.

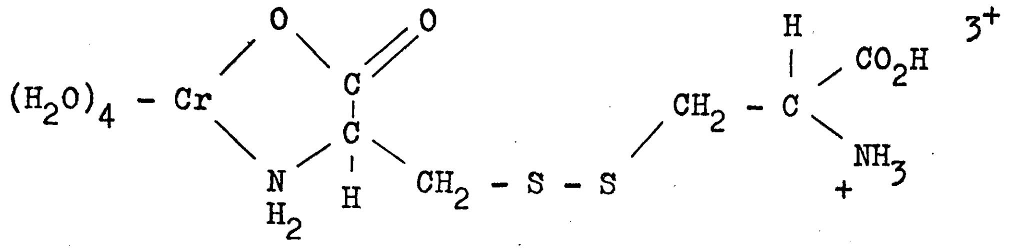
Both by using the method of King and Dismukes[198] and by using $Cr(H_2O)_6^{3+}$ and $Cr(H_2O)_5Cl^{2+}$ as references for comparison of elution rates it was possible to show that the purple species eluted with 1 M HNO_3 was doubly charged and contained about 60% of the total chromium. Also identified were $Cr(H_2O)_6^{3+}$ and a purple species which could not be eluted with 2 M HNO_3 but appeared to aquate on prolonged elution to yield $Cr(H_2O)_6^{3+}$ which could of course be eluted with this eluent. This latter purple complex is considered to be a dimeric 4+ species formed by parallel reaction of $Cr_2O_7^{2-}$, a fact which contrasts with currently held views on the reactivity of this species compared with $HCrO_4^-$.

Assuming that the measured stoicheiometry of 3.05 is not a composite value resulting from consumption of L-cysteine not only by oxidation but also by co-ordination to Cr(III), followed by separation on the ion-exchange column,

Fig. 3.8.



Spectrum of Complex Final Products of Reaction of Chromate(VI) with L-cysteine the conclusion seems inevitable that it is cystine which is co-ordinated to Cr(III) in the purple complexes. The structure proposed for the monomeric complex is



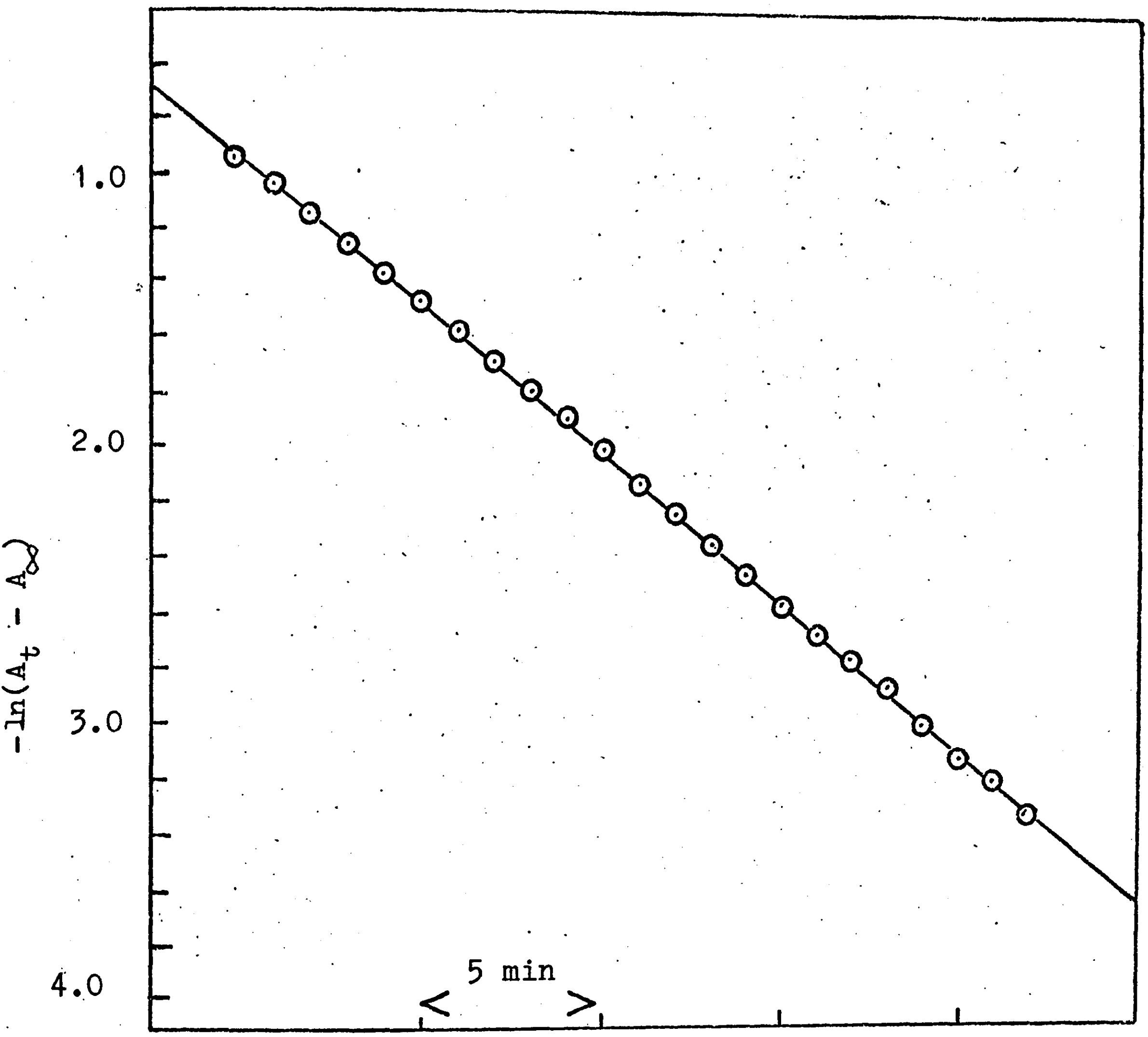
Although the overall charge on this species is 3^+, the charge separation would seem to be sufficiently great for it to behave as a doubly-charged species on the ion-exchange column.

2. Kinetics of the Electron-Transfer Reactions

In order to simplify the redox kinetics, a sufficient excess of L-cysteine was used such that no free $HCrO_4^-$ was present in the redox step. Plots of $\ln(OD_t - OD_\infty)$ against time were linear to 85-90% reaction (Fig. 3. 9). The pseudo-first-order rate constants, k_{obs}, obtained as the slopes of these plots were found to be independent of the wavelength at which measurements were made. Rate constants at various H^+ and L-cysteine concentrations are presented in Table 3.8 . Degassing reactant solutions had no effect on reaction rates. No difference was observed in one experiment where 0.0416 M Mn(II) was present.

Plots of k_{obs} as a function of $[\text{L-cysteine}]_0$ yielded straight lines with positive intercepts (Fig. 3.10.). The

Fig. 3.9.



Linearisation of Pseudo-First-Order Decay of Chromate(VI)-Cysteine Esters

$[Cr(VI)] = 4.00 \times 10^{-4}M$; [L-cysteine] = $1.69 \times 10^{-3}M$; $[H^+] = 0.040M$; $\lambda = 420$ nm; temp = 25°C

Table 3.8.

Rate constants for the Redox Reaction

$[Cr(VI)]_0 = 4 \times 10^{-4}M$; $I = 1.00M$; $\lambda = 420nm$

temp. 15.0°C

$10^2[\text{L-cysteine}]_0/M$	$10^3 k_{obs}/s^{-1}$	$10^2[\text{L-cysteine}]_0/M$	$10^3 k_{obs}/s^{-1}$
$[H^+]_0 = 0.025M$		$[H^+]_0 = 0.075M$	
0.9461	0.473	0.9583	0.770
1.892	0.888	1.917	1.29
2.838	1.27	2.875	1.73
3.875	1.75	3.833	2.15
4.731	2.11	4.792	2.58
$[H^+]_0 = 0.050M$		$[H^+] = 0.100M$	
0.9386	0.589	0.9012	0.917
1.877	1.05	1.802	1.44
2.816	1.50	2.704	1.98
		3.605	2.35
		4.506	2.80

temp. 25.0°C

$10^2[\text{L-cysteine}]_0/M$	$10^3 k_{obs}/s^{-1}$	$10^2[\text{L-cysteine}]_0/M$	$10^3 k_{obs}/s^{-1}$
$[H^+]_0 = 0.020M$		$[H^+]_0 = 0.080M$	
0.9274	0.947	0.9792	1.72
1.855	1.75	1.958	2.84
2.782	2.64	2.938	3.69
3.710	3.61	3.917	4.68
4.637	4.79	4.896	5.47

$[H^+]_o$ = 0.040M

10^2[L-cysteine]$_o$/M	$10^3k_{obs}/s^{-1}$
0.8479	0.987
1.696	1.83
2.544	2.67
3.392	3.23
4.240	4.10

$[H^+]_o$ = 0.100M

10^2[L-cysteine]$_o$/M	$10^3k_{obs}/s^{-1}$
0.8954	1.93
1.791	2.89
2.686	3.86
3.582	4.85
4.477	5.61
3.078	3.85
3.078$^{(a)}$	3.94

$[H^+]_o$ = 0.060M

10^2[L-cysteine]$_o$/M	$10^3k_{obs}/s^{-1}$
0.8189	1.23
1.638	2.05
2.457	2.83
3.276	3.58
4.095	4.33

$[H^+]_o$ = 0.100M$^{(b)}$

10^2[L-cysteine]$_o$/M	$10^3k_{obs}/s^{-1}$
0.9500	1.92
1.900	2.98
2.850	3.97
3.800	4.81
4.750	5.63

temp. 35.0°C

$[H^+]_o$ = 0.050M

10^2[L-cysteine]$_o$/M	$10^3k_{obs}/s^{-1}$
0.955	2.39
1.910	3.86
2.865	5.66
3.820	7.40
4.775	8.40

$[H^+]_o$ = 0.100M

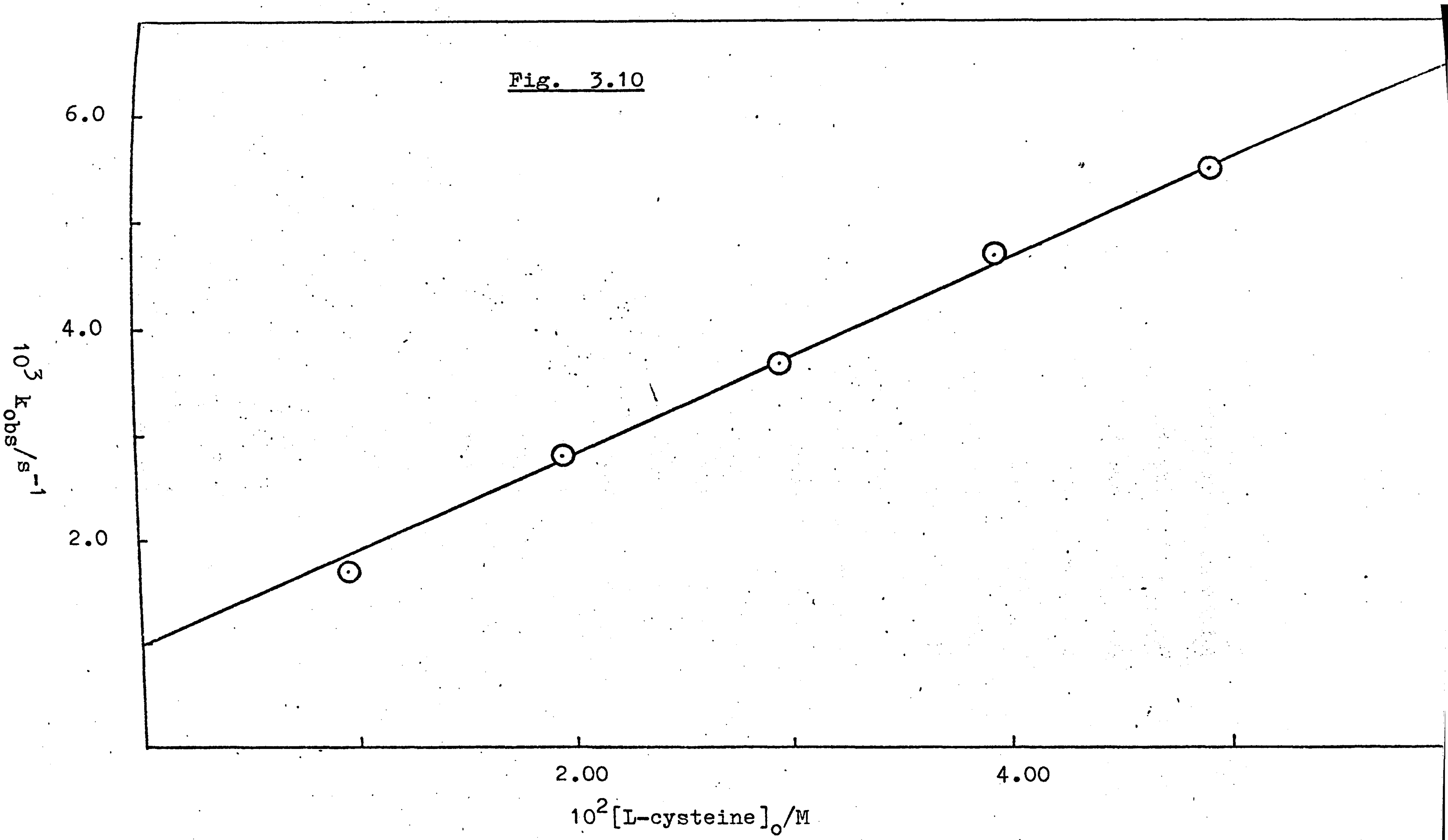
10^2[L-cysteine]$_o$/M	$10^3k_{obs}/s^{-1}$
0.9782	4.03
1.956	6.12
2.935	7.66
3.913	9.43
4.891	11.08

10^2[L-cysteine]$_o$/M	10^3k_{obs}/s^{-1}	10^2[L-cysteine]$_o$/M	10^3k_{obs}/s^{-1}
$[H^+]_o$ = 0.075			
0.928	2.92		
1.855	4.73		
2.783	6.39		
3.711	7.66		
4.639	9.12		

(a) Mn(II) added

(b) solutions degassed

Fig. 3.10



Ligand dependence of the pseudo-first-order rate constant for the Cr(VI)/L-cysteine redox reaction. $[Cr(VI)] = 4.00 \times 10^{-4}M$; $[H^+] = 0.06M$; $I = 1.0M$; $T = 25^{\circ}C$ $\lambda = 420$ nm.

slopes of these lines were acid independent, although the cysteine-independent pathway is hydrogen-ion dependent.

If H_2L and H_3L^+ react at different rates it would be expected that the slopes of plots of k_{obs} against ligand would be acid dependent since the proportions of these two species vary much more with $[\text{L-cysteine}]_o$ at the lowest acid concentration employed than at the highest. Thus, as in the kinetic and equilibrium studies of the formation of the intermediate complex it would appear that distinction is not possible in this work either between the reactions of these two species, or between those of the corresponding complexes $HLCrO_3^-$ and H_2LCrO_3.

Plots of intercept against $[H^+]_o$ (Fig. 3.11) suggested that this redox route is first-order in hydrogen ion. The decrease in absorbance at 420 nm is due solely to the disappearance of the intermediate complexes and the linearity of plots of $\log(OD_t - OD_\infty)$ against time indicated a reaction order of unity with respect to complex.

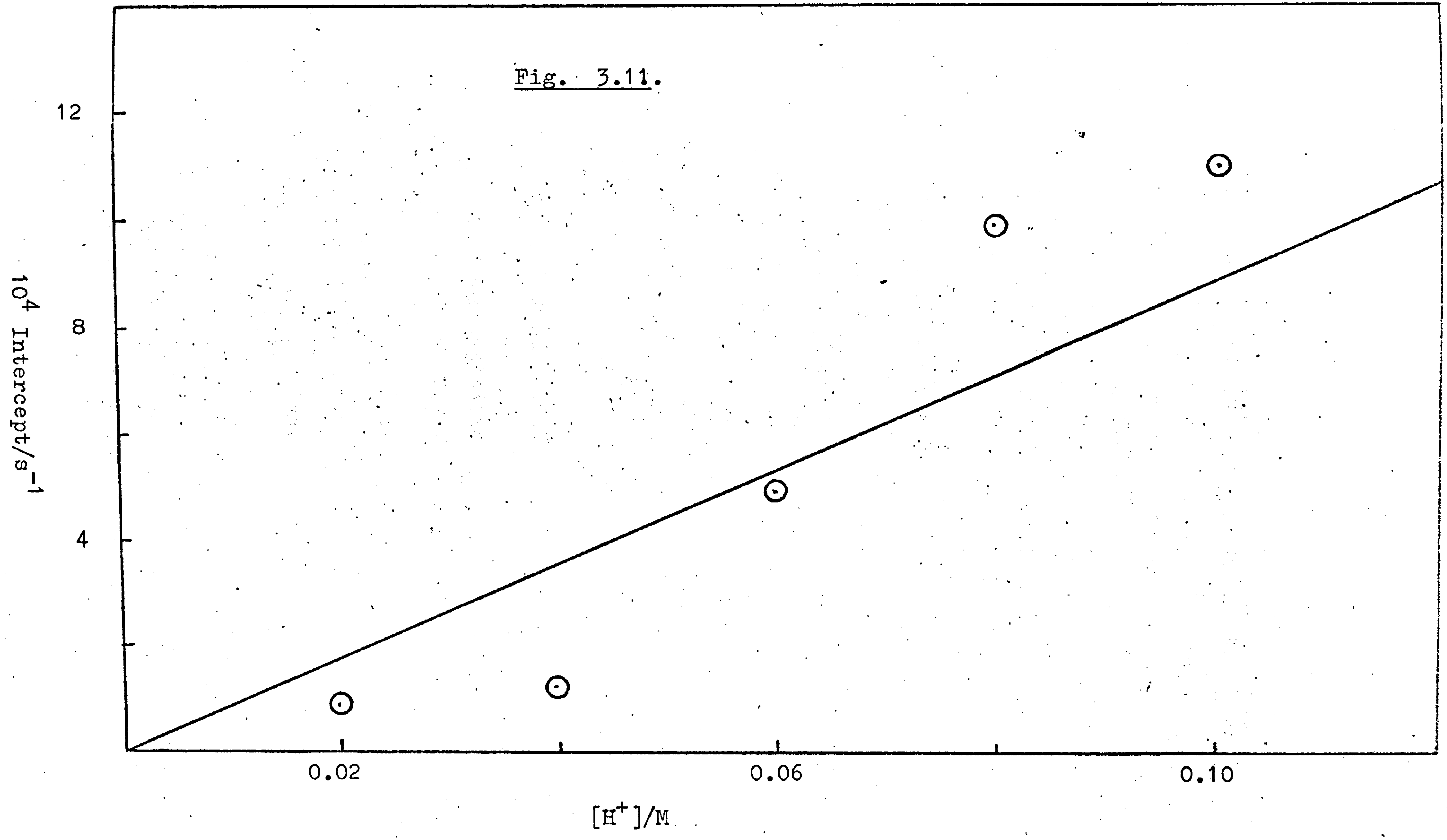
These results are consistent with the rate scheme given by equations (19), (50) and (51)

$$H_2RSCrO_3 + H^+ \xrightarrow{k_1} Cr(V) \qquad (50)$$

$$H_2RSCrO_3 + H_2RSH^+ \xrightarrow{k_2} Cr(IV) \qquad (51)$$

Hence the rate-law given by equation (52) may be derived

Fig. 3.11.



Hydrogen-ion dependence of rate of ligand-independent redox pathway.

temp = 25°C; I = 1.00M.

$$\frac{-d[\mathrm{Cr(VI)}]_{tot}}{dt} = \frac{K_1(k_1[\mathrm{H}^+] + k_2[\mathrm{H_2RSH}^+])[\mathrm{H_2RSH}^+][\mathrm{Cr(VI)}]_{tot}}{1 + K[\mathrm{H_2RSH}^+]}$$

$$= k_{obs}[\mathrm{Cr(VI)}]_{tot} \qquad (52)$$

where $[\mathrm{Cr(VI)}]_{tot} = [\mathrm{Cr(VI)}]_o$

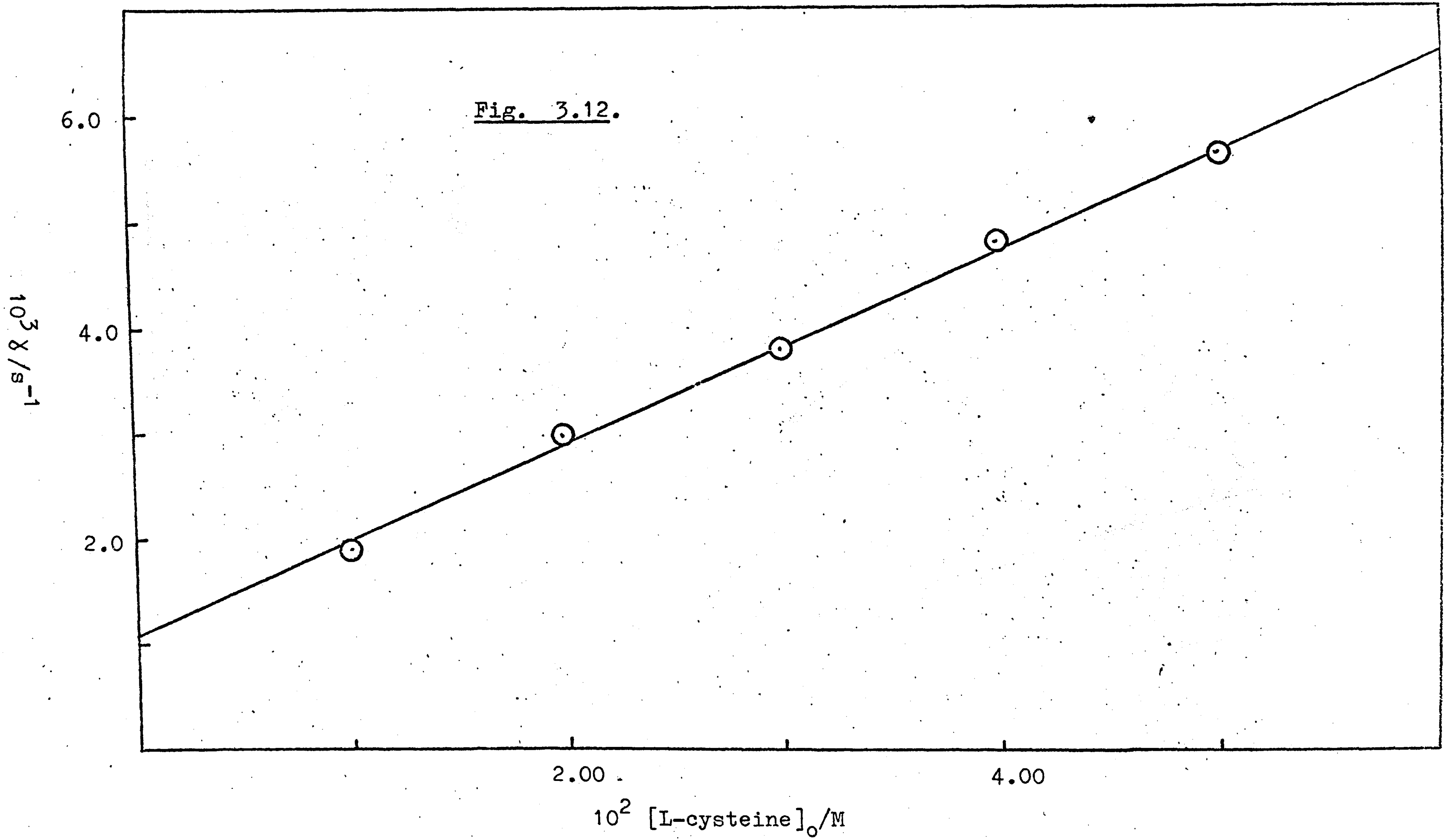
$\dfrac{k_{obs}(1 + K_1[\mathrm{H_2RSH}^+])}{K_1[\mathrm{H_2RSH}^+]}$, γ, evaluated using the appropriate values of K_1 in Table 3.3. was found to be a linear function of $[\mathrm{H_2RSH}^+]$. Plots of γ as a function of $[\mathrm{H_2RSH}^+]$ (Fig. 3.12.) yielded k_2 directly. k_1 was derived from plots of intercept against $[\mathrm{H}^+]_o$ (Fig. 3.13.). The variation of k_1 and k_2 with temperature is indicated in Table 3.9.

3. Mechanism of the Redox Processes

The route corresponding to k_1 is considered to involve three consecutive one-electron transfers, according to the conventional mechanism discussed earlier for reactions of one-electron reductants, with the first of the three steps being rate-determining.

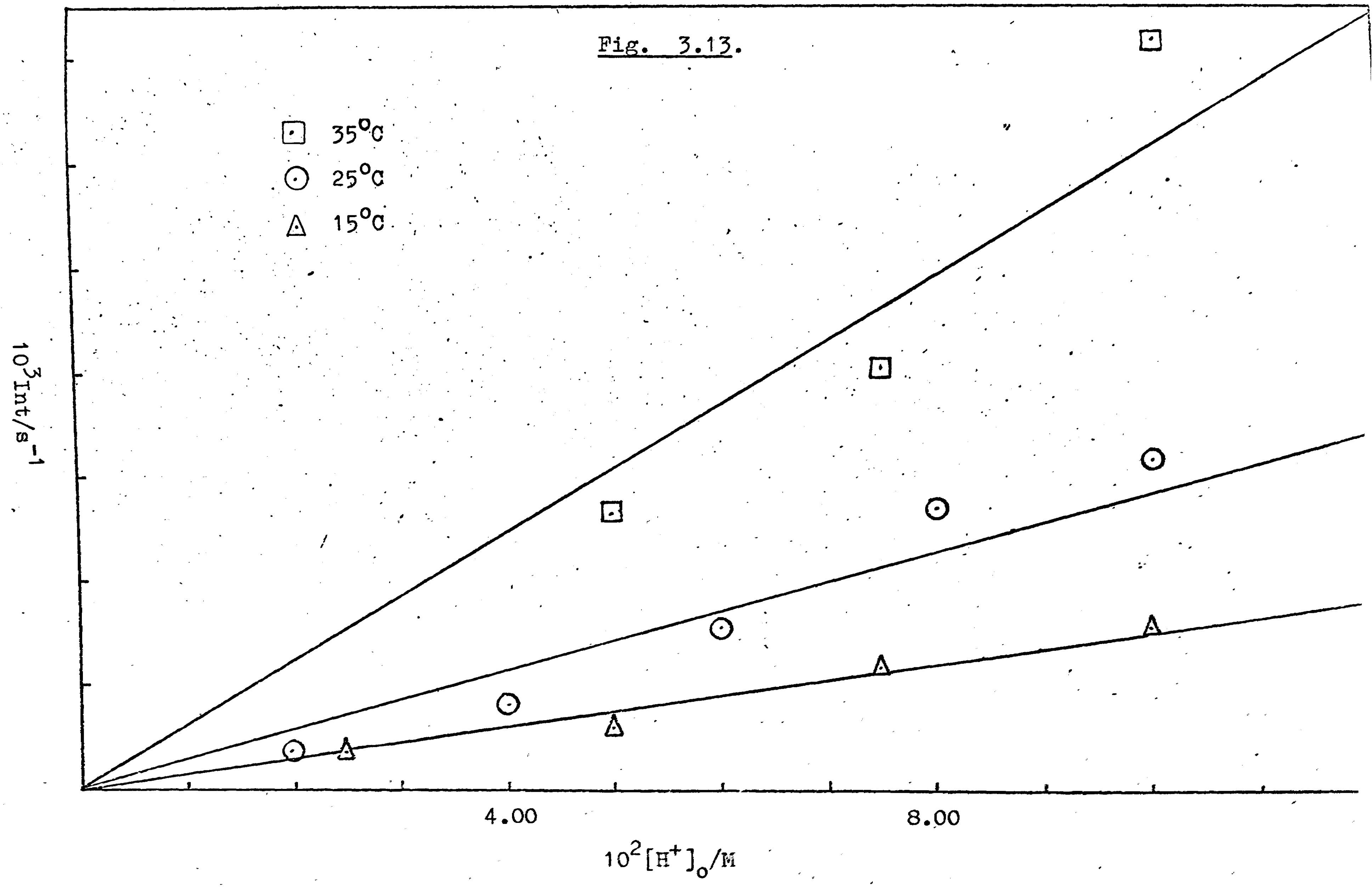
Table 3.10. enables a comparison to be made of $\Delta H_2^{\ddagger}$ and $\Delta S_2^{\ddagger}$ with activation parameters of corresponding routes in other chromate oxidations involving second-order ligand dependences. These values indicate that such routes involve similar processes with negligible dissociative character. The significance of such second-order processes has been discussed.[133]

Fig. 3.12.



Ligand dependence of γ (eqn. 52); $[H^+]$ = 0.080M; temp = 25°C

Fig. 3.13.



Hydrogen-ion dependence of intercepts of plots of vs [L-cysteine]$_o$

Table 3.9.

Dependence of k_1 and k_2 on temperature

temperature/^oC	$10^2k_1/l^2\ mol^{-2}\ s^{-1}$	$10^3k_2/l^2\ mol^{-2}\ s^{-1}$
15.0	4.6 ± 0.4	6 ± 1
25.0	9.4 ± 0.4	12 ± 3
35.0	16.9 ± 0.6	26 ± 4

$$\Delta H_1^{\ddagger} = 12 \pm 2\ \text{kcal mol}^{-1};$$

$$\Delta S_1^{\ddagger} = -27 \pm 7\ \text{cal K}^{-1}\ \text{mol}^{-1};$$

$$\Delta H_2^{\ddagger} = 10.8 \pm 0.8\ \text{kcal mol}^{-1};$$

$$\Delta S_2^{\ddagger} = -27 \pm 3\ \text{cal K}^{-1}\ \text{mol}^{-1}$$

Although the form of the redox rate-law found for this system could possibly suggest that the second cysteine molecule in the activated complex is acting as a general acid catalyst, similar second-order terms can be seen(Table 3.10)to be encountered with substrates such as iodide, thiocyanate and thiourea where no such role could be readily envisaged for the extra reductant molecule.

At some stage in the overall reduction of chromium(VI) to chromium(III), a change of co-ordination number from four to six is necessary. Chromium(IV) is generally considered[133] to be octahedral and it is possible that the additional substrate molecule may assist in expanding the co-ordination sphere to produce, with the participation of water molecules, an octahedral activated complex. This is thought[133] to be the function of two-equivalent reductants which are involved in such transition states.

For sulphur-containing one-electron reductants such as L-cysteine, routes corresponding to such terms are considered to provide a low energy pathway for formation of disulphide in a "template"-type reaction. The evidence obtained in this study that product disulphide is co-ordinated to Cr(III) supports this theory because, since Cr(III) is kinetically inert, cysteine must co-ordinate to either Cr(V) or Cr(IV). The latter alternative is considered more likely.

Regardless of whether chromium(IV) is formed by way of two consecutive one-electron transfers, pathway (50), or <u>via</u> an activated complex is which there is incipient

Table 3.10.

Activation Parameters for Chromate(VI) Oxidation Paths involving Second-Order Reductant Terms

Reductant	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}
L-cysteine (1)	10.8	-27
Pencillamine (2)	7.4	-37
Thiourea (a)(3)	11	-19
Thiosulphate (4)	8.2	-20.8
Sulphite (5)	4.5	-13
Oxalic Acid (6)	12.8	-18.6
Iodide (7)	9.7	-16

(a) First-order acid path

(1) This work

(2) ref. 25

(3) ref. 27

(4) ref. 6

(5) G.P. Haight, Jnr., E. Perchonock, F. Emmenegger, and G. Gordon, J. Amer. Chem. Soc., 1965, 87, 3835.

(6) G.V. Bakore and C.L. Jain, J. Inorg. Nuclear Chem., 1969, 31, 805.

(7) ref. 28

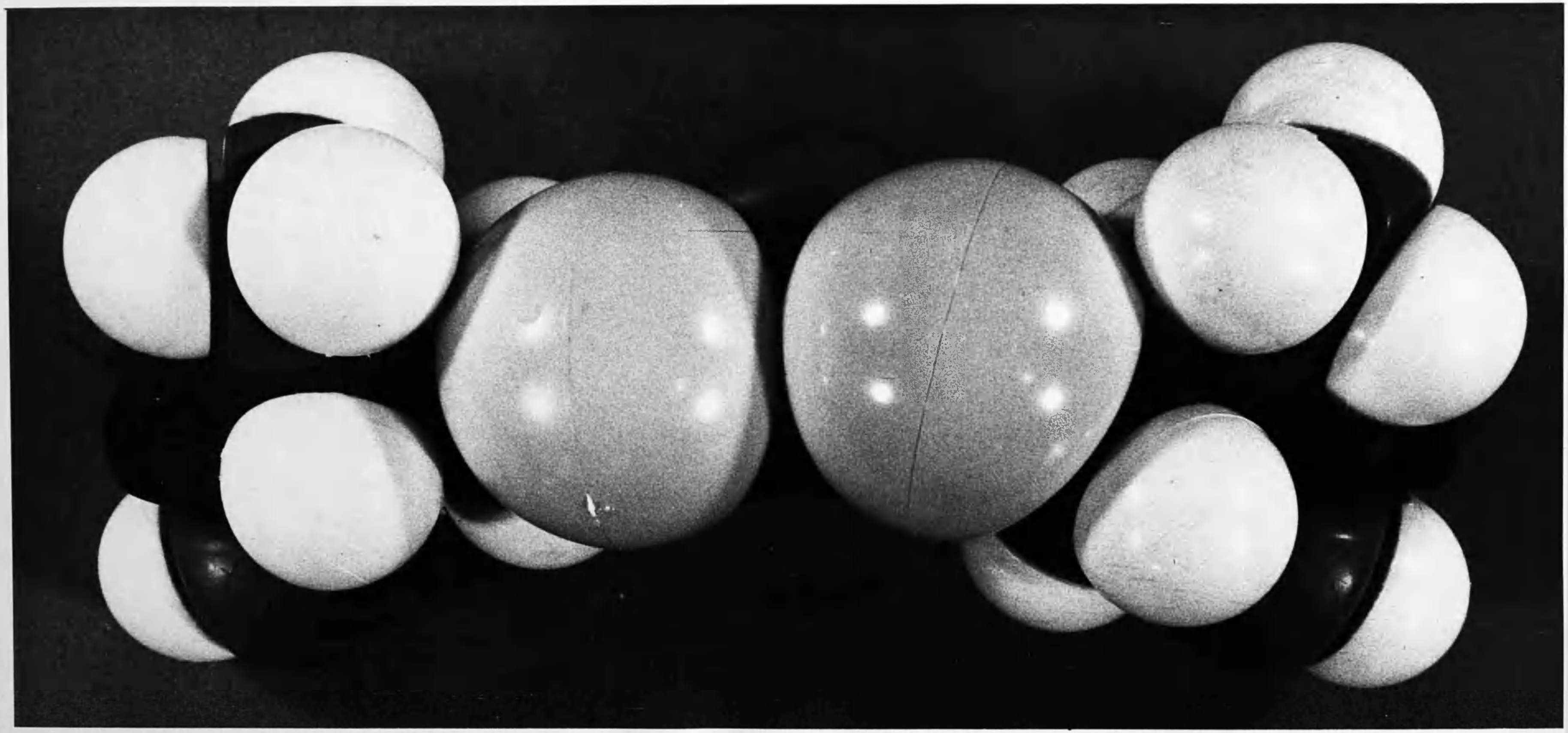


Fig. 3.14

cysteine, which was more abundant in solution.

No effect of Mn(II) on the reaction rate was observed in studies of the Cr(VI) oxidations of thiourea,[199] ethylenethiourea,[199] thiocyanate[185] and iodide.[200] The halving of the rate of other Cr(VI) oxidations upon addition of Mn(II) has been attributed to removal of Cr(IV) by reaction with Mn(II) thus rendering impossible reaction of a second Cr(VI) species with either Cr(IV) or the radical produced if the latter were to react with another substrate molecule. Thus on the basis of the mechanism we propose for reduction of Cr(VI) by L-cysteine, addition of Mn(II) would not be expected to affect its rate. Mn(II) is reported to inhibit the oxidation of thiosulphate by Cr(VI).[185] It is difficult to envisage how this phenomenon would occur under conditions where tetrathionate is produced. However, at high acidities and Cr(VI) concentrations where sulphate is produced[184] reaction of Cr(VI) with either Cr(IV) or $\cdot S_2O_3^-$ is considered to take place.

Further work is required before the mechanism of this reaction can be established with certainty. The use of E.P.R. in an attempt to clarify the role of chromium(VI), the trapping and identification of radicals, and the isolation and characterisation of the chromium(III) product complexes, remain to be used in the investigation of this system.

CHAPTER IV

A COMPARISON OF THE MODES OF OXIDATION OF MALIC AND THIOMALIC ACIDS BY CHROMIUM(VI)

Introduction

Malic acid and thiomalic acid (α-mercaptosuccinic acid) both react with a number of metal-ions. It has often proved possible to detect intermediate complexes of these ligands where such reactions involve redox processes.

An early study[201] of the reduction of cerium(IV) by malic acid in sulphuric acid media, in the presence of an excess of ligand, showed the immediate oxidation product to be an organic free radical. No complexation was observed. In another reported investigation[202] where similar conditions were employed, kinetic evidence was presented for the existence of an intermediate complex. Fission of a carbon-carbon bond was postulated to be the rate-determining step. The measured stoicheiometry indicated that the overall organic product was almost exclusively formic acid.

A recent study[203] of the cerium(IV) oxidation of this substrate in perchlorate media, where there is less competition with the counter-anion in complex formation with the oxidant, provided conclusive spectrophotometric proof of the existence of transient cerium(IV)-malate complexes. The formation of the intermediates was considerably more rapid than the decay, the former process being too fast to be detectable by stopped-flow methods. In addition, it was confirmed[203] that the formation of a free radical is the rate-determining step, as would be expected for a one-equivalent oxidant. A stoicheiometry almost identical to that reported by Dayal and Bukore[202] was found[203] for oxidation of an excess of ligand. The previous determination[202] of the stoicheiometry had been carried out using a excess of metal-ion.

The oxidation of malic acid by manganese(III)[204] and by vanadium(V)[205] is believed in each case to proceed by way of reversible formation of chelate complexes which break down with loss of carbon dioxide and formation of an organic radical. A fast one-equivalent oxidation of this latter species then follows. If an excess of metal-ion is present, further oxidation of the resultant keto-acid takes place. The evidence for participation of an intermediate is in each case based entirely on kinetic data; no direct observation of these species was reported.

Spectrophotometric characterisation of a transient complex was achieved in a study[206] of the oxidation of malic acid by cobalt(III) in which an excess of substrate over oxidant was maintained. No ligand dependence of the oxidation rate was detected. It appeared that the free radical initially formed was immediately oxidised further to the final product, oxaloacetic acid.

The chromium(VI) oxidation of malic acid appears to have been previously studied in detail by two research groups.[207,208] The mechanistic proposals concerning the results of one of these investigations[208(a)] are largely invalidated by the authors' erroneous assumption[208] that the reactant chromium(VI) entity is $HCrO_3^+$; all the available information[133] shows that it was in fact mainly

$HCrO_4^-$ which was present in the reaction mixtures.

Both groups were in agreement[207,208] that the overall redox reaction is first order in each of chromium(VI) and malic acid. Neither group of investigators reported a product analysis. In one case chromium(IV) was postulated as an intermediate while in another report[208(a)] there was a reference to the observation of a purple intermediate which was found to be stable for a week and was presumed to be a complex of one of the intermediate oxidation states of chromium, probably chromium(II). (This ion is in fact only stable for such a period of time if oxygen is excluded from its environment, in the presence of oxygen it rapidly reduces water.[133])

The observation in this laboratory that a much shorter-lived intermediate is involved in this reaction has led to its reinvestigation, the results of which will be presented in this chapter.

In several instances it is possible to make a direct comparison between the reactions of malic and thiomalic acids with a given metal-ion. Differences in their modes of reaction are directly attributable to the replacement of oxygen by sulphur.

Most metal-ion oxidations of thiols yield disulphides if the reductant is present in excess.[31,209] Thiomalic acid is no exception, although it has been shown[210] to be susceptible to overoxidation by both neptunium(VI) and cerium(IV) in an argon atmosphere to an extent which appears to be governed only by the magnitude of the initial thiol concentration.

A kinetic study[211] of the cerium(IV) sulphate oxidation of thiomalic acid showed, however, that the product is exclusively disulphide under the reaction conditions used therein. No complex formation was reported,[211] the reaction being simply first order in each of the two reagents.

Intermediate complexes have been identified spectrophotometrically in the oxidation of thiomalic acid by both vanadium(V)[212] and cobalt(III).[213] In the former system the kinetic data[212] suggest the involvement of pathway in addition to the more usual first-order process, whereby a ligand molecule interacts with the complex. Disulphide was found[212,213] to be the exclusive organic product of both redox processes.

The blue intermediate formed in the reduction of iron(III) by thiomalic acid has also been characterised[189] spectrphotometrically. Disulphide and iron(II) are the overall reaction products. The difference in reactivity conferred by replacement of oxygen by sulphur is illustrated especially well by the absence, under normal conditions, of any measurable redox reaction of the iron(III) malate complex.[214]

A transient orange colouration was observed when chromate(VI) solutions were mixed with thiomalic acid. In view of the interest currently centred on sulphur-bonded esters of this oxidant it was decided to undertake a kinetic investigation of this system. It was hoped also that a direct comparison might be possible between the reactions of malic and thiomalic acids with $HCrO_4^-$

Experimental

DL-malic acid (B.D.H. reagent grade) and DL-thiomalic acid (B.D.H. reagent grade) were used without further purification. Chromium(VI) stock solutions were prepared using potassium dichromate (B.D.H. AnalaR grade). Stock solutions of sodium perchlorate and perchloric acid were prepared and standardised as described in chapters 2 and 3.

The kinetics of the reaction of chromate(VI) with malic acid were studied using the "slow" hand-driven apparatus described in chapter 1. For the corresponding thiomalic acid reaction, this device was used in addition to the stopped-flow apparatus, also described in chapter 1, which was equipped with a Unicam S.P.500 monochromator as light-source. Calculation of the traces obtained with this latter machine was carried out using a Nova 1200 computer.

A Nova 2100 computer was used in calculating simulated kinetic traces for the reaction of $HCrO_4^-$ with thiomalic acid; the relevant program is reproduced in an appendix.

Results and Discussion

1. The Reaction of Chromate(VI) with Malic Acid

(a) Preliminary observations

Under the conditions used in this work, $[H^+]$ = 0.04-1.00M, T = 15^oC and I = 1.00M, $HCrO_4^-$ and undissociated malic acid (pKa's >3[127]) were the principal reactants. Dissociation of the organic substrate was assumed to be entirely negligible.

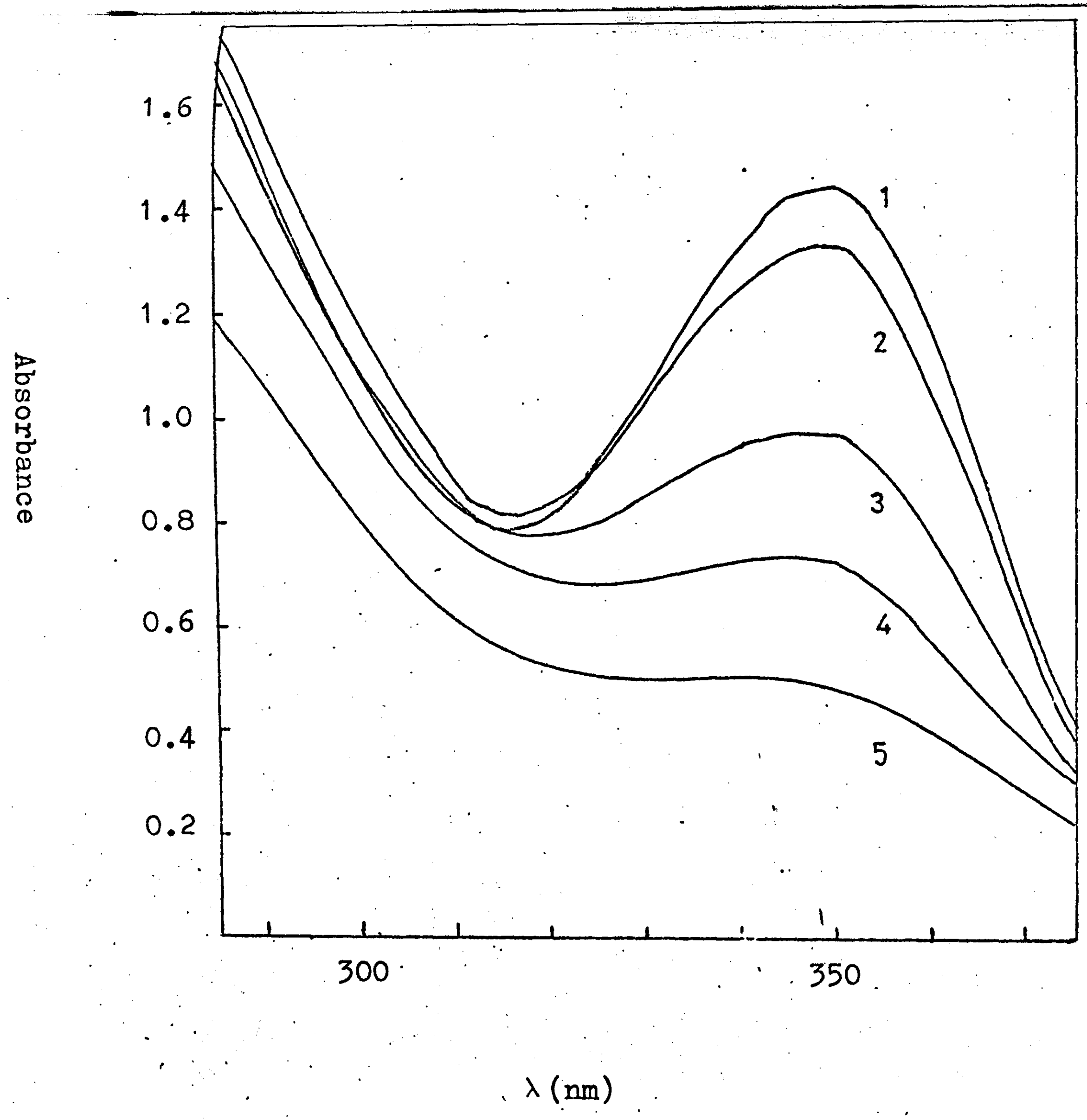
Scanning the spectrum of mixed reactants at frequent time intervals provided direct evidence for the existence of an isosbestic-point in the early stages of reaction, as illustrated in Fig. 4.1. This indicates the existence of an intermediate chromium-containing entity.

(b) The nature of the intermediate

As has been discussed in the previous chapter, three oxidation states of chromium, namely +6, +5, and +4, can be expected to be present in transient complexes formed in the course of reduction of $HCrO_4^-$. There have been no published reports of the direct observation of chromium(IV). The available spectra of chromium(V), species[133,142,149,215,216] have generally been quite different from that of the corresponding chromium(VI) complex. Moreover, chromium(V) is believed[151,152] to disproportionate rapidly in aqueous solution.

It has been noted,[158,184] however, that substitution of the -OH group of $HCrO_4^-$ by a functional group of similar

Fig. 4.1.



[Cr(VI) = 10^{-3}M

[Malic Acid] = 0.109M

[H^+] = 0.30M

I = 1.00M

temp = 35°C

1 t = 1 min

2 t = 3 min

3 t = 10 min

4 t = 16 min

5 t = 24 min

path-length = 1.00 cm

electronegativity, such as -OR where R is an alkyl substituent, leads to only minor changes in the spectrum of this ion. It is likely, therefore, that the transient species formed in this system is an oxygen-bonded chromate ester which reacts in the manner proposed by Westheimer.[130]

(c) The treatment of the absorbance data

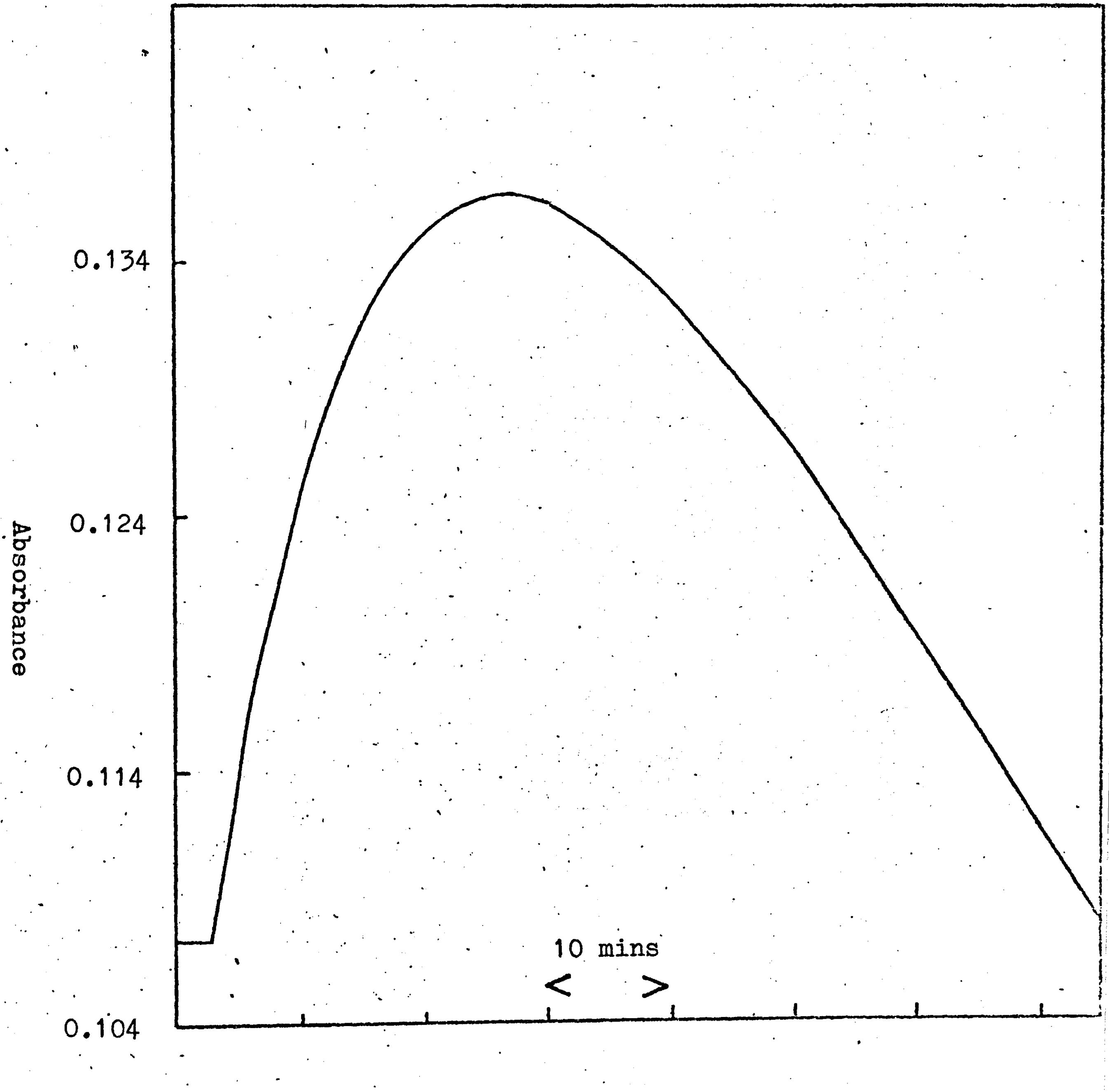
The initial absorbance increase was greatest in the region of 312 nm. The progress of reaction was therefore monitored at this wavelength. A typical trace is shown in Fig. 4.2.

It would have been advantageous to employ experimental conditions whereby intermediate formation occurred much more rapidly than did the subsequent process which presumably involves electron-transfer. The consequent attainment of equilibrium at the absorbance maximum would have permitted the use of a treatment such as that described in the previous chapter for the reaction of $HCrO_4^-$ with L-cysteine. Unfortunately, despite experimentation with a wide variety of temperatures and reagent concentrations it was not found possible to achieve this aim.

A spectrophotometric investigation of the redox step itself was rendered impracticable by the occurrence of a slower minor absorbance decay which is thought to be caused by aquation of the product chromium(III) species.

Fig. 4.2.

Complex Formation and Decay in the Reaction of Chromate(VI) with Malic Acid



[Cr(VI)] = 1.00 x 10^{-4}M;

[M.A.] = 0.2146M;

[H^+] = 0.100M; I = 1.00M; l = 0.5 cm.

temp = 15.0°C λ = 312 nm

The only other approach available for a kinetic study of the transient species was the method of initial rates.

(d) The kinetics of intermediate formation

It was possible to measure the initial reaction rate quite precisely. The variation of such rate constants with ligand and hydrogen-ion concentrations is shown in Table 4.1.

As shown in Figs. 4.3. and 4.4, this technique enabled establishment of the order of reaction with respect to both $HCrO_4^-$ and malic acid. It can be seen from Fig. 4.4. that the dependence of the rate of formation of the complex, x, on the ligand concentration, [L], can be expressed as in equation (1),

$$\frac{d[x]}{dt} = a[L] + b[L]^2 \qquad (1)$$

where a and b are constant at constant concentrations of metal- and hydrogen-ions. Such a rate expression indicates the existence of either higher-complex formation or general acid catalysis.

The hydrogen-ion dependences of a and b are illustrated in Fig. 4.5 and 4.6. At sufficiently low hydrogen-ion concentrations it was possible to observe a ligand-dependence which was purely second order. It is difficult to assess the significance of the highly unusual hydrogen-ion dependence of a.

In order to derive, using initial rates, the rate

Table 4.1.

The Effect of Variation of Reagent Concentrations on the Initial Rate of Formation of the Intermediate Species Formed in the Reaction of Chromate(VI) with Malic Acid.

$[Cr(VI)]_o$ = 1.00×10^{-3}M; temp. = 15.0°C; I = 1.00M
λ = 312 nm; path-length = 0.5 cm.

10^2[M.A.]/M	10^2I.R./s^{-1}	10^2[M.A.]/M	10^2I.R./s^{-1}
$[H^+]$ = 0.0400M		$[H^+]$ = 0.500M	
3.72	0.75	3.73	6.4
7.43	3.0	7.46	15.5
14.91	11.5	11.19	27.5
22.16	27.0	14.92	42.9
32.72	54.7	22.38	84.5
$[H^+]$ = 0.100M		$[H^+]$ = 0.800M	
3.72	1.4	3.80	10.5
7.46	5.2	7.45	23.9
14.92	19.2	11.20	40.8
22.38	42.4	14.92	60.5
29.54	74.1	22.38	11.0

$[H^+]$ = 0.250M

10^2[M.A.]/M	10^2I.R./s^{-1}
3.73	3.5
7.47	9.6
11.19	18.2
14.92	30.4
22.36	62.7

$[H^+]$ = 1.00M

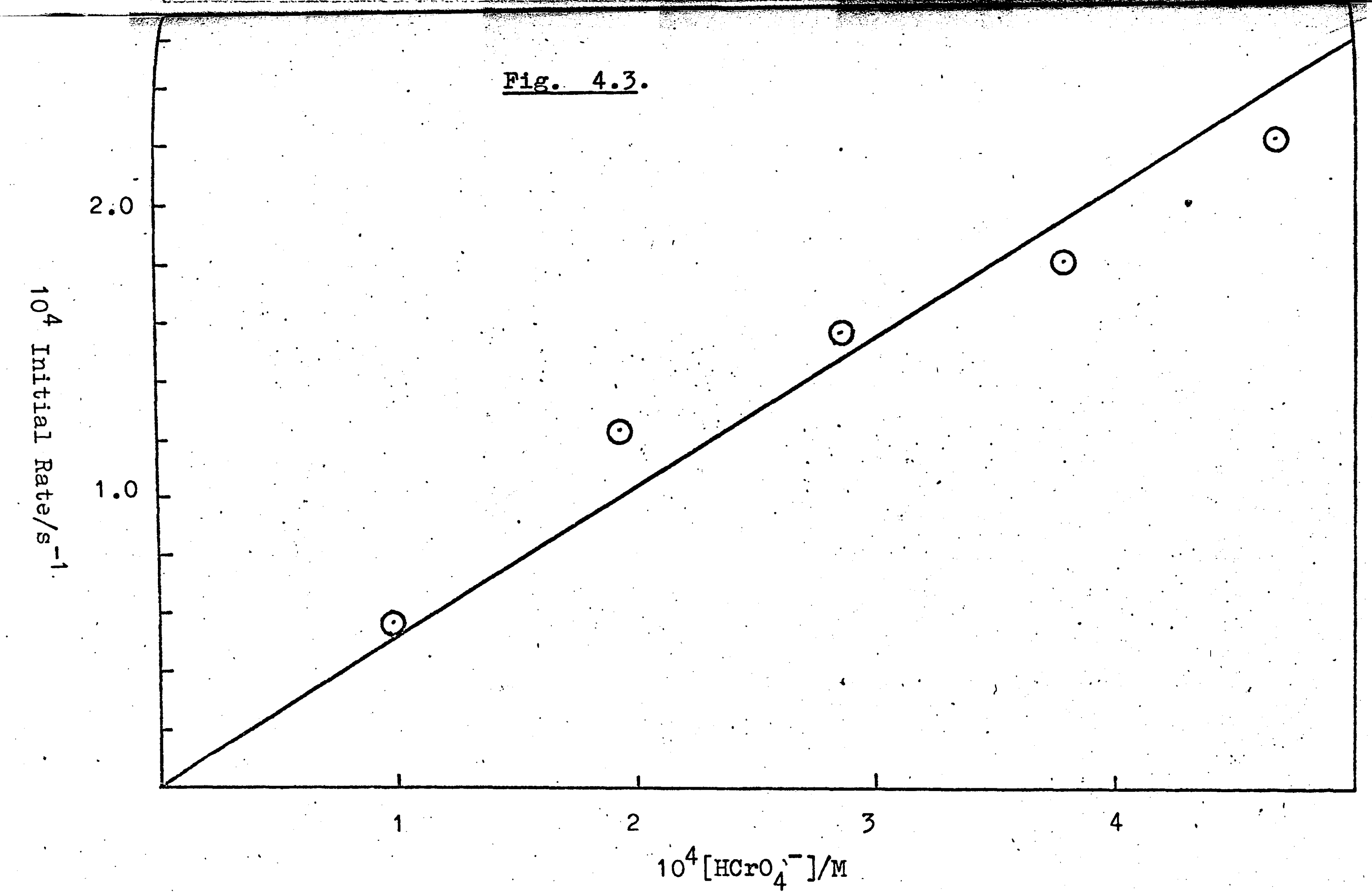
10^2[M.A.]/M	10^2I.R./s^{-1}
3.86	13.8
7.56	31.4
11.61	52.5
14.96	75.5
21.69	131.0

[M.A.] = 0.2146M

$[H^+]$ = 0.100M

10^4[Cr(VI)]/M	10^2I.R./s^{-1}
1.00	5.7
2.00	12.3
3.00	15.7
4.00	17.8
5.00	22.1

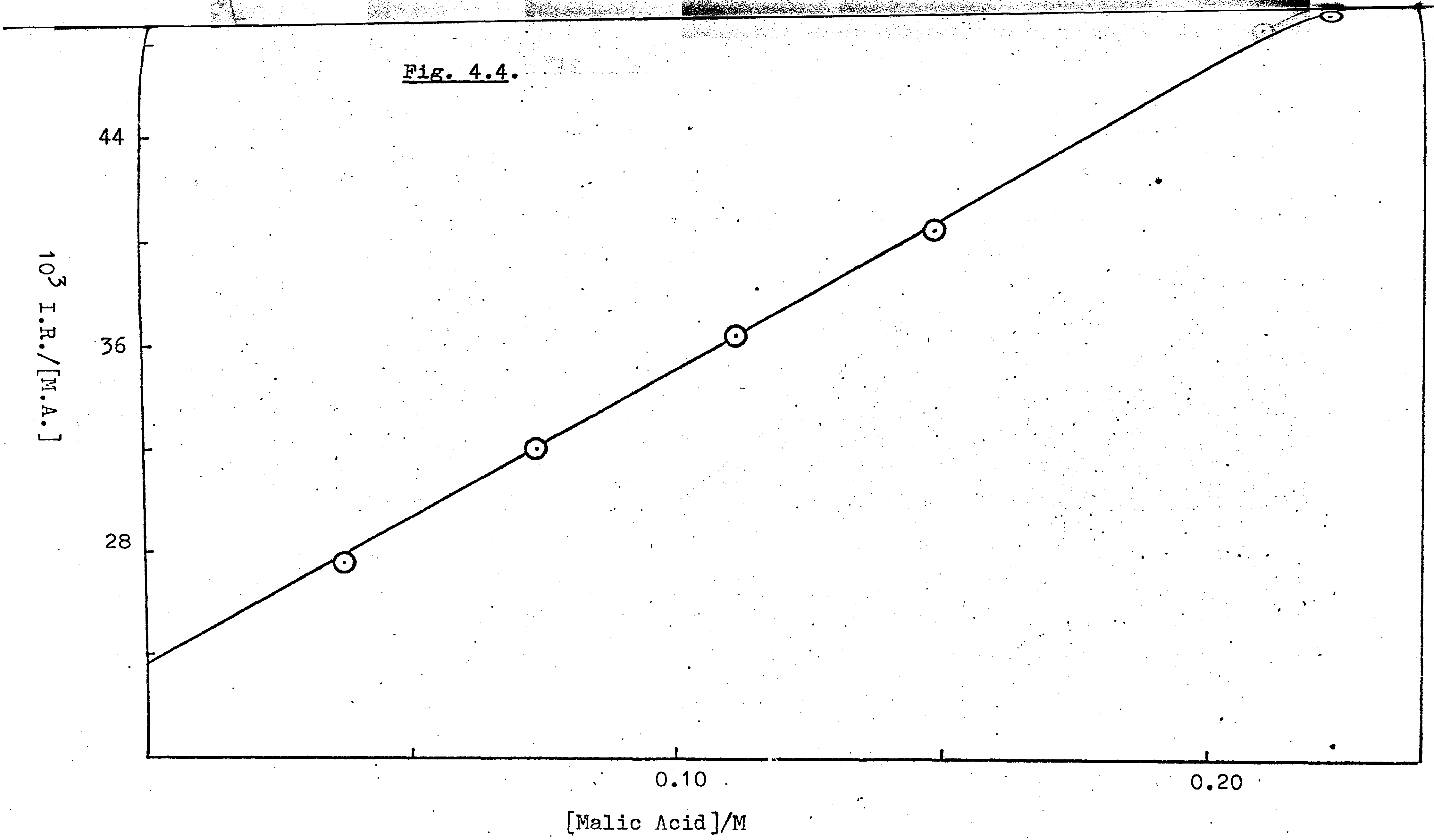
Fig. 4.3.



Dependence of Initial Rate of Chromate(VI) Malate Ester Formation on $[HCrO_4^-]$

$[MA] = 0.215M$; $[H^+] = 0.100M$; temp = 15^oC; $\lambda = 312$ nm; $l = 0.5$ cm.

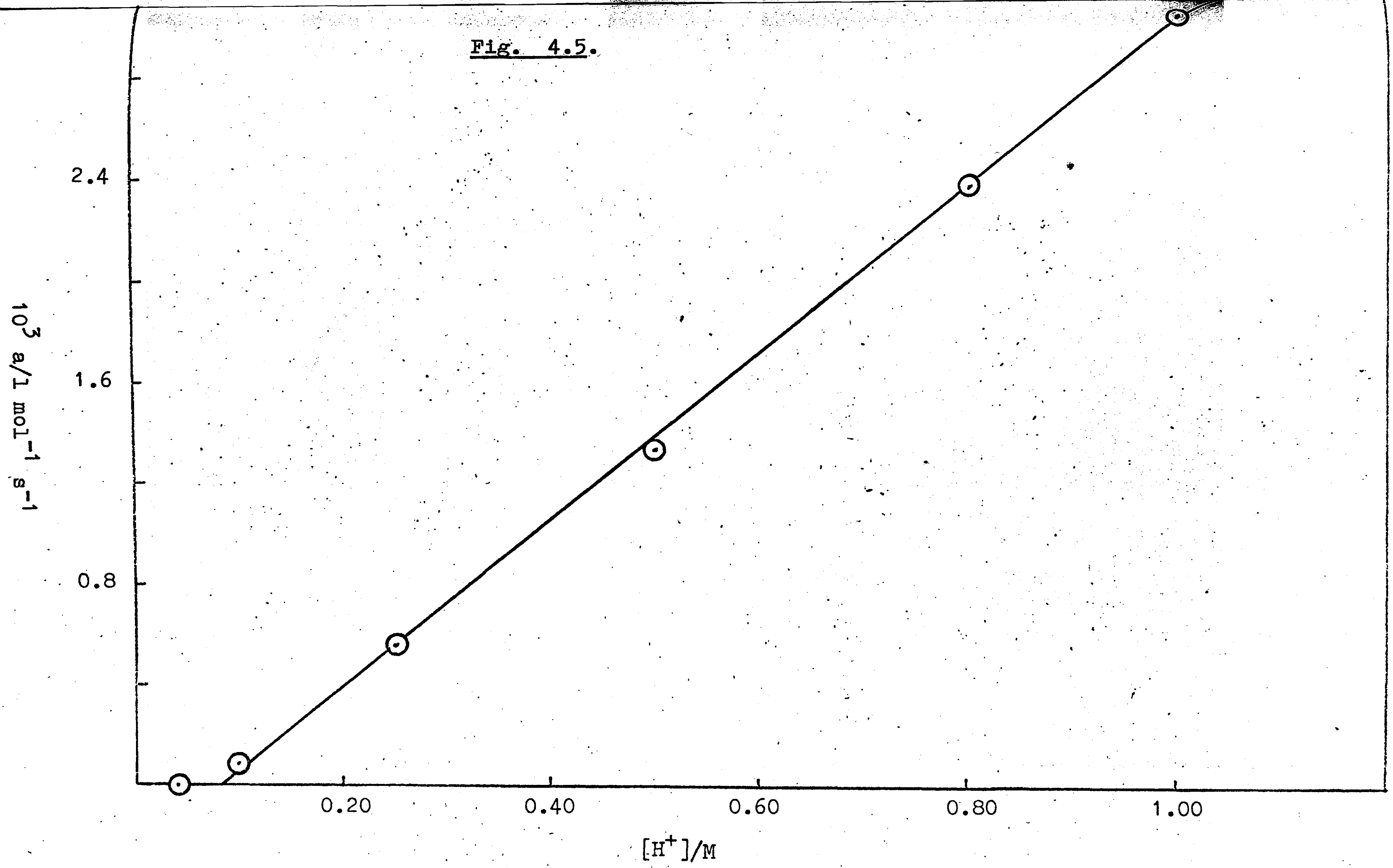
Fig. 4.4.



Dependence of Initial Rate of Chromate(VI) Malate Ester Formation on [Malic Acid].

[Cr(VI)] = 1.00 x 10^{-3}M; [H^+] = 0.80M; I = 1.0M; temp = 15°C; λ = 312 nm; l = 0.5 cm.

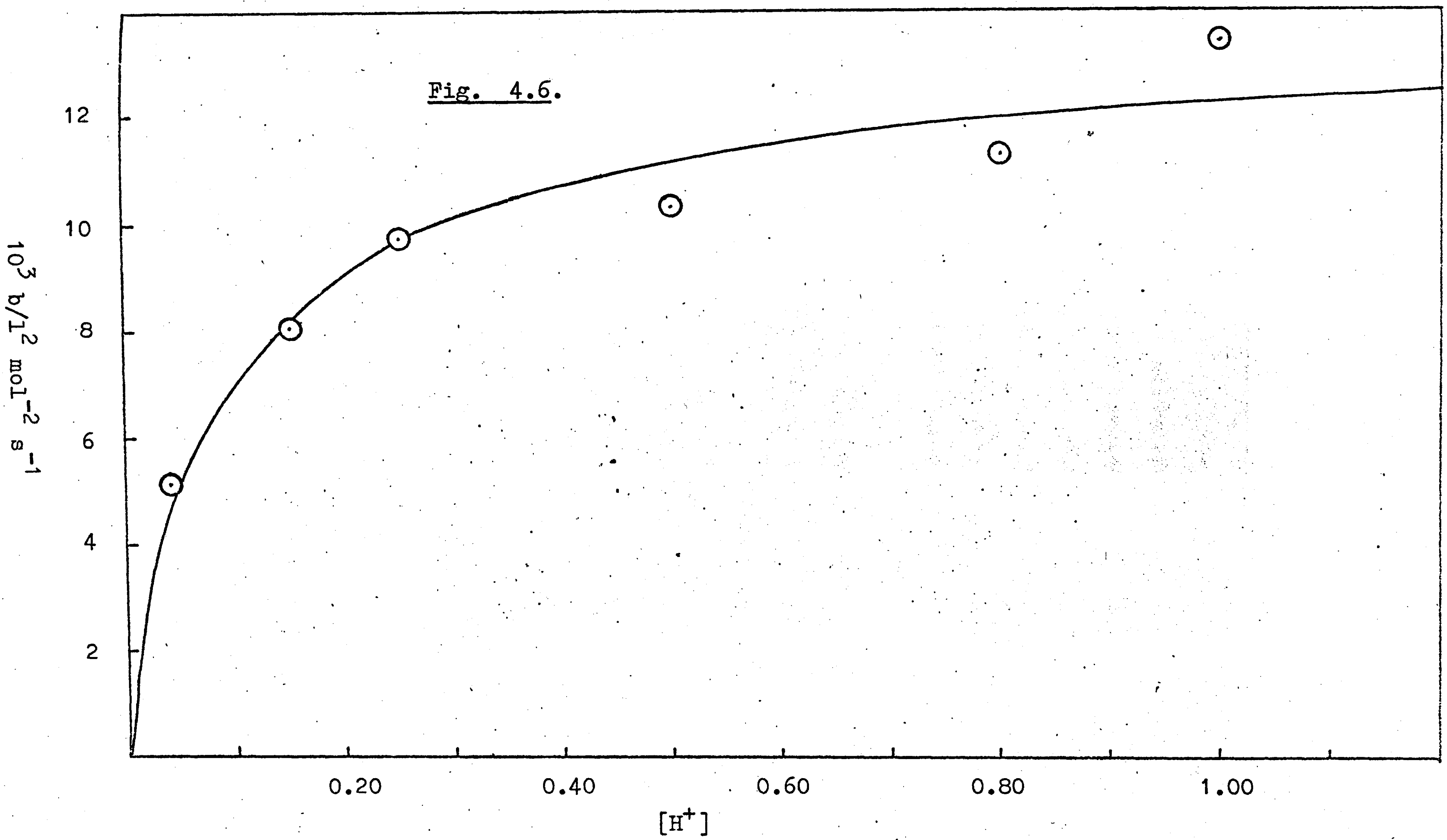
Fig. 4.5.



Dependence of Rate of First-Order Malic Acid Route on [H$^+$] .

[Cr(VI)] = 1.00 x 10^{-3}M; I = 1.0M; temp = 15°C; λ = 312 nm; l = 0.5 cm

Fig. 4.6.



Dependence of Rate of Second-Order Malic Acid Route on [H^+].

[Cr(VI)] = 1.00 x 10^{-3}M; I = 1.0M; temp = 15° C; λ = 312 nm; l = 0.50 cm.

constants for the individual pathways leading to ester formation it is clearly necessary to know the value of $\Delta\varepsilon$, the difference between the extinction coefficients of $HCrO_4^-$ and the transient species. $\Delta\varepsilon$, however, can normally only be measured if the equilibrium absorbance is known. (If the redox kinetics are straightforward this difficulty can be overcome, as will be seen in section 2). As stated in section 1(c), it appears to be impossible to measure the equilibrium absorbance directly.

Another complicating factor arose from the considerable magnitude of the ligand concentrations which it was necessary to employ in order to obtain significant absorbance increases. Under such conditions the probability of other than solely monocomplex formation is substantial.

Although, because of the above considerations no unambiguous evaluation of parameters was achieved by this study, it did establish that the reaction of $HCrO_4^-$ with malic acid is significantly more complicated than previously believed.

It is possible that further work incorporating such techniques as computerised curve-fitting, e.p.r. etc. could elucidate the mechanism of what is clearly a highly interesting reaction.

2. The Reaction of Chromate(VI) with Thiomalic Acid

(a) General experimental back-ground

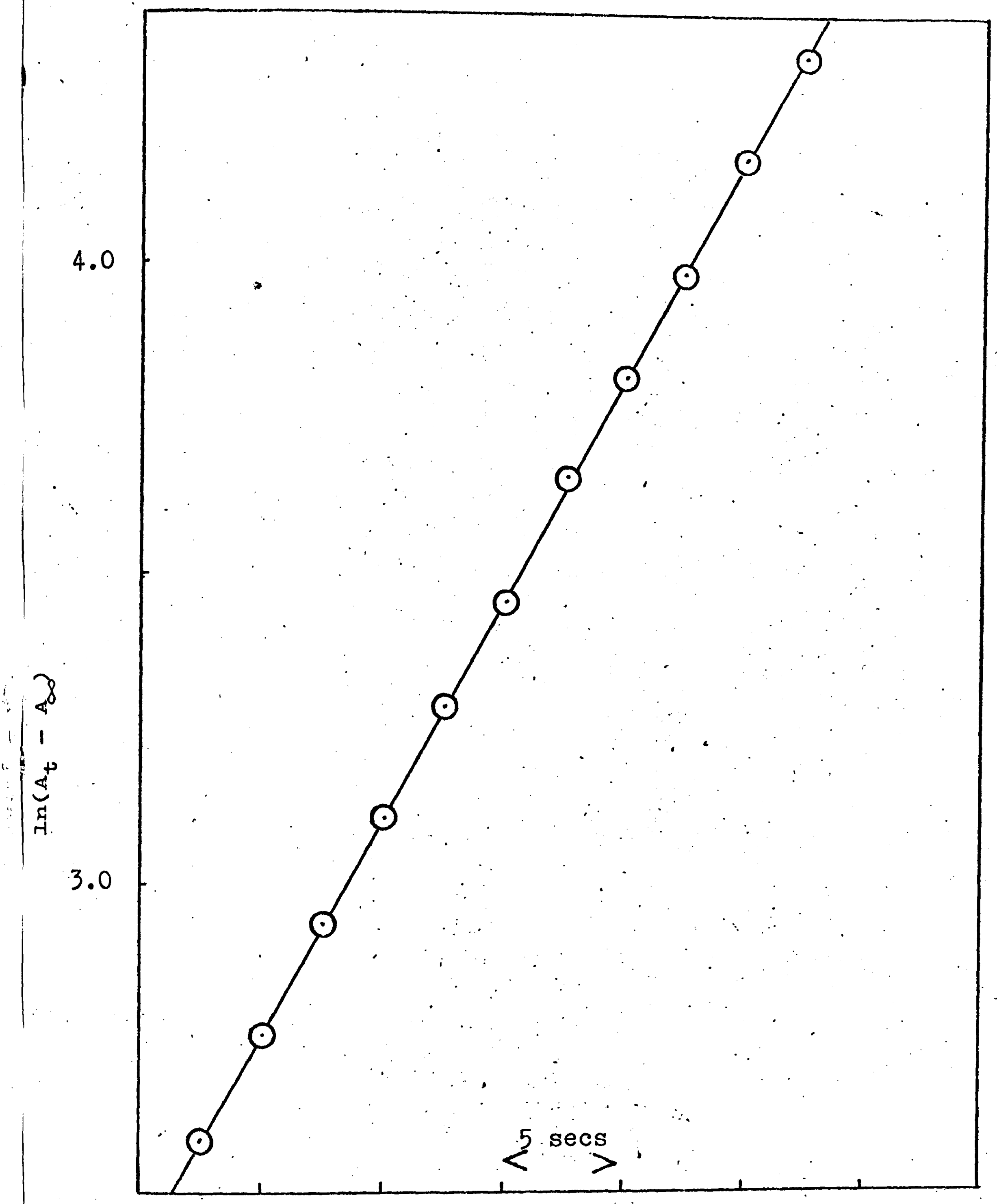
This system was investigated using experimental conditions such that $HCrO_4^-$ and the undissociated acid were the principal reactant species. Dissociation of the organic substrate was negligible (all pKa's $> 3^{217}$).

It was observed that the orange intermediate formed and decayed at comparable rates. Variation of the wavelength used to monitor these processes showed that the difference between the extinction coefficients of $HCrO_4^-$ and the transient complex, was greatest in the region of 420 nm. In order to minimise the error in measurements, this wavelength was adopted for use in the remainder of the study.

An attempt was made to establish experimental conditions whereby the absorbance decay was retarded with respect to the increase, as was achieved for the chromate(VI)/L-cysteine system, so that the maximum absorbance reached corresponded approximately to attainment of equilibrium in complex formation. However, as was the case with the reaction of chromate(VI) with malic acid, such a search proved unsuccessful despite the trial of a wide variety of conditions.

An investigation of the decomposition step was undertaken with a view to gaining some insight into the equilibria involved in intermediate formation. As can be seen by inspection of Fig. 4.7., $\log_e(A_t - A_\infty)$ is a linear function of time in the latter stages of reaction. The

Fig. 4.7.



Linearisation of Pseudo-First-Order Absorbance Decay in the Reaction of $HCrO_4^-$ with Thiomalic Acid. [Cr(VI)] = 4.00×10^{-4}M; [T.M.A.] = 2.91×10^{-3}M; $[H^+]$ = 0.050M; temp = 25°C; I = 1.0M; λ = 420 nm.

slopes of such plots, k_{obs}, are directly proportional to ligand concentration, with no deviation from linearity being observed at high values of the latter; see Fig. 4.8. k_{obs} can hence be expressed as $k'[L]$. A list of the values of k_{obs} under various conditions is given in Table 4.2.

As can be seen by reference to Table 4.3, substantial variation of the hydrogen-ion concentration caused no significant variation in the measured values of k'.

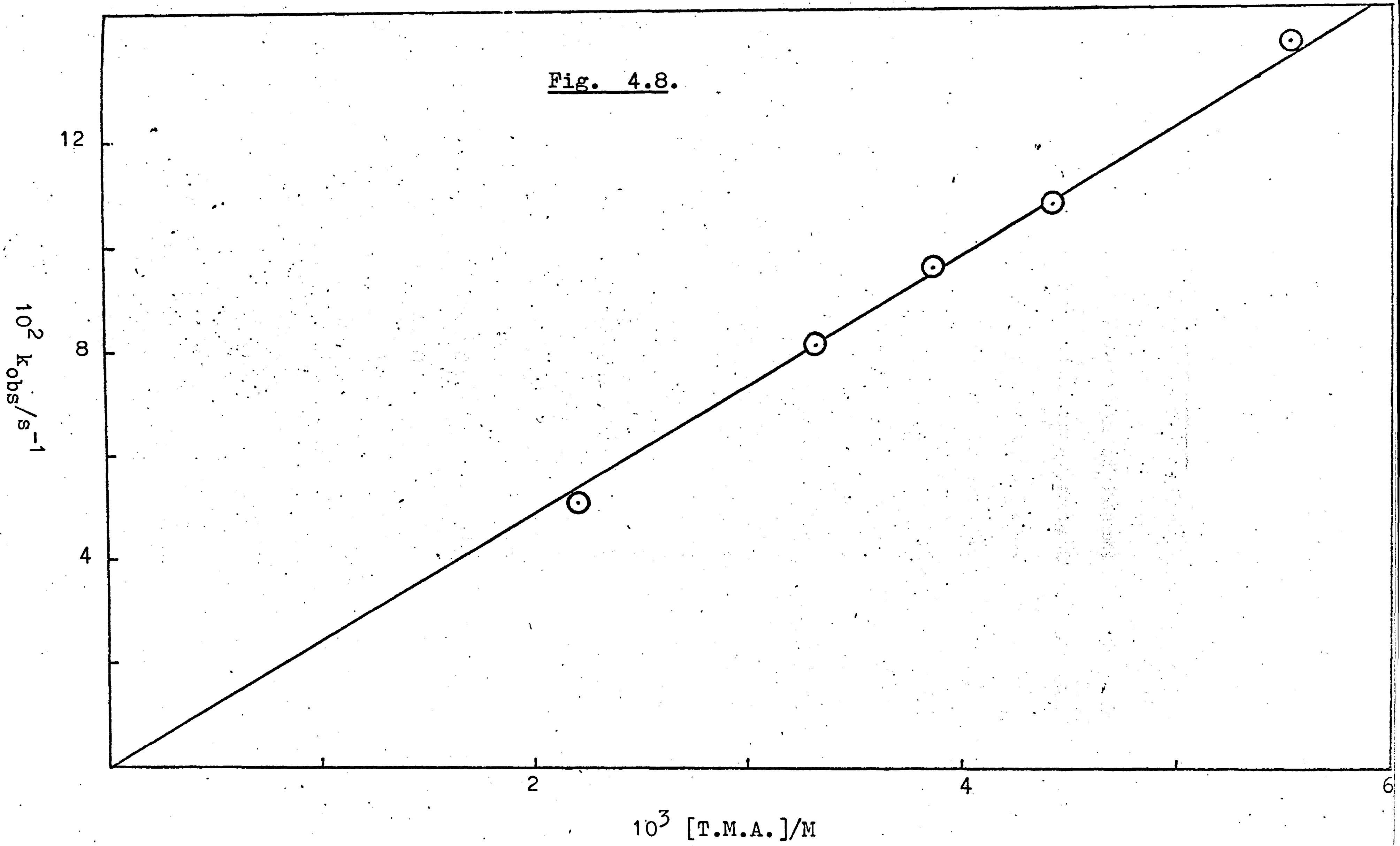
The initial rate of intermediate formation, I.R., was found to exhibit the same ligand dependence as the decay step; see Fig. 4.9. Values of I.R. under various conditions are listed in Table 4.4. The slopes of such plots, k_1, are also acid independent, as shown in Table 4.5.

Estimation of the minimum value of $\Delta\varepsilon_{420}$ was achieved by dividing the maximum absorbance by the initial concentration of chromium(VI) i.e. the maximum possible concentration of complex. The value thus obtained, $\sim$600 l ml^{-1} cm^{-1}, showed that λ_{max} was indeed close to 420 nm.

From a knowledge of similar systems,[133,199] it is anticipated that a chromate ester would be formed and that chromium(V) would not be important spectrophotometrically. Since the orange species has a strong spectral similarity to such esters, almost certainly sulphur-bonded, encountered with sulphydryl-containing ligands[192,218] and relatively little to chromium(V),[133,142,149,215,216] it is concluded that this is such a chromate(VI) complex.

The exclusively first-order dependence of the initial

Fig. 4.8.



The Variation of k_{obs} with Thiomalic Acid Concentration. [Cr(VI)] = 4.00×10^{-4}M; $[H^+]$ = 0.050M; I = 1.0M; temp = 25^{o}C; λ = 420 nm.

Table 4.2.

The Effect of Variation of Reaction Conditions on k_{obs}, the Pseudo-first-order Rate Constant relating to the Absorbance Decay Observed at 420 nm in the Reaction of Chromate(VI) with Thiomalic Acid at Unit Ionic Strength.

temp. = 25.0°C

$10^2[H^+]_o$/M	$10^4[Cr(VI)]_o$/M	$10^3[T.M.A.]_o$/M	$10^2k_{obs}/s^{-1}$
2.00	4.00	1.83	3.75
2.00	4.00	2.74	5.95
2.00	4.00	3.65	8.40
2.00	4.00	5.48	12.6
2.00	4.00	7.30	16.6
2.00	4.00	10.95	23.5
2.00	4.00	18.25	39.6
5.00	4.00	2.21	5.14
5.00	4.00	3.31	8.15
5.00	4.00	3.87	9.59
5.00	4.00	4.42	10.8
5.00	4.00	5.52	13.9
5.00	4.00	2.91	7.03
5.00	4.00	5.82	15.2
5.00	4.00	8.73	22.2
5.00	4.00	11.6	27.3
5.00	4.00	14.6	30.8

$10^2[H^+]_o$/M	$10^4[Cr(VI)]_o$/M	$10^3[T.M.A.]_o$/M	$10^2k_{obs}/s^{-1}$
8.00	1.00	2.11	4.81
8.00	1.00	2.63	5.68
8.00	1.00	3.16	6.86
8.00	1.00	3.69	8.61
8.00	1.00	4.21	9.63
8.00	1.00	5.27	11.63
10.0	4.00	2.02	6.11
10.0	4.00	4.04	13.05
10.0	4.00	5.05	15.7

temp. = 11.4°C

10.0	4.00	5.12	8.5

temp. = 34.8°C

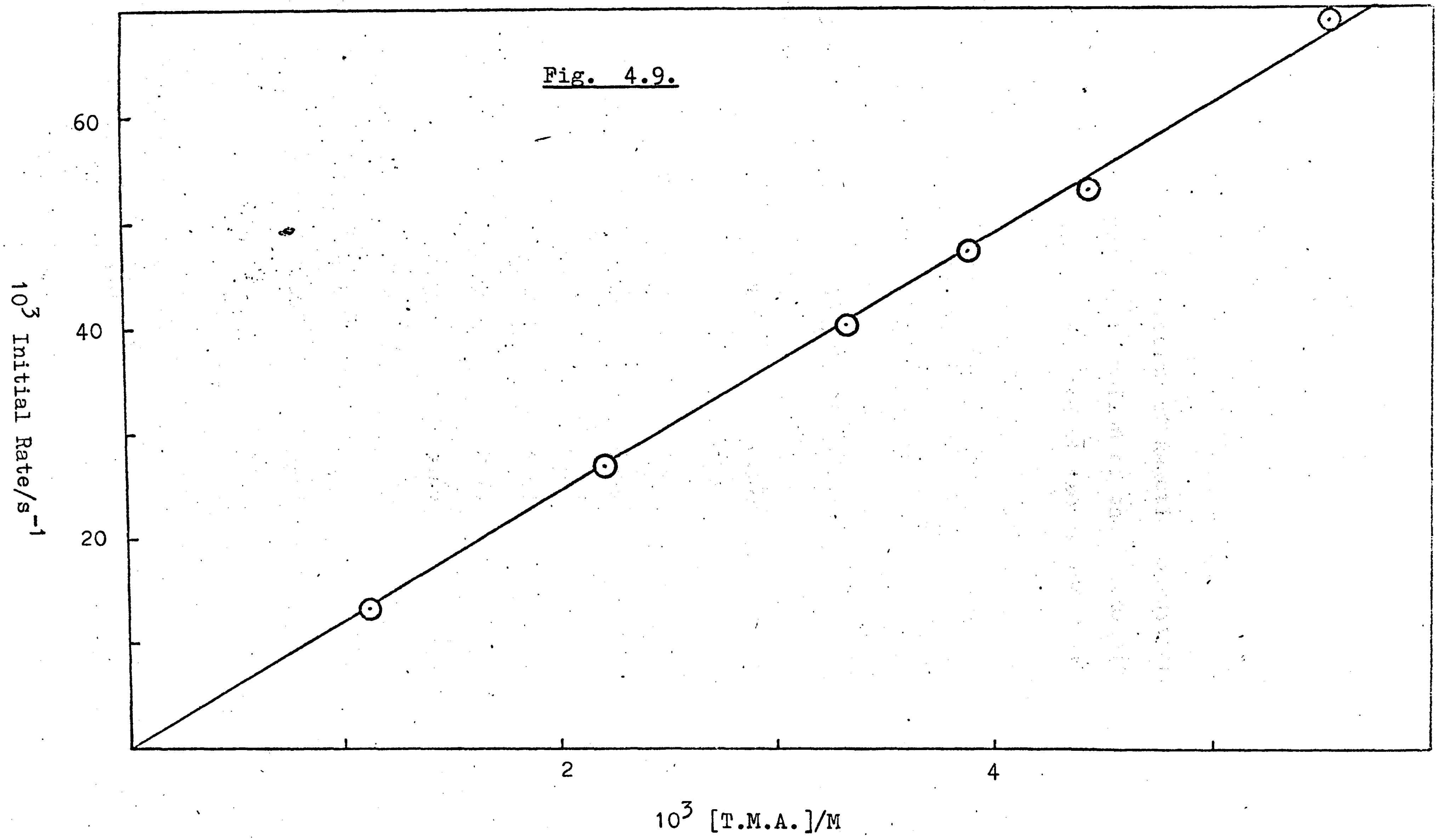
10.0	4.00	5.12	24

Table 4.3.

The Independence of k'(= $\frac{k_{obs}}{[\mathrm{T.M.A.}]_o}$ or $\frac{\lambda_2}{[\mathrm{L}]}$) of Hydrogen-Ion Concentration at 25.0°C.

$10^2[\mathrm{H}^+]/\mathrm{M}$	$k'/\mathrm{l\ mol^{-1}\ s^{-1}}$
2.00	21.9
5.00	24.6, 23.1
8.00	22.2
10.0	31.3

Fig. 4.9.



Variation of Initial of Absorbance Increase with [T.M.A.]. λ = 420 nm; l = 1.0. cm; [Cr(VI)] = 4.00×10^{-4}; [H^+] = 0.50M; I = 1.0M; temp = 25°C.

Table 4.4.

The Effect of Variation of Reaction Conditions on the Initial Rate of Formation of the Chromate(VI)-Thiomalate Species as Measured at 420 nm and Unit Ionic Strength.

temp. = 25.0°C

$10^2[H^+]_o$/M	$10^4[Cr(VI)]_o$/M	10^3[T.M.A.]$_o$/M	path-length/cm	10^2I.R./s^{-1}
1.00	4.00	0.873	0.50	0.753
1.00	4.00	1.75	0.50	1.48
1.00	4.00	2.62	0.50	2.20
1.00	4.00	3.49	0.50	2.92
1.00	4.00	4.37	0.50	3.67
2.00	4.00	1.83	1.00	2.53
2.00	4.00	2.74	1.00	3.76
2.00	4.00	3.65	1.00	5.07
2.00	4.00	5.48	1.00	8.22
5.00	4.00	1.11	1.00	1.32
5.00	4.00	2.21	1.00	2.66
5.00	4.00	3.31	1.00	4.02
5.00	4.00	3.87	1.00	4.64
5.00	4.00	4.42	1.00	5.30
5.00	4.00	5.52	1.00	6.88
5.00	4.00	2.91	0.50	1.79
5.00	4.00	8.73	0.50	5.31
5.00	4.00	11.6	0.50	6.79
5.00	4.00	14.6	0.50	8.92

$10^2[H^+]_o$/M	$10^4[Cr(VI)]_o$/M	10^3[T.M.A.]$_o$/M	path-length/cm	10^2I.R./s^{-1}
8.00	1.00	2.11	1.00	0.68
8.00	1.00	2.63	1.00	0.73
8.00	1.00	3.16	1.00	0.96
8.00	1.00	4.21	1.00	1.25
8.00	1.00	5.27	1.00	1.52
10.0	4.00	1.01	0.50	0.83
10.0	4.00	2.02	0.50	1.53
10.0	4.00	3.03	0.50	2.10
10.0	4.00	4.04	0.50	3.00
10.0	4.00	5.05	0.50	3.85
temp. = 11.4°C				
10.0	4.00	5.12	0.50	1.92
temp. = 34.8°C				
10.0	4.00	5.12	0.50	6.11

Table 4.5.

The Independence of $\frac{\text{I.R.}}{[\text{T.M.A.}]}$* of Hydrogen-Ion Concentration at 25.0°C.

$10^2[H^+]/M$	10^4I.R./l mol^{-1} s^{-1}
1.00	4.20
2.00	3.48
5.00	3.08, 3.03
8.00	3.02
10.00	3.71

* normalised to 1·00 cm path-length.

reaction rate on ligand concentration suggests, but in no way proves, that only monocomplex is present. Under comparable conditions cysteine and other substrates form only 1:1 complexes with $HCrO_4^-$.[133]

(b) Derivation of the rate law

All the evidence presented above points to the occurrence of the two consecutive processes in equation (2)

$$M + L \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X \xrightarrow[k_2]{+L} P \qquad (2)$$

Since X is the species being monitored, it is desirable to express the rate law in terms which describe its behaviour.

$$\frac{d[X]}{dt} = k_1[M][L] - k_{-1}[X] - k_2[X][L] \qquad (3)$$

A sufficient excess of ligand over metal-ion was maintained in this study for pseudo-first-order kinetics to be obtained. Hence equation (3) can be rewritten as

$$\frac{d[X]}{dt} = k_f[M] - k_b[X] - k[X] \qquad (4)$$

where $k_f = k_1[L]$, $k_b = k_{-1}$ and $k = k_2[L]$. The rate of change of concentration of metal-ion and product are given in equations (5) and (6)

$$\frac{d[M]}{dt} = -k_f[M] + k_b[X] \qquad (5)$$

$$\frac{d[P]}{dt} = k[X] \qquad (6)$$

Differentiation of equation (4) yields equation (7)

$$\frac{d^2[X]}{dt^2} = k_f\frac{d[M]}{dt} - (k_f + k)\frac{d[X]}{dt} \qquad (7)$$

Elimination of [M] and $\frac{d[M]}{dt}$ by use of equations (4), (5) and (7) leads to the homogeneous second-order differential equation, (8).

$$\frac{d^2[X]}{dt^2} + (k_f + k_b + k)\frac{d[X]}{dt} + k_f[X] = 0 \qquad (8)$$

$e^{-\lambda t}$ is a solution of equation (8), with λ being given by equation (9).

$$\lambda = \tfrac{1}{2}\left((k_f + k_b + k) \pm \sqrt{(k_f + k_b + k)^2 - 4k_fk}\right) \qquad (9)$$

The general solution of (8) is therefore as given in equation (10)

$$[X] = \alpha e^{-\lambda_1 t} + \beta e^{-\lambda_2 t} \qquad (10)$$

where λ_1 is λ with the positive sign in equation (9), and λ_2 is λ with the negative sign.

If, as is the case in this system, only M and L are present at time zero,

$$0 = \alpha + \beta$$

Differentiation of equation (10) leads to equation (11)

$$\frac{d[X]}{dt} = -\alpha\lambda_1 e^{-\lambda_1 t} - \beta\lambda_2 e^{-\lambda_2 t} \tag{11}$$

If, as is also true for this system, no X is present a time zero, equation (12) holds.

$$\left(\frac{d[X]}{dt}\right)_{t=0} = -k_f[M]_o \tag{12}$$

Combining equations (11) and (12), equation (13) follows.

$$k_f[M]_o = -\alpha\lambda_1 + \beta\lambda_2 \tag{13}$$

Hence

$$\beta = -\alpha = \frac{k_f[M]_o}{\lambda_1-\lambda_2} \tag{14}$$

By substituting equation (14) into equation (10), it can be seen that the instantaneous concentration of the intermediate complex, X, is given by equation (15).

$$[X]_t = \frac{k_f[M]_o}{\lambda_1-\lambda_2}(-e^{-\lambda_1 t} + e^{-\lambda_2 t}) \tag{15}$$

Differentiation of equation (15) yields firstly an expression for $\frac{d[X]}{dt}$ and then one for $\frac{d^2[X]}{dt^2}$, both of which can be substituted in equation (7) to give, upon integration of $\frac{d[M]}{dt}$, equation (16).

$$[M]_t = \frac{[M]_o}{\lambda_1-\lambda_2}\left((k_f - \lambda_2)e^{-\lambda_1 t} + (\lambda_1 - k_f)e^{-\lambda_2 t}\right) \tag{16}$$

Combining equations (15) and (16), and assuming that only M and X absorb to any significant extent, which is valid for 420 nm (ε for $Cr(H_2O)_6^{3+}$ at 420 nm is only 4.3 $l\ mol^{-1}\ cm^{-1}$)[149] the instantaneous absorbance of the solution, A_t, = $(\varepsilon_M[M]_t + \varepsilon_X[X]_t).l$, is given by equation (17) with ε_M and ε_X being the

$$A_t = \frac{[M]_o.l.\varepsilon_M}{\lambda_1-\lambda_2}\Big((k_f\varepsilon_M - k_f\varepsilon_X - \lambda_2\varepsilon_M)e^{-\lambda_1 t} + (\lambda_1\varepsilon_M - k_f\varepsilon_M + k_f\varepsilon_X)e^{-\lambda_2 t}\Big) \quad (17)$$

extinction coefficients of $HCrO_4^-$ and the orange species respectively.

(c) Derivation of the physical parameters

The linear final portion of plots of $\log_e(A_t-A_\infty)$ against time can easily be shown to be λ_2, equation (18),

$(k_f = k_1[L]\ ;\ k_b = k_{-1}\ ;\ k = k_2[L])$

$$\lambda_2 = \tfrac{1}{2}\Big((k_1[L] + k_{-1} + k_2[L]) - \sqrt{(k_1[L] + k_{-1} + k_2[L])^2 - 4k_1k_2[L]^2}\Big) \quad (18)$$

As λ_2 has been found to be directly proportional to [L], Fig. 4.8., it seems that $k_1[L] + k_2[L] >> k_{-1}$. λ_2 thus reduces to either $k_2[L]$, if $k_1 > k_2$, or $k_1[L]$, if $k_1 < k_2$. Hence λ_1 and λ_2 can be replaced by $k_1[L]$ and $k_2[L]$ respectively without presuming, however, that k_1 is larger than k_2.

Equation (17) then simplifies to equation (19)

$$A_t = \frac{[M]_o . l}{k_2 - k_1}\left((k_1\Delta\varepsilon + k_2\varepsilon_M)e^{-k_1[L]t} - k_1\varepsilon_X e^{-k_2[L]t}\right) \quad (19)$$

This expression, (19), which holds regardless of the relative magnitudes of k_1 and k_2, is identical to that which describes the absorbance behaviour where the first step of equation (2) is irreversible. This indicates that $k_1 >> k_{-1}$, consistent with the intermediate being a sulphur-bonded chromate(VI) complex, such species generally being found to have quite large formation constants.[133,192,199,218]

The slopes of the initial rate plots, Fig. 4.9, are clearly of the form shown in (20)

$$\text{Slope} = \frac{I.R.}{[L]} = k_1\Delta\varepsilon . l . [M]_o \quad (20)$$

Lack of a direct means of measurement of $\Delta\varepsilon$ precludes the determination of k_1 directly from such data.

$k_1\varepsilon$, evaluated graphically (Fig. 4.9.) by way of this approach, can, however, be used indirectly to extract values for k_1 and k_2.

The effect of temperature variation can aid the decision as to whether $\frac{\lambda_2}{[L]}$ is k_1 or k_2.[219] Assuming that $\frac{\lambda_2}{[L]}$ is k_2, the activation parameters for the formation and redox processes might be sufficiently different for this solution to be established, with the activation enthalpies of $k_1\Delta\varepsilon$ and λ_2 being demonstrably dissimilar.

In the reaction of $HCrO_4^-$ with thiomalic acid, however, the ratio of $\Delta\varepsilon k_1$ to λ_2 is invariant with temperature, with ratios of 1150 at 11.4°C, 1360 at 25°C and 1280 at 34.8°C. This in itself clearly does not prove that $\frac{\lambda_2}{[L]}$ is in fact k_1, since the activation enthalpies of k_1 and k_2 could, by chance, be experimentally indistinguishable.

The values of ε obtained on the basis of an assumed identity of $\frac{\lambda_2}{[L]}$ with k_1 are, however, strikingly similar to all values so far measured for sulphur-bonded chromate(VI) esters, as is illustrated in Table 4.6. Although the above evidence is circumstantial in nature, it is nevertheless highly likely that $\frac{\lambda_2}{[L]}$ equals k_1.

(d) Measurement of k_2 and mathematical simulation of overall kinetic traces

At the time when A_t is a maximum, $\frac{dA_t}{dt} = 0$. Hence differentiation of equation (19) allows derivation of equation (21).

$$t_{max} = \frac{1}{(k_1-k_2)[L]} \log_e\left(\frac{k_1\varepsilon_X + \varepsilon_M(k_2-k_1)}{k_2\varepsilon_X}\right) \qquad (21)$$

where t_{max} is the time taken for the absorbance to reach its maximum value where $\varepsilon_X > \varepsilon_M$.

Using 228 l mol^{-1} cm^{-1} as the value of ε_M[157] and employing the values of ε_X and k_1 listed in Tables 4.6 and 4.7, trial of various values of k_2 in order to obtain agreement between values of t_{max}, calculated according to equation (21), and those found experimentally yielded the

Table 4.6.

Extinction Coefficients of Sulphur-Bonded Chromate(VI) Esters at Unit Ionic Strength.

Ligand	λ_{max}/nm	ε_{max}/l mol^{-1} cm^{-1}	ref.
thiomalic acid	420	1490[*]	a
mercaptoethylamine	430	1300	b
L-cysteine	420	1410	a
DL-penicillamine	420	1250	b
glutathione	430	1280	b
thiourea	380	1270	b
ethylenethiourea	380	1260	b
N-methylthiourea	380	1290	b
N,N'-dimethylthiourea	380	1180	b
thiosulphate	390	1400[†]	c

(a) This work.

(b) M.A. Olatunji and A. McAuley.

(c) I. Baldea and G. Niac, Inorg. Chem., 1968, 7, 1232.

[*] $\varepsilon^{420}_{HCrO_4^-} = 228$ l mol^{-1} cm^{-1}.[157]

[†] $I = 0.11M$.

Table 4.7.

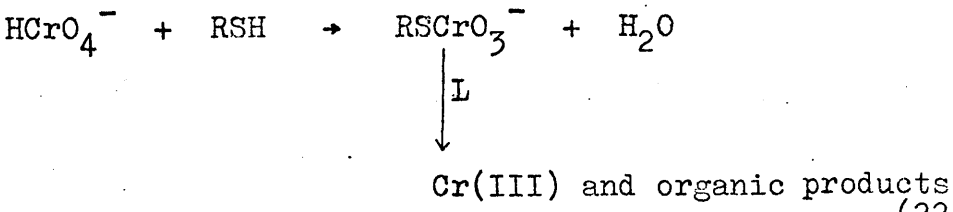
The Variation with Temperature of $k_1(\frac{\lambda_2}{[L]})$ and k_2 (as evaluated using equation (21)).

temp./^oC	k_1/l mol^{-1} s^{-1}	k_2/l mol^{-1} s^{-1}
11.4	17 ± 3	21 ± 1
25.0	25 ± 5	40 ± 3
34.8	47 ± 9	65 ± 5

values of k_2 in Table 4.7.

Simulation of experimentally derived traces of absorbance against time was achieved by the use of equation (19) with k_1, k_2 and $\Delta\varepsilon$ all being varied to give the closest fit ; see Figs. 4.10. and 4.11.

Synthesis of such curves involves two main approximations namely (a) the intermediate formation processes, while almost certainly reversible, are assumed to be irreversible and (b) the absorbance of the reaction products is neglected. In view of these factors and also the quality of the fit achieved with parameters not very different from those derived by the methods given above it would appear that equation (22) is an adequate description of the consecutive processes involved in the reaction of chromate(VI) with thiomalic acid in acidic solution with the ligand in excess

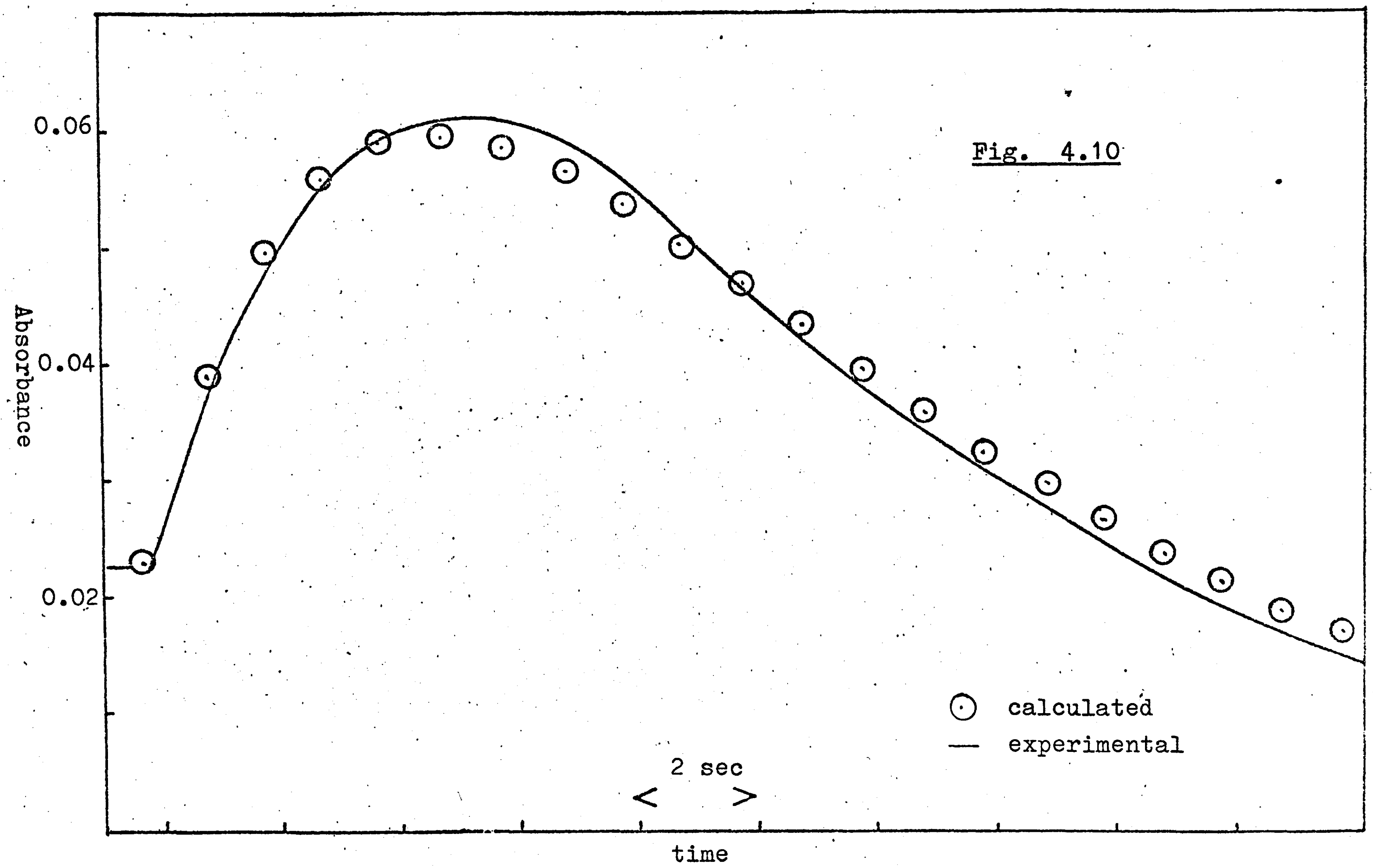


$$\begin{tikzcd} HCrO_4^- + RSH \arrow[r] & RSCrO_3^- + H_2O \arrow[d, "L"] \\ & \text{Cr(III) and organic products} \end{tikzcd} \qquad (22)$$

It is considered unlikely to be coincidence that when a very large excess of ligand over metal-ion is present, and hence conditions for pseudo-first-order behaviour are optimised, that the closest fit of the three simulated traces is obtained with, moreover, parameter values closest to those listed in Table 4.7.

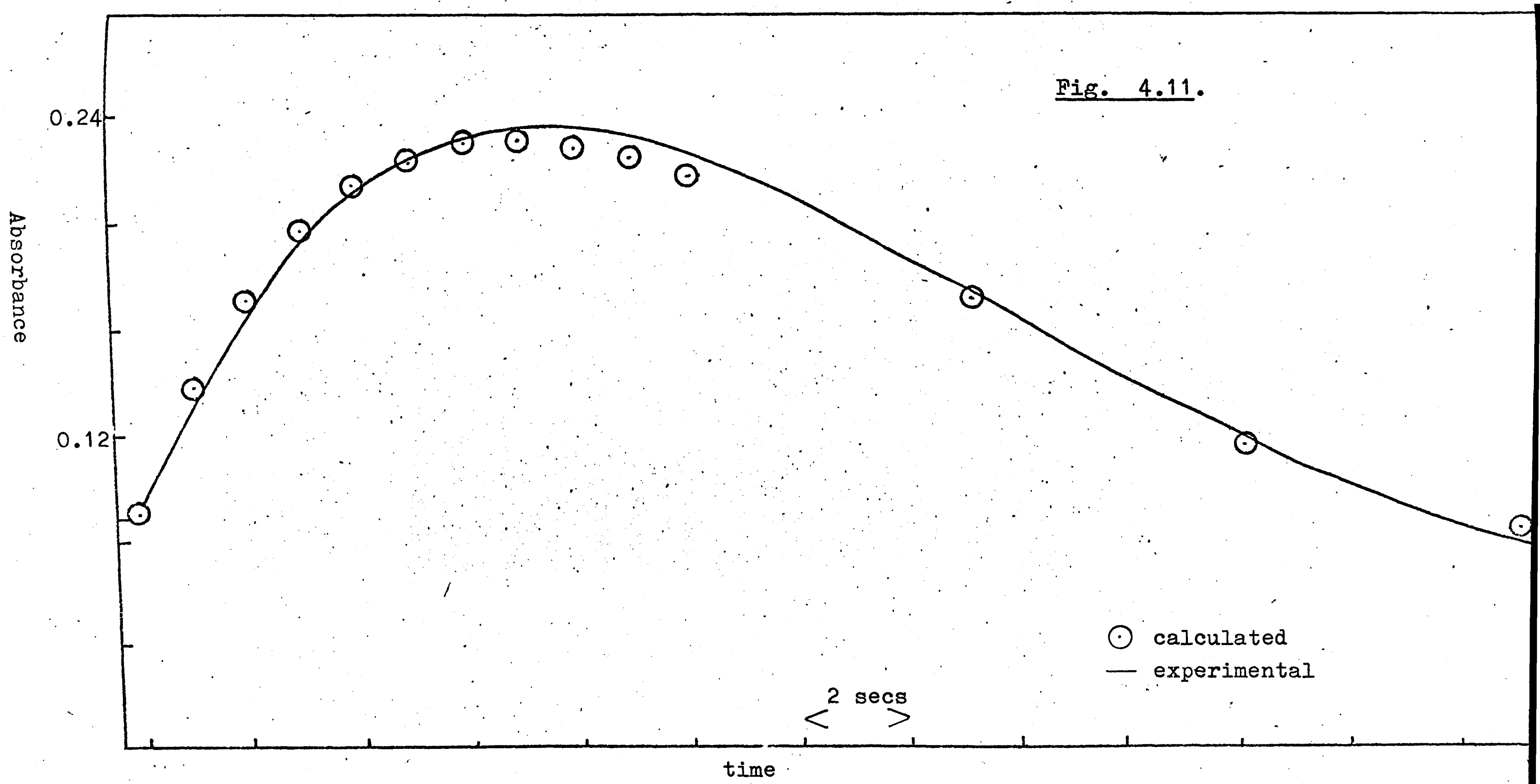
It was discovered that the use of values of k_2 less

Fig. 4.10



Simulation of the Absorbance Changes at 420 nm in the Reaction of $HCrO_4^-$ with Thiomalic Acid using $k_1 = 26$ l mol^{-1} s^{-1}; $k_2 = 40$ l mol^{-1} s^{-1}; and $\Delta\varepsilon = 1440$ l mol^{-1} cm^{-1}. l = 1.0 cm; [Cr(VI)] = 1.00 x 10^{-4}M; [T.M.A.] = 5.27 x 10^{-3}M; $[H^+]$ = 0.08M; temp = 25°.

Fig. 4.11.



Simulation of the Absorbance Changes at 420 nm in the Reaction of $HCrO_4^-$ with Thiomalic Acid, using $k_1 = 28\ l\ mol^{-1}\ s^{-1}$; $k_2 = 47\ l\ mol^{-1}\ s^{-1}$; and $\Delta\varepsilon = 1440\ l\ mol^{-1}\ cm^{-1}$.

$[Cr(VI)] = 4 \times 10^{-4}M$; $[T.M.A.] = 3.31 \times 10^{-3}M$; $[H^+] = 0.05M$; temp = 25°C; l = 1.0 cm.

than $\sim 38\ l\ mol^{-1}\ s^{-1}$ and greater than $\sim 48\ l\ mol^{-1}\ s^{-1}$ did not allow the production of synthetic reaction curves which bore any resemblance to the corresponding experimentally measured trace, regardless of the chosen values of k_1 and $\Delta\varepsilon$

In the light of these findings, the values of the constants used in successful trace simulations and the results given in Table 4.7, the most reasonable values of k_1 and k_2 at 25°C and ε_X^{420} are 25 ± 5 and $43 \pm 5\ l\ mol^{-1}\ s^{-1}$ and $1550 \pm 100\ l\ mol^{-1}\ cm^{-1}$.

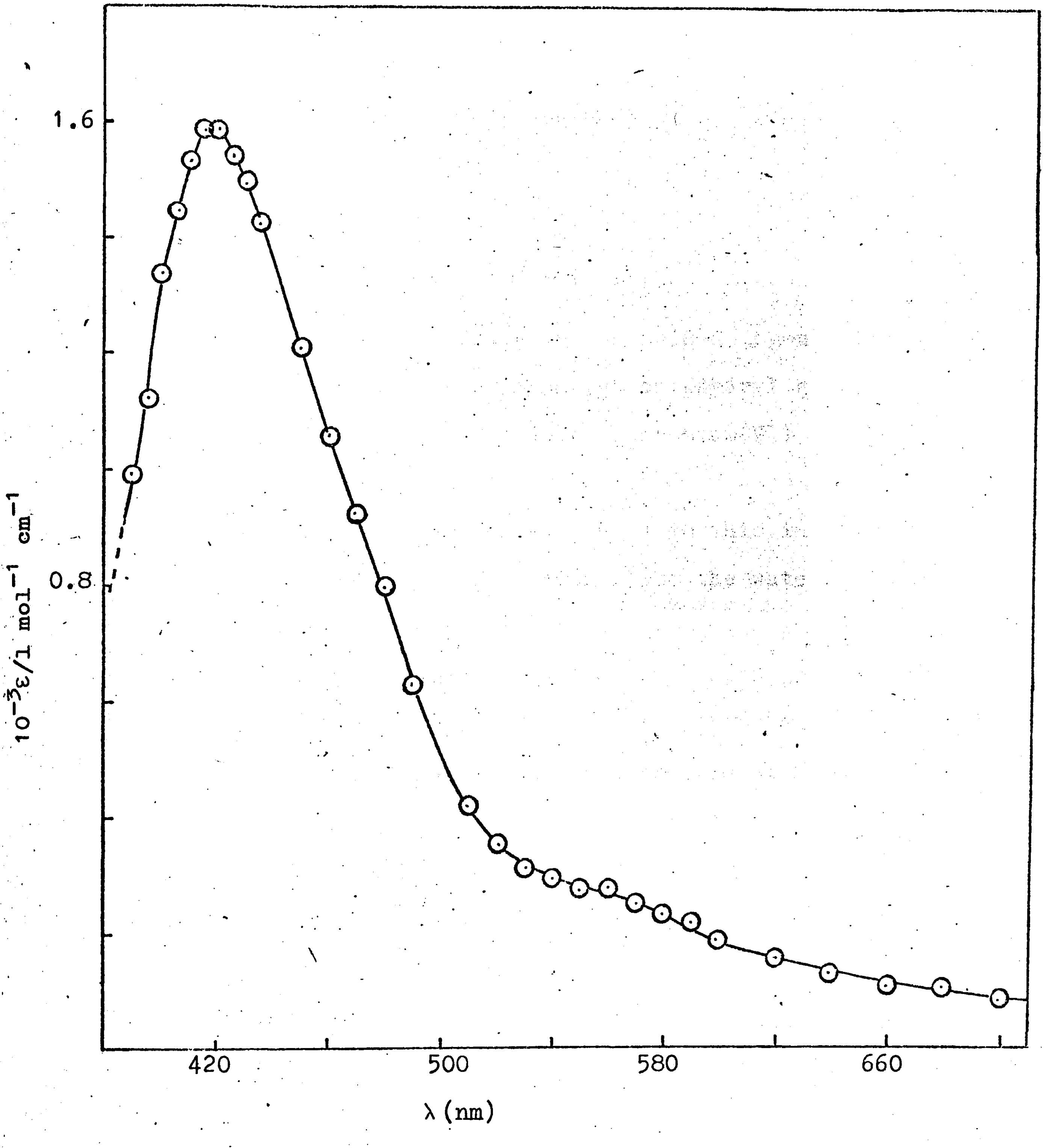
In conclusion it should be noted that there is a possible alternative solution, although it is not so probable viz. $\frac{\lambda_2}{[L]} = k_2 = 25\ l\ mol^{-1}\ s^{-1}$ and $k_1 = 43\ l\ mol^{-1}\ s^{-1}$. $\varepsilon_X 420$ in this case would be approximately $1000\ l\ mol^{-1}\ cm^{-1}$. The evidence which favours the interpretation adopted in this study is not conclusive; it cannot be stated with certainty that the alternative solution given above is not correct. However, even it it were the true situation, the similarity in magnitude between k_1 and k_2 is such that the discussion of the significance of their values would not be invalidated by this circumstance.

(e) The spectrum of the intermediate

Knowledge of ε_X^{420}, together with the known variation of ($O.D._X - O.D._{HCrO_4^-}$) with wavelength, derived in a manner similar to that described in the previous chapter, allowed compilation of the spectrum illustrated in Fig. 4.12.

Its similarity to that of the spectrum of the chromate(VI)

Fig. 4.12.



Spectrum of the Intermediate formed during the Reaction of Chromate(VI) with Thiomalic Acid.

L-cysteinate ester is quite pronounced. It follows that the same conclusions may be drawn regarding the nature of the metal-ligand linkage.

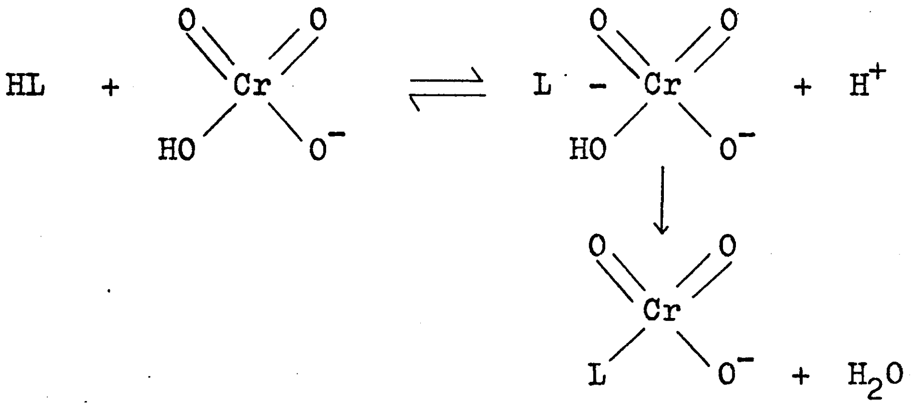
(f) The significance of k_1

The net process involved in the acid-independent ester formation is proton-transfer from the sulphydryl group to the hydroxyl ion co-ordinated to the chromium(VI) centre thus forming water, the leaving group.

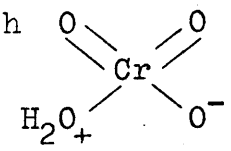
In such acidic media as were used in this investigation it need not be the -SH proton which forms the water molecule expelled by that particular sulphur. No extra protons are involved in the transition state, but rapid proton-loss by the sulphydryl group and protonation of the co-ordinated -OH group prior to the slow step is still consistent with the observed acid-independence of the formation rate. In this case the rate-limiting process would be either loss of water or co-ordination to chromium by RS^-.

As was found for L-cysteine in the previous chapter, the general mechanism proposed[158] by Haight and co-workers to describe such reactions as this is clearly unsatisfactory (pK_a of -SH in thiomalic acid is ~ 10). The scheme which they proposed explained the proportionality of k_f (equivalent to k_1 above) to the acidity of the substrate by postulating that the rate-determining process is transfer of the sulphydryl proton to the hydroxyl ion within a very loosely-bond complex. In effect, since protonation is generally diffusion-controlled, and could be effected by extraneous protons, it might be concluded that breaking of the S-H bond is the critical process according to this model. However, the transition state, if the above took place, would involve an extra proton and a hydrogen-ion dependence would be observed.

In order to take account of the high value of k_f, 80 l mol^{-1} s^{-1}, for $Co(NH_3)_5OH^{2+}$, which has a pK_a of 14, Haight found it necessary to put forward[196] an alternative mechanism involving initial fast formation of a strongly-bound aggregate, accompanied by elimination of a proton, with proton-assisted water loss being the rate-determining process.



(23)

This mechanism is similar in essence to one of the two alternatives mentioned at the beginning of this sub-section. The other alternative proposed there, rate-determining interaction of L^- with  involves two species both of whose formation equilibria are unfavourable and is consequently less likely.

In-sufficient evidence is available to test the validity of the second of Haight's schemes[196] but it is less inconsistent with the data found in this laboratory for k_f in this reaction of both L-cysteine and thiomalic acid with $HCrO_4^-$.

(g) The significance of k_2

Electron-transfer in the reaction of $HCrO_4^-$ with thiomalic acid appears to proceed by a pathway analogous to the predominant redox route encountered in the corresponding process with L-cysteine. The significance of such second-order ligand terms in redox rate-laws was discussed in the previous chapter. An insufficient number of these acid-independent paths have been characterised to enable a meaningful comparison to be made between that of thiomalic acid and that of L-cysteine.

Runs at a single ligand and hydrogen-ion concentration were carried out at 11.4°C and 34.8°C primarily to aid the decision concerning whether $\frac{\lambda_2}{[L]}$ equalled k_1 or k_2, as described earlier. Approximate activation parameters derived from these data are :- $\Delta H^{\ddagger} = 7 \pm 1$ kcal mol^{-1} and $\Delta S^{\ddagger} = -27 \pm 4$ cal K^{-1} mol^{-1}. Comparison of these values with those in Table 3.10 shows that they are not significantly different. The presumably associative character of such pathways is consistent with the quite negative values of $\Delta S^{\ddagger}$.

It is noteworthy that this study helps confirm the widespread incidence of such second-order ligand routes in the chromate(VI) oxidations of one-equivalent non-metal reductants, especially those containing sulphur. The driving-force which favours such pathways appears to be the ease with which it is possible, in such circumstances, to form disulphides, clearly the preferred oxidation product for most thiol compounds.

COMPARISON OF THE REACTIONS OF MALIC AND THIOMALIC ACIDS WITH $HCrO_4^-$

The active sites in these two reductants are -OH and -SH respectively. As the two molecules are otherwise identical, any variation in reactivity must surely stem from differences in the characteristics of the two functional groups above.

Of all the hydroxyl-containing reducing agents those whose reactions with $HCrO_4^-$ have been most widely and extensively studied are alcohols and hydrated aldehydes. The general mechanism in these cases consists of formation of an oxygen-bonded ester followed by a two-equivalent internal redox step. The overall oxidation products are usually similar to those yielded by other oxidants i.e. ketones and acids.[133] In the case of reductants whose active site contains sulphur the most common oxidation product is disulphide, formed via a sulphur-bonded chromate ester.[180,184,192,199,218] Further oxidation can in some circumstances take place.[184,218] This difference in the nature of the products can be rationalised on the basis of the following factors.

Firstly the larger and more diffuse sulphur atom appears to be more capable of accommodating an unpaired electron than does the smaller, "harder", oxygen. The longer life-times of sulphur-containing radicals enables them to encounter and interact with each other more readily than the corresponding oxygen-containing entities.[31]

Secondly, the catenation properties of sulphur seem stronger than those of oxygen. The disulphide group is common in biological systems both in providing the cross-linkages in proteins and in electron-transfer processes in enzymes.[209] The peroxo group is of no comparable importance.

Although the products of the reactions of malic and thiomalic acids with $HCrO_4^-$ have not as yet been adequately investigated, it is unlikely that this oxidant yields organic products significantly different from those found with other metal-ion oxidants.

In general, factors governing chromate(VI) ester formation and substrate oxidation appear to be more favourable for thio ligands than for those incorporating hydroxyl groups. The principal reason is probably the greater size, and hence polarisability, of sulphur as compared with oxygen.

One of the most striking differences between the reactions with chromate(VI) of these two acids is the apparently much greater simplicity of that involving thiomalic acid. Although this is perhaps partly a result of exclusive formation of disulphide, it should not be overlooked that it was not necessary in the case of thiomalic acid to use as large an excess of ligand as was used for malic acid.

Because of the much greater difference in electronegativity between -SR and -OH than between -OR and -OH, the spectrum of the thiomalate intermediate is sufficiently different from that of $HCrO_4^-$ for the practical employment of experimental conditions which favour formation of monocomplex only, thus simplifying the kinetics.

The reason for the radically different hydrogen-ion dependences of the two formation reactions is not immediately apparent. One speculative explanation is that in the case of malic acid three different oxygen atoms are capable of electron-donation to chromium(VI). There is thus a possibility that isomers may form. With thiomalic acid, where only one sulphur can participate, a comparable possibility does not exist.

APPENDIX TO CHAPTER IV

Computer Program (In Extended Basic) Used To Simulate The Absorbance Changes Occurring In The Course Of The Reaction Of Chromium(VI) With Thiomalic Acid.

```
0010  PRINT   "M",
0020  INPUT    M
0030  PRINT   "P",
0040  INPUT    P
0050  PRINT   "K",
0060  INPUT    K
0070  PRINT   "E"
0080  INPUT    E
0090  PRINT   "L",
0100  INPUT    L
0110  PRINT   "X",
0120  INPUT    X
0130  PRINT   "T",
0140  PRINT   "I",
0150  INPUT    I
0160   LET    T = 0
0170  GO TO   0190
0180   LET    T = T + I
0190   LET    J = -1*K*L*T
0200   LET    N = -1*X*L*T
0210   LET    O = (K*E) + (228*X)
0220   LET    Q = K*(228 + E)
0230   LET    R = M*P/(X-K)
0240   LET    V = O*EXP(J)
0250   LET    W = Q*EXP(N)
0260   LET    Y = R*(V-W)
0270  PRINT   Y
0280  GO TO   0180
```

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