A THESIS

entitled

~~THE~~ OXIDATION OF THIOLS IN GAS-LIQUID SYSTEMS

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ABSTRACT

This thesis describes research into the kinetics and mechanism of the oxidation by gaseous oxygen of simple thiols (mercaptans) in aqueous alkaline solution at 30 - 50°C. The reactions were studied both in the nominal absence and in the presence of metal ions, complexing agents, and disulphides.

In the Introduction a survey is made of previous work in this field. This has been concerned mainly with carboxy-thiols, such as cysteine, although some important papers on simple thiols have appeared since 1961.

The Experimental section describes the techniques and apparatus used. The aqueous solutions were shaken under oxygen, the pressure of which was automatically kept constant, the decrease in volume taking place as reaction proceeded being measured in a gas burette. Methods for sampling and analysis of the reagents are described.

The Results section gives details of the stoichiometric and kinetic experimental results. Most of the work was carried out on 0.5 M ethanethiol solutions in 0.5 - 4.0 M sodium hydroxide. The disulphide was the principal final product under almost all conditions. An account is given of the effect of various parameters upon the kinetics both of the uncatalysed reaction and of the reaction catalysed by metal ions. The oxidisability of the thiols decreased in the order: n-alkanethiols > phenylmethanethiol > thiophenol > t-butanethiol. Metal ions were added as sulphates and their order of effectiveness as catalysts was: $\mathrm{Cu} > \mathrm{Co} > \mathrm{Mn} \approx \mathrm{Fe} > \mathrm{Cr} \approx 0$. The effect of copper was appreciable at concentrations as low as 10^{-7}M. Of the various complexing agents investigated, cyanide ions were the most effective in suppressing catalysis by metal ions. The uncatalysed and copper-catalysed oxidations of ethanethiol had activation energies of 15.5 and 11 kcal/mole respectively.

The experimental findings are critically examined in the Discussion section. Oxidation in the nominal absence of additives appears to be partly catalysed by impurities, which may be traces of metals or oxy-sulphur acids. The catalytic effect of metal ions is correlated with the oxidation-reduction potentials of their common valencies. Mechanisms are proposed in which metal ions promote electron transfer from thiol anions to oxygen in a redox cycle. The effect of other additives is due mainly to modification of the ligand shell of the metal ion.

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J.D.H.

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1 INTRODUCTION 1

1.1 Historical

The oxidation of thiols (mercaptans) in basic media is a subject which has occupied a large number of research workers, and there have been few periods in the past century when some work in this field has not been in progress. The subject has proved surprisingly difficult to conquer. Much of the data have been in conflict, and the various interpretations even more so, and this has continued in some of the work published quite recently. The chief reason for this confusion appears to be the extreme sensitivity of the systems to traces of impurity, and real progress has been made only when the catalytic role of metals and in particular metal ions has been appreciated.

The first published work on the subject appeared in 1865, when Maercker[1] prepared some sulphur derivatives of toluene, and noted that what is now known as phenylmethanethiol (toluene-omega-thiol, or benzyl mercaptan) was oxidised by air faster if ammonia was present. Among subsequent papers published before 1900, the work of Klason[2] is noteworthy; studies were made of the oxidation of thioglycolic acid by iron and copper salts, as well as by iodine and gaseous oxygen, and catalysis of the autoxidation of potassium thioglycolate by ferric chloride was observed. Investigations were carried out on the autoxidation of sodium ethanethiolate in aqueous and alcoholic solutions[3]. 1.1

Biochemists have also been greatly interested in the role of metals as catalysts in physiological systems. Thiol autoxidation provided an excellent model system for quantitative study, and biochemists were therefore responsible for the sustained activity which followed the papers of Matthews and Walker in 1909[4]. It was desirable to study the oxidations under conditions comparable to those <u>in vivo</u>, and hence solutions buffered to low pH values were used, in which only carboxy-thiols, such as thioglycolic acid and cysteine, are soluble, and the oxidation of simple thiols in strong alkali was almost wholly neglected.

The removal of thiols ('sweetening') is an important step in the refining of petroleum, and their extraction with alkali has long been used, with simultaneous or subsequent regeneration of the alkali with blown air, which oxidises the thiols to the less undesirable disulphides[5]. Numerous patents have been taken out for improvements on this process, including the use of various solutisers and catalysts, but it is only recently that the industry has made a significant contribution to our understanding of the oxidation of simple thiols in strongly basic conditions. This has included the first reliable work on the truly uncatalysed (i.e. only base-catalysed) reaction.

A little work on the problem has also been carried out by the rubber industry[6], although here the emphasis has naturally been placed more on factors contributing to the deterioration of vulcanised rubber, such as the oxidation of sulphur-sulphur bonds in disulphides.

This brief historical survey has shown that a considerable amount of research has been carried out on the subject by workers with several different points of interest. In the following survey of previously published work it is proposed to review the relevant general chemistry of thiols and to establish the present state of knowledge on their liquid-phase oxidation.

1.2 Properties of thiols

The resemblance of thiols to alcohols is mainly a formal one. Thiols are considerably more acidic than alcohols, and while their solubility in water decreases rapidly from methanethiol up the series, they are readily soluble in alkaline solutions from which crystalline thiol salts (mercaptides, thioalkoxides, or thiolates) are obtainable. Some physical properties of the more common thiols and the corresponding alcohols are compared in Table 1. The boiling-points of the low molecular weight thiols are much lower than those of the alcohols, and this is certainly due to association by hydrogen bonding in the latter. The greater solubility in water of the alcohols is due to similar association with the solvent.

Table 1. Comparison of physical properties of some thiols 1.2 and alcohols. Bracketed figures are temperatures in °C. Sources: refs. 7, 8, 9, 10, 11, 12, 13, 14, 15.

	RSH				ROH			
R	m.pt. (°C)	b.pt. (°C)	water solubility (g/l, 20°)	pK$_a$	m.pt. (°C)	b.pt. (°C)	water solubility (g/l, 20°C)	pK$_a$
H	- 82.9	- 61.8	0.63(0) 0.28(40)	7.0 (25)	0.0	100.0	inf.	14.0 (25)
CH$_3$	-123.0	6.0	23.3		-97.0	64.5	inf.	13.5 (27)
C$_2$H$_5$	-147.3	34.7	6.76	10.6(20) 10.9(25)	-114.6	78.3	inf.	14.5 (27)
nC$_4$H$_9$	-115.9	98.0	0.57	10.7(20)	-89.8	117.7	79	14.3 (27)
tC$_4$H$_9$	1.2	64	0.96	11.1(20)	25.5	82.8	inf.	>14.4 (27)
nC$_6$H$_{13}$	- 81.0	151.5	0.043		-51.6	156.5	5.9	
C$_6$H$_5$	- 14.9	169.5	0	7.8(20) 6.5(25)	41	182	67(16)	9.9 (25)
C$_6$H$_5$CH$_2$	<20	195	0	9.4(25)	-15.3	205.2	40(17)	13.5 (27)
HOOC.CH$_2$	- 16.5	105		10.3(20)	63,79	dec.		

As the series are ascended, the growing hydrocarbon chain increasingly dictates the properties of both types of molecule, and the difference between alcohols and thiols diminishes.

1.3 Oxidation of organic sulphur compounds

The oxidation of pure thiols proceeds extremely slowly at room temperatures. The oxidation of methanethiol and ethanethiol by oxygen in the gas phase was studied by Cullis and Roselaar[16], who found that the reaction rate was suitable for study only above 210°C. The reacting gases were analysed at hourly intervals, and the main product was found to be sulphur dioxide. The alkyl fragments were recovered as carbon monoxide, formaldehyde, and methanol (from methanethiol), or acetaldehyde (from ethanethiol). Higher ratios of thiol to oxygen favoured the formation of an increasing proportion of the corresponding disulphide. The results were compatible with a mechanism initiated by the reaction:

$$RSH + O_2 \rightarrow RS^\bullet + HO_2^\bullet \qquad (1)$$

and continued by the reactions:

$$RSH + HO_2^\bullet \rightarrow RS^\bullet + H_2O_2 \qquad (2)$$

$$RS^\bullet + O_2 \rightarrow R^\bullet + SO_2 \qquad (3)$$

the latter in oxygen-rich mixtures; in oxygen-lean mixtures:

$$RS^\bullet + RS^\bullet \rightarrow RSSR \qquad (4)$$

The oxygenated products are derived from other reactions of the various intermediates, especially $R^\bullet$ radicals.

Bateman et al.[17,18,19] have studied the oxidation of 1.3
various organic sulphur compounds by a number of reagents including gaseous oxygen. ~~Acyclic~~ Monosulphides and disulphides with saturated side-chains (except thiacyclohexane) were inert to autoxidation at temperatures from 45° to 75°C. Sulphides with allylic or vinylic groups were, however, more readily oxidised, the initial attack taking place on hydrogen atoms attached to alpha carbon atom. This leads to the formation of the corresponding hydroperoxide in a free-radical chain-reaction. The hydroperoxide may oxidise the residual sulphide to sulphoxide, or decompose to give ultimately a variety of oxygenated products.

From these results it appears that the autoxidation of pure thiols and other sulphur compounds is very similar to that of the hydrocarbons from which they are derived[20,21] and of the corresponding oxygenated compounds[22].

There have been a number of studies of the low-temperature oxidation of organic sulphur compounds by oxidants other than gaseous oxygen. In the case of thiols a good recent review by Tarbell is available[23], and this provides many references. The reagents used include hydrogen peroxide, whose oxidation of 2-mercaptophenylacetic acid was studied by Pascal and Tarbell[24]. The rate in the presence of excess hydrogen peroxide was zero order in thiol and was inhibited by hydrogen ions according to the equation:

$$-\frac{d[RSH]}{dt} = k_0[RSH]^0 = k_0'[H_2O_2][H^+]^{-0.5} + k_0''[H^+]^{-0.5} \qquad (i)\ 1.3$$

Iron ions increased the rate linearly, but copper ions, iodine, the corresponding disulphide, and sodium sulphate at ionic strengths of 0.05 and 0.1, had no effect. Over the temperature range 20 to 40°C the activation energy was 17.8 kcal/mole. In the presence of ethylenediaminetetracetic acid at pH 2.6 to 5.6, and with excess peroxide, the rate was given by:

$$-\frac{d[RSH]}{dt} = k_1[RSH]^1 = k_1'[RSH][H_2O_2][H^+]^{-0.5} \qquad (ii)$$

k_1 was independent of the EDTA and iron concentrations, and showed no salt-effect with sodium sulphate. The activation energy was 16.2 kcal/mole. Pascal and Tarbell did not postulate a mechanism to explain their observations, but pointed out that a complex with the empirical formula $M_{1/2}[H_2O][OH^-][RSH]$ could be formed as an intermediate. Disulphide was found to be the sole product.

The kinetics of the oxidation of some aliphatic thiols (n-butane-, n-octane-, and n-dodecane-thiols) by potassium persulphate in slightly aqueous acetic acid has been studied[25]. The initial product was the disulphide, but 3 moles of persulphate were ultimately consumed per mole of thiol, and the disulphide was presumably oxidised further, since the ratio 2:1 is expected from oxidation only to disulphide. The rate was first order in persulphate ion and zero order in thiol, becoming first order at low thiol concentrations. The energy of activation was 26 kcal/mole. Two mechanisms have been put forward, depending upon either the homolysis[25] or heterolysis[26] of the persulphate ion as the rate-determining step. In the latter mechanism the disulphide is produced through a sulphenyl cation (RS^+) intermediate, and in the former through thiyl radicals ($RS^\bullet$).

The oxidation of thiols with a dye provides a convenient spectrophotometric method for rapid estimation of their relative ease of oxidation. Methylene blue was employed as the oxidising agent by Dixon and Tunnicliffe[27], but the method has been used more fully in recent work using 2,6-dichlorophenolindophenol or its sodium salt. In neutral solution the kinetics and stoichiometry depend upon the nature of the oxidising thiol[28]. The mechanism appears to involve sulphenyl ions:

$$RSH + I + H^+ \rightarrow RS^+ + IH_2 \qquad (5)$$

where I represents the dye molecule. The cation may then react to give the sulphenic acid RSOH or its anhydride ('monoxide') RS.O.SR. This gives a fast reaction with 1:1 (dye:thiol) stoichiometry. If the RS^+ ion reacts with more thiol:

$$RS^+ + RSH \rightarrow RSSR + H^+ \qquad (6)$$

then a slow reaction is observed with 1:2 stoichiometry. The latter reaction appears to be favoured by Cu^{2+}, Ni^{2+}, and Fe^{2+} ions, while EDTA reverses this effect, accelerates the reaction, and gives the 1:1 stoichiometry.

In this system at pH 10, Overberger and Ferraro[29,30] found that, in a series of monothiols and dithiols, aromatic thiols were considerably more stable to oxidation than saturated aliphatic thiols.

The absolute and relative rates of oxidation of thiols appear to depend on a number of factors, especially the pH value. pH 10 is very near the pK_a values for the majority of thiols (see Section 2.1), and it is doubtful whether useful comparisons can be made under these conditions. However, Overberger's and Ferraro's conclusions were confirmed by Xan et al.[31] for the oxidation by gaseous oxygen of thiophenol, phenylmethanethiol, and a series of saturated aliphatic thiols in strong alkali. Among these thiols (RSH) the oxidation rate decreased in the order $nPr > nBu > nPen > PhCH_2 > Ph$. On the other hand, Kharasch et al.[32] compared the rates of oxidation of thiols by 'a variety of agents', and found the order to be $Ar > HOOC.CH_2 \gg RCH_2 > RR'CH > RR''R'C$, thus largely reversing the former order. It may be seen, however, that the latter order is that of the ease of oxidation of the molecules RSH, while the former applies to the ions RS^- [33].

The autoxidation of thiols is a thermochemically favourable process. Taking the most probable values for the energies of the bonds involved, viz. $D(C_2H_5S{-}H) = 87$ kcal/mole, $D(C_2H_5S{-}SC_2H_5) = 70$[34], $D(O{=}O) = 118$, and $D(H{-}O{-}H) = 219$ kcal/mole[35], the reaction:

$$C_2H_5SH + 1/4\ O_2 \rightarrow 1/2\ C_2H_5SSC_2H_5 + 1/2\ H_2O \quad (7)\ 1.4$$

is exothermic by about 30 kcal/mole. Taking $D(C_2H_5O\text{-}H)$ = 110 kcal/mole and $D(C_2H_5O\text{-}OC_2H_5)$ as 40 kcal/mole, the analogous oxidation reaction for ethanol would be endothermic by about 10 kcal/mole. It is therefore not surprising that ethanethiol is oxidised to the disulphide under conditions which do not affect ethanol.

The autoxidation of a pure dry thiol to the disulphide has probably not been observed. This is presumably because the energy of activation is so high that temperatures are required such that oxidation takes place by a different mechanism, which leads to the formation of more highly oxidised products, as observed by Cullis and Roselaar[16]. However the base-catalysed oxidation of most thiols proceeds at a reasonable rate at room temperature, and this is certainly due to the much lower activation energy needed for oxidation of the anion RS^-. The reactions are also very strongly catalysed by a number of metals and metal ions.

In the following Sections the oxidation of thiols in basic media, both in the absence and presence of metallic and other catalysts, will be discussed in detail.

1.4 Uncatalysed autoxidation of thiols in basic media

Previous work on the uncatalysed oxidation of thiols under alkaline conditions is clearly divided into two classes. Firstly, there are some earlier papers on the oxidation of

carboxy-thiols such as cysteine in buffered solutions. 1.41
Secondly, there is a considerable amount of more recent work on the autoxidation of simple thiols in strongly basic media.

1.41 Carboxy-thiols

The autoxidation of the amino-carboxy-thiol, cysteine, $HOOC.CHNH_2.CH_2SH$, at low alkaline pH values was the subject of early work by Matthews and Walker[4], who found that the rate was a maximum at pH 8. The autoxidation of three carboxy-thiols was studied by Dixon and Tunnicliffe[27]. The compounds investigated were reduced glutathione (a dipeptide of cysteine and glutamine), cysteine, and thioglycolic acid, and the oxidations were carried out over a wide range of alkaline pH values. The reaction was followed by the decrease in the oxygen pressure at constant volume, and by titration of unchanged thiol with iodine, the final solutions being tested with nitroprusside for complete oxidation. The chief result of this work was the discovery that the reactions were catalysed by deliberate addition of disulphides, although in the absence of added disulphide the reactions were not autocatalytic. This result is discussed later in Section 1.53.

The rate of autoxidation of glutathione was highest at pH 7 to 7.5, fell off rapidly outside this range, and at pH 13.8 was less than 10% of the maximum. With thioglycolic acid, however, the rate increased steadily with pH. Benesch and Benesch[37] suggest that increasing pH produces a higher concentration of thiol anions RS^-, which are the active 1.41 species, and thus favours autoxidation. With glutathione and cysteine, however, this positive effect is offset above pH 7 by the loss of a proton from the substituted ammonium group $>NH_2^+$, which increases the nett negative charge on the thiyl radical, and discourages its dimerisation. This explanation is not, however, wholly satisfactory, since it is the reaction which produces the radicals, and not their dimerisation, which is rate-controlling. Some effect of the higher overall negative charge on the proportions of the products would be expected, however, due to the participation of the thiyl radicals in alternative processes to dimerisation: this was apparently not observed.

The probable effect of contaminants on the results of previous workers prompted Gerwe[38] to take special precautions to exclude iron from his reagents. However, the effect of iron would probably still be considerable below the 10^{-6}M concentration limit to which the thiocyanate test which he used is sensitive. Furthermore, no special precautions were taken by Gerwe to exclude copper ions, which are about 16 times more effective than iron in promoting the oxidation of cysteine[39].

The results available for the uncatalysed oxidation of carboxythiols are therefore inconclusive, but it is likely that the kinetics are similar to those found more recently for simple thiols, which are the subject of the next Section.

1.42 Simple aliphatic and aromatic thiols

Whereas the liquid-phase autoxidations of the carboxy-thiols has been studied over the complete range of alkaline pH values, this has generally not been possible with the simple thiols, RSH, where R is an alkyl or aryl group, since these thiols are almost insoluble in water unless ionised. As most of them have pK_a values in the range 10 to 11, moderately strong basic conditions are necessary, and for this reason the uncatalysed oxidation is often referred to as a base-catalysed reaction. The bases most commonly used have been the alkali metal hydroxides and alkoxides, while the solvents are water or alcohols or binary mixtures: highly polar solvents have also been used to increase the basicity, and in a few cases base and solvent properties have been included in the same molecule, such as in dimethylformamide (DMF) or tetramethylguanidine (TMG).

The necessity for strongly alkaline conditions has generally obviated the use of buffers, which have been a constant source of contamination and kinetic irreproducibility in the carboxy-thiol systems. The brief study by Fruton and Clarke[40] of the autoxidation of ethanethiol in solutions buffered to pH 7.5 to 9 gave little simple kinetic data. The rate appeared, however, to be independent of pH, which is perhaps not surprising, since the thiol was unionised over this range of pH. 1.42

A fuller investigation of the autoxidation of some simple thiols in aqueous sodium hydroxide solution was published by Xan, Horton, et al.[31] A very simple apparatus was used in which a roughly constant pressure was maintained by raising a mercury resevoir manually. The concentrations of sodium hydroxide were between 0.05 and 2.7 N. The ease of oxidation of the different thiols decreased in the order nPr $>$ nBu $>$ nAm $>$ PhCH$_2$ $>$ Ph. While the total consumption of oxygen corresponded to the formation of disulphide at low alkali concentrations, the final uptake was 50% higher in the strongest alkali. Thiophenol was an exception, and absorbed the theoretical volume of oxygen under all the conditions used. This confirmed the early results of Engler and Broniatowsky[41], who found that thiophenol absorbed 98.2 to 107.9% of the theoretical amount of oxygen in 1 N sodium carbonate solution, and 92.3 to 104.8 % in 0.2 N ammonia. More recently Cole[6] has found that p-nitrophenol was oxidised with extensive breakage of the C-S bond. Three times the theoretical quantity of oxygen required for oxidation to disulphide was absorbed, and twice as much monosulphide as disulphide was produced, the remaining sulphur appearing as sulphite and sulphate.

The most extensive investigation of the base-catalysed oxidation of simple thiols is that of Wallace and Schriesheim[33],

who suggest that the base-catalysed oxidation of thiols 1.42
can proceed without the intervention of metal ions according to the scheme:

$$RSH + B \rightleftharpoons RS^- + BH \tag{8}$$

$$RS^- + O_2 \rightarrow RS^\bullet + O_2^- \tag{9}$$

$$RS^- + O_2^- \rightarrow RS^\bullet + O_2^{--} \tag{10}$$

$$2RS^\bullet \rightarrow R_2S_2 \tag{11}$$

$$O_2^{--} + H_2O \rightarrow 2OH^- + 0.5O_2 \tag{12}$$

With reaction (9) rate-determining, this mechanism predicts that the rate of oxidation depends upon the proportion of RS^- ions in the solution, and this was strikingly confirmed by measurement of the oxidation rates of n-butanethiol with sodium methoxide as the base in (a) strongly basic solvents of low dielectric constant, and (b) polar, aprotic solvents of high dielectric constant. The oxidation rates (which were not corrected for changes in oxygen solubility) were first order in thiol, and were from 35 to 300 times faster than in methanol. The effect of various alkoxide bases were compared, and again the strongest bases gave the highest rates.

In further experiments a series of thiols was oxidised under a variety of conditions[42]. The reactivity depended upon the alkyl group in the order: benzyl > n-butyl > p-aminophenyl > cyclohexyl > phenyl > p-nitrophenyl ≈ 0, confirming that the most acidic thiols are most resistant to oxidation, and that the rate-determining step is therefore that in which the anion is destroyed, viz. reaction (9), and not that which produces it, viz. reaction (8). The reactions were followed to 30% conversion and were first order in thiol. The conclusion that electrophilic beta-substituents decrease the ease of oxidation of aliphatic thiols[43] is probably another case of anion-stabilisation. 1.42

The nature of the rate-determining transfer of the electron from the thiol anion to the oxygen molecule has been further elucidated[42]. n-Butanethiol was oxidised in binary solutions of methanol with DMF and with diglyme, with sodium methoxide as the base. The relative rates of oxidation decreased in the same manner in the two solvent mixtures as the proportion of methanol increased, suggesting that similar transition states operate in each medium. A series of ion-pair complexes was suggested to explain this. An electron is transferred from the ion-pair complex of the thiol anion with methanol to an oxygen molecule less readily than from the complex with DMF or diglyme.

Berger[44] has studied the oxidation of octane-1-thiol and thiophenol in t-butanol containing various proportions of potassium t-butoxide. The amount of oxygen absorbed, and the corresponding products formed, depended upon the relative amounts of thiol and base present. With the thiol in excess, disulphides were formed, but with excess base the products were sulphinic acids ($R.SO.OH$) and sulphonic acids ($R.SO_2.OH$).

It was concluded that disulphides are formed from thiol molecules, RSH, and acids, primarily sulphinic, from the thiol anion, RS^-. The higher yields of acids from thiophenol were put down to its lower pK_a value. The oxygen uptake rates were zero order in thiol, and the final uptake values varied from the O_2:RSH ratio of 1:4 (theoretical for oxidation to disulphide) with excess thiol to more than 1:1 (theoretical for oxidation to sulphinate) with excess base. In oxidations giving finally about 50% disulphide and 50% sulphinate, the disulphide was the main product until the thiol ceased to be in excess, when sulphinate became the major product. Berger proposed a chain mechanism to explain these results: 1.42

$$RSO^- + O_2 \rightarrow R.SO.OO^- \tag{13}$$

$$R.SO.OO^- + RS^- \rightarrow RSO^- + RSO_2^- \tag{14}$$

$$RSO_2^- + RSH \rightarrow RSSR + HO_2^- \tag{15}$$

$$HO_2^- + 2RSH \rightarrow RSSR + H_2O + OH^- \tag{16}$$

or alternatively, and better:

$$RS^- + O_2 \rightleftharpoons RSO_2^- \text{ (triplet)} \tag{17}$$

$$RSO_2^- \text{ (triplet)} \rightarrow RSO_2^- \tag{18}$$

$$2RSH + RSO_2^- \text{ (triplet)} \rightarrow RSSR + RS^- + H_2O_2 \tag{19}$$

$$2RSH + H_2O_2 \rightarrow RSSR + 2H_2O \tag{20}$$

The above conclusions are most remarkable, ane it is rather surprising that no account was taken of the highly plausible explanation that the oxygenated acids are not primary products at all, but are derived from hydrolysis of the disulphide.

This would of course be favoured by excess base.

Wallace and Schriesheim[45] have shown that thiols may be oxidised to disulphides or sulphonic acids at will, simply by varying the basicity of the solution and the temperature. It may be concluded however that the primary product of the base-catalysed oxidation of simple thiols is the corresponding disulphide, which is produced by a mechanism at least similar to that of Wallace and Schriesheim. Under strongly basic conditions other products may be formed by hydrolysis and oxidation of the disulphide.

1.5 Catalysed autoxidation of thiols in basic media

1.51 Catalysis by metallic ions and complexes

The autoxidation of thiols under basic conditions is very sensitive to traces of metals. In many cases the metal may be in the pure elemental form, but more usually it is added as the aquo-ion or some other complex, such as phthalocyanine.

Recorded work may again be conveniently subdivided into work on carboxy-thiols and work on simple thiols. The lower alkaline pH values available when carboxy-thiols are employed has led generally to the formation of more clearly defined complexes, and the metal-ion catalysed oxidation of this class of thiol is therefore at present rather more clearly understood.

1.511 Carboxy-thiols

Earlier workers surveyed the effect of a variety of metals, ions, and complexes on the autoxidation of cysteine[4,46], thioglycolic acid[47,48], and glutathione[49]. Although there are some differences between these thiols, and also some conflicting results, the ions (and in some cases the free metals also) of transition and B sub-group elements are generally catalytic, and among these the effects of manganese, iron, cobalt, copper, and arsenic have repeatedly been demonstrated. Among inorganic anions, both cyanide and iodide have been found to be inhibitors.

Further studies of the iron-catalysed oxidation of cysteine showed that the rate in solutions buffered to about pH 7 was first order in iron[50,51] and zero order in thiol[52]. The catalysis was inhibited by cyanide. In the presence of cupric ions in solution buffered to pH 7.6 with pyrophosphate the kinetics were zero order in cysteine to over 50% oxidation[53]. The role of haemin as a catalyst for the oxidation of cysteine was investigated by Krebs[54]. The catalysis was again very sensitive to cyanide.

All these results showed that the most probable mechanism for this catalysis by metal ions was through formation of intermediate metal-thiol complexes, and schemes for the iron-catalysed oxidation of cysteine[55] and thioglycolic acid[56] were proposed. However the first frontal attack on the problem was that of Michaelis, assisted chiefly by Barron[57,58] and 1.511 Schubert, who studied the cysteine complexes of iron, cobalt, and nickel and their oxidation at pH 7 and 8. The oxygen uptake curves were again zero order in cysteine. Cobalt and nickel, however, were not catalysts in this system. It was concluded that the difference between iron and the latter metals in this system is due to decomposition of the iron-cystine complex, which allows the iron to take part in an oxidation-reduction cycle. The corresponding cobalt complex is stable, and the cobalt cannot therefore be recycled. The cobalt complex in question probably has the composition $Co(SCH_2.CHNH_2.COO)_3H_2$[59], the sequence of reactions being[60]:

$$\begin{aligned} Co(II) + 3RS^- \rightarrow Co(II)[RS^-]_3 &\xrightarrow{O_2} [Co(III)[RS^-]_3] \\ &\rightarrow Co(II)[RS^-RSSR] \end{aligned} \qquad (21)$$

With iron replacing the cobalt, the ferrocysteinecystine complex reacts further with two molecules of free cysteine to complete the cycle:

$$Fe(II)[RS^-RSSR] + 2RS^- \rightarrow Fe(II)[RS^-]_3 + RSSR \qquad (22)$$

Nickel was not a catalyst since 'it is inconceivable that the nickelic state would ever be established by exposing any nickelous complex to air'[60]. More recent work by Neville[61] confirmed the above conclusions.

Michaelis and Schubert[62] also studied the complexes of cobalt and iron with thioglycolic acid. The stable brown complex formed when solutions of thioglycolic acid containing cobalt ions were aerated was found to have two cobalt 1.51 atoms and four thioglycolate groups per molecule of complex. Its exact nature could not be established, but it is possible to write both cobalti-thiol and cobalto-disulphide formulae. It seems probable that the rearrangement of bonds by which the former could become the latter might be responsible for the catalysis of thioglycolate by both cobalt and iron[63,64].

The kinetics of the oxidation of cysteine and some derivatives in the presence of 10^{-3}M iron were studied by Fruton and Clarke[40]. The reaction was zero order in thiol for cysteine and thioglycolic acid, but first order for a series of N-acylated cysteines. The solutions were buffered with a series of phosphate, borate, and veronal buffers at M/15 concentration, which evidently modified the catalytic effect of the iron, since, while little dependence of the rate on pH was found within the range of a single buffer, the rates differed sharply from one buffer to the next. Presumably the metal ions formed complexes with the buffer molecules.

The cysteine-cystine redox system in the presence of iron has been studied polarographically by Kolthoff et al.[65]. At pH 10 to 11 in aerated solutions there is an equilibrium between the complexes $Fe[(RS)_3]^{3-}$ and $Fe[(OH)(RS)_2]^{2-}$, where RS is the group $^{-}S.CH_2.CHNH_2.COO^{-}$. The equilibrium constants show that the ferrodisulphide complex is strongly favoured[66]. There was evidence however for a reverse reduction of cystine by ferrous ions, possibly through the equilibrium[67]: 1.511

$$\mathrm{Fe(II)} + \mathrm{RSSR} \rightleftharpoons \mathrm{Fe(III)} + \mathrm{RS}^- + \mathrm{RS}^\bullet \qquad (23)$$

However, it is possible that the back-reaction was induced by the polarographic mercury. The catalytic effect of iron in this system was eliminated by EDTA and much pyrophosphate, but was unaffected by tartrate.

Following Michaelis and Schubert's studies of the thioglycolic acid system in the presence of iron and cobalt, the kinetic work was extended to copper and manganese ions by Kharasch et al.[68]. The effect of copper was optimum at pH 6 and 9, due presumably to stepwise ionisation of the thioglycolic acid. Combinations of copper and manganese were more effective than either metal alone. Phosphates inhibited catalysis by manganese and iron, but accelerated that by copper.

A photometric study of iron-thioglycolate complexes was made by Kolthoff and Leussing[69]. They observed an intensely coloured ferric complex which was formed from the precipitated ferric hydroxide when thioglycolate was added to alkaline solutions. This complex was found to be $\mathrm{Fe(III)[(OH)(RS)_2]^{2-}}$. Leussing and Newman followed the anaerobic bleaching of the complex[70], and produced an elaborate mechanism involving a succession of one- and two-centred complexes to explain their findings.

The simple formal mechanism for the iron-catalysed autoxidation of thioglycolate:

$$\mathrm{Fe(II)} + {}^{-}\mathrm{RSH} \rightarrow \mathrm{Fe(II)[{}^{-}RSH\ complex]} \qquad (24)$$ 1.51

$$\mathrm{Fe(II)[{}^{-}RSH\ complex]} + \mathrm{O_2} \rightarrow \mathrm{Fe(III)[{}^{-}RSH\ complex]} \qquad (25)$$

$$\mathrm{Fe(III)[{}^{-}RSH\ complex]} \rightarrow \mathrm{Fe(II)[{}^{-}RSH\ complex]} + {}^{-}\mathrm{RSSR}^{-} \qquad (26)$$

in which the nature of the complex is uncertain, was rejected by Lamfron and Nielsen[71] on the grounds that the separately measured rates of reactions (24) and (25) were much lower than the overall rate of autoxidation. They proposed further free-radical steps to account for the higher rate of oxidation:

$$\mathrm{Fe(II)[{}^{-}RSH\ complex]} + \mathrm{O_2} \rightarrow \mathrm{Fe(III)[{}^{-}RSH\ complex]} + \mathrm{O_2}^{\dot{-}} \qquad (27)$$

$$\mathrm{O_2}^{\dot{-}} + {}^{-}\mathrm{RSH} \rightarrow \mathrm{HO_2}^{-} + {}^{-}\mathrm{RS}^{\cdot} \qquad (28)$$

$${}^{-}\mathrm{RS}^{\cdot} + \mathrm{Fe(III)[{}^{-}RSH\ complex]} \rightarrow \mathrm{Fe(II)[{}^{-}RSH\ complex]} + {}^{-}\mathrm{RSSR}^{-} \qquad (29)$$

This appears reasonable, and it is also one of few attempts to explain the fate of the oxygen. The hydroperoxide ion would presumably produce further oxidation. These free radical steps receive some support from the reported positive effect of hydroquinone (Section 1.52) and the detection of hydrogen peroxide as an intermediate under certain conditions (Section 1.6).

Although the oxidation of cysteine and thioglycolic acid has been most extensively investigated, a little work has also been carried out on glutathione. In contrast to the former thiols, the latter was not catalysed by iron at pH 7, although copper was effective, and this may have been due to the use of pyrophosphate buffers. The kinetics were zero order in thiol[74]. The effectiveness of copper increased with pH, but haemin had an optimum effect at pH 8, and was surprisingly insensitive to cyanide, in marked contrast to the corresponding cysteine system. With 1 molar % cuprous chloride in 0.02 mM glutathione at pH 8.7, the oxygen uptake curve was first order in thiol, and the final uptake was theoretical for oxidation to disulphide. 1.51

The detailed kinetics and rate of oxidation in any particular system appear to depend therefore upon the formation of a suitable metal-thiol complex, its oxidation to a metal-disulphide complex, and the decomposition of the latter by thiol. In such a system there will clearly exist a delicately balanced mechanism, which is easily upset by changes of pH, and by competing ligands such as cyanide, or the buffers used to maintain the pH, such as phosphate, borate, and organic anions. It is probably for these reasons that such a variety of kinetic results has been observed in systems of this type.

1.512 Simple aliphatic and aromatic thiols

The catalytic effect of metal salts and complexes on the oxidation of simple thiols is probably the least understood aspect of thiol autoxidation. This is probably because such reactions take place only under strongly basic conditions, when most of the catalysts are precipitated as hydroxides, which may have an heterogeneous effect, while such metal-thiol complexes as are formed are of uncertain composition 1.51 and concentration. Certainly this is a much more difficult problem than the case of carboxy-thiols.

As with cysteine and the carboxy-thiols, the catalytic effect of a considerable number of metals and salts has been recorded[75]. Again the most remarkable and most fully investigated effects are those obtained with the transition elements generally, and with copper, iron, and cobalt especially. The presence of the ions of these metals appears to favour the formation of disulphide as the product[44,75]. Catalysis seems to take place through the formation of some kind of metal-thiol complex[76], but little is known of these or their stability constants, and the kinetic data are not simple. Thus although ferric ions had a positive effect on the rate of autoxidation of ethanethiol, the rate was almost independent of the iron concentration from 10^{-4} to 10^{-2}M [40]. In aqueous solutions this must have been due to the minute solubility product of ferric hydroxide (10^{-36}). Cobalt (III) hydroxide also has a low value (10^{-43}), but copper (II) hydroxide has a much higher value (10^{-19}), and it is therefore not surprising that copper ions are a very effective catalyst[43].

Striking effects have been observed when metals are added to thiol autoxidation systems in the form of complexes other than the usual aquo-ions. Investigations of various complexes with a view to use in commercial sweetening processes has been made by Wallace et al.[77]. Work with 2M butane-1-thiol and 2M sodium hydroxide solution in the presence of 100 mg of the complexes showed that cobalt phthalocyanine (whose commercial use has been patented[78]) and pyrophosphate were of similar catalytic activity which was much greater than that of the phosphomolybdate, phosphotungstate, or phosphate. The activity was attributed to the formation of six-membered rings in the phthalocyanine and pyrophosphate complexes, and this facilitates the transfer of an electron from the complex to oxygen[79]. The order of activity for a series of pyrophosphates was Co $>$ Cu $>$ Ni $>$ Fe, and this may be explained in terms of the stability of the 3d electron-shells. Thus the oxidation-reduction of cobalt (II) and copper (I) pyrophosphates would be expected to proceed readily, but the Co(II) ($3d^9$) would be more easily oxidised than Cu(I) ($3d^{10}$ or $4p^6$), which is also stable in the Cu(II) state. Oxidation of Ni(II) ($3d^{10}$) to Ni(III) is possible but not as favourable. The Fe(II) catalyst ($3d^6$) would undergo oxidation to Fe(III) ($3d^5$), but the reduction step would be difficult due to the stability of the half-filled 3d electron-shell. 1.512

Kinetically, Wallace's oxygen uptake versus time curves show that the reaction is generally zero-order in thiol, although with cobalt phthalocyanine and pyrophosphate it is possibly first order. In experiments with various ratios of thiol to cobalt pyrophosphate, either zero-order kinetics in thiol of first-order in catalyst are deducible from the linear graph of reaction time for 40% conversion of thiol versus the thiol/catalyst ratio. 1.5

Patents have also been taken out for the catalytic use of other cobalt complexes in sweetening processes[80,81].

Little work appears to have been carried out on the possible modifying effect of the common ligands such as ethylenediamine (en), ethylenediaminetetracetic acid (EDTA), or cyanide, on simple metal-catalysed thiol autoxidation systems. Pascal and Tarbell[24] have, however, reported an interesting effect of EDTA on the oxidation of 2-mercaptophenylacetic acid by hydrogen peroxide at pH 2.4 to 7.2, which was quoted in Section 1.3.

The oxidation of octane-1-thiol by ferricyanide has been studied by Kolthoff et al.[82]. In 60-70% aqueous acetone solution at 50°C the kinetics were first order in ferricyanide, thiol, and hydroxide. In the absence of excess cyanide the reaction proceeds through an intermediate complex in which a thiol anion has displaced a cyanide ligand, i.e. the mechanism is 'inner sphere':

$$\mathrm{Fe[CN]_6{}^{3-} + RS^- \rightleftharpoons Fe[(CN)_5(SR)]^{3-} + CN^-} \qquad (30)$$

$$\mathrm{Fe[(CN)_5(SR)]^{3-} \xrightarrow{fast} Fe[CN]_5{}^{3-} + RS^{\bullet}} \qquad (31)$$

$$\mathrm{Fe[CN]_5{}^{3-} + CN^- \xrightarrow{fast} Fe[CN]_6{}^{4-}} \qquad (32)$$

$$\mathrm{2RS^{\bullet} \rightarrow R_2S_2} \qquad (33)$$

The reaction is slowed by excess cyanide, the reaction then proceeding by electron transfer from the thiol anion to the iron through its intact ligand shell of six cyanide ions, i.e. by an 'outer sphere' mechanism:

$$RS^- + Fe[CN]_6^{3-} \rightarrow Fe[CN]_6^{4-} + RS^\bullet \qquad (34)$$

Although it is possible that these reactions could in the presence of oxygen form part of an oxidation-reduction cycle, no detailed mechanism has been worked out for any practical system.

1.52 Catalysis by other compounds

The role of metal ions as catalysts in the autoxidation of thiols in basic solution is essentially to provide a more facile route by which electrons may pass from the thiol anion to an oxygen molecule. Therefore any molecule which can easily absorb an electron and then transfer it to an oxygen molecule is a potential catalyst.

Wallace et al.[83] have investigated the oxidation of butane-1-thiol by nitrobenzene in dimethylformamide containing potassium hydroxide. They observed colour changes to yellow, to red, and then slowly to dark blue. Electron spin resonance and u.v. and visible absorption spectra showed that the nitrobenzene had been reduced to the radical-anion. Analysis of the oxidation products revealed that 99% of the thiol had been oxidised to give the disulphide in 98% yield. The reaction was followed spectrophotometrically for 100 minutes, and first-order kinetics were observed, suggesting a rate-

determining transfer of the electron from thiol anion to 1.52
nitrobenzene. In other experiments phenylmethanethiol and thiophenol were oxidised to give 81% and 2% yields respectively of their disulphides. Other oxidising agents for thiols were 2-nitrothiophene, ethylenetetracetonitrile, and 4-nitropyridine oxide. The latter was the most effective, and oxidised both butanethiol and thiophenol at the same rate.

All these compounds can be catalysts proper only, of course, if their reduced form, the anion, is oxidisable by O_2. It was found that exposure of the nitrobenzene-butanethiol system to oxygen reduced the absorption at 457 mμ, showing destruction of the radical-ion. This is unlikely to have been other than a simple electron-transfer to O_2, thus allowing recycling of the nitrobenzene as a true catalyst:

$$PhNO_2 + nBuS^- \rightarrow PhNO_2^{-} + nBuS^{\cdot} \qquad (35)$$

$$PhNO_2^{-} + O_2 \rightarrow PhNO_2 + O_2^{-} \qquad (36)$$

$$2\ nBuS^{\cdot} \rightarrow nBu_2S_2 \qquad (37)$$

The catalytic effect of nitrotoluene on the autoxidation of octane-1-thiol has been recorded[44].

The oxidation of hexane-1-thiol in the presence of base and of various quinones was studied by Meguerian[72]. With hydroquinone (QH_2) and sodium hydroxide the kinetics were consistent with the following mechanism:

$$QH_2 + OH^- \rightleftharpoons QH^- + H_2O \qquad (38)$$

$$QH^- + O_2 \rightarrow QH^{\cdot} + O_2^{-} \qquad (39)$$

$$QH^{\bullet} + RSH \rightarrow QH_2 + RS^{\bullet} \qquad (40)1.53$$

$$2\ RS^{\bullet} \rightarrow R_2S_2 \qquad (41)$$

According to this scheme the hydroquinone catalyses the oxidation of undissociated thiol molecules, but there is no apparent reason why the anion should not react similarly to give QH^- and $RS^{\bullet}$.

Patents have also been taken out for oxidations of thiols in which both hydroquinone and a water-soluble iron salt are used as catalysts[84]. The rate of oxidation in the presence of both catalysts was three times higher than the sum of the rates with either used alone. At a constant concentration of hydroquinone the rate seemed to bear a second-order relationship to the sodium hydroxide concentration. No explanation of these facts was put forward.

1.53 The effect of disulphides

Several workers have reported that the rate of oxidation of thiols in alkaline media may be increased by adding an organic disulphide[27], not necessarily identical with the disulphide product from the thiol undergoing oxidation[85]. The catalytic effect is maintained in systems in which metal catalysts also are present[68].

The best explanation for the catalytic effect of disulphides is that put forward some time ago by Harrison[85]. He had found that the aerobic and anaerobic oxidation of thiol groups were accelerated by the disulphide, dithioglycolic acid.

Aware that this catalysis might be put down to impurities 1.53 such as metal salts in his disulphide, he purified the latter by recrystallisation from ethyl acetate, and showed that the catalysis was not inhibited by cyanide, but disappeared when the S-S bond had been destroyed by treatment with bromine. Aware that the disulphide bond was liable to alakline hydrolysis[86], Harrison proposed that the catalysis might be due to the setting up of a sulphenate-sulphinate oxidation-reduction cycle:

$$RSSR + H_2O \rightleftharpoons RSH + RSOH \qquad (42)$$

$$RSOH + O \rightleftharpoons RSOOH \qquad (43)$$

$$2\ R'SH + RSOOH \rightleftharpoons R'SSR' + RSOH \qquad (44)$$

From studies of the hydrolysis of a number of disulphides, it has been concluded[87] that only disulphides with aryl, carbonyl, or alpha-unsaturated groups are susceptible to hydrolytic attack by nucleophilic reagents such as hydroxide ions. However, susceptibility is a matter of degree, and some small catalytic effect from dialkyl disulphides might be expected.

In view of the catalytic nature of disulphides, it would be expected that an autocatalytic increase in rate would be observed in thiol autoxidation experiments. It is remarkable that this has not generally been recorded, even in the autoxidation of carboxy-thiols. Autocatalysis has, however, been discovered in the oxidation of some carboxy-thiols with methylene-blue, a system which was also catalysed by added disulphide[27]. Presumably in the case of alkanethiols any such autocatalytic effect would be very small owing to the resistance of the disulphide to hydrolysis. 1.5

It has been shown that besides the structure of the thiol the basicity of the solution chiefly determines the proportion of disulphide and higher oxidation products in the system. Using comparatively weakly basic conditions (e.g. aqueous sodium hydroxide or sodium methoxide in methanol) n- and s-butanethiols and phenylmethanethiol gave 77 to 85%, and thiophenol 67% yields of their disulphides[88], whereas solutions of thiols in DMF containing potassium hydroxide gave sulphonic acids in yields of 90% or more[45].

Those disulphides which are most liable to hydrolysis are also most liable to oxidation, probably because both involve initial nucleophilic attack. It is possible therefore that, even when the hydrolysis necessary for catalysis takes place, the products are too easily oxidised to take part in an oxidation-reduction cycle with oxygen and thiol. Thus it is observed that the base-catalysed autoxidation of thiophenol is a slow reaction, not autocatalytic, but which in strongly alkaline media produces larger yields of higher oxidation products than are obtained in the much faster oxidations of alkanethiols[45].

It may be concluded therefore that catalysis and autocatalysis by disulphide requires certain conditions of alkalinity and reactivity in which a redox cycle may be established and maintained. The requirements are evidently more exacting than those which apply in the case of catalysis by other agents, summarised above.

1.6 The role of peroxide

In the preceding Sections, mechanisms have been put forward to account for the kinetic features of thiol autoxidation both in the absence and presence of various catalysts. In all of these one stage has necessarily involved electron-transfer onto an oxygen molecule to give a peroxy radical-ion, which then acquires either an electron or a hydrogen atom and becomes a peroxide ion. The peroxide then oxidises more thiol, but the mechanisms quoted in previous Sections would obviously be supported if peroxide, even in traces, could be detected in the system.

Early attempts to show that peroxide was present in autoxidising systems of thiophenol[41] and iron-containing cysteine[89] were not successful, although the rate of consumption of oxygen in the latter system was increased by adding hydrogen peroxide. Schoeberl[90] considered peroxide to be an intermediate in this system, and this was confirmed by Holtz and Triem[91] and by Schales[73], who added luminol (5-amino-2,3-dihydro-1,4-phthalazinedione) and observed luminescence: this test is sensitive to 10^{-5} parts % of peroxide. This evidence is generally accepted by modern workers including Wallace and Schriesheim[33].

1.7 The present work 1.7

The research reported in this thesis was started before the appearance of the recent series of papers by Wallace, Schriesheim, and others[33,42,44,45,77,83,88], which are discussed in the previous Sections. At that time (1961) the only information on the oxidation of simple thiols in strong aqueous alkali appeared to be provided by the work of Xan, Horton, and others[31]. Publication of the recent papers mentioned above has shed considerable light on the reaction under certain conditions, especially in non-aqueous solutions, but has not removed the need for further work on simple aqueous systems.

The present work was therefore directed towards enlarging upon the previous data in this field, and in particular to examining the effects of some metal ions and complexing agents.

2 EXPERIMENTAL 2

2.1 Materials and reagents

2.11 Thiols

The thiols used in this work were all obtained from Kodak Ltd. They were distilled in an all-Pyrex apparatus, which had been cleaned by the method described in Section 2.24. The apparatus had a water-cooled condenser, was built from Quickfit components, and was completely gas-tight except for an outlet tube which was closed with a calcium chloride drying tube. The apparatus was first purged with a stream of nitrogen, and the thiol was then introduced and distilled, the middle fraction being collected in the special storage vessel shown in Fig. 1, which was cooled in ice. The boiling points and refractive indices of the collected fractions are compared with literature values in Table 2.

Distilled samples of ethanethiol were found to be oxidised generally at a lower rate than undistilled samples (Table 3). In view of the extreme sensitivity of thiol autoxidation systems to traces of catalytic impurities, especially metal ions (Section 1.5), this lower rate was taken as evidence of higher purity, and the distillation of thiol samples was therefore justified.

The thiols were stored under one atmosphere of nitrogen in the same special vessel into which they had been distilled (Fig. 1). The vessel had a capacity of about 50 ml, and

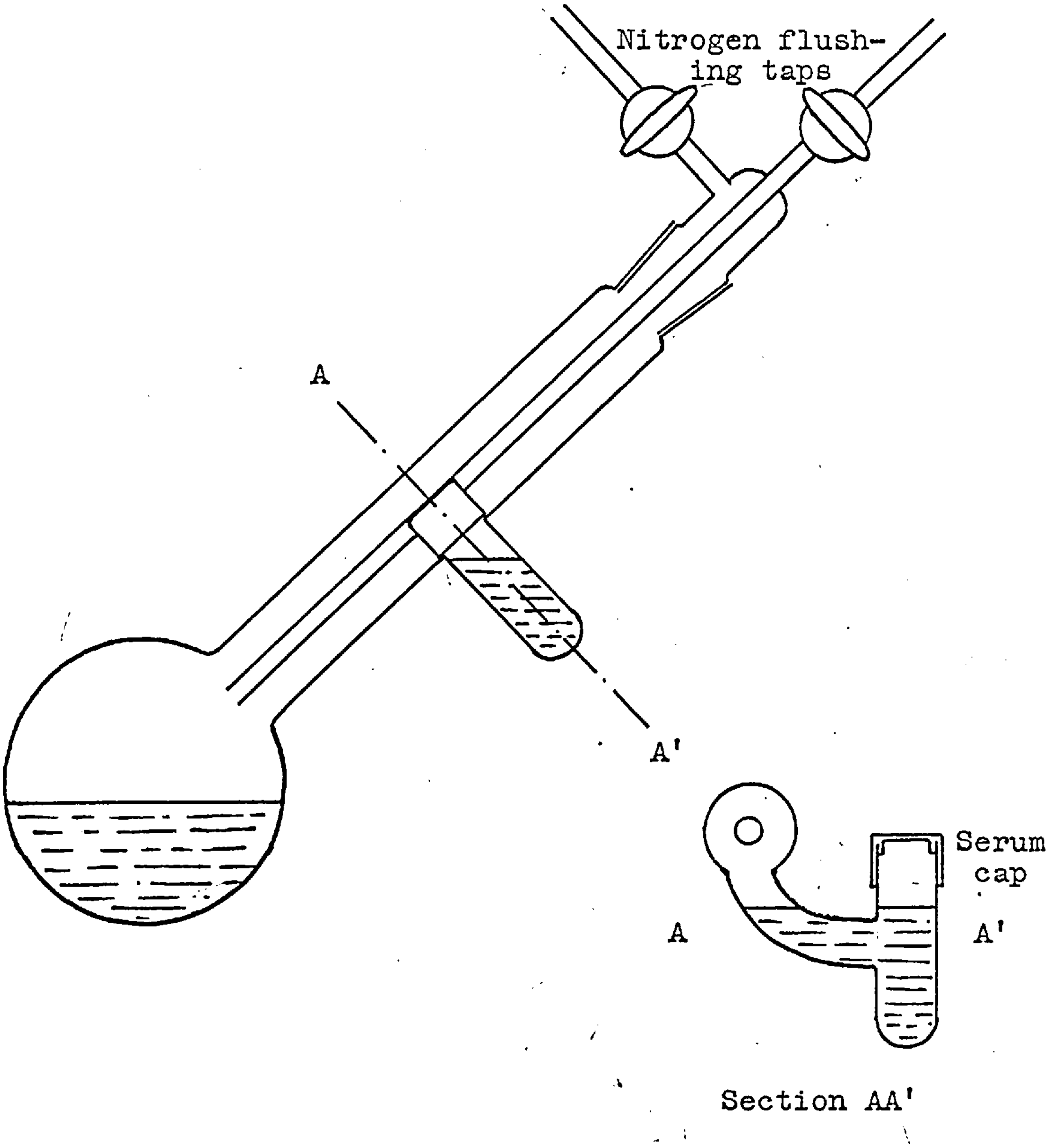


Fig. 1. Thiol storage vessel

Table 2. Distillation of thiols and diethyl disulphide: boiling points and refractive indices. 2.11

Compound	Literature values[7,8]		Collected fraction	
	b.pt.	n_D^{25}	b.pt.	n (≈20°)
EtSH	34.7	1.4270	34.5-37.0[a]	1.4290[a]
n-BuSH	98.0	1.4401	97.4-99.2	1.4403
n-HexSH	151.5	1.4473	148.0-150.0	1.4476
t-BuSH	64	1.4201	62.0-63.0	1.4201
PhSH	169.5	1.5805	166.8-169.4	1.5801
$PhCH_2SH$	195	1.5779[b]	196.2-198.5	1.5741
Et_2S_2	153-154	1.5063	151.0-152.5	1.5060

a - Mean of several batches. b - n_D^{20}

Table 3. Oxidation of ethanethiol: effect of distillation on oxygen uptake rate under standard conditions. 0.5 M EtSH, 2.0 M NaOH, 70 cm O_2, 30°C.

Etanethiol sample	Rates (mmole/l/min)	Mean Rate
Undistilled	0.17, 0.18, 0.20, 0.134, 0.104, 0.070, 0.098	0.134 ± 0.046
Distilled	0.050, 0.051, 0.114, 0.12	0.084 ± 0.033

incorporated a side-limb of about 5 ml into which the thiol could be tipped for extraction through a Suba-seal 30 serum-cap by a hypodermic needle and syringe. The vessel was normally kept immersed to the neck in crushed ice.

2.12 Water

All aqueous reagent solutions for use in kinetic experiments were prepared with deionised water. Under otherwise identical conditions, the rate of oxidation of ethanethiol was lowered by as much as 90% by the use of deionised water in place of laboratory-distilled water in the reagents. This was almost certainly due to the very considerable reduction in the concentration of metal-ion impurities.

Deionised water was prepared by passing distilled water through a 'Deeminac' model 32-6 deioniser, which consisted of a polyethylene bottle inverted over a 12 cm cylindrical bed of absorbent, through which the water ran slowly under gravity.

The deionised water, and all reagent solutions prepared from it, were stored in screw-topped polyethylene bottles.

2.13 Alkali

The alkalies used were sodium and potassium hydroxides. Most of the work was carried out using 'Analar' grade sodium hydroxide from Hopkins and Williams Ltd. A number of experiments was also conducted with 'Analar' potassium hydroxide, and with 'Judactan' sodium and potassium hydroxides from the General Chemical and Pharmaceutical Company Ltd.

To minimise contamination, the aqueous hydroxide solutions were prepared by weighing the required deionised water and solid hydroxide directly into polyethylene storage bottles, which were cooled in ice during mixing.

The solutions were standardised against hydrochloric acid which had in turn been standardised against sodium carbonate. The concentration of the stock solution of alkali prepared in the above manner was usually 5 M. When not in use, the storage bottles were sealed by air-tight screw caps.

2.14 Metallic salts and complexes

Metal ions were usually added to reagent solutions as measured volumes of standard solutions of their sulphates. The solids used were $CuSO_4.5H_2O$, $CoSO_4.7H_2O$, $MnsO_4.7H_2O$, $FeSO_4.7H_2O$, and $K_2SO_4.Cr_2(SO_4)_3.24H_2O$, which were all of 'Analar' grade from Hopkins and Williams Ltd. According to the makers' specifications these sulphates were sufficiently pure for the present purpose, and no further purification was undertaken.

The standard solutions were prepared directly from the dried solids by weighing. This was adequate, since the effects of the salts were to be studied over a range of concentrations differing by several orders of magnitude.

Two methods for introducing metal complexes into the reagents were used:

(1) The metal complexes were prepared in situ by mixing appropriate volumes of the standard sulphate solutions and standard aqueous solutions of the required complexing agents, which were variously ethylenediaminetetracetic acid (EDTA), ethylenediamine (en) dihydrochloride, and cyanide ion. The EDTA (disodium salt) and potassium cyanide were 'Analar' reagents, and the en.2HCl was the best grade available from Koch-Light Laboratories Ltd. Standard aqueous solutions were prepared by direct weighing, using deionised water and were stored in polyethylene bottles.

(2) For comparative purposes, crystalline samples of copper, cobalt, and manganese EDTA complexes were obtained from ~~Light and Company~~ Koch-Light Laboratories Ltd. Standard aqueous solutions of the complexes were prepared by direct weighing.

2.15 Other additives

The kinetic effects of the complexing agents EDTA, en, and cyanide were also studied in the absence of added metal salts. The preparation of their standard solutions is described in Section 2.14.

Diethyl disulphide was used as an additive in some experiments. This was purified by distillation exactly as were the thiols (Section 2.11). The disulphide fraction was collected in the Pyrex bottle in which it was stored. The boiling point and refractive index are given in Table 2.

Diphenylamine was purified by recrystallisation from 20% aqueous ethanol. It was dried at the pump and in a desiccator, and the required quantity weighed directly into the reaction vessel.

Di-t-butyl peroxide was obtained as a 98% solution from Laporte Chemicals Ltd., and no further purification was carried out. Taking the density as 0.79 g/ml the required quantity of the peroxide was added to the reaction vessel from a small graduated pipette.

2.16 Gases

Oxygen and nitrogen were obtained from cylinders supplied by the British Oxygen Company Ltd. The section of apparatus concerned with the admission and purification of the gases is described in Section 2.215.

Oxygen from the cylinder was condensed at just below atmospheric pressure in the trap cooled to -180°C with liquid nitrogen. The condensed gas was then alternately pumped upon and left to stand in equilibrium with its own vapour at this temperature until its vapour pressure was unchanged by further pumping. This was taken as indicating the complete removal of nitrogen from the condensed oxygen. The liquid nitrogen bath was then removed, the condensed gas allowed to boil off, and the middle fraction admitted to the working line or the storage globe as required. 2.17

Nitrogen (B.O.C. 'oxygen-free') was admitted to the storage globe through the trap, which was surrounded by liquid nitrogen to condense any oxygen and other less volatile gases. It was passed again through the trap immediately prior to use.

2.17 Reagents for non-kinetic work

Reagents used in volumetric analyses (Section 2.4) were of 'Analar' grade from Hopkin and Williams Ltd. Reagents used in spectrophotometric measurements were of the highest purity available, generally 'Analar'. All the aqueous solutions used in non-kinetic experiments were prepared with laboratory distilled water.

2.2 Apparatus

2.21 Apparatus for measurement of gas uptake by solutions

All measurements of the uptake of gas by solutions were made with the apparatus shown in Plate I and diagrammatically in Fig. 2. The system was in principle similar to the standard apparatus described by Bolland[92]. It may be termed static inasmuch as the reagents were shaken together in a closed system. The reaction was followed by measuring the decrease in the volume of gas at a pressure which was automatically maintained at a constant pre-set value.

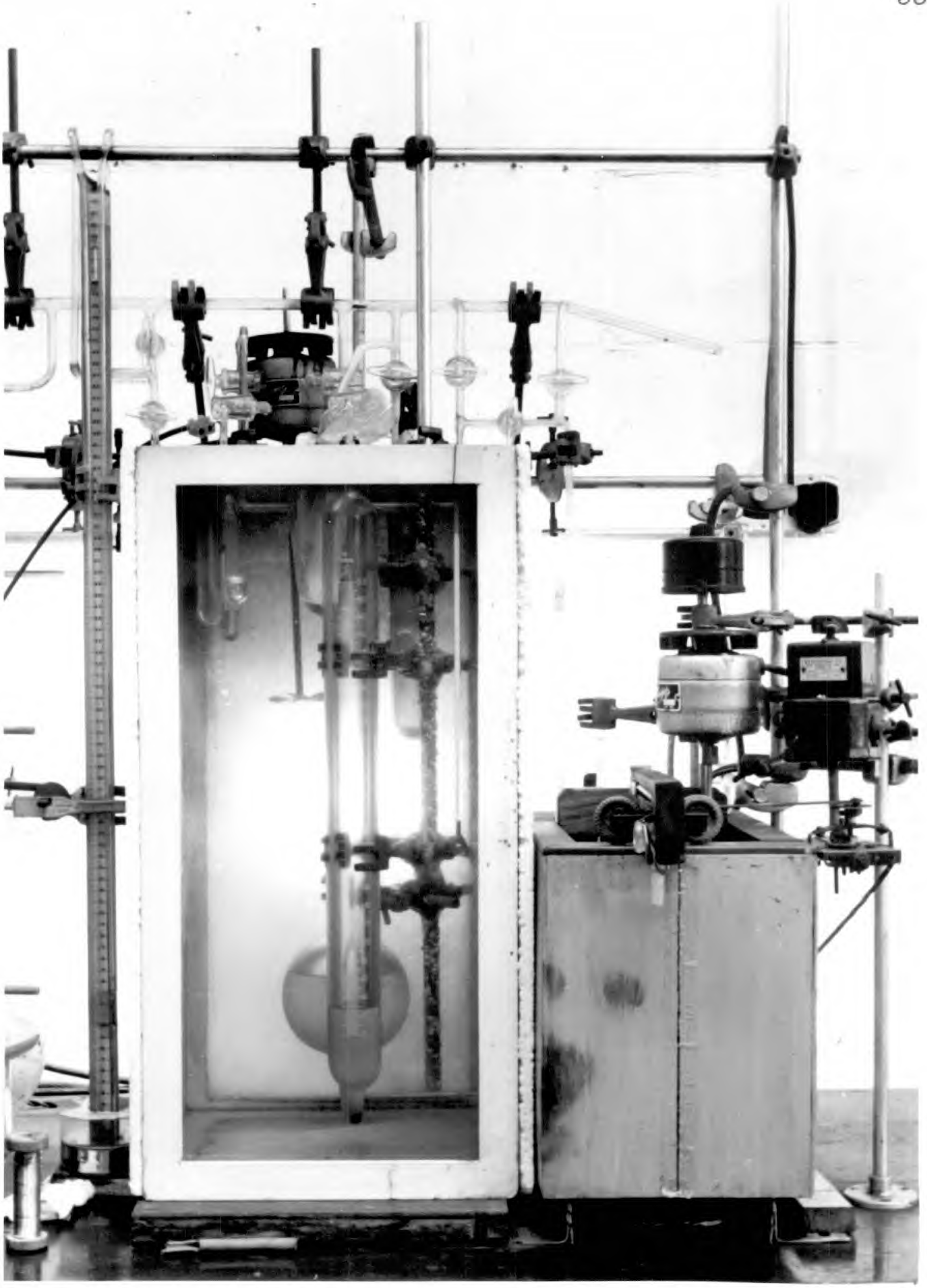


Plate I. Apparatus for measuring gas uptake by solutions.

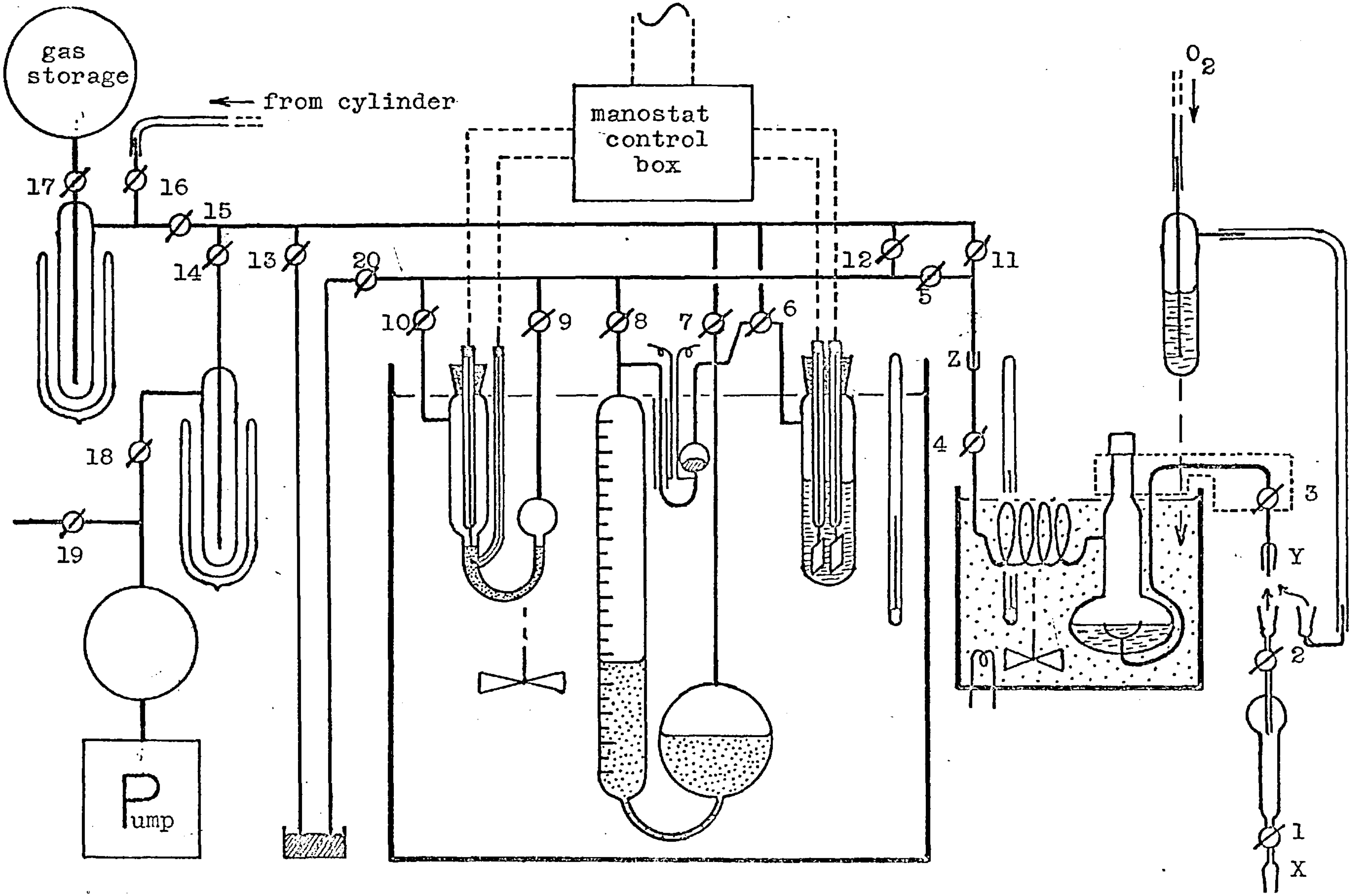


Fig. 2. Apparatus for measuring gas uptake by solutions

The apparatus will be described in the following 2.211 Sections. The parts described in Sections 2.211 to 2.214 may be described collectively as the 'working line', since they are directly involved in making kinetic measurements: these include the reaction vessel and sampler, the burette, manostat, etc. The parts described in Sections 2.215 and 2.216, i.e. the gas inlet and pumping lines, serve the working line, and are therefore subsequently referred to as the 'service lines'.

2.211 Reaction vessel and sampler

The reaction vessel and sampling system are shown schematically in Fig. 3.

The reaction vessel consisted of a flattened spherical flask, fitted with a sampling cup, which was connected by a capillary tube to tap 3 and a ground glass cone Y through an internal seal in the bottom of the vessel (Tap numbers and ground joint letters refer to the Figures). The narrow neck of the vessel was closed by a rubber serum cap (Suba-seal 30). A side-tube led from the vessel through a flexible glass spiral, which had 6 turns of 5 cm diameter, made from 3 mm bore thin-walled tubing. The spiral led to tap 4 and a ground joint Z which was used to connect the vessel to the working line. The neck of the reaction vessel and part of the sampling tube were clamped into a recessed wooden

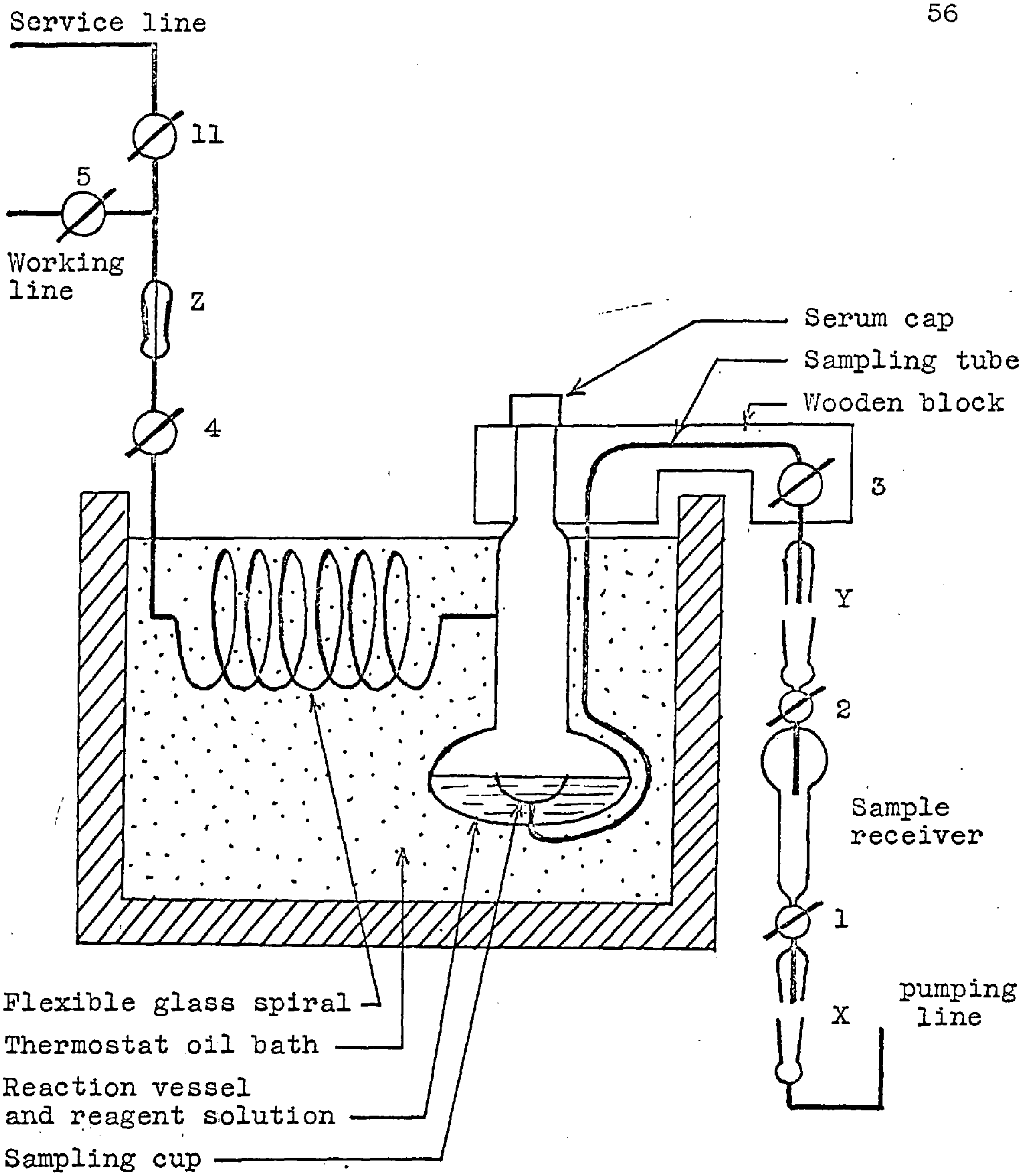


Fig. 3. Reaction vessel and sampling system

block to which the shaker was attached. 2.211

The form of the reaction vessel described above was developed through a series of modifications to give maximum contact between the gaseous and liquid reagents when shaken, and thus to minimise the effects of diffusion. Early forms had cylindrical and spherical bulbs of various capacities. The bulb of the vessel shown in Fig. 3 had a capacity of 50 ml up to its equator, the surface/volume ratio of the liquid at rest then being about 0.7 cm^{-1}.

The cup mounted in the reaction vessel was developed as a device for sampling a heterogeneous mixture of liquids in their bulk proportions. The rim of the cup was arranged to be about 1 mm above the surface of the solution (50 ml) when the reaction vessel was at rest. When the unit was shaken, the homogenised liquid phase slopped into and out of the cup, which therefore collected a representative sample. This sample was isolated immediately the shaking ceased and the liquid came to rest, and although the immiscible phases then rapidly settled out, the isolated sample still comprised the phases in their bulk proportions. The capacity of the cup was 3.8 ml, but the actual volume of samples was of course determined by chance, and was usually 1 - 2 ml. In an earlier sampling arrangement, a simple tube, dipping below the surface of the reagents, was used in place of the cup, the other parts being as described above. The removal of samples was carried out by the procedure described in Section 2.33. 2.211

The reaction vessel and flexible spiral were immersed in a bath of liquid paraffin, the temperature of which was controlled by a Sunvic F 103-S thermostat unit. The temperature could be pre-set to any value from 25 to 70°C, and was automatically controlled to within 0.1C° at 30°C.

The reaction vessel was shaken in a direction perpendicular to the plane of Fig. 3 by a device made from Meccano parts. The frequency of the shaking could be varied by shunting the electric motor. The motor was geared down and was attached to the wooden block, which held the reaction vessel, through a crank-wheel and connecting rod. The reaction vessel was thus shaken with a reciprocating motion. A Meccano beam was attached to one end of the wooden block and was mounted above the glass spiral and parallel to its axis. The vibrating length of the beam was adjusted by means of a slotted wooden clamping block to give a steady resonant frequency of oscillation. Wear on the moving parts was thus minimised by avoiding forced vibrations. The wooden block which held the reaction vessel was mounted on two small rubber-tyred wheels, which ran in tandem on the broad smooth rim of the thermostat tank. This reduced the tendency of the reaction vessel to pitch owing to the viscous drag of the oil in which the lower parts of the vessel were immersed.

2.212 Gas burette 2.212

The consumption of gas in kinetic experiments was measured as a decrease in volume at constant pressure by means of the gas burette, which is shown schematically in Fig. 2. The left-hand (or front) limb of the burette had an etched scale reading to 500 ml by 2 ml divisions, and 1 mm length on the scale corresponded to about 1 ml volume. The burette contained silicone oil type MS 550, which is well suited for this use, having a low density and negligible vapour pressure. The sharply contrasted meniscus obtained by diffuse illumination from the rear, permitted reading of the burette to 0.1 ml.

The burette and the manostat cells (see Section 2.214) were immersed in water in a large glass-walled tank (1 ft x 1 ft x 2 ft ht.). The water served as a large thermal capacity which damped the effect of variations in ambient temperature on the gas in the burette and the cells. The water in the tank was stirred but not thermostatted, and was insulated on three sides by half-inch sheets of expanded polystyrene. Variations of 0.5 - 1 C° in the water temperature were observed during day-long experiments, and the burette readings were therefore always corrected to a standard temperature for each experiment. The burette readings were also corrected for the small pressure variations which occurred during the manostat switching cycle (Details of these corrections are given in Appendix 1).

2.213 Automatic burette recorder 2.213

The gas-uptake measuring apparatus was adapted for automatic recording of the burette level after it had been in use for some time. The arrangement is shown in Fig. 2 and its principle in Fig. 4.

Changes in the burette oil level were paralleled by smaller changes in the level of mercury in a small U-tube bridging the two limbs of the burette, both levels being determined by the same pressure difference. The U-tube was adapted so that changes in the mercury level produced corresponding changes in electrical capacity. This capacity cell was made the variable arm of a Fielden Electronics 'Telstor' capacity bridge unit. The out-of-balance current was amplified and passed to a Fielden 'Servograph' circular chart recorder.

The front limb of the U-tube was blown out into a bulb, so that changes in pressure produced the maximum movement in the mercury level in the rear limb, which was the capacity limb. This consisted of a piece of glass tubing of uniform bore (4 mm) and wall thickness (1 mm). The tube was surrounded by a sleeve of aluminium foil bound tightly with copper wire. The sleeve formed one plate of the capacity cell, the other being the mercury itself, to which electrical contact was made through a platinum-glass seal. The dielectric material was therefore the 1 mm thick Pyrex wall of the tube.

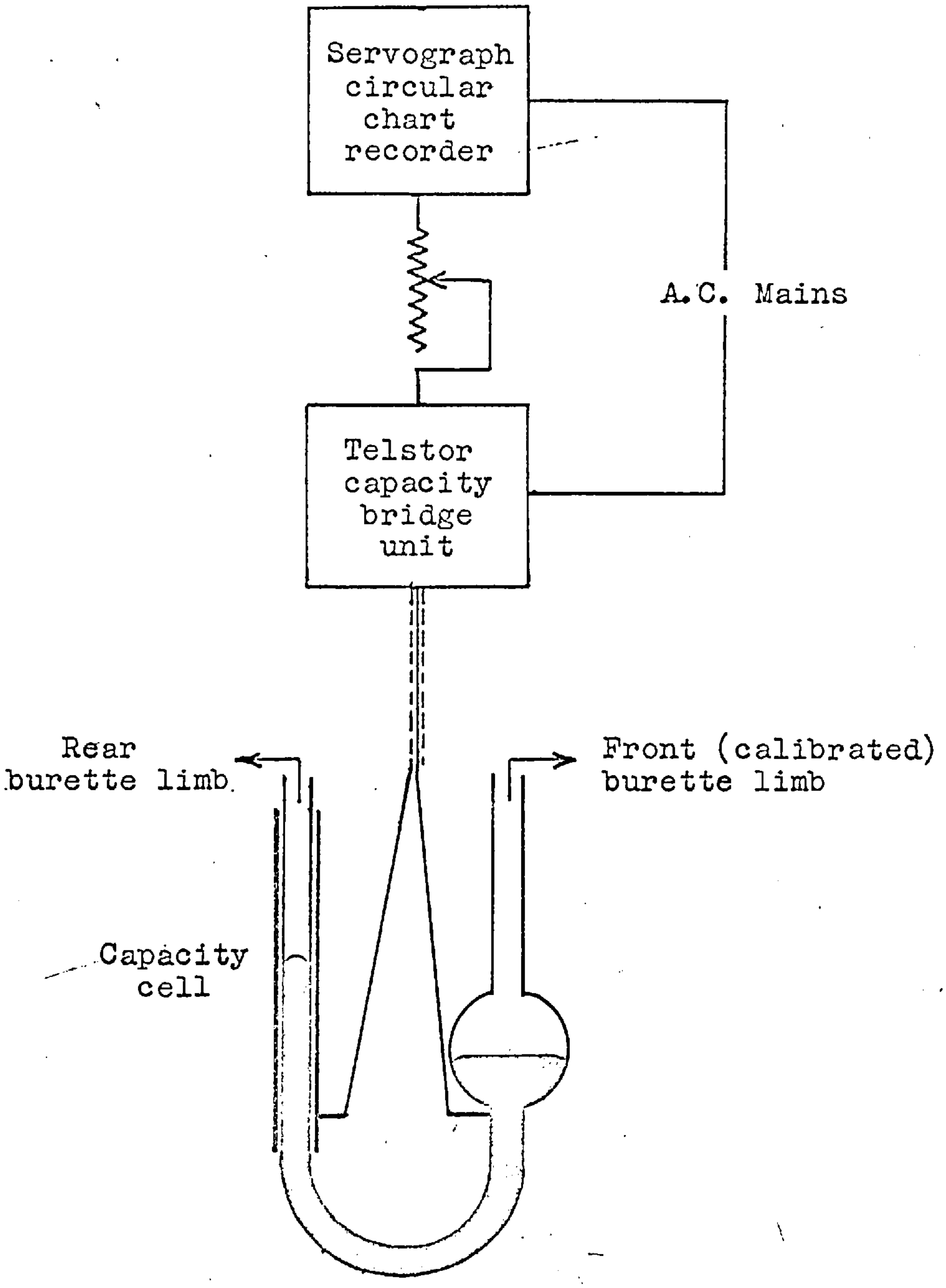


Fig. 4. Automatic burette level recorder (schematic)

The outer cylindrical metal plate was insulated by a thick coating of Picien wax, and the entire U-tube unit was surrounded by a water-proof polyethylene bag, with spacers of expanded polystyrene to minimise the capacity effect of the water in the earthed tank.

The U-tube capacity cell was connected to the Fielden 'Telstor' capacity unit type LF 3 by coaxial cable. The output from the 'Telstor' unit was passed through an attenuating rheostat to the Fielden 'Servograph' circular chart recorder type RF 1, which had a 24 hour period of rotation. The chart was graduated in 100 arbitrary units (a.u.).

It was found that a full-scale deflection on the 'Servograph' (100 to 5 a.u.) was produced by a change of approximately 0 to 400 ml on the burette scale. The calibration curve was very nearly linear between these limits, and the stability of the instruments was found to be excellent (± 1%). However, the device was not satisfactory in use due to hysteresis, especially near the start of kinetic runs. The design and performance of this and other possible burette-level recording devices are discussed in Appendix 2.

2.214 <u>Manostat</u>

Constant pressure in the working line of the apparatus was maintained during kinetic experiments by means of an automatic manostat. This consisted of three parts: the pressure-sensing cell, the electronic switching device, and the

electrolytic gas-generating cell. The two cells are 2.214
shown in Fig. 2.

When the pressure in the working line fell below a pre-set standard value, the electric circuit through the sensing cell was broken, and the switching device caused a small current to pass through the electolytic cell. The pressure of the generated gas was applied to the back limb of the burette, thus raising the level and decreasing the volume in the front limb until the working pressure was restored to the standard value. The circuit in the sensing cell was thereby closed, and gas-generation stopped.

The sensing cell contained an electrolyte consisting of a saturated solution of sodium nitrite in trimethylene glycol. This electrolyte was chosen because it has a negligible vapour pressure and does not release any gas when passing a current. During the experiments one limb was open to the working line, while the other was closed by tap 10 (Fig. 2), and provided the constant pre-set reference pressure. The closed limb of this cell was fitted with two sealed-in platinum wire electric contacts. One of these was sealed into the U-tube well below the surface of the electrolyte, while the other was held vertically above the electrolyte surface, and was ground to a point in order to reduce the effect of surface tension. The manostat system was controlled by making and breaking contact between this probe and the electrolyte, and any tailing due to surface tension would have increased unnecessarily the pressure fluctuation in the switching cycle.

The electrolytic cell had two platinum electrodes each of about 1 cm^2, 1 cm apart, immersed in approximately 50% sulphuric acid. Passage of a direct current through the cell thus generated hydrogen and oxygen.

The circuit for the switching device is shown is Fig. 5. Two separate 12-volt power supplies were used to minimise the voltage drop when current passed through the transistor OC 35. The variable resistor VR 1 was used to adjust the current passed through the electrolytic cell. The grid-bias battery B 1 was used to overcome the effects of polarisation in the sensing cell: about 4.5 to 6 volts was found to be a suitable value.

The limits within which the pressure may be controlled with this manostatic arrangement were found to depend chiefly upon the absolute pressure and the design of the sensing cell. Defining the sensitivity of the cell as the change in the electrolyte level in the reference limb per unit pressure change in the working line, the simple Boyle's Law calculation given in Appendix 3 shows that the sensitivity would be increased by enlarging the volume of the (closed) reference limb, and by decreasing the bore of the glass tubing where contact was made and broken in the cell. The cell was designed with these principles in mind, and was found to control the pressure

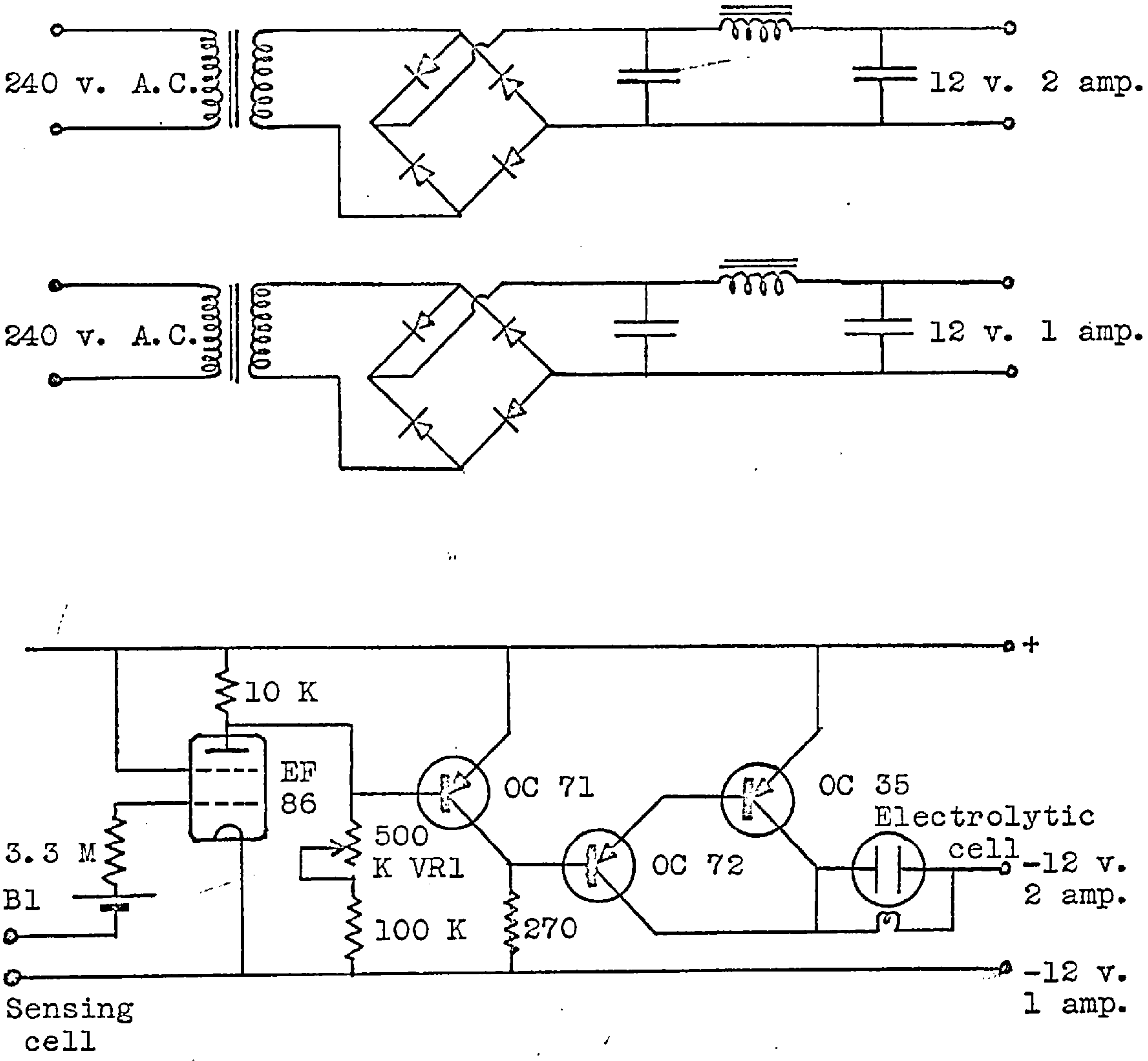


Fig. 5. Circuit diagram for manostat control box

to within ± 0.2 mm at 760 mm.

The two cells of the manostat were immersed in the water tank with the gas burette, thus allowing correction of the burette readings for fluctuations in temperature and pressure (see Section 2.212 and Appendix 1).

2.215 Gas-introduction line

The gas-introduction line consisted of an inlet to which gas storage cylinders could be connected, a combined manometer and blow-off tube, a trap which could be surrounded by an appropriate coolant, and a 5-litre storage globe. The arrangement is shown in Fig. 2. The use of this arrangement to collect, purify, and store gases is described in Section 2.16.

2.216 Pumping line

The entire apparatus was served by one Metrovac DR 1 two-stage rotary vacuum pump (Fig. 2). This enabled the apparatus to be pumped rapidly down to below 0.05 mm pressure.

2.22 Lubricants

All taps and ground joints were greased with Silicone High Vacuum Grease from Edwards High Vacuum Ltd. Taps were cleaned with trichloroethylene prior to regreasing.

2.23 Hypodermic needles and syringes

Thiols were extracted and transferred from their storage vessel in measured volumes by means of a hypodermic needle and syringe (Sections 2.11 and 2.31). This method minimised the exposure of thiols to the atmosphere, and thereby reduced 2.24 aerial contamination of the thiol and the escape of objectionable odours. To further the latter objective and also to reduce contamination of the thiol by the metallic needle, the syringe and needle were stored in the deepfreeze of a refrigerator, and the thiol was handled only at a low temperature. An effort was made to reduce contamination further by coating the needle and syringe with PTFE from an aerosol spray obtained from Fison's Scientific Ltd.

All-glass 2 ml and 5 ml syringes of the 'Acossan' brand supplied by McCarthy (Romford) Ltd. and No. 15 stainless steel needles were used. The syringes were calibrated to 0.05 ml and any necessary allowance was made for the calibrated 0.15 ml volume of the needle and Luer fitting.

2.24 Method for cleaning glassware

All glassware used in this work was made from Pyrex. All vessels which came into contact with any of the reagents used in kinetic experiments were cleaned by prolonged treatment with concentrated nitric acid followed by rinsing with deionised water.

Glassware used for other purposes was cleaned with chromic acid and rinsed with distilled water. Where necessary, glassware was finally dried with pure methanol.

2.3 Experimental procedure 2.3

The experimental methods used to obtain kinetic curves for the uptake of gas with time, and to sample the liquid reagents, are reported in the following Sections. The apparatus is described in Section 2.21, and the analytical techniques are reported in Section 2.4.

2.31 Starting experiments

In order to decide upon a suitable technique for starting kinetic runs, several requirements had to be taken into account besides the usual need to bring the correct amounts of reagents together at the right temperature and at a certain time. Most people find the odour of thiols very unpleasant, and there was an obvious need to minimise the escape of thiol vapour. The extreme sensitivity of the kinetics of thiol autoxidation to traces of metals and their salts became apparent in the earliest runs: it was therefore essential to minimise contamination of this kind.

The procedure for starting kinetic runs was developed progressively to satisfy these requirements, but it is proposed to describe here only the technique finally developed.

The reaction vessel was first demounted as described in Section 2.211, and cleaned thoroughly by the methods given in Section 2.24. It was finally rinsed with deionised water and its taps refitted. It was then remounted and connected to the working line. The vessel was pumped on until dry. At the

2.31 same time the oil-bath thermostat was set to the temperature required for the experiment.

With tap 4 closed (see Fig. 3), the reaction vessel was brought to atmospheric pressure by opening tap 3, and the serum cap was removed. The appropriate volumes of the reagent solutions were then measured into the reaction vessel with pipettes, the order of admission being: (1) deionised water, (2) standard metal salt solution, (3) standard solution of complexing agent, (4) any other additives, (5) standard alkali from stock. The final total volume of the aqueous solution was arranged usually to be 50 ml. Separate pipettes were used for the different reagents in order to avoid contamination, and the pipettes were left to stand in measuring cylinders filled with concentrated nitric acid when not in use.

After admission of the aqueous reagents the serum cap was replaced, and the air was displaced from the reaction vessel by passing a stream of oxygen. The oxygen was first passed through a bubbler attached to the sampling outlet of the reaction vessel, and containing alkali at the same concentration and temperature as in the reaction vessel in order to equalise the partial pressure of water vapour and to remove any carbon dioxide. The gas passed through tap 3 into the vessel, sweeping the air out through taps 4 and 11, and through taps 15 and 16 to the atmosphere.

With the reaction vessel once more isolated, the rest of the apparatus was pumped out. Oxygen (and nitrogen when required) was introduced into the rest of the working line to the required pressure. This was carried out as described in Section 2.16, oxygen being fractionated direct from the trap and nitrogen being passed from the storage globe through the same trap, which was cooled in liquid nitrogen. The reaction vessel was then opened to the working line through tap 4 and the manostat was switched on. Taps 7, 11, and 12 were then closed and tap 6 was turned to connect the electrolytic cell to the rear limb of the burette. The working line was then left to settle down for as long as possible, generally 15-30 min. 2.31

With taps 4 and 5 closed, the reaction vessel was separated from the working line at the ground joint Z, and from the shaker, and was transferred to a fume cupboard. The required volume of thiol was then extracted from the storage vessel and injected through the serum cap into the closed reaction vessel which was immediately shaken manually to dissolve the thiol in the alkali. The reaction vessel was remounted on the shaker, connected to the working line through the joint Z, which with taps 4 and 5 closed was pumped out through tap 11. Tap 11 was then closed, and taps 4 and 5 opened, and the shaker was switched on. Tap 10 was closed to isolate the standard pressure in the manostat sensing cell, and this was taken as zero time, when readings commenced. 2.32

Although the oxidation must have started as soon as the thiol began to dissolve in the alkali, it was convenient to take the end of the starting procedure as zero time. This was generally about 2 min after injection of the thiol. In any event it was not possible to take useful readings earlier since the thiol was incompletely dissolved and its vapour pressure not equilibriated.

2.32 Taking readings

In order to obtain a point on the graph of gas-uptake versus time in visually observed runs, the gas burette had to be read and the value corrected for any deviations from the standard temperature and pressure. The set of necessary readings was carried out in the order:- (1) both manometers to give by difference the actual working-line pressure, the service-line manometer being under vacuum; (2) gas burette; (3) water-tank temperature; (4) oil-bath temperature (as a check for constancy). These sets of readings were made at regular intervals as frequent as necessary to follow the gas uptake accurately.

Corrected burette readings were obtained by the method described in Appendix 1. The volume of gas taken up under the standard conditions was obtained by subtracting the corrected burette readings from the value at the start of reaction, i.e. at zero time.

The uptake was finally expressed in either of two ways: (a) as a percentage of the theoretical amount of oxygen required to oxidise all the thiol in the reaction vessel to disulphide according to the equation,

$$RSH + 1/4\ O_2 \rightarrow 1/2\ R_2S_2 + 1/2\ H_2O\ ;$$

(b) as the number of millimoles of oxygen consumed per litre of reagent solution.

2.33 Sampling the liquid during experiments

The provisions in the apparatus for sampling the reacting liquid phase are described in Section 2.211.

To carry out running sampling, the sampler tube was first evacuated by connecting it at X (Figs. 2 and 3) to the pumping line. Tap 4 was closed, the shaker stopped, and the sampler tube attached to the reaction vessel at Y. Taps 2 and 3 were then opened, and tap 3 was closed as soon as all the sample had passed over into the sampler tube, which was then detached. The shaker was restarted, and tap 4 reopened.

In order to allow for the unavoidable loss of a small quantity of gas from the working line, readings were taken immediately before and after sampling, and the gas-uptake figures corrected appropriately.

The sample was rinsed with distilled water from the sampler tube into a bottle containing 20 ml carbon tetrachloride and the alkali was titrated as soon as possible to minimise further oxidation (see Section 2.4).

2.34 Terminating experiments 2.34

At the end of experiments tap 4 was closed, and the manostat and thermostat were switched off. The reaction vessel was disconnected at Z and demounted from the shaker, and its contents taken for analysis (as in Section 2.35) or discarded into a residues beaker containing chromic acid to destroy any residual thiol.

The reaction vessel was cleaned in the manner described in Section 2.24, being left to stand filled with concentrated nitric acid until required for the next experiment.

2.35 Preparation of reaction products for analysis

The procedure used to obtain samples for analysis from oxidising solutions was explained in Section 2.33. When the whole of the product mixture was to be taken for analysis, it was transferred from the reaction vessel to a bottle, whence 2 ml samples were pipetted for titration of the alkali, care being taken not to remove any of the floating disulphide. The bulk of the mixture was then acidified and extracted twice with 25 ml carbon tetrachloride. The phases were separated after each extraction and the extracts (containing the thiol and disulphide) were combined. 2 ml samples of the extract were then analysed by the standard procedure (Section 2.42).

In the case of one analysis carried out on the reaction products from thiophenol (Section 3.153), the mixture was extracted twice with 25 ml carbon tetrachloride <u>before</u>

neutralisation. The aqueous phase was then acidified and extracted twice again with 25 ml portions of carbon tetrachloride. The two extracts separately contained the disulphide and thiol respectively, and were sampled and analysed by the standard procedure.

2.4 Analytical methods and procedure

2.41 Method

The method used for the quantitative estimation of thiols and disulphides in the present work was chosen for its simplicity and convenience, and was based on standard techniques.[93,94,95] Use was made of the fact that, whereas iodine oxidises alkanethiols quantitatively to the corresponding disulphides, bromine oxidises both thiols and disulphides to sulphonic acids:

$$2RSH + I_2\ (Br_2) \rightarrow R_2S_2 + 2HI\ (2HBr) \qquad (1)$$

$$R_2S_2 + 5Br_2 + 6H_2O \rightarrow 2RSO_2OH + 10HBr \qquad (2)$$

If any monosulphide is present it is also oxidised by the bromine: $R_2S + Br_2 + H_2O \rightarrow R_2SO + 2HBr$ (3)

Equations (2) and (3) show that monosulphide interferes with the determination of disulphide only to the extent of one fifth of its molar proportion in the mixture.

It was convenient to carry out these titrations with the same standard solution of potassium bromate, in the presence of excess iodide or bromide as appropriate:

$$BrO_3^- + 6I^- \; (6Br^-) + 6H^+ \rightarrow 3I_2 \; (3Br_2) + Br^- + H_2O \qquad (4)$$ 2.42

2.42 Procedure

Analyses for alkali, thiol, and disulphide were carried out in three stages on the same sample:

(1) Titration with standard hydrochloric acid solution;

(2) Titration with standard bromate solution in the presence of acid and excess iodide;

(3) Titration with standard bromate solution in the presence of acid and excess bromide.

The details of these stages were as follows:

(1) The sample containing alkali, thiol, and disulphide was added to 20 ml carbon tetrachloride in a stoppered bottle. The alkali was then titrated with standard acid: this served to determine the approximate volume of each running sample, or the actual alkali concentration in the case of measured volumes of the product liquid. Phenolphthalein was used as the indicator since its colour did not interfere with the next stage.

(2) The neutralised sample was acidified with about 5 ml 4N hydrochloric acid, and 20 ml of 0.5M potassium iodide solution were added. The mixture was titrated with approximately 0.025M standard bromate solution until the persistence after shaking of a faint iodine colour in the carbon tetrachloride layer indicated complete oxidation of the thiol.

The two liquid phases were then separated in a funnel, and the aqueous phase was washed with 20 ml carbon tetrachloride. The layers were again separated, and the carbon tetrachloride solutions, combined in a stoppered bottle, were subjected to the third stage of analysis. 2.42

(3) To the carbon tetrachloride solution, now containing dissolved disulphide, were added 20 ml water, 5 ml 4N hydrochloric acid, and 20 ml of 4M potassium bromide solution. The mixture was then titrated with the same standard bromate solution as in stage (2) until the yellow colour of free bromine persisted in the non-aqueous layer. The bromine-disulphide reaction was rather slow, and was assisted by slight warming. The end-point could be accurately determined provided that the bromate was added in small portions and the bromine was consumed between each addition. This minimised the loss of bromine as vapour and in side-reactions (brominations). A single titration required 10-20 min. The end-point was more easily detected in the presence of a little free iodine (that from stage (2) was generally sufficient), since excess bromine decolorised the latter with the formation of interhalogen compounds.

It was found that vigorous shaking to ensure thorough mixing of the phases increased the rapidity and precision of all three titrations.

2.43 Trials 2.43

Trials of the above method were carried out on standard thiol-disulphide solutions. In one of these, a solution was made up containing 0.74 ml ethanethiol (EtSH) and 0.62 ml diethyl disulphide (Et_2S_2) in 20 ml carbon tetrachloride. When 2 ml of this solution were added to 18 ml carbon tetrachloride and 20 ml water, the resulting mixture was similar to the mixtures obtained at the start of the second stage of analysis of samples withdrawn during oxidation experiments, being equivalent to a reagent solution containing 0.50M EtSH and 0.25M Et_2S_2. The results in Table 4 are expressed in terms of this equivalent reagent solution.

Table 4. Trial of procedure for analysis of thiols and disulphides.

Sample no.	EtSH molarity		Total Et_2S_2 molarity		Actual Et_2S_2 molarity	
	made	found	made	found	made	found
1	2	3	4	5	6	7
1	0.50	0.50	0.50	0.50	0.25	0.25
2	0.50	0.51	0.50	0.48	0.25	0.22
3	0.50	0.49	0.50	0.49	0.25	0.25

Columns 4 and 5 give the figures for the total Et_2S_2 as analysed in stage (3) (see above), and these include disulphide derived from oxidation of the thiol in the sample in stage (2), while columns 6 and 7 give the Et_2S_2 molarity present originally in the sample, and were obtained by subtracting half the thiol molarity from the total disulphide molarity of columns 4 and 5.

In these results the scatter is probably due mainly to the uncertainty in pipetting 2 ml of carbon tetrachloride solution. These figures and other results showed that the method was adequate for the present purpose, since errors of 5% were acceptable in running analyses of small samples. The accuracy of the method using larger samples was even better. The tendency for the disulphide titres to be low, noted by Siggia and Edsberg,[94] was not observed in these tests.

In some early analyses thiol alone was titrated with standard iodine solution.[93] This method worked most satisfactorily, but was abandoned in favour of the more convenient bromate method.

2.44 Reduction of disulphides

Some experiments were carried out to determine whether disulphides could be simply and quantitatively reduced to thiols, since this would avoid the possible interference of monosulphides. The quantitative reduction of disulphides by zinc amalgam and dilute acid in the Jones' reductor has been described.[96] Owing to the volatility of free ethanethiol it was preferable to reduce it in alkaline media. Zinc dust, amalgamated zinc, and hydroxylamine were each tried, the reduced disulphide being estimated as thiol with standard iodine solution. No satisfactory method was found, and the attempts were abandoned when there were other reasons to believe that the amounts of monosulphide formed in the oxidation of ethanethiol were negligible (Section 3.131). 2.5

2.5 Efficiency of shaker

In measuring rates of consumption of oxygen by aqueous reagent solutions it is obviously important to know the limiting conditions under which the liquid phase ceases to be saturated with oxygen and diffusion affects the measured rate. This limit is determined by the pressure and solubility of the gas, the rate of the chemical reaction, the geometry of the reaction vessel, and the efficiency of the shaking.

In the present work the rate of shaking could be controlled by a shunting rheostat on the shaker motor, which had ten settings. Tests for diffusion control of rate were carried out on the fast zero-order copper-catalysed thiol oxidations (Section 3.22), by measuring the rate of gas uptake at the normal (no. 6) and maximum (no. 10) settings of the rate of shaking. Although the shaking rate was thereby increased only from 330-350 to 360-400 c.p.m., the increase in violence was such that the risk of fracturing the apparatus made continuous operation at the higher settings inadvisable. The use of different volumes of liquid provided another method of testing for diffusion control. These tests showed the upper limit at which the rate of consumption of oxygen ceased to be wholly chemically controlled. The important results are gathered in Table 5.

The results show that the surface/volume ratio was not alone responsible for the limit for diffusion control of rate, for the small increase in the ratio from vessels 2 to 3 raised the limiting rate from about 0.35 to over 0.9 mmole O_2/ml/min. Evidently the mixing in vessel 3 was much better than in vessel 2. Vessel 3 was the final version, described in Section 2.211, with which most of the important results were obtained. Results in which diffusion control was operative are so noted as they arise in the following Sections.

Table 5. Efficiency of shaking: dependence of measured reaction rates on surface/volume ratio (S/V) and total volume of aqueous phase and rate of shaking.

Reaction vessel geometry (r=radius in cm)	Total liquid volume (ml)	S/V (cm^{-1})	Reagent concns. [RSH] (M)	[NaOH] (M)	$[Cu^{2+}]$ (M)	p_{O_2} (cm)	Slow shake: Shake rate (cpm)	Slow shake: Reaction rate (mmole/l/min)	Fast shake: Shake rate (cpm)	Fast shake: Reaction rate (mmole/l/min)
(1)			MeSH							
Vertical	20	0.35	0.70	1.54	-	55	365	0.53	-	-
cylinder	30	0.24	0.65	1.54	-	76	405	0.34	-	-
r = 1.5	40	0.18	0.70	1.54	-	76	375	0.30	-	-
(2)			EtSH							
	30	0.65	0.5	2.00	10^{-5}	68	335	0.83	400	1.35
Sphere	30	0.65	0.5	2.00	10^{-6}	68	345	0.44	395	0.54
r = 2.5	50	0.35	0.5	2.00	10^{-6}	67	-	-	380	0.39
	30	0.65	0.5	2.00	$5x10^{-7}$	67	340	0.35	400	0.35
(3)			EtSH							
Flattened sphere: equatorial r = 3.3	50	0.70	0.5	2.0	10^{-5}	69	345	0.92	365	0.91

3 RESULTS 3

3.0 Notes on the presentation of results

(a) The rates of nominally uncatalysed reactions were reproducible only within fairly wide limits, and any inconsistencies between data in the following Figures and Tables are due to this. The results quoted for comparison with experiments with additives were obtained so far as possible under the most comparable conditions - generally with samples from the same batches of reagents.

(b) Reagent concentrations given in the Figures and Tables are initial values unless otherwise indicated. Values of the oxygen pressure given in captions are mean values for the series of experiments. There were slight differences from run to run due to the difficulty in adjusting the pressure exactly to the required value, but actual pressures were within 2 cm of the mean.

(c) Reaction rates are normally expressed as rates of consumption of oxygen per unit volume of solution, viz. mmole O_2 per litre per min., and the term 'rate' used without qualification refers to this.

(d) Rate constants are written as k or k' with the reaction order in thiol as a subscript. k is not an absolute rate constant, and includes one or more constant concentration terms, such as those for oxygen or metal ions. The true rate constants are written as k', and these nominally exclude any reagent concentration terms.

(e) E_{a0} and E_{a1} represent the energy of activation for reactions which are respectively zero and first order in the thiol concentration.

3.1 Oxidation of thiols in the absence of added metal salts

3.11 Oxidation of methanethiol

Some early experiments were carried out with methanethiol, and few of the refinements in the technique described in Section 2 were used. The oxygen-uptake increased linearly with time, and some results are given in Table 6.

Table 6. Oxidation of methanethiol. 30°C.

MeSH concn. (M)	NaOH concn. (M)	Oxygen pressure (cm)	Shaking rate (c.p.m.)	Vol. of soln. (ml)	Reaction rate (mmole O_2 /1/min)	Final oxygen uptake (% theor.^{a})
0.70	1.54	55	365	20	0.53	88
0.70	1.54	76	375	40	0.30	98
0.65	1.54	76	405	30	0.34	102

a - 100% is uptake required for oxidation of thiol to disulphide.

Titration with standard iodine solution showed the final thiol concentration to be < 1% of the initial values.

3.12 Preliminary work on the oxidation of ethanethiol 3.1

Considerable difficulty was experienced in obtaining reproducible kinetics of oxidation in early experiments, and technical refinements were made progressively to reduce the possibility of contamination of the reagents, especially by metal ions. The results of a number of experiments, carried out under nominally similar conditions, but separated in time, are shown in Table 7. The final oxygen uptake in Run 22, which was followed to completion, was 110% of the theoretical requirement for oxidation of thiol to disulphide.

Table 7. Oxidation of ethanethiol: effect of progressive technical refinements on the steady rate of oxygen uptake. 0.5 M EtSH.

Run no.	NaOH concn. (M)	Oxygen pressure (cm)	Temperature (°C)	Rate (mmole O_2 /l/min)
22	1.00	74	30.1	0.45
48	2.04	67	30.3	0.182
93	2.04	67	30.0	0.104
123	2.00	72	30.0	0.052
160	2.0	71	29.9	0.050

3.13 Later work on the oxidation of ethanethiol 3.13

The following results were obtained after refinements in technique had reduced the rates of uncatalysed oxidation to the lower levels in Table 7.

3.131 Stoichiometry

Fifteen uncatalysed oxidations of ethanethiol were followed to completion, i.e. until there was no significant further uptake of gas for 15 min. In Table 8 the values of the total oxygen consumption are expressed as percentages of that required for oxidation of the thiol to disulphide, according to the equation:

$$4EtSH + O_2 \rightarrow 2Et_2S_2 + 2H_2O \qquad (1)$$

The stoichiometry was further examined by the analysis of samples withdrawn from oxidising solutions, and of some solutions in which the oxidation had gone to completion.

In an early series of experiments samples taken from the oxidising solutions were analysed for their thiol content. The consumption of thiol and that of oxygen are compared on the kinetic curves reproduced in Fig. 6. The conclusion from these two experiments, viz. that the stoichiometry of equation (1) is closely followed at all stages of oxidation, was supported by the results of nine other similar experiments. The samples in these experiments were withdrawn through the dipping tube described in Section 2.211.

Table 8. Oxidation of ethanethiol: stoichiometry of oxygen uptake. 74 cm O_2, 30°C. 3.13

NaOH concentration (M)	EtSH concentration (M)	Final oxygen uptake (%)[a]
0.4	0.29	107
0.5	0.30	103
0.5	0.31	104
0.5	0.36	100
0.9	0.64	102
1.0	0.14	99
1.0	0.19	89
1.0	0.30	100
1.0	0.45	95
1.0	0.60	90
1.0	0.80	90
2.0	0.35	105
2.0	0.52	113
2.0	0.55	102
2.0	0.60	113

a - 100% is oxygen uptake required for oxidation of thiol to disulphide.

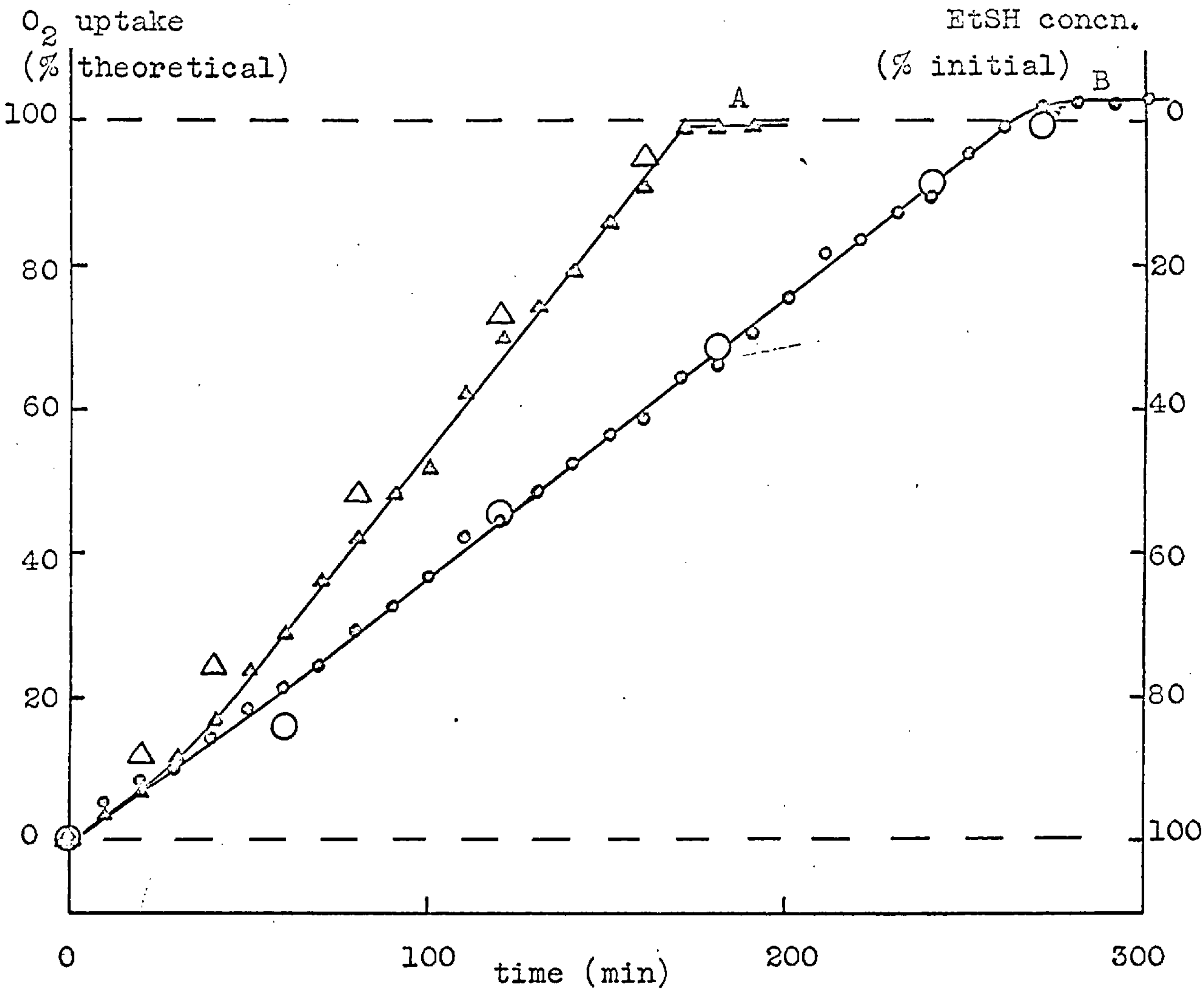


Fig. 6. Oxidation of ethanethiol: stoichiometric relationship between oxygen uptake and decrease in thiol concentration. 75 cm O_2, 30°C.

A - 0.36 M EtSH, 0.5 M NaOH
B - 0.46 M EtSH, 1.0 M NaOH

▲ ● - Oxygen uptake: 100% is theoretical for stoichiometry:

$$4\ \mathrm{EtSH} + O_2 \rightarrow 2\ \mathrm{Et_2S_2} + 2\ H_2O$$

△○ - EtSH concentration

Further experiments were carried out using the cup-sampler also described in Section 2.211, the analyses being extended to include both thiol and disulphide. The results of three experiments are shown in Table 9. The table also shows the results obtained from analyses of the whole product mixture. Further details of these and a number of other experiments are given in Table 10, in which the last three columns of Table 8 have become columns 5, 6, and 7. In column 8 the disulphide is related to the oxygen uptake, while in column 11 the decrease in alkali is correlated with the deficit of disulphide in the products. 3.13

The results show that at all stages the main reaction was the oxidation of thiol to disulphide, but the deficiency of disulphide in the products increased with time and was greater in the presence of more concentrated alkali. There was a slight decrease in the alkali concentration, but correlation between this and the disulphide deficit was uncertain; however, the formation of acids as minor oxidation products appears to be indicated.

3.132 Effect of oxygen pressure

An early series of six experiments with ethanethiol in sodium hydroxide solution was carried out using from 5 to 62 cm oxygen made up with nitrogen to about 63 cm total pressure. The results are given in Table 11. In the experiments with the lowest partial pressures of oxygen the oxidation did not go to

Table 9. Oxidation of ethanethiol: results of sample analyses for thiol and disulphide. 3.131

Conditions	Time (min)	Sample volume (ml)	O_2 uptake (% theor.[a])	EtSH consumed (% init.)	Et_2S_2 produced (% theor.[a])
0.30M EtSH 1.0 M NaOH 74 cm O_2 30.2°C	0	0.68	0	0	0
	20	0.67	18	10	7
	60	0.85	44	26	27
	90	0.49	60	42	40
	120	0.58	72	61	53
	1200	b	89	98	89
0.80M EtSH 1.0 M NaOH 74 cm O_2 30.0°C	0	-	0	-	-
	5	0.94	3	1	2
	60	0.57	24	4	0
	90	0.61	32	24	27
	120	0.45	39	42	42
	150	0.30	44	42	< 47
	180	0.36	48	40	35
	210	0.45	52	51	42
	1230	0.33	90	98	46
	1490	0.35	90	98	56
	1490	b	90	100	92

a - 100% is theoretical uptake and yield for oxidation of thiol to disulphide.

b - Entire product mixture taken for analysis.

Table 9 is continued overleaf.

Table 9. (continued)

Conditions	Time (min)	Sample volume (ml)	O_2 uptake (% theor.^{a})	EtSH consumed (% init.)	Et_2S_2 produced (% theor.^{b})
0.55M EtSH 2.0 M NaOH 74 cm O_2 30.0°C	0	-	0	0	0
	5	0.27	2	0	-
	15	0.56	4	3	- 9
	30	1.06	10	12	0
	50	0.38	15	11	6
	70	0.35	21	3	12
	90	0.55	25	20	21
	132	0.70	33	37	15
	150	0.48	37	32	<46
	1190	0.50	101	91	48
	1270	0.40	102	98	52
	1340	b	102	-	73

a - 100% is theoretical uptake and yield for oxidation of thiol to disulphide.

b - Entire product mixture taken for analysis.

Table 10. Oxidation of ethanethiol: stoichiometry. 74 cm O_2.

Initial concns.		Temp.	Reactn. time at analysis	O_2 uptake	EtSH consumed	Et_2S_2 produced		NaOH consumed		
EtSH (M)	NaOH (M)	(°C)	(min)	(% theor. on init. EtSH)	(% of init.)	% theor. on init. EtSH	% theor. on O_2 uptake	Concn. decrease (M)	% of init. concn.	Mole % of Et_2S_2 deficit
1	2	3	4	5	6	7	8	9	10	11
0.30	0.994	30.2	1200	89	98	89	100	0.036	3.6	180
0.45	0.995	30.1	1560	95	>99.3	85	90	0.021	2.1	60
0.60	0.999	30.1	3000	90	>99.5	74	82	0.030	3.0	38
0.80	0.995	30.0	1490	90	100	92	102	0.035	3.5	175
0.35	2.049	30.1	6000	106	99.7	69	65	0.096	4.7	167
0.50	2.00	30.0	1170	57	47	35	61	a	a	a
0.52	1.958	34.7	1530	113	a	84	74	0.067	3.4	167
0.55	1.994	30.0	1340	102	a	73	72	0.052	2.6	110

a - Residue not determined.

Table 11. Oxidation of ethanethiol: effect of partial pressure of oxygen. 0.50 M EtSH, 2.0 M NaOH, 30°C.

Oxygen pressure (cm)	Total pressure (cm)	Initial rate (mmole/l/min)	Final uptake (% theor.[a])
5	63	0.038	9
14	64	0.064	18
15	63	0.115	-
23	64	0.237	30
37	63	0.096	-
62	62	0.226	-

a - 100% is theoretical for oxidation of thiol to disulphide.

completion owing to lack of oxygen.

The rates were not very reproducible, but evidently increased with the oxygen pressure.

A later series of experiments was carried out when uncatalysed rates were generally lower and more reproducible: oxygen pressures from 13 to 71 cm were used without diluent nitrogen. These reactions were followed only long enough for steady rates of oxygen uptake to be established and measured. The results are shown in Fig. 7. There was a linear dependence of rate on the oxygen pressure, but the graph does not pass through the origin: with the lowest oxygen pressure, 13 cm, a steady <u>increase</u> in the gas-phase volume was observed.

3.133 Effect of ethanethiol concentration

A series of experiments was carried out with ethanethiol concentrations from 0.1 to 1.0 M in 2.0 M sodium hydroxide. The resulting kinetic curves are shown in Fig. 8. The slower reactions commence with an apparent induction period, and this was generally observed in the slower oxidations. The rate then rapidly reached a maximum, and subsequently decreased slightly until a constant zero-order rate was established and the graphs were straight lines. The general shape of these curves was supported by the full oxygen-uptake curves for two experiments which were followed for long reaction times, one of them to completion: these are shown in Fig. 9.

In order to investigate the kinetics of the reaction in

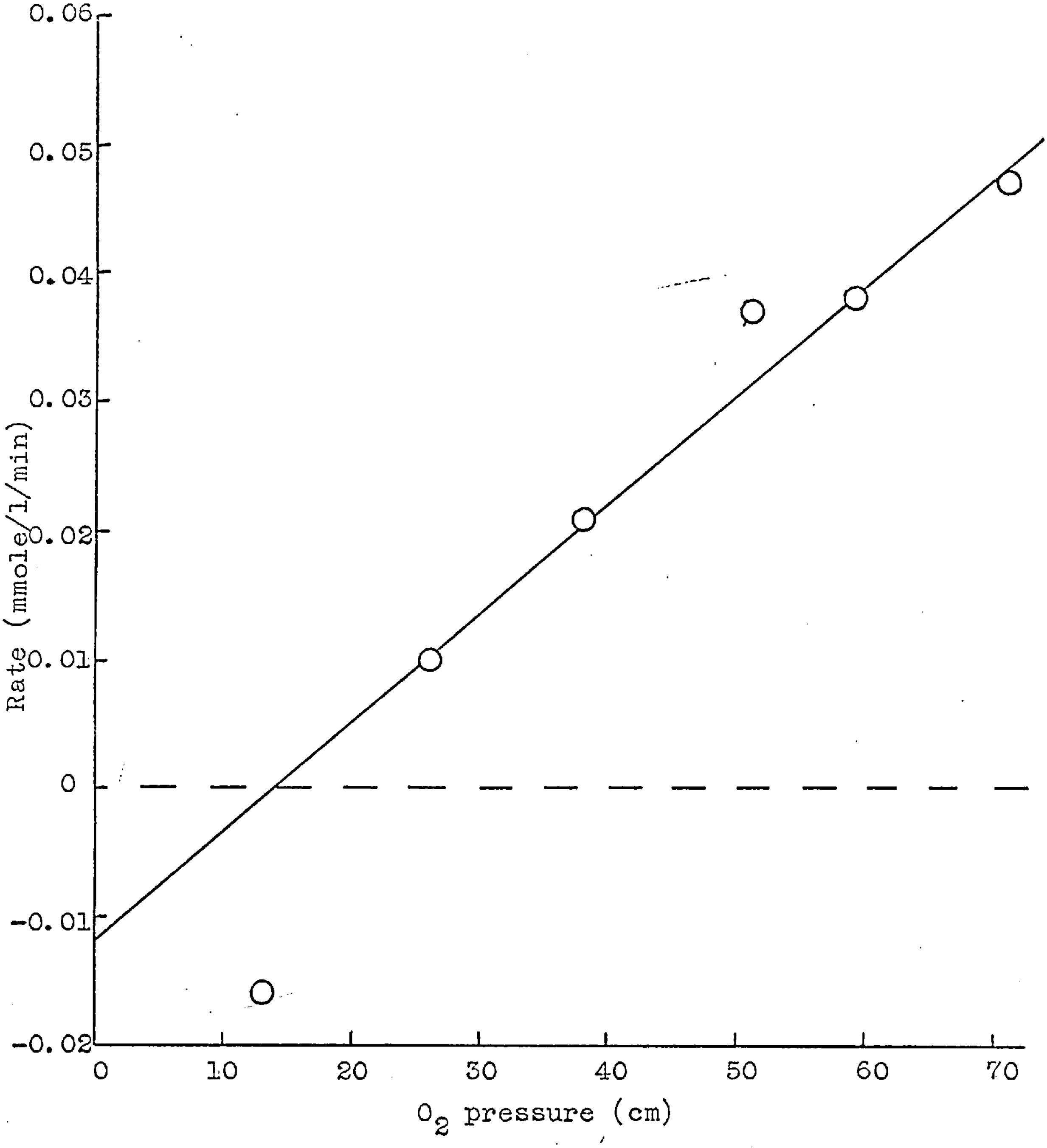


Fig. 7. Oxidation of ethanethiol: effect of oxygen pressure on the steady (zero-order) rate of reaction. 0.2 M EtSH, 2.0 M NaOH, 30°C.

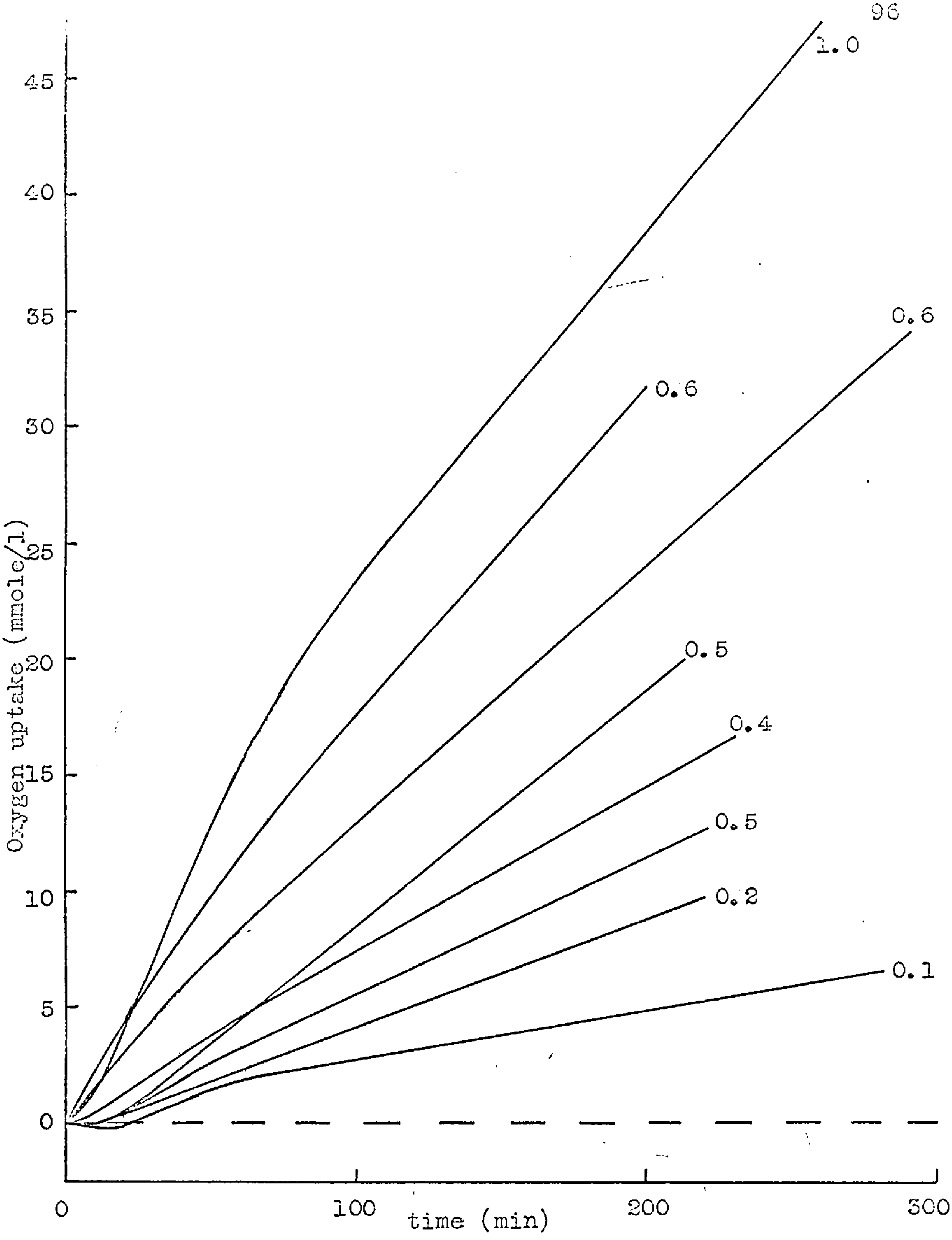


Fig. 8. Oxidation of ethanethiol: effect of initial thiol concentration (values in M beside curves). 2.0 M NaOH, 70 cm O_2, 30°C.

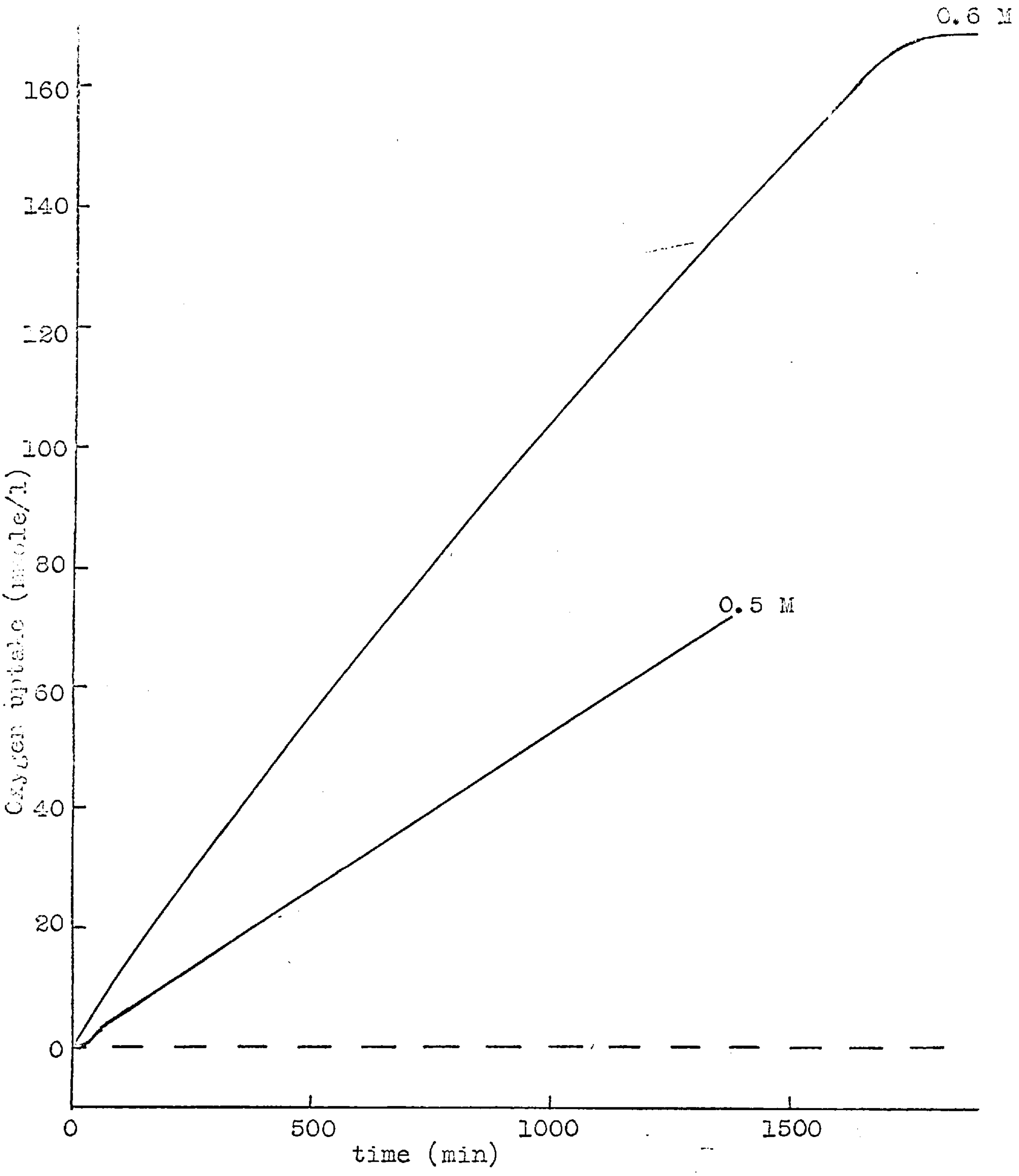


Fig. 9. Oxidation of ethanethiol: kinetic curves for long experiments. 2.0 M NaOH, 71 cm O_2, 30°C, initial thiol concentrations beside curves.

the early part of the oxidation, graphs of $-\log_{10}[\mathrm{EtSH}]$ 3.13 versus time were plotted for the runs shown in Fig. 8, the thiol concentrations being obtained from the oxygen consumption, assuming the 1:4 (oxygen:thiol) stoichiometric ratio. The resulting graphs were nearly all straight lines (especially when their curvature was compared with that of a typical zero-order curve), and provided values of the first-order rate constant for the early part of the oxidation (i.e. initial k_1) shown in Table 12. The Table also shows the values of the initial (post-induction period) and steady (zero-order) rates, and these are plotted against the initial thiol concentrations in Fig. 10.

The general conclusion from these results, that the kinetics may be first-order in thiol near the start of reaction but soon becomes zero-order, was supported by the kinetic curves from a large number of other experiments in which these points were not explicitly under consideration.

The rate constant for the early part of the reaction was $k_1 \approx 10^{-3}\mathrm{min}^{-1}$, which includes the oxygen concentration term. Taking the Bunsen absorption coefficient α as 0.0114 and the oxygen partial pressure as 70-15=55 cm (the 15 cm being the apparent pressure for which zero rate of reaction was obtained, q.v. Section 3.132), the true first order rate constant was $k_1' \approx 4.5 \times 10^{-3}\mathrm{l.mole}^{-1}\mathrm{sec}^{-1}$ in 2 M sodium hydroxide at 30°C, the rate equation being:

Table 12. Oxidation of ethanethiol: rates of reaction and initial first-order rate constants from experiments with various initial thiol concentrations. 2.0 M NaOH, 70 cm O_2, 30°C. 3.133

Initial thiol concn. (M)	Reaction rates (mmole/l/min)			Initial $k_1 \times 10^3$ (min^{-1})
	initial	steady	ratio	
0.1	≈0.035	0.020	1.7	1.12
0.2	0.047[a]	0.047	1.0	1.10
0.4	0.108	0.072	1.5	0.79
0.5	0.074	0.052	1.4	0.50
0.5	0.104[a]	0.104	1.0	0.90
0.6	0.146	0.111	1.3	0.88
0.6	0.22	0.144	1.5	1.18
1.0	0.29	0.142	2.0	1.13[b]

a - Apparent zero-order reaction from start: k_1 for comparison only.

b - k_1 decreasing to 0.72×10^{-3}.

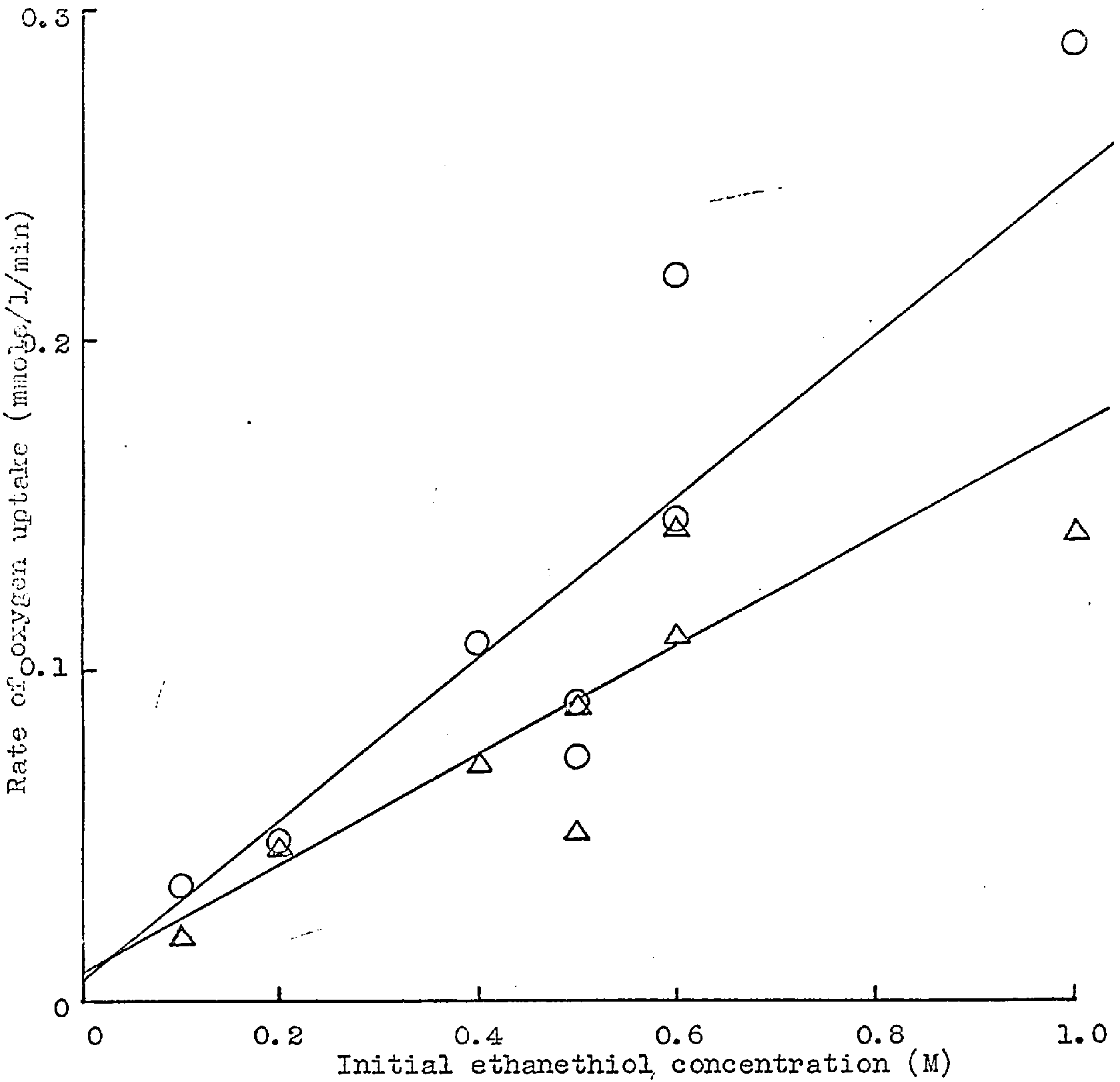


Fig. 10.
Oxidation of ethanethiol: effect of initial thiol concentration on rate of oxygen uptake. 2.0 M NaOH, 70 cm O_2, 30°C.
○ - initial (maximum) rate
△ - steady (zero-order) rate

3.13

$$-\frac{d[EtSH]}{dt} = k_1[EtSH] = k_1'[O_2][EtSH] \qquad (i)$$

For the steady zero-order reaction at the higher thiol conversions, the oxygen uptake rate was roughly 0.1 mmole/l/min, and hence $k_0' \approx 1.8 \times 10^{-2}$ sec^{-1}, where:

$$-\frac{d[EtSH]}{dt} = 4\frac{d[O_2]}{dt} = k_0 = k_0'[O_2][EtSH]^0 \qquad (ii)$$

3.134 Effect of source, nature, and concentration of alkali

A series of experiments was made using ethanethiol in aqueous solutions of sodium and potassium hydroxides. Two samples of each hydroxide - from the 'AnalaR' and 'Judactan' branded reagents - were used. The gas uptake was followed until the definite steady (zero-order) rate had been established and measured: this was generally about 200 min. The rates of oxidation were corrected for the different solubilities of oxygen in the various concentrations of alkali by dividing by the Bunsen absorption coefficient α (see Appendix 4). The results are given in Fig. 11. The corrected rates increased rather more than linearly with the alkali concentration, potassium hydroxide giving slightly higher rates than sodium hydroxide.

3.135 Effect of temperature

The temperature coefficient of the rate of reaction was determined by increasing the temperature stepwise from 30 to 40 and 50°C, allowing sufficient time at each temperature for

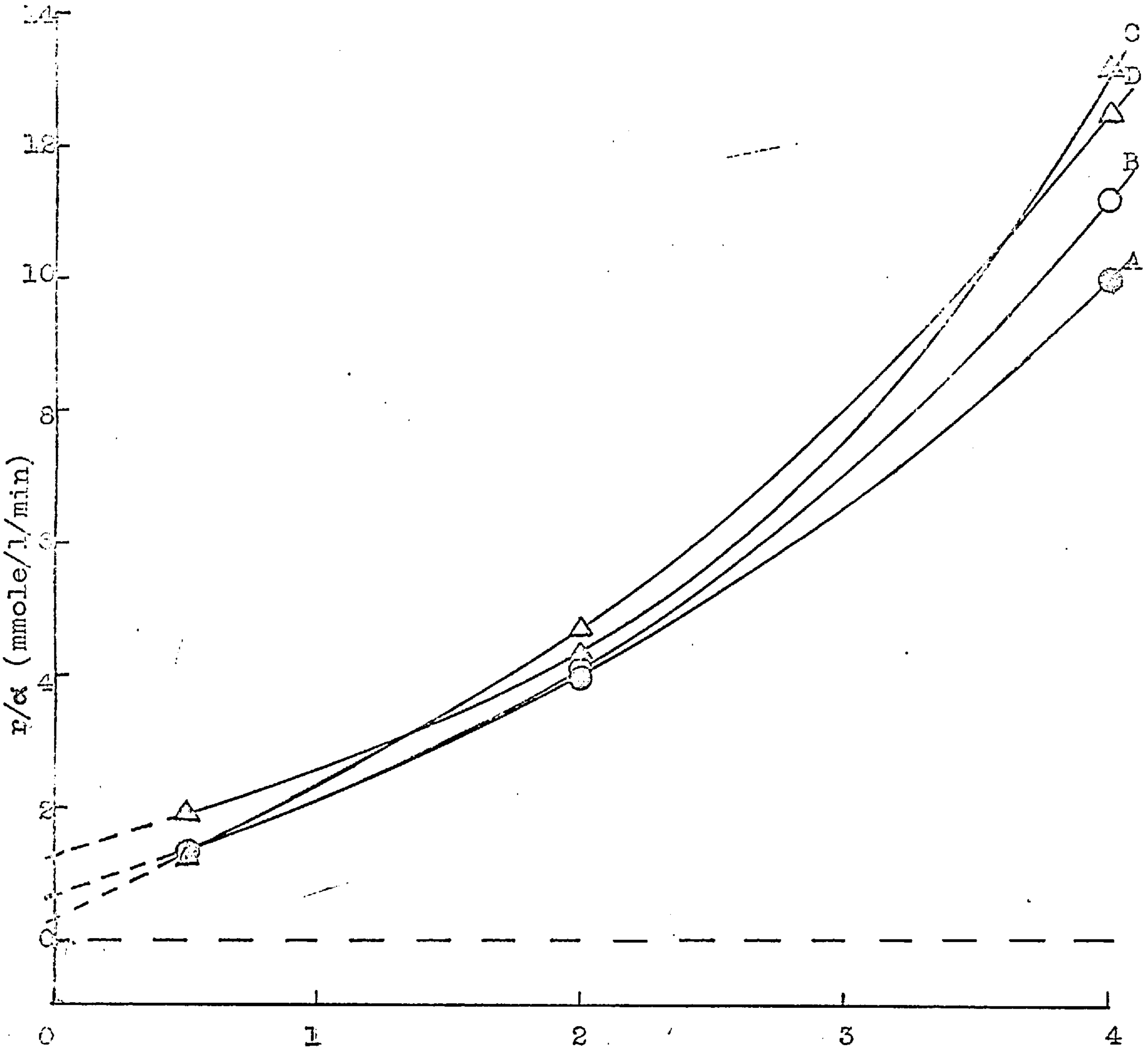


Fig. 11. Oxidation of ethanethiol: effect of source, nature, and concentation of alkali. 0.2 M EtSH, 69 cm O_2, 30°C.

A - 'Analar' NaOH; B - 'Judactan' NaOH; C - 'Analar' KOH; D - 'Judactan' KOH.

the steady rate to be established and measured. The kinetic curves are shown in Fig. 12. The straight-line sections of these curves are joined sometimes by slight discontinuities, due to readjustment of gas and vapour pressures in the reaction vessel. 3.135

The zero-order rates of reaction, r, obtained from these curves were corrected for changes in oxygen solubility (q.v. Section 3.134), and the values of $\log_{10}(r/\alpha)$ plotted against 1/T, as shown in Fig. 13. The best straight line through these points gives the following values for the zero-order energy of activation:

$$0.6 \text{ M NaOH}, \ E_{a0} = 16.6 \text{ kcal/mole}$$

$$2.0 \text{ M NaOH}, \ E_{a0} = 16.4 \text{ kcal/mole}$$

The mean value of E_{a0} = 16.5 kcal/mole, taken with the value of $k_0' = 1.8 \times 10^{-2}$ sec^{-1} (Section 3.133) and the Arrhenius equation:

$$k_0' = A_0 e^{-E_{a0}/RT} \qquad \text{(iii)}$$

gives a value of $A_0 = 10^{10.2}$ sec^{-1}.

3.136 Effect of added diethyl disulphide

The kinetic curve for an experiment to which 0.5 M diethyl disulphide was added is shown in Fig. 14, together with those for a similar experiment with an additional 0.1 M ethylenediamine, and corresponding experiments without added disulphide. The Figure also shows the curve obtained for a run carried out with 0.5 M disulphide in the absence of thiol. The consumption of oxygen was negligible even after 1260 min,

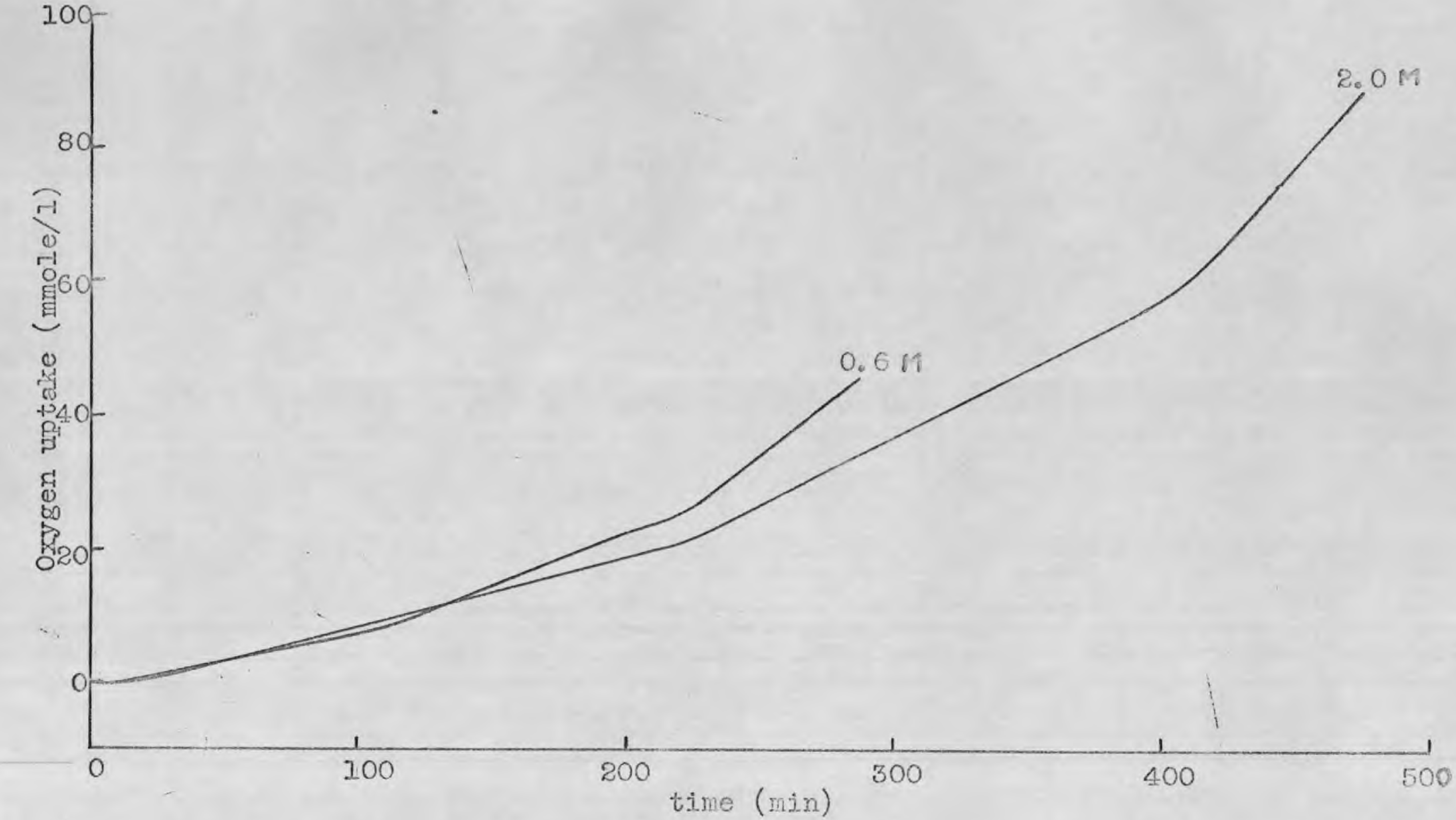


Fig. 12. Oxidation of ethanethiol: effect of stepwise increase in temperature. 0.5 M EtSH, 67 cm O_2, NaOH concentrations beside curves; 30 → 40 → 50°C.

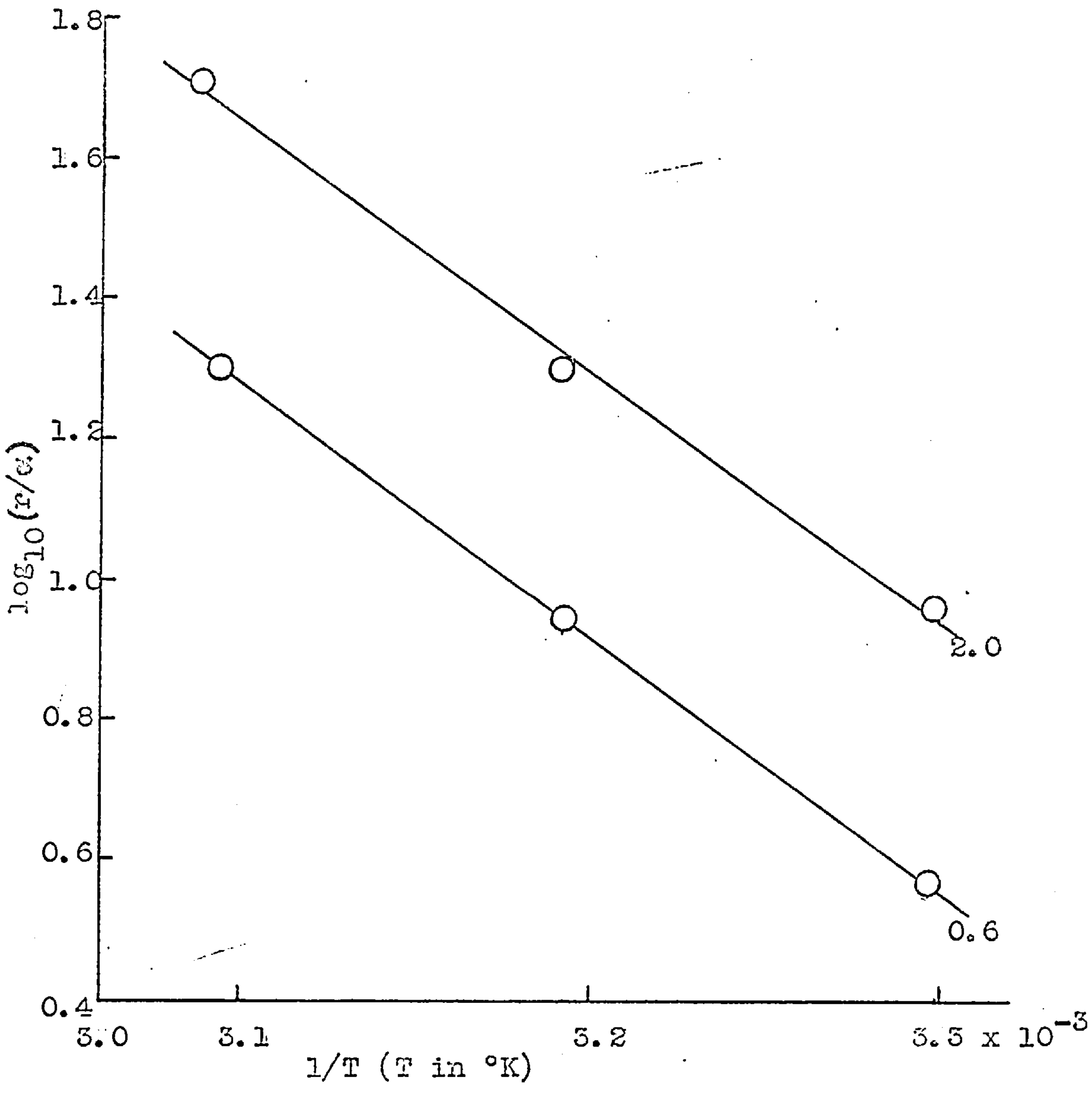


Fig. 13. Oxidation of ethanethiol: effect of temperature. 0.5 M EtSH, 67 cm O_2, NaOH concentrations (M) beside curves.

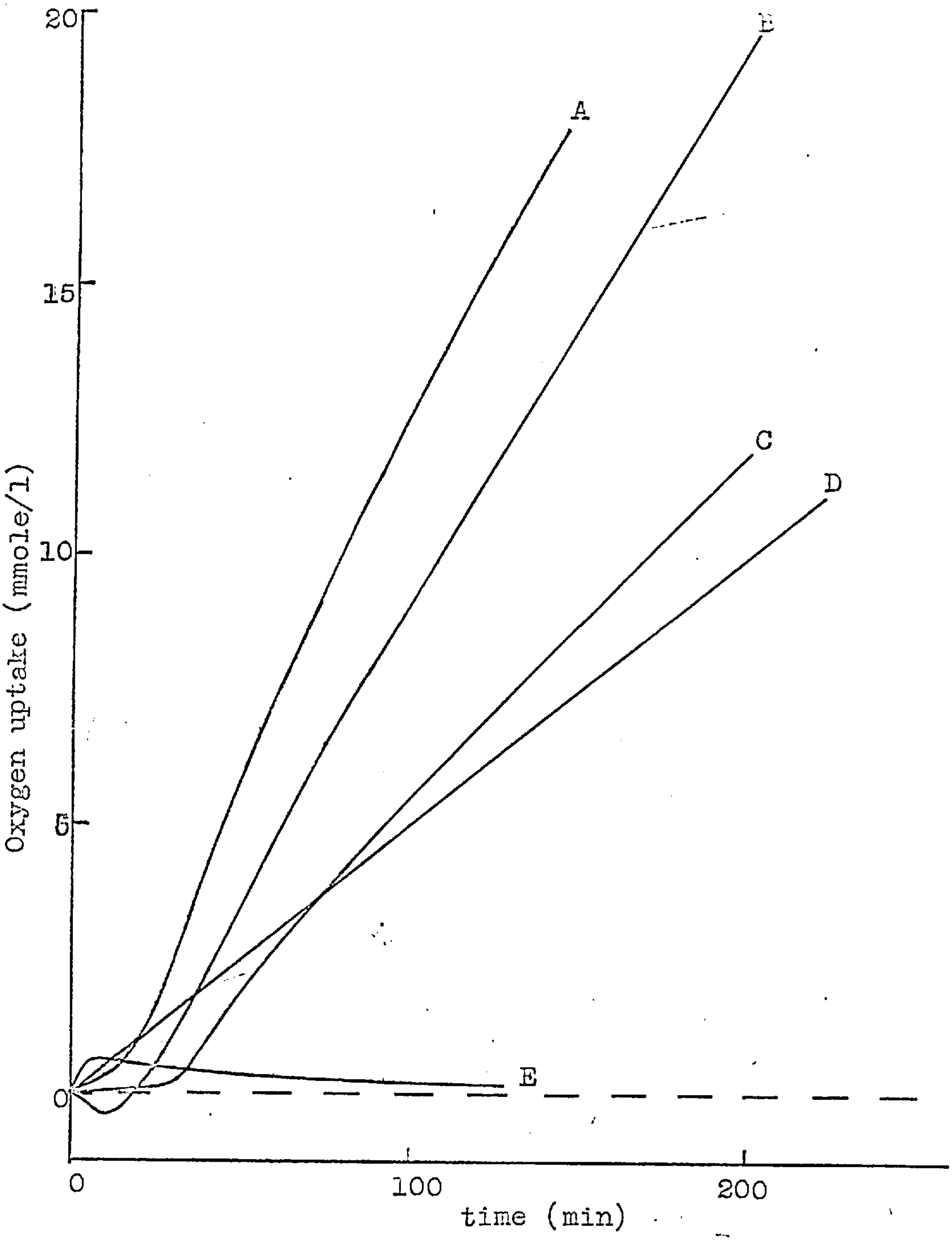


Fig. 14. Oxidation of ethanethiol: effect of added diethyl disulphide, 0.5 M EtSH, 2.0 M NaOH, 70 cm O_2, 30°C; A - 0.5 M Et_2S_2; B - 0.5 M Et_2S_2, 0.1 M en; C - 0.1 M en; D - no additives; E - no thiol, 0.25 M Et_2S_2.

when the solution was analysed: the decrease in the disulphide concentration was 0.027 M (11%) and in the alkali was 0.08 M (4%).

3.137 Effect of ethylenediamine

The effect of 10^{-1} M ethylenediamine (en) is shown in Table 13, which gives the results of experiments with pure and impure samples of thiol. The diamine reduced the higher rate but increased the lower.

Table 13. Oxidation of ethanethiol: effect of added ethylenediamine. 0.5 M EtSH, 2.0 M NaOH, 70 cm O_2, 30°C.

Ethanethiol sample	en concn. (M)	Rate (mmole/l/min)
Distilled	0	0.050
	10^{-1}	0.065
Undistilled	0	0.206
	10^{-1}	0.114

A further experiment was conducted with 0.2 M en, the temperature being increased stepwise. The rates were corrected for oxygen solubility, and the values of $\log_{10}(r/\alpha)$ are plotted against 1/T to give curve A in Fig. 15. The resulting graph is markedly curved, and as the oxygen-uptake versus time plots also had shown slight curvature, indicating possible first-order kinetics, the oxygen consumption was converted to equivalent thiol concentrations, a graph of

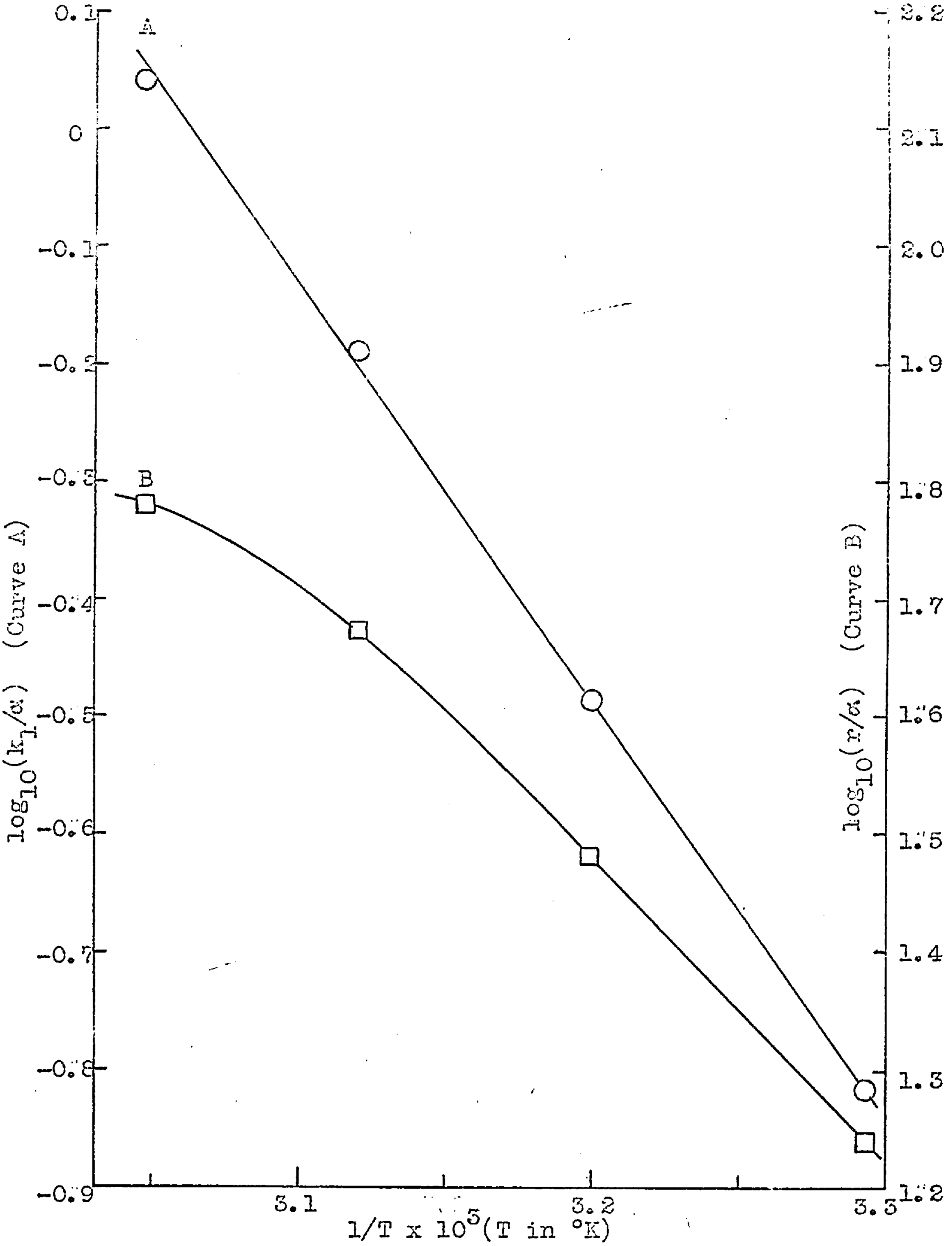


Fig. 15. Oxidation of ethanethiol: effect of temperature on reaction in presence of added ethylenediamine. 0.5 M EtSH, 2.0 M NaOH, 71 cm O_2.

$\log_{10}$[EtSH] versus time constructed, and values of k_1 obtained for each temperature. These were corrected for oxygen solubility and the values of $\log_{10}(k_1/\alpha)$ are plotted against 1/T as curve B in Fig. 15. The best straight lines through the points on curves A and B gave the following values for the zero- and first-order activation energies:

Curve A, E_{a0} = 11.4 kcal/mole

Curve B, E_{a1} = 15.0 kcal/mole

3.138 Effect of ethylenediaminetetracetic acid

The oxidation of ethanethiol was studied in a series of experiments in which from 10^{-3} to 10^{-1} M ethylenediaminetetracetic acid (EDTA) was added to the reagents. The kinetic curves are shown in Fig. 16. The two runs with 10^{-1} M EDTA were from different series of experiments. Fig. 16 also shows a run with 10^{-1} M EDTA and 10^{-1} M en. The reactinn rates are detailed in Table 14.

One of the experiments with 10^{-1} M EDTA was followed to completion (1230 min) and the oxygen uptake was 118% of theoretical for conversion of thiol to disulphide.

3.139 Effect of cyanide

Two experiments were made with ethanethiol in the presence of 0.25 M potassium cyanide. In the second of these the temperature was increased stepwise from 30.0 to 51.3°C. Both zero-order and first-order data were calculated for the reason given in Section 3.137. The results and values of the

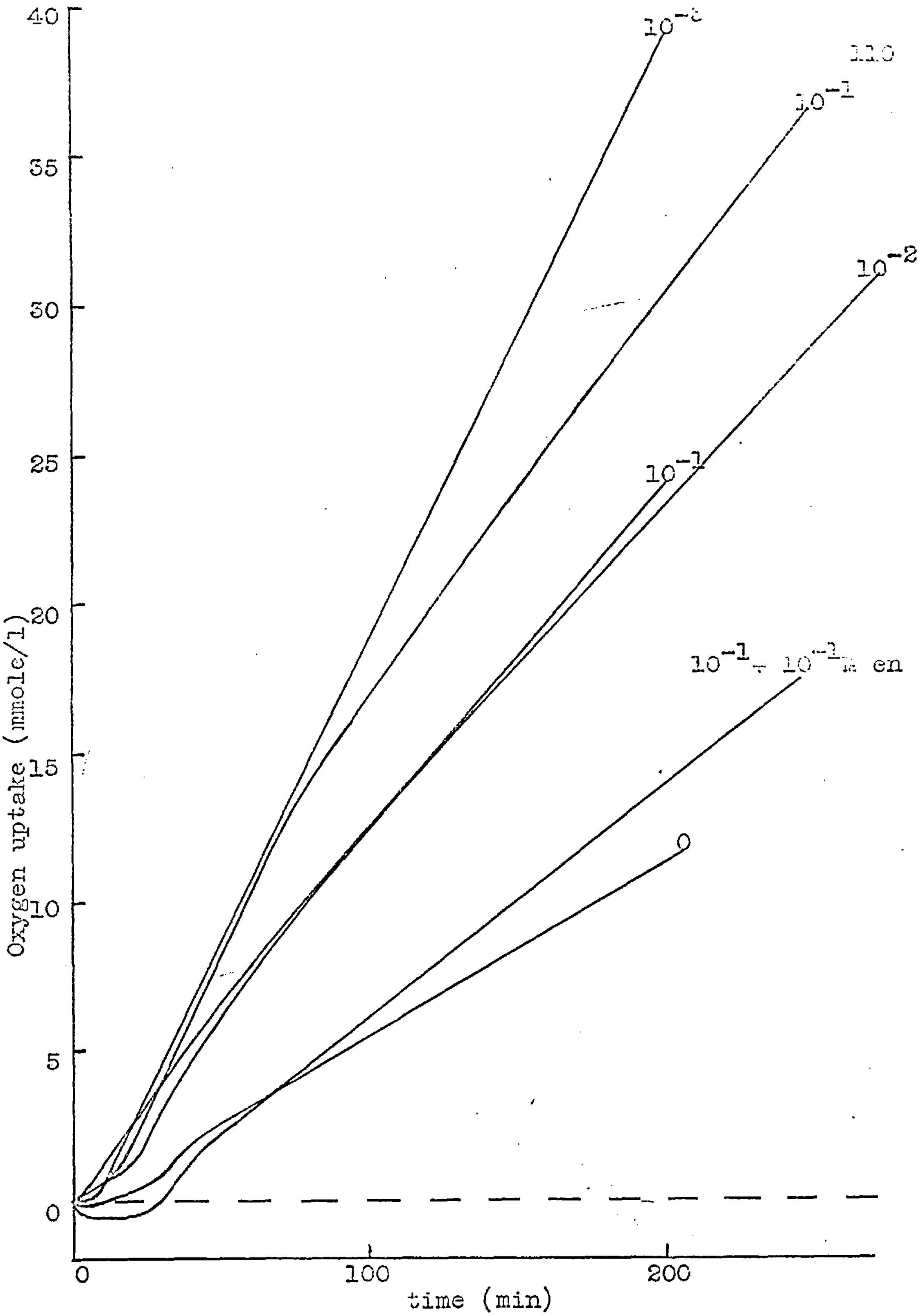


Fig. 16. Oxidation of ethanethiol: effect of added ethylenediaminetetracetic acid. 0.5 M EtSH, 2.0 M NaOH, 69 cm O_2, 30°C; EDTA concentrations (M) beside curves.

Table 14. Oxidation of ethanethiol: effect of EDTA. 3.13

0.5 M EtSH, 2.0 M NaOH, 69 cm O_2, 30°C.

EDTA concn. (M)	Rate (mmole/l/min) initial	Rate (mmole/l/min) steady
0	0.10	0.059
10^{-3}	0.21	0.200
10^{-2}	0.14	0.107
10^{-1}	0.20	0.122
10^{-1} a	0.11	0.078

a - plus 10^{-1} M en.

Table 15. Oxidation of ethanethiol: effect of added potassium cyanide. 0.5 M EtSH, 2.0 M NaOH, 71 cm O_2.

KCN concn. (M)	Temp. (°C)	Rate=r (mmole /l/min)	r/α (mmole /l/min)	E_{a0} (kcal/mole)	$k_1 \times 10^3$ (min^{-1})	k_1/α (min^{-1})	E_{a1} (kcal/mole)
0	30	0.12	10.5				
0.25	30	<0.015	<1.3				
0.25	30.0	0.069	6.05	17.4	0.51	0.045	20.4
	42.4	0.18	18.9	18.0	1.6	0.170	21.0
	51.3	0.35	41.6		3.6	0.428	

activation energy are shown in Table 15. The discrepancy 3.14 between the two rates at 30°C is remarkable, and is due to the trend towards higher rates with successive experiments with added cyanide: this is shown in greater detail in Table 26 in Section 3.2217.

The last experiment in Table 15 was continued at + 50°C for a total reaction time of about 1285 min, when the oxygen uptake was 191% of theoretical for oxidation of the thiol to disulphide. The consumption of oxygen had not ceased at this time, and over the final 148 min the mean rate was 0.066 mmole/l/min, or about 20% of the initial rate at this temperature.

3.140 Effect of di-t-butyl peroxide and of diphenylamine

Experiments were conducted with ethanethiol in the presence of 0.05 M di-t-butyl peroxide and of 0.1 M diphenylamine. In a further experiment both 0.05 M peroxide and 0.1 M ethylenediamine were added. The results are shown in Fig. 17, which includes for comparison an experiment without additives.

4.15 Comparison of different thiols

Comparative oxidation experiments were carried out on a series of different thiols in the absence and presence of ethylenediamine. The oxygen-uptake versus time curves are shown in Figs. 18 and 19, and the rates are compared in Table 16. In the case of the slow reactions with t-butanethiol and thiophenol, measurements were not made during the middle

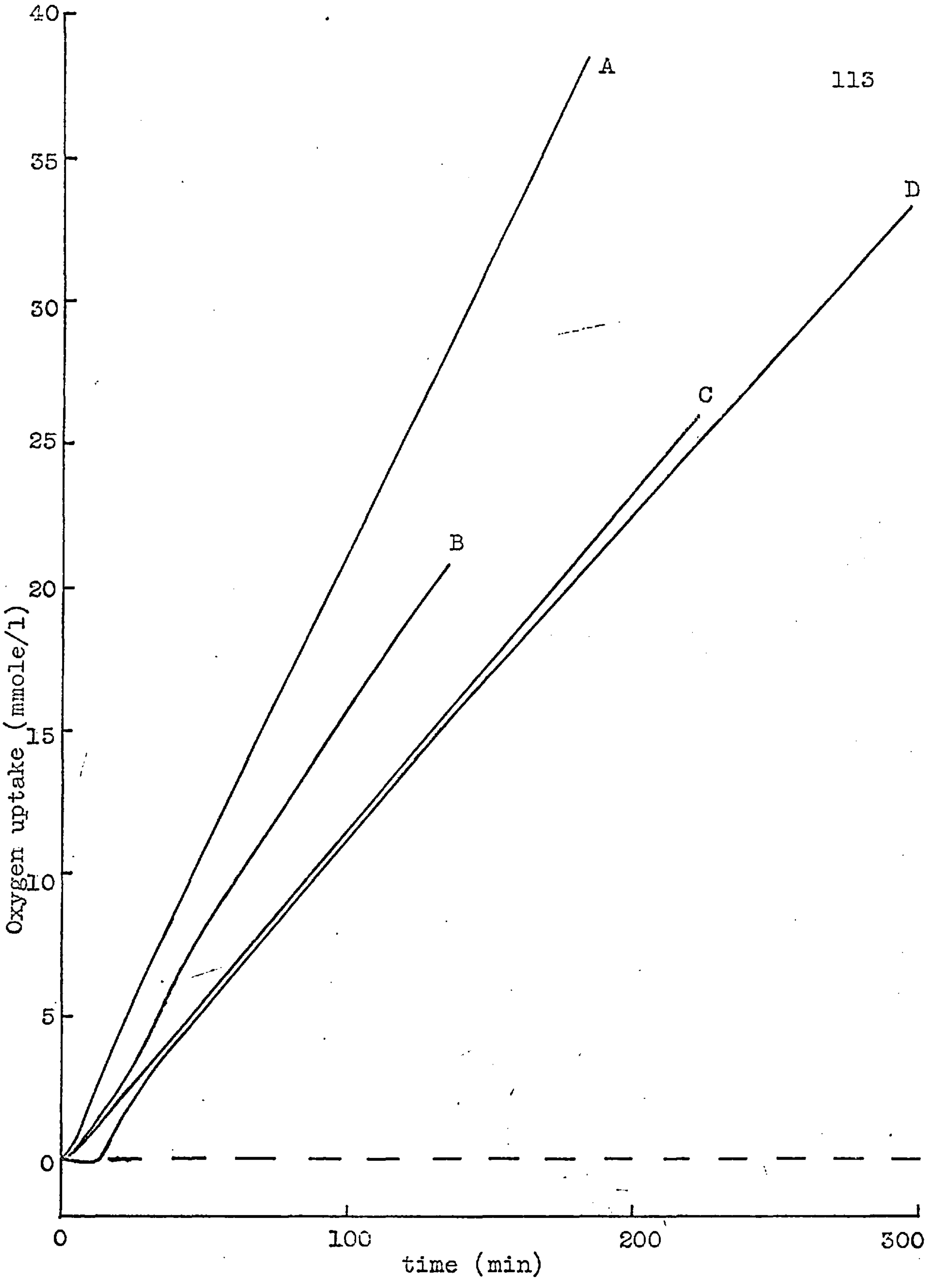


Fig. 17. Oxidation of ethanethiol: effect of added di-t-butyl peroxide and diphenylamine. 0.5 M EtSH, 2.0 M NaOH, 72 cm O_2, 30°C; A - 0.05 M tBu_2O_2; B - 0.1 M Ph_2NH; C - 0.05 M tBu_2O_2 + 0.1 M en; D - no additives.

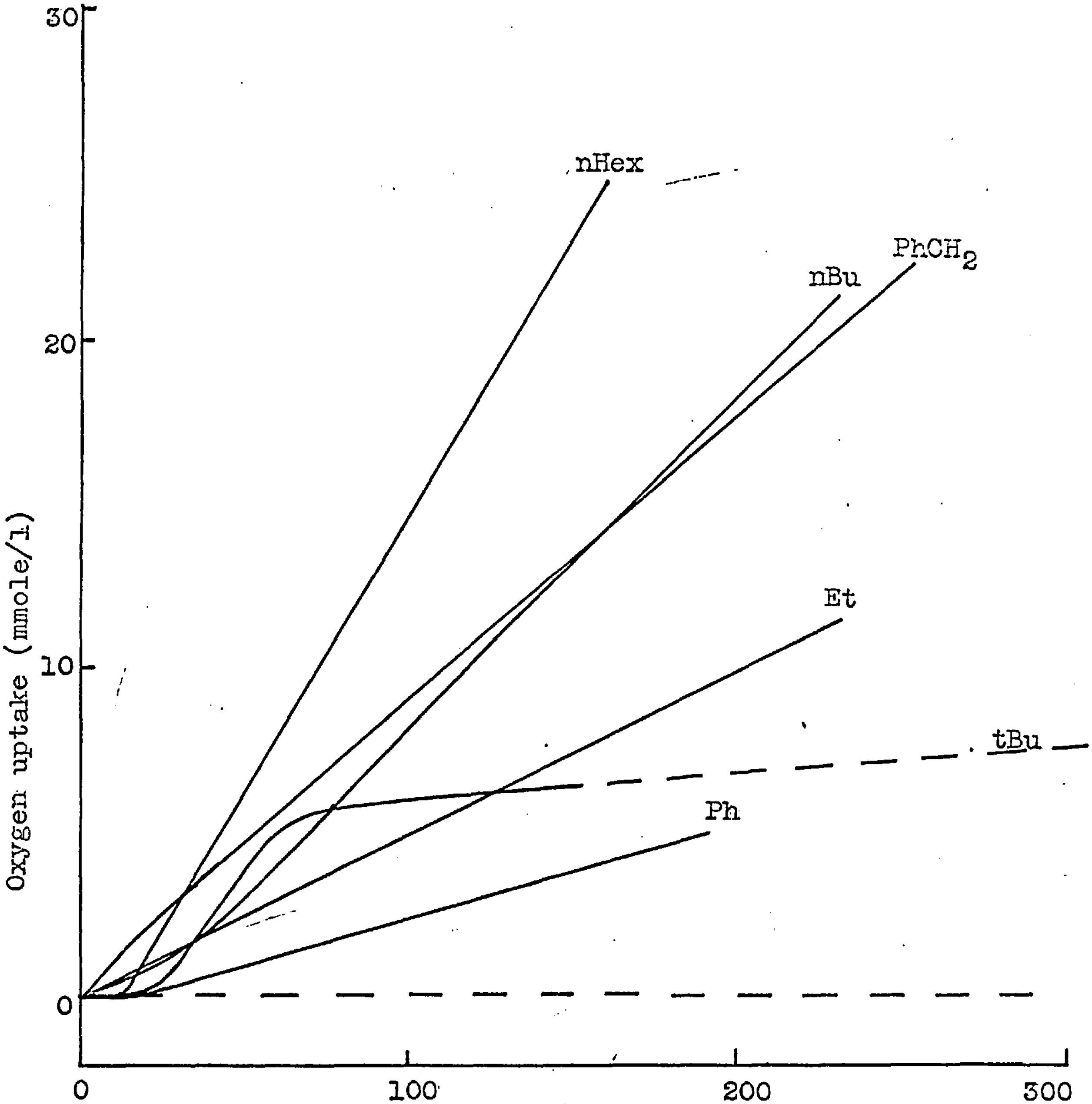


Fig. 18. Oxidation of various thiols. 0.5 M RSH, 2.0 M NaOH, 70 cm O_2, 30°C.

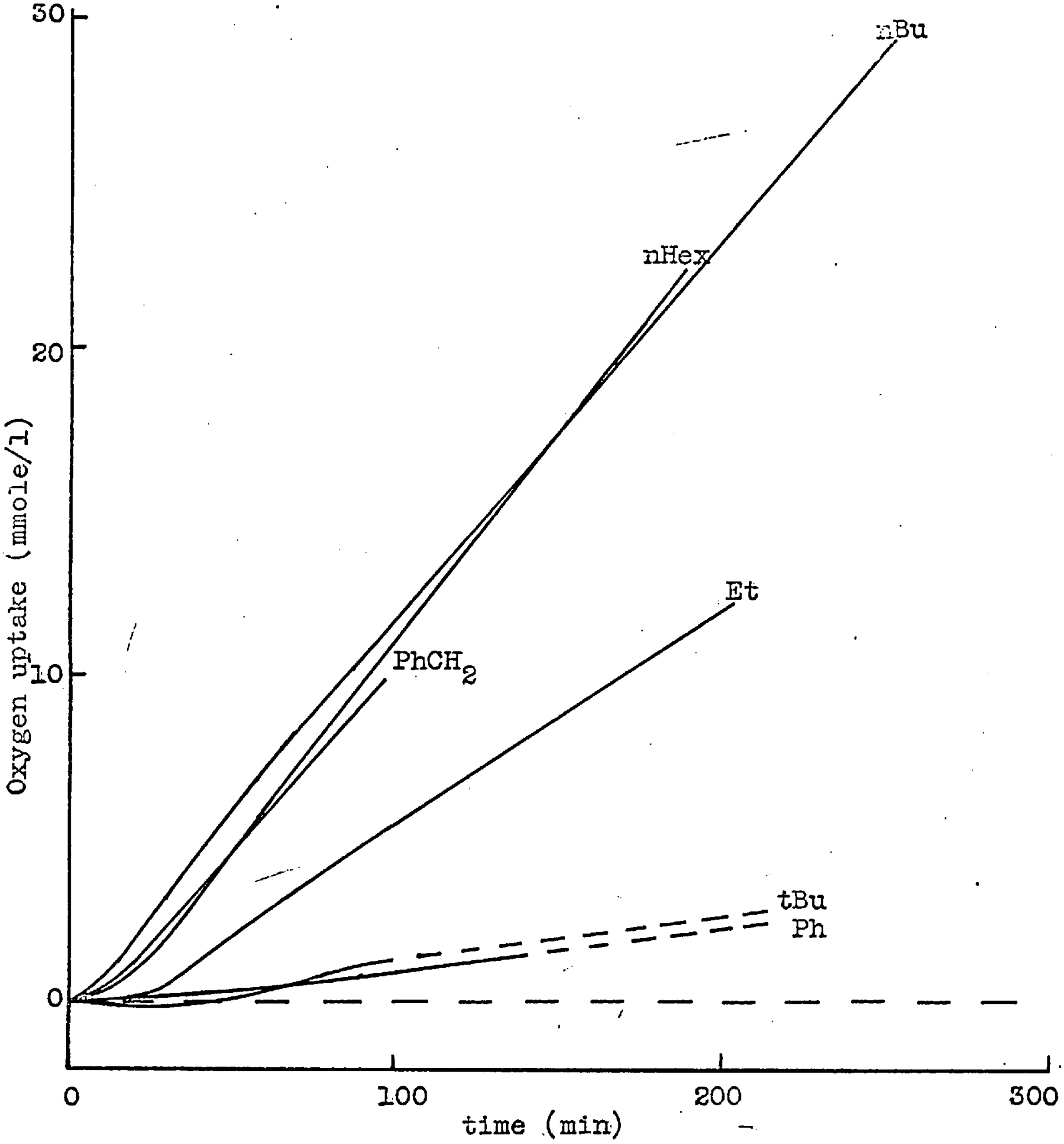


Fig. 19. Oxidation of various thiols in presence of ethylenediamine. 0.5 M RSH, 2.0 M NaOH, 70 cm O_2, 30°C; 0.1 M en except Ph and PhCH$_2$ 0.2 M.

Table 16. Rates of oxidation of various thiols in the absence of additives and the presence of ethylenediamine. 0.5 M RSH, 2.0 M MaOH, 70 cm O_2, 30°C. 3.15

Thiol	No additives	Ethylenediamine present	
	Rate (mmole/l/min)	En concn. (M)	Rate (mmole/l/min)
EtSH	0.052	0.1	0.065
n-BuSH	0.10	0.1	0.119
n-HexSH	0.166	0.1	0.129
t-BuSH	0.006[a]	0.1	0.013[b]
PhSH	0.0289	0.2	0.011
$PhCH_2SH$	0.0859	0.2	0.11

a - Rate near start of reaction ≈ 0.14 mmole/l/min (Fig. 18).

b - Rate near start of reaction ≈ 0.03 mmole/l/min (Fig. 19).

Table 17. Oxidation of t-butanethiol: effect of temperature. 0.5 M t-BuSH, 2.0 M NaOH, 72 cm O_2.

Temp. (°C)	Rate = r (mmole/l/min)	r/α [a] (mmole/l/min)	E_{a0} (kcals/mole)
30.4	0.006	0.535	22.5
40.4	0.017	1.747	32.1
51.3	0.080	9.52	

a - α is the Bunsen absorption coefficient for oxygen in alkali.

stage of the oxidation. The broken lines for t-butanethiol on Figs. 18 and 19 and for thiophenol on Fig. 19 are interpolated from oxygen-uptake readings of 14.0 mmole/l at 1100 min, 16.5 mmole/l at 1225 min, and 12.4 mmole/l in 1035 min respectively, and the rates shown in Table 16 are mean values over these periods. 3.1

3.151 n-Hexanethiol

The experiment with n-hexanethiol in the presence of 0.1 M ethylenediamine, the start of which is shown on Fig. 19, was allowed to contimue for two days. The full kinetic curve is given in Fig. 20. The three periods over which readings were made are shown as full lines, the intervening periods by broken lines which must be regarded as conjectural. The mean rates for the three periods were 0.129, 0.043, and 0.021 mmole/l/min respectively. The highest measured uptake was 155.7 mmole/l or 124% of theoretical for oxidation of the thiol to disulphide.

3.152 t-Butanethiol

The experiment with t-butanethiol whose kinetic curve is plotted in Fig. 18 was continued for 1480 min with stepwise increase in temperature to 51.3°C. The oxygen-uptake versus time curve had straight-line sections joined by slight discontinuities, similar to those in Fig. 12. The rates of reaction and the derived energies of activation are given in Table 17.

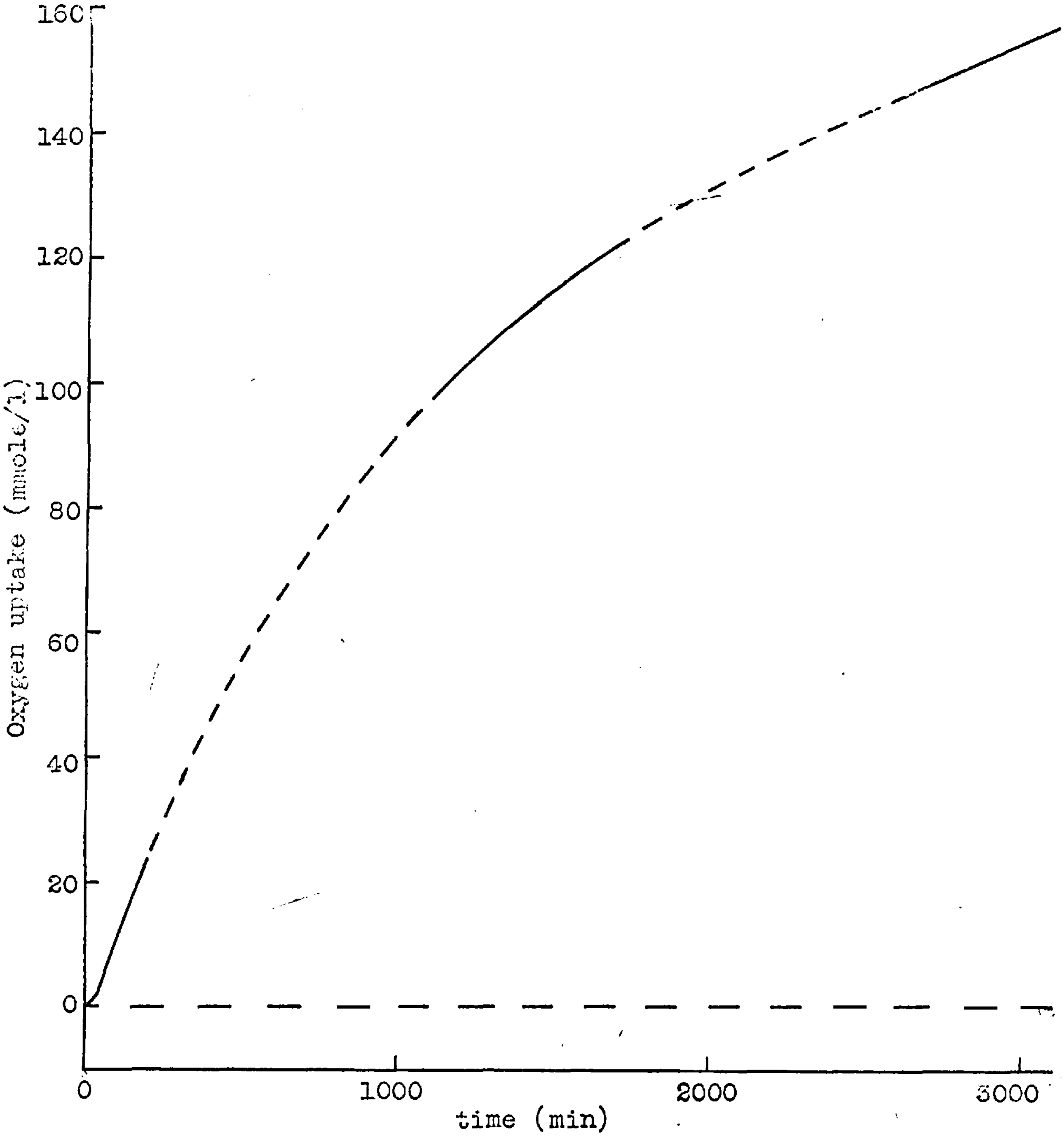


Fig. 20. Oxidation of n-hexanethiol. 0.5 M nHexSH, 2.0 M NaOH, 0.1 M en, 70 cm O_2, 30°C. Theoretical uptake for conversion to disulphide - 125 mmole/l.

Attempts to analyse the product mixture by the standard procedure (Section 2.42) were unsuccessful owing to the formation of the red sulphenyl iodide in the non-aqueous phase[7], the iodine and bromine titres being the same: the former was twice that expected, and the latter two-fifths. 3.152

3.153 Thiophenol

The two experiments with thiophenol whose kinetic curves were given in Figs. 18 and 19 were both continued with a single stepped increase in temperature from 30 to 40°C. The zero-order rates and energies of activation are shown in Table 18. The final products from the incomplete oxidation in the second of these experiments were analysed as described in Section 2.42. The results are shown in Table 19. While the titration of thiol with iodine appears to have been normal, no disulphide was found by titration with bromine in the next stage.

3.2 Oxidation of thiols in the presence of added metal salts

As with the uncatalysed oxidation of thiols, most of the work on metal-ion-catalysed reactions was carried out with ethanethiol, and the effect of the salts of five metals was studied. The effect of copper and cobalt sulphates was examined in some detail.

Table 18. Oxidation of thiophenol: effect of temperature.

0.5 M PhSH, 2.0 M NaOH, 70 cm O_2.

Ethylenediamine concentration (M)	Temp. (°C)	Rate = r (mmole/l/min)	r/α (mmole/l/min)	E_{a0} (kcals/mole)
0	30.0	0.029	2.55	23.6
	40.0	0.086	8.80	
0.2	30.4	0.012	1.07	20.4
	40.5	0.031	3.17	

Table 19. Oxidation of thiophenol: product analyses.

0.5 M PhSH, 2.0 M NaOH, 0.2 M en, 70 cm O_2, 30.4°C (0-1040 min), 40.5°C (1040-1300 min). Analysis at 1300 min, when oxygen uptake 15.7% of theoretical for oxidation of thiol to disulphide.

Extract	Thiophenol concn. (M)		Total disulphide concn.[a] (M)	
no.	Expected	Found	Expected	Found
1	0	0	0.037	< 0.04
2	0.425	0.455	0.212	0

a - Total disulphide includes both reaction product and disulphide from thiol titration (if any).

3.21 Effect of added metal salts on ethanethiol oxidation 3.21

The oxidation of ethanethiol was carried out in the presence of the ions of five metals, viz. copper, cobalt, iron, manganese, and chromium, added as sulphates over wide ranges of concentration. The effect of the ions at 10^{-5}M and 10^{-3}M in 2.0 M sodium hydroxide solution are shown in Fig. 21. The order of catalytic effectiveness and the shape of the uptake curves were confirmed in a similar series of experiments with 0.6 M alkali.

3.22 Effect of added copper sulphate on the oxidation of thiols

The effect of 10^{-5}M copper sulphate on the oxidation of six thiols is shown in Fig. 22. The rates are compared with those for the corresponding reactions in the absence of copper sulphate in Table 20.

~~Examination of~~ The final section of the curve for hexanethiol was found to be first order in thiol with $k_1 = 7.7 \times 10^{-3}$ min^{-1}.

Table 20. Effect of 10^{-5}M $CuSO_4$ on rates of oxidation of thiols
0.5 M RSH, 2.0 M NaOH, 70 cm O_2, 30°C.

Thiol	$CuSO_4$ absent Rate (mmole/l/min)	$CuSO_4$ present Rate (mmole/l/min)	Rate ratio
EtSH	0.070	1.10	16
n-BuSH	0.10	0.995	10
n-HexSH	0.166	1.38	8.3
t-BuSH	0.006	0.099	16
PhSH	0.029	0.07	2.4
$PhCH_2SH$	0.0859	0.55	6.4

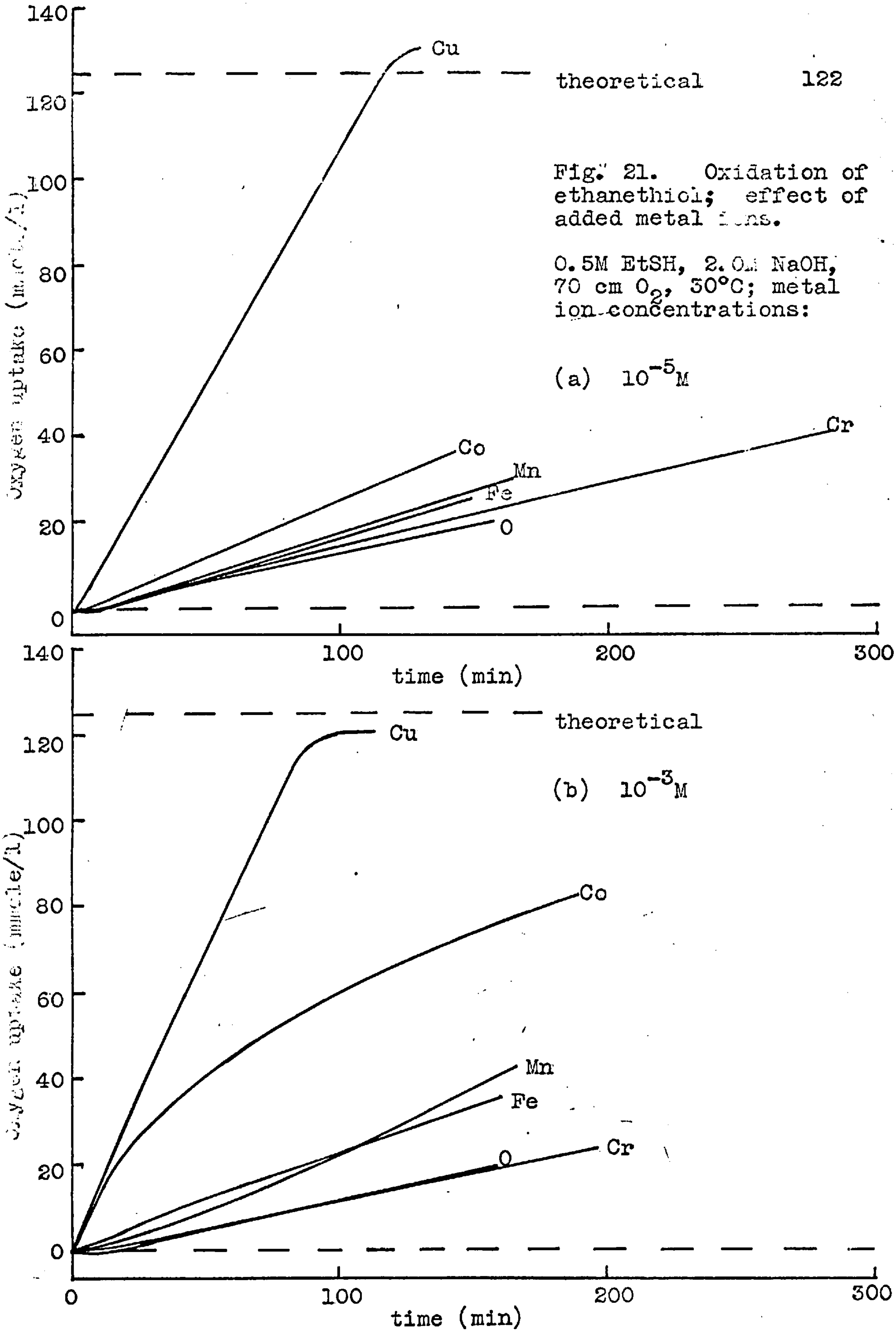


Fig. 21. Oxidation of ethanethiol; effect of added metal ions.

0.5M EtSH, 2.0M NaOH, 70 cm O_2, 30°C; metal ion concentrations:

(a) 10^{-5}M

(b) 10^{-3}M

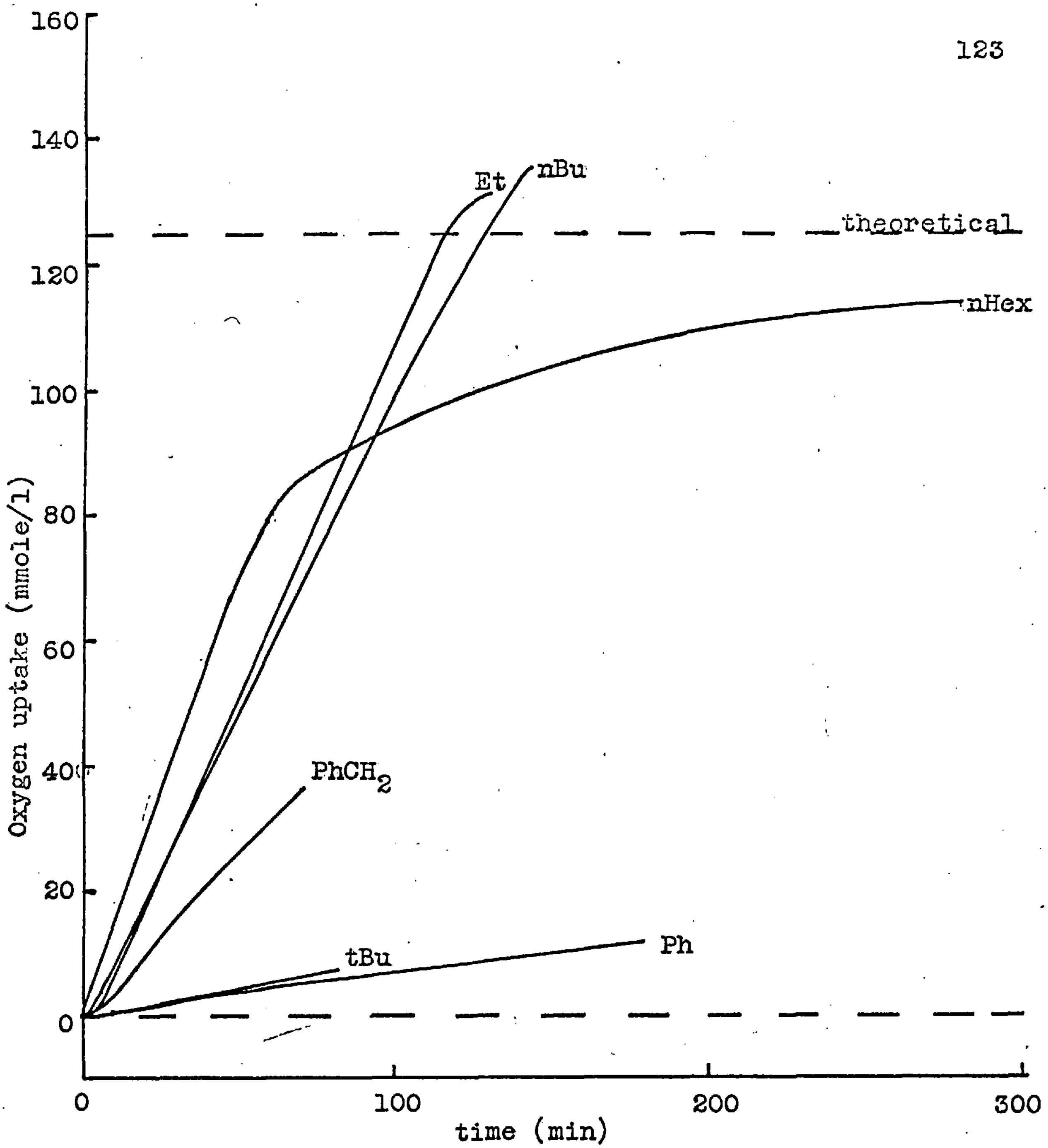


Fig. 22. Oxidation of various thiols in the presence of 10^{-5}M copper sulphate. 0.5 M RSH, 2.0 M NaOH, 70 cm O_2, 30°C.

3.221 Oxidation of ethanethiol in the presence of added copper sulphate

Graphs of oxygen-uptake versus time for two series of experiments with different concentrations of sodium hydroxide are reproduced in Figs. 23 and 24. The dependence of the rate of reaction upon the copper concentration is expressed graphically in Fig. 25. The various curves on the latter Figure are discussed in Sections 3.2212 and 4.21.

The product mixture from the single experiment with 10^{-2}M $CuSO_4$ was observed to contain a considerable quantity of a brown precipitate whose nature was not determined.

3.2211 Stoichiometry

The effect of copper sulphate was studied mainly from the kinetic viewpoint, and stoichiometric evidence consists chiefly of the final consumption of oxygen in reactions which were followed to completion. The results are given in Table 21.

3.2212 Effect of concentration of added copper sulphate and of sodium hydroxide

The effect of the concentration of added copper was shown by the uptake curves in Figs. 23 and 24, and more exactly in Fig. 25, in which the results of a number of sets of experiments have been plotted. The rates are shown as values of r/α, i.e. they have been corrected for variations

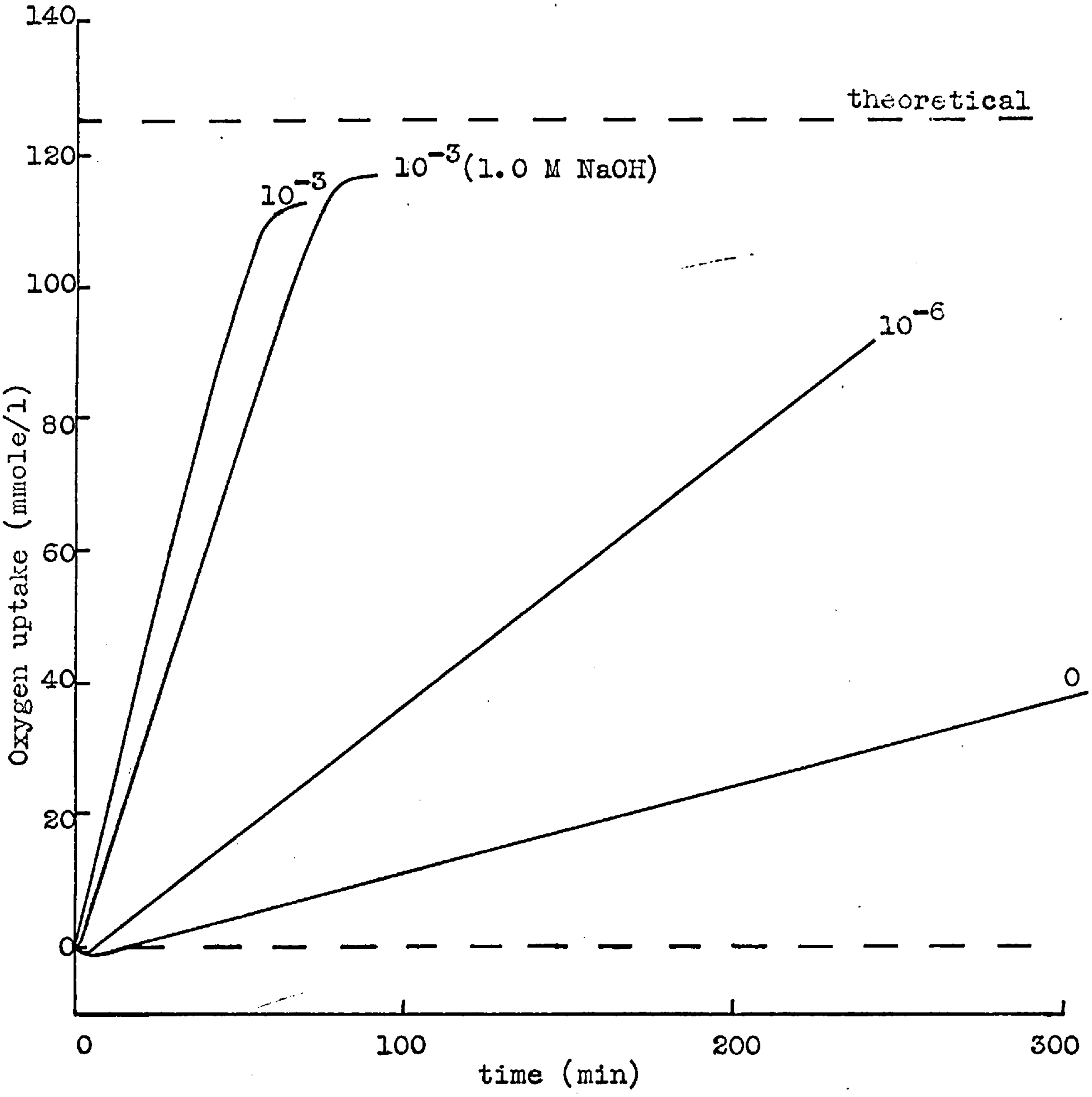


Fig. 23. Oxidation of ethanethiol: effect of added copper sulphate. 0.5 M EtSH, 0.6 M NaOH, 68 cm O_2, 30°C; Cu concn. beside curves.

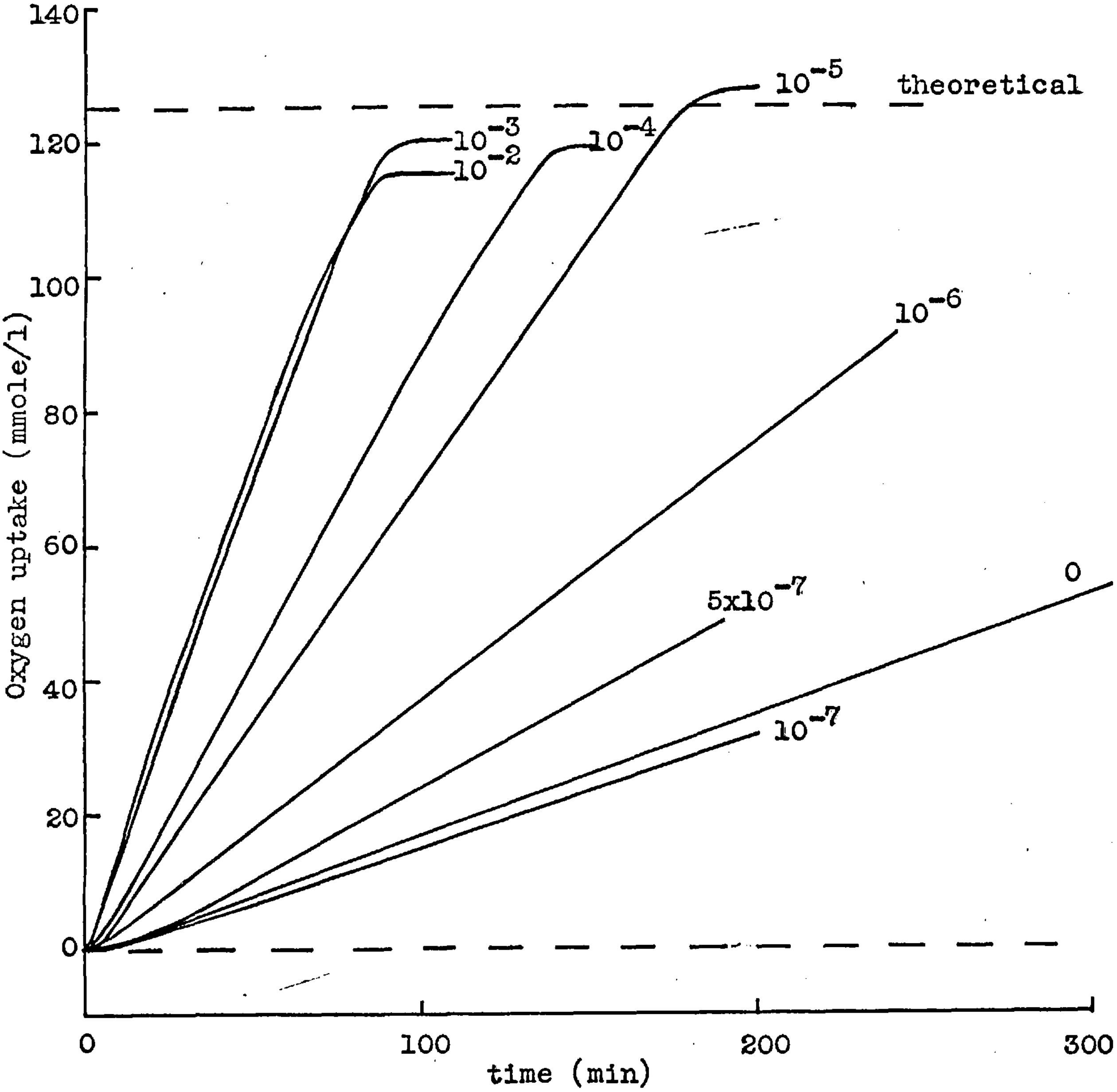


Fig. 24. Oxidation of ethanethiol: effect of added copper sulphate. 0.5 M EtSH, 2.0 M NaOH, 68 cm O_2, 30°C; Cu concentration beside curves.

Table 21. Oxidation of ethanethiol in presence of added 3.221 copper sulphate: final oxygen uptake in completed reactions. 0.5 M EtSH, 68 cm O_2, 30°C.

$CuSO_4$ concn. (M)	NaOH concn. (M)	en concn. (M)	EDTA concn. (M)	Final oxygen uptake (% theor.[a])
10^{-3}	0.6	-	-	90
10^{-3}	1.0	-	-	93
$2x10^{-3}$	1.0	-	-	100
10^{-5}	2.0	-	-	103, 101[b], 112[c]
10^{-4}	2.0	-	-	95
10^{-3}	2.0	-	-	96
10^{-2}	2.0	-	-	92
10^{-5}	2.0	0.1	-	102
10^{-5}	2.0	-	10^{-5}	107
10^{-5}	2.0	-	10^{-4}	113
10^{-5}	2.0	-	10^{-3}	111
10^{-5}	2.0	-	0.5	106
10^{-5} [d]	2.0	-	10^{-5} [d]	109

a - 100% is theoretical uptake for oxidation of thiol to disulphide.

b - Stepwise reduction in O_2 pressure from 72 to 60 cm.

c - Stepwise reduction in O_2 pressure from 49 to 34 cm.

d - Added 10^{-5}M Cu[EDTA].

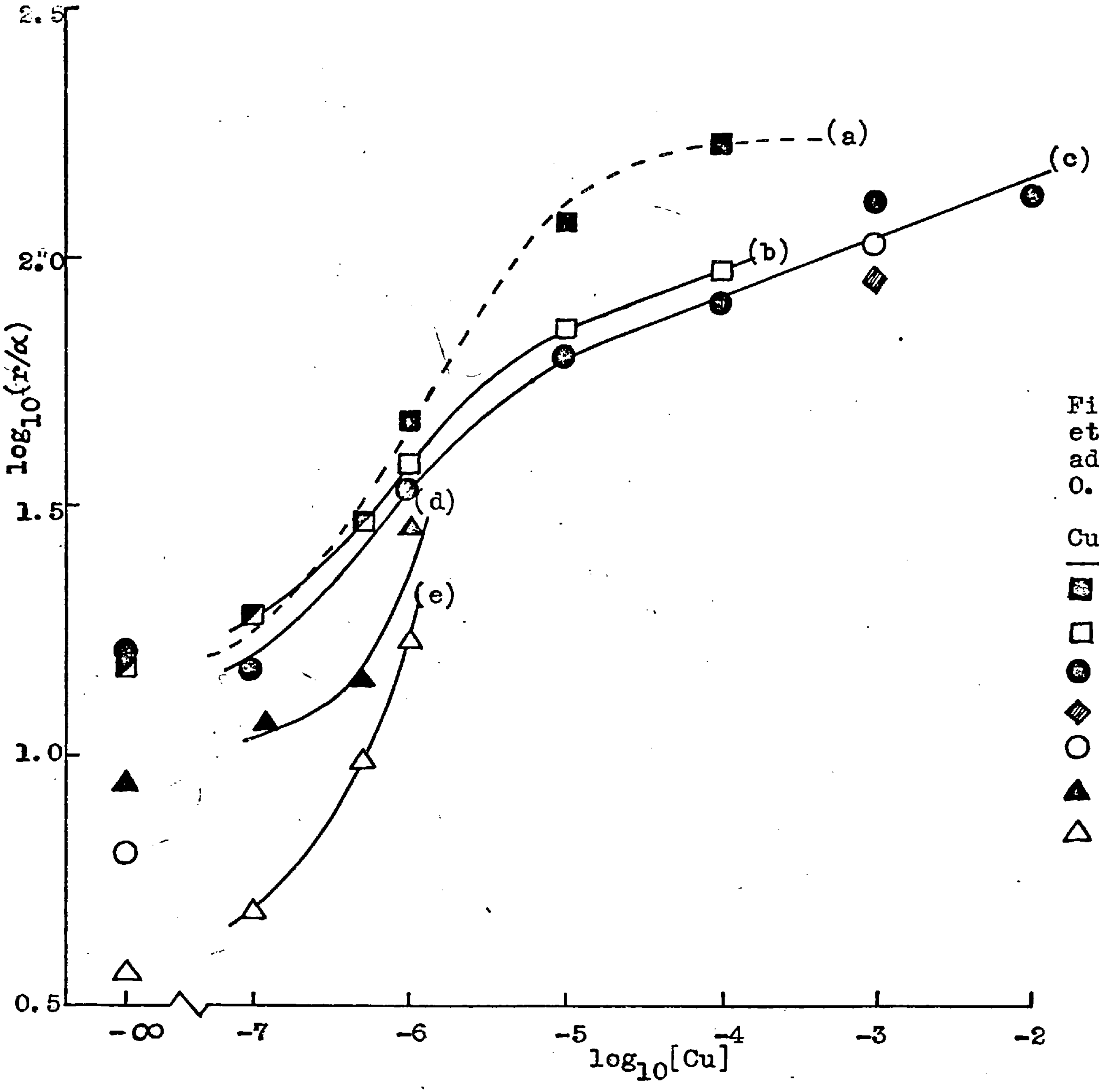


Fig. 25. Oxidation of ethanethiol: effect of added copper sulphate. 0.5 M EtSH, 70 cm O_2, 30°C.

Curve	NaOH concn.	Shaking rate	Soln. vol.
▩ (a)	2.0 M	400 cpm	30 ml
□ (b)	2.0	350	30
● (c)	2.0	360	50
◈	1.0	360	50
○	0.6	360	50
▲ (d)	2.0	350	50
△ (e)	0.6	350	50

in oxygen solubility with the concentration of alkali. The set of experiments presented in Fig. 24 forms curve (c) in Fig. 25. Curves (a) and (b) are from a set carried out with a smaller volume of reagent solution and a rate of shaking which was increased from medium (≈350 c.p.m.) to maximum (≈400 c.p.m.) at about 50% complete reaction. Curves (d) and (e) are later sets of reactions and reflect the lower rates of uncatalysed oxidation which had by then been attained.

3.2213 Effect of oxygen pressure

In one series of experiments with the copper-catalysed oxidation of ethanethiol the oxygen pressure was reduced stepwise at 50 min. intervals during the reaction. This method was possible because it had been shown that the reaction was zero-order in thiol, a roughly constant rate being maintained throughout a single kinetic run (q.v. Figs. 23 and 24). The dependence of the uptake rate on the oxygen pressure is shown in Fig. 26.

3.2214 Effect of temperature

A series of experiments with from 10^{-7}M to 10^{-6}M added $CuSO_4$ in 0.6 M and 2.0 M NaOH solution was carried out, and the temperature was increased stepwise from 30 to 50°C, as in Section 3.135. The graphs of oxygen-uptake versus time consisted of straight-line sections. The rates were corrected for oxygen solubility and values r/α and $(r-r_0)/\alpha$ (where

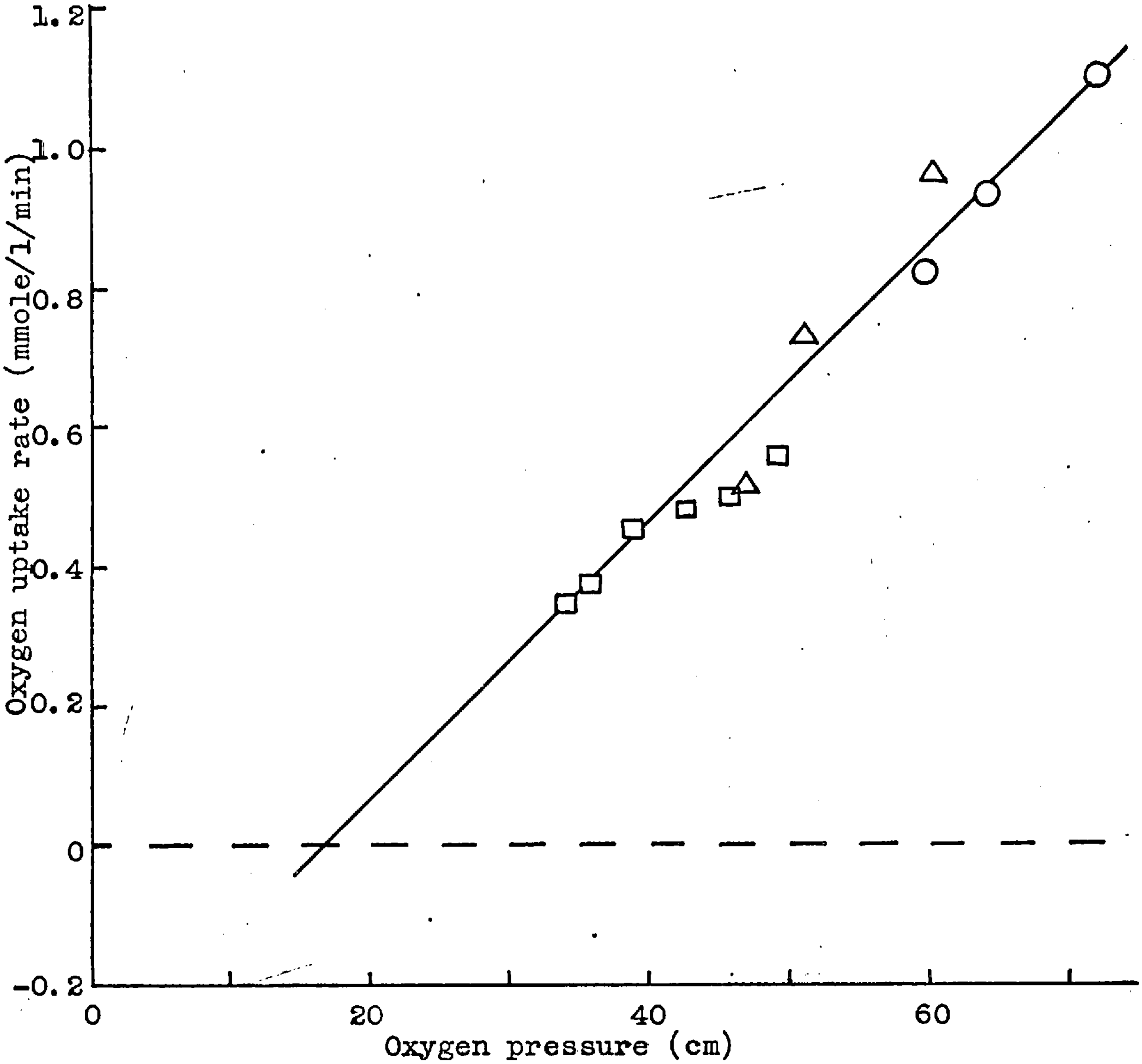


Fig. 26. Oxidation of ethanethiol in presence of copper sulphate: effect of oxygen pressure. 0.5 M EtSH, 2.0 M NaOH, 10^{-5} M $CuSO_4$, 30°C. The different symbols refer to three experiments.

r_0= the corresponding 'uncatalysed' rate) are given in Table 22. The values of $(r-r_0)/\alpha$ for the weaker alkali at all temperatures and for the stronger at 30°C show a reasonably good linear dependence on the added $CuSO_4$ concentration, and provide a value of $k'_0 \approx 7 \times 10^3$ $l.mole^{-1}.sec^{-1}$ at 30°C, where k'_0 is the rate constant for the equation: 3.2214

$$4(r-r_0) = k'_0[Cu][O_2][EtSH]^0 \qquad \text{(iii)}$$

and $[O_2]$ is based upon a gas pressure of 67-17 = 50 cm O_2, the correction of 17 cm being derived from Fig. 26.

Arrhenius plots of $\log(r/\alpha)$ and $\log(r-r_0)/\alpha$ versus $1/T$ were constructed. Few of these gave straight lines, and the values of the activation energy E_{a0} are therefore given separately for each temperature step in Table 23.

If the above value of k'_0 is taken together with the appropriate value of $E_{a0} \approx 10.6$ kcal/mole from Table 20, the equation[97]:

$$k'_0 = (kT/h)e^{-\Delta H^\ddagger/RT}e^{\Delta S^\ddagger/R} \qquad \text{(iv)}$$

where $\Delta H^\ddagger = E_{a0}-RT$, gives a value of $\Delta S^\ddagger = -8.1$ e.u.

3.2215 Effect of ethylenediamine

The effect of added ethylenediamine upon the rate of the copper-catalysed oxidation of ethanethiol is shown by the data in Table 24. The kinetic curves were all straight lines similar to those in Figs. 23 and 24. The last two rows in Table 24 show for comparison the effect of ethylenediamine on the uncatalysed rate of reaction.

Table 22. Oxidation of ethanethiol in the presence of low concentrations of added copper sulphate: effect of temperature upon the rate of reaction. 0.5 M EtSH, 67 cm O_2.

Corrected rate (mmole /1/min)	Temp. (°C)	Alkali concentration (M)							
		0.6				2.0			
		Added $CuSO_4$ concentration (M)							
		0	10^{-7}	$5x10^{-7}$	10^{-6}	0	10^{-7}	$5x10^{-7}$	10^{-6}
r/α	30	3.59	4.86	9.50	18.8	8.61	10.4	14.4	29.4
	40	8.91	12.2	19.35	34.5	21.4	20.6	28.0	52.0
	50	20.7	26.1	32.9	48.9	48.6	48.6	47.9	73.8
$\frac{r-r_0}{\alpha}$	30	0	1.27	5.91	13.4	0	1.8	5.8	20.8
	40	0	3.3	10.4	25.6	0	-0.8	6.6	30.6
	50	0	5.4	12.2	28.2	0	0	-0.7	25.2

Table 23. Oxidation of ethanethiol in the presence of added copper sulphate: values of the activation energy, E_{a0}, in kcal/mole: (1) for the observed total rates of reaction, r, (2) for the rates of reaction after subtracting the 'uncatalysed' rates, i.e. $(r-r_0)$. 0.5 M EtSH, 67 cm O_2.

	$CuSO_4$ concn. (M)	0.6 M NaOH		2.0 M NaOH	
		30 - 40°C	40 - 50°C	30 - 40°C	40 - 50°C
(1)	0	16.7	16.4	14.6	18.1
	10^{-7}	16.8	15.2	12.2	17.7
	$5x10^{-7}$	12.8	10.7	13.2	10.4
	10^{-6}	12.9	6.9	10.7	7.2
(2)	0	0	0	0	0
	10^{-7}	17.3	10.2	a	a
	$5x10^{-7}$	10.2	3.2	2.3	a
	10^{-6}	11.7	1.9	7.0	-3.9

a - Not calculated as $(r-r_0)$ very small.

Table 24. Oxidation of ethanethiol in the presence of added copper sulphate: effect of added ethylenediamine. 0.5 M EtSH, 2.0 M NaOH, 70 cm O_2, 30°C.

$CuSO_4$ concn. (M)	en concn. (M)	Rate (mmole/l/min)
10^{-5}	0	1.10
10^{-5}	0.1	0.804
10^{-5}	0.5	0.537
0	0	0.050
0	0.1	0.065

3.2216 Effect of ethylenediaminetetracetic acid 3.2216

Experiments were made to investigate the effect of added ethylenediaminetetracetic acid (EDTA) upon the oxidation of ethanethiol in the presence of added copper sulphate. In further experiments the copper and EDTA were added as a solution of the complex Cu[EDTA]. The resulting kinetic curves, reproduced in Fig. 27, show that the reactions were autocatalytic over a large part of the oxidation: this feature was not observed in the absence of EDTA. The broken line on one curve is conjectural owing to a break in readings. The reaction rates are given in Table 25.

Table 25. Oxidation of ethanethiol in the presence of added copper sulphate: effect of added EDTA. 0.5 M EtSH, 2.0 M NaOH, 71 cm O_2, 30°C.

$CuSO_4$ concn. (M)	EDTA concn. (M)	Oxygen uptake rate (mmole/l/min) Initial (approx.)	Maximum
10^{-5}	0	1.10	1.10
10^{-5} a	10^{-5} a	1.00	1.08
10^{-5}	10^{-5}	0.68	0.80
10^{-5}	10^{-4}	0.51	0.57
10^{-5}	10^{-3}	1.00	1.08
10^{-5}	0.5	0.86	0.88
0	0	0.10	0.059
0	10^{-3}	0.21	0.200

a - Added as Cu[EDTA].

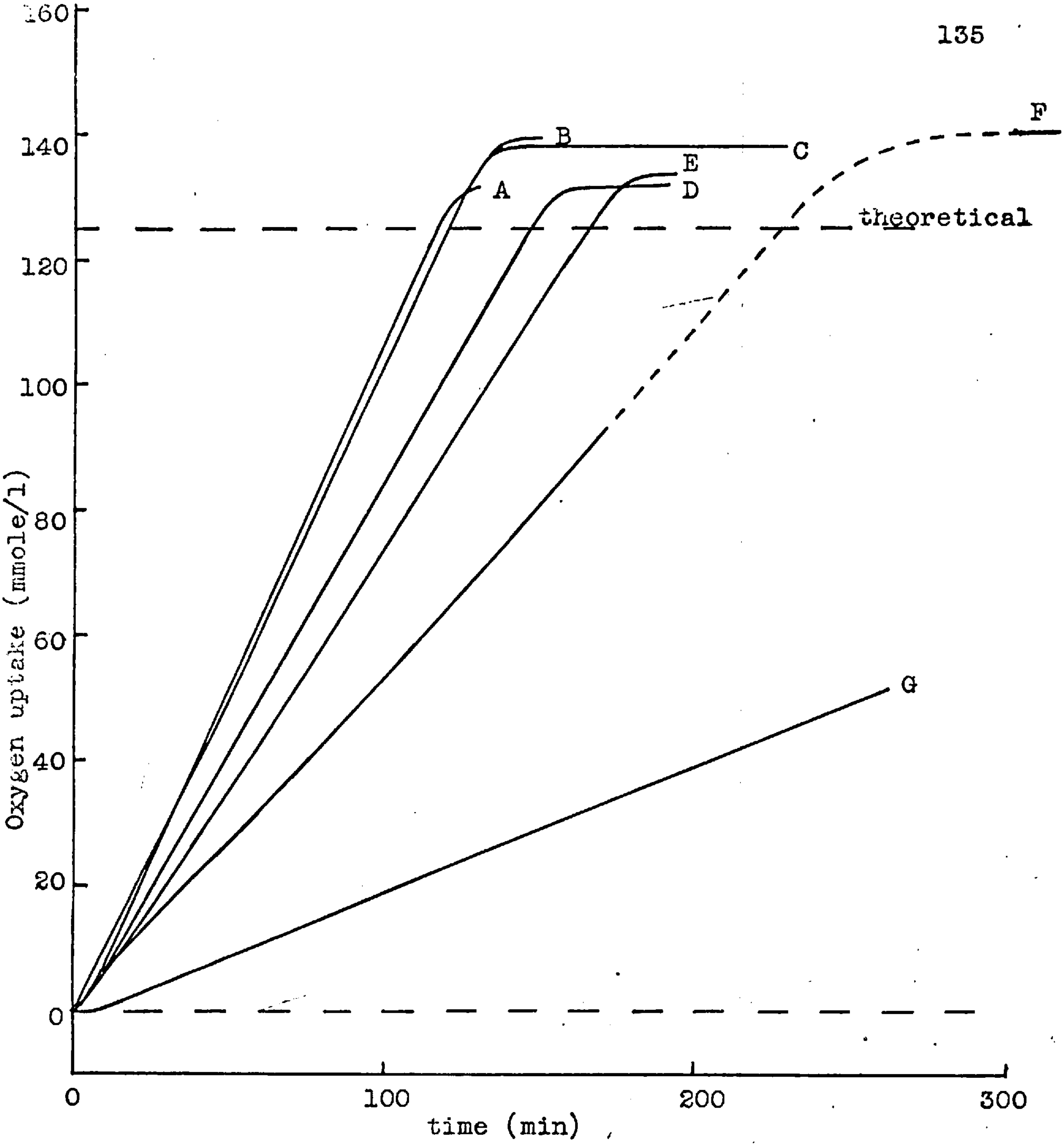


Fig. 27. Oxidation of ethanethiol in presence of added copper sulphate: effect of EDTA. 0.5 M EtSH, 2.0 M NaOH, 71 cm O_2, 30°C, 10^{-5}M $CuSO_4$ except B and G.

A - no EDTA; B - 10^{-5}M Cu[EDTA] added as complex; C - 10^{-3}M EDTA; D - 0.5 M EDTA; E - 10^{-5}M EDTA; F - 10^{-4}M EDTA; G - no Cu, 10^{-3}M EDTA.

4.2217 Effect of cyanide

A single experiment was made to find the effect of added potassium cyanide upon the oxidation of ethanethiol in the presence of 10^{-5}M added copper sulphate. The results of this and three other experiments with added cyanide are collected in Table 26.

The products from the copper-cyanide run were analysed after 1125 min of reaction by the standard procedure, except that the mixture was first poured into 25 ml of 0.25 M ferrous ammonium sulphate solution, which was then acidified, precipitating the cyanide as Prussian blue. The results of analyses for thiol and disulphide are given in Table 27.

3.222 Oxidation of other thiols in the presence of added copper sulphate: effect of temperature

The copper-catalysed oxidation of thiols other than ethanethiol was studied only under the standard conditions of 10^{-5} M added $CuSO_4$ in 2.0 M sodium hydroxide, and the results have been presented in Fig. 22. The reactions with thiophenol and t-butanethiol were continued with stepwise increase in temperature in order to estimate the energies of activation. The results are given in Table 28.

The rates, $(r-r_0)$, obtained for the two thiols with 10^{-5}M added $CuSO_4$ at 30°C correspond to values of $k_0' = 80$ $1.mole^{-1}sec^{-1}$ for thiophenol and $k_0' = 132$ $1.mole^{-1}sec^{-1}$ for t-butanethiol, where k_0' is given by the rate equation:

$$4(r-r_0) = k_0'[Cu][O_2][EtSH]^0 \qquad \text{(iii)}$$

Table 26. Oxidation of ethanethiol in the presence of potassium cyanide. 0.5 M EtSH, 2.0 M NaOH, 71 cm O_2, 30°C. 4.2217

Additives and concns.	Uptake (mmole/l)		End of expt.		Mean rate
	at 60 min	at 120 min	Time (min)	Uptake (mmole/l)	(mmole/l /min)
0.25 M KCN	0	0	1092	14.6	<0.015
10^{-5} M $CuSO_4$, 0.25 M KCN	0	1.2	1125	20.2	0.019
10^{-3} M $CoSO_4$, 0.25 M KCN	0.8	5.3	1255	46.4	0.038
0.25 M KCN	3.3	7.4	-	-	0.066
None [a]	5.8	13.6	294	33.1	0.12
10^{-5} M $CuSO_4$ [a]	62.9	128.1	130	131.0	1.1
10^{-3} M $CoSO_4$ [a]	39.2	57.9	150	65.9	1.06→0.26

a - Experiments without added cyanide for comparison.

Table 27. Oxidation of ethanethiol in presence of added copper and cyanide: final product analyses. 0.5 M EtSH, 2.0 M NaOH, 71 cm O_2, 30°C.

Time (min)	Oxygen uptake (mmole/l /min)	EtSH concn. (M)	Et_2S_2 concn. (M)	Reagents consumed (%[a])		Disulphide produced (%[a])
				O_2	EtSH	
1125	20.2	0.43	-0.01	16	14	Nil

a - 100% is theoretical for oxidation of thiol to disulphide.

Table 28. Oxidation of thiols in the presence of added copper sulphate: effect of temperature. 0.5 M RSH, 2.0 M NaOH, 70 cm O_2.

Thiol	Temp. (°C)	Total reaction			Cu - cat. reaction [a]		
		r (mmole /l/min)	r/α	E_a^0 (kcal /mole)	$(r-r_0)$ (mmole /l/min)	$(r-r_0)/\alpha$	E_a^0 (kcal /mole)
PhSH	30.0	0.060[b]	5.3	16.4	0.031	2.8	8.0
	40.0	0.128	13.15		0.042	4.3	
t-BuSH	30.1	0.055[b]	4.9	-3.2	0.050	4.4	-10.5
	39.5	0.041	4.1	-9.3	0.026	2.6	-
	47.9	0.026	2.9		-0.020	-2.2	

a - r_0 ('uncatalysed' rate) obtained from Tables 18 (PhSH) and 17 (t-BuSH).

b - These rates are rather lower than in Table 20 because rates decreased slightly with time.

3.23 Effect of added cobalt sulphate on the oxidation of thiols 3.23

The graphs of oxygen-uptake versus time for the oxidation of six thiols in the presence of 10^{-3}M added cobalt sulphate are shown in Fig. 28. The uptake curves in the faster reactions were found to follow a rate law which was first order in thiol with a fairly abrupt change of rate constant k_1 (see Section 3.2311). The slower reactions with phenylmethanethiol, n-butanethiol, and possibly thiophenol also showed a change in rate at low extents of reaction, but the experiments were not taken far enough for the order to be certain, and the straight lines on the graph fitted the points as well as any curve. The initial rates of reaction in the absence and presence of 10^{-3}M added cobalt sulphate are compared in Table 29, which also shows the values of k_1 before and after any change (i.e. initial and final k_1).

Those hydroxide solutions with more than about 10^{-4}M added cobalt were all found to contain a brown precipitate before injection of thiol to start the run. All the product mixtures from the cobalt-catalysed oxidations, except those from t-butanethiol and thiophenol, were found to contain some deep red solid product suspended in the disulphide layer. Some experiments made to discover the nature of this product are described in Section 3.233.

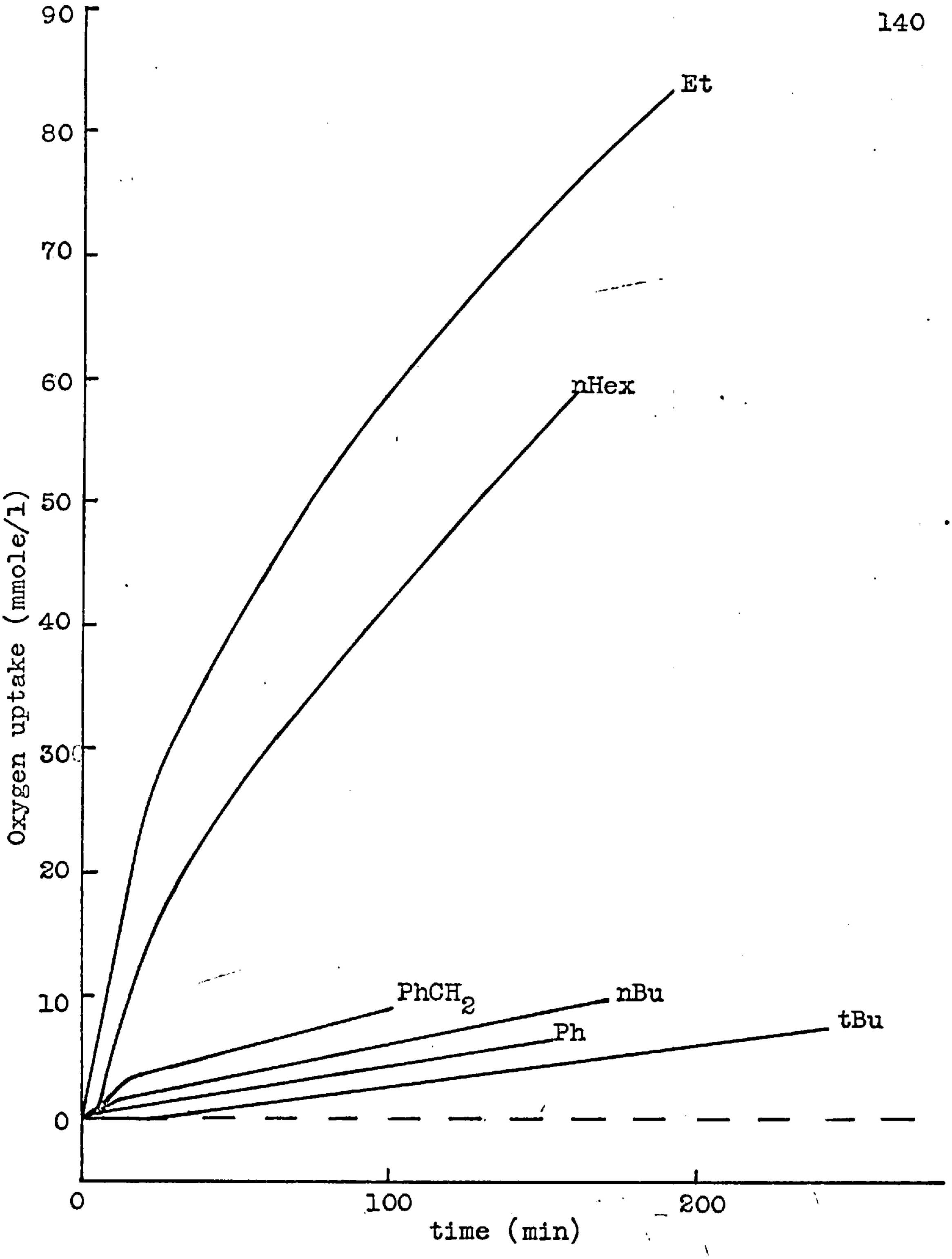


Fig. 28. Oxidation of various thiols in the presence of 10^{-3}M cobalt sulphate. 0.5 M RSH, 2.0 M NaOH, 70 cm O_2, 30°C.

Table 29. Oxidation of thiols in the presence of added cobalt sulphate. 0.5 M RSH, 2.0 M NaOH, 10^{-3}M $CoSO_4$, 70 cm O_2, 30°C.

Thiol	Initial rate (mmole/l/min)		Initial rate ratio	Results with $CoSO_4$ present			
				k_1 change obs. at		k_1 x 10^3 (min^{-1})	
	$CoSO_4$ absent	$CoSO_4$ present	Co pres /Co abs	time (min)	O_2 uptake (mmole/l)	Initial	Final
EtSH	0.10	1.1	11	22	25	10.8	5.2
n-BuSH	0.10	0.15	1.5	20	3	0.7	0.4
n-HexSH	0.166	0.85	5	23	15	7.1	3.6
t-BuSH	0.006	0.035	6	-	-	0.3	0.3
PhSH	0.029	0.06	2.1	10	1	0.5	0.3
$PhCH_2SH$	0.0859	0.27	3.1	11	3	2	0.6

3.231 Oxidation of ethanethiol in the presence of added cobalt sulphate

The oxygen-uptake versus time curves for a series of experiments with ethanethiol in the presence of a range of concentrations of added cobalt sulphate are shown in Fig. 29. The product mixtures from 10^{-4}, 10^{-3}, and 10^{-2}M added $CoSO_4$ contained the deep red product in the disulphide layer, and in the case of 10^{-2}M Co this had coagulated into a single large lump.

3.2311 Effect of the concentrations of ethanethiol, added cobalt sulphate, and alkali

Assuming the stoichiometry of oxidation of thiol to disulphide, the oxygen-uptake values shown in Fig, 29 were converted to thiol concentrations. Some of the resulting curves of log[EtSH] versus time are drawn in Fig. 30, and show first order kinetics in thiol. The results with 10^{-3}M added $CoSO_4$ show a change in the first-order rate constant k_1 20-40 min after the start of reaction: this was found to be a reproducible feature. Numerical details of these experiments are given in Table 30.

3.2312 Effect of oxygen pressure

The results of three experiments with different pressures of oxygen are shown in Table 31. Both the initial and final rates of oxygen uptake increased approximately linearly with the oxygen pressure.

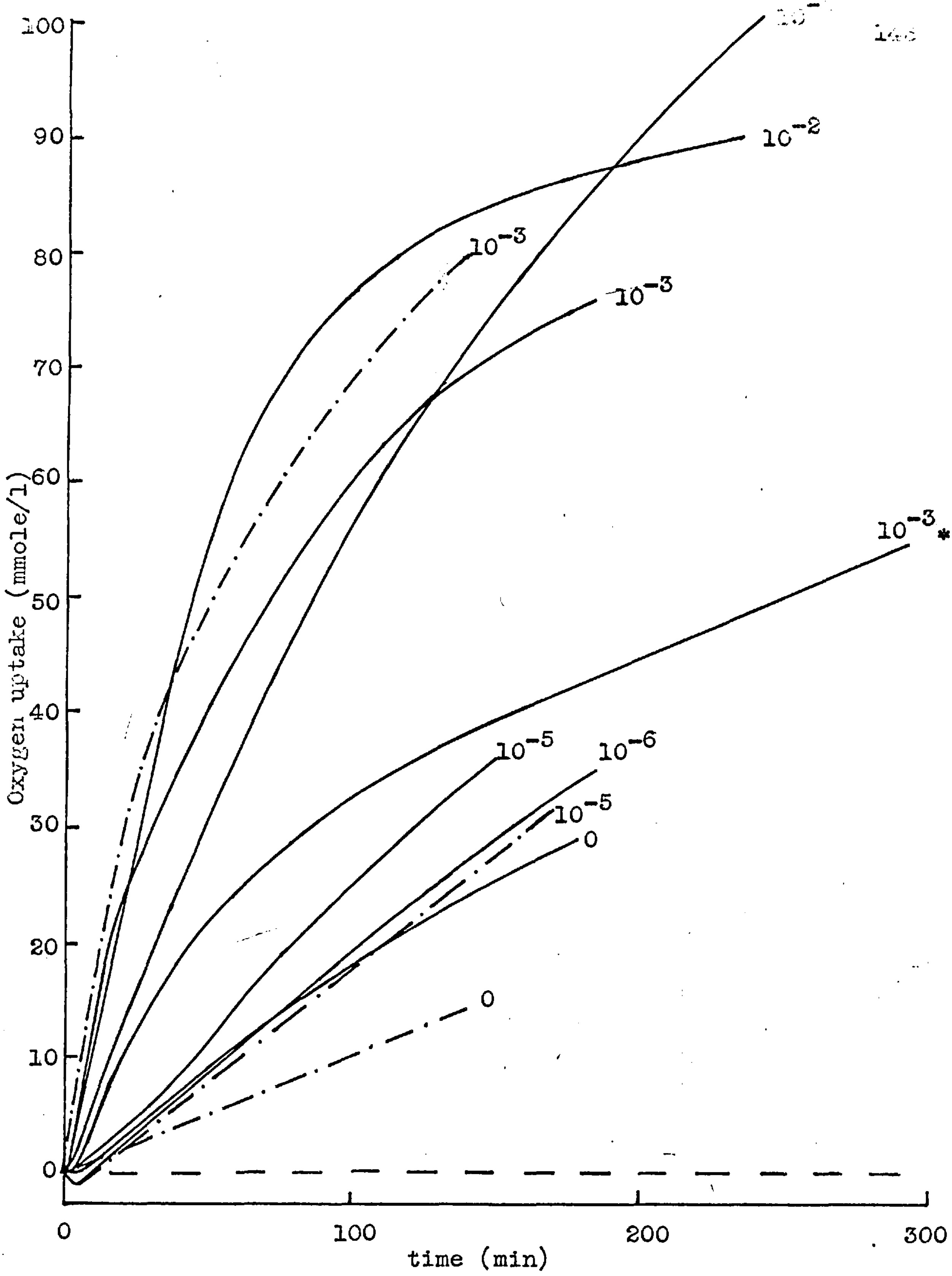


Fig. 29.
Oxidation of ethanethiol: effect of added cobalt sulphate.
0.5 M EtSH, 70 cm O_2, 30°C; Co concentrations beside curves.
—·— 0.6 M NaOH; ——— 2.0 M NaOH. * 0.28M init. EtSH.

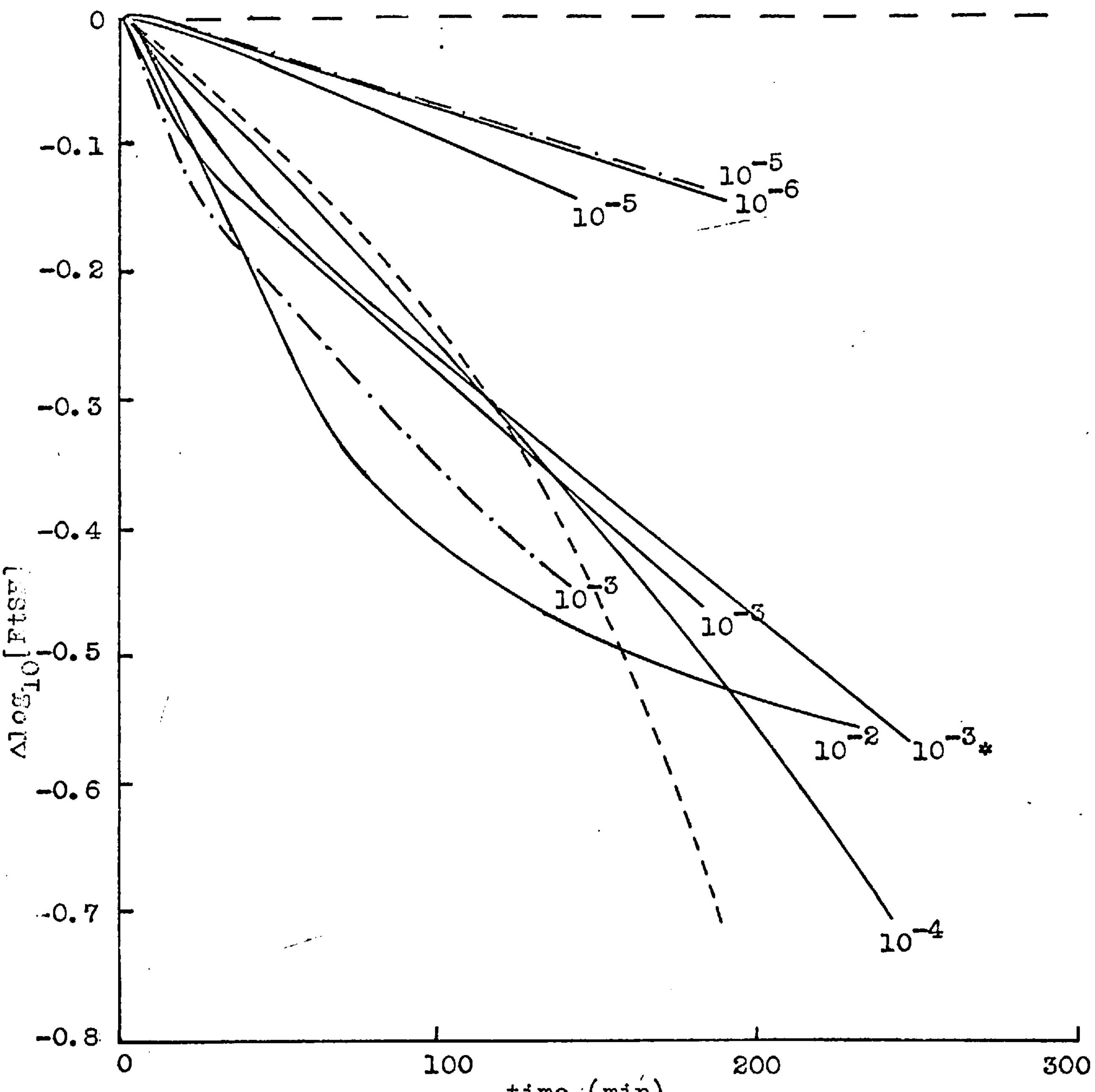


Fig. 30. Oxidation of ethanethiol in presence of added cobalt sulphate: effect of consumption of thiol. Graph of $\Delta\log_{10}[EtSH] = \log_{10}[EtSH]_t - \log_{10}[EtSH]_{t=0}$ vs. time. 70 cm O_2, 30°C; 0.5 M EtSH except *, 0.28 M.

—·— 0.6 M NaOH, ——— 2.0 M NaOH; – – – – theoretical zero-order curve.

. S.2311

Table 30. Oxidation of ethanethiol in the presence of added cobalt sulphate: dependence of k_1 upon reagent concentrations. 70 cm O_2, 30°C.

EtSH concn. (M)	NaOH concn. (M)	$CoSO_4$ concn. (M)	k_1 change obs. at Time (min)	Uptake (mmole/l)	$k_1 \times 10^3$ (min^{-1})[a]	$(k_1-k_{1,0}) \times 10^3$ (min^{-1})[b]	$(k_1-k_{1,0}) \times 10^3/\alpha$ (min^{-1})
0.5	0.6	0	-	-	$1.0=k_{1,0}$	0	0
0.5	0.6	10^{-5}	-	-	1.8	0.8	39
0.5	0.6	10^{-3}	21	31	13.2,6.6[c]	12.2,5.6	595,273
0.5	2.0	0	-	-	$1.5=k_{1,0}$	0	0
0.5	2.0	10^{-6}	-	-	1.9	0.4	35
0.5	2.0	10^{-5}	-	-	2.5	1.0	88
0.5	2.0	10^{-4}	--	-	6.1	4.6	404
0.5	2.0	10^{-3}	23	26	10.8,5.2[d]	9.3,3.7	816,325
0.28	2.0	10^{-3}	47	21	9.0,4.6	8.0,3.6[e]	702,316
0.5	2.0	10^{-2}	65	64	12.2,4.1	10.7,2.6[f]	929,228

a - Where two values are given, these refer to rates before and after the change in k_1.

b - $k_{1,0}$ is the value of k_1 in the absence of added cobalt.

c - $k_1/\alpha = 6.5,3.2 \times 10^{-5}$ min^{-1}.

d - $k_1/\alpha = 9.6,4.6 \times 10^{-5}$ min^{-1}.

e - $k_{1,0}$ taken as 1.0×10^{-3} min^{-1} due to lower initial thiol concentration (see Fig. 8).

f - k_1 (final) decreased with time.

Table 31. Oxidation of ethanethiol in the presence of added cobalt sulphate: effect of oxygen pressure. 0.5 M EtSH, 2.0 M NaOH, 30°C, 10^{-3}M $CoSO_4$. 3.2312

Oxygen pressure (cm)	k_1 change observed at Time (min)	O_2 uptake (mmole/l)	$k_1 \times 10^3$ (min^{-1}) Initial	Final
38	100	26	1.5	0.44
51	40	25	5.6	2.0
68	22	25	10.8	5.2

Table 32. Oxidation of ethanethiol in the presence of added cobalt sulpnate: effect of additives. 0.5 M EtSH, 2.0 M NaOH, 70 cm O_2, 30°C, 10^{-3}M $CoSO_4$.

Additive and concn. (M)	k_1 change observed at Time (min)	O_2 uptake (mmole/l)	$k_1 \times 10^3$ (min^{-1}) Initial	Final
0	22	25	10.8	5.2
0.5 M Et_2S_2 [a]	70	38	5.6	4.9
10^{-3}M EDTA	70	60	10.8	5.9
10^{-2}M EDTA	65	62	10.8	8.0
0.1 M EDTA	20	13	5.4	4.7
0.1 M en	-	-	0.42	
0.25 M KCN	125	6	0.6	0.38

a - Only partially dissolved.

3.2313 Effect of added diethyl disulphide

The first-order graph for one experiment with added diethyl disulphide is shown in Fig. 31. The results are compared with those in the absence of added disulphide in Table 32.

3.2314 Effect of ethylenediaminetetracetic acid

The effect of adding various concentrations of EDTA is shown in Fig. 31, and the rate constants are listed in Table 32. The cobalt-EDTA-alkali solutions were quite clear, and were pale pink or violet which deepened when the thiol was added. The product mixtures all contained the red precipitate.

The experiments in this group were the only cobalt-catalysed reactions which were followed to apparent completion, and oxygen uptakes of 105, 104, and 116% of theoretical for conversion of thiol to disulphide were obtained with 10^{-3}, 10^{-2}, and 0.1 M EDTA respectively.

3.2315 Effect of ethylenediamine

The effect of 0.1 M ethylenediamine on the oxidation of ethanethiol in the presence of cobalt is shown in Table 32, where a value of k_1 is given. However, after 240 min the oxygen uptake was only 7.1% of theoretical for conversion of thiol to disulphide, and the order of reaction was therefore not clear. No coloured product was found.

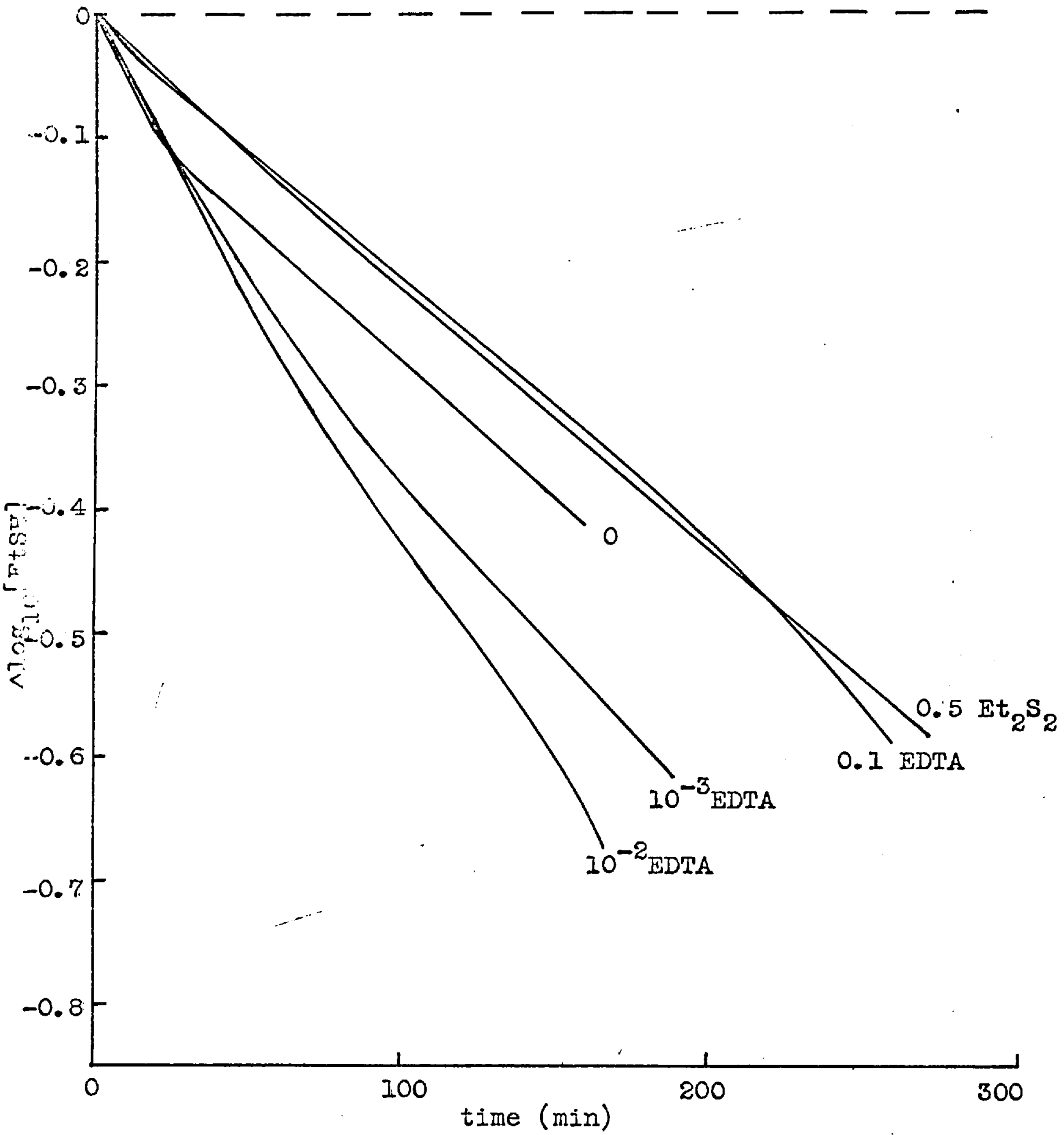


Fig. 31. Oxidation of ethanethiol in presence of added cobalt sulphate: effect of added diethyl disulphide and EDTA. Graph of $\Delta\log_{10}[\text{EtSH}] = \log_{10}[\text{EtSH}]_{t=t} - \log_{10}[\text{EtSH}]_{t=0}$ vs. time. 0.5 M EtSH, 2.0 M NaOH, 70 cm O_2, 30°C; additive concentrations (M) beside curves.

3.2316 Effect of cyanide

In an experiment with added 0.25 M potassium cyanide, the catalytic effect of cobalt was again found to be suppressed. A value of k_1 is given in Table 32, but the order of reaction was not clear. No coloured product was observed.

3.232 Oxidation of t-butanethiol in the presence of added cobalt sulphate: effect of temperature

Attempts to measure the energy of activation for the oxidation of thiols in the presence of added cobalt sulphate were made only in the case of t-butanethiol. Stepwise increase in temperature from 30.5 to 40.8°C increased the rate from 0.035 to 0.046 mmole/l/min, which after correcting for the decrease in oxygen solubility in 2.0 M aqueous NaOH solution, gave an activation energy, $E_{a0} = 7.6$ kcal/mole.

3.233 Identity of red products

As noted in Sections 3.23 and 3.231, the oxidation of several thiols with 10^{-3}M $CoSO_4$ produced deep red products apparently suspended in the disulphide phase in the product mixture and which separated with it into an upper layer on standing. The product was insoluble in water, and formed red suspensions (which separated very slowly to the surface) with trichlorethylene and carbon tetrachloride. It adhered tenaciously to the walls of glass vessels and seemed to be most easily removed with disulphide. It was insoluble in ammonia and dilute nitric acid but was dissolved slowly by 1:1 nitric acid to give a pale green solution. 3.233

A series of experiments was conducted to discover the nature of this precipitate. It was found to be formed in systems containing cobalt ions, diethyl disulphide, and aqueous sodium hydroxide only if ethanethiol was present. In the absence of the latter a blue coloration was produced on adding the $CoSO_4$, and a brown precipitate slowly formed. The latter was much less red, went to the bottom of the solution, and was not absorbed into the disulphide layer. When 10^{-3}M $CoSO_4$ was added to a partially (15%) oxidised solution of 0.5 M ethanethiol in 2 M sodium hydroxide, the solution immediately became blue, but the red precipitate was f~~ro~~ormed in about 15 min and appeared to be identical with the product from cobalt-catalysed oxidations.

Similar experiments were carried out with the alternative reductant formaldehyde replacing the thiol. A little formaldehyde prolonged the blue coloration, and pink and violet solutions were obtained with excess: however all the solutions slowly turned green and gave the brown precipitate.

The products from the oxidation of ethanethiol in the presence of 10^{-2}M added cobalt were transferred to a separating funnel, and the aqueous phase removed. The non-aqueous phase included a large lump of coagulated red product. This was broken up by the addition of 25 ml trichlorethylene, and the suspension filtered under gravity through a .. 3.24 sintered glass disc. The red solid was collected and dried to constant weight in a vacuum desiccator. About 120 mg of the solid remained, and half of this was analysed for elements. The result was: Co, 20.9 %; S, 25.64%; C, 27.55%; H, 5.76%. This corresponds to the empirical formula $CoS_{2.25}C_{6.49}H_{16.3}O_{3.56}$ if the unanalysed residue to 100% is taken as oxygen.

The remainder of the sample was used for magnetic susceptibility measurements. The material was found to be only very slightly paramagnetic, and it was concluded that it was a diamagnetic Co(III) ($3d^8$) complex with traces of Co(II) as impurity.

3.24 Oxidation of ethanethiol in the presence of added ferrous sulphate

The catalytic effect of added ferrous sulphate was investigated only with ethanethiol. The kinetic curves are shown in Fig. 32. The rate (0.18 mmole/l/min) of the blank run in the series with the stronger alkali is probably much too high. The experiments with 10^{-4} and 10^{-3}M added $FeSO_4$ in 2.0 M NaOH solution show a change in rate similar to those found with added cobalt sulphate: the products from these runs contained a brown precipitate. Details of these series of experiments are given in Table 33.

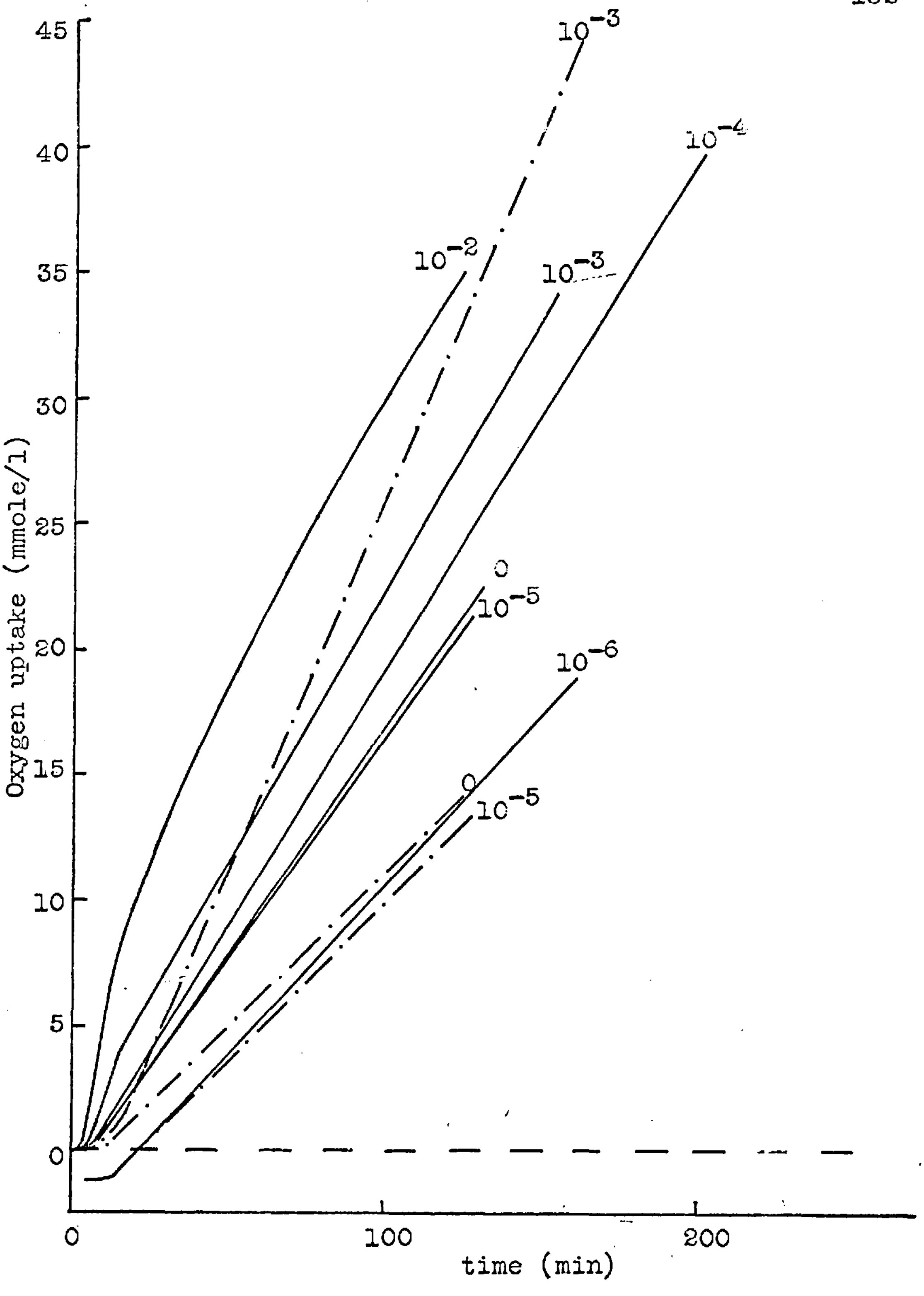


Fig. 32. Oxidation of ethanethiol: effect of added ferrous sulphate. 0.5 M EtSH, 67 cm O_2, 30°C; $FeSO_4$ concentrations (M) beside curves.

—·— 0.6 M NaOH, ——— 2.0 M NaOH.

Table 33. Oxidation of ethanethiol in the presence of added ferrous sulphate. 0.5 M EtSH, 67 cm O_2, 30°C. 3.24

NaOH concn. (M)	$FeSO_4$ concn. (M)	Rate-change obs. at		Rate (mmole/l/min)	
		Time (min)	O_2 uptake (mmole/l)	Initial	Final
0.6	0	-	-	0.12	
0.6	10^{-5}	-	-	0.12	
0.6	10^{-3}	-	-	0.30 [a]	
2.0	0	-	-	0.18	
2.0	10^{-6}	-	-	0.13	
2.0	10^{-5}	-	-	0.18	
2.0	10^{-4}	-	-	0.21	
2.0	10^{-3}	16	4	0.35	0.21 [b]
2.0	10^{-2}	15	8	0.69 [c]	0.22 [c]

a - r/α = 14.7 mmole/l/min.

b - r/α = 18.4 mmole/l/min.

c - $k_1 = 5.7,\ 2.1 \times 10^{-3}\ \text{min}^{-1}$.

3.25 Oxidation of ethanethiol in the presence of added manganese sulphate

The effect of added manganese sulphate upon the oxidation of ethanethiol is shown in Fig. 33. In 2.0 M sodium hydroxide the kinetics were zero order in thiol, the reaction with 10^{-3}M $MnSO_4$ being apparently autocatalytic. The two runs with 0.6 M alkali were first order, that with 10^{-3}M manganese showing a change in k_1. Details of the results are given in Table 34. The products from the experiments with 10^{-3}M added $MnSO_4$ contained a brown precipitate.

Table 34. Oxidation of ethanethiol in the presence of added manganese sulphate. 0.5 M EtSH, 67 cm O_2, 30°C.

NaOH concn. (M)	$MnSO_4$ concn. (M)	Rate (mmole/l/min) Initial	Rate (mmole/l/min) Final
0.6	0	0.10	
0.6	10^{-5}	0.18^{a}	0.11^{a}
0.6	10^{-3}	0.51^{b}	0.18^{b}
2.0	0	0.13	
2.0	10^{-5}	0.19	
2.0	10^{-4}	0.18	
2.0	10^{-3}	0.19	0.29

a - $k_1 = 1.23 \times 10^{-3}$ min^{-1} (one value only).

b - $k_1 = 4.4,\ 2.4 \times 10^{-3}$ min^{-1}.

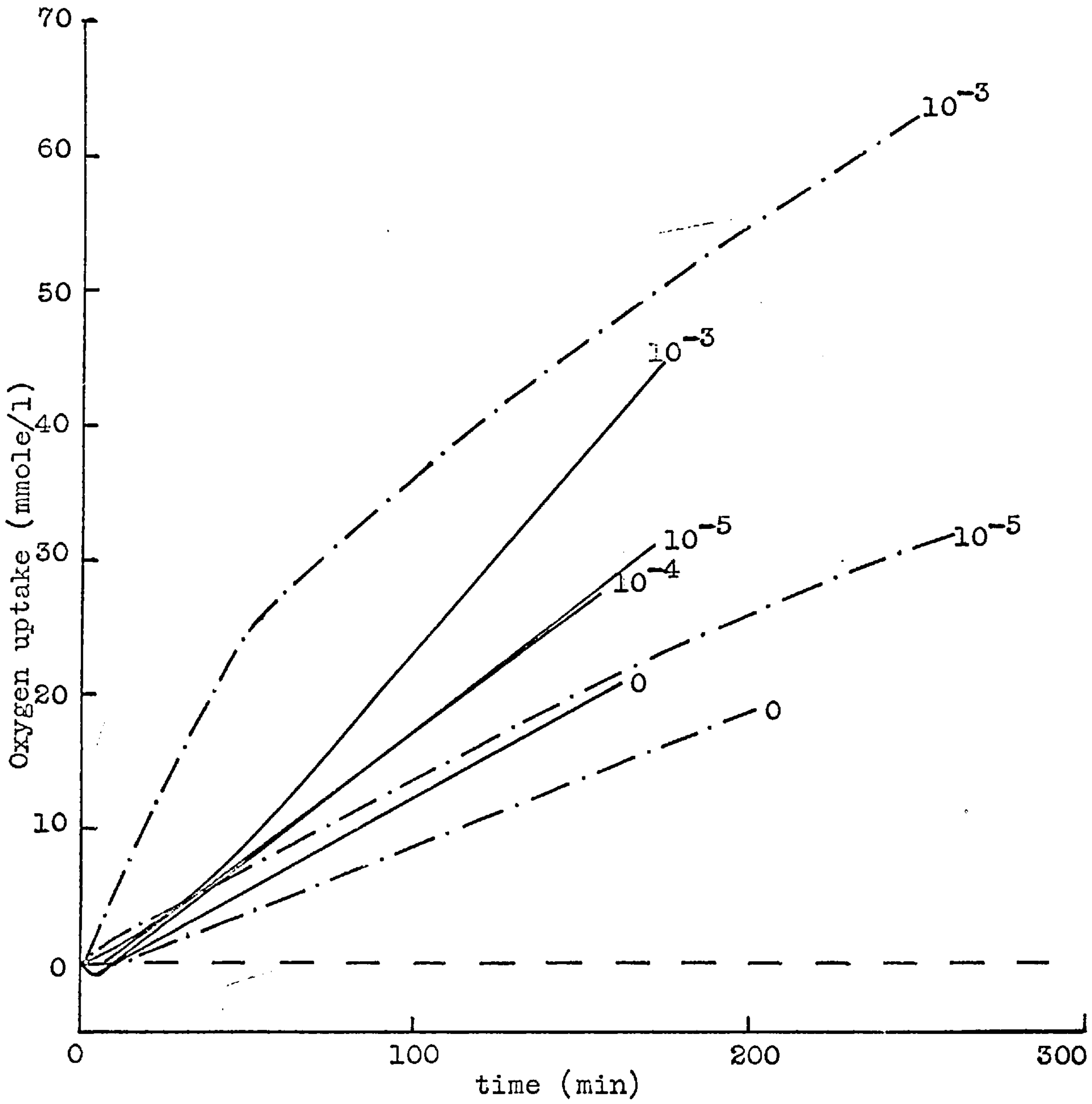


Fig. 33. Oxidation of ethanethiol: effect of added manganous sulphate. 0.5 M EtSH, 67 cm O_2, 30°C; $MnSO_4$ concentrations (M) beside curves.

—·— 0.6 M NaOH, ——— 2.0 M NaOH.

4.26 Oxidation of ethanethiol in the presence of added chrome alum

The results of experiments with added chrome alum are given in Fig. 34 and Table 35. The catalytic effect was extremely small.

Table 35. Oxidation of ethanethiol in the presence of added chrome alum. 0.5 M EtSH, 68 cm O_2, 30°C.

NaOH concn. (M)	Chrome alum concn. (M)	Rate (mmole/l/min)
0.6	0	0.10
0.6	10^{-5}	0.11
0.6	10^{-3}	0.11
2.0	0	0.13
2.0	10^{-5}	0.25, 0.14[a]
2.0	10^{-3}	0.12

a - Faster reaction briefly near start.

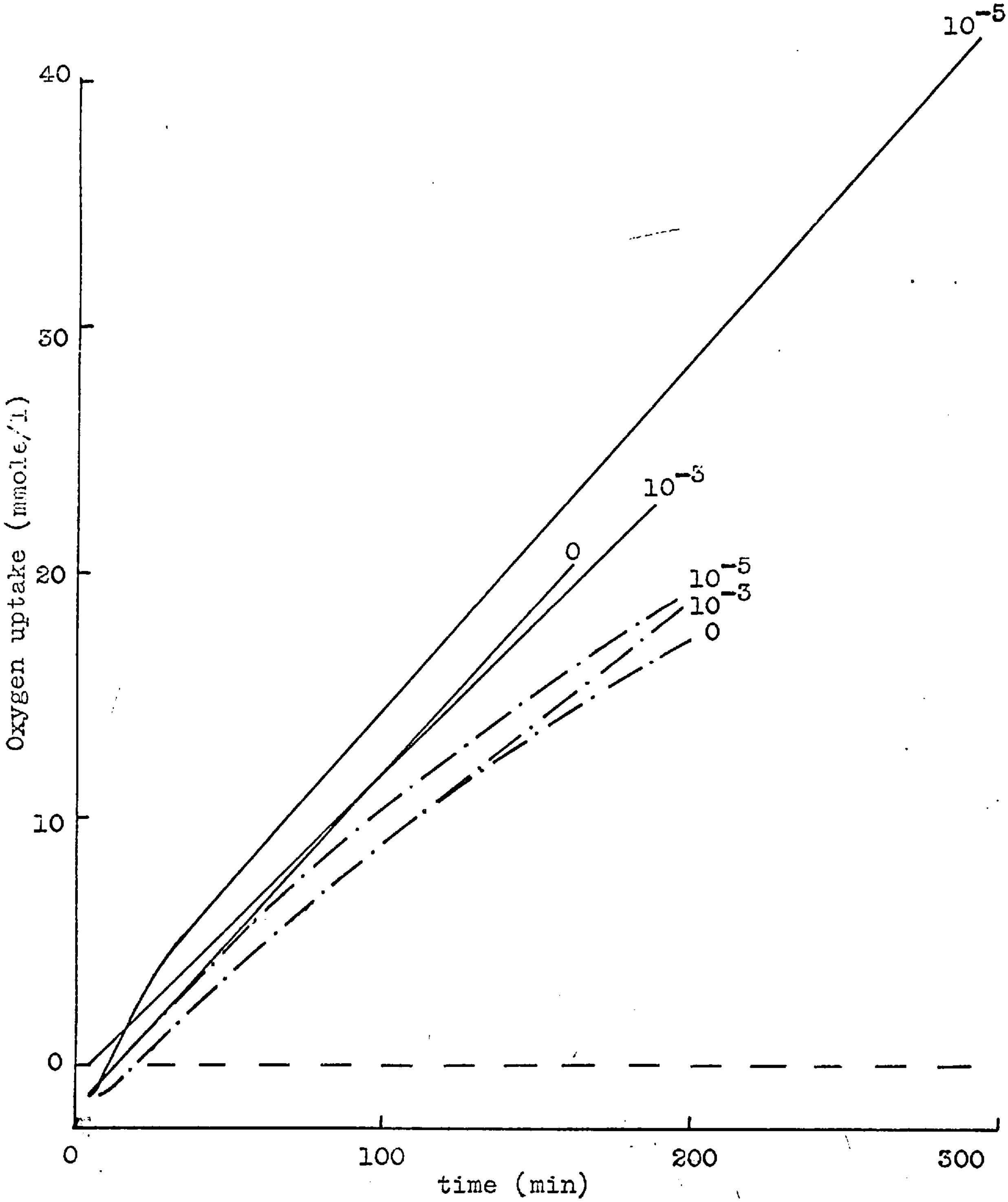


Fig. 34. Oxidation of ethanethiol: effect of added chrome alum. 0.5 M EtSH, 68 cm O_2, 30°C; Cr concentrations (M) beside curves.
—·— 0.6 M NaOH, ——— 2.0 M NaOH.

3.3 Solubility of diethyl disulphide in aqueous sodium hydroxide 3.3

The solubility of diethyl disulphide was estimated roughly by adding the pure disulphide dropwise from a graduated 1 ml pipette into bottles containing 50 ml of 0.6 M or 2.0 M aqueous sodium hydroxide solutions, shaking, and observing the onset of turbidity. The results are given in Table 36. Both solutions were still turbid after standing for 24 hours.

Table 36. Solubility of diethyl disulphide in aqueous sodium hydroxide. 30°C.

NaOH concn. (M)	Limits of Et_2S_2 solubility (ml/l)	(M)
0.6	<0.36	<0.0029
2.0	0.36-0.70	0.0029-0.0057

3.4 Spectra of oxidation products

The spectra of the products from some thiol oxidations were examined, mainly on a Perkin-Elmer recording spectrophotometer and some on an Unicam SP.500. Spectral examination was carried out on both the aqueous products (A) from which the disulphide layer had so far as possible been separated, and on the disulphide layer itself after extraction with trichlorethylene (TCE) or with carbon tetrachloride (CTC).

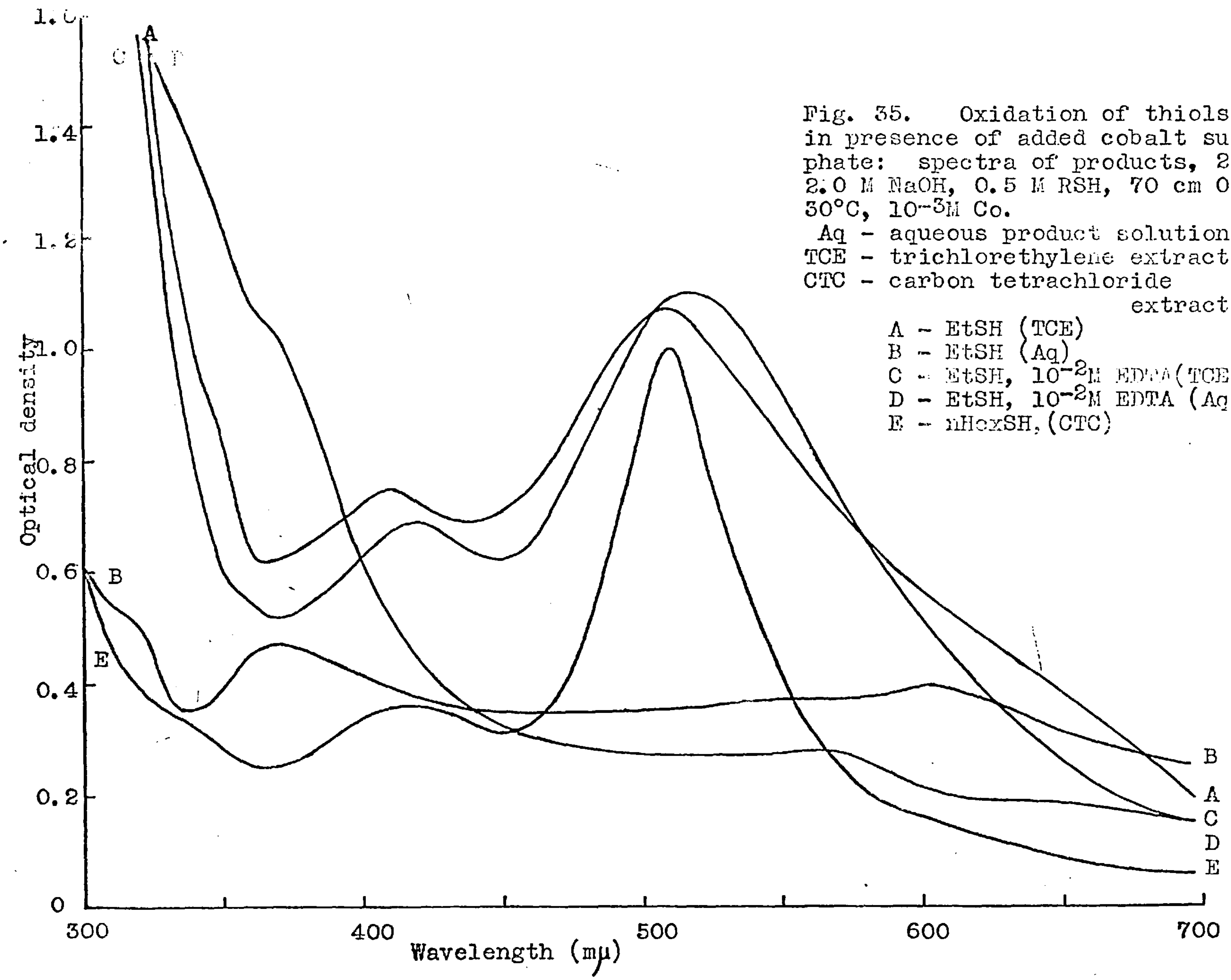


Fig. 35. Oxidation of thiols in presence of added cobalt sulphate: spectra of products, 20° 2.0 M NaOH, 0.5 M RSH, 70 cm O_2, 30°C, 10^{-3}M Co.

Aq - aqueous product solution
TCE - trichlorethylene extract
CTC - carbon tetrachloride extract

A - EtSH (TCE)
B - EtSH (Aq)
C - EtSH, 10^{-2}M EDTA (TCE)
D - EtSH, 10^{-2}M EDTA (Aq)
E - nHexSH, (CTC)

The latter extracts included the suspended red product formed in some cobalt-catalysed oxidations (Section 3.233). Some of these spectra are shown in Fig. 35, and details of the absorption peaks in these and other spectra are given in Table 37.

Turbidity in the liquids gave rise to an irreproducible level of 'background' absorption which increased with decreasing wavelength. The peak heights (ΔD) quoted in Table 37 have been adjusted so far as possible to allow for this.

Non-aqueous suspensions of the red products from cobalt-catalysed oxidations of ethane- and hexane-thiols had characteristic strong absorption peaks at about 415 and 510 mμ, the latter being more intense than the former by a factor of rather over 3 with ethanethiol, and about 6 with hexanethiol.

Table 37. Oxidation of thiols: principal peaks in product spectra. 2.0 M NaOH, 30°C.

Thiol concn. (M)	Metal concn. (M)	Additive concn. (M)	Aqueous phase		Non-aqueous phase		
			Peak (mμ)	ΔD^a	Solvent^c	Peak (mμ)	ΔD^a
0.5 Et	10^{-5}Cu	-	<250 307	c.o.^{b} 0.20			
0.5 Et	10^{-5}Cu	10^{-5}EDTA	<320 310s^d	c.o. 0.09			
0.5 Et	-	10^{-3}EDTA	<320	c.o.			

Table 37 (cont.)

Thiol concn. (M)	Metal concn. (M)	Additive concn. (M)	Aqueous phase		Non-aqueous phase		
			Peak (mu)	ΔD^a	Solvent^c	Peak (mu)	ΔD^a
0.5 Et	-	10^{-2}EDTA	<355	c.o.	TCE	<340	c.o.[b]
0.5 Et	-	0.1 EDTA	<350 390	c.o. 0.08	TCE	<350	c.o.
0.28 Et	10^{-3}Co	-	<270 292s 310s 370	c.o. 0.14 0.22 0.03	TCE	<315 420 510	c.o. 0.09 0.29
0.5 Et	10^{-3}Co	-	<265 294s 310s 370	c.o. 0.15 0.14 0.11	TCE	<325 415 508	c.o. 0.19 0.64
0.5 n-Hex	10^{-3}Co	-			CTC	<285 416 511	c.o. 0.14 0.84
0.5 Et	10^{-3}Co	0.5 Et_2S_2			CTC	<335 415 510	c.o. 0.03 0.20
0.5 Et	10^{-3}Co	10^{-3}EDTA	<290	c.o.	TCE	<310 415 510	c.o. 0.30 0.93
0.5 Et	10^{-3}Co	10^{-2}EDTA	<325	c.o.	TCE	<320 419 517	c.o. 0.23 0.75
0.5 Et	10^{-3}Co	0.1 EDTA	<380	c.o.	TCE	<360	c.o.

a - ΔD is additional optical density over approximate level of density due to turbidity.

b - 'c.o.' means 'cut-off', i.e. lowest wavelength at which the transmission was measurable.

c - TCE = trichlorethylene; CTC = carbon tetrachloride.

d - 's' denotes peaks appearing as shoulders.

4 DISCUSSION 4

4.1 Oxidation of thiols in the absence of added metal salts

4.11 Early experiments

The results of the early experiments on the oxidation of methanethiol (Section 3.11) and ethanethiol (Section 3.12) show how the prolonged development of techniques for the storage and handling of the reagents produced a considerable decrease in the general level of uncatalysed rates of reaction. The rates obtained with methanethiol are three times higher than those with the other alkanethiols (Section 3.15) and this is probably due to the high level of impurity obtained with the early technique. The results show a dependence of the rate upon the total volume of reagents and/or the rate of shaking due to poor mixing in the cylindrical reaction vessel then in use. In view of this the results with methanethiol will not be further considered.

4.12 Oxidation of ethanethiol in the absence of added metal salts

Alkaline solutions of ethanethiol generally absorbed the theoretical quantity of oxygen for oxidation of the thiol to the disulphide:

$$4EtSH + O_2 \rightarrow 2Et_2S_2 + 2H_2O \qquad (1)$$

and this stoichiometry held approximately for all stages of the reaction (Section 3.131). However, a slight excess oxygen uptake of about 10% was observed with the strongest alkali (2 M) with which stoichiometric studies were made. The analysed yields of the disulphide were generally rather lower than theoretical, and decreased with the alkali concentration. Titration showed small decreases also in the concentration of alkali in the final solution, indicating the formation of small quantities of acids in the products, but the differences were too near the limit of experimental error for correlation with the deficiency in disulphide to be established.

Although an excess uptake as high as 24% was found with hexanethiol, the final oxygen uptake figures for ethanethiol were generally close to those expected for production of disulphide. The fifteen experiments in Table 8, Section 3.131, gives a mean uptake of 101% of theoretical with a standard deviation of 7%. The present results are not in agreement with those of Xan, Horton, et al[31], who found that alkanethiols in 2 M alkali absorbed up to 50% more than the stoichiometric quantity of oxygen at 30°C. However, these workers appear to have used initial thiol concentrations less than 10% of those in the present work (see below), and their alkali/thiol ratios were therefore from 1.6 to 75, compared with 1.2 to 6 covered in the present stoichiometric experiments. The excess oxygen consumed leads to the formation of higher oxidation products such as sulphinic and sulphonic acids, and it has been shown that the yields of these 4.12 compounds increases with the basicity of the solution and the temperature[45]. Since saturated disulphides in the pure state are generally inert to oxidation[17,18,19], the formation of the higher oxidation products is probably started by the hydrolysis of the disulphide:

$$RSSR + OH^- \rightleftharpoons RSOH + RS^- \qquad (2)$$

and the sulphenic acid is then oxidised. The extent of further oxidation would therefore increase with the concentration ratio $[OH^-]/[RS^-]$, and some difference between the present results and those of Xan, Horton, et al. is therefore to be expected.

Kinetically, the oxidation of ethanethiol was found to be first order in oxygen and initially also in thiol (Sections 3.132 and 3.133), but later became zero order in the <u>decreasing</u> thiol concentration within each experiment, although the zero-order rate constant increased linearly with the <u>initial</u> thiol concentration. There was a positive dependence on the alkali concentration (Section 3.134). The initial orders of reaction appear to agree with those expected from the mechanism of Wallace and Schriesheim[33,77]:

$$EtSH + OH^- \rightleftharpoons EtS^- + H_2O \qquad (3)$$

$$RS^- + O_2 \rightarrow RS^\bullet + O_2^{\bar{\bullet}} \qquad (4)$$

$$RS^- + O_2^{\bar{\bullet}} \rightarrow RS^\bullet + O_2^{--} \qquad (5)$$

$$RS^\bullet + RS^\bullet \rightarrow R_2S_2 \qquad (6)$$

in which reaction (4) is rate-determining. 4.12

Although the dependence of the rate on the oxygen pressure was found to be linear, the rate actually reached zero and became negative below about 15 cm pressure. This and the apparent induction periods in slow reactions were probably due to the reagent vapour pressures, and to the setting up of the disulphide vapour pressure as the reaction proceeded. The similar limiting pressure found for the copper-catalysed reaction (Fig. 26, Section 3.2213) supports this view, and the value of $k_1' = 4.5 \times 10^{-3}$ l.mole^{-1}sec^{-1} was therefore calculated for an oxygen pressure 15 cm below the nominal value.

It is difficult to compare the reaction rates obtained in the present work with those of Xan, Horton, et al.[31], who worked under similar conditions, because their paper states unequivocally neither their initial thiol concentrations nor their total reagent volumes. From such data as they provide it appears that their usual initial thiol concentration was 0.036 M. In this case the initial zero-order rates (9 - 15% theoretical uptake per min. for 0.0576 M to 2.71 M sodium hydroxide, see their Fig. 1) were 0.8 to 1.4 mmole/ml/min, which is about ten times the rate obtained with 2 M sodium hydroxide in the present work, and is of the same order as the rates with about 10^{-3} M added copper. These rates are also about twice those obtained here with methanethiol in alkali prepared with laboratory-distilled water. Xan et al. do not give details of the purification of their water, and in view of this it is possible that their solutions contained very high levels of impurity (see below). 4.12

The change in kinetics from first-order to zero order in thiol as the reactions proceeded was probably due to the increasing importance of reactions involving catalytic impurities. The positive dependence of the zero-order rate on the alkali concentration (Fig. 11, Section 3.134) is unlikely to have been due to increasing ionisation of the thiol ($pK_a \approx 11$), which would have been 99% ionised in even the weakest alkali used (0.6 M). The effect was presumably due to catalytic impurities introduced with the thiol and/or produced by the alkali in subsidiary reactions, such as hydrolysis (see below).

According to the analysis given on the label ('actual batch analysis' in the case of Judactan) a molar solution of sodium hydroxide contains about 2×10^{-6}M iron, 0.6×10^{-6}M lead, and 0.1×10^{-6}M arsenic, and the potassium hydroxide solution contains no iron or arsenic, but about 0.3×10^{-6}M lead. The 'Analar' reagent labels give maximum impurity limits several times higher. The catalytic effect of iron was investigated in the present work (Section 3.24), and from this the uncatalysed would apparently be compatible with the presence of about 10^{-5}M iron. While lead has been reported

as ineffective in the oxidation of cysteine[46], arsenic 4.12
is a good catalyst for the oxidation of both cysteine[4] and thioglycolate[48]. However, all four samples of the two hydroxides used in the present work gave closely similar results, potassium hydroxide giving slightly higher rates of reaction despite its supposed greater purity. It is possible that the impurity in all the solid samples increased during storage, especially in the case of potassium hydroxide, which is more hygroscopic: further contamination in preparing, storing, and measuring out the standard solutions was also inevitable.

Since the final rate of reaction, although zero order, increased with the initial thiol concentration, it is probable that additional impurities were introduced into the system with the thiol. The most obvious source was the stainless steel needle used to inject the thiol into the reaction vessel, although contamination from this source was minimised by using dry thiol, and performing the operation at a low temperature.

The energy of activation of about 16.5 kcal/mole obtained for the zero-order reaction (Section 3.135) is consistent with a mechanism involving metal ion catalysis, a value of 10 to 12 kcal/mole having been measured for the copper-catalysed reaction (Section 3.2215). The low value of $A_0 = 10^{10.2} \text{sec}^{-1}$ (Section 3.135) shows that a further low concentration term should probably be included in the rate equation: 4.12

$$-\frac{d[EtSH]}{dt} = k'_0[O_2][EtSH]^0 \qquad (i)$$

and this may be an unknown impurity concentration term.

Despite the probability of catalysis by metal ion impurities, the possibility of autocatalysis by disulphide cannot be ignored. It was shown in Section 3.135 that added disulphide increased the rate of all stages of the reaction, and that its effect was only slightly less in the presence of ethylenediamine, and cannot therefore be wholly ascribed to impurities introduced with it. It is likely also that the added disulphide was of higher purity than the thiol since it was introduced from a pipette rather than through an hypodermic needle, although disulphides are probably more effective metal scavengers than thiols.

It should be emphasised that catalysis by disulphide would not necessarily give rise to any marked autocatalytic increase in the rate of reaction. It was shown in Section 3.3 that the solubility of diethyl disulphide in aqueous alkali is very low, and a 0.5 M solution of ethanethiol in 2 M sodium hydroxide would become saturated with disulphide at 2% or even smaller conversion of thiol. The solution would therefore contain a constant disulphide concentration for nearly the whole period of oxidation.

The catalytic effect of disulphides, and dithiodiglycolic acid in particular, is now fairly well established[68], 4.12 and the effect has been ascribed to a cyclic process involving sulphenic and persulphinic acids[44], details of which were given in Section 1.53. Sulphenic acids are produced by the hydrolysis of disulphides (equation 2, above)[86], and the autocatalytic effect of disulphide should therefore increase with the alkali concentration, as observed. However, sulphenic and sulphinic acids normally disproportionate according to the scheme[36]:

$$2RSOH \rightarrow RSH + RSOOH \tag{7}$$

$$2RSOOH \rightarrow RSOH + RSO_2OH \tag{8}$$

$$RSH + RSOH \rightarrow RSSR + H_2O \tag{9}$$

$$RSOOH + RSOH \rightarrow RSOOSR + H_2O \tag{10}$$

These reactions would break the redox cycle envisaged by Berger[44] and lead to the formation of higher oxidation products. This was not generally observed in the present work, and it must be concluded either that disulphide does not catalyse the reaction (the observed effect being due to impurities) or that the catalytic mechanism is very efficient compared with the disproportionation reactions which require bimolecular collisions of very dilute reagents (Reactions 7, 8, and 10: 9 is the reverse reaction of the equilibrium equation 2).

From these considerations it appears most probable that the oxidation of ethanethiol was catalysed both by metal ion impurities and by oxy-sulphur derivatives of the disulphide.

In the experiments in which ethylenediamine was added to solutions of pure and impure samples of ethanethiol, the reaction rate of the pure sample was increased, and that of the impure sample was decreased. The two nominally uncatalysed reaction rates represent the limits of irreproducibility within which a large number of experiments fell. These results are consistent with the introduction of further (metallic) impurity with the diamine, which however diminished its catalytic effect, presumably by complexing with the metal ions. This effect was demonstrated in experiments in which copper and cobalt ions were added to the reagents containing the diamine (Sections 3.2215 and 3.2315).

The values obtained for the zero-order and first-order activation energies (11.4 and 15.0 kcal/mole) were both lower than the zero-order value in the absence of ethylenediamine, and this is consistent with modification of the reacting species.

The rather complicated dependence of the kinetics and rate of oxidation of ethanethiol in the presence of added EDTA may be due to similar causes; for instance, the minimum rate found with 10^{-2}M EDTA compared with 10^{-3} and 10^{-1}M EDTA is explicable in this way (but see also Section 4.21). The addition of 0.1 M ethylenediamine to the reagents containing 0.1 M EDTA gave a rate only slightly above that in the absence of additives, confirming this view.

The results in Table 26 (Section 4.2217) show that the slowest oxidations of ethanethiol were obtained in the presence of 0.25 M potassium cyanide. The catalytic effect of added copper and cobalt were completely suppressed, but there was a progressive fourfold increase in rate over the four experiments carried out. This may have been due to increasing contamination of the stock cyanide solution in storage, but it is difficult to imagine what the contaminants might have been. The lowest rate measured (with fresh cyanide solution) was 0.015 mmole/l/min at 30°C. This rate is 15 - 30% of the supposedly uncatalysed rates obtained in the absence of additives. A rate of a little over 0.015 mmole/l/min is obtained by extrapolating the curves in Fig. 11 (Section 3.134) back to zero hydroxide concentration. It appears, therefore, that this rate is a measure of the rates to be expected in the absence of impurities, and the similar rates obtained with added and copper ions in the presence of cyanide confirm this view. It is unfortunate that the experiments with added cyanide were conducted too late in this research for an extensive investigation to be made.

In one of the experiments with added cyanide the highest oxygen uptake of 191% of theoretical for conversion of thiol to disulphide was recorded, and the reaction was still continuing at 20% of the initial rate. In the absence of cyanide under otherwise identical conditions the final uptake was (4.12 only 113%, and the reaction had virtually ceased. It has been shown[98] that the cyanide ion is more effective than hydroxide in causing scission of the sulphur-sulphur bond, which is the preliminary step in the formation of higher oxidation products. The thiocyanate produced by the scission[87]:

$$\mathrm{RSSR + CN^- \rightarrow RSCN + RS^-} \qquad (11)$$

would be stable to oxidation, and the final consumption of oxygen would be twice that required for oxidation to disulphide, although the results here do not confirm this as the oxidation was not taken to completion.

The higher rate of oxidation of ethanethiol in the presence of 0.05 M di-t-butyl peroxide was suppressed by the further addition of 0.1 M ethylenediamine, and was therefore probably due to an impurity effect rather than to free-radical initiation. The base-catalysed oxidation of ethanethiol was thus shown not to occur through a free-radical chain mechanism, such as occurs for example in the low-temperature oxidation of olefins[20] and indeed in the gas-phase oxidation of ethanethiol itself[16].

Diphenylamine was added as a potential free-radical inhibitor, a role which it plays for example in the oxidation of hydrocarbons, by reacting with the chain-propagating radicals to form other radicals with much lower activity[99]. In the present system diphenylamine had a small positive effect

on the rate. This may have been another impurity effect, 4.13
although as was mentioned in Section 1.52 any species which can accept an electron is a potential catalyst. Diphenylamine is an extremely weak base, due to the strong electron-withdrawing character of the two phenyl groups. It would in fact be expected to form anions in the presence of strong base. This could lead to catalysis through the reaction scheme:

$$Ph_2NH + OH^- \rightleftharpoons Ph_2N^- + H_2O \qquad (12)$$

$$Ph_2N^- + O_2 \rightarrow Ph_2N^\bullet + O_2^{\bullet-} \qquad (13)$$

$$Ph_2N^\bullet + RS^- \rightarrow Ph_2N^- + RS^\bullet \qquad (14)$$

followed by equation 6 ($RS^\bullet$ dimerisation). The role of N,N'-dialkylaromatic amines in the 'antioxidant' sweetening of gasoline has been worked out by Barringer[100], but in this case the anions are oxidised by $RO_2^\bullet$ radicals derived from unsaturated hydrocarbons in the feedstock.

4.13 Oxidation of other thiols

The order of oxidisability of various thiols (Section 3.15) was comparable with the results of previous workers, the order being n-Hex > n-Bu > Et ≈ $PhCH_2$ > Ph > t-Bu, although Xan et al.[31] found that n-Pr > n-Bu > n-Am. The rates quoted for ethanethiol in Table 16 (Section 3.15) are somewhat lower than expected from other experiments, and its reactivity is probably similar to that of phenylmethanethiol. The above order follows approximately the order of stability of the anions given by the values of pK_a in Section 1.2: this stability is decreased by nucleophilic alkyl chains and increased by electrophilic aromatic groups. However, factors other than stability of the anion must be involved in the extreme slowness of oxidation of t-butanethiol after the brief period of comparatively rapid reaction at the start which cannot at present be explained (Section 3.152). The slow oxidation is associated with an exceptionally high activation energy, which appeared to increase from about 22 to 32 kcal/mole from 30 to 50°C, compared with the constant value of 16.5 kcal/mole for ethanethiol. The activation energy for thiophenol oxidation was also, at 24 kcal/mole, higher than for ethanethiol. Somewhat higher values would be expected for sterically hindered reactions, and, in the case of thiophenol, from the stability of the anion. However, the values for the activation energy correspond to values of the pre-exponential factor A some 10^6 and 10^5 times *higher* for t-butanethiol and thiophenol respectively, compared with ethanethiol, whereas *lower* values would have been expected from steric considerations. In view of this and the paucity of data obtained, the values for the activation energy for the oxidation of t-butanethiol and thiophenol, especially the high values with the former, must be regarded as suspect.

4.2 Oxidation of thiols in the presence of added metal salts 4.2

Experiments with added metal salts showed that under the conditions studied the order of catalytic effectiveness was Cu $>$ Co $>$ Mn $>$ Fe $>$ Cr $\approx$ 0. Copper and cobalt were selected for more detailed study due to their large effect, and the different types of kinetic behaviour which they gave.

4.21 Oxidation of ethanethiol in the presence of added copper sulphate

Copper-catalysed oxidations were all found to absorb nearly theoretical amounts of oxygen for the production of disulphide as the sole product (Section 3.2211).

The kinetics of the oxidation were zero order in thiol, and first order in oxygen and copper ions (the latter at low concentrations only). The relevant data appear in Sections 3.22, 3.2212, and 3.2213. After allowing for the different solubility of oxygen, the effect of the alkali concentration diminished with increasing amounts of added copper, and the rate of the copper-catalysed reaction was probably independent of the alkali strength. At low concentrations of copper the measured rates were largely those of the 'uncatalysed' reaction, and it is for this reason that the curves (d) and (e) in Fig. 25 (Section 3.2212), derived in later experiments, are lower than the other curves.

The apparent upper limit to the rate of reaction, 4.21 reached at between 10^{-3} and 10^{-2}M added $CuSO_4$, was accompanied by the production of a brown precipitate, which was probably cuprous oxide, or a copper-disulphide complex. However the limit was not necessarily due only to removal of copper ions from the solution. In one series of experiments the reaction rates at the higher copper concentrations were affected by the rate of shaking (curves (a) and (b), Fig. 25), and therefore by the rate of diffusion of oxygen gas into the liquid phase. The reaction vessel was subsequently modified to reduce this effect; however, the dependence of the reaction rate on the copper concentration in these diffusion-affected reactions was used in the following interesting reflections.

Assuming homogeneous distribution of oxygen in the liquid phase, the following equation would appear reasonable for the rate of diffusion of oxygen at the liquid-gas interphase:

$$r_D = D[O_2]_G\left(a - \frac{[O_2]_L}{[O_2]_G}\right) \qquad \text{(ii)}$$

$[O_2]_L$ and $[O_2]_G$ are the oxygen concentrations in the liquid and gaseous phases respectively; <u>a</u> is the value of the concentration ratio when the solution is saturated; and D is a diffusion rate constant which is dependent upon the geometry of the system. If the oxygen reacts chemically in bimolecular reactions with dissolved catalytic impurities and cuprous ions, the chemical rate of reaction may be written as: 4.21

$$r_C = [O_2]_L(k'[Cu] + k''[Imp]) \qquad (iii)$$

In this equation [Cu] is the total concentration of copper ions; the reaction between cupric and thiol ions is assumed to be very fast. Equating r_D and r_C for the steady state, where $[O_2]_L$ is constant:

$$r_C = r_D = r = \frac{k'[Cu]/D + r_0/(r_\infty - r_0)}{k'[Cu]/D + r_\infty/(r_\infty - r_0)} r_\infty \qquad (iv)$$

In this equation r_0 and r_∞ are the observed rates at [Cu] = 0 and ∞ respectively. The broken curve (a) in Fig. 25 is based on this equation. Although the upper and lower rate limits and the position of the curve with respect to the log[Cu] axis were chosen to fit the experimental data, the agreement with the three intermediate points confirms the validity of the assumptions upon which equations (ii) and (iii) are based. The curves (b) and (c) in Fig. 25 cannot be made to fit any theoretical relationship, and are probably the result of heterogeneous distribution of dissolved oxygen in the liquid phase.

The kinetics of the copper-catalysed oxidations are consistent with the following type of mechanism:

$$Cu(I) + O_2 \rightarrow Cu(II) + O_2^{-} \qquad (15)$$

$$Cu(I) + O_2^{-} \rightarrow Cu(II) + O_2^{--} \qquad (16)$$

$$Cu(II) + RS^{-} \rightarrow Cu(I) + RS^{\cdot} \qquad (17)$$

$$2RS^{\cdot} \rightarrow RSSR \qquad (18)$$

Equation (15) is rate-determining. Probably, the copper 4.21
ions are in the form of complexes with OH^-, RS^-, and subsequently also RSSR. The sulphur compounds would be expected to give stronger complexes, and species such as $Cu[RS]_2^-$ are likely to be involved in reaction (15). Values of the activation energy E_{a0} for the reaction in the absence and presence of low concentrations of added copper sulphate are given in Table 23 (Section 3.2.14). After allowing for the uncatalysed reaction, a value of $E_{a0} \approx 10$ or 11 kcal/mole emerges from measurements in 0.6 M alkali in the lower temperature range, but in the higher temperature range, and over both ranges with 2.0 M alkali, E_{a0} decreased both with increasing temperature and copper concentration. This must reflect changes in the composition and concentration of the active complexes with temperature, and the details are likely to be complicated.

The values of $E_{a0} = 10$ or 11 kcal/mole and $\Delta S^{\ddagger} \approx -8$ e.u. obtained for ethanethiol are similar to values obtained for redox reactions involving metal ions, but it is at present not possible to derive mechanistic details from such data[101].

The three additives ethylenediamine (en), ethylenediaminetetracetic acid (EDTA), and cyanide ion were all found to inhibit the catalysis, the last of them completely. It is possible to calculate the approximate concentrations of these additives required to displace hydroxide from its complexes with copper and cobalt. Considering the following equilibria:

$$M + xOH^- \rightleftharpoons M[(OH^-)_x](s) \qquad (19)$$ 4.21

$$M + yL \rightleftharpoons M[L_y] \qquad (20)$$

it can be shown that the concentration of the complex $M[L_y]$ is given by the equation:

$$[\text{Complex}] = \frac{B_y k_{so}[L]_0^{\,y}/[OH^-]_0^{\,x}}{1 + B_y k_{so} y^2 [L]_0^{(y-1)}/[OH^-]_0^{\,x}} \qquad (v)$$

where k_{so} is the solubility product according to equation (19), and B_y is the formation constant for the complex $M[L_y]$ (equation (20)). The subscript zero denotes initial total reagent concentrations. Values of k_{so} and B_y are available in the literature[102], and equation (v) was used to calculate the value of $[L]_0$ for which $[\text{Complex}] = [M]_0$, when the concentrations were those used in the present work, viz. $[Cu]_0 = 10^{-5}$M, $[Co]_0 = 10^{-3}$M, $[OH^-]_0 = 2$ M, temperature = 30°C. The results are given in Table 38. It is acknowledged that these values apply only to the complete exchange of ligands, and that complexes with mixed ligands would be formed at concentrations of the additive ligands lower than these. Considering the case of catalysis by copper ions, the first-order kinetics in copper and the rate constant obtained make it very improbable that the copper was present as an all-hydroxide complex, which would have been precipitated under all the conditions studied. Complexes involving thiol or disulphide are much more probable, and since values of B_y for these are

not available, a precise explanation of the details of 4.21
the effect of additives is not possible. However, the ligand concentrations in Table 38 may be regarded as probable minima for displacement of thiol from its complexes.

Table 38. Ligand concentrations (in moles/l. (M)) required to dissolve precipitated hydroxides and oxides. For conditions see text.

Metal oxidation state	$\log k_{so}$	Ethylenediamine			EDTA			Cyanide		
		$\log B_y$	y	$[en]_0$	$\log B_y$	y	$[EDTA]_0$	$\log B_y$	y	$[CN^-]_0$
Cu(I)	-15^a	10.8	2	0.5	b		b	27.3	4	$5x10^{-4}$
Cu(II)	-24^a	19.3	2	1	17.8	1	80	25	4	$5x10^{-2}$
Co(II)	-14.9	13.8	3	0.5	15.4	1	10^{-3}	19.1	6	0.1
Co(III)	-43	48.7	3	10^{-2}	36	1	10^{5}	64	6	0.1

a - k_{so} estimated from data in Ref. 102, p. 30, and refer only to 10^{-5}M Cu.

b - B_y not available.

The added 0.25 M cyanide was obviously adequate to complex with and deactivate all the copper ions in solution. This reaction was interesting because, although the consumption of oxygen and thiol corresponded closely to the stoichiometry expected for oxidation to disulphide, none was

recovered. Two explanations of this are possible. 4.21
The disulphide may have been removed in the treatment with ferrous ammonium sulphate (to remove cyanide prior to acidification for titration), or it may have been completely hydrolysed. The latter would have led however to twice the observed consumption of oxygen per mole of thiol oxidised (Section 4.12), and the results do not show this, unless an inadvertent deficiency as large as 8% in the amount of injected thiol may be assumed.

The concentrations of added ethylenediamine were hardly sufficient completely to displace hydroxide from its copper complexes, and therefore probably insufficient to compete effectively with thiol and disulphide as ligands. The deactivation was therefore only partial, whereas with cobalt it was complete.

Added concentrations of EDTA were all well below the values needed to displace hydroxide from complexes with Cu(II), although the necessary data for Cu(I) are unfortunately not available. As with the 'uncatalysed' oxidation of ethanethiol, the minimum rate was observed at a concentration of EDTA below the maximum used: the rate was halved by 10^{-4}M, but almost unaffected by 10^{-3}M EDTA. Rising concentrations of EDTA could lead to the formation first of complexes with mixed ligands, perhaps with Cu-EDTA-Cu bridging, and finally to the simple Cu[EDTA] complexes when the EDTA concentration was high enough. The minimum at 10^{-4}M EDTA (10:1 excess EDTA over copper) may have been due to such changes. 4.211

4.211 Oxidation of other thiols in the presence of added copper sulphate: effect of temperature

The energy of activation for the oxidation of thiophenol was lowered by the presence of copper ions. After allowing for the 'uncatalysed' reaction, the value for the contribution of the copper ions was about 8 kcal/mole with thiophenol, compared with about 10 or 11 kcal/mole for ethanethiol. Taking the rate constant as 132 $l.mole^{-1}sec^{-1}$ for thiophenol at 30°C, the entropy of activation was -23.5 e.u. The value for ethanethiol was -8.1 e.u., and the decrease is consistent with the greater bulk of the thiophenol anion.

t-Butanethiol was anomalous in giving rates which decreased with increasing temperature. The result can only be explained by changing composition and concentrations in the reagents. Although apparently absurd, this result does serve to confirm the participation of thiol in the rate-determining step, despite its zero power in the rate equation. The copper species involved in this step (reaction (15)) cannot therefore be a simple hydroxide, or similar values for the rate constants and their thermodynamic constants would be expected irrespective of the nature of the thiol.

4.212 Mechanism for the copper-catalysed oxidation of thiols 4.212

The mechanism for the copper-catalysed oxidation of thiols, the outline of which was expressed in equations (15) and (18), can now be envisaged in greater detail:

$$\mathrm{Cu(I)[(SR)_2]^- + O_2 \rightarrow Cu(II)[(SR)_2O_2]^-} \qquad (21)$$

$$\mathrm{Cu(II)[(SR)_2O_2]^- + 2RS^- \rightarrow Cu(I)[(SR)_2S_2R_2]^-} \qquad (22)$$

$$\mathrm{Cu(I)[(SR)_2RSSR]^- \rightarrow Cu(I)[(SR)_2]^- + RSSR} \qquad (23)$$

$$\mathrm{2O_2^{--} + 2H_2O \rightarrow 4OH^- + O_2} \qquad (24)$$

The addition of oxygen in reaction (21), which is rate-determining, is stabilised by the internal transfer of an electron from copper to oxygen. Thiol anions then displace a peroxide ion (22), and the resulting quadricovalent Cu(I) complex eliminates disulphide to give the more stable bicovalent thiol complex, which re-enters reaction (21). There are several routes by which reaction (22) could be accomplished, including the formation of free radical intermediates. However, most probably the two RS^- ions are coordinated in two steps, the second of which eliminates peroxide from a trithiolatoperoxo intermediate. Whatever the details of the mechanism, it is almost certainly based on reaction (21), and through this on the increase in the more favoured coordination number from 2 to 4 when Cu(I) is oxidised to Cu(II).

The change in kinetics to first order in thiol at high conversions in the copper-catalysed oxidation of hexanethiol

may be interpreted as a change in rate-determining step 4.22
to reaction (22) (or one of its component steps) due to the steric effect of the alkyl hydrocarbon chains.

The small effect of added ethylenediamine may be due to the fact that two coordinated positions are unchanged throughout the above reaction cycle, and hence could be occupied by en without much disturbing the kinetics.

4.22 Oxidation of ethanethiol in the presence of added cobalt sulphate

The initial rate of oxidation of ethanethiol in the presence of added cobalt sulphate was found (Section 3.2311) to increase with the cobalt concentration up to about 10^{-3}M, the effect being roughly linear between 10^{-6} and 10^{-4}M cobalt (Table 30). The initial rate also depended linearly upon the oxygen pressure, but the results (Table 31, Section 3.2212) can be extrapolated to give zero rate with as much as 33 cm oxygen.

The most interesting feature was the well-defined, and often abrupt, decrease in the first-order rate constant as the reaction proceeded, when the cobalt concentration was 10^{-3}M or more (Fig. 30). The result of this was that in the later stages of the reaction the rate was higher in the presence of 10^{-4}M cobalt than with 10^{-3}M (Fig. 29). Details of the rate-constants and conditions under which the change in k_1 took place are all given in Tables 30 and 31 (Sections

3.2311 and 3.2312). From the results with 10^{-3}M cobalt, 4.22
the change in k_1 appears to be determined by the disulphide content of the mixture. With 10^{-2}M cobalt the change took place at a thiol conversion some three times higher. The values of $(k_1 - k_{1,0})/\alpha$ show that both the initial and final cobalt-catalysed rates were higher in stronger alkali.

The dependence of the change in k_1 upon the disulphide content was shown by adding disulphide to the reagents (Section 3.2313). The rate constant throughout the reaction was then close to the final values in the runs without added disulphide. An apparent slight decrease of about 10% in k_1 was observed. but this is much smaller than the 50% in the absence of added disulphide.

In the presence of 10^{-3} and 10^{-2}M added ethylenediaminetetracetic acid (Section 3.2314) the initial period was prolonged, and the initial rate constant was unaltered, whereas the final value was rather higher. However, 10^{-1}M EDTA shortened the initial period so much that its rate could not be exactly determined: the final value of k_1 was close to that in the absence of EDTA. These reactions were followed until oxygen uptake had ceased. The final uptakes were only slightly more than theoretical for the production of disulphide in the case of 10^{-3} and 10^{-2}M EDTA, but was some 16% higher with 0.1 M EDTA. All the EDTA- containing solutions were clear before the addition of thiol, whereas those without

EDTA contained the brown hydroxide. Table 38 shows that EDTA concentrations over 10^{-3}M should keep the cobalt in solution as the Co(II) complex. 4.22

All the experiments with 10^{-3}M or more added cobalt, with and without EDTA, were found finally to produce a red solid product suspended in the droplets of disulphide. The nature of this product is discussed below in Section 4.221.

The addition of ethylenediamine or cyanide completely suppressed the catalytic effect of the cobalt. No coloured product was obtained, and the reactions were similar to those in the absence of added cobalt.

Some data are available which allow some comparison of the relative stability of amine and thiol complexes of Co(II)[102]. The formation constants for the stepwise addition of ethylenediamine are $K_1 = 5.9$, $K_2 = 4.8$, and $K_3 = 3.2$, whereas for 2-aminoethanethiol the values are $K_1 = 7.7$ and $K_2 = 7.0$, and no value is available for K_3. Although the latter values refer to addition of the unionised aminothiol, they do demonstrate the greater affinity of Co(II) for sulphur. However, in this example the thiol group forms part of a bidentate chelating ligand, and it is doubtful whether non-chelating thiol groups such as ethanethiol itself could displace ethylenediamine from its complexes, especially from the highly stable Co(III)en$_3$, and the present results appear to confirm this.

No temperature coefficients for the cobalt-catalysed oxidations of thiols were obtained except for the case of t-butanethiol, for which a value of 7.6 kcal/mole was obtained from the overall measured rates. No allowance was made for the 'uncatalysed' contribution as the differences were so small, but the value is very much lower than the 22 - 32 kcal/mole obtained for the 'uncatalysed' oxidation of this thiol.

4.221 Mechanism of the cobalt-catalysed oxidation of thiols

Two types of mechanism for the cobalt-catalysed oxidation of thiols can be envisaged. These may be termed 'inner sphere' and 'outer sphere' by analogy with the use of these terms to describe the two basic ways in which exchange reactions between complex ions can take place[101].

In an outer sphere reaction electron transfer takes place without disturbance to the ligand shell of the complexed metal. Thus in the present case the cobalt complex would act only as a bridge between the thiol anion and an oxygen molecule, through which the electron could be readily transferred:

$$\begin{aligned} & RS^{-}\ldots Co(III)[X_6]\ldots O_2 \\ & \qquad \rightarrow RS^{\bullet}\ldots Co(II)[X_6]\ldots O_2 \qquad (25) \\ & \qquad\qquad \rightarrow RS^{\bullet}\ldots Co(III)[X_6]\ldots O_2^{\bullet-} \end{aligned}$$

This mechanism does not imply that trimolecular collisions are necessary, since the bimolecular collision between the cobalt complex and either reagent (but especially the anion) could be 'sticky' and persist as an outer sphere complex until a further collision completed the exchange. 4.221

The ligands X occupying the six inner-sphere co-ordination positions on the cobalt ion take no direct part in the reaction, i.e. no bonds are made or broken, but the different polarisability of various ligands would be expected to affect the rate of electron transfer. It has been found for similar electron transfers between two complex ions that outer sphere reactions are characterised by the comparative insensitivity of the rate constant to changes in the inner sphere ligands, but this has been confirmed mainly for series of complexes in which only one co-ordination position is changed[103]. In the present case the rates vary by a factor of about 17 from cyanide to EDTA, but the changes in the complexes were probably drastic, involving most of or all the co-ordination positions, and such a range of rates does not therefore necessarily preclude an outer sphere mechanism.

As an alternative, an inner sphere mechanism, with actual co-ordination of oxygen, can be envisaged. While free-radical intermediates may take part, the following scheme does not require this:

$$\mathrm{Co(II)[X_4(S_2R_2)] + O_2 \rightleftharpoons Co(III)[X_4(SRSR)(OO^-)]} \qquad (26)^{4.221}$$

$$\mathrm{Co(III)[X_4(SRSR)(OO^-)] + RS^- \rightarrow Co(III)[X_4(SR^-)(OO^-)] + RSSR} \qquad (27)$$

$$\mathrm{Co(III)[X_4(SR^-)(OO^-)] + RS^- \rightarrow Co(II)[X_4(S_2R_2)] + O_2^{--}} \qquad (28)$$

In these equations only the atoms written first in the ligand formulae are actually co-ordinated: i.e. (SRSR) occupies only one, but (S_2R_2) two co-ordination positions. Equation (27) is rate-determining.

Both outer and inner sphere mechanisms would give a rate equation of the type:

$$\mathrm{Rate} = k'[\mathrm{Co(II)}[\mathrm{O_2}][\mathrm{RS^-}] \qquad \text{(vi)}$$

Although the observed dependence of the rate upon reagent concentrations was not straightforward, equation (vi) appears to be indicated by the results.

The discontinuous change in the measured rate constant during reactions with 10^{-3}M or more cobalt, with and without EDTA, was always accompanied by the formation of the insoluble red complex. Experiments showed that this could only be obtained from solutions containing both cobalt and thiol. Non-aqueous suspensions of the product were found to have absorption maxima at 415 and 510 mμ, the latter being about three times stronger than the former with ethanethiol, and six times with n-hexanethiol. Spectra of this type are characteristic of Co(III) complexes[104], and this was confirmed

by the diamagnetism, since Co(II) ($3d^9$) has an 4.221
unpaired electron. The red product was therefore a Co(III)-thiol/disulphide complex. The elemental analysis did not provide a simple empirical formula, but in view of the probable presence of C_2H_5S units, the complex evidently contained either a $Co(C_2H_5S)_2$ or $Co(C_2H_5S)_3$ grouping, depending upon whether the sulphur or carbon analyses are accepted (c.f. empirical formula $CoS_{2.25}C_{6.49}H_{16.3}O_{3.56}$, Section 3.233). It seems likely that the precipitate contained an assortment of Co-S-S-Co bridged chains and lattices, giving overall the indefinite composition shown by analysis. The formation of such structures could effectively put a proportion of the cobalt atoms in an extensive ligand cage, and thereby prevent their interaction with oxygen and thiol.

The time of reaction at which the complex was formed would be determined mainly by the disulphide content of the solution, since this is changing most rapidly near the start of the reaction. Although the abrupt decrease in the rate constant k_1 was probably connected with the formation and precipitation of the complex, the precise relationship is not clear. When disulphide was deliberately added to the reagents the slower rate was observed from the start. However, the rate-constant changes were observed at reaction times at which the disulphide content of the reagents was several times greater than its solubility in the alkali

(Section 3.3), and was dependent upon the cobalt content. 4.221 This shows that more than a simple equilibrium of complexes is involved, and the effect of the relative proportions of precipitate, aqueous phase, and disulphide on the physical state of the precipitate may be responsible for the kinetic details. For example, with 10^{-2}M Co, coagulation of the larger amount of precipitate evidently led progressively to the complete removal of cobalt from the oxidising system, and therefore to a decreasing rate constant (Fig. 30, Section 3.2311). With 10^{-3}M cobalt, however, the smaller quantity of precipitate remained finely divided in the droplets of disulphide, and equilibrium with the aqueous phase was maintained, giving a constant concentration of dissolved cobalt, and the observed uniform value of the lower k_1.

While it is possible in this way to explain certain features of the observed reaction kinetics, it must be concluded that the present limited data do not permit any decision concerning the mechanism of the basic cobalt-catalysed reaction, such as whether it is outer or inner sphere. To achieve this an intensive investigation of the complexes of cobalt ions with hydroxide, thiols, and disulphides is required.

4.222 Oxidation of other thiols in the presence of added cobalt sulphate 4.222

The rate and kinetics of oxidation of n-hexanethiol in the presence of added cobalt sulphate were very similar to those found with ethanethiol, and the same mechanism was doubtless operative. The rates were somewhat lower, and this could be ascribed to the greater bulk of the thiol anion leading to a slower reaction. In view of this the very slow reaction obtained with n-butanethiol is remarkable, and this anomaly cannot be explained at present. The slow reaction with t-butanethiol parallels the results obtained with this thiol in 'uncatalysed' and copper-catalysed systems. The energy of activation was found to be 7.6 kcal/mole, which would be of the order expected for a metal-ion catalysed reaction, and if the reagent concentrations are taken as their nominal values, the entropy of activation can be calculated as -47 e.u., a large negative value being expected for a sterically-hindered reaction.

The slow reaction with thiophenol is probably due both to steric effects and to the stability of the anion, i.e. the difficulty of removing an electron from sulphur combined to an electrophilic group.

The rate of the cobalt-catalysed oxidation of phenylethanethiol was intermediate between those for thiophenol and the alkanethiols (except the butanethiols), as in its uncatalysed and copper-catalysed oxidation.

4.23 Oxidation of ethanethiol in the presence of other metal sulphates

The oxidation-reduction potentials for the aquo-complex ions of the five metals used in the present work are given in Table 39.

Table 39. Redox potentials for aquo-ions of various metals.[105]

Couple	Standard redox potential (Volts)
$Cu^{+} \rightleftharpoons Cu^{2+} + e^{-}$	-0.167
$Co^{2+} \rightleftharpoons Co^{3+} + e^{-}$	-1.82
$Mn^{2+} \rightleftharpoons Mn^{3+} + e^{-}$	-1.51
$Fe^{2+} \rightleftharpoons Fe^{3+} + e^{-}$	-0.771
$Cr^{2+} \rightleftharpoons Cr^{3+} + e^{-}$	+0.41

While the couples would of course change with the substitution of other ligands for water, the values in the Table should provide a general guide to the relative stability of the metal ions in the oxidation states considered. In each case the oxidation states are those most likely to be involved in the catalysis of thiol oxidation, and there is no reason to believe that any other states take part. The two most active catalysts, copper and cobalt, are seen to have widely different redox potentials, with the two less effective catalysts, iron and manganese, between them.

The value for chromium ions shows that reduction of the chromic state is very difficult, and the ineffectiveness of chromic ions as a catalyst is almost certain to be due to the inability of thiol ions to accomplish this (Section 3.26).

The present results **show** that the slow (rate-determining) step in the cobalt-catlysed oxidation of thiols is that involving the reduction of Co(III) ions. The corresponding states of manganese and iron are even more stable, and their reduction correspondingly more difficult, and hence their lower catalytic effect is to be expected (Sections 3.24 to 3.25). The rather limited kinetic results obtained in the presence of these metals show that both probably take part in a cobalt-type oxidation-reduction cycle, since initially rapid oxidation with abrupt decreases in the first-order rate constants was observed under certain conditions with the ions of both metals. In the case of iron the decrease occurred at lower conversions of thiol compared with cobalt, and this may indicate the higher stability of Fe(III)-disulphide complexes, which - as in the case of cobalt - would make the higher oxidation state more resistant to reduction by thiol, especially by the inner-sphere mechanism.

In the case if manganese, high initial rates were obtained only in the presence of the weaker alkali. This may show the special stability of Mn-hydroxide complexes to substitution by thiol in the inner-sphere mechanism: therefore despite the closeness of the redox potential to that for cobalt, the reaction is much slower.

Under the most favourable conditions, the rate constants for the iron- and manganese-catalysed oxidations were from one-third to one-half of those obtained with cobalt, the values for iron being somewhat higher than those for manganese.

4.3 Conclusions

The present researches have shown that the uncatalysed oxidation of thiols in aqueous basic solutions is probably very slow at 30-50°C. The reaction is extremely sensitive to catalysis by metal ions, and in view of this it would probably be unprofitable to attempt to obtain lower levels of impurity than those in the present work. The apparent suppression of the catalytic effect of metal ions by the addition of cyanide is likely to provide a simpler method of achieving uncatalysed oxidations. As reported in Section 1.42, it has been shown that the uncatalysed oxidation of thiols is considerably faster in highly polar solvents containing organic bases. However, the latter are all Lewis bases in the broader definition, and as such are likely to be strong ligands and metal-scavengers, and hence easily contaminated. It is therefore at least as necessary to take care to exclude metals from these as from aqueous systems. Workers have not always explicitly considered this.

The results obtained in the present work on oxidation experiments with added metal ions suggest that the mechanisms are essentially similar to those proposed by Schubert and others for the corresponding catalysed oxidations of carboxy-thiols, which were discussed in Section 1.511. Some differences would of course be expected from competition by OH^- ions in the present strongly alkaline aqueous solutions, for most of the earlier work has been carried out at low alkaline pH values. Further differences in detail are expected from the relative stabilities and solubilities of hydroxide, thiol, and disulphide complexes. The thiols and derived disulphides concerned in the present studies do not of course possess hydrophilic groups, which ensure solubility in the case of carboxy-thiols. Precipitation is especially likely to occur when sufficient disulphide has accumulated in the system to form complexes with no overall charge. This leads to the removal of metal ions from the aqueous phase, and the changes in rate constant observed with cobalt, iron, and manganese. This process does not appear to occur in the cobalt system when certain concentrations of EDTA are present. From the point of view of commercial operation of metal-catalysed petroleum sweetening processes, the use of aqueous alkali containing metal ions homogeneously dissolved as a complex is likely to have the advantage in simplicity and

efficiency over the slurry methods to which the present 4.4
research of other workers on catalysis by pyrophosphate and other insoluble complexes appears to be leading. For these purposes suitable complexes of copper would appear most promising.

From the academic viewpoint, details of the process which the present work shows only in outline should clearly be sought. More data on complexes with simple thiols and disulphides is required, and it may prove feasible to measure the rates of oxidation of thiol anions by metal ions in anaerobic systems, for comparison with the metal-ion-catalysed rates of autoxidation, since with cobalt, iron, and manganese at least it is these reactions which appear to determine the overall rates of reaction.

APPENDICES

A 1 Correction of gas burette readings

The gas burette readings were corrected for variations from standard values in the water-bath temperatures and in the working pressure. This was carried out by means of the following Boyle's Law treatment.

If p_s, T_s are the standard pressure and water-bath temp.,
p_o, T_o are the observed pressure and water-bath temp.,
T_{oil} is the oil-bath temperature,
v is the volume of gas in the reaction vessel (at T_{oil}),
V is the volume of the working line at T_o, with the burette at the zero mark, and excluding the volume at T_{oil},
b_o is the observed, b_c the corrected burette readings.

If the effect of the vapour pressures of the reagents is neglected, then the observed and corrected burette readings may be connected by the equation:

$$\frac{p_s(V - b_c)}{RT_s} + \frac{p_s v}{RT_{oil}} = \frac{p_o(V - b_o)}{RT_o} + \frac{p_o v}{RT_{oil}} \qquad (i)$$

This may be rearranged to give the equation:

$$b_c = b_o + \frac{p_s(T_o - T_s) - T_s(p_o - p_s)}{T_o p_s}(V - b_o) + \frac{vT_s}{T_{oil}p_s}(p_s - p_o) \qquad (ii)$$

The apparatus used in this work was calibrated by application of Boyle's Law, and the volumes were found to be V = 612 ml, v = 92 ml (with 50 ml reagent solution in the reaction vessel). Taking T_{oil} as the common 30°C (303°K), equation (ii) becomes:

$$b_c = b_o + \frac{p_s(T_o-T_s) + T_s(p_s-p_o)}{T_s p_s}(612-b_o) + 0.3035\frac{T_s}{p_s}(p_s-p_o) \qquad \text{(iii)}$$

The denominator of the first quotient in this equation should be $T_o p_s$, to which $T_s p_s$ is a simplifying approximation. The form of this equation enables burette readings, b_o, to be corrected rapidly and simply, p_s and T_s being chosen to minimise the corrections necessary in each experiment.

A 2 Automatic recording of burette levels

A device for the automatic recording of burette level as a function of reaction time was described in Section 2.213. Several methods of achieving this were in fact considered. All depended upon the movement of mercury in a U-tube spanning the two limbs of the gas burette, which (as described in Section 2.212) was filled with silicone oil, and three methods of detecting and recording the movement were considered.

1. By the change in resistance of a dipping single-crystal graphite rod. Trials were conducted with a rod of about 0.1 ohm/cm. A fairly good linear calibration was found, but it was considered that the performance of the cell would

deteriorate seriously with use, as the mercury became dirty.

2. By floating a steel ball on the mercury, and detecting the change of inductance as the ball moved between two coils, which formed the variable arms of an inductance bridge circuit. This system worked very well in mock-up, but in the event it was not used since the necessary electronic equipment was not available.

3. By making the mercury-filled U-tube a capacity cell. This was the method adopted, because the necessary 'Telstor' and 'Servograph' units were available, as described in Section 2.213.

After calibration had given good linear curves connecting the Servograph and burette readings, it was disappointing to find that the device failed to follow changes in burette level during actual experiments. At the start of runs no uptake was registered until the burette level had risen by about 10 ml (about 6% of the usual total uptake). The recorder subsequently followed the burette, but the readings fell progressively further behind the calibration, and tended to move in steps.

It is likely that this behaviour was due to sticking of the mercury in the capicity limb, in which the mercury fell as the burette level rose. Although this arrangement was perhaps unwise, it had been considered that the vibration

A 3

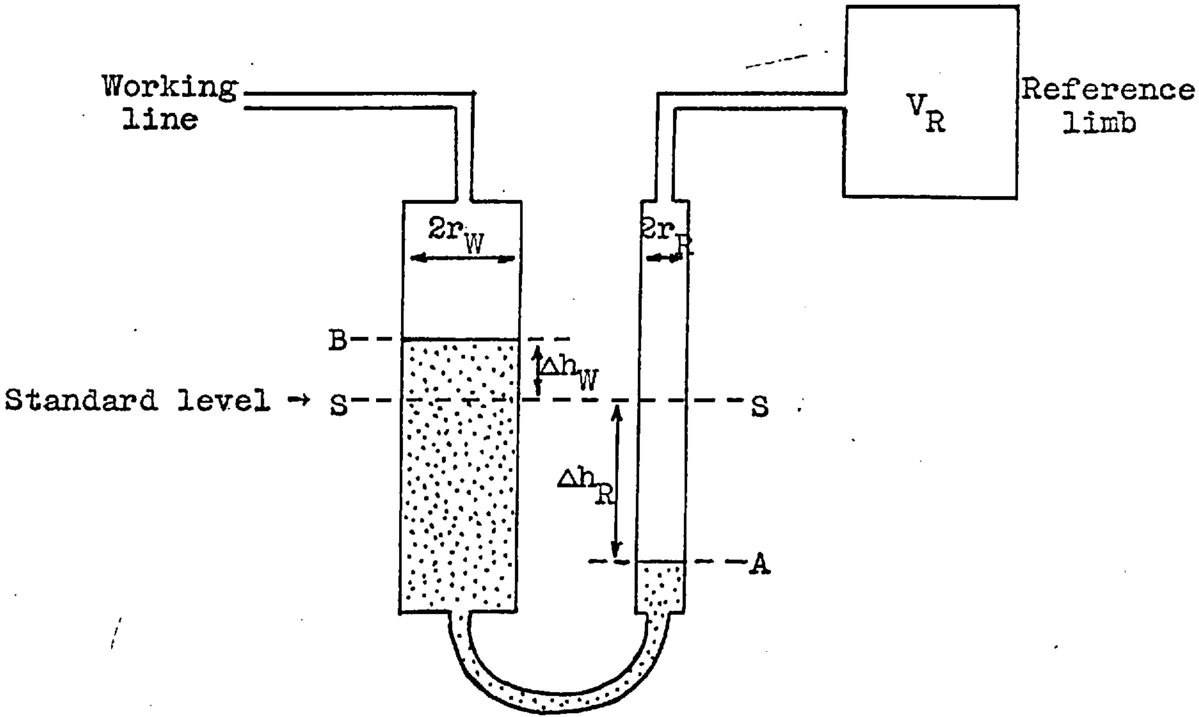


Fig. 36. Manostat sensing cell (diagrammatic) showing dimensions.

from the shaker would prevent sticking: evidently this was not so. Since the discrepancy between the calibration curves and actual working values increased during experiments, it is likely that the recording device was subject to a further steady drift.

Since some time had been spent developing this device, and there was doubt if it could be made to work in a reasonable time, further development was abandoned, and readings were recorded visually.

A 3 Sensitivity of the manostat sensing cell

The manostat sensing cell is shown diagrammatically in Fig. 36. The fall SA in the electrolyte level in the reference limb (Δh_R) and the corresponding rise SB in the working limb (Δh_W) are caused by a pressure decrease from P_W to $P_W-\Delta P_W$ in the working line, there being a corresponding decrease from P_R to $P_R-\Delta P_R$ in the reference limb. Applying Boyle's Law to the gas enclosed in the reference limb:

$$P_RV_R = (P_R-\Delta P_R)(V_R+\pi r_R^2\Delta h_R) \qquad \text{(i)}$$

For equilibrium at level A:

$$P_R-\Delta P_R = P_R-\Delta P_W+dg(\Delta h_R+\Delta h_W) \qquad \text{(ii)}$$

where d = density of the fluid in the sensing cell.

But, since the volume of fluid in the sensing cell is constant,

$$\pi r_R^2\Delta h_R = \pi r_W^2\Delta h_W \text{ , or } \Delta h_W = \Delta h_R.\frac{r_R^2}{r_W^2} \qquad \text{(iii)}$$

Substituting from (iii) into (ii):

$$\Delta P_R = \Delta P_W - dg\Delta h_R(1 + \frac{r_R^2}{r_W^2}) \qquad \text{(iv)}$$

Substituting from (iv) into (i) gives the following expression for the sensitivity of the cell:

$$\frac{\Delta h_R}{\Delta P_W} = \frac{V_R}{P_R \pi r_R^2 - V_R dg(1+r_R^2/r_W^2)} \qquad \text{(v)}$$

For optimum sensitivity, therefore, the volume of the reference limb, V_R, should be large, and the tube diameter, r_R, small. This was applied in constructing the cell described in Section 2.214.

A 4 Solubility of oxygen in aqueous alkali

Data are available for the Bunsen absorption coefficient, α, for solutions of oxygen in aqueous sodium and potassium hydroxides[106]: α is the volume of oxygen, corrected to 0°C, dissolved in unit volume of alkali.

For the purpose of the present work these data were interpolated and extrapolated using the equations[107]:

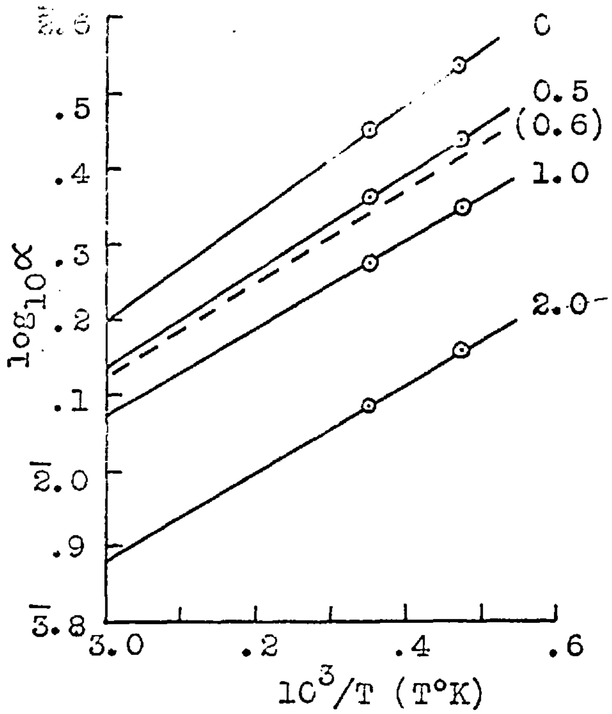
$$\ln \alpha = - \frac{\Delta H}{RT} + \text{constant} \qquad \text{(i)}$$

at constant alkali concentration, c, and:

$$\ln \alpha = kc + \text{constant} \qquad \text{(ii)}$$

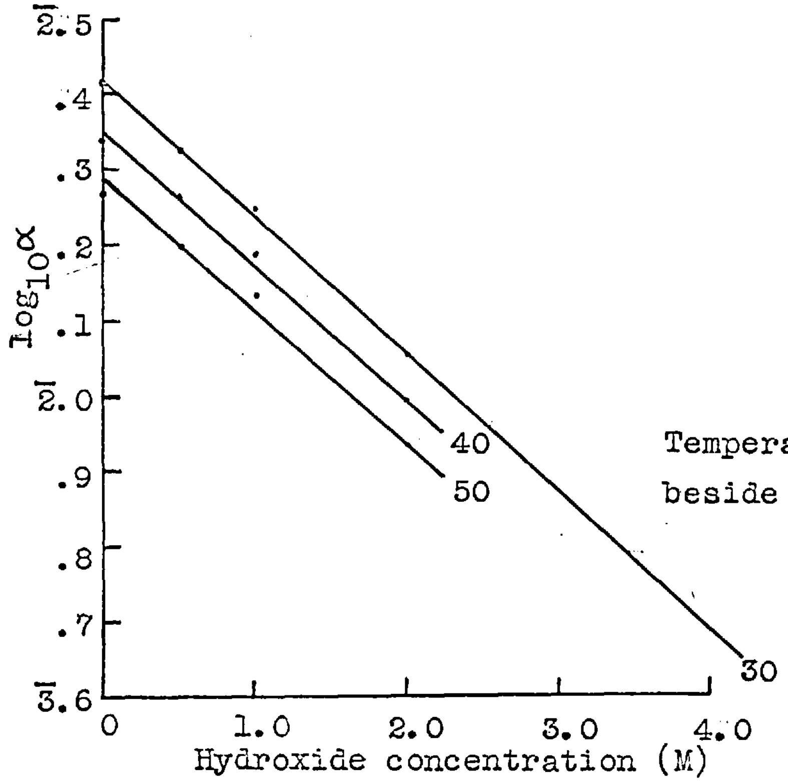
at constant temperature, T, where k is a constant.

The available data are plotted in Fig. 37, values of α



Hydroxide concentration (M) beside curves.

Fig. 37. Solubility of oxygen in aqueous sodium and potassium hydroxides: dependence of Bunsen absorption coefficient α on temperature.



Temperature (°C) beside curves.

Fig. 38. Dependence of α on hydroxide concentration.

for solutions of sodium and potassium hydroxides being so A 4 close that the mean has been plotted as a single point. The results obtained by extrapolating to higher temperatures are shown in Fig. 38. Although the three extrapolated points obtained for each temperature appear to fall on a curve, the best straight line has been used to extrapolate to 4 M alkali at 30°C (see Section 3.134).

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