THE KINETIC AND THERMODYNAMIC BEHAVIOUR OF SOME PLATINUM METAL COMPLEXES

A Thesis submitted for the degree of

Doctor of Philosophy

by

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ABSTRACT

The construction and operation of a stopped flow apparatus is described, which is capable of studying the rates of moderately fast chemical reaction by observation of the change in absorbance of visible or ultraviolet light. Half lives as low as 5 m-sec. can be measured over a temperature range of 0 to 50°C.

The assembly was used to investigate the rates of reduction of sodium chloroiridate (IV) by iodide and nitrite ions. These reactions have been found to be much slower than other electron transfer reactions of chloroiridate (IV) being less than 10^3 l mole^{-1} sec.^{-1} compared with about 10^6 l mole^{-1} sec.^{-1} when the electron is donated from either Fe^{2+} or $IrBr_6{}^{3-}$.

The relative stabilities of the chloride, bromide iodide and thiocyanate complexes of the type Pd dien X^+ and $PdEt_4$ dien X^+ have been examined (dien = diethylenetriamine and Et_4dien = 1,1,7,7,tetra-ethyl diethylene tnaimine). The order of stability constants, $Cl < Br < I < SCN$ indicates that both sets of complexes are class (b). The values of ΔH^o for the interchange of various ligands give the stability order

$Cl < Br < I < SCN$ for the dien complexes and $Cl > Br \ll I < SCN$ for the Et_4 dien system. The results and the ultraviolet absorbance spectra of related compounds are consistent with a slight increase in class (b) character being opposed by steric effects in the tetra ethyl complexes. The thiocyanate ion in $PdEt_4$dien SCN is nitrogen bonded and it therefore appears that (in this case also) steric factors overrule the increase in class (b) character which should reinforce the tendency towards sulphur bonding.

The displacement of bromide ion in sodium bromoplatinate (IV) by iodide is conveniently studied by conventional spectrophotometric techniques. The reaction proceeds in three stages which probably correspond to the formation of trans $PtBr_4I_2^{2-}$ and trans $PtBr_2I_4^{2-}$ as intermediates. The bromide replacement resembles the $PtCl_6^{2-} + I^-$ reaction in some ways and a general mechanism for substitution into PtX_6^{2-} complexes by way of reduction and reoxidation is proposed.

ACKNOWLEDGEMENT

I wish to thank my supervisor, Dr. A. J. Poë, for his interest, guidance and encouragement during the past three years; also the many people in the Radiochemistry Laboratory and elsewhere who have assisted me "beyond the call of duty" on innumerable occasions.

CONTENTS

CHAPTER 1

The Construction and Operation of a Stopped Flow Assembly for the Study of Moderately Fast Chemical Reactions.

INTRODUCTION

Conventional methods for studying the rate of chemical reactions are satisfactory if the half life is greater than 20 seconds or so. The reaction studied has to be initiated, usually by mixing the reagents, and its progress followed by direct chemical analysis or measurement of some physical property, for example conductance or pH. In the study of faster reactions, it is important to ensure that the time taken to start the reaction and to make observations during the run are still negligible when compared with the half life of the reaction.

In 1923 Hartridge and Roughton[1] described a continuous flow (CF) technique by which reaction rates 100 times faster than those hitherto studied could be measured. The major disadvantage of the method was the large volume of reagents required. At the present time, Stopped Flow (SF) and Accelerated Flow (AF) assemblies[2] developed from the CF technique are in operation where reactions whose half lives are a few milliseconds can readily be studied and only 0.1 ml. of each reagent is necessary per run.

The fastest reaction that can be studied by a flow technique is determined by the time taken to mix the reagents. In most of the mixing devices currently in use, this time is between one and five milliseconds, and it appears unlikely that appreciable reduction of mixing time will result from improved design. Faster reactions are studied by methods that avoid mixture of the reagents, relying instead on a sudden displacement from equilibrium conditions. The Temperature Jump, Ultrasonic Absorption and E.S.R. methods are examples of such techniques, and are fully described elsewhere.[3]

The Stopped Flow method is applicable to reactions in the gas or liquid phase that are complete in times greater than 0.01 seconds. The advantages of SF over CF and AF are the small volumes of reagents necessary; the simplicity of the electronic apparatus required, and the ability to follow changes of several different physical properties.

The design of apparatus currently in use is for the greater part derived from that developed by Gibson[2d] although both Roughton and Chance had used the technique earlier.

Principle of the SF method

Two reagent solutions are forced by means of syringes through a mixer into an observation tube. The flow is suddenly arrested and the mixture comes to rest in 1-2 msec. provided there is no air in the system. The solution coming to rest at 1 cm. from the mixing chamber will have been mixed for about 5 msec. and the remainder of the reaction may be studied at the one fixed point by following the alteration in any physical property that can be measured in microseconds.

A convenient method of observing the response is to convert the measurements to a voltage and to photograph or "store" the trace obtained on an oscilloscope when the measured signal is combined with a suitable time base. Suitable properties for measurement include[4] conductance and ultra-violet or visible light absorption.

Description of the present assembly

The apparatus constructed during the course of this work was built to a basic design by Dr. J. Moore (Northwestern University). Reactions that proceed with changes of visible or ultra-violet light absorption between 750 and 230 mμ can be followed so long as the change in transmittance is greater than 10% and that the initial transmittance of the reagent is less than 50%. That is, under normal conditions a change in optical density of 0.04 can be studied, but if there is high initial adsorption, a larger change may be necessary. The temperature range at present accessible is 10°C to 50°C from a water circulating device, but this could easily be extended.

The time for complete reaction can be from 2 secs. to 0.05 secs. if the oscilloscope is used; slower reactions may be studied by means of a suitable chart recorder and potential divider.

The mixing chamber was made from three plates of teflon, and has a total volume of about 2.5 μl. The quartz observation cell (Thermal Syndicate) rests immediately on top of the mixer and has a pathlength of 2.00 mm. and a volume of 0.08 ml. The solutions are stored in 2 ml. "luer lok" metal and glass syringes (Chance) which are connected via a three-way tap system to reservoir syringes and to the mixing chamber. In this assembly, 0.5 ml. of reagent is completely

STOPPED FLOW
ASSEMBLY

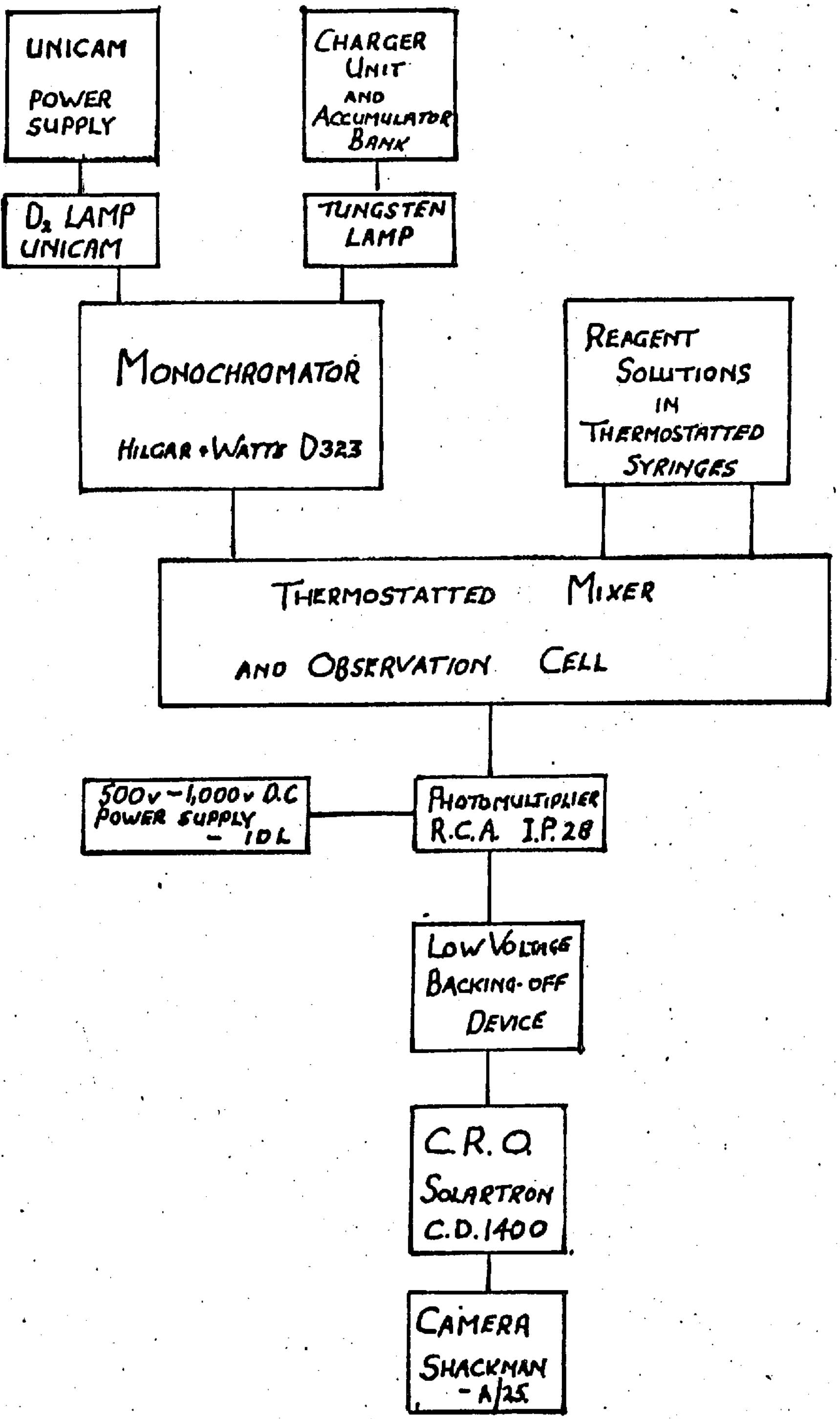


FIG 1.

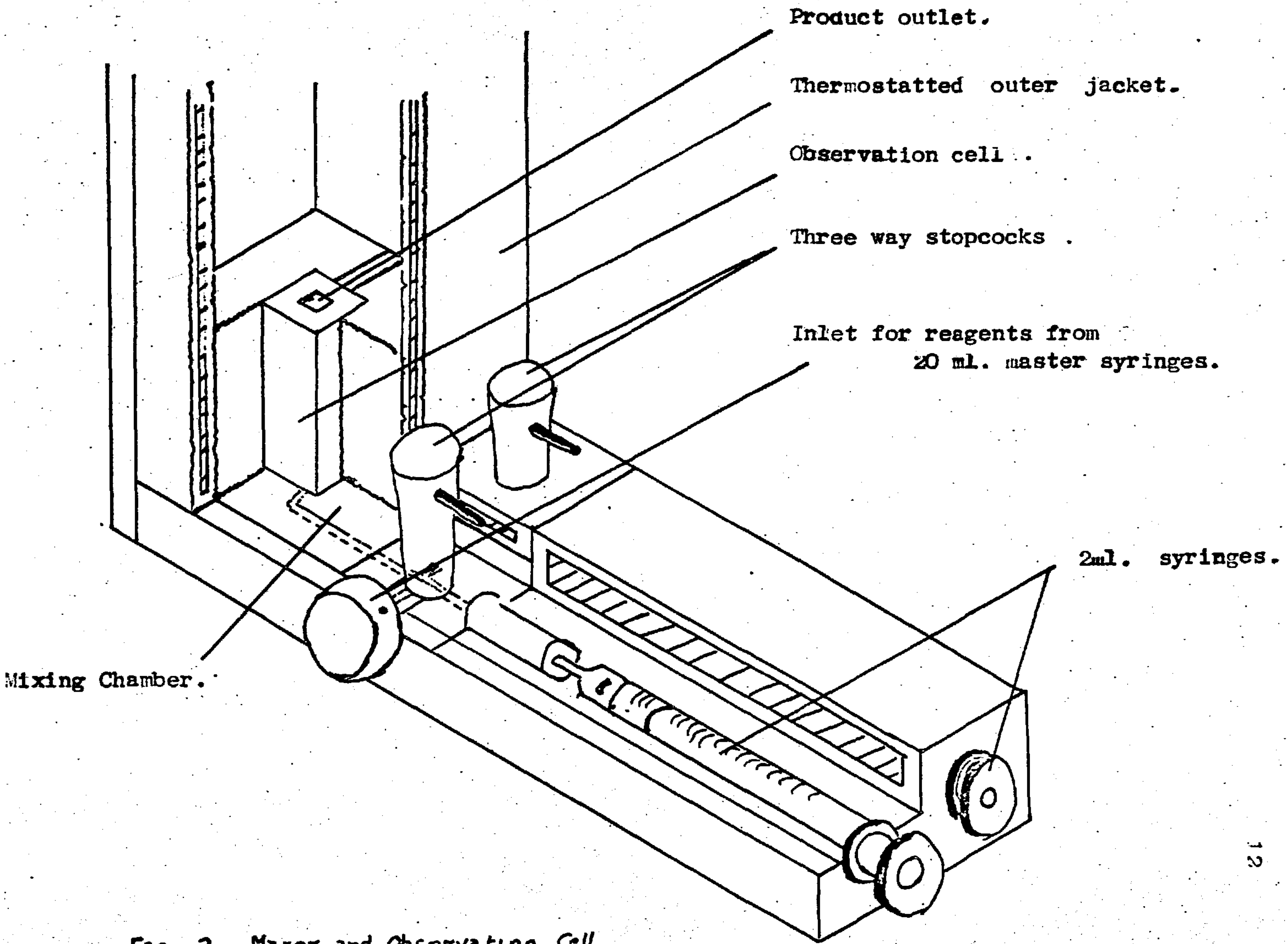


Fig. 2. Mixer and Observation Cell.

adequate to flush the reacted liquid out of the reaction cell, and allow the new reaction to be studied. Six to ten shots can therefore be observed with one filling.

The complete mixer and observation assembly is surrounded by a copper jacket through which liquid maintained by a Shandon Ultra Thermostat (E6) may be circulated. The temperature of the observation block is found by measuring the resistance of a themistor (Brimar F. 23) embedded in the syringe housing, by means of a simple Wheatstone Bridge circuit. The necessary calibration curve was constructed by referring to calibrated thermometers.

Visible (6V. 26W. Tungsten lamp - Unicam) or ultraviolet light (Deuterium lamp - Unicam) is coupled to a monochromator (Hilger and Watts D 246) and passed through the observation cell. The energy transmitted is detected by a photomultiplier (R.C.A. IP28) powered by a high tension unit (I.D.L. 532/A). The change in optical density during a reaction produces a change in voltage across the load resistor which is recorded against the time base on an oscilloscope (Solartron CD 1400). The second set of Y plates on the C.R.O. is used to take a standard signal (50 c.p.s.) to allow direct calculation of the rate constant without having to calibrate the oscilloscope time bases. Each shot results in a curved signal trace and the sinusoidal calibration trace both appearing on the screen which is photographed (Shackman AC/2/25 35 mm. oscilloscope camera) Fig. 3.

The tungsten lamp is run from a pair of accumulators which are charged by a simple rectifier bridge circuit arranged so as to charge one battery while the other is in use (Fig. 4). Full charge rate is 6 amps and trickle charge approximately 1 amp.

If changes in transmittance from 60% to 40% were to be studied, the photomultiplier voltage might change, typically, from 4.6 volts to 3.1 volts. A better display of the reaction on the screen can be obtained by applying a back potential by means of dry batteries of, in this case, 3.0 volts, and then increasing the amplification of the oscilloscope. In this manner, the range 60% to 40% transmittance may be made to fill the whole screen. The circuit arranged to do this (Fig. 6) was combined with a 1,000 pF condenser to act as a high frequency filter. In all but the fastest reactions, (those complete in 0.05 sec.) this capacitor was used

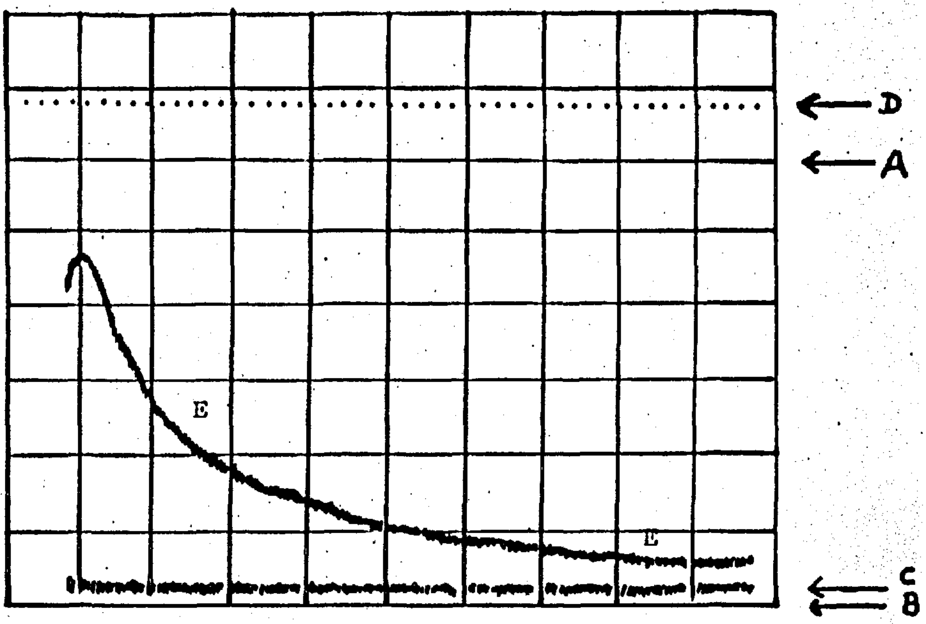


Fig. 3. A Typical Oscilloscope Trace.

A	Low Transmittance Line
B	High Transmittance Line
C	Infinite time transmittance
D	Time Calibration.
E	Reaction Trace.

to reduce the noise arising from the power supply used which makes the trace diffuse.

A few alterations have been incorporated into the basic design with some improvement in performance. The joint between the tap block and the mixer was originally a butt joint, and leaked quite badly on occasions, so the workshop fitted two 'straw' connections as in Fig. 7. This has greatly improved the position, but means that extreme care is needed in parting these two pieces for cleaning.

The removal of air from the system was made easier by the attachment of a third syringe and three-way tap on the outflow (Fig. 8). Air can be removed by alternately pushing and pulling the reagent syringes while the apparatus is filled with boiled out distilled water. All gas rises into the top syringe where it is readily visible and easily expelled.

Rather than use standard solutions for calibration purposes, it was preferred to use where possible neutral density glass filters (Chance) while the observation cell was filled with water. (Fig. 9.) This allows checking and rechecking of maximum and minimum absorbance traces in rapid succession; the necessity for which arises from the interlocking of some of the oscilloscope controls.

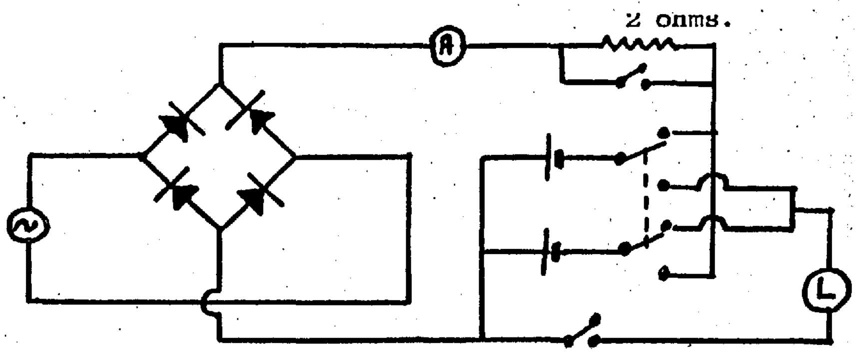


Figure 4. Accumulator Charger Circuit.

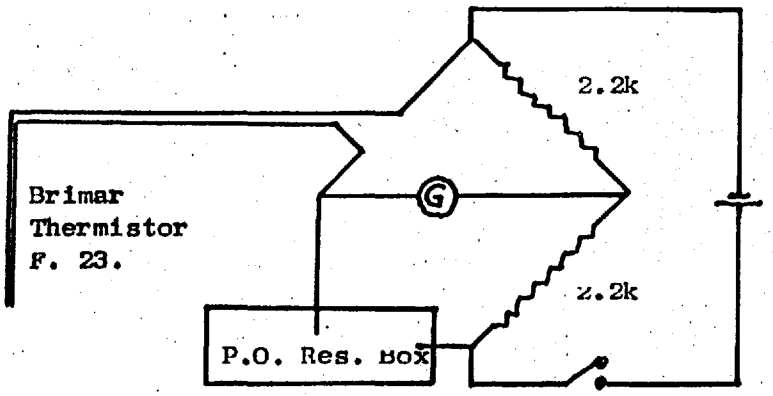


Figure 5. Thermistor Resistance Measurement.

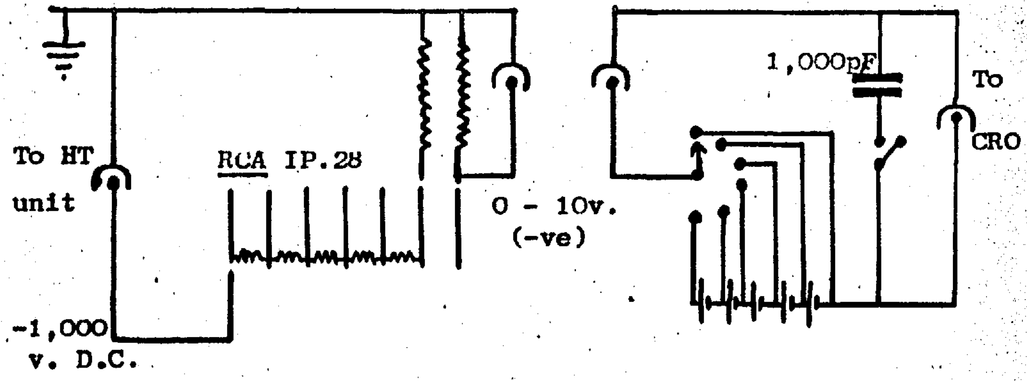


Figure 6. Photomultiplier and Bias Voltage.

(all resistors 100k.)

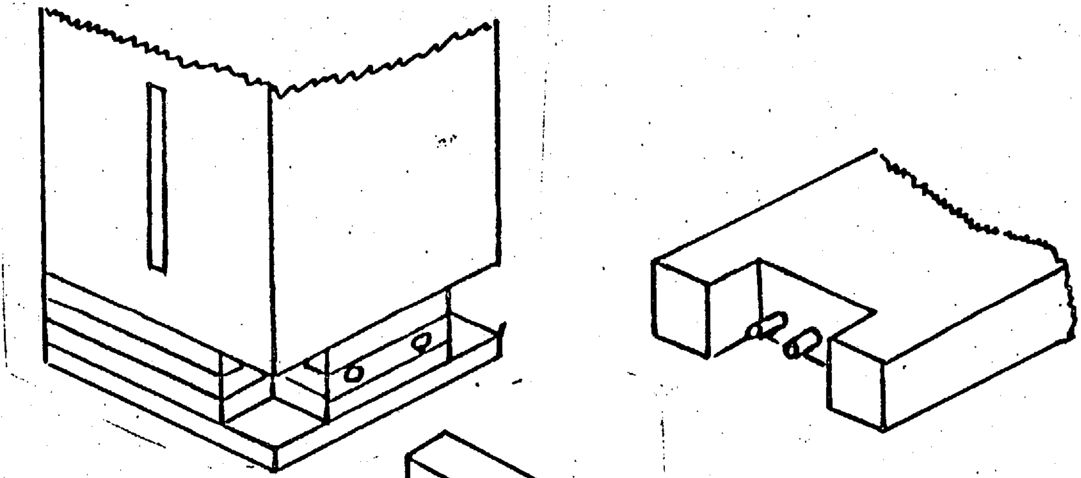


FIG 7. TAP BLOCK AND MIXER MODIFICATION.

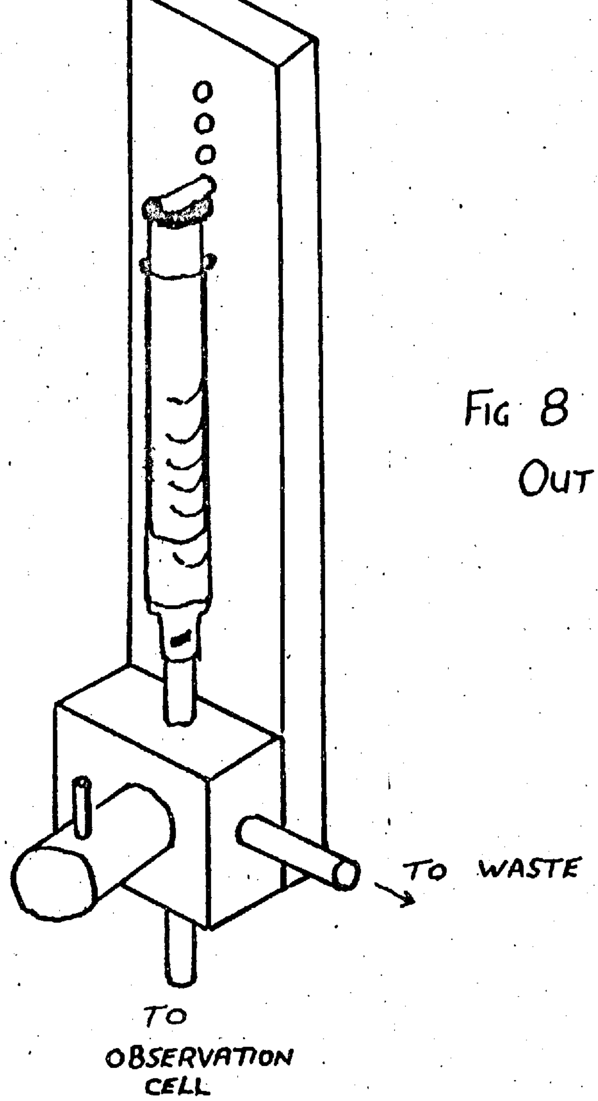


FIG 8 OUT FLOW SYSTEM.

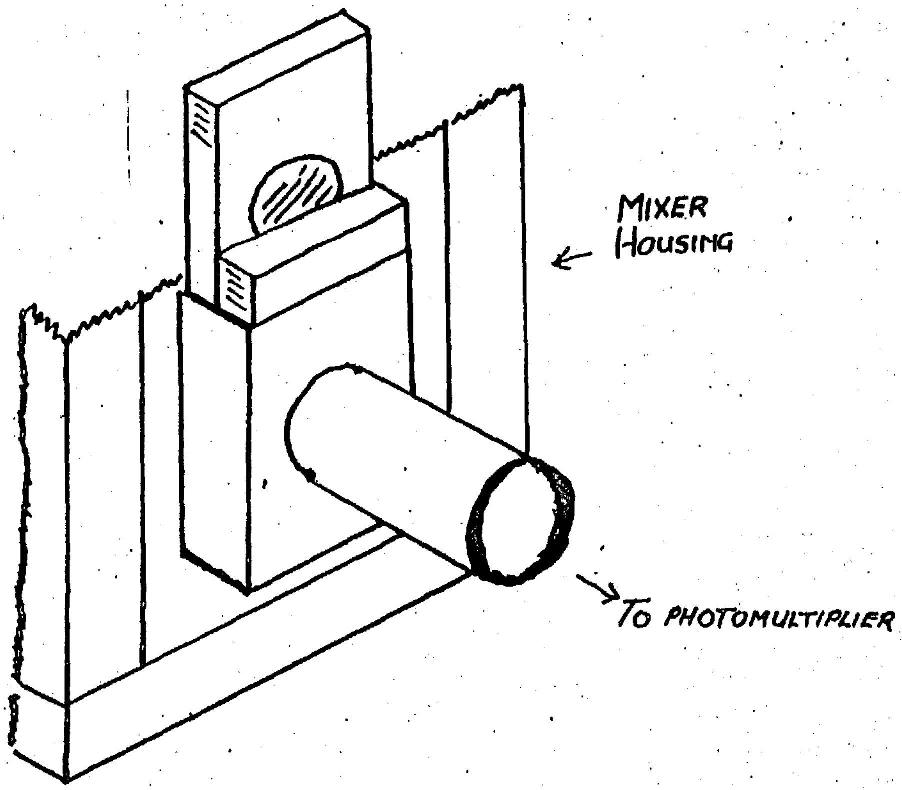


FIG 9. CALIBRATION FILTERS

Tests on the performance of the apparatus

1. The volume delivered by each syringe was identical.

The dimensions of the pistons were measured with a micrometer and found to be the same. A standard solution of potassium permanganate was placed in one syringe and distilled water in the other. The optical density of the mixed solutions was compared with that obtained when the solutions were interchanged. With the oscilloscope covering the range 0.172 to 0.340 the signal was the same to within a millimetre over the eight centimetre screen. The equivalence of volume delivered is at least ± 1% and probably much better than this.

2. The C.R.O. screen was found to give a linear response to changes in voltage across the Y plates, and the photomultiplier and oscilloscope combined also responded linearly.

With the oscilloscope amplifier on 2 volts/cm., increments of $1\frac{1}{2}$ volts were made in the voltage across the Y plates, and the corresponding deflection in centimetres read off the photograph of the trace.

Slight deviations from linearity were observed at the extreme top of the screen (up to -3%) when the lower set of Y plates were used, and all the kinetic runs were done using the lower portion of the screen for optical measurements and the top two centimetres for the time calibration.

The set of four glass filters ~~were~~ was placed in various combinations between the photomultiplier and observation cell with water in the cell, and the response of the oscilloscope compared with values calculated from the individual transmittance (Table I).

3\. The accuracy of the monochromator calibration was checked using holmium glass.

Although this was found to be not particularly good, it is adequate since the band width of radiation used under normal conditions is about 10 mμ when the slit-width is 0.5 mm.

4\. The speed and efficiency of mixing the reagents was investigated using a very fast reaction.

Sodium hydroxide (0.09M) contain~~ed~~ing sufficient phenol phthalein to give an optical density of 0.9 at 600 mμ in the observation cell was mixed with 0.10M hydrochloric acid at 24.5°C. The acid-base reaction has a rate constant of the order of 10^{11} l mole^{-1} sec^{-1} at this temperature and the rate of interconversion of

TABLE I

Filter	Screen deflection (in cms. from top)	$\frac{I_o}{I}$	$OD_{obs.}$	$OD_{calc.}$	Δ
Zero trans.	2.0	∞	∞		
N.D. 3	3.05	5.71	0.757		
N.D. 2	4.4	2.50	0.398		
N.D. 1	5.7	1.62	0.210		
U.V. 1	7.4	1.11	0.045		
100% trans.	8.0	1.00	0		
2 + UV	4.2	2.725	0.435	0.443	+2%
1 + UV	5.3	1.82	0.260	0.255	+2%
2 + 1	3.45	4.14	0.617	0.608	+1.5%
3 + 2	2.40	15.0	1.17	1.155	-1.5%
UV + UV	6.85	1.238	0.093	0.090	-3%

TABLE II

Absorbance maxima in a holmium glass

Experimental	Actual
288	287.5
335	333.7
362	360.1

the indicator is in the temperature-jump range, so any colour observed after mixing would arise from incomplete mixture rather than incomplete reaction.

No change from 100% transmittance was, however, observed; and since an absorbance change of 2% would be easily detected, mixture is said to be at least 98% complete by the time the liquid reaches the observation cell.

Volume between mixer and observation cell = 0.02 ml.
Time taken to push in syringes (estimated) = 0.1 to 0.5 sec.
Volume mixed in this time = 1 ml.
Rate of flow = 2 to 10 ml/sec.
Time for solution to travel from mixer to cell = 0.01 to 0.002 sec.

The fastest reaction capable of being studied on this apparatus will thus have a half life of 5 msec. or so. A faster flow rate would increase this fractionally.

5. A brief study of a previously studied reaction was carried out as an overall check on the apparatus.

Mr. D. H. Vaughan studied the reaction of carbonic acid in water, following the method described by Dalziel.[5] Three runs were carried out at each of three temperatures, and rate constant and activation parameters compared with existing data (Table III).

TABLE III

Carbonic acid decomposition

Temperature	Observed rate ($sec.^{-1}$)	Average rate ($sec.^{-1}$)	
18.4	11.57 11.91 12.36	11.94	
24.7	21.59 20.91	21.25	E_A = 16.0 Kcal/mole
35.0	53.38 52.65 51.83	52.62	

Comparison with existing data

Worker	Observed[(a)] rate (18°C) $sec.^{-1}$	Temp. range	E_A	Technique
Moore[(b)]	11.5	23 - 30	15.9	SF
Scheurer[(c)]	11.8	23 - 37	16.1	SF
Dalziel[(d)]	12.3	19 - 23	16.9	CF
Brinkman[(e)]	12.9			
Vaughan	11.48	18 - 35	16.0	SF

(a) Calculated from the activation energy where necessary

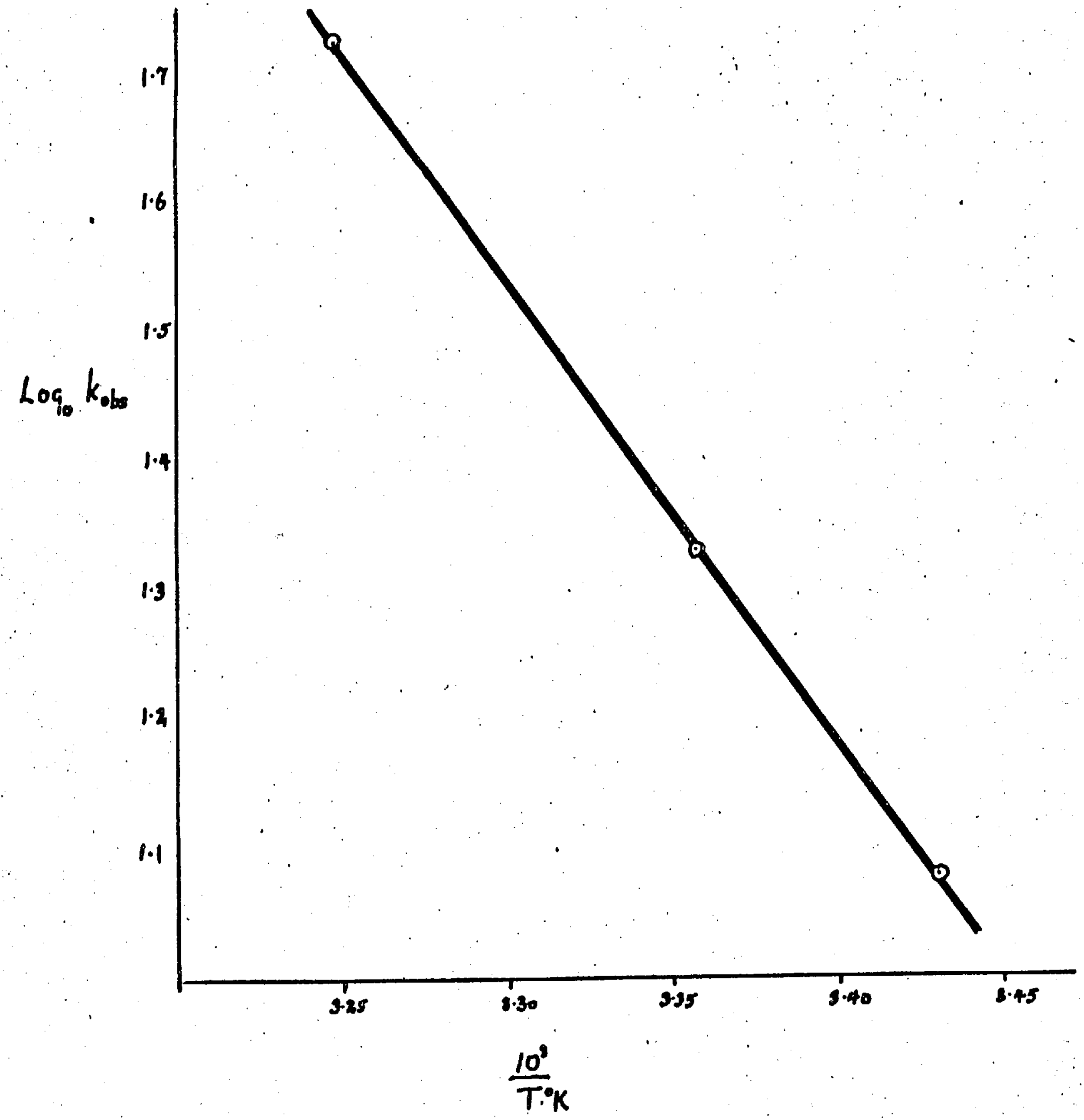
(b) J. Moore. Thesis, Northwestern University.

(c) P. Scheurer, R. Brownell and J. LuValle; J. Phys. Chem., 1958, 62, 809.

(d) K. Dalziel, Reference 5.

(e) R. Brinkman, K. Nargaria and F.W.J. Roughton, Phil. Trans. Roy. Soc., 1933, A232, 65.

DETERMINATION OF THE ACTIVATION ENERGY FOR DECOMPOSITION OF CARBONIC ACID



Use of the apparatus

In order to facilitate the operation of the assembly by other workers, a set of instructions has been compiled.

1. A supply of suitable developer (e.g. Kodak D.K.20) and fixer should be available, and the camera loaded with an adequate length of 35 mm. film. Wind on four frames at the start in order to clear the exposed film.
2. Switch on power - left-hand wall switch.
3. Switch on thermostat and adjust temperature.
4. Switch on photomultiplier power supply - (I.D.L. power pack bench - mains on - wait 1 minute - E.H.T. on). Check E.H.T. = 500 to 700 volts.
5. Switch on oscilloscope. Turn right-hand knob on the main frame clockwise until the graticule is faintly lit, but still plainly visible.
6. Leave to stabilise for about 60 minutes.
7. Switch on deuterium lamp power supply or tungsten lamp accumulator charger.
8. Select wavelength by rotating monochromator drum. Check entry slit width fully open and leaving slit-width = 0.1 to 0.5 mm.

9. Fill the mixing chamber with distilled water and expel all air in the system by alternately pulling and pushing the mixer syringe plungers when the taps are arranged to connect the mixer to all three syringes. Air will then rise into the outflow syringe, and can be removed.

10. Select top (minimum) and bottom (maximum) transmittance from the range of filters and 100% and 0% which occur when no filter is used and when the shutter is closed, respectively.

11. Check that the Bias voltage is zero.

12. Rotate 'level' and 'stability' controls on the oscilloscope fully clockwise. With the top limit arranged adjust Y Shift on the lower set of Y plates until the trace occurs on the third horizontal line on the graticule, i.e. 2 cms. from the top.

With the bottom limit arranged, adjust 'Y Gain' on the lower set of Y plates until the trace occurs on the bottom horizontal line, i.e. 8 cms. from the top of the graticule.

13. Repeat operations 11 and 12 until both conditions are met.

14. If this is found to be impossible:

(a) the distance between the two traces may be increased by:

(i) increasing the photomultiplier voltage NOT above 1000v;

(ii) increasing the slit width of the monochromator;

(iii) increasing the amplification in volts per centimetre of Y lower on the C.R.O.

(b) The pair of lines may be moved vertically without altering their distance apart by using 'Y shift' or altering the bias voltage.

Then repeat steps 11 and 12 until conditions are fulfilled.

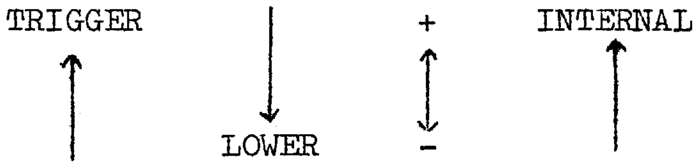
15. Push syringes in to expel the distilled water.

16. Put reagents into syringes by means of the 20 ml. storage syringes and allow to come to temperature.

17. Alter the time base on the oscilloscope to 200 msec/cm., wait until a trace has just started, and then push the trolley firmly in one stop. Note the approximate time for reaction and whether the trace is adequately displayed with respect to transmittance changes. If no sign of a deflection is observed, it is probable that the reaction is too fast.

18. From the rough determination, select a suitable time scale and switch on the 4 v. a.c. supply. Make sure that the signal on Y upper occupies the top two centimetres of the screen.

19. For relatively slow reactions (those complete in 0.2 secs. or more) the removal of reacted liquid should be used to trigger the sweep, but for faster rates the start of the reaction has to be used. For example: a reaction proceeds with increasing optical density. The removal of reacted solution will then cause a sudden increase in transmittance and the spot will move downwards followed by a more gradual positive shift as the reaction continues. If this reaction were fairly slow, a negative trigger would be used. Check the four trigger controls on the X control panel:



20. Turn 'stability' anticlockwise until continous sweep ceases. Then turn 'level' anticlockwise until trace just reappears and continue turning until it just disappears again.

21. Push in the syringes one hole. Check that there is only one trace of the spot across the screen. If the trace continues to run after the reaction turn 'level' and/or 'stability' a little anticlockwise.

22. Refill the syringes and allow to come to temperature.

23. Open camera shutter.

Push in trolley, keeping the hand on trolley so as to prevent the syringes filling with reacted solution.

Close camera shutter.

Place pegs in slots to hold trolley ready for the next shot.

Remove 50 c.p.s. signal.

Open camera shutter, alter trigger +ve -ve switch and reset.

Close camera shutter.

24. Wind on film and replace a.c. calibration.

25. Run at least three shots under identical conditions and then repeat at other conditions as required.

26. At end of series, wind on the film by four frames, open camera and remove exposed cassette. Reconnect the unexposed film to the stand-by cassette and close camera.

27. Switch off the individual pieces of apparatus and the main power supply. Rinse the mixer assembly by passing at least two storage syringes full of distilled

water. Leave the assembly full of water and with all taps pointing at 45° to the direction of flow.

28. Develop and fix the film in the normal way.
29. Put the film into an enlarger and fit the image on the 7" x 9" template provided. Note the wavelength of the calibrating trace in centimetres on the graticule; the distance (again in cms. on the screen) of the infinite time trace from the top transmittance line, and a reference number by which the computer result may be correlated with the negative.
30. Record approximately ten pairs of coordinates on the reaction curve in the order X_1, Y_1, X_2, Y_2, each measurement to be in centimetres from the top transmittance line with respect to the C.R.O. screen.
31. Punch Fortran cards in the columns indicated as outlined overleaf.

The treatment of data

The computer programme as written will convert the information read into optical densities at various time intervals. The dependability of each point is tested by introducing an error of 0.1 cm. both in the original reading at each time, and the infinity value, and calculating the function:

$$F = \frac{1}{[(OD_t - OD_{inf}) - (OD_{t*} - OD_{inf*})]}$$

ARRANGEMENT OF RESULTS FOR CARD PUNCHING

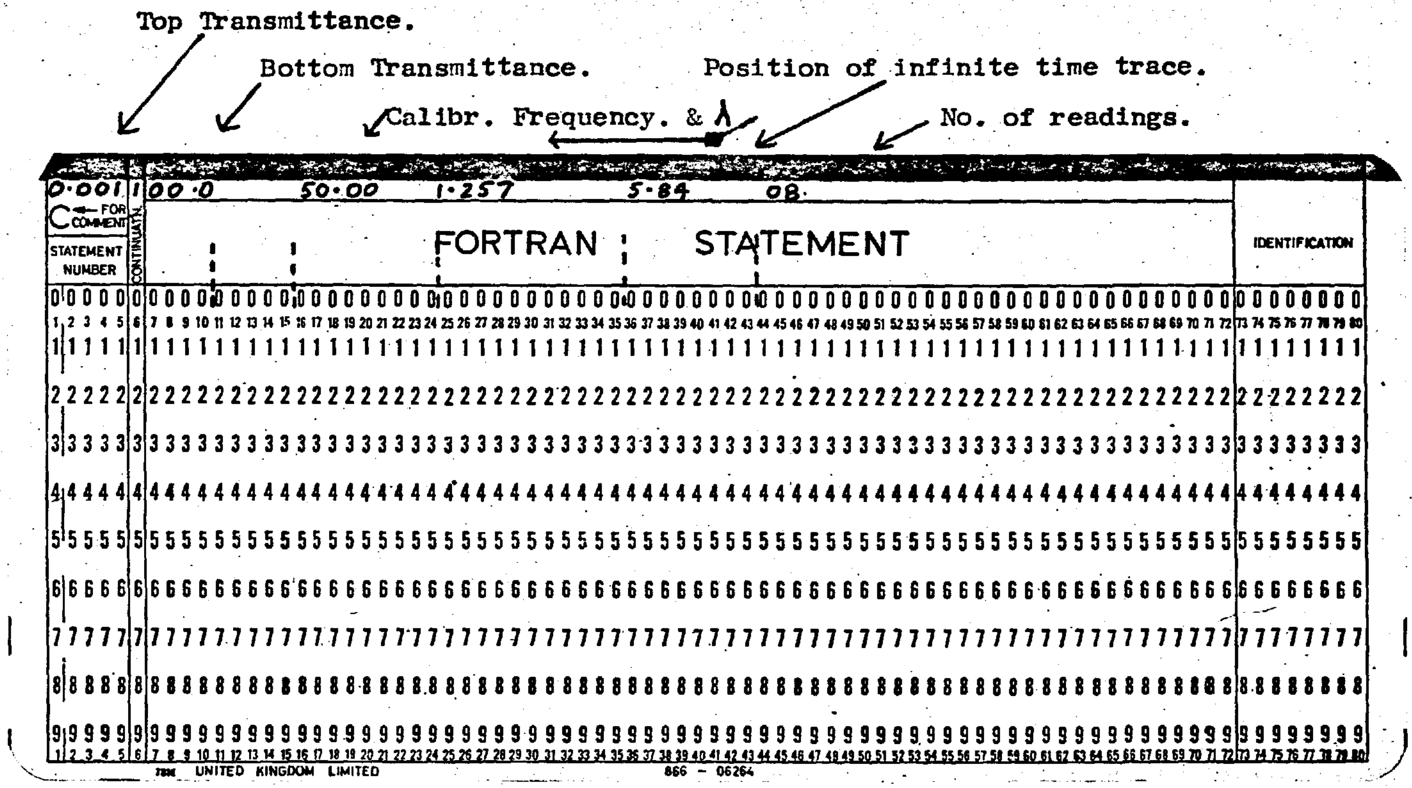
		Column No's	Example
At beginning of results:		1 - 5	$DATA
First shot:			
CARD 1	Shot reference number	1 - 4	1234
CARD 2	Top transmittance	1 - 5	0.001
	Bottom transmittance	6 - 10	100.0
	Frequency of calibration	16 - 19	50.0
	Wavelength of calibration	25 - 30	1.257
	Infinite time trace distances	36 - 40	5.84
	Number of readings	44 - 45	08
CARD 3	Horizontal reading, X_1	1 - 10	2.00
	Vertical reading Y_1	11 - 20	1.25
	Vertical reading X_4	61 - 70	4.40
	Vertical reading Y_4	71 - 80	5.28

CARDS 4,5 Pairs of readings as card 3 until the number of readings on card 2 has been reached.

Last shot:

CARD 1 Shot reference number must be 0099.
CARDS 2,3,4 as usual.
FINAL CARD End of file card 1 - 3 EOF

An example of CARD 2 is shown in Fig. 10.



0·001 1 00·0 50·00 1·257 5·84 08

Figure 10. Card 2 of a data set.

The method of least squares is used to fit the values of $\log._e (OD_t - OD_{inf})$ and t to a straight line,[6] each point being counted F times. The slope of the line, k_{obs}, is printed out. Each value of the optical density is then compared with the value read off the straight line graph, and the residual is quoted together with its sign, thus indicating any curvature in the rate plot. If more than one third of the readings deviate by more than 10% a rate constant based on a second order reaction is calculated as before so long as a value of the initial optical density of the system and the cell path length have been read in.

The variance in the slope is calculated and printed out in both cases, and the standard deviation of the rate constant is given by the square root of the variance.

Possible future developments

Although the set up works reasonably well, several improvements could be made. The mains frequency is at present used as a standard for time calibration on each run, but a more reliable signal could be obtained from

Cont^d on P.38

```
      C
      C    S T O P P E D   F L O W   R E A C T I O N   K I N E T I C S
      C
      C
      C           USING RESULTS WEIGHTED ACCORDING TO THE EFFECT OF AN ERROR
      C
      C                    OF 0.1 IN BOTH Y(J) AND YINF.
      C
            DIMENSION ECD(100),  Z(100),Y(100),X(100),OD(100),DIFF(100),
           A   TIME(100),RESID(100),  YBAR(100),  XSRES(100),  PLOT(100)
      C
      C     INFORMATION ON EXPERIMENTAL CONDITIONS
      C
      C      INFORMATION ON EXTINCTION COEFFICIENT AND PATH LENGTH
      C      APPLY TO THIS RUN ONLY
            ED=2400.0
      C
          2 WRITE(6,7)
          7 FORMAT(1H1,40X,36H STOPPED FLOW REACTION KINETIC DATA.,/////)
            READ(5,3)NOSHOT
          3 FORMAT(I4)
            WRITE(6,5) NOSHOT
          5 FORMAT(14H SHOT  NUMBER, I4///)
            WRITE(6,8)
          8 FORMAT(20X,36H REACTANT A            CONCN            ,//
           B   20X,        36H REACTANT B            CONCN            ,///
           C  60H  LAMBDA                                                ,
           D//30X,   12H TEMP=        ,  10X,  21H IONIC STRENGTH =     ,///
           E30H FILM NO          FRAME  NO         ,/////)
      C
      C
            READ(5,1) TOPTR,BOTTR,FREQ,WVLNTH,YINF,N,(X(J),Y(J),J=1,N)
          1 FORMAT (2F5.1,3F10.2,I5/( 8F10.3))
            DFJSUM=0.0
            SUMX=0.
            SUMY=0.
            SUMXSQ=0.
            SUMXY=0.
```

```
      DARKY=6.0*TOPTR/(BOTTR-TOPTR)
      YLIGHT=DARKY/(TOPTR/100.0)
      EODINF=ALOG10(YLIGHT/(DARKY+YINF+0.1))
      ODINF=ALOG10(YLIGHT/(DARKY+YINF))
      DO 6 J=1,N
      IF((Y(J).LE.0.).OR.(DARKY.LE.0.).OR.(YLIGHT.LE.0.))    GOTO98
      Z(J)=Y(J)
      OD(J)=ALOG10(YLIGHT/(DARKY+Z(J)))
      EOD(J)=ALOG10(YLIGHT/(DARKY+Z(J)-0.1))
      PLOT(J)=ALOG (ABS(ODINF-OD(J)))
      DIFF(J)=1.0/(ABS(PLOT(J)-ALOG(ABS(EODINF-EOD(J)))))
      TIME(J)=X(J)/(FREQ*WVLNTH)
C
C     LEAST SQUARES FIT TO FIRST ORDER RATE PLOT
C
      PRODXY=PLOT(J)*TIME(J)
      SUMXY=SUMXY+PRODXY   *DIFF(J)
      SUMX=SUMX+TIME(J)   *DIFF(J)
      SUMY=SUMY+DIFF(J)   *PLOT(J)
      SUMXSQ=SUMXSQ+DIFF(J)*(TIME(J)**2.0)
      DFJSUM=DFJSUM+DIFF(J)
    6 CONTINUE
      BETA= (SUMXY-SUMX*SUMY/DFJSUM   )/(SUMXSQ-SUMX*SUMX/DFJSUM   )
      RATE=(-1.0)*BETA
      WRITE(6,12) RATE
   12 FORMAT (30X, 41H K OBS PSEUDO FIRST ORDER RATE CONSTANT =,E12.4,
     F  7H SEC -1,/////)
      ALPHA=(SUMY/DFJSUM   -BETA*SUMX/DFJSUM   )
      ORDER=0.0
C
C     RESIDUALS TO SEE IF PLOT IS LINEAR
C
   49 REJECT=0.0
      SMSQRS=0.0
      DO10  J=1,N
      YBAR(J)= ALPHA+BETA*TIME(J)
      RESID(J)=YBAR(J)-PLOT(J)
      SMSQRS=SMSQRS+(ABS(RESID(J))**2.0)*DIFF(J)
      IF(ABS(RESID(J)) .LT.(YBAR(J)          *0.1)) GOTO50
         FS J)=FLOAT(J)
```

```
      REJECT=REJECT+1.0
      GOTO10
   50 XSRES(J)=0.0
   10 CONTINUE
      YERROR=(SMSQRS/DFJSUM)**0.5
      U=(DFJSUM*SUMXSQ)-(SUMX**2.0)
      RERROR=(DFJSUM/U)*(YERROR**2.0)
      WRITE(6,59)  RERROR
   59 FORMAT(1H0,20X, 32H WEIGHTED  STANDARD DEVIATION = ,E13.4//)
      IF((REJECT.GT.5.0).AND.(ORDER.EQ.0.0))GOTO611
      WRITE(6,60)
   60 FORMAT(1H0, 10X,80H                 OD(J)              PLOT(J)      RESID(J)
     N                    TIME(J)             ,  30H  EXCESS RESID ON READING NO
     0    ///)
      WRITE(6,61)( OD(J),PLOT(J),RESID(J), TIME(J),  XSRES(J),    J=1,N)
   61 FORMAT      (12X,E13.4,8X,E13.4,8X,E13.4,8X,F7.5,   15X,F6.3)
  611 WRITE(6,62)    REJECT
   62 FORMAT(1H0  10X,     30H,  NO OF RESULTS TO REJECT =    ,  F5.2)
      IF((REJECT.LT.3.0).OR.(ORDER.EQ.2.0))   GOTO70
C
C      IF A POOR FIRST ORDER PLOT HAS BEEN OBTAINED TRY SECOND ORDER
C
      WRITE(6,63)
   63 FORMAT(1H1,  60H,    APOOR FIT TO FIRST ORDER HAS BEEN FOUND  TRY
     0SECOND          ///)
      DFJSUM= 0.0
      SUMXSQ=0.0
      SUMX=0.0
      SUMY=0.0
      SUMXY=0.0
      DO65 J=1,N
      PLOT(J)=1.0/(OD(J)-ODINF)
      DIFF(J)=1.0/(ABS(PLOT(J)-(     1.0/(OD(J)-ODINF+0.2))))
```

```
      PRODXY=PLOT(J)*TIME(J)
      SUMXY=SUMXY+PRODXY*DIFF(J)
      SUMX=SUMX+TIME(J) *DIFF(J)
      SUMY=SUMY+PLOT(J)  *DIFF(J)
      SUMXSQ=SUMXSQ+(TIME(J)**2.0)*DIFF(J)
      DFJSUM=DFJSUM+DIFF(J)
   65 CONTINUE
      BETA= (SUMXY-SUMX*SUMY/DFJSUM  )/(SUMXSQ-SUMX*SUMX/DFJSUM  )
      ALPHA=(SUMY/DFJSUM  -BETA*SUMX/DFJSUM  )
      RATE=BETA*EC
      WRITE(6,66)  RATE
   66 FORMAT( 1H0,40H,   PSEUDO SECOND ORDER RATE CONSTANT  =,  E13.4  )
      ORDER=2.0
      GOTO49
   98 WRITE(6,99)
   99 FORMAT(1H0,50H  OPTICAL DENSITY CALCULATED TO BE NEGATIVE       ,//
     C60H PROBABLY ERROR IN DATA INPUT FOR THIS SHOT                  ///
     D60H              Y O U   T W I T      YOU HAVE DONE IT AGAIN    ,)
   70 IF(NOSHOT.LT.99)  GOTO2
      STOP
      END
```

a crystal controlled oscillator running at about 1k/c coupled to a decade reducing system.

An extension to the range of filters could be made by constructing quartz cells that would fit into the existing filter support. The cells could contain two calibrating liquids, and could be interchanged as required.

The triggering mechanism on the oscilloscope sometimes allows a second trace to run and makes the photograph less easy to read. A single shot could be arranged by means of a microswitch attached to the trolley.

The metal and glass syringes at present in use should be changed to teflon and glass gas-tight type to remove any possibility of acid attack on the stainless steel parts of the present syringes.

Hydraulic operated syringes would probably increase the flow rate slightly and enable faster reactions to be studied.

Experiments carried out using the apparatus will be described in the following chapters as they arise.

CHAPTER 2.

Linkage Isomerism in Thiocyanate Complexes of Palladium.

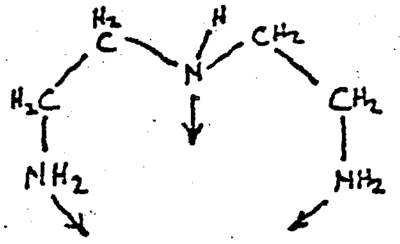
INTRODUCTION

Until recently, Jørgensen's discovery that the nitrite ion could be bound to cobalt[7] either through oxygen or through nitrogen provided the only known example of linkage isomerism. Other metals were then found that gave both nitro and nitrito complexes[8] and it was pointed out that thiocyanate ion should also be capable of forming linkage isomers under certain conditions since the first row transition metals form isothiocyanates whereas the heavier metals usually form sulphur bonded complexes.[9]

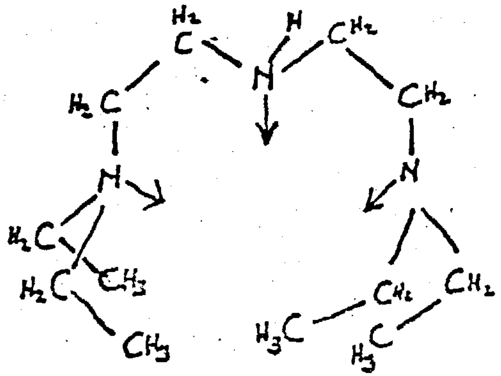
Thiocyanate and isothiocyanate complexes of the same metal, platinum, were reported[10] in 1961, and a related discovery that $[Co(CN)_5SCN]^{3-}$ is sulphur bonded while $[Co(NH_3)_5NCS]^{2+}$ is an isothiocyanate[11] followed. The factors determining the outcome of the choice between sulphur and nitrogen bonding were discussed and as a result several examples of linkage isomerism came to light[12] involving thiocyanate complexes of palladium and manganese. Other less stable isomers have been prepared in solution.[13]

The nature of the metal thiocyanate bond is influenced by the electronic natures of the metal and ligands, and also by steric effects.[10,14] The change-over from nitrogen to sulphur bonding corresponds approximately to the change in relative strengths of the halogen complexes from Cl > Br > I (class (a)[15]) to I > Br > Cl (class (b)). For example, Co^{2+} and Fe^{3+} show typical class (a) behaviour and are found to form isothiocyanate complexes, whereas class (b) metal ions such as Pt^{2+} and Pd^{2+} form sulphur bonded tetra-thiocyanates. In some cases the natures of the ligands bound to the metal can determine whether a particular system is class (a) or class (b); that is, whether the system forms more stable complexes with "Hard" or "Soft" ligands respectively.[16] The cobalt(III) pentammine ion ha~~ve~~s been classed as hard and the pentacyano-cobalt(III) ion is soft.[17]

The electronic natures of the metal and its surrounding ligands may not, however, provide a complete answer. The thiocyanate-complexes of palladium with diethylene-triamine (dien) and 1,1,7,7, tetraethyldiethylene-triamine (Et_4dien) (See Fig. 11) were shown to be sulphur and nitrogen bonded, respectively, in the crystalline state.[18, 14(a)] Neither of the amine ligands can form π bonds, and any inductive effect of the four ethyl groups would



diethylene triamine (dien)



4,7,7-tetraethyl diethylene triamine (Et_4dien)

FIG. 11

increase the softness of the metal, and hence the tendency to form a sulphur bonded complex.

The relative stability of the isomers may, therefore, also be controlled by steric factors. The M-N=C=S system is usually linear, whereas thiocyanato complexes are always angular at the sulphur atom.[19,14(b)] The steric hindrance imposed in the "pseudo octahedral" complexes of the tetra-ethyl ligand[20] would be expected to favour the linear isothiocyanate, and indeed molecular models indicate that this system can accommodate a sulphur bonded ligand only under considerable strain.

We have made spectrophotometric studies of the relative stabilities of the complex of the general form Pd dien X^+ and Pd Et_4dien X^+ where X was Cl, Br, I or SCN, in order to see whether the relationship between class (b) behaviour towards halide ions and sulphur bonding on one hand, and class (a) behaviour and nitrogen bonding on the other, is maintained in these complexes, and also to see to what extent steric factors are discernible in this system.

EXPERIMENTAL

The complexes Pd dien X^+ and Pd Et_4dien X^+ were prepared by published methods.[21] The visible and ultraviolet absorption spectra were found to agree reasonably well with existing data[21,22] and the complexes were not in general analysed. The compositions of the dien chloride and Et_4 dien bromide complexes were, however, investigated and the results given below:

(a) N 15.4% Cl 24.6% $PdC_4H_{13}N_3Cl_2$
required N 15.0 Cl 25.3.

(b) N 9.0 Br 33.9 $PdC_{12}H_{19}N_3Br_2$
requires N 8.8 Br 33.4.

The extinction coefficient of [Pd dien I] I is considerably higher than the earlier value, possibly because it was found to be only slightly soluble, and errors could have been caused in the earlier work by precipitation.

All extinction coefficients were measured in 0.5 M halide solution to remove the possibility of hydrolysis which occurs particularly in the Et_4 dien complexes. The spectra of the Pd dien complex was found to be the same in water and in excess halide solutions and therefore any effects due to ion pairing were ignored.

TABLE IV

Ultraviolet absorption spectra at 25°C of Pd dien X^+ and Pd Et_4dien X^+

X	Pd dien X^+			Pd Et_4dien X^+		
	λ max. (mμ)	ε (cm.$^{-1}$ l mole^{-1}.)		λ max. (mμ)	ε (cm.$^{-1}$ l mole^{-1}.)	
		(a)	(b)		(a)	(c)
Cl	330	480	500	350	900	860
Br	340	480	450	362	730	755
I	370	680	500	390	710	654
SCN	310	840	-	-	-	-
NCS	-	-	-	327	1500	1360

(a) This work.

(b) Ref. 22(a)

(c) Ref. 21, 22(b).

In the case of a one-stage replacement reaction,

M-X + Y = M-Y + X,

the equilibrium constant can be calculated from the equation:

$$K = \frac{[\varepsilon_x - \varepsilon_{xy}]\,[X]}{[\varepsilon_{xy} - \varepsilon_y]\,[Y]}$$

where ε_x ε_y and ε_{xy} are the extinction coefficients of the solution when it contains the complex and large excesses of X, Y, and an X:Y mixture of concentration ratio $\frac{[X]}{[Y]}$ respectively.

A solution of one or other of the complexes was mixed with a solution containing two halides, or a mixture of halide and thiocyanate, in a known concentration ratio and total ionic strength of 0.5 or 1.0 Molar. The solution was allowed to come to equilibrium in a fused silica cell$_{X}$ placed in a thermostatted compartment of a spectrophotometer, and absorbance measured at a convenient wavelength (where $/\varepsilon_x - \varepsilon_y/$ was as large as possible). The temperature of the cell compartment was then changed, and the absorbance recorded when the new equilibrium position had been reached. Concentrations of the complexes were such that optical densities in the range 0.3 to 1.0 were measured.

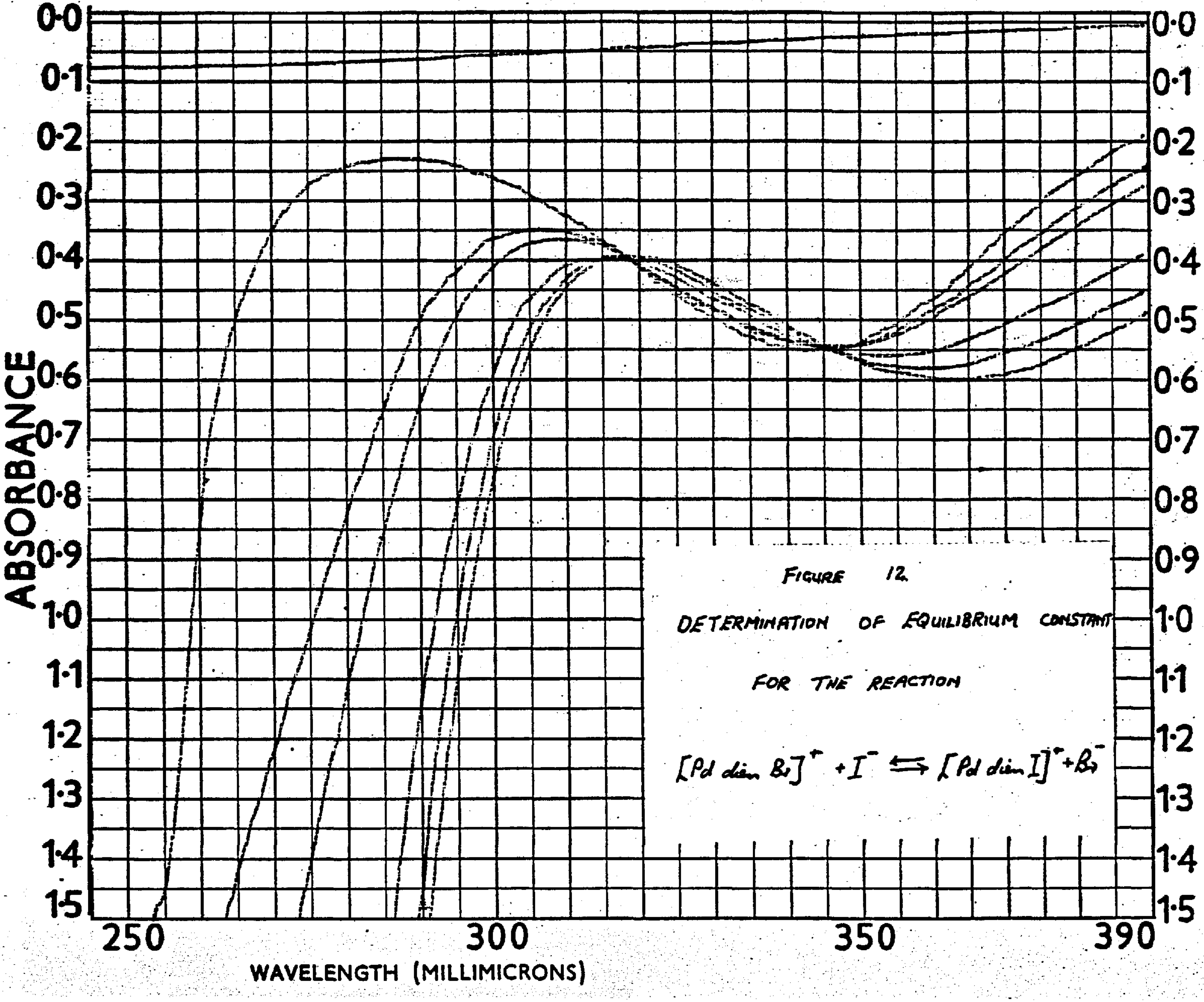


FIGURE 12.

DETERMINATION OF EQUILIBRIUM CONSTANT FOR THE REACTION

$[Pd\ dien\ Br]^+ + I^- \rightleftharpoons [Pd\ dien\ I]^+ + Br^-$

When the equilibrium constant was greater than 30 a convenient method of altering the concentration ratio was to start with 3.0 ml. of a solution containing a suitable concentration of complex and being 0.5 Molar in NaX. This solution was placed in a 1 cm. cell, and up to 0.03 ml. of NaY solution of suitable concentration was then added by means of a micro syringe. The concentration of complex, and the ionic strength of the solution change by less than 1% , that is by less than the experimental error, and the technique is capable of giving very precise values for the concentration ratio.

For the Pd dien complexes, equilibrium was attained immediately on mixing, but with the Et_4 dien complexes sufficient time (calculated from the known rate constants, or observed directly) was allowed for equilibration after the requisite temperature had been reached.

Kinetic studies of interchange were carried out on Pd Et_4dien X^+ complexes, by mixing solutions of thermostatted reagents in a silica cell, placing the cell in a thermostatted compartment of the spectrophotometer, and following changes in absorbance with time at a suitable wavelength. When readings were required every five seconds or so, a double beam recording instrument, PE 137, was used at a fixed wavelength, and the pen tapped on to the paper at the required time intervals.

It was not found possible to prepare the aquo complex Pd Et_4dien OH_2^{2+} without decomposition even in neutral solution. Pd Et_4dien OH^+ was obtained on treatment of Pd Et_4dien Br^+ with sodium hydroxide (λmax. = 319 mμ). Acidifying this compound caused an immediate change in spectrum (presumably due to the formation of the aquo complex (λmax. = 329 mμ)) but this spectrum changed with time probably because of the dissociation of the amine from the complex. A solution of the hydroxide complex, when neutralised and rapidly treated with a borate buffer solution (pH 9), gave a stable spectrum between that of the hydroxide and aquo complexes, indicating a mixture containing approximately 10% aquo complex.

Pd Et_4dien OH^+ was found to be unaffected by bromide ion (0.6 M) at room temperature after 12 hours, whereas buffered solutions of the neutralised complex reacted within a few minutes with 0.06 M bromide ion. It was concluded that solutions buffered at pH 9 contain a small constant percentage of the aquo complex and that pseudo first order rate constants of anation reactions with various halides and at different temperatures would be in the same ratio as if the aquo complex was exclusively present.

To study the anation reactions of Pd Et_4dien OH_2^{2+} the bromide complex was dissolved in 0.1 M NaOH to give a 5×10^{-3}M solution. 1.0 ml. of this stock solution was pipetted into a cell containing 2.0 ml. of a solution that was 0.05 M in borax, 0.05 M in perchloric acid, and contained various halide concentrations.

RESULTS

The experimental data, together with the equilibrium constants derived from them, are given in Table V. The variation of the extinction coefficient of Pd dien SCN^+ with temperature is barely significant and is within the range of variation found with other systems.[23]

The changes in enthalpy, entropy and free energy for each system were obtained by using a least squares fit[24] to a straight line plot of $\log_e K$ against $\frac{1}{T^\circ K}$, and the results are quoted in Table VI.

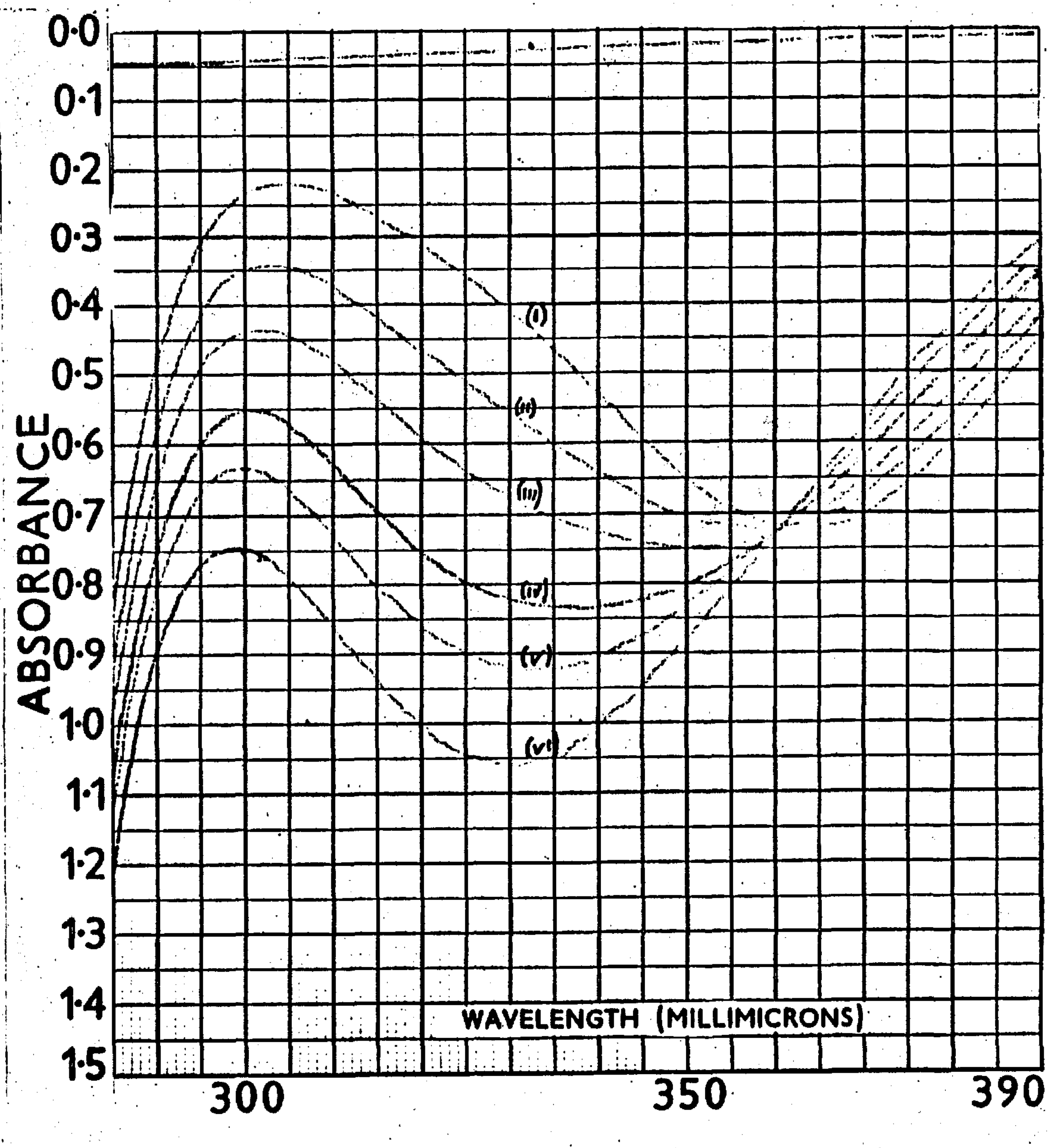
Although the errors on individual constants are quite large, the uncertainty in the thermodynamic parameters is considerably reduced by the wide variation in temperature. The calculation was carried out using a simple Fortran IV programme on an I.B.M. 7090 computer because it would have been tedious, and probably less accurate, to use a desk calculator.

The determination of stability constants in the Pd Et_4dien X^+ system was hampered by side reactions. Although the kinetics of interchange for reactions of the type:

$$\text{Pd Et}_4\text{dien Br}^+ + \text{I}^- \rightleftharpoons \text{Pd Et}_4\text{dien I}^+ + \text{Br}^-$$

have been found to be reasonably clean[21] and to give good isosbestic points practically up to complete reaction, a slow decomposition was observed when mixtures were left to equilibrate. This effect was most noticeable with iodide, and is attributed to acid attack on the complex causing the removal of one of the tertiary amine groups of the ligand. The removal of the first amine group in Pd Et_4dien Cl^+ is fast.[25]

The amount of such decomposition could be controlled and reduced by carrying out all observations in solutions buffered at pH 6.8 (phosphate) or pH 9 (borax). Information was obtained on the chloride-



Dropwise addition of Na SCN to $[Pd(Et_4dien)Br]^+$ at 82·3°

(buffered at pH 6·8)

Figure 13.

TABLE V

Equilibrium constants for the equilibria $PdLX^+ + Y^- \rightleftharpoons PdLY^+ + X^-$

(a) X = Cl, Y = I, L = dien, $\mu = 0.5$ M, $\lambda = 370 m\mu$
$\varepsilon_{Cl} = 180$ cm.$^{-1}$1.mole^{-1}, $\varepsilon_{I} = 690$ cm.$^{-1}$1.mole

Temp.	$[Cl^-]/[I^-]$	ε_{ClI}	K
24.0°	49.0	520	98.4
	99.0	430	96.1
29.8	49.0	509	89.2
37.7	49.0	480	70.5
	99.0	394	72.0
48.0	49.0	460	59.8
	99.0	373	60.2
62.9	49.0	427	46.5
	99.0	348	48.3

$\sigma_K = \pm 2.7\%$

TABLE V (Continued)

(b) X = Br, Y = I, L = dien, μ= 0.5 M, λ= 370 m.,
ε_{Br} = 290 cm.$^{-1}$1.mole^{-1}, ε_{I} = 690 cm.$^{-1}$1 mole^{-1}

Temp.	$[Br^-]/[I^-]$	ε_{BrI}	K
19.1°	19.5	550	36.9
24.0	19.0	541	33.0
	32.3	479	29.6
	49.0	450	33.4
24.2	19.5	546	35.2
29.8	19.0	532	30.5
	32.3	468	26.5
	49.0	440	30.2
34.8	19.5	530	30.1
37.9	19.0	524	26.8
	32.3	459	24.1
	49.0	434	28.2
41.9	19.5	525	29.3
47.8	19.0	502	23.2
50.4	19.5	514	24.9
52.1	32.3	442	20.4
56.4	19.5	497	21.0
58.5	19.0	497	20.8
65.4	19.5	489	19.7
73.7	19.5	480	17.9
85.2	19.5	468	15.9

$\sigma_K = \pm$ 7.0%

TABLE V (Continued)

(c) X = Br, Y = $\underline{S}$CN, L = dien, μ = 0.5M λ = 310 mμ, ε_{Br} = 178 cm.$^{-1}$1.mole^{-1}, ε_{SCN} = variable

Temp.	[Br$^-$]/[SCN$^-$]	ε_{SCN}	ε_{BrSCN}	K
10.6°	315.9	840	504	302
	157.6		616	308
11.1	315.9	840	503	304
	157.6		612	298
	78.3		702	298
	38.8		766	307
30.5	315.9	840	407	167
	157.6		517	165
	78.3		632	171
	38.8		715	165
48.2	315.9	840	358	108
	157.6		431	97
	78.3		572	113
	38.8		676	116
63.0	315.9	820	311	81.5
	78.3		500	78.6
	38.8		608	80.5
80.4	78.3	800	453	61.7
	38.8		549	57.1
81.8	78.3		429	52.8
	38.8		558	61.4

σ_K = ± 5.3%

TABLE V (Continued)

(d) X = Cl, Y = Br, L = Et$_4$dien, μ = 1.0 M
λ = 340 mμ ε_{Cl} = 770 cm.$^{-1}$ l.mole^{-1}
ε_{Br} = 520 cm.$^{-1}$ l.mole^{-1}

(Buffered at pH 9.)

Temp.	$\frac{[Cl]}{[Br]}$	ε_{ClBr}	K	
20.0	0.922	619	1.46	
	1.33	640	1.49	
33.2	0.922	614	1.59	
	1.33	637	1.56	
48.2	0.922	609	1.70	
	1.33	636	1.59	
63.4	0.922	610	1.71	σK = 6.0%
	1.33	636	1.69	

(e) *X = Br, Y = NCS$^-$, μ = 0.5 M λ = 325 mμ,
ε_{Br} = 370, ε_{NCS} = 1450.

(Buffered at pH 6.8.)

Temp.	TOTAL [SCN$^-$] (l^{-1} moles) x 10^3	ε_{BrNCS} (l.mole^{-1}cm.$^{-1}$)	K	
20.0	3.77	878	135	
	5.67	1000	137	
	7.53	1067	133	
32.2	1.88	660	114	
	3.77	845	118	
	5.67	948	112	
45.0	3.77	790	94.1	
	5.67	900	93.0	
	8.67	1035	99.6	σK = 11%
82.5	3.77	598	37.5	
	7.53	755	38.6	
	11.3	858	34.7	
	18.8	1003	38.8	

* The micro syringe technique was used. The total thiocyanate ion concentration given above was corrected to the concentration of free thiocyanate ion by subtraction of the concentration of isothiocyanato complex formed.

TABLE VI

Thermodynamic functions* for the reaction:

$$PdLX^+ + Y^- \rightleftharpoons PdLY^+ + X^-$$

L	X	Y	ΔG^o* (kcal./mole)	ΔH^o (kcal./mole)	ΔS^o (e.u.)
dien	Cl	I	-2.68	-3.7 ± 0.1	-3.4 ± 0.3
dien	Br	I	-2.05	-2.5 ± 0.12	-1.6 ± 0.13
dien	Br	SCN	-3.12	-4.7 ± 0.06	-5.4 ± 0.2
dien**	Cl	Br	-0.63	-1.2 ± 0.16	-1.8 ± 0.3
Et_4dien	Cl	Br	-0.24	+0.65 ± 0.06	+3.0 ± 0.2
Et_4dien	Br	NCS	-2.81	-4.4 ± 0.10	-4.0 ± 0.5

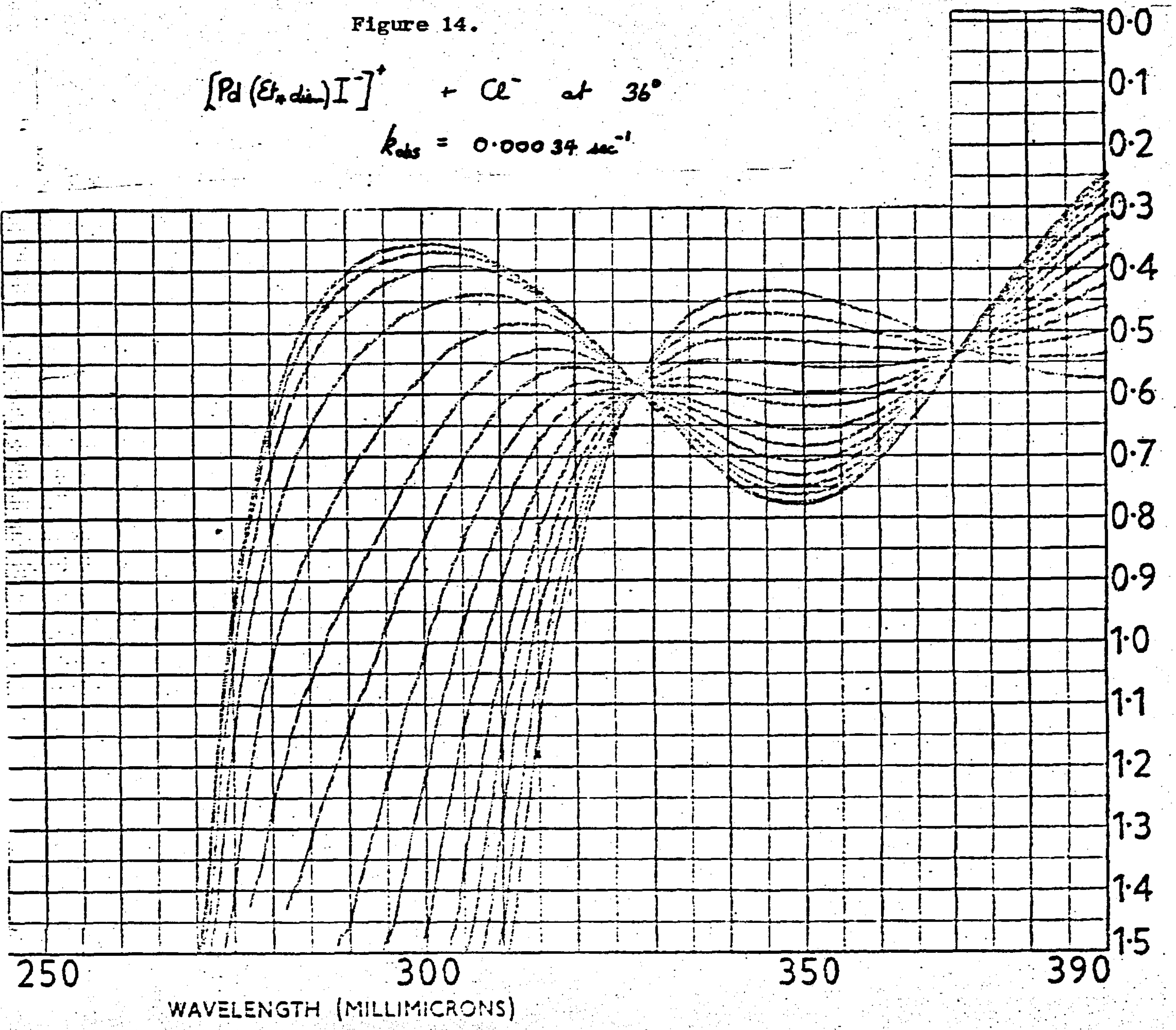
* ΔG^o values are at 300^oK.

** Obtained by subtraction.

Figure 14.

$[Pd(Et_4dien)I^-]^+ + Cl^-$ at 36°

$k_{obs} = 0{\cdot}00034 \ sec^{-1}$

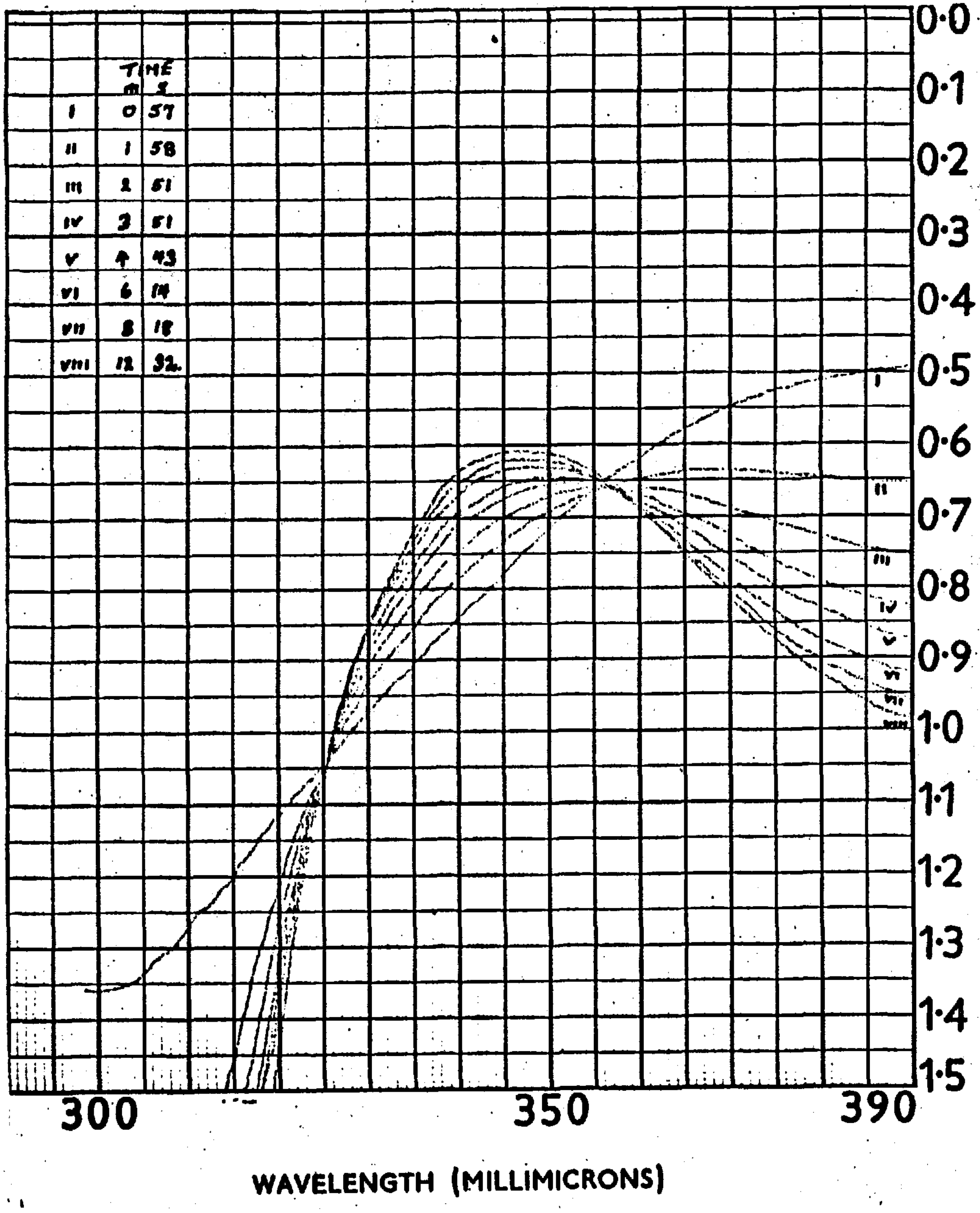


bromide and bromide-thiocyanate systems in this way, but no reliable data could be obtained on the iodide exchanges. Such values that were obtained indicate a stability constant of between 6 and 8 for bromide-iodide exchange at pH 9 and 30°.

The kinetics of interchange reactions involving Pd Et_4dien X^+ were investigated over a temperature range in order to obtain information concerning the stability of the iodide complex. A representative set of spectral changes for replacement of iodide by chloride is shown in Fig. 14. The rate of interchange has been shown to be independent of the nature and concentration of incoming halide at several temperatures, and on combining results obtained during this study with those already published[21,26] activation parameters were estimated graphically (Table VII).

In the study of the rates of anation, quite good isosbestic points were observed for the slower reactions (Fig. 15) at 294 and 330 mμ, 288 and 340 mμ and 326 and 357 mμ for the chloride, bromide and iodide anations, respectively. The results are indicated graphically overleaf, and the plausibility of the straight-line graphs indicating a definite first-order

Cont^D on P. 64



$[Pd(Et_4dien)OH_2]^{2+}$ ANATION BY IODIDE ION

FIGURE 15

TABLE VII

Pseudo first order rate constants for the reaction: Pd Et$_4$dien X$^+$ + Y$^-$ == Pd Et$_4$dien Y$^+$+X$^-$

X	Y	k_{obs} (sec^{-1})	T$^{\circ}$C	E_a (kcal/ mole)	ΔS (cal.deg.$^{-1}$ mole^{-1})
I	Br	0.0050	63.0	20.4	-10.3
I	Cl	0.00485			
I	Br	0.00113	46.4		
I	Cl	0.00115			
I	Cl	0.00034	35.0		
Br	I	0.014	63.0	11.9	-33.6
Br	I	0.00515	46.4		
Br	I	* 0.0014	25.0		
Cl	I	* 0.00087	14.3	13.3	-27.0
Cl	I	* 0.0020	25.0		
Cl	I	* 0.0046	36.5		
NCS	Br	⌿ 0.00051	35.0	18.1	-17.0
NCS	Br	⌿ 0.00128	45.0		
SCN	Br	⌿ 0.00026	20.0	17.1	-18.5
SCN	Br	⌿ 0.00108	35.0		
SCN	Br	⌿ 0.00256	45.0		

* Rate constants from reference 21.

⌿ Parameters recalculated from reference 26.

TABLE VIII

Second order rate constants and energies of activation for the anation by X^- of Pd Et_4dien OH_2^{2+}

X	Temp. °C	$k_{obs.}$ ($1\ mole^{-1} sec^{-1}$)	E_a kcal/mole	S* e.u.
	24.2	0.096		
Cl	36.7	0.195	10.5	-28.2
	44.8	0.270		
	24.2	0.053		
Br	36.7	0.141	12.3	-25.2
	44.8	0.216		
	24.2	0.056		
I	36.7	0.140	12.4	-23.8
	44.8	0.225		
CNS	20.0	0.68		
	40.0	0.97		

TABLE IX

Enthalpy of interchange for the reaction

$$\text{Pd L X}^+ + \text{Y}^- == \text{Pd L Y}^+ + \text{X}^-$$

X	Y	L = dien	L = Et_4dien	
			kinetic	equilibrium
Cl	Br	-1.2 ± 0.16	+1.4 ± 2	+0.65 ± 0.06
Cl	I	-3.7 ± 0.1	-7.2 ± 2	
Br	I	-2.5 ± 0.12	-8.6 ± 2	
Br	NCS		-6.2 ± 2	-4.0 ± 0.16
Br	SCN	-4.7 ± 0.06	-5.3 ± 2	

dependence on the concentration of the incoming group will be discussed later. The second order rate constants calculated from the slopes of the graphs are given in Table VIII together with respective energies of activation.

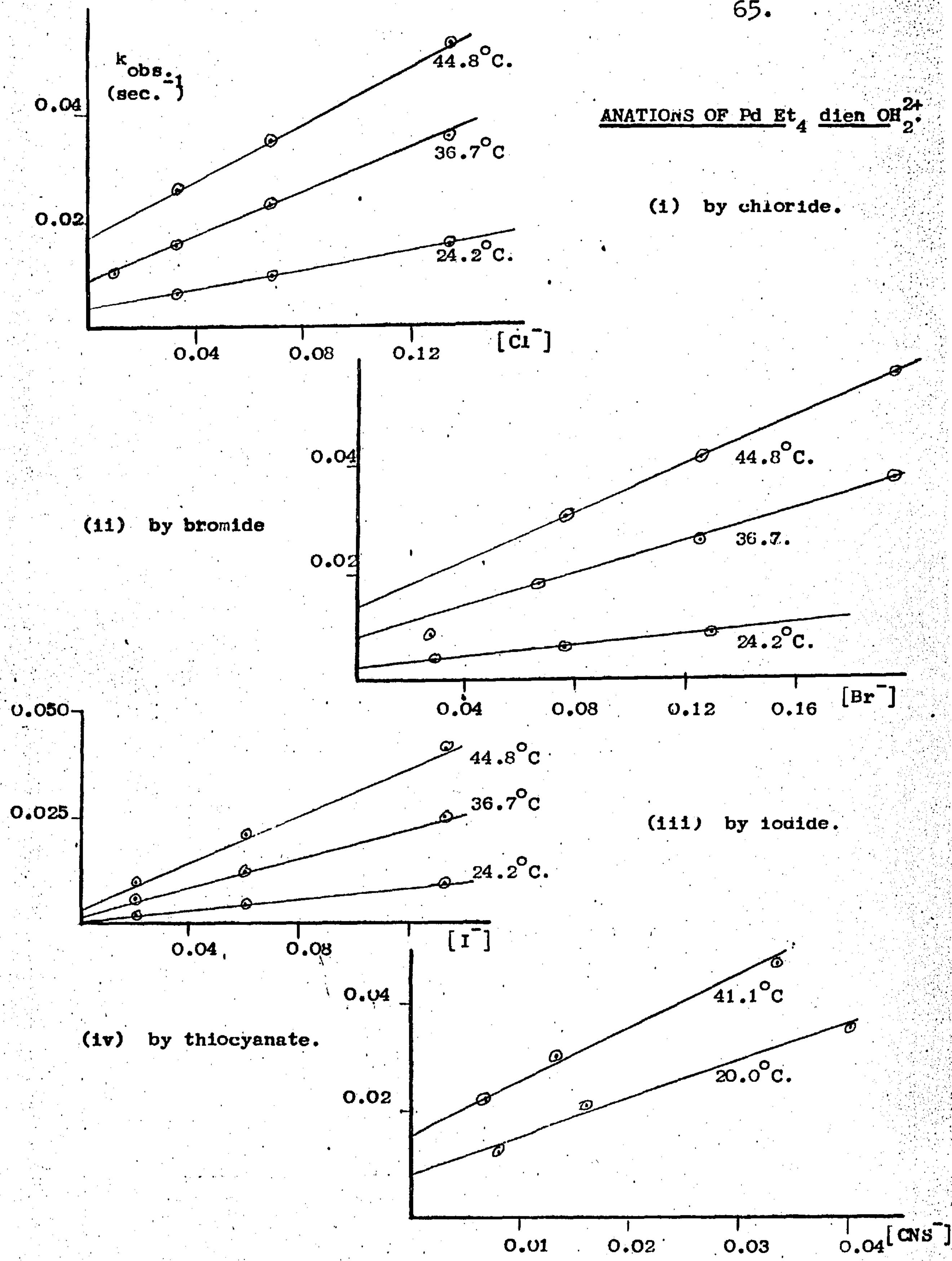
DISCUSSION

Although direct values for the thermodynamic functions of equilibria involving Pd $\mathrm{Et_4}$dien $\mathrm{I^+}$ were not obtained, approximate answers can be deduced from the kinetic results.

The proposed mechanism of the interchange reactions is that the initial (dissociative) step is rate determining, and that subsequent anation of the intermediate is rapid.[21] For example in the reaction:

$$\mathrm{Pd\ Et_4dien\ I^{+}} \underset{k_{+I}}{\overset{k_{-I}}{\rightleftharpoons}} \mathrm{Pd\ Et_4dien\ OH_2^{+2}} \underset{k_{+Br}}{\overset{k_{-Br}}{\rightleftharpoons}} \mathrm{Pd\ Et_4dien\ Br^{+}}$$

k_{-I} and k_{-Br} are both much smaller than k_{+I} and k_{+Br}. A study of the anation of the aquo complex by Cl, Br, I and CNS has therefore to be combined with the results from the interchange reactions to give values for the stability constants of the halide complexes with respect to water.



ANATIONS OF Pd Et_4 dien OH_2^{2+}.

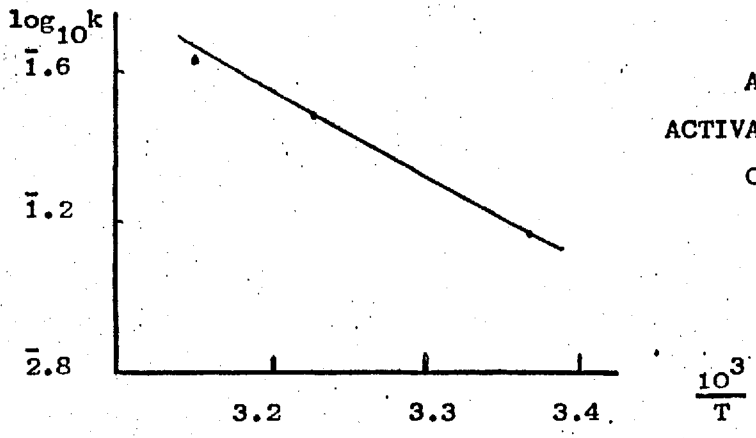
(i) by chloride.

(ii) by bromide

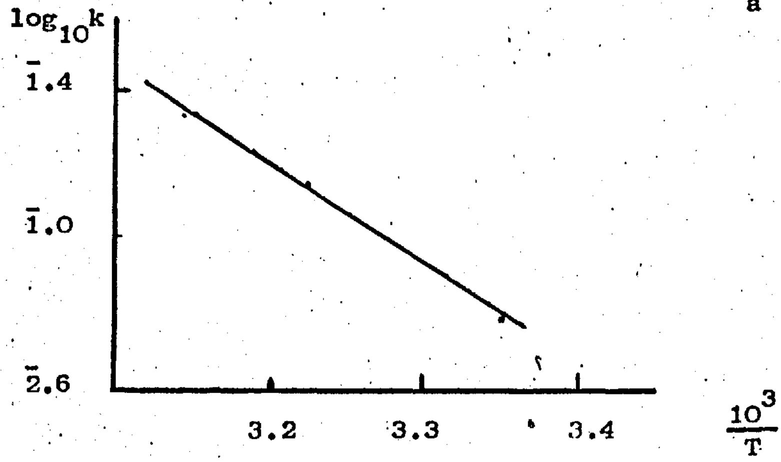
(iii) by iodide.

(iv) by thiocyanate.

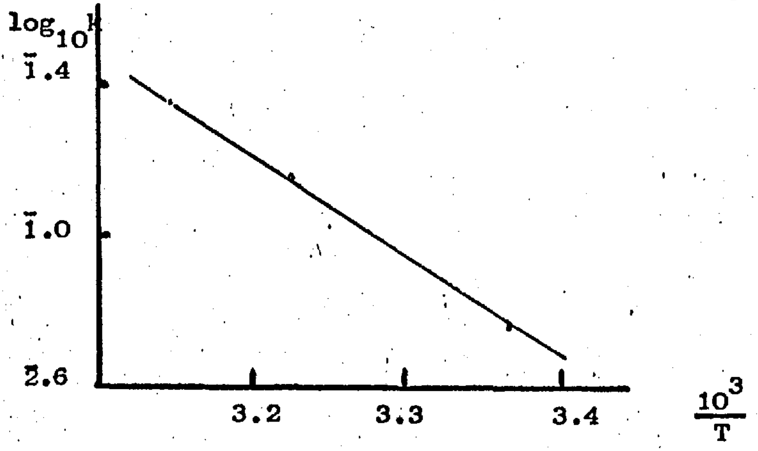
ARRHENIUS ENERGIES OF ACTIVATION FOR THE ANATION OF Pd Et_4dien OH_2^{2+}



(i) chloride E_a = 12.6 kcal/mole



(ii) bromide E_a = 12.3 Kcal/mole

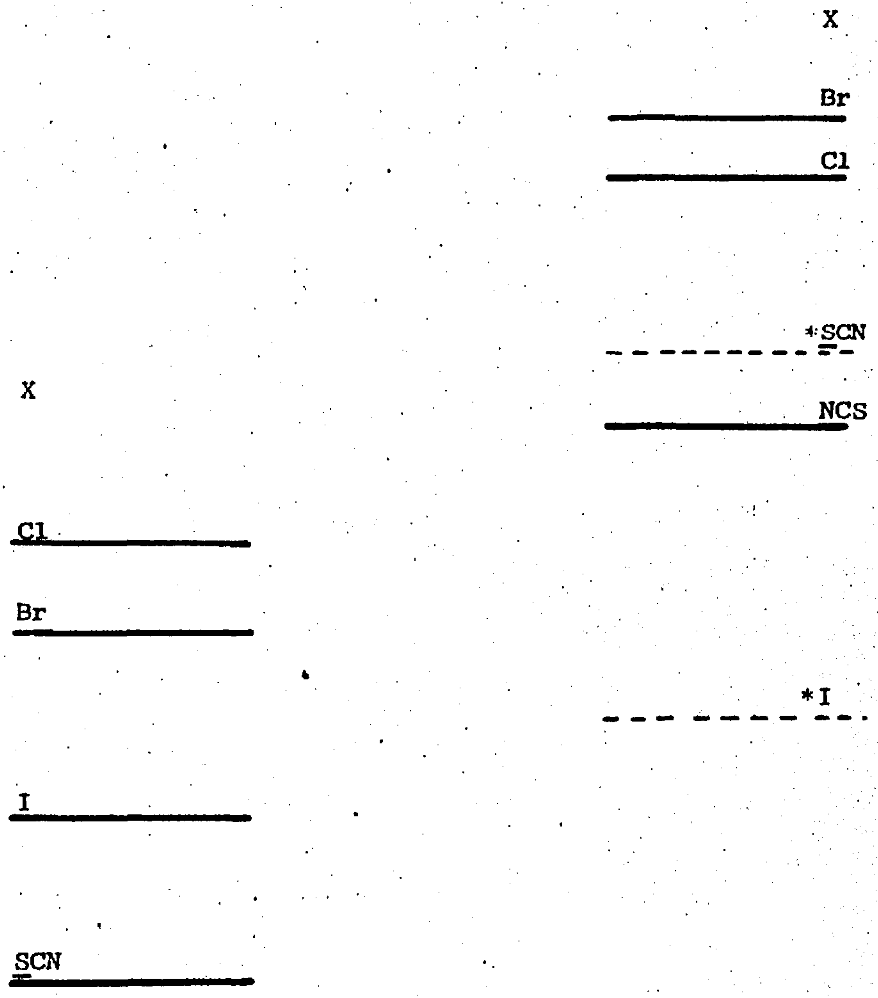


(iii) iodide E_a = 14.2 kcal/mole

Preliminary results indicate that although the rates of anation of Pd Et_4dien OH_2^{2+} by X^- vary with the concentration of incoming group, the activation energy, calculated from the slopes of graphs of observed rates at T°C versus concentration of X^-, is practically independent of X^- and has a value of 11.5 ± 1.0 kcal./mole. Hence, pairs of activation energies from the aquations of Pd Et_4dien X^+ may be subtracted and the result compared with the enthalpy changes in equilibrium measurements. (Table IX).

The agreement between equilibrium and kinetic measurements is within the assigned error in the two cases where comparison can be made, and so the kinetic results may be used in systems where direct measurement was not possible, so long as the large probable error is taken into account. (Figure 16.)

As far as the relative stabilities of the halogeno complexes is concerned, the effect of changing the triamine to the N-alkyl form produces a slight decrease in the class (b) character, the equilibrium constants for halide exchange being reduced by a factor of 2 to 3. The stability of all the halogeno complexes relative to the aquo complex, as



(i) A_3 = dien.

(ii) A_3 = Et_4dien.

Figure 16. The standard enthalpies of complexes of the type $[Pd\ A_3X]X$

approx. 1 kcal/mole

* Estimated value from kinetic expts.

seen from the anation studies, is also reduced considerably.

When the enthalpy values for the various interchanges are considered, the situation is more complicated. The order of stability is then $Cl > Br \ll I$ in the Et_4 dien complex compared with $Cl < Br < I$ in the dien system. A parallel stability order is indicated by the electronic spectra. The first absorption band in these complexes has been assigned to an electronic transition from an antibonding π^* orbital, comprising $p\pi$ and $d\pi$ orbitals from the metal, and $p\pi$ ligand orbitals, to a σ^* antibonding orbital of mainly $d_{x^2-y^2}$ character. The transition can therefore be used as a rough measure of the metal-ligand bond strength. The inductive effect of N-alkyl substitution would be expected to increase the the strength of σ bonding without causing much change in the π bonding, and the transitions would then be expected to appear at higher energy. This is observed on comparison of the wavelengths for this transition in $Pd(NH_3)_4^{2+}$ and $Pd(en)_2^{2+}$ and also in <u>cis</u> $Pd(NH_3)_2Cl_2$ and Pd en Cl_2 (Table 10). The introduction of further alkyl groups onto the nitrogen, however, causes the energy of this transition to decrease, as in N,N,N',N', tetramethyl-ethylenediamine complexes, and this has been attributed to a reduction in the σ overlap due to steric repulsions.[27]

The energies for the $\pi^* \longrightarrow \sigma^*$ transition in Pd dien and Pd Et_4dien complexes have been calculated and are given in Table XI. The transitions are all at lower energy in the Et_4 dien complexes, and so it is assumed that steric repulsions outweigh electronic effects. The decrease is least for the iodide and greatest for the bromide which is identical with the situation shown by the enthalpy values.

Since the halides increase in size from chloride to iodide, one would expect steric effects to decrease the relative stability of the Pd Et_4dien I^+ complex with respect to chloride. This will be opposed, however, by the greater polarisability of the iodide, and its greater ability to take advantage of the higher effective ionic charge on the metal to form a stronger covalent bond.

The stability of the bromide complex expected from electronic considerations appears more than counteracted

TABLE X

Wavelength of maximum absorbance for some Pd^{2+} complexes

		λ max.(mμ)	Ref.
(a)	Pd $(NH_3)_4^{2+}$	367	28
(b)	Pd $(en)_2^{2+}$	340	28
(c)	Pd(NN'dimethyl-en)$_2^{2+}$	350	27
(d)	Pd(NNN'N'tetramethyl-en)$_2^{2+}$	425	27
(e)	cis Pd $(NH_3)_2Cl_2$	375	25
(f)	Pd en Cl_2	362	25
(g)	Pd (NN'dimethyl-en)Cl_2	388	27
(h)	Pd (N,N,N',N',tetramethyl-en)Cl_2	392	27

TABLE XI

The energies of $\pi^* \longrightarrow \sigma^*$ electronic transition (in kcal/mole) in complexes of the type Pd L X^+

X	L = dien	L = Et_4dien	
Cl	86.4	81.5	-4.9
Br	83.9	78.8	-5.1
I	77.0	73.0	-4.0

by the steric repulsion and the net result is that Pd Et$_4$Cl is more stable than the bromide.

The decrease in absolute metal halide bond strengths has been shown in other systems to parallel an increase in class (b) character.[29] In this case enthalpy values show that the chloride and bromide complexes are destabilised with respect to the iodide, while ultraviolet absorption spectra indicate an all-round decrease in metal ligand bond strengths.

Entropy changes for the reactions of Pd dien X$^+$ and Pd Et$_4$dien X$^+$ counteract the irregular enthalpy values and a misleading smooth change, and net decrease in class (b) nature is observed if the entropy differences are not allowed for.

The stability of the dien and Et$_4$dien complexes with thiocyanate show small differences when the equilibrium constants are considered, the dien complex being six times as stable and the Et$_4$dien being approximately ten times more stable than the corresponding iodo complexes. The enthalpy differences show a more noticeable effect, the enthalpy change on replacing iodide by thiocyanate being -2.2 ±0.2 and +3 ± 2 kcal/mole respectively. The complex

Pd Et_4dien NCS^+ has been shown to be stable as the nitrogen bonded isomer in the solid and in aqueous solution. The analogous thiocyanato complex has been shown to isomerise readily to the more stable isothiocyanate,[26] and our ultraviolet and infrared spectra agree with those previously reported for Pd Et_4dien NCS^+. In Pd dien SCN^+ the solid is sulphur bonded, but no investigation of the aqueous solution had been made. From a comparison with the ultraviolet spectrum of Pd Et_4dien SCN^+ a maximum would be expected at about 360 $m\mu$. A shoulder is observed in this region, but the main peak is at 310 $m\mu$ and is similar to bands that have been assigned to a metal independent intraligand transition in sulphur bonded thiocyanates.[30] Infrared spectra of the solids show peaks at 2130 $cm.^{-1}$ and 2100 $cm.^{-1}$ in Pd dien SCN^+ and Pd Et_4dien NCS^+ respectively, in addition to an intense absorption at 2060 $cm.^{-1}$ due to free thiocyanate ion. An aqueous solution of Pd dien SCN^+ absorbed at 2100 $cm.^{-1}$, but a sufficiently concentrated solution of the tetra ethyl complex could not be obtained. However, in nitromethane, absorbances at 2110 $cm.^{-1}$ and 2090 $cm.^{-1}$ were recorded for the dien and Et_4dien complexes respectively. The large solvent effects are not uncommon and the absorbance maximum for Pd $(SCN)_4^{2-}$ is at 2108 $cm.^{-1}$ in acetophenone[19] so it is likely that the dien compound is sulphur bonded in both nitromethane and water. The absence of an absorbance around 840 $cm.^{-1}$ in Pd dien SCN^+ also favours the view that the complex is a thiocyanate, but unfortunately the C - S stretch expected in these systems at 710 $cm.^{-1}$ also remained undetected.

The replacement equilibria involving interchange of bromide and thiocyanate were quantitatively consistent with the Pd Et_4dien NCS^+ complex's being exclusively bound through the nitrogen atom. Therefore, although the N-alkyl system has greater class (b) character as indicated by the enthalpy values for halide interchanges, the thiocyanate has been forced by steric constraint to override electronic effects, and coordinate through the nitrogen atom.

The activation energy for the replacement of X in Pd Et_4dien X^+ by water is 17.3 for X = $\underline{S}CN$ and 18.2 for X = $\underline{N}CS$. The enthalpy change on changing Pd_4Et dien I^+ to Pd Et_4dien SCN^+ will be approximately 1 kcal/mole greater than for the isothiocyanato complex, i.e. +4 ± 2 kcals/mole. Remembering that the enthalpy change for the conversion of Pd dien I^+ to Pd dien SCN^+ is -2.2 ± 0.2 it can be seen that the replacement of dien by Et_4dien decreases the strength of the Pd - S bond by at least 4kcal/mole more than the Pd - I bond.

This supports the view that the complex Pd dien SCN^+ is entirely sulphur bonded in aqueous solution.

There are at least three possible mechanisms by which anation of Pd Et_4dien H_2O^{2+} could occur. In square planar complexes, it is usual to observe a combination of S_{N2} attack by solvent and by incoming ligand. The observed rate constant then obeys the expression:

$$k_{obs} = k_1 + k_2[X]$$

This particular complex, has, however, been found to behave similarly to a hexacoordinated system.[20] Anation studies of octahedral complexes are usually discussed in terms of the general scheme outlined in Figure 17.

Two general paths are available and the observed kinetics may result from either I, III, IV or I, II, IV, or a combination of both. Path I, III, IV involves a rapidly established equilibrium, followed by slow reversible reaction of the ion pair to give product.

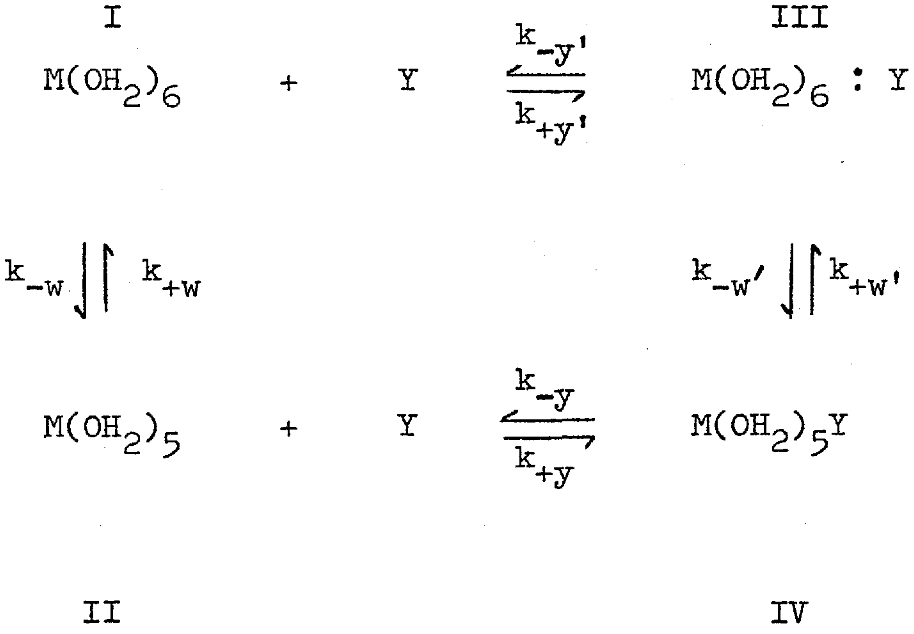


FIGURE 17. General reaction scheme for anation of octahedral complexes.

Let concentrations of the various species be represented by square brackets, and a suffix t indicate the same arbitrary time throughout.

$$\frac{+d\ \mathrm{IV}}{dt} = \frac{-d\ \mathrm{III}}{dt} = (k_{-w'} + k_{+w'})\ [\mathrm{III}]t$$

The ion pairing constant, K, $= \dfrac{k_{+y}}{k_{-y}} = \dfrac{[III]_t}{[I]_t[Y]_t}$

Let the total concentration of unreacted aquo complex and ion pair after a time t be $[M]_t$.

$$\text{Then} \quad [I]_t = [M]_t - [III]_t$$

$$\text{And} \quad K = \frac{[III]_t}{([M]_t - [III]_t)[Y]_t}$$

From which a value of $[III]_t$ may be calculated which, when substituted into the rate equation, gives:

$$+\frac{d\,IV}{dt} = \frac{(k_{-w'} + k_{+w'}) . K . [Y]_t . [M]_t}{1 + K[Y]_t} = \frac{-d\,M}{dt}$$

From which:

$$\frac{1}{k_{obs}} = \frac{1}{K(k_{-w'} + k_{+w'})} \times \frac{1}{[Y]_t} + \frac{1}{(k_{-w'} + k_{+w'})}$$

It can be seen that a plot of k_{obs} against halide ion concentration under pseudo first order conditions would pass through the origin, and be expected to rise to a limiting rate (the rate of reaction of the ion pair). Small values of K would lead to a linear dependence on halide ion concentration. Plots of

$\frac{1}{k_{obs}}$ against $\frac{1}{[Y]}$ would also be straight lines of gradient $\frac{1}{K(k_{-w'} + k_{+w'})}$ and intercept $\frac{1}{(k_{-w'} + k_{+w'})}$.

Path I, II, IV involves loss of water to give a five coordinate intermediate followed by anation. The rate law for this process has been derived[31]

$$k_{obs} = \frac{k_{-w}\,[Y] + \frac{k_{+w}k_{-y}}{k_{+y}}}{[Y] + \frac{k_{+w}}{k_{+y}}}$$

If $k_{+w} \gg k_{+y}$ a linear dependence on $[Y]$ would be expected for k_{obs} and the intercept should equal the rate of back reaction k_{-y}.

The reproducibility of individual rate constants was poor and experimental difficulties were increased by the speed of reactions at high halide concentrations, and the incomplete reaction at low concentrations. Although straight lines have been drawn through the points, many of the plots curve slightly and always in the same sense. If this is coupled with the observation that aquation reaction reactions resemble those observed in octahedral

TABLE XII

Stability constants for the equilibrium:

$\mathrm{Pd\ Et_4dien\ X + Y = Pd\ Et_4dien\ Y + X}$

derived from the rates of aquation and anation at 44.8°C

X	$\frac{k_{-w}k_{+y}}{k_{+w}}$ (1 mole^{-1}sec^{-1})	k_{-y}(sec^{-1})	$K\ \frac{X}{H_2O}$	$K\ \frac{X}{Br}$
Cl	0.270	0.0087	31	0.72
Br	0.216	0.0051	43	
I	0.225	0.0011	204	4.8
NCS*	0.97	0.00084	1150	

*Values for 40°C.

systems there are reasonable grounds for rejecting the simple S_{N2} reaction path which occurs in square planar complexes.

The chloride and bromide anation studies have noticeable intercepts and, although these are greater than the observed values for k_{-y} in each case, the presence of an intercept at all is taken as indication of a dissociative mechanism. The ionic strength varied during these studies from 0.1 to 0.3 and so little importance can be attached to any quantitative data from this system. It is of interest to note, however, that whichever reaction path is assumed, the activation energies are independent of anion to the limits of experimental error.

Assuming a dissociative mechanism, the slopes of the graphs of k_{obs} against Y give values of $\frac{k_{-w}k_{+y}}{k_{+w}}$. If these are divided by k_{-y} for the same temperature and halide ion, rough values for the stability constants for halide interchange may be obtained. (Table XII.)

Thelow stability of the complexes with respect to water indicates that some hydrolysis is to be expected even in solutions containing 0.5 M excess halide, and it can also be seen that the equilibrium constants are in fair agreement with those obtained directly.

CHAPTER 3.

The Reaction of Sodium Chloro-iridate with Nitrite, Iodide and Thiocyanate Ions.

INTRODUCTION

The rate constants for the aquation of hexachloro-iridate (IV) and hexachloro-iridate (III) are both approximately 10^{-6} sec.$^{-1}$1.mole^{-1} at 25°C, whereas electron transfer reactions of these ions occur readily, many of the rate constants lying in the range 10^6 to 10^9 1.mole^{-1}.sec.$^{-1}$. Since substitution reactions occur so slowly for these ions, the electron transfer reaction:

$$*IrCl_6^{2-} + IrCl_6^{3-} \rightleftharpoons *IrCl_6^{3-} + IrCl_6^{2-}$$

has been classified as outer sphere[33] and other rapid reactions of iridium (IV) have been discussed in terms of this mechanism.[34,35]

However, the oxidation of Cr^{2+} by $IrCl_6^{2-}$ is believed to be an inner sphere process,[36] the nature of the products being determined by the greater stability of Cr^{3+}(aq.) and $IrCl_6^{3-}$ than the monochloro chromium (III) complex and $IrCl_5H_2O^{2-}$. The ligand displacement during an inner sphere transfer occurs at the reducing species and distinction between inner and outer sphere mechanisms is poorly defined in cases where there is no atom transfer.

The inner sphere mechanism however requires the electron to be transferred through a particular atom, and so diffusion controlled rates would not be expected in these reactions. It has been pointed out that inner and outer sphere mechanisms are probably only extreme limits of a general case.[37]

Small amounts of $IrCl_6^{2-}$ (about 5 mole per cent) have been found[38] to inhibit the light catalysed substitution reactions of $PtCl_6^{2-}$. However, during studies on $PtBr_6^{2-}$ and PtI_6^{2-}, it was found that the spectrum of $IrCl_6^{2-}$ rapidly and completely disappeared in the presence of iodide ion, although the inhibitory properties appeared to be retained. A related reaction was observed when sodium nitrite or sodium thiocyanate was used instead of sodium iodide, and in these cases the reaction was slightly slower.

The reduction of $IrCl_6^{2-}$ with iodide, nitrite, and thiocyanate was studied by the stopped flow technique. The mechanism of these relatively slow electron transfer reactions is discussed in terms of previously published data.

RESULTS

The product of the reaction of $IrCl_6^{2-}$ with I^-, NO_2^- or SCN^- can be precipitated in each case by mixing alcoholic solutions containing stoichiometric quantities of $IrCl_6^{2-}$ and the sodium salt. The ultraviolet spectrum of the greenish yellow powder obtained was identical to the product of the reaction when carried out in water, and no iodide or thiocyanate was detected in the product. The spectra of the $Ir(III)Cl_n(H_2O)_{6-n}$ ions have been found to be very similar[39] and the absorbances are weak in the easily accessible part of the spectrum, with the result that it is difficult to identify a particular chloroaquo species of iridium (III). The various Ir(IV) species are however easily distinguished, and can be prepared by bubbling chlorine gas through an aqueous solution of the corresponding Ir(III) complex.[39] The total time taken to oxidise and obtain the spectrum of a solution ~~of~~ is four minutes or so, completely negligible in comparison with the time taken for detectable amounts of substitution to occur. The resulting spectrum was the same in each of the three cases and was that of $IrCl_6^{3-}$. The

Dependence of $k_{obs.}$ on $[I^-]$ at 20.1°C

For the reaction:

$$2IrCl_6^{2-} + 3I^- = 2IrCl_6^{3-} + I_3^-$$

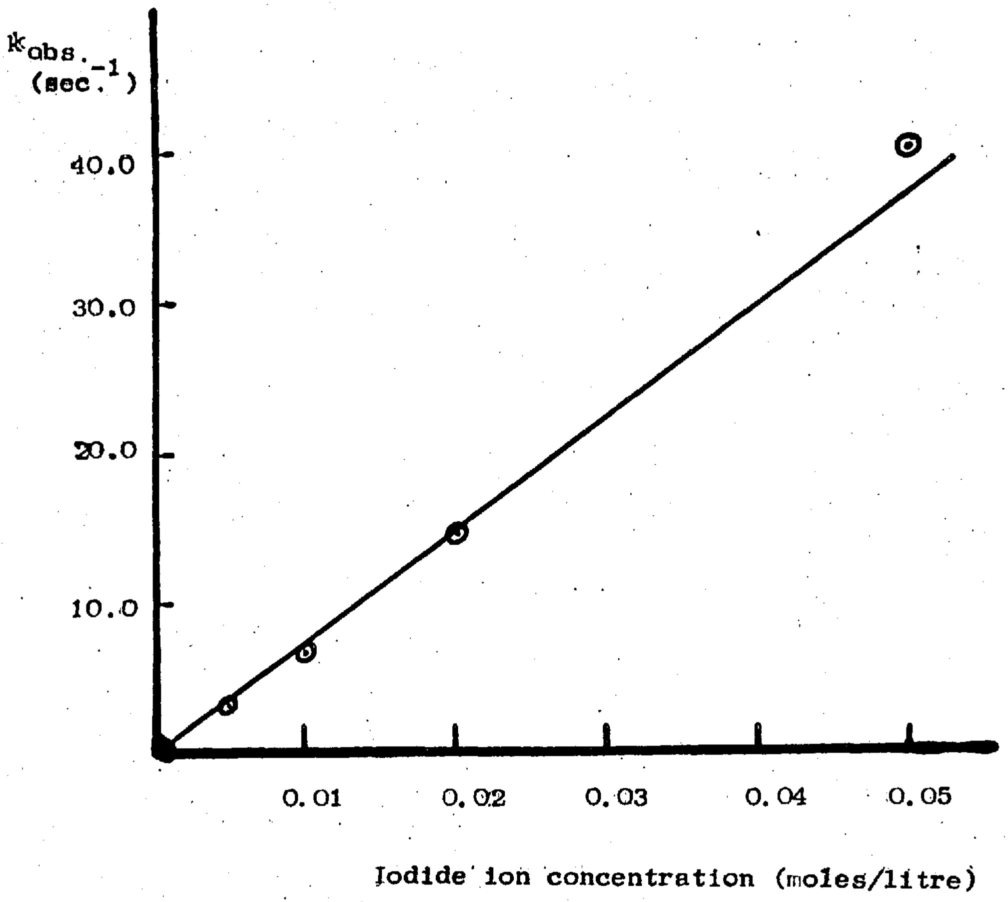


Figure 17

reactions therefore consist simply of the donation of an electron to $IrCl_6^{2-}$ by various anions.

In the case of iodide reduction, one of the products is I_3^- which has an intense and characteristic spectrum.[40] In a 1.0 M solution of sodium iodide, the amount of I_3^- formed only corresponded to 72% of that expected from the equation:

$$2IrCl_6^{2-} + 3I^- \rightleftharpoons 2IrCl_6^{3-} + I_3^-$$

The discrepancy cannot be explained on the basis of the equilibrium between I_2 and I_3^- and probably therefore arises from reaction of $I^{\bullet}$ or I_3^- with H_2O or OH^-. The rate of formation of I_3^- followed at 353 mμ was very similar to the rate of disappearance of $IrCl_6^{2-}$ followed at 485 mμ, and so the progress of the reaction was followed by the increase of absorbance at 353 mμ where the extinction coefficient of I_3^- is 26,400, and that of $IrCl_6^{2-}$ is less than 400 ($cm.^{-1} l. mole^{-1}$).

The results are given in Table XIII; the reaction is first order with respect to both reagents, and k_2 = 700 $l. mole^{-1} sec.^{-1}$ at 20.1°C.

CONT^D ON P 90

TABLE XIII

The reduction of $IrCl_6^{2-}$ by iodide ion

λ = 353 mμ $[IrCl_6^{2-}]$ = 2 x 10^{-4} M

$[I^-]$	Temp.°C	Ionic Strength (mole/1)	k_{obs} (sec.$^{-1}$)	k_2 (1.mole^{-1} sec^{-1})
0.01	15.1	0.1	5.64	564
0.01	20.5	0.1	6.84	684
0.02	20.1	0.1	14.44	722
0.05	20.1	0.1	40.68	801
0.005	20.1	0.1	3.05	610
0.01	20.5	1.0	41.1	4110
0.01	20.5	0.01	5.03	503
0.01	28.8	0.1	9.28	928
0.01	29.0	0.1	9.19	919
0.01	38.9	0.1	13.02	1302
0.01*	20.5	0.1	6.34	634

*λ = 485 mμ

TABLE XIV

The reduction of $IrCl_6^{2-}$ by nitrite ion

λ = 485 mμ $[IrCl_6^{2-}]$ = 6 x 10^{-4} M

$[NO_2^-]$	Temp. °C	μ	k_{obs} (sec.$^{-1}$)
0.50	20.5	1.0	117.0
0.50	20.3		112.4
0.35	20.3		75.4
0.25	20.5		49.7
0.10	20.5		9.52
0.05	20.5		2.73
0.005	20.5		0.083
0.00005	20.5		0.00523
0.25	30.1	1.0	59.4
0.25	38.6		70.7
0.25	47.0		85.9

The Reduction of Na_2IrCl_6 by NO_2^- :

(a) k_{obs} plotted against $[NO_2^-]$.

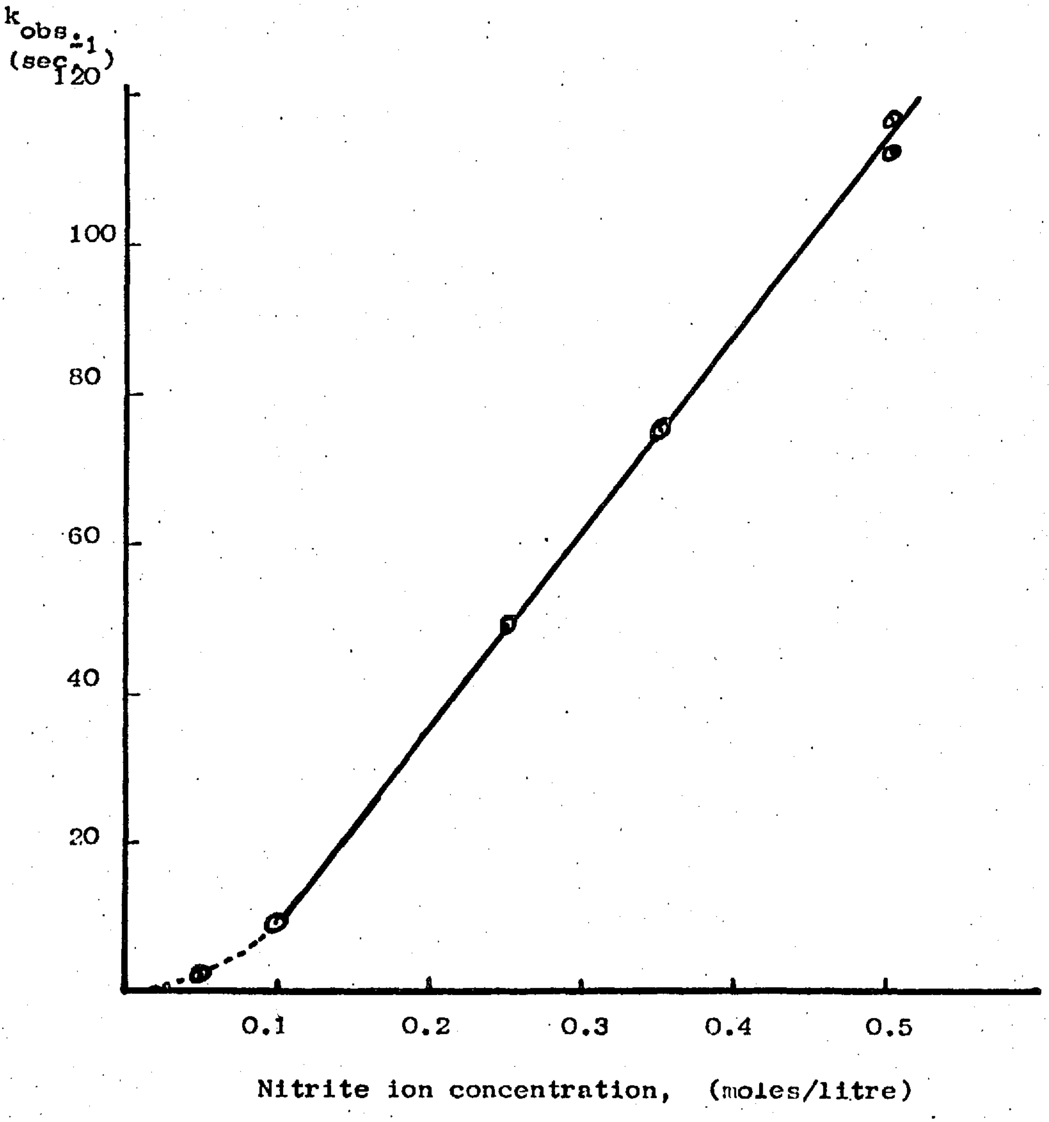


Figure 18

The Arrhenius energy is 6.4 ± 0.5 kcal.per mole, and the variation in ionic strength indicates that the reagents are of the same sign, but no information can be obtained concerning the magnitude of the charges because the Debye Hückel limiting law does not hold at such high ionic strength.

The reaction with nitrite ion with $IrCl_6^{2-}$ was studied at 485 mμ at an ionic strength of 1.0 M. Pseudo first-order rate plots were obtained and the results are quoted in Table XIV. It can be seen from the Table and Figures 18 and 19 that the reaction is first order in nitrite above 0.1 M and k_2 is 250 $1.mole^{-1}$ $sec.^{-1}$. The Arrhenius energy is 4.1 ± 0.2 kcal per mole.

At lower nitrite ion concentrations the pseudo first order rate constant became approximately second order in nitrite ion. A related dependence has been found in the nitrosation of $Co(NH_3)_5H_2O^{3+}$ where the rate law has been found to be[41]

$$R = k\,[\text{hydroxo complex}]\,[HNO_2]^2$$

The interpretation given in the cobalt case is that the reagent actually involved in the activated complex is N_2O_3

The Reduction of Na_2IrCl_6 by NO_2^-:

(b) $\sqrt{k_{obs.}}$ plotted against $[NO_2^-]$

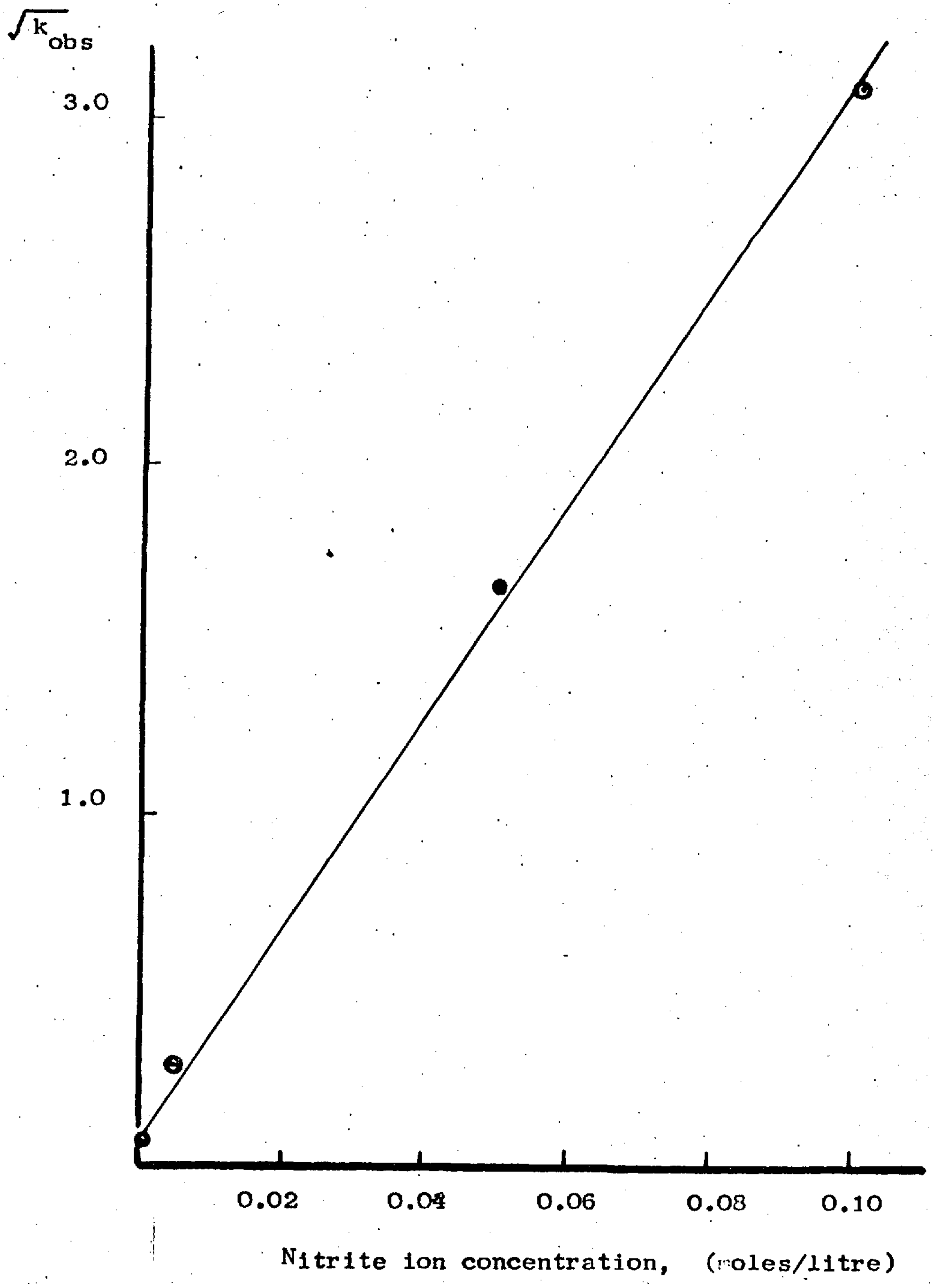


Figure 19.

$$NO_2^- \quad + \quad H^+ \quad \rightleftharpoons \quad HNO_2$$

$$2HNO_2 \quad \rightleftharpoons \quad N_2O_3 \quad + \quad H_2O$$

At low NO_2^- concentrations in distilled water at about pH 5, the proportion of N_2O_3 could be quite considerable, and the electron transfer might be expected to be more favourable from the π-bonded system. The N_2O_3 path would then have control and the reaction would be second order in nitrite. As the small amount of acid is removed, proportionately less undissociated acid is formed with increasing nitrite ion concentration, and at high concentrations the NO_2^- path takes control.

A single run was carried out using 0.01 M sodium thiocyanate at unit ionic strength and 25°C. The pseudo first order rate constant was found to be 0.02 $sec.^{-1}$ and assuming that the reaction is first order in both reagents, a bimolecular rate constant of approximately 2 $1.mole^{-1}$ $sec.^{-1}$ is calculated.

Determination of the Arrhenius energy of Activation, for the reduction of Na_2IrCl_6 by iodide.

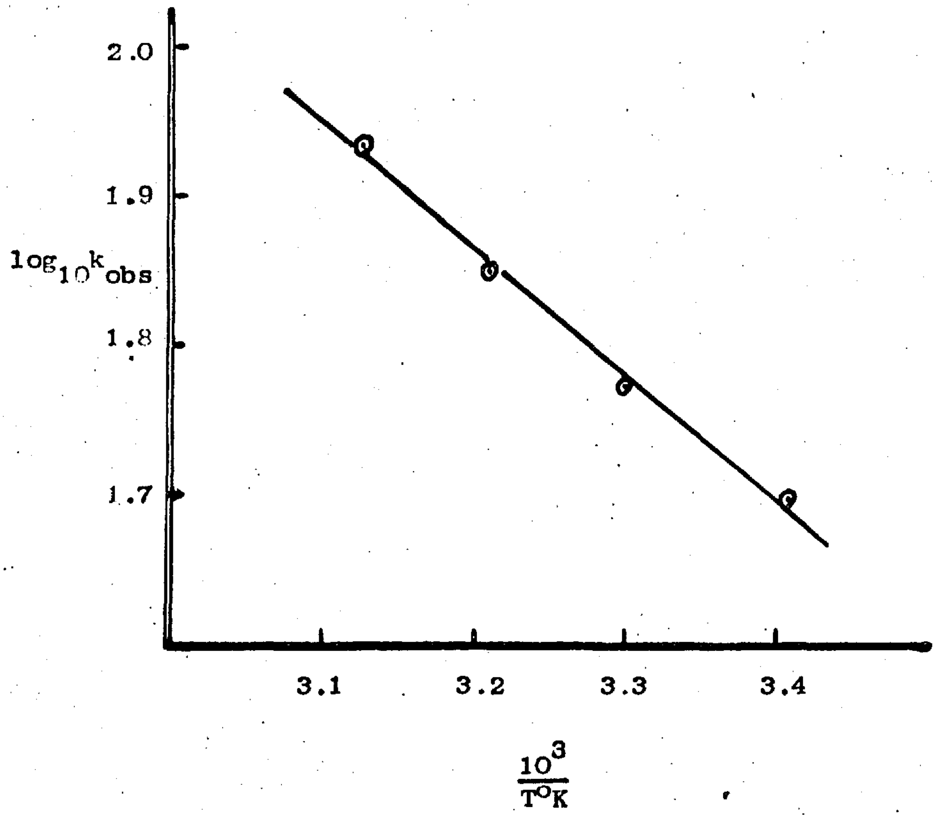


Figure 20.

TABLE XV

Some electron transfer reactions of Ir(IV)

Ref.	Reagents	k_2(1 mole^{-1}sec.$^{-1}$)	ΔH^*	ΔS^*
35	$^*IrCl_6^{2-} + IrCl_6^{3-}$	/ 2.3×10^5		
35	$IrCl_6^{2-} + IrBr_6^{2-}$	1.2×10^7	5.7	-8.7
35	$IrBr_6^{2-} + IrCl_6^{2-}$	1.8×10^6	7.5	-6.3
45	$IrCl_6^{2-} + Fe^{2+}$	3.2×10^6	1.9	-25
46	$IrCl_6^{2-} + Fe(DMP)^{2+}$	1.2×10^9	0.5	-18
	$IrCl_6^{2-} + I^-$	700	5.8	-25.7
	$IrCl_6^{2-} + NO_2^-$	250	3.5	-35.6
	$IrCl_6^{2-} + SCN^-$	2		
47	$IrCl_6^{2-} + W(CN)_8{}^{4-}$	6.1×10^7		
47	$IrCl_6^{2-} + Mo(CN)_8{}^{4-}$	1.9×10^6		

DISCUSSION

The reactions studied involve the transfer of an electron from various reducing agents to the $IrCl_6^{2-}$ ion. The kinetic parameters found during this work are listed in Table XV together with other published results.

The mechanism of electron transfer reactions has been reviewed by Halpern.[33] When the rate of electron transfer is less than that at which substitution occurs in the reducing species, it is possible that an inner sphere mechanism is occurring as in the reduction[42] of certain Co(III) complexes by Cr^{2+}

$$\begin{array}{l} (NH_3)_5Co - X \; + \; Cr(H_2O)_6 \rightleftharpoons (NH_3)_5 - X - Cr(H_2O)_5 \\ \hspace{9em} \downarrow \\ \hspace{6em} (NH_3)_5Co\,(H_2O) + CrX(H_2O)_5 \end{array}$$

The rates of inner sphere reactions are very sensitive to the ability of the bridging ligand to "conduct" the electron,[43] and also depend considerably on the non-bridging ligands.[44] The probability that an electron will be conducted by a particular bridging group has been measured and found to be capable of producing changes in ΔS^* of up to 30 e.u. and changing the rate by a factor of 10^6.

Where the electron transfer occurs at a rate much greater than those substitution reactions which occur in the reducing species, an outer sphere mechanism is usually proposed. The rearrangement of reactants before electron transfer can take place is an essential part of the theoretical treatment of outer sphere reactions by Marcus.[49] The Franck Condon restriction permits a radiationless transition only between two states at some non-equilibrium (vibrationally excited) region where their energies are equal. The energy required to excite the reagents to the position where such a transition can happen is called the reorganisation energy and it is greatest for exchange reactions where the Gibbs free energy change during the reaction is zero. In reactions where there is some driving force it is possible to form the products in an excited state, and less rearrangement energy may be necessary before reaction can occur.

This argument leads to the prediction that all electron transfer reactions that take place with a net decrease of free energy should occur greater rates than exchange reactions.

The rate of the exchange reaction:

$$IrCl_6^{2-} + {}^*IrCl_6^{3-} = IrCl_6^{3-} + {}^*IrCl_6^{2-}$$

. has been studied using radio-iridium, but the technique used would appear only to justify use of the rate constant quoted[35] (2.3 x 10^5 l.mole^{-1} sec.$^{-1}$) as a lower limit. The forward and reverse rate constants for the reaction of chloroiridate with bromoiridite are 1.2 x 10^7 and 1.8 x 10^6 l.mole^{-1} sec.$^{-1}$ respectively. Since the reverse reaction is thermodynamically unfavourable, the products of this step cannot be formed in an excited state, and the amount of reorganisation energy required would be expected to be similar to that for the chloroiridate chloroiridite exchange. It is therefore probable that the rate constant for the isotopic exchange is too low, a more acceptable value being 2 x 10^6 l.mole^{-1} sec.$^{-1}$.

The electron transfer reactions between iridium complexes are clearly outer sphere, and the reactions with other complexed metal ions have faster rates than that expected for the isotopic exchange. In general, the rates of reduction of $IrCl_6^{2-}$ show few trends, and it is only when enthalpies and entropies of activation are calculated that major differences become apparent. Thus, although the rates of reaction of chloroiridate with ferrous ion and with bromoiridate are within a factor of four of one another, they have very different values of ΔH^* and ΔS^*.

The amount of data giving energies and entropies of activation is small and so the factors that determine the observed values of ΔH^* and ΔS^* are uncertain. However, if it is assumed that ΔH^* is largely a function of the work required to bring the reagents together; that is the respective charges and the internuclear distance in the activated complex; and that ΔS^* indicates the ease of electron transfer in that complex, a reasonably consistent picture can be built up.

Reactions of $IrCl_6^{2-}$ with $Fe(DMP)_6^{2+}$(DMP = 4,7, dimethyl ortho-phenanthroline) might be expected to have a low ΔH^* because the ligands would probably prevent very close approach of the reagents in the activated complex and the charges are of opposite sign. The relative difficulty in transferring an electron as indicated by the fairly large negative value of ΔS^* is more difficult to understand. The large negative entropy of activation in reductions by Fe^{2+}ion is thought to be caused by the electron being conducted through several water molecules.[50]

E.S.R. studies have shown that the unpaired electron in Ir(IV) complexes spends a fair proportion of its time on the ligands, in a π-type antibonding orbital, and the antiferromagnetic behaviour[51] found in $IrCl_6^{2-}$ supports this. The intermolecular distance in the activated complex formed during the reaction of $IrCl_6^{2-}$ and $IrBr_6^{3-}$ could be quite large and the enthalpy of activation is not very much more than that observed in the Fe^{2+} + $IrCl_6{}^{2-}$ reaction, despite the large negative charge on the intermediate. The ease with which an electron is tranferred during overlap of the π antibonding orbitals of the two iridium species is indicated by the small negative entropy values.

The iodide and nitrite ions are uninegative and hence their reactions with chloroiridate would be expected to have lower activation energies than the exchange between $IrCl_6^{2-}$ and $IrBr_6^{3-}$. It is possible that the relatively similar values found experimentally indicate that iodide and nitrite ions have to approach $IrCl_6^{2-}$ more closely than does $IrBr_6^{3-}$. The large difference in the bimolecular rate constants is due to the entropy term. This could possibly simply reflect the difficulty of transferring an electron from widely different species such as I^- and NO_2^- to $IrCl_6^{2-}$. An alternative reason could be that in these cases, the activated complex is more highly ordered and a partially bound structure exists for example:

$$Cl - Ir - Cl \ldots\ldots I$$

(four planar chloride ligands have been omitted).

The rates of reaction of chloroiridate with iodide and nitrite are far below the lower limit observed for the isotopic exchange and so some approximation to an inner sphere mechanism where the rate is controlled by the rate of removal of water from the hydration sphere of the iodide ion is by no means unlikely.

CHAPTER 4

The reaction of hexabromoplatinate (IV) with iodide ion.

INTRODUCTION

Platinum (IV) complexes have a t_{2g}^{6} configuration and would therefore be expected to resemble Co(III) and Ir(III) in its inertness to nucleophilic attack. Indeed, the higher positive charge and small size of Pt(IV) would tend to attract the ligands closer to the metal and result in increased bond strength and crystal field splitting, suggesting that Pt(IV) may be expected to be more inert than Rh(III) etc. to nucleophilic substitution

However, many rates have been measured, and in some cases a surprising degree of labitity has been observed which arises from the ability of the reaction to proceed by an alternative path to the usual S_N mechanisms. Much recent work has been based on compounds of the type $Pt(NH_3)_4X_2^{2+}$ and $Pt(en)_2X_2^{2+}$. The rates of these reactions have been explained[52,53] in terms of Pt(II) catalysis, and the general mechanism is usually as outlined below (four equatorial ammonia molecules have been omitted on each platinum atom for clarity).

$$Pt^{II} + Y^- \leftrightharpoons Pt^{II} - Y$$

$$Y - Pt^{II} + X - Pt^{(IV)} - X \leftrightharpoons Y - Pt^{(IV)} - X + {}^{II}Pt - X$$

followed by:

$$Y - Pt^{(II)} + Y - Pt^{(IV)} - X \rightleftharpoons Y - Pt^{(IV)} - Y + {}^{(II)}Pt - X$$

Although many of the reactions of Pt(IV) can be understood in this light, the bridged redox mechanism does not always apply. Ion pairing has been observed in the complex $Pt(en)_2Br_2^{2+}$ with free bromide and it has been suggested that these ion pairs may be formed in an alternative mechanism for non catalytic substitution involving only free halide ion and the Pt(IV) complex.[54]

The exchange of $PtCl_6^{2-}$ with radiochloride has been shown to be a light catalysed chain reaction[55] and is attributed to the formation of labile $Pt(III)\ Cl_5^{2-}$. The catalyst could be formed by the addition of one of a variety of reducing agents including Na_2SO_3 and $SnCl_2$ and the reaction was shown to be inhibited by oxidising agents such as Cl_2 and Na_2IrCl_6.

The catalytic action of light on the exchange reaction of $PtBr_6^{2-}$ with free bromide ion has been attributed to a similar chain mechanism[56] and quantum yields of up to 500 have been reported.

(Both $Br^{\cdot}$ and $PtBr_5^{2-}$ exchange rapidly with Br^-)

$$PtBr_6^{2-} \rightleftharpoons PtBr_5^{2-} + Br^{\cdot}$$

$$PtBr_6^{2-} + PtBr_5^{2-} \rightleftharpoons PtBr_5^{2-} + PtBr_6^{2-}$$

The inhibitory natures of $Fe(CN)_6^{3-}$ and $IrCl_6^{2-}$ have been investigated quantitatively[57] for the $PtBr_6^{2-}$ – Br^- exchange, and found to obey the relationship:

$$R \propto [\text{Inhibitor}]^{-\frac{1}{2}}$$

for $\left[\dfrac{\text{Pt}}{\text{Inhibitor}}\right]$ ratios from 10^2 to 10^5.

A detailed study of the reaction of $PtCl_6^{2-}$ with iodide using both radiochemical and spectroscopic methods has been reported.[58] The presence of a labile Pt(III) intermediate was postulated because the reaction was found to be light sensitive and catalysed by small amounts of ferrous and thiosulphate ions. Additions of $PtCl_4^{2-}$ had only a small effect on the rate and so the Pt(II) bridge mechanism was thought unlikely. The rate was inhibited by 1 - 5% sodium chloroiridate, and the residual reaction assumed to react by a non-catalytic path.

Preliminary investigations of the $PtBr_6^{2-}$ replacement reaction[58,59] showed that the reaction was considerably faster than the $PtCl_6^{2-}$ replacement, consisted of three stages, and was only slightly light sensitive. Inhibition by small amounts of $IrCl_6^{2-}$ (up to 5%) was observed, and since larger additions had no further effect, the residual reaction was assumed to represent the non-photochemical replacement.

Radiochemical work showed that the product of the first stage is probably cis or trans $PtBr_4I_2^{2-}$ and that the second stage produces $PtBr_nI_{6-n}^{2-}$ where $n = 1$ or 2.

In the present work an attempt has been made to identify with more certainty the species involved as intermediate products. The amount of kinetic data for each stage has been increased, and some possible mechanisms discussed.

METHOD

The ultraviolet spectra of the species formed during the reaction of $PtBr_6^{2-}$ with iodide ion are given in Figure 21. The rate constants were obtained under pseudo first order conditions by dissolving solid $PtBr_6^{2-}$ in thermostatted reagent solutions containing the required amounts of sodium iodide, sodium perchlorate and sodium chloroiridate. For the first stage observations were made at 435 mμ at the required time intervals, and the infinity time value estimated by a short graphical extrapolation of the recorded absorbance.

The spectral change during the second step is not large and the results obtained are not particularly consistent. The kinetic measurements were made at about 470 mμ where an isobestic point prevented the subsequent stage from interfering (Figure 23). The exact wavelength of this point varied by ± 2 mμ with changing temperature.

The final stage of the reaction results in the formation of PtI_6^{2-} with a maximum of 495 mμ (Figure 23).

The oxidation of Pt(II) to Pt(IV) by chlorine gas in the presence of chloride ion has long been

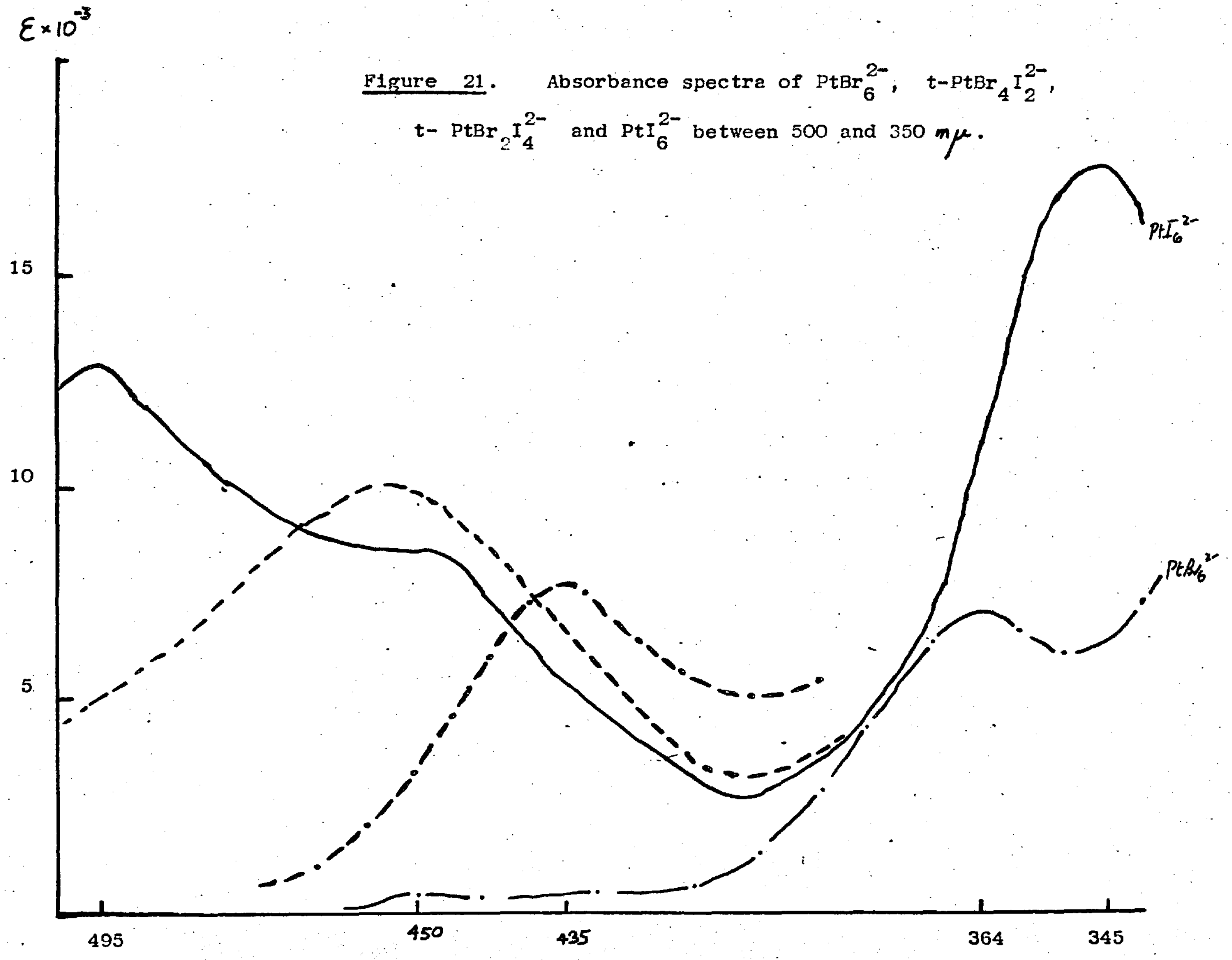


Figure 21. Absorbance spectra of $PtBr_6^{2-}$, t-$PtBr_4I_2^{2-}$, t- $PtBr_2I_4^{2-}$ and PtI_6^{2-} between 500 and 350 mμ.

Spectral Changes during the reaction of

$PtBr_6^{2-}$ with iodide.

Fig. 23

second and third steps.

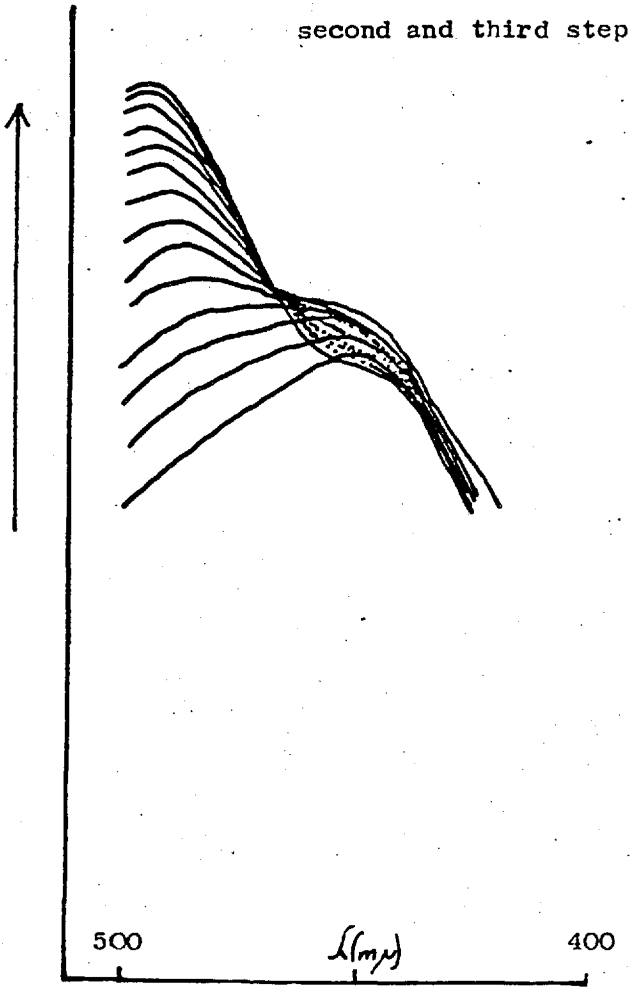
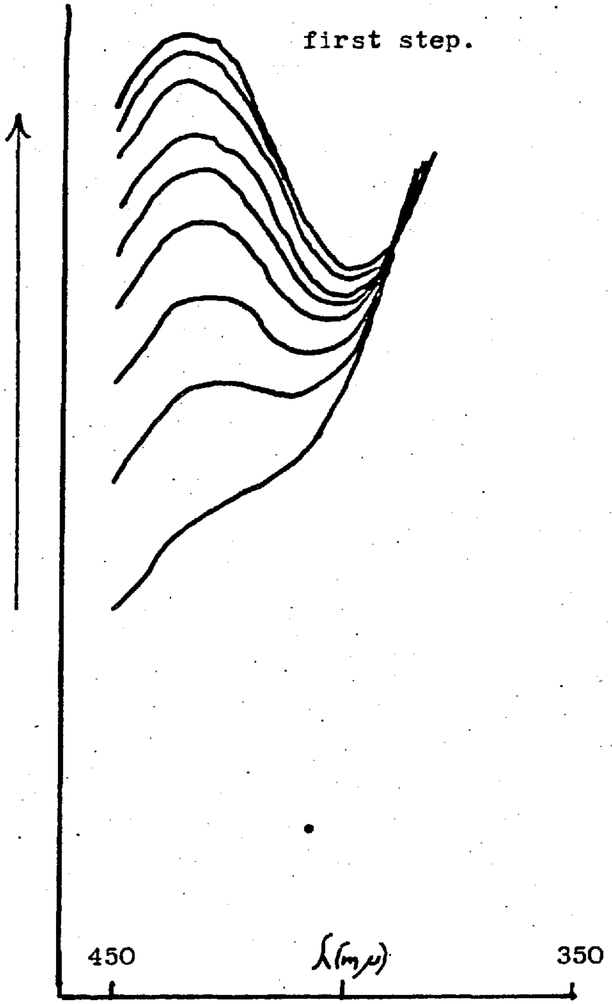


Fig. 22

first step.



known and used as a preparative route to the octahedral Pt(IV) complexes. When a solution of PtI_4^{2-} is treated with iodine dissolved in sodium iodide, the rapid oxidation to PtI_6^{2-} is too fast to be measured on the stopped flow assembly. ($k_2 > 10^8$ l. mole^{-1} sec.$^{-1}$).

On treatment of $PtBr_4^{2-}$ with the same solution, an equally rapid reaction occurred to give a spectrum similar to that observed at the end of the first substitution process. Two slower steps were then observed and the kinetics of these compared with those found in the substitution process. The kinetic study of these reactions was carried out in thermostatted four centimetre cells into which were pipetted various volumes of I_3^-(7.2×10^{-5} M) dissolved in 0.01 M sodium iodide, sodium iodide (0.01 M) sodium perchlorate (0.01 M), containing sodium chloro-iridate (8×10^{-6} M) and $PtBr_4^{2-}$ dissolved in 0.01 M sodium perchlorate. The concentrations of I_3^- and Na_2PtBr_4 (which was supplied in solution) were determined from their published extinction coefficients:

ε_{354} for I_3^- is 26,400 and ε_{267} for $PtBr_4^{2-}$ is 6,700.[28,40]

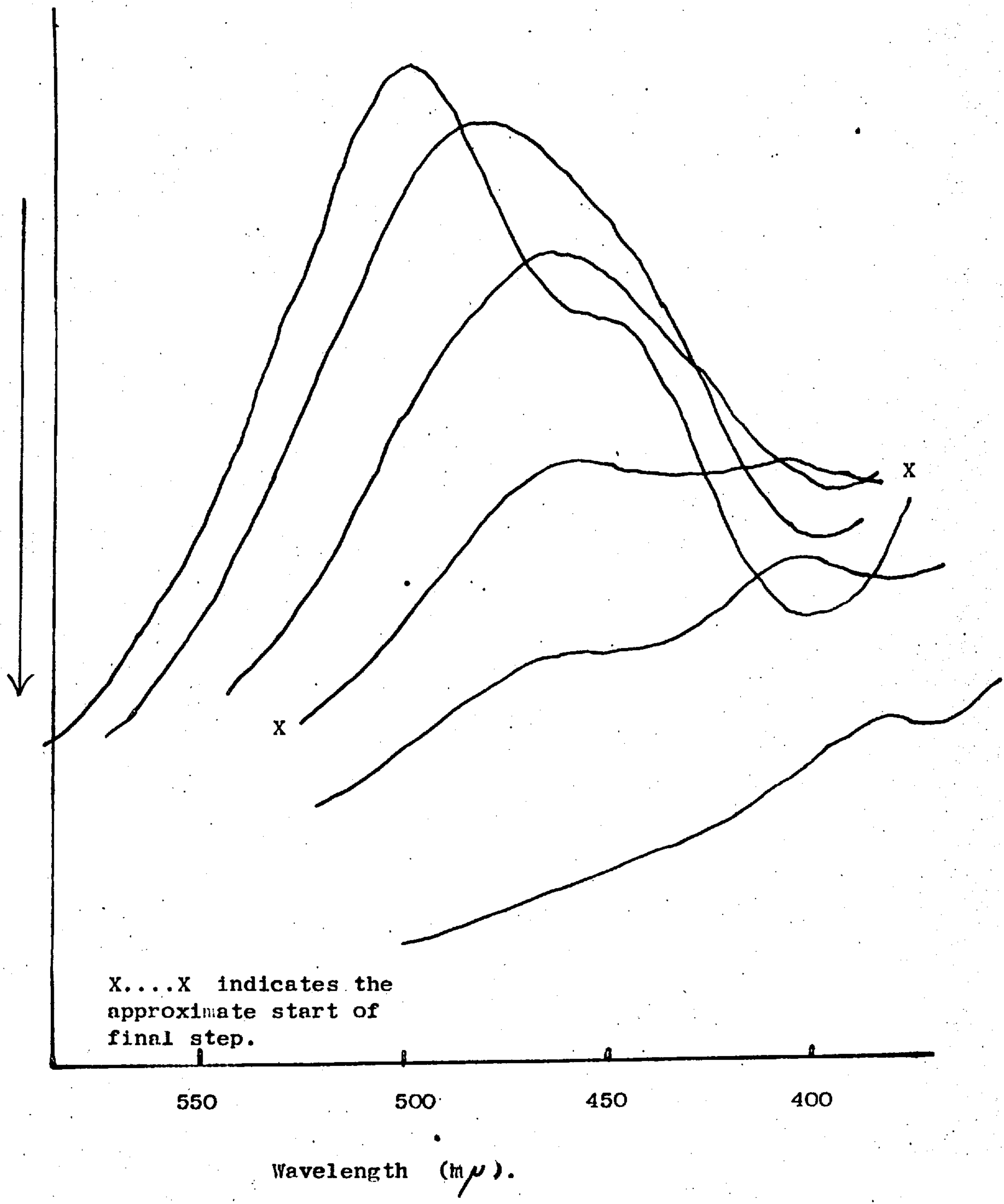
A short investigation of the reaction of PtI_6^{2-} with bromide ion was also carried out. The final product was found to be $PtBr_6^{2-}$ and the kinetics of the final stage of the reaction studied by conventional methods using solid PtI_6^{2-} and strong sodium bromide solutions (1 - 5 M) containing sodium chloro-iridate (10^{-5}M). The spectral change that occurs during the stepwise addition of Br^- to PtI_6^{2-} is shown in Figure 24 and the rate of the final reaction was followed at 290 mμ so that the absence of the decomposition could be checked during each run (Figure 25).

RESULTS

The rate constants for the substitution reactions found during earlier work have been combined with new data and are given in Tables XVI to XVIII. Ionic strength variation is consistent with the activated complex formed during the first stage of the reaction comprising two similarly charged species.

Figure 24.

Absorbance changes on addition of
bromide ion to iodo-platinate(IV)



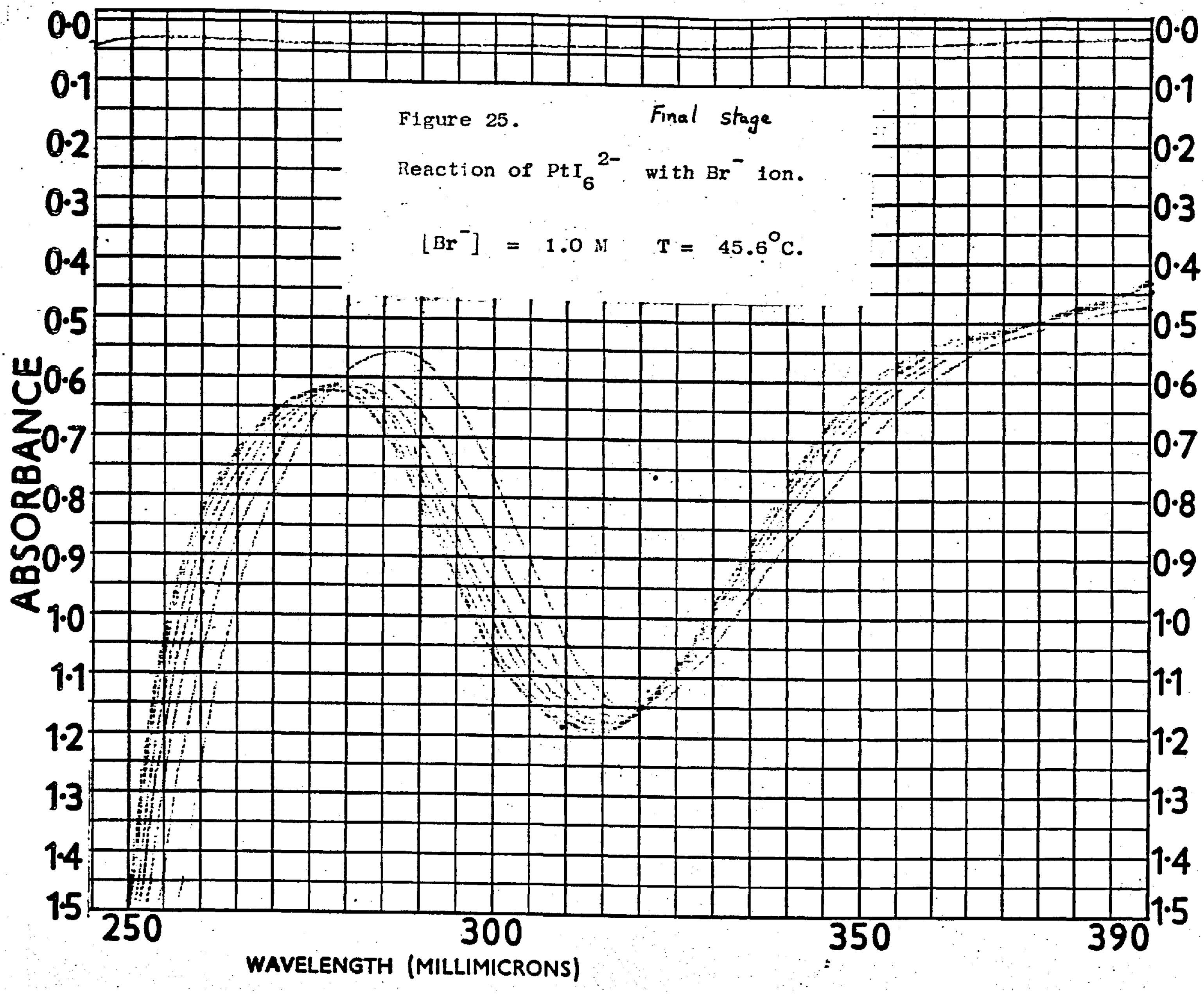


Figure 25. *Final stage*

Reaction of PtI_6^{2-} with Br^- ion.

$[Br^-]$ = 1.0 M T = 45.6°C.

The ultraviolet spectrum of the product of the rapid oxidation of $PtBr_4^{2-}$ by iodine was found to be identical with that observed at the end of the first stage of the substitution reaction. The kinetic data obtained from the two subsequent slow steps are presented in Tables XIX and XX. It is deduced from the Arrhenius activation energy plots compiled from both oxidation and substitution results (Figures 27 and 28) that the two stages of substitution that follow the rapid oxidation are identical with the latter two stages of reaction of $PtBr_6^{2-}$ with iodide ion.

The final stage of the reverse reaction, PtI_6^{2-} + Br^- has also been studied and the kinetic parameters set out in Table XXI.

Although none of the rate constant data is particularly reproducible fairly good pseudo first order rate plots were obtained over about three half lives. The activation energies and their probable errors were estimated graphically from a combination of $PtBr_6^{2-}$ and $PtBr_4^{2-}$ data where applicable.

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Figure 26.

Arrhenius Activation Energy Plot for the reaction:

$PtBr_6^{2-} + 2I^- == t\text{-}PtBr_4I_2^{2-}$

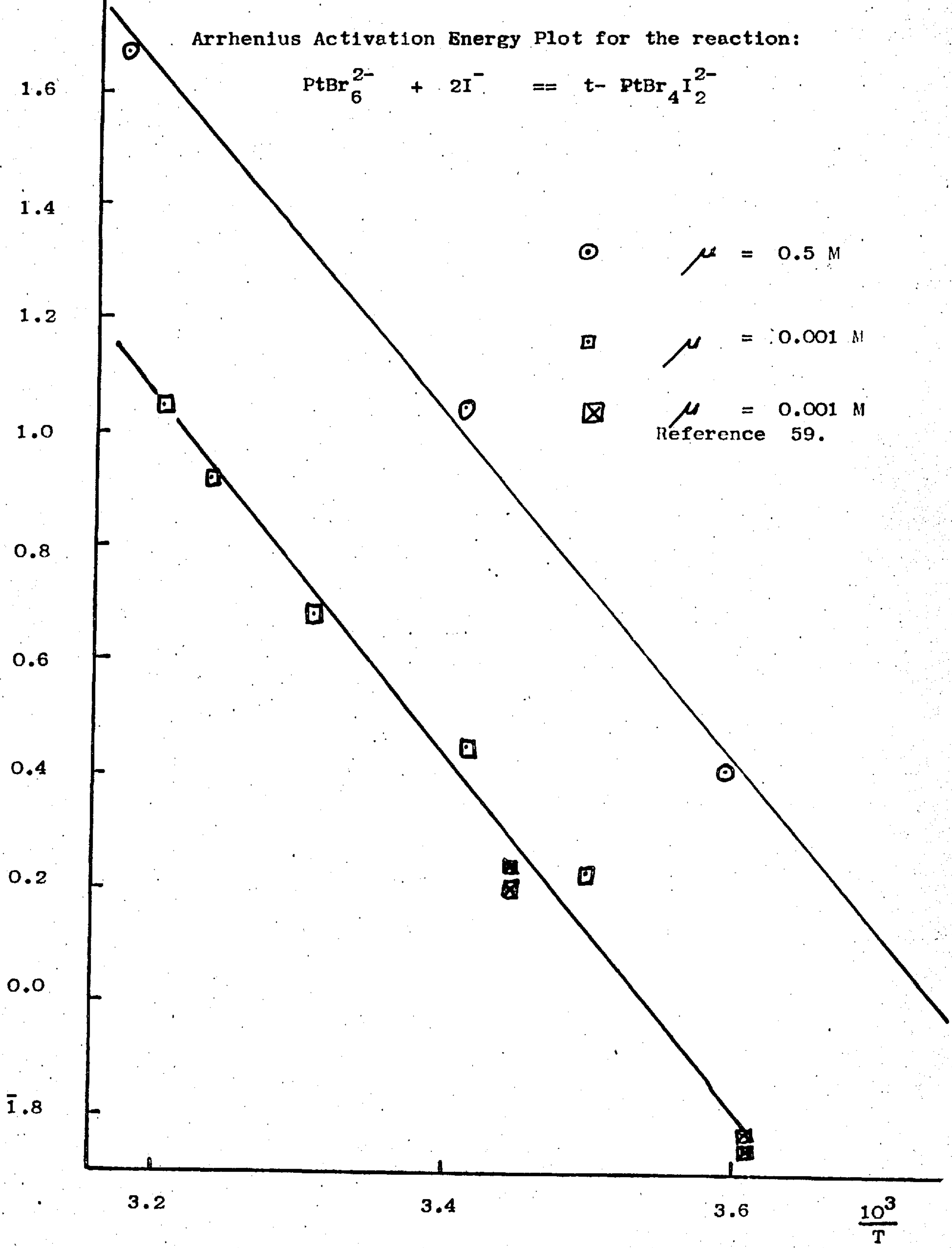


TABLE XVI

$PtBr_6^{2-}$ + I^- substitution reaction (first stage)

Studied at 435 mμ $[PtBr_6^{2-}]$ = 6 x 10^{-5} to 10^{-4} M
$[IrCl_6^{2-}]$ = 2 x 10^{-5} M

k_{obs} sec.$^{-1}$	$[I^-]$ mole/l x10^{-4}	k_2 sec.$^{-1}$ l mole^{-1}	T°C	μ mole/l
0.0122	50	2.51	5.1	0.5
0.00576	20	2.88	5.1	0.5
0.00127	5	2.54	5.1	0.5
0.00690	5.97	11.05	20.0	0.5
0.0233	5	46.7	40.0	0.5
0.000845	5	1.69	13.0	0.001
0.00140	5	2.80	20.1	0.001
0.00422	5	8.45	35.7	0.001
0.00650	5	13.0	39.1	0.001
0.0024	5	4.8	29.0	0.001
*0.000574	10	0.574	3.8	0.0005
*0.000272	5	0.544	3.8	0.0005
*0.0087	5	1.74	17.0	0.0005
*0.00079	5	1.59	17.0	0.0005

*Reference 59

E_a = 15.5±1 kcal/mole

Figure 27. Arrhenius Activation Energy Plot for the reaction t- $PtBr_4I_2^{2-}$ with iodide.

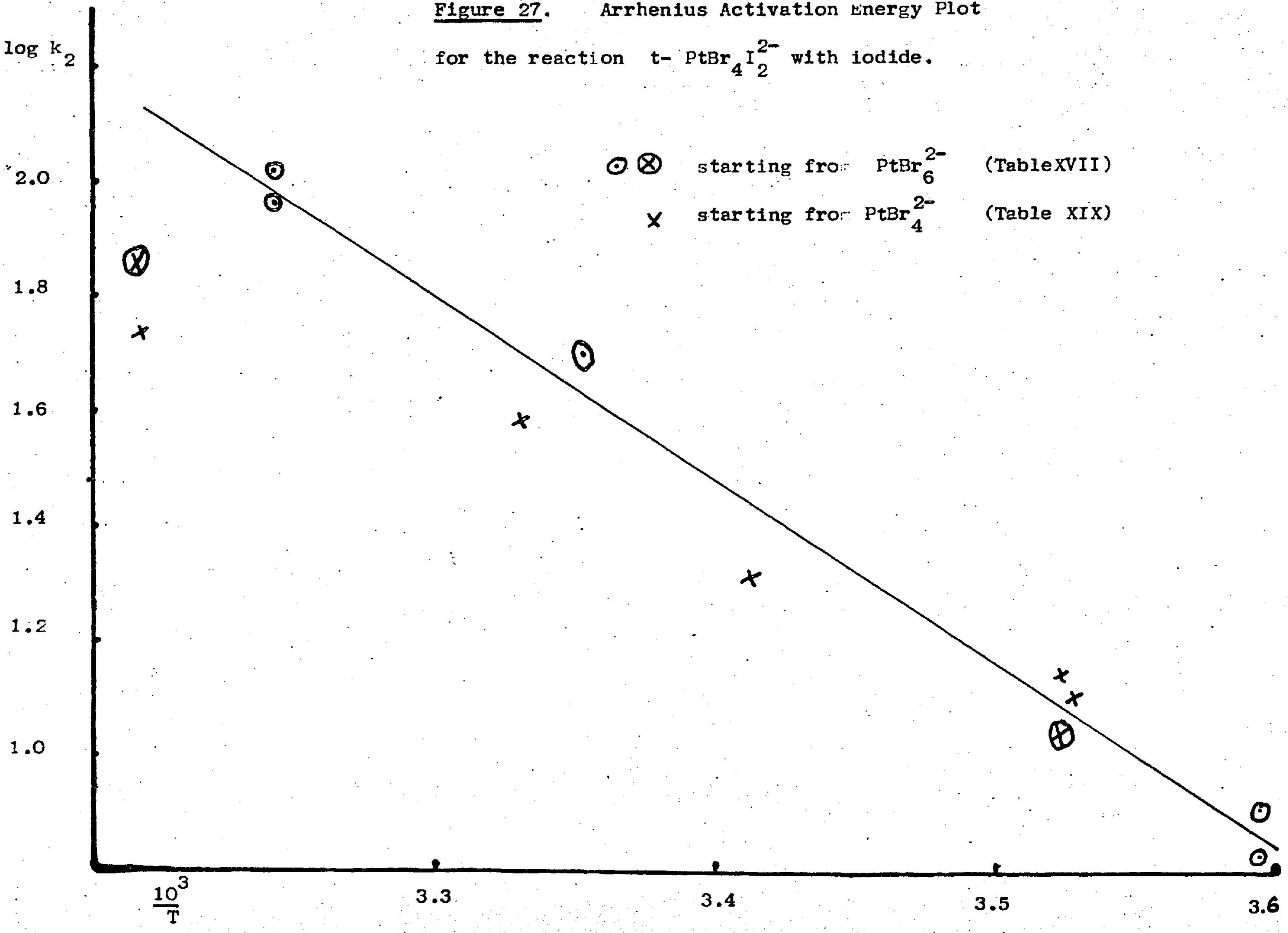


TABLE XVII

$PtBr_6^{2-}$ + I^- substitution reaction (second stage)

Studied at various wavelengths between 464 and 472 mμ

$[IrCl_6^{2-}]$ = 10%

k_{obs}	$[I^-]$	k_2	T°C	μ	Worker
0.0016	0.02	0.08	5.0	0.02	EJB
0.0014	0.02	0.07	5.0	0.02	EJB
0.00502	0.01	0.502	25.0	0.01	DH
0.00251	0.005	0.502	25.0	0.005	DH
0.00502	0.005	1.004	35.0	0.005	DH
0.00462	0.005	0.924	35.0	0.005	DH
0.000634	0.006	0.104	11.2	0.01	DJH
0.0044	0.006	0.733	40.0	0.01	DJH

E_a = 12 ± 1.5 kcal/mole

TABLE XVIII

$PtBr_6^{2-}$ + I^- substitution reaction (third stage)

Studied at 495 mμ.

k_{obs}	$[I]$	k_2	T°C	μ	Worker
0.00047	0.04	0.0115	4.0	0.04	EJB
0.000625	0.01	0.0625	25.0	0.01	DH
0.000788	0.01	0.0788	30.0	0.01	DH
0.00105	0.01	0.105	35.0	0.01	DH
0.000089	0.006	0.0149	11.2	0.01	DJH
0.001212	0.006	0.202	40.0	0.01	DJH

E_a = 16.8 ± 1.0 kcal/mole

TABLE XIX

$PtBr_4^{2-} + I_3^-$ oxidation reaction (first substitution step)

Followed at 470 ± 2 mμ　　$[IrCl_6^{2-}] = 3 \times 10^{-6}$

$\mu = 0.01$ M　　$[PtBr_4^{2-}] = 1.36 \times 10^{-5}$

k_{obs}	$[I^-]$	k_2	T°C
0.00291	0.00545	0.535	39.6
0.00214	0.00545	0.394	30.2
0.00113	0.00545	0.208	19.8
0.00069	0.00545	0.126	10.3
0.00070	0.00545	0.129	11.2

TABLE XX

$PtBr_4^{2-} + I_3^-$ oxidation reaction (second substitution step)

Followed at 495 mμ　　$[IrCl_6^{2-}] = 3 \times 10^{-6}$

$\mu = 0.01$ M　　$[PtBr_4^{2-}] = 1.36 \times 10^{-5}$

$k_{obs} \times 10^4$	$[I^-] \times 10^3$	k_2	T°C		
0.634	5.45	0.0116	10.3		
0.704	5.45	0.0129	11.2		
2.38	5.45	0.0436	19.8		
1.35	3.63	0.0370	20.2	(a)	(b)
3.52	8.18	0.0431	20.2	(a)	
2.03	5.45	0.0372	20.2		
3.43	5.45	0.093	30.7	(a)	
6.72	8.18	0.82	30.4	(a)	(b)
4.14	5.00	0.83	30.2		
9.75	9.00	0.108	30.2		(d)
9.24	3.63	0.236	39.8		(c)
11.3	5.45	0.208	39.8		
7.93	3.63	0.218	39.7		(b)
11.7	5.45	0.214	39.6		

(a) double Pt concentration　　(c) 5 x $IrCl_6^{2-}$

(b) no chloro-iridate　　(d) 4.5 x I_3^-

Figure 28. Arrhenius Activation Energy Plot for the reaction of t-$PtI_4Br_2^{2-}$ with iodide.

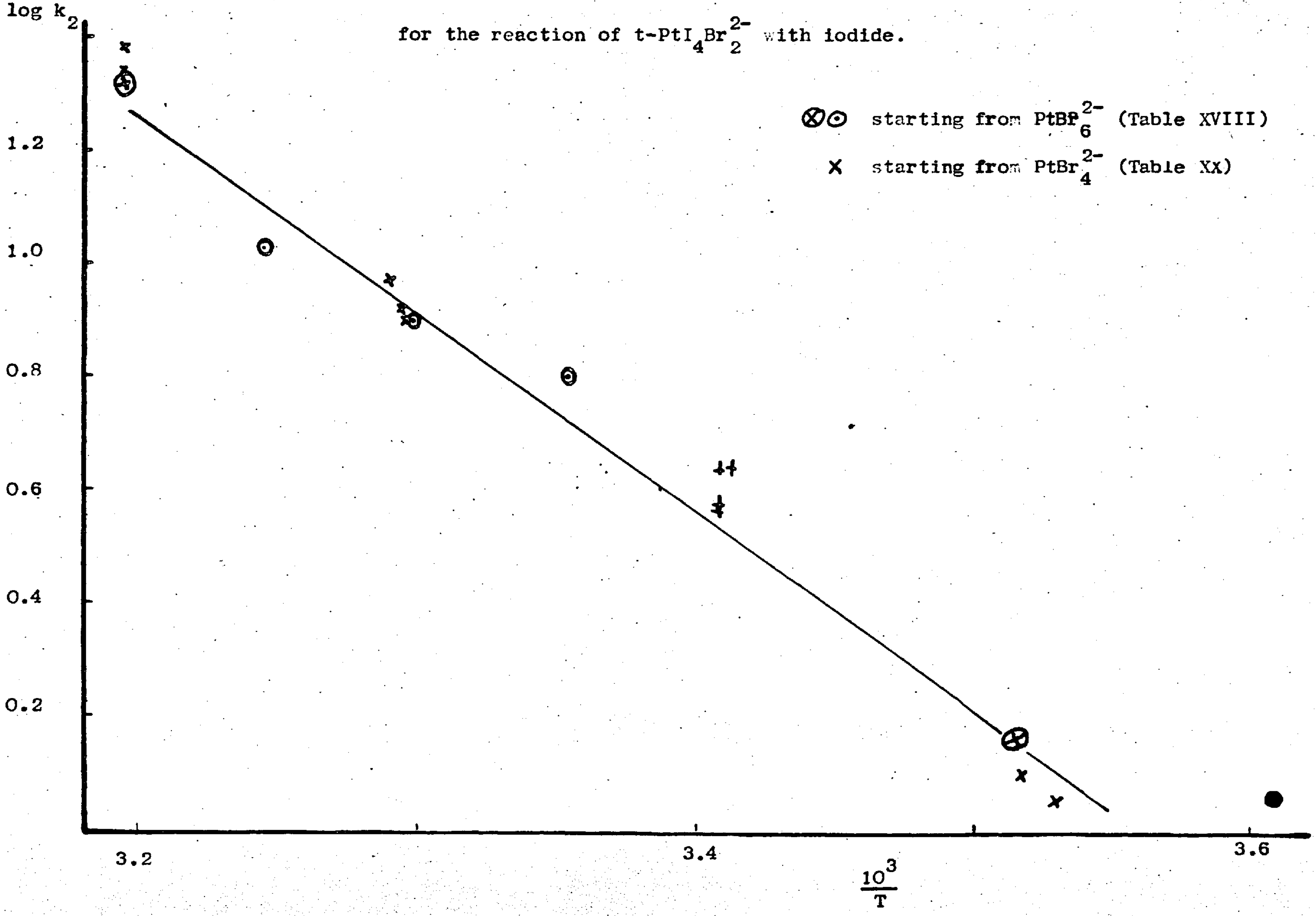


TABLE XXI

PtI_6^{2-} + Br^- substitution reaction (final stage)

Studied at 290 mμ

μ = $[Br^-]$ i.e. not constant

$[IrCl_6^{2-}]$ = 10%

k_{obs}	Br^-	k_2	T°C
0.000405	1.0	0.000405	19.6
0.00045	1.0	0.00045	19.6
0.000864	2.0	0.00043	19.4
0.00087	2.0	0.000435	19.4
0.00384	5.0	0.0007	19.4
0.0043	5.0	0.0008	19.5
0.00182	2.0	0.00091	24.5
0.00155	2.0	0.00075	25.1
0.00240	1.0	0.00240	35.0
0.00532	2.0	0.00266	36.0
0.0079	5.0	0.0035	35.0
0.00437	1.0	0.00437	44.7
0.00469	1.0	0.00469	45.6
0.00468	1.0	0.00468	44.7

E_a = 17.3 kcal/mole

DISCUSSION

When tetramine Pt(II) is treated with chlorine in the presence of chloride ion, the trans dichloro-Pt(IV) complex is formed.[60] Also, oxidation of 1-Pt(i-bn)(m-stien)$^{2+}$ by one or two electron oxidising agents followed by reduction using similar reducing agents resulted in little or no racemisation.[61] (1-bn = 2 methyl,1,2, propane diamine and m stien = meso 1,2, diphenyl,1,2, ethane diamine).

It is therefore assumed that oxidation of planar Pt(II) species results in trans addition and that the first products of oxidation of $PtBr_4^{2-}$ by I_3^- and of substitution into $PtBr_6^{2-}$ by iodide are both t-$PtBr_4I_2^{2-}$. It then seems likely that the two subsequent steps in the substitution process yield $PtBr_2I_4^{2-}$ and PtI_6^{2-}.

From electrode potentials[62] it can be deduced that although each halogen will oxidise its respective PtX_4^{2-} complex the values given for the $PtBr_4^{2-}/PtBr_6^{2-}$ and I^-/I_3^- couples are -0.643 and -0.536 volt and no reaction would be expected if $PtBr_4^{2-}$ and I_3^- were mixed. Since the reaction is observed, and found to be practically complete, one of the figures may be in error or another redox couple may be involved.

An S_{N2} mechanism for these reactions appears improbable. The rate constants observed during this study are comparable with those found in the Pt(II) catalysed exchange reactions of $Pt(NH_3)_4X_2^{2+}$ if allowance is made for the change in order, and both are much greater than nucleophilic substitution into rhodium (III). The rate constants in Pt(IV) substitution reactions depend on the concentration of incoming ligand whereas in Rh(III) and Co(III) bond breaking is rate determining and the nature and concentration of the incoming ligand has little effect. The high charge on Pt(IV) might however be expected to cause this.

The activation energy for most nucleophilic substitution reactions is in the range 22 - 30kcal/ /mole for both Co(III) and Rh(III). Those for Pt(IV) ligand exchange are between 12 and 17kcal/mole for the PtX_6^{2-} system and between 3 and 11kcal/mole for the Pt(II) catalysed $Pt(NH_3)_4X_2^{2+}$ reactions.

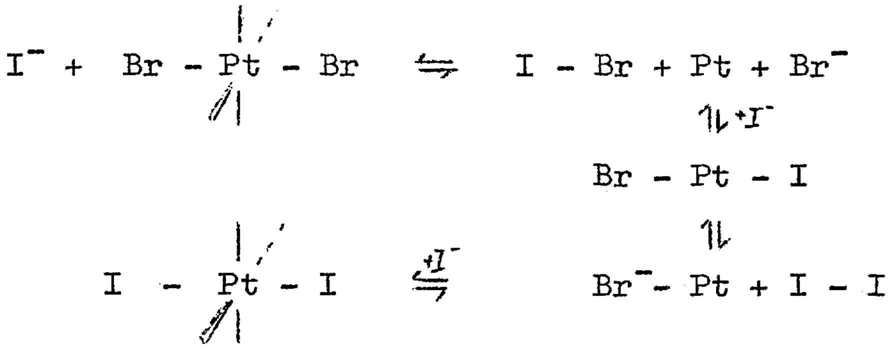
Although Pt(II) was often available in the reaction mixtures, no evidence of the bridging mechanism was observed. An equilibrium between the iodide complexes:

$$PtI_6^{2-} + I^- \rightleftharpoons PtI_4^{2-} + I_3^- \qquad K = 10^{-5.2}$$

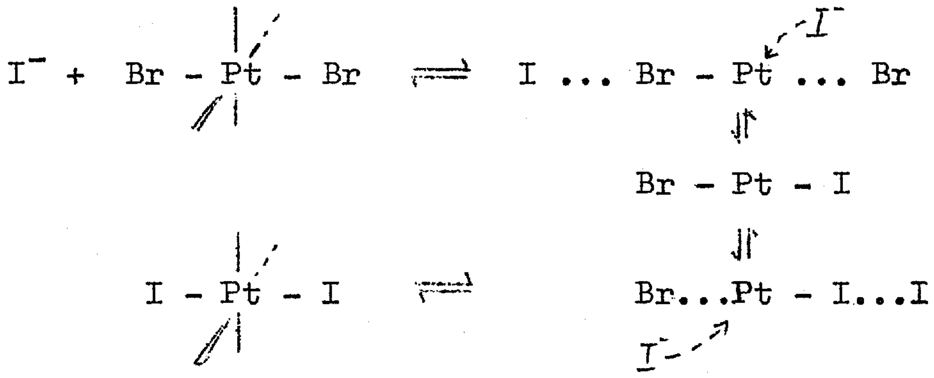
is rapidly maintained, but addition of I_3^- tended to accelerate the rate slightly whereas the reverse would be expected if Pt(II) catalysis were taking place.

A possible alternative involves the formation of an ion pair which then forms a transient Pt(II) species capable of rapid reoxidation,

e.g.



A less extreme view would be to assume that the iodide ion can increase the trans bond weakening effect of the bromide in the ion pair, which then undergoes the usual S_{N1} type of reaction.



Intermediates of the type $L_5M - X - Y$ have been postulated on several occasions[63] but evidence is sparse. However, the presence of halogen in contrast to halide in solutions of $PtBr_6^{2-}$ and PtI_6^{2-} was demonstrated by the observation of complete reduction of Pt(IV) when small quantities of aniline or phenol were added.

The "two-by-two" replacement of bromide by iodide in $PtBr_6^{2-}$ may be due to the mechanism of the reaction (for example, reduction followed by oxidation) or may simply reflect the greater trans bond weakening effect of the iodide ligands. In the reverse reaction, PtI_6^{2-} with bromide ion it should be possible to distinguish between these two possibilities since the greater trans bond weakening effect might, naively, be expected to favour the formation of cis $PtI_3Br_3^{2-}$ as an intermediate product, whereas the trans isomers $PtBr_4I_2^{2-}$ and $PtI_4Br_2^{2-}$ would be expected if a redox mechanism dictates the course of the reaction.

Unfortunately the evidence from the replacement of iodide in PtI_6^{2-} by bromide is not conclusive. In a large excess of bromide the final product was found to be $PtBr_6^{2-}$, the rate is slow and approximately bimolecular (the ionic strength was not held constant) and the activation energy is 17.3kcal/mole. If it is accepted that the first observed stage of the reaction of $PtBr_6^{2-}$ with iodide results in the formation of t-$PtBr_4I_2^{2-}$ then it can be said that the rate of formation of $PtBr_5I^{2-}$ has a rate constant greater than 11.05 $1.mole^{-1}$ $sec.^{-1}$ at 20°C and high ionic strength. Since the final observed stage of the reaction of PtI_6^{2-} with bromide has a rate constant of 0.00045 $1.mole^{-1}$ $sec.^{-1}$ and the equilibrium constants is approximately 1200, the last observed stage of the $PtBr_6^{2-}$ reaction cannot consist of the removal of a single iodide ligand.

The ultraviolet spectrum of the starting material for this stage does not however agree with that found for t- $PtBr_4I_2^{2-}$ and, although it is possible that the observed spectrum arises from a mixture of $t\text{-}PtBr_4I_2^{2-}$ and $t\text{-}PtBr_2I_4^{2-}$, it could also be due to the less symmetrical cis $PtBr_3I_3^{2-}$. N.M.R. studies on Pt^{195} and polarographic studies were unsuccessful in resolving this question, but now infra red spectra may be obtained down to 60 $cm.^{-1}$ it may be possible to reach a conclusion so long as precipitate induced exchange does not occur when Cs^+ ion is added to equilibrium mixtures.

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