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The Mechanism of Halide Interchange Reactions of Hexahalogenoplatinate(IV) Complexes. The $PtBr_6^{2-}$-I^- Reaction.

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The reaction of iodide ions with the hexabromoplatinate(IV) ion proceeds through three distinct stages, each of which probably corresponds to the replacement of two bromide ions trans *to each other. The reactions are all first order in both iodide and complex concentrations, and the mechanism is believed to involve a rate determining reduction of the complex to platinum(II) by what is effectively the transfer of* Br^+ *to the iodide. This is followed by re-oxidation to platinum(IV), the iodine atom of the IBr appearing to end up in the product complex. The reaction of the complex* PtI_6^{2-} *with bromide does not proceed through the same intermediates as are formed in the forward reaction. Activation parameters for these reactions lie in the ranges* $\Delta H^* = 12$ *to 18 kcal./mole, and* $\Delta S^* \approx$ *—10 to —20 cal.mole*$^{-1}$ *deg.*$^{-1}$*.*

Introduction

Substitution reactions of halogeno-platinum(IV) complexes have received considerable attention in the last few years and several different mechanisms appear to be possible.[1,2] The reaction of hexachloroplatinate (IV) with iodide has been shown to proceed, under some conditions, through a slow rate determining reaction between $PtCl_6^{2-}$ and I^-, subsequent replacement reactions being fast and no products other than PtI_6^{2-} being detectable.[2] The slow step is first order in both complex and iodide, but the S_N2 mechanism which was tentatively proposed[2] does seem to be rather unlikely. The corresponding reaction with the hexabromoplatinate(IV) ion was similar in many respects, except that the first substitution was not the only slow step.[2] This reaction has been studied spectrophotometrically in greater detail with a view to obtaining a better understanding of the special mechanism which operates in these systems, and of the factors which govern the occurrence of this mechanism.

Experimental Section

Sodium hexabromoplatinate(IV) hexahydrate and sodium hexachloro-iridate(IV) hexahydrate were obtained from Johnson, Matthey and Co., Ltd., and were used as received. Reagent grade sodium salts were used, standard solutions being made up by weighing out the dry, finely powdered salts into graduated flasks.

Spectrophotometric measurements were made with Perkin Elmer 137UV and 350 recording spectrophotometers, or with a Unicam SP 500 spectrophotometer. Solutions were contained in silica cells and were thermostatted as required, usually to within ±0.1° or better, at temperatures between 1 and 40° in suitable cell holders. The solutions were made up by dissolving the solid platinum complex in thermostatted solutions containing sodium iodide, sodium perchlorate, and sodium hexachloro-iridate(IV). The concentrations of iodide were sufficiently high for pseudo first order kinetics to be followed, and the sodium perchlorate was present to control the ionic strength. The pseudo first order rate plots were obtained by graphical plotting of log $(A_t - A_\infty)$ against t, A_t and A_∞ being the absorbances, at a convenient wavelength, measured at time t and at the end of the reaction, respectively.

Some radiochemical studies were made in which iodide solutions labelled with $^{131}I^-$ were used. The reaction between the bromo complex and iodide was quenched after suitable reaction times by the addition of 1 ml. of cold, saturated caesium nitrate solution to a few ml. of the reaction mixture. The caesium complex so precipitated was separated by centrifugation, and was washed twice with cold distilled water. The supernatant solution and the two washings were together made up to 10 ml. and the activity of 5 ml. of this was measured with a sodium iodide gamma-ray scintillation counter adjusted so as to detect the 0.64 MeV gamma-rays from the radioactive $^{131}I^-$. The precipitated caesium salt was dissolved in ethylenediamine, the solution made up to 10 ml., and the activity determined as before. Good agreement was obtained between the total activity from the precipitate and the supernatant solution, and that from solutions to which no separation procedure had been applied. In other cases, hexa-iodoplatinate(IV) was labelled[3] by the

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[1] (a) R. L. Rich and H. Taube, *J. Amer. Chem. Soc.*, 76, 2608 (1954); (b) F. Basolo, P. H. Wilks, R. G. Pearson and R. G. Wilkins, *J. Inorg. and Nuclear Chem.*, 6, 161 (1958); (c) A. G. Sharpe, *J. Chem. Soc.*, 3444 (1950); (d) R. C. Johnson, F. Basolo and R. G. Pearson, *J. Inorg. and Nuclear Chem.*, 24, 59 (1962); (e) A. W. Adamson and A. H. Sporer, *J. Amer. Chem. Soc.*, 80, 3865 (1958).

[2] A. J. Poë and M. S. Vaidya, *J. Chem. Soc.*, 2981 (1961).

[3] A. J. Poë and M. S. Vaidya, *J. Chem. Soc.*, 187 (1960).

addition of carrier-free $^{131}I^-$, and the iodide subsequently replaced by bromide was estimated in exactly the same way.

Results

Radiochemical studies confirmed that the initial substitution, in the dark and in the presence of hexachloroiridate(IV), did not result in the replacement of all the bromide ions after one rate determining step. Spectrophotometric studies showed that substitution proceeded through three quite well defined stages which we shall call Stages I, II and III. The spectral changes characteristic of each stage are shown in Figure 1. Stage I involves a decrease in the intensity of the peak at 310 mμ, due to the $PtBr_6^{2-}$ ion,[4] and the growth of peaks at ~350 and 430 mμ. Clear isosbestic points occur at 287, 338, 370 and 394 mμ. Stage II is accompanied by the complete disappearance of the maxima at 310 and 430 mμ, by the continued growth of the maximum at 350 mμ, and by the appearance of new maximum at 450 mμ. Isosbestic points at 287, 338, 360 and 435 mμ are observed. Stage III is characterised by a further shift towards low energies of the absorption maximum below ~250 mμ, by a continued slight growth in the intensity of the maximum at 350 mμ, by a decrease of the maximum at 450 mμ, and the appearance of a new maximum at 495 mμ. The final spectrum corresponds to that of the PtI_6^{2-} ion,[4] and isosbestic points at 303, 360 and 464 mμ are observed.

The kinetics of Stage I were followed by measuring the growth in the absorbance at ~430 mμ. The absorbance at the end of the reaction was not directly measurable, because of the overlap between Stages I and II, so the rate constants were derived either by means of Guggenheim plots,[5] or by extrapolating the plot of absorbance against time to give an approximate measure of A_∞, and then adjusting this slightly to give linear plots of $\log(A_t - A_\infty)$ against time. The reaction was studied over a range of temperatures and ionic strengths, and the results are given in Table I. Activation parameters were obtained graphically (Figure 2) and are given in Table 5. The rates are hardly affected by a change in ionic strength from 5 to 10, $\times 10^{-4}M$, but a further increases to $0.5M$ increases the rate by about a factor of 4 without affecting the activation enthalpy.

An attempt was made to determine radiochemically the number of bromide ions which were replaced in Stage I. The results were in good agreement with those obtained by Poë and Vaidya.[2] After allowing for precipitation induced exchange, the data were treated according to the method used for the $PtCl_6^{2-}$-I^- reaction,[2] i.e. the reaction was assumed to be the second order replacement of Pt-Br bonds by Pt-I bonds, and normal second order rate equations were applied. Unlike the plot for the $PtCl_6^{2-}$-I^- reaction, which was linear over the whole range of substitution, linear plots were obtained only up to about 33% substitution. This suggested that two bromide ions were replaced during

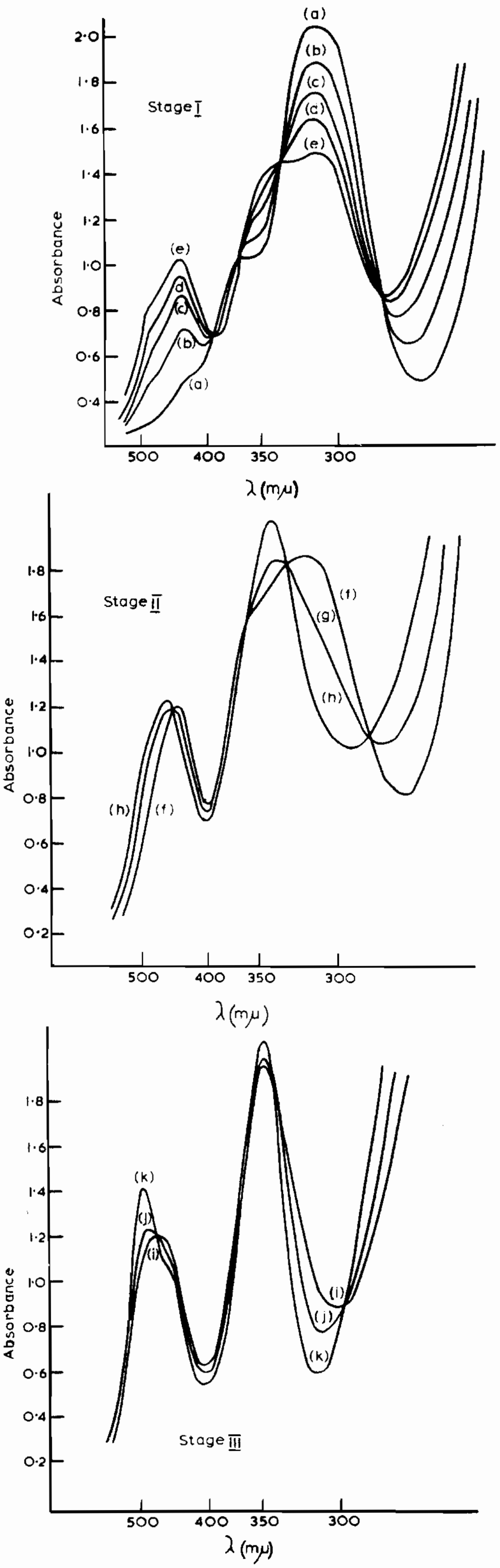

Figure 1. Spectral changes in four cm. cells during Stages I, II and III of the reaction of iodide with $PtBr_6^{2-}$. Complex concentrations are $\sim 10^{-4}M$; (a) is the spectrum of $PtBr_6^{2-}$ and (k) is that of PtI_6^{2-}; (b), (c) and (d) are during Stage I, while (e) is towards the end of Stage I; (h) is towards the end of Stage II.

(4) C. K. Jorgensen, *Acta Chem. Scand.*, *10*, 518 (1956); *idem*, *Mol. Phys.*, *2*, 309 (1959).

(5) A. A. Frost and R. G. Pearson, «Kinetics and Mechanism», Wiley, New York, 2nd Edn., pp. 49-50 (1961).

Table I. Rate constants for Stage I of the $PtBr_6^{2-}$-I^- reaction. $[PtBr_6^{2-}]$ = 6 to 10, $\times 10^{-5}M$; $[IrCl_6^{2-}] = 2\times10^{-5}M$.

T (°C)	$10^4[I^-]$ (M)	μ (M)	10^4k_{obs} (sec.$^{-1}$)	k_2 (l.mole^{-1}sec.$^{-1}$)
5.1	50.0	0.5	122	2.51
5.1	20.0	0.5	57.6	2.88
5.1	5.0	0.5	12.7	2.54
20.0	5.97	0.5	69.0	11.1
40.0	5.0	0.5	233	46.7
13.0	5.0	0.001	8.45	1.69
20.1	5.0	0.001	14.0	2.80
29.0	5.0	0.001	24.0	4.80
35.7	5.0	0.001	42.2	8.45
39.1	5.0	0.001	65.0	13.0
3.8	10.0	0.001	5.74	0.574
3.8	5.0	0.0005	2.72	0.544
17.0	5.0	0.0005	8.70	1.74
17.0	5.0	0.0005	7.95	1.59

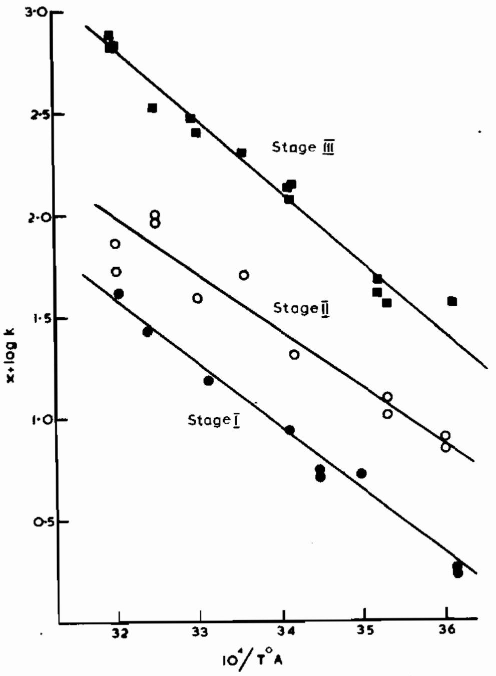

Figure 2. Arrhenius plots for Stages I, II and III of the reaction of iodide with $PtBr_6^{2-}$. x = 0.5, 0 and 1.5 for Stages I, II and III, respectively.

Stage I but a more detailed analysis of the data showed that they were not sufficiently accurate to distinguish between two and three bromides being replaced. Thus the stoicheiometry of Stage I was considered to be either (a) $PtBr_6^{2-}+2I^- \rightarrow PtBr_4I_2^{2-}+2Br^-$, or (b) $PtBr_6^{2-}+3I^- \rightarrow PtBr_3I_3^{2-}+3Br^-$. Knowing the initial concentrations of $PtBr_6^{2-}$ and iodide, it was possible to calculate a value for the second order rate constant from each measurement of iodide uptake taken during the first three minutes of the reaction. The average of about 20 determinations based on four different sets of runs by three different people was 0.7±0.05 and 0.40±0.02 l.mole^{-1} sec.$^{-1}$ for reactions (a) and (b), respectively, at an ionic strength of $10^{-2}M$ and at 1°. No systematic differences were noticed between different sets of data, and no systematic trends with time were observable such as might have been expected from an incorrect choice of stoicheiometry. This was largely because of the low precision of an individual measurement (± ~20%).

Two measurements of the rate of Stage I were made under conditions of temperature and ionic strength identical with those used for the radiochemical measurements. When $[I^-]$=5.34 and 3.00, $\times10^{-4}M$ the second order rate constants were 0.54 and 0.66 l.mole^{-1} sec.$^{-1}$, respectively, giving an average of 0.60±0.06 l.mole^{-1} sec.$^{-1}$ This is in better agreement with the result obtained radiochemically by assuming stoicheiometry (a) rather than (b).

An alternative method of determining the product of Stage I of the reaction was attempted. It has long been known that the oxidation of platinum(II) complexes by halogens in the presence of halide ions produces platinum(IV) complexes in which the two halogen atoms have effectively been added above and below the plane of the original platinum(II) complex.[1a,6] The reaction between PtI_4^{2-} and iodine in iodide solutions produces PtI_6^{2-} at rates too fast to be measured by the «stopped flow» technique.[7] Similarly it was found that treatment of a solution of $PtBr_4^{2-}$ with iodine dissolved in iodide solution led to the instantaneous formation of a new spectrum characteristic of that at the end of Stage I of the $PtBr_6^{2-}$-I^- reaction. The spectrum subsequently underwent slow changes identical in nature and rate with those observed for the second and third stages of the substitution reaction. The kinetics of Stage II were followed by measuring the growth in absorbance at the isosbestic point for Stage III at about 470 mμ. This eliminated the difficulty of estimating the extinction coefficient at the end of this stage, but the absorbance changes were small so that the precision of the results was quite low. The results for Stage II obtained by both methods are given in Table II, and the activation parameters derived graphically (Figure 2) are given in Table V. The oxidation of $PtBr_4^{2-}$ by I_3^- was found to be too fast to be measured by the «stopped flow» technique, and no further substitution was observed other than that which corresponded to Stages II and III of the $PtBr_6^{2-}$-I^- reaction.

Table II. Rate constants for Stage II of the $PtBr_6^{2}$ -I^- reaction. (a) $[PtBr_6^{2-}]$ = 1.7 to 9, $\times10^{-5}M$; $[IrCl_6^{2-}] \approx$ 10 mole %. (b) $[PtBr_4^{2-}] = 1.36\times10^{-5}M$; $[I_3^-] = 1.38\times10^{-5}M$; $[IrCl_6^{2-}] = 3\times10^{-6}M$.

T (°C)	$10^3[I^-]$ (M)	μ (M)	10^4k_{obs} (sec.$^{-1}$)	10^2k_2 (l.mole^{-1}sec.$^{-1}$)
(a) 5.0	20.0	0.02	16.0	8.0
(a) 5.0	20.0	0.02	14.0	7.0
(b) 10.3	5.45	0.01	6.90	12.6
(a) 11.2	6.00	0.01	6.34	10.4
(b) 11.2	5.45	0.01	7.00	12.9
(b) 19.8	5.45	0.01	11.3	20.8
(a) 25.0	10.0	0.01	50.2	50.2
(a) 25.0	5.00	0.005	25.1	50.2
(b) 30.2	5.45	0.01	21.4	39.2
(a) 35.0	5.00	0.005	50.2	100
(a) 35.0	5.00	0.005	46.2	92.4
(b) 39.6	5.45	0.01	29.1	53.5
(a) 40.0	6.00	0.01	44.0	73.3

(6) F. A. Cotton and G. Wilkinson, «Advanced Inorganic Chemistry», Interscience, New York, 2nd Edn., p. 1026 (1966).

(7) B. Corain and D. J. Hewkin, unpublished work.

Stage III was also followed in these two ways by measuring the growth in absorbance at 495 mμ. The results are given in Table III and the activation parameters (Figure 2) in Table V. The presence of an equivalent of $PtBr_4^{2-}$, or the absence of hexachloro-iridate(IV), have no effect on the rate, the latter indicating, perhaps, the presence of a slight amount of iridium(IV) impurity in the platinum complex such as has been found before.[2] The presence of five times the usual amount of hexachloro-iridate(IV) has no effect on the rate, but an excess of I_3^- does seem to have a noticeable accelerating effect.

Table III. Rate constants for Stage III of the $PtBr_6^{-2}$-I^- reaction. $\mu = 0.01M$; (i) $[PtBr_6^{2-}] = 1.7$ to 9, $\times 10^{-5}M$; $[IrCl_6^{2-}] \approx 10$ mole %. (ii) $[PtBr_4^{2-}] = 1.36\times10^{-5}M$; $[I_3^-] = 1.38\times10^{-5}M$; $[IrCl_6^{2-}] = 3\times10^{-6}M$.

T (°C)	$10^3[I^-]$ (M)	10^4k_{obs} (sec.$^{-1}$)	10^2k_2 (l.mole^{-1}sec.$^{-1}$)
(i) 4.0	40.0 [a]	4.70	1.15
(ii) 10.3	5.45	0.63	1.16
(i) 11.2	6.00	0.89	1.49
(ii) 11.2	5.45	0.70	1.29
(ii) 19.8	5.45	2.38	4.36
(ii) 20.2	3.63	1.35	3.70 [b,c]
(ii) 20.2	8.18	3.52	4.31 [b]
(ii) 20.2	5.45	2.03	3.72
(i) 25.0	10.0	6.25	6.25
(i) 30.0	10.0	7.88	7.88
(ii) 30.2	9.00	9.75	10.8 [d]
(ii) 30.2	5.00	4.14	8.30
(ii) 30.4	8.18	6.72	8.20 [b,c]
(ii) 30.7	5.45	3.43	9.30 [b]
(i) 35.0	10.0	10.5	10.5
(ii) 39.6	5.45	11.7	21.4
(ii) 39.7	3.63	7.93	21.8 [c]
(ii) 39.8	5.45	11.3	20.8
(ii) 39.8	3.63	9.24	23.6 [e]
(i) 40.0	6.00	12.1	20.2

[a] $\mu = 0.04M$; [b] $[PtBr_4^{2-}] = 2.72\times10^{-4}M$; [c] $[IrCl_6^{2-}] = 0M$; [d] $[I_3^-] = 6.3\times10^{-5}M$; [e] $[IrCl_6^{2-}] = 1.5\times10^{-5}M$.

Some studies were also made of the reaction of bromide with the PtI_6^{2-} ion. Large excesses of bromide are necessary owing to the unfavourable equilibrium constants for the replacement[8] but it was clear that an initial very fast reaction occurred, and this was followed by a much slower reaction which could be studied by conventional techniques. This slow stage led to the formation of $PtBr_6^{2-}$, provided sufficiently large concentrations of bromide were used. Some spectra in the visible region are shown in Figure 3. These were obtained by the successive addition of solid sodium bromide to a solution of PtI_6^{2-}. The rates of the spectral changes were too great to be detected by eye until the spectrum marked x———x was reached, and the earlier spectra are therefore of equilibrium mixtures. The later spectra, however, were taken during the slow stage following the addition of enough sodium bromide to make the solution about 5*M* in bromide. In the ultraviolet region there was a move to higher energies of an absorption maximum at 315 mμ without any change in absorbance. This led to the existence of isosbestic points at ~277 and 320 mμ. The spectral changes during this slow step are not those expected if the reaction went through the same intermediates as the $PtBr_6^{2-}$-I^- reaction. In particular, no absorption maximum at ~400 mμ is shown by any of these species, and the spectral changes during the first (forward) stage and the last (reverse) stage both involve isosbestic points, but these are quite different. The results of following the increase of absorbance at 290 mμ are given in Table IV, and the activation parameters derived from them are given in Table V. Rather small effects of changing the ionic strength from 1.0 to 2.0*M* are found, but a further change to 5.0*M* does produce a significant increase in rate. The activ-

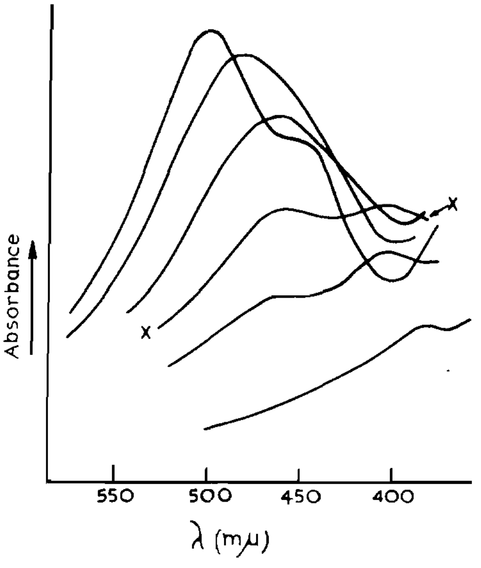

Figure 3. Spectral changes following the addition of bromide to PtI_6^{2-}. The top three spectra are of equilibrium mixtures formed rapidly after addition of up to ~1*M* bromide. The lower three spectra are spectral changes changes during the slow reaction following the addition of 5*M* bromide to PtI_6^{2-}.

Table IV. Rate constants for the last stage of the PtI_6^{2-}-Br^- reaction. $[PtI_6^{2-}] \approx 10^{-4}M$; $[IrCl_6^{2-}] = 2\times10^{-5}M$; $\mu = [Br^-]$.

T (°C)	$[Br^-]$ (M)	10^4k_{obs} (sec.$^{-1}$)	10^4k_2 (l.mole^{-1}sec.$^{-1}$)
19.4	2.0	8.64	4.30
19.4	2.0	8.70	4.35
19.4	5.0	38.4	7.00
19.5	5.0	43.0	8.00
19.6	1.0	4.05	4.05
19.6	1.0	4.50	4.50
24.5	2.0	18.2	9.10
25.1	2.0	15.5	7.50
35.0	1.0	24.0	24.0
35.0	2.0	53.2	26.6
44.7	1.0	43.7	43.7
44.7	1.0	46.8	46.8
45.6	1.0	46.9	46.9

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(8) A. J. Poë and M. S. Vaidya, *J. Chem. Soc.*, 3431 (1961).

Table V. Rate parameters for halide interchange reactions of some hexahalogenoplatinate(IV) compexes [a]

	ΔH* (kcal./mole)	ΔS* (cal.mole⁻¹deg.⁻¹)	10^2k_2 (25°) (l.mole⁻¹sec.⁻¹)	μ
$PtCl_6^{2-} + I^-$ [2]	12.1 ± 0.5	—26 ± 2	1.4	0.04
$PtBr_6^{2-} + I^-$	14 ± 1	— 9 ± 3	400	0.001
trans-$PtBr_4I_2^{2-} + I^-$	12 ± 2	—20 ± 7	35	0.005 or 0.01
trans-$PtBr_2I_4^{2-} + I^-$	15.5 ± 1	—13 ± 3	6	0.01
$PtBr_nI_{6-n}^{2-} + Br^-$ [b]	17.5 ± 1	—14 ± 3	8×10^{-2}	1.0 or 2.0

[a] The limits are approximate estimates of the maximum uncertainties based on the Arrhenius plots. [b] $n \geqslant 3$; configuration almost certainly is *cis* if n = 3 or 4.

ation parameters were derived by using only those data obtained at $\mu = 1.0$ or $2.0M$.

The extent of the initial fast reaction between PtI_6^{2-} and Br^- was studied radiochemically. PtI_6^{2-} labelled with carrier-free $^{131}I^-$ [3] was reacted with Br^-, in the dark and in the presence of 10 mole % of hexachloro-iridate(IV) at room temperature. The product complex was separated as its caesium salt, and the activity of free and complexed iodide was measured. When the initial ratio $[Br^-]/[PtI_6^{2-}]$ was between 500 and 700, only about 40% of the coordinated iodide was replaced, but when this ratio was increased to about 1300 an average of the results of four experiments showed that 47.8±0.7% of the iodide had been replaced within three minutes, the minimum convenient separation time.

Discussion

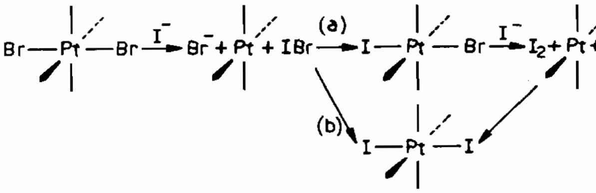
The reactions which were observed were all independent of the concentration of hexachloro-iridate(IV) although its presence is probably required in small amounts to avoid the occurence of a chain reaction, involving Pt(III) intremediates, of the type which has been found in other similar systems.[1a,1e,2] The presence of $PtBr_4^{2-}$ has a negligible effect on the rates, and the reactions are certainly not first order in $[PtBr_4^{2-}]$. This would be required if the reaction proceeded through a bridged intermediate species such as I..Pt(II)...Br-Pt(IV)-Br.[1b] The only interchange reactions of hexa-halogenoplatinate(IV) complexes which appear to go *via* this mechanism is the interchange of chloride and bromide.[9] The mechanism of the $PtBr_6^{2-}$-I^- reaction appears, therefore, to be the same as that of the $PtCl_6^{2-}$-I^- reaction.[2]

The three stages almost certainly correspond to the stepwise replacement of three pairs of coordinated bromide ions. Stage I cannot involve the replacement of only one bromide ion. In the radiochemical studies the separation procedure induces the replacement of an average of about one bromide ion from each complex[2] but the subsequent replacement occurs at a rate characteristic of Stage I observed spectrophotometrically, and not of Stage II. The fact that the two reactions observed after the oxidation of $PtBr_4^{2-}$ by I_3^- are identical in spectral changes and rates with Stages II and III of the substitution reaction, is strong evidence that the product of Stage I is *trans*-$PtBr_4I_2^{2-}$. This complex must be formed as the first product of the oxidation, but if the product of Stage I were $PtBr_3I_3^{2-}$ then the reaction of iodide with *trans*-$PtBr_4I_2^{2-}$ would have to be faster than with $PtBr_6^{2-}$. Although this in itself is not unreasonable, no reactions other than Stages II and III are observed after the oxidation, even by the stopped flow technique, so that the reaction of *trans*-$PtBr_4I_2^{2-}$ with I^- would have to be quite unreasonably fast. Finally, the radiochemically determined rate constants show better agreement with those determined spectrophotometrically when the former are calculated by assuming that two bromides are replaced rather than three.

Stage III cannot correspond to the replacement of the sixth and last bromide ion. The equilibrium constant for this reaction is approximately 100 at 25° [10] so that the rate constant for the reaction $PtI_6^{2-} + Br^- \rightarrow PtBrI_5^{2-} + I^-$ would be 6×10^{-4} l.mole⁻¹ sec.⁻¹, and not extremely large as is actually the case.[7] Since the last stage therefore involves the replacement of at least two bromide ions, it seems most probable that all three stages involve the replacement of two bromide ions *trans* to each other, the two intermediates being *trans*-$PtBr_4I_2^{2-}$ and *trans*-$PtBr_2I_4^{2-}$.

The reaction of PtI_6^{2-} with bromide, on the other hand, proceeds *via* the very rapid replacement of at least three iodide ions. The spectral changes observed during the replacement of iodide by bromide do not correspond with any of those found during the $PtBr_6^{2-}$-I^- reaction, and a completely different path must, therefore, be followed.

These facts can all be explained in terms of the reaction scheme (1) in which the iodide ion causes a rate determining two electron reduction, by what is effectively the transfer of Br^+ from the platinum(IV) to the iodide.[11] The IBr formed then re-oxidises the platinum(II) complex, but the excess of iodide present ensures that it is an iodide ion which adds on in the position *trans* to the site of oxidation by IBr. Whether



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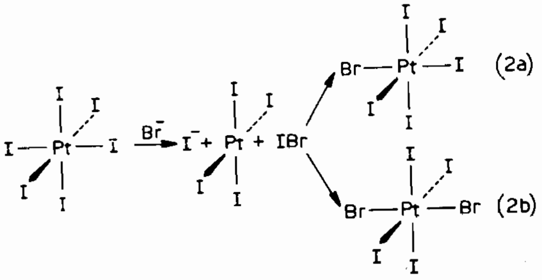
(9) G. B. Schmidt and W. Herr, Z. *Naturforsch.*, *16a*, 748 (1961).

(10) A. J. Poë, unpublished calculations based on data in ref. 8.

(11) This type of mechanism was proposed to one of us (A.J.P.) by Professor A. W. Adamson in 1960, and is closely related to the mechanism proposed for the oxidation of $PtCl_4^{2-}$ by chlorine to form $PtCl_5OH^{2-}$. (See ref. 1a).

the *trans*-di-iodo complex is formed directly, (path 2b), or by a two step reaction involving the same sort of mechanism, depends on which atom of the IBr molecule ends up in the platinum(IV) complex. This mechanism would explain a sequence of three successive replacements of two bromide ions *trans* to each other. If the *trans*-$PtBr_4I_4^{2-}$ is formed by a two step reaction (path 1a), then the second step must be fast, as would be expected from the very rapid reversible reactions of the type $Pt(IV)\text{-}I + I^- \rightleftharpoons Pt(II) + I_2$.[7]



The fact that the PtI_6^{2-}-Br^- reaction does not go through the same sequence of intermediates as the $PtBr_6^{2-}$-I^- reaction suggests that it is the iodine atom in the IBr which ends up attached to the platinum(IV), as shown in reaction scheme 2a. If it were the bromine atom then the first product should be *trans*-$PtBr_2I_4^{2-}$ (path 2b) and a similar subsequent reaction should then give *trans*-$PtBr_4I_2^{2-}$. The reaction of $PtBr_6^{2-}$ with iodide to form *trans*-$PtBr_4I_2^{2-}$ is, therefore, essentially a one step reaction which does not involve $PtBr_5I^{2-}$ as an intermediate. The fact that it is the iodine atom of IBr which becomes attached to the platinum after oxidation, is consistent with the reactions being the transfer of X^+ to the platinum(II). The iodine in IBr already has a partial positive charge before reaction and the eventual production of a bromide ion rather than an iodide ion is favoured by solvation effects. The fact that it is an iodine atom which becomes attached to the platinum could also be explained if the IBr reacts, before oxidising the platinum(II), either with water to form IOH and HBr, or with iodide to form I_2 and Br^-. The former reaction is known to occur rapidly[12] and the second is thermodynamically favourable[13] although its rate is apparently unknown. It is, however, thermodynamically most unlikely that, in the reaction of bromide with PtI_6^{2-}, the IBr reacts with bromide to form Br_2 and I^-. Possible combination of the halogen molecule with free halide ion to form a trihalide is unlikely to affect our conclusions. Trihalide ions should oxidise platinum(II) almost as rapidly as the halogens do, so that no kinetic effects should be observed. Any thermodynamic effects would have caused some reduction to occur, but this was not detected.

The proposed mechanism is supported by all the known redox behaviour of the platinum(II) and (IV) system. PtI_6^{2-},[7] Pt $en_2I_2^{2+}$,[14] and $Pt(CN)_4I_2^{2-}$,[15] all undergo rapid reduction by sufficiently large amounts of iodide, with removal of two iodide ions *trans* to each other. Pt $diars_2Cl_2^{2+}$ and other arsine complexes of platinum(IV), have been shown to undergo complete reduction by I^-, SCN^- and $SeCN^-$ with release of two *trans* chloride ions.[16] The formation of species such as ClSCN which decompose rather than reoxidise the platinum(II) was proposed. The halogen compound which is formed in the substitution reactions of PtX_6^{2-} is sufficiently stable towards decomposition for reoxidation to occur preferentially but, in the reaction of PtI_6^{2-} with bromide or iodide, addition of the halogen scavengers phenol or aniline resulted in the formation of only $PtBr_4^{2-}$ or PtI_4^{2-}.

It is implicit in this mechanism that oxidation of platinum(II) by halogen under these conditions results in only one atom from the halogen molecule becoming attached to the metal rather than the addition of both atoms to form a *cis* product. The latter type of reaction may well occur when other oxidants react with d^8 complexes under rather different conditions.

The activation parameters in Table V show that there are no systematic trends for this system, except that the activation enthalpy for the formation of $PtBr_6^{2-}$ is the highest. This would be expected from the thermodynamic behaviour, the average value of ΔH° for replacing a coordinated iodide by bromide being ~ 4 kcal./mole.[8] The values of ΔS^* are quite compatible with a bimolecular reaction between doubly and singly charged ions of the same sign, as is the qualitative nature of the dependence on ionic strength.

The lack of observable intermediates in the reaction of $PtCl_6^{2-}$ with iodide merely shows that the rate of reaction of iodide with complexes such as *trans*-$PtCl_4I_2^{2-}$ is ~ 10 times faster than the reaction with $PtCl_4^{2-}$ itself. Although the first stage of the reaction of iodide with $PtBr_6^{2-}$ is about 300 times as fast as the reaction with $PtCl_6^{2-}$, the last stage is only about four times faster. This kinetic behaviour shows some parallel with the thermodynamic behaviour. Thus the successive replacement of bromide by iodide tends to become progressively more difficult as more bromides are replaced, whereas the opposite is true for replacement of chloride.[8,10]

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