# 572. *The* $PtCl_6^{2-}$–$I^-$ *and* $PtBr_6^{2-}$–$I^-$ *Replacement Reactions.*

By A. J. Poë and M. S. Vaidya.

The replacement reactions of iodide ions with $PtCl_6^{2-}$ and $PtBr_6^{2-}$ ions have been studied by radio-tracer and spectrophotometric methods. In the presence of $IrCl_6^{2-}$, the reactions are of first order in both iodide and Pt–Cl or Pt–Br bond concentrations, and probably involve an $S_N2$ mechanism. For the $PtCl_6^{2-}$–$I^-$ reaction, $k_{25} = 0{\cdot}85 \pm 0{\cdot}05$ l. mole$^{-1}$ min.$^{-1}$, the rate-determining step being the replacement of the first chloride ligand. The $PtBr_6^{2-}$–$I^-$ reaction, at 1°, has a rate constant of about 12 l. mole$^{-1}$ min.$^{-1}$ for replacement of the first two bromide ligands, but subsequent reaction is slower. Increasing lability along the series chloro-, bromo-, and iodo-platinate is ascribed, in part at least, to decreasing bond strengths.

In the absence of $IrCl_6^{2-}$, the reactions are faster and are photosensitive. The $PtCl_6^{2-}$–$I^-$ reaction is greatly accelerated by small amounts of thiosulphate and of ferrous ions, and Pt(III) intermediates are probably formed. Chloroplatinate, containing a negligible quantity of iridium, exchanges relatively slowly with chloride ions and the reaction is greatly accelerated by very small amounts of thiosulphate.

Replacement reactions of a series of related complex ions with a single ligand species can give more information about the differing natures of the complexes than can the ligand exchange reactions in which both reactants change from case to case.[1] We have therefore studied the reactions of hexachloro-, hexabromo-, and hexaiodo-platinates with iodide ion. In addition, it was hoped that the relative reactivity of the intermediate mixed halogeno-complexes would throw some light on the relative effects of the halide ligands on the reactivity of other Pt(IV)–Hal bonds in the same ion. The $PtI_6^{2-}$–$I^-$

---

[1] Zvyagintsev and Karandasheva, *Proc. Acad. Sci.* (*U.S.S.R.*), 1956, **108**, 277.

exchange reaction has already been described [2] and results for the two replacement reactions have been reported briefly.[3]

The replacement reactions are reversible but the equilibrium constants are such that the reverse reactions have negligible kinetic effect.[4] The reactions were studied by making use of the insolubility of cæsium hexahalogenoplatinates and by using radioactive $^{131}I^-$ to indicate the extent of uptake of iodide by the complex. The replacement reactions involve a changing proportion of various mixed halogeno-complexes, and each of these would be expected to exhibit a characteristic rate constant in its reaction with iodide ions. To simplify this kinetic problem the reactions were considered to be between the iodide ions and Pt–Cl or Pt–Br bonds and the effects of the other ligands attached to the platinum were ignored. In this way statistical effects were eliminated and any transmitted effects due to the other ligands would be expected to be revealed by changes in the derived " rate constants " during the reactions. The order of the reaction could be determined by comparing the rate constants, calculated according to the first- or second-order rate-equations from data obtained at different initial concentrations.

## RESULTS

*The* $PtCl_6^{2-}$–$I^-$ *Reaction.*—Recent confirmatory runs,[5] performed some time after the main group [3] of experiments had been completed and making use of a recently obtained chloroplatinate sample, showed that the reaction is both light-sensitive and inhibited by the addition of small amounts of hexachloroiridate ions. The reaction observed in the presence of 1—5% of hexachloroiridate conformed to the earlier results, some of which are given in Table 1. These show no effects caused by laboratory light or hexachloroiridate, and an inhibitor, probaby chloroiridate itself, must have been present which eliminated the induced reaction so that no further inhibition could be produced. The reaction is then not affected by the presence of small amounts of acid. The addition of a small amount of tetrachloroplatinite ions to the reaction mixture had only a small accelerating effect on the rate of the reaction in the light. The addition of excess of $Cs^+$ ions to this reaction mixture evidently precipitated the Pt(II) species in addition to those of Pt(IV) since the supernatant solutions were colourless. The concentration of Pt(II)–Cl bonds was therefore included in the value of the Pt–Cl bond concentrations used and the reaction would be expected to be somewhat faster merely because of the increased Pt–Cl concentration. The reaction is also sensitive to traces of thiosulphate ions. When present to about 5% of the $PtCl_6^{2-}$ concentration, 50% replacement occurred in 1 minute followed by a much slower reaction. The effect of the thiosulphate evidently overcame that of any inhibitor which was present in the sample. Qualitative experiments, in which the reaction was followed visually by observing the colour change, showed that the reaction is also accelerated by ferrous ions.

TABLE 1. *Typical results for the* $PtCl_6^{2-}$–$I^-$ *reaction.*

$[PtCl_6^{2-}]_0 = 5{\cdot}58 \times 10^{-3}$M, $[I^-]_0 = 6{\cdot}03 \times 10^{-2}$M. Temp. = 25°.

| | Replacement (%) after (min.) | | | | | | |
|---|---|---|---|---|---|---|---|
| Other conditions | 2 | 10 | 25 | 50 | 75 | 100 | 150 |
| In light; $1 \times 10^{-6}$M-$S_2O_3^{2-}$ | 22·8 | 48·0 | 71·9 | — | 92·0 | — | 98·8 |
| ,, No $S_2O_3^{2-}$ | 25·0 | 48·5 | 69·8 | 85·1 | 92·9 | 96·0 | — |
| In dark; No $S_2O_3^{2-}$ | 24·4 | 48·3 | 70·4 | 84·9 | 93·0 | 96·4 | — |
| In light; No $S_2O_3^{2-}$; $2{\cdot}5 \times 10^{-4}$M-$IrCl_6^{2-}$ | 24·6 | 47·2 | 69·5 | 84·9 | 95·9 | 97·2 | — |
| ,, No $S_2O_3^{2-}$; $5 \times 10^{-3}$M-$HClO_4$ | 26·0 | 48·3 | 73·0 | 86·2 | 93·5 | 96·9 | — |
| ,, No $S_2O_3^{2-}$; $3{\cdot}9 \times 10^{-4}$M-$PtCl_4^{2-}$ | 31·5 | 57·1 | 79·2 | 92·7 | 97·8 | 102 | —* |

* These figures refer to uptake of iodide by both Pt(IV) and Pt(II) species.

The rate of the reaction was found to depend on the initial concentrations of both chloroplatinate and iodide ions. The second-order rate equation can be expressed in terms of the

---

[2] Poë and Vaidya, *J.*, 1960, 187.

[3] Poë and Vaidya, *Proc. Chem. Soc.*, 1960, 118.

[4] Poë and Vaidya, *J.*, 1960, 3431.

[5] Poë, unpublished work.

fraction, *f*, of the total possible reaction which has occurred by time *t*, and the initial concentrations of the iodide ions and Pt–Cl bonds. Thus:

$$kt = \{2{\cdot}303/([I^-]_0-[PtCl]_0)\}\log\{(1 - [PtCl]_0 f/[I^-]_0)/(1 - f)\}$$

The rate constant, *k*, was therefore obtained by plotting the function on the right-hand side of this equation against time. The results obtained from thirteen runs at 25° in which $[I^-]_0$ varied from 0·0214M to 0·0643M, and $[Pt{-}Cl]_0$ varied from 0·015M to 0·045M, were expressed graphically. A straight line was obtained, up to about 90% replacement, which did not go through the origin and which gave a rate constant of 0·9 l. mole$^{-1}$ min.$^{-1}$. The finite value of the logarithmic term at $t = 0$ suggests some separation-induced replacement. This was confirmed by runs in which the complex was separated within about 15 sec. of mixing the reactants. The amount of replacement varied up to about 18%, but it was not constant at 17% as would have been the case if rapid replacement of one of the chloride ligands had occurred. It was not due to inadequate washing of the precipitate since the distribution of the activity after completion of the reaction was very close to that predicted from the known concentrations. Precipitation-induced reaction therefore seems most likely. The rate-constant graph can be made to go through the origin by using corrected values of the replacement obtained from the equation:

$$f_{\text{apparent}} = f_{\text{correct}} + 0{\cdot}12(1 - f_{\text{correct}})$$

based on the assumption that at any time about 12% of the reaction which has still to occur will occur during the separation process. Since only the earlier points are much affected by this, the graph is not very sensitive to the exact amount of separation-induced reaction assumed. The graph obtained is shown in the Figure. Where more than one point is available for any one time, the spread of the points is given by the length of the vertical line, where this is greater than the radius of the closed circle which indicates the average value. Single points are indicated by open circles. The gradient corresponds to a rate constant of 0·85 l. mole$^{-1}$ min.$^{-1}$ with an uncertainty of about ±0·05 l. mole$^{-1}$ min.$^{-1}$. Three runs, involving identical solutions, were performed at 1°, 25°, and 44° and the results are given in Table 2. The initial concentration of iodide ions was only slightly greater than that of Pt–Cl bonds, and the absolute values of the rate constants obtained were rather inaccurate since they depend partly on the difference between these concentrations. However, since the solutions were identical, and good straight-line rate-constant graphs were obtained from the data corrected for separation-induced reaction, the relative values of the rate constants were quite accurate. The value for 25° being set at 0·85 l. mole$^{-1}$ min.$^{-1}$, the graphically obtained values for 1° and 44° are 0·111 and 3·12 l. mole$^{-1}$ min.$^{-1}$. These results are well expressed by the equation:

TABLE 2. *Temperature dependence of the* $PtCl_6^{2-}$–$I^-$ *reaction.*

$[I^-]_0 = 3{\cdot}62 \times 10^{-2}$M; $[PtCl]_0 = 3{\cdot}35 \times 10^{-2}$M.

(The value of $[I^-]_0$–$[PtCl]_0$ is adjusted so that graphical determination gives $k_{25} = 0{\cdot}85$ mole$^{-1}$ min.$^{-1}$. This requires a decrease of 14% in the difference, which corresponds to an uncertainty in one of the absolute values of about 1%).

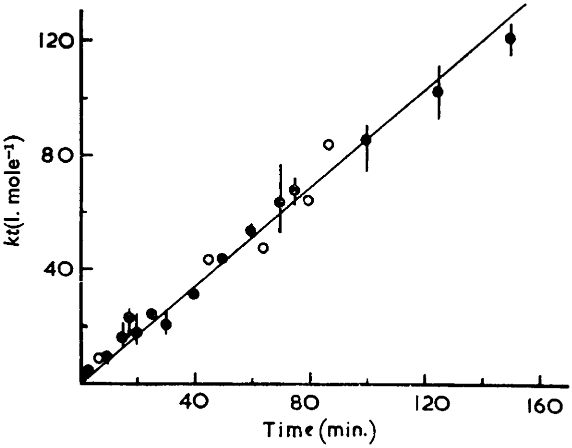
| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 25° | Time (min.) | 10 | 25 | 50 | 75 | 100 | | | | | |
| | 100 $f_{\text{corr.}}$ | 21 | 39 | 57 | 68 | 75 | | | | | |
| | 100 $k_{\text{calc.}}$ (l. mole$^{-1}$ min.$^{-1}$) | 86 | 83 | 83 | 86 | 88 | | | | | |
| | $k_{\text{graph}}$ (l. mole$^{-1}$ min.$^{-1}$) | | | 0·85 | | | | | | | |
| 1° | Time (min.) | 30 | 73 | 90 | 150 | 195 | 240 | 300 | 360 | 420 | 480 |
| | 100 $f_{\text{corr.}}$ | 9·3 | 20 | 28 | 33 | 41 | 46 | 51 | 56 | 58 | 62 |
| | 1000 $k_{\text{calc.}}$ (l. mole$^{-1}$ min.$^{-1}$) | 112 | 110 | 136 | 104 | 112 | 112 | 111 | 110 | 102 | 105 |
| | $k_{\text{graph}}$ (l. mole$^{-1}$ min.$^{-1}$) | | | 0·111 | | | | | | | |
| 44° | Time (min.) | 3 | 6 | 9 | 11 | 13 | 15 | 18 | 20 | 25 | 30 |
| | 100 $f_{\text{corr.}}$ | 24 | 38 | 47 | 52 | 58 | 61 | 67 | 68 | 70 | 75 |
| | 100 $k_{\text{calc.}}$ (l. mole$^{-1}$ min.$^{-1}$) | 332 | 322 | 302 | 298 | 330 | 318 | 336 | 318 | 287 | 284 |
| | $k_{\text{graph}}$ (l. mole$^{-1}$ min.$^{-1}$) | | | 3·12 | | | | | | | |

$$k = (60\boldsymbol{R}Te/\boldsymbol{N}h)\exp(-26{\cdot}31/\boldsymbol{R})\exp(-12{,}730/\boldsymbol{R}T)\ \text{l. mole}^{-1}\ \text{min.}^{-1},$$

which gives values of 0·114, 0·817, and 3·20 l. mole$^{-1}$ min.$^{-1}$ for *k* at 1°, 25°, and 44°, respectively. Since the uncertainty in each of the values of *k* is not more than about ±5% the values of

$E$ and $\Delta S^{\ddagger}$ are $12{\cdot}7_3 \pm 0{\cdot}5$ kcal./mole and $-26{\cdot}3 \pm 2$ cal./deg. mole, respectively. (These values differ from those previously quoted [3] owing to the improved treatment of the data.)

A spectrophotometric examination of equilibrium mixtures containing 0·001M-$PtHal_6^{2-}$, 0·5M-$Cl^-$ and various small amounts of iodide showed that the intermediate species have absorptions at the same wavelengths as the hexaiodoplatinate (*i.e.*, 340, 420, and 495 mμ) but that the 420 mμ absorption is more intense than that at 495 mμ in the species containing less iodide. In the hexaiodoplatinate the absorption at 420 mμ shows only as a shoulder to the more intense absorption at 495 mμ. An examination of the changing spectrum during the reaction, in the presence of sufficient chloroiridate to minimise photochemical effects, revealed a steady growth of the hexaiodoplatinate spectrum and, therefore, no intermediate species were formed in appreciable concentrations. The straight-line rate-constant graph is obtained, therefore, because the reaction involves a rate-determining replacement of one of the chloride ligands, followed by rapid replacement of the remaining five, rather than a series of successive replacements governed by approximately the same rate constant and leading to a constant average value (cf. ref. 3).



*The* $PtCl_6^{2-}$–$I^-$ *reaction at* 25°. *A graphical representation of the rate constant data obtained from thirteen runs, involving over 70 points.*

The kinetics of the replacement in the presence of chloroiridate and at room temperature were examined spectrophotometrically in the presence of chloroiridate by following the changing absorption at 495 mμ. Provided the solutions were not left continuously in the light beam, linear rate-constant graphs were obtained, but the rate constants were larger than those obtained by the tracer method at corresponding ionic strengths. Thus the lowest rate constant observed at $I = 0{\cdot}05$M was 1·6 l. mole$^{-1}$ min.$^{-1}$ and we assume that this is because some extra reaction is caused by the light beam in spite of the presence of chloroiridate. On decreasing the ionic strength to 0·01M the rate constant dropped to 0·6 mole$^{-1}$ min.$^{-1}$ which is, qualitatively at least, the drop expected according to the simple Debye–Hückel equation. The difficulty in obtaining reproducible results by this method, in contrast with the good reproducibility obtained by the radiotracer method, shows that the latter is more reliable.

*The* $PtBr_6^{2-}$–$I^-$ *Reaction.*—This reaction is considerably faster than that of the chloroplatinate and its study has been much less thorough. Table 3 shows most of the results in detail. The reaction is not sensitive to thiosulphate in the same way as the chloroplatinate reaction, but the runs were nevertheless performed in its absence. It is retarded a little by acid, in the light, and it is slightly photosensitive. The addition of a small amount of tetrabromoplatinate slightly accelerates the reaction in the dark over the early stages. The reaction in the dark is partially inhibited by small amounts of $IrCl_6^{2-}$, but additional quantities have no further effect and the residual reaction is presumably a genuine, non-photochemical replacement reaction.

When precipitation was effected within 15 seconds of mixing the reactants at 1°, about 17% replacement was found to have occurred. Although this corresponds closely to the fast replacement of one of the six bromide ligands, this correspondence is probably fortuitous, the rapid replacement being precipitation-induced, as in the chloroplatinate reaction. Thus, spectrophotometric observation of the reaction of $10^{-4}$M-$PtBr_6^{2-}$ and $10^{-3}$M-$I^-$, in the presence of

$3 \times 10^{-5}$M-$IrCl_6^{2-}$ and at room temperature, shows no sudden initial increase in absorption such as would have been expected if the first stage of substitution had been rapid. Precipitation-induced reaction might be expected to occur more easily in the more labile bromoplatinate system.

The reacting solutions, in the presence of chloroiridate, showed absorption maxima at 340, 420, and 495 mμ but the 420 mμ absorption was more intense than that at 495 mμ until the later stages of the reaction: then the 495 mμ peak became more intense, as in the hexaiodoplatinate spectrum. This shows that intermediate species must be present in significant quantities, in contrast with the chloroplatinate reaction.

TABLE 3. *The* $PtBr_6^{2-}$–$I^-$ *reaction.*

| | Replacement (%) after (min.) | | | | | | |
|---|---|---|---|---|---|---|---|
| | ½ | 1 | 1½ | 2¼ | 3 | 7 | 12 |
| (a) *At* 1°, *and* $[I^-]_0 = 9{\cdot}74 \times 10^{-3}$M, $[PtBr]_0 = 6{\cdot}12 \times 10^{-3}$M. | | | | | | | |
| In light | 28·0 | — | 41·6 | 50·2 | 55·1 | 65·4 | 76·5 |
| ,, $PtBr_6^{2-}$ previously in dark for 24 hr. | 29·8 | — | 40·1 | 50·6 | 55·6 | 68·7 | 77·2 |
| In light; $10^{-3}$M-$HClO_4$ | 20·0 | — | 39·7 | 43·7 | 48·3 | 58·4 | 67·2 |
| In dark | 32·7 | 36·0 | 42·2 | 45·9 | 48·4 | 57·7 | 64·1 |
| ,, $7{\cdot}7 \times 10^{-5}$M-$PtBr_4^{2-}$ | 35·9 | 41·7 | 45·2 | — | 50·7 | 59·9 | 64·8 * |
| ,, $5 \times 10^{-5}$M-$IrCl_6^{2-}$ | 18·7 | 22·6 | 29·4 | 35·2 | 37·3 | 43·7 | 50·5 |
| ,, $1 \times 10^{-4}$M-$IrCl_6^{2-}$ | 17·2 | 21·5 | 25·7 | 34·6 | 36·7 | 44·0 | — |
| (b) *At* 1°, *and* $[I^-]_0 = 7{\cdot}3 \times 10^{-3}$M, $[PtBr]_0 = 6{\cdot}12 \times 10^{-3}$M. | | | | | | | |
| In dark; $5 \times 10^{-5}$M-$IrCl_6^{2-}$ | 17·7 | 20·1 | 22·5 | 25·7 | 28·3 | 37·4 | 38·5 |
| (c) *At* 25°, *and* $[I^-]_0 = 9{\cdot}74 \times 10^{-3}$M, $[PtBr]_0 = 6{\cdot}12 \times 10^{-3}$M. | | | | | | | |
| In dark; $5 \times 10^{-5}$M-$IrCl_6^{2-}$ | 41·8 | 46·6 | 57·2 | 54·7 | 58·3 | 64·5 | 68·8 |
| (d) *At* 1°, *and* $[I^-]_0 = 10^{-2}$M, $[PtBr]_0 = 5{\cdot}62 \times 10^{-3}$M. | | | | | | | |
| | ¼ | 1 | 2 | 3 | 4 (min.) | | |
| In dark; $10^{-4}$M-$IrCl_6^{2-}$ | 17·2 | 22·8 | 30·5 | 36·8 | 36·0 | | |
| ,, ,, | 17·6 | — | — | 33·9 | 36·8 | | |

* These figures give the uptake of iodide by both the Pt(IV) and the Pt(II) species.

The rate of the reaction is dependent on the initial concentration of the iodide. After allowance for the precipitation-induced reaction as before, and with a second-order rate equation, the rate-constant plot is linear only up to a total of about 35% replacement, corresponding to the replacement of two chloride ligands, after which the gradient decreases, showing that the complexes containing more iodide react more slowly than the less substituted species. The gradient of the straight line corresponds to a rate constant of about 12 l. mole$^{-1}$ min.$^{-1}$ at 1°.

## DISCUSSION

The inhibition of the $PtCl_6^{2-}$–$I^-$ reaction by chloroiridate, and the sensitivity of the reaction to light and to traces of thiosulphate or ferrous ions, show that it can involve a labile Pt(III) intermediate in the same way as does the $PtCl_6^{2-}$–$Cl^-$ exchange reaction.[6] The residual reaction, after addition of chloroiridate, must, however, go by some other mechanism. A redox mechanism, involving a bridged intermediate and chlorine-transfer, and similar to that proposed for the Pt $en_2Cl_2^{2+}$–$Cl^-$ exchange,[7] would be of first order in a Pt(II) species. The small effect of adding chloroplatinate ions to the reaction mixture, and the unlikelihood of there being a substantial amount of Pt(II) in the chloroplatinate samples, make such a mechanism unlikely. The reaction is also faster than it would be if aquation were the mechanism.[3]

In the absence of evidence for yet another devious path (and previous studies of platinum complexes give little reassurance here) the second-order kinetics suggest an $S_N2$ mechanism. The size of the entropy of activation, and the decrease in rate with decreasing ionic strength, are both consistent with this. The only other $S_N2$ reactions of chloroplatinates which have been studied in detail involve the attack of neutral or

---

[6] Rich and Taube, *J. Amer. Chem. Soc.*, 1954, **76**, 2608.

[7] Basolo, Wilks, Pearson, and Wilkins, *J. Inorg. Nuclear Chem.*, 1958, **6**, 161.

cationic complexes by pyridine, and activation energies of about 20 kcal./mole were found.[1] The value of 12·7 kcal./mole for the $PtCl_6^{2-}$–$I^-$ reaction, though rather small, is consistent with the greater nucleophilic character of the iodide ion and with the presumed lower strength of the Pt–Cl bond in the anionic complex. Solvation of the highly charged transition state may well help to offset the repulsion between the similarly charged reactants. The rapidity with which further replacement occurs, after the slow introduction of the first iodide ion, shows that the labilising effect of the iodide ligand, even on chloride ligands in the *cis*-positions, must be large relative to that of the chloride ligand. Although kinetically the system proceeds rapidly from $PtCl_5I^{2-}$ to $PtI_6^{2-}$ the system at equilibrium does contain the intermediate species in significant proportions.[4]

The $PrBr_6^{2-}$–$I^-$ reaction is partly inhibited by chloroiridate and can therefore involve a Pt(III) intermediate. The residual reaction, in the presence of chloroiridate, cannot go by this mechanism. The redox mechanism [7] involving bromoplatinite can also be rejected, and aquation is also too slow to provide a reaction path.[8] In the absence of other evidence, the second-order kinetics can be taken to indicate an $S_N2$ mechanism. The rate constant for replacement of the first two bromide ligands is about 100 times as great as that for the $PtCl_6^{2-}$–$I^-$ reaction and, if the entropies of activation are similar, then the activation energy must be 2—3 kcal./mole smaller. In the reactions of the corresponding cationic complexes with pyridine the activation energy for the reaction of the bromo-complex was about 1·5 kcal./mole smaller, and the entropy of activation somewhat lower, than that for the corresponding chloro-complex.[9] A lower activation energy would parallel the weaker bond strength in the hexabromoplatinate, the Pt–Br bond being, on the average, about 6 kcal./mole weaker than the Pt–Cl bond.[10] On going to the iodoplatinate exchange reaction, a further increase in the rate constant by a similar amount would result in a value of $10^3$ l. mole$^{-1}$ min.$^{-1}$. This would give a half-time for exchange of about 8 seconds in the most dilute solutions studied.[2] This would hardly have been detectable, with the technique used, especially if there were an appreciable amount of precipitation-induced exchange. Although it is possible that the rapid and complete exchange observed was entirely precipitation-induced this would be an alternative manifestation of the increasing lability along the series chloro-, bromo-, and iodo-platinate. The slow replacement of the third and subsequent bromide ligands, compared with the replacement of the first two, is in contrast with the increased rate observed with the chloroplatinate. A similar contrast exists in the replacement equilibria for which the average spreading factors [11] in the chloride–iodide and bromide–iodide systems are 0·9 and 1·1, respectively.[4]

The observations on the reactions which apparently involve Pt(III) intermediates can be considered together with some results for the $PtCl_6^{2-}$–$Cl^-$ exchange reaction [12] which differ from those reported by Rich and Taube.[6] Sodium hexachloroplatinate was used which had been shown spectrographically to contain less than $5 \times 10^{-4}$ % of iridium. This underwent relatively slow exchange with chloride, and half times of about 2½ hr. were obtained at 25° in the light. With sodium chloroplatinate, of normal grade rapid exchange was induced by addition of less than 1% of thiosulphate ions, relative to the chloroplatinate. These results suggest that laboratory light is a relatively poor generator of Pt(III) species compared with chemical, one-electron, reducing agents but that, when generated, these species provide a path for rapid exchange or replacement reactions. Ions such as $PtI_5^{2-}$ must, therefore, be capable of extracting chlorine or bromine atoms rapidly from $PtCl_6^{2-}$ or $PtBr_6^{2-}$, thereby propagating the reaction by regeneration of $PtCl_5^{2-}$ or $PtBr_5^{2-}$.

---

[8] Archibald, *J.*, 1920, **117**, 1104; 1922, **121**, 2849.

[9] Grinberg, *J. Inorg. Chem.* (*U.S.S.R.*), 1959, **4**, 683.

[10] Poë and Vaidya, *J.*, 1961, 1023.

[11] Bjerrum, " Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1957.

[12] Burford and Poë, unpublished work.

## EXPERIMENTAL

The radiotracer procedures were those used in the study of the $PtI_6^{2-}$–$I^-$ exchange reaction.[2] The agreement between the total activity added and the sum of activities in the free and combined iodide, measured after replacement, was usually within ±1—2%. Sufficient activity was used to keep statistical uncertainties below ±1%. Platinum complexes were supplied by Messrs. Johnson, Matthey and Co. Ltd. and "AnalaR" halide salts were used.

A Perkin–Elmer recording spectrophotometer (model 4000) was used to study the changing spectra during the reactions, and changing absorption at a single wavelength was measured on a Unicam S.P. 500 spectrophotometer.

We are grateful to Messrs. Johnson, Matthey and Co. Ltd. for the loan of the spectrographically analysed sodium hexachloroplatinate.

INORGANIC CHEMISTRY RESEARCH LABORATORIES,
IMPERIAL COLLEGE, LONDON, S.W.7.

[*Received, January* 19*th*, 1961.]