

37. *The Iodoplatinate Iodide Exchange.*

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The exchange of free iodide ions with iodide in the complex hexaiodoplatinate has been studied under a variety of conditions by using $^{131}\text{I}^-$. In all cases the rate of exchange was immeasurably fast, even in the presence of customary inhibitors or in the absence of customary catalysts. The exchange was also fast and complete with iodide in hydrolysed forms of the complex. Possible mechanisms for the exchange are discussed and some which have been proposed for analogous reactions are rejected in this case. It is possible that the exchange proceeds by a simple substitution with a low activation energy, although catalysis cannot be completely ruled out.

Preliminary studies of the hydrolysis of the iodoplatinate and of the reactions of iodide ion with chloro- and iodo-platinites are reported. Unsuccessful attempts have been made to prepare solid potassium tetraiodoplatinite.

EXCHANGE studies on the complex hexaiodoplatinate in aqueous solution have not previously been reported in detail. Grinberg, Kozlova, Nikolskaya, and Shagisultanova¹ have stated that, with $0.0047\text{M}[\text{PtI}_6]^{2-}$, 56% exchange occurs in 30 min. at 18° but no further results were given.

The Exchange Reaction.—The exchange was studied with solutions made by dissolving the complex in potassium iodide solution, where hydrolysis was minimised. The reaction was initiated by addition of carrier-free $^{131}\text{I}^-$ and quenched by precipitation of caesium iodoplatinate. No separation-induced exchange occurs in other cases involving precipitation of similar caesium salts. After separation of the precipitate, and dissolution in sodium thiosulphate solution, the activities in the complex iodide and free iodide forms

¹ Grinberg, Kozlova, Nikolskaya, and Shagisultanova, *J. Appl. Chem. (U.S.S.R.)*, 1955, **28**, 5.

were each measured under standard conditions and compared with the total activity added initially. The fraction of exchange was given by the ratio of the measured activity in the complex to that calculated for an even distribution of the activity among all the iodide ions present, the complex being assumed to be $[\text{PtI}_6]^{2-}$.

Typical results are given in Table I. In no case was a measurable reaction rate observed even with very dilute solutions at 0° in the absence of light and thiosulphate ions (the tracer was supplied in sodium thiosulphate solution). Each of these is known to accelerate reactions of other halogen complexes of platinum(IV).^{2,3} The addition of

TABLE I. *Typical results of $[\text{PtI}_6]^{2-}$ -I⁻ exchange.*

(Solutions prepared by dissolving the complex in KI solution.)

| Concn. (M) | | | | Exchange (%) after: | | | | | Average (%) |
|--------------------------|----------------------|----------------------|---------------------------------|---------------------|-------|------------|------|------|-------------|
| $[\text{PtI}_6]^{2-}$ | I ⁻ | Other reagents | | 30 | 60 | 90 sec. | 120 | 180 | |
| <i>At 0° in the dark</i> | | | | | | | | | |
| 5×10^{-3} | 4×10^{-3} | 1.5×10^{-5} | $[\text{S}_2\text{O}_3]^{2-}$ | 99.0 | 102.3 | 98.8 | 97.5 | 97.5 | 99.0 |
| 1×10^{-3} | 4×10^{-3} | 1×10^{-4} | $[\text{S}_4\text{O}_6]^{2-}$ | 99.8 | 99.1 | 96.9 | | | 98.5 |
| 5×10^{-4} | 2×10^{-3} | „ | | 99.4 | 98.5 | 99.0 | | | 98.9 |
| <i>At 25° in light</i> | | | | | | | | | |
| 5×10^{-3} | 2.7×10^{-2} | 1×10^{-5} | $[\text{S}_2\text{O}_3]^{2-}$ | 100.9 | 100.1 | 98.4 | | | 99.8 |
| | | 2.8×10^{-3} | $[\text{Fe}(\text{CN})_6]^{3-}$ | | | | | | |
| „ | „ | 1×10^{-5} | $[\text{S}_2\text{O}_3]^{2-}$ | 100.2 | 100.1 | 100.1 | | | 100.1 |
| | | 2×10^{-4} | $[\text{IrCl}_6]^{2-}$ | | | | | | |
| „ | „ | 1×10^{-5} | $[\text{S}_2\text{O}_3]^{2-}$ | 99.7 | 99.8 | 99.6 | | | 99.7 |
| | | 6×10^{-3} | Quinol | | | | | | |

oxidising agents such as hexachloroiridate(IV) and ferricyanide ions, or a reducing agent such as quinol, all of which are effective inhibitors of the $[\text{PtCl}_6]^{2-}$ -Cl⁻ exchange,⁴ also had no effect.

Hydrolysis of $[\text{PtI}_6]^{2-}$.—Preliminary studies of the hydrolysis of the iodoplatinate ion were made by measuring the release of activity from the complex which had previously been labelled by addition of carrier-free $^{131}\text{I}^-$, making use of the rapidity of the exchange. As judged by the colourless supernatant solutions obtained, the complex species in solution were completely precipitated as caesium salts even when the degree of hydrolysis was as large as 60%. The results are listed in Table 2 and show that the hydrolysis is strongly dependent on free iodide-ion concentration and is not appreciably sensitive to light, in contrast to the hydrolysis of the chloro- and bromo-platinates.⁵ The pH of the solutions was measured, with a Cambridge Portable pH meter, and indicated that the hydrolysed species were weak acids, the hydrogen-ion concentration being considerably lower than that of iodide released from the complex.

The initial rate at 25° corresponds to a rate constant of about 0.1 min.^{-1} for the hydrolysis of $[\text{PtI}_6]^{2-}$.

Exchange with Partially Hydrolysed Species.—The addition of carrier-free $^{131}\text{I}^-$ to aged solutions of the iodoplatinate enabled the exchange of free iodide with the iodide in hydrolysed forms of the complex to be studied. The exchange is still rapid and the equilibrium distribution of the activity is consistent with all the iodides' being involved in the exchange, *i.e.*, none of them is stabilised by the presence of water molecules or hydroxide groups in the complex. This is shown in Table 2 where the degree of hydrolysis calculated from the equilibrium activity distribution after exchange is compared with that indicated by iodide release from the fully labelled complex.

Exchange using iodoplatinate solutions which were about an hour old was studied by

² *E.g.*, Stranks and Wilkins, *Chem. Rev.*, 1957, **57**, 743.

³ Poë, unpublished work.

⁴ Rich and Taube, *J. Amer. Chem. Soc.*, 1954, **76**, 2608.

⁵ Archibald, *J.*, 1920, **117**, 1104; 1922, **121**, 2849.

the addition of a finite amount of labelled iodide solution. About 85% exchange occurred rapidly, followed by a relatively slow uptake of activity by the complex to an extent consistent with the complex species' finally becoming $[\text{PtI}_6]^{2-}$. This slower reaction can be ascribed to a reversal of the hydrolysis in its early stages which was not detected with

TABLE 2. *The hydrolysis of $\sim 5 \times 10^{-3}\text{M}$ - $[\text{PtI}_6]^{2-}$: (a) by release of I^- , (b) from equilibrium distribution of activity after exchange.*

| Method | | | Initial I^- concn. (M) | | Hydrolysis (%) after: | | | | | | | |
|--------|----------------------|----------------------------|------------------------------------|------|-----------------------|------|------|------------|------|------|------|------|
| | | | | | 5 | 10 | 15 | 20 min. | 50 | 80 | 300 | |
| (b) | 0 | 25°, in light | 5.4 | 6.8 | | 8.7 | 12.8 | 14.3 | | | | |
| (a) | 0 | " " | 4.0 | 5.8 | | 8.7 | 12.4 | 13.2 | 17.6 | | | |
| (b) | 0 | " " | 4.3 | 5.1 | | 8.1 | 12.9 | 13.7 | 18.2 | | | |
| (a) | 0 | $\sim 19^\circ$, in dark | | 4.2 | 4.8 | 5.4 | 7.2 | 9.1 | 11.7 | | | |
| (a) | 0 | $\sim 20^\circ$, in light | | 5.0 | 5.5 | 6.3 | 8.7 | 10.5 | 13.8 | | | |
| | | | Hydrolysis (%) after: | | | | | | | | | |
| | | | 1 | 4 | 5 | 6 | 8 | 12 | 13 | 15 | 21 | 27 |
| (a) | 3.6×10^{-3} | 25°, in light | 2.2 | 15.2 | 17.5 | 18.0 | 20.0 | 22.5 | | 25.5 | 27.7 | 30.5 |
| (a) | " | " in dark | 2.7 | 15.3 | 17.7 | 18.7 | 21.3 | 22.7 | | 25.5 | 27.9 | 31.2 |
| (b) | 0 | Room temp., in dark | 29 | | 36 | | 47 | 54 | 60 | | | |

older solutions. The reversibility is supported by the large effect of free iodide on the rate of hydrolysis. Fast exchange without detectable reversal of hydrolysis was still observed on a 13-day old solution when 60% of the iodides originally in the complex had been hydrolysed.

Discussion.—Since no studies of the kinetics of this fast reaction were made there is no positive indication of the mechanism. However, some mechanisms previously suggested for analogous reactions of other halogenoplatinates can be rejected in this case.

The absence of inhibition by substances such as hexachloroiridate(IV) suggests strongly, although it does not prove, that there is no catalysis by platinum(III) species of the kind postulated by Rich and Taube⁴ for the $[\text{PtCl}_6]^{2-}-\text{Cl}^-$ exchange. The rapid exchange even of iodides in the complex which are slowly released by hydrolysis precludes aquation as a reaction path. Basolo, Wilks, Pearson, and Wilkins⁶ have shown that platinum(II) species catalyse the exchange of chloride ions with *trans*- $[\text{Pt}(\text{en})_2\text{Cl}_2]^{2+}$ (en = ethylenediamine), and propose a group-transfer mechanism for the exchange. They suggest that such catalysis should always be looked for in reactions of platinum(IV) complexes. If analytically undetectable amounts of platinum(II) species catalyse the iodoplatinate exchange by a similar mechanism, then the exchange of iodide with iodoplatinate, in the presence of iodoplatinate, would be very fast. Although Grinberg and his co-workers¹ reported half-times of about 2 min. for 0.12M - $[\text{PtI}_4]^{2-}$ and 0.48M - I^- at 5° our preliminary observations reported below indicate considerably shorter half-times even in much more dilute solutions. This made it very difficult to discover experimentally whether the exchange is affected by iodoplatinate. However, the mechanism proposed by Basolo and his co-workers involves a transition state comprising two doubly charged positive ions and one singly charged negative ion, whereas in the iodoplatinate exchange three ions bearing a total negative charge of five units would have to be involved. The latter seems very much less likely.

Finally, the reaction of 0.03M -iodide with $5 \times 10^{-3}\text{M}$ -hexachloroplatinate at 25° has a half-time of about 10 min. and is not light-sensitive; that of $4 \times 10^{-3}\text{M}$ -iodide with $5 \times 10^{-4}\text{M}$ -hexabromoplatinate, also at 25° , has a half-time of about 30 sec.⁷ The Pt-I

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

bond is also known ⁸ to be weaker than the Pt-Cl and the Pt-Br bond by ~ 12 and ~ 5 kcal. mole⁻¹, respectively. Although the possibility of an undetected catalysis cannot be completely ruled out, these facts, together with the rejection of the more complicated mechanisms mentioned previously, make it reasonable to suppose that fast exchange takes place by a simple S_N1 or S_N2 substitution with a low activation energy, the S_N1 mechanism not involving aquation.

EXPERIMENTAL

Tracer.—Carrier-free ¹³¹I⁻ ($t_{1/2} = 8.1$ days) was obtained from the Radiochemical Centre, Amersham, in 0.01N-sodium thiosulphate solution. The thiosulphate was usually converted into tetrathionate by adding an excess of iodine and removing unchanged iodine with carbon tetrachloride. The activity in solution was measured by using an Isotope Development Ltd. scintillation spectrometer adjusted to count 364 Kev gamma-rays. The background count was about 240 counts/min. and the samples were counted to 1% statistical accuracy in an annular plastic container which fitted tightly over the cap enclosing the sodium iodide phosphor. Decay corrections were avoided by counting several samples within a short time.

Chemicals.—Sodium hexaiodoplatinate and potassium tetrabromo- and tetrachloro-platinite were obtained from Messrs. Johnson, Matthey and Co. Ltd. Otherwise "AnalaR" reagents were used. Solutions were made up in normal distilled water.

[PtCl₄]²⁻-I⁻ Reaction.—The rate of iodide replacement of chloride in the platinum(II) complex was measured at initial concentrations of 0.005M-[PtCl₄]²⁻ and 0.04M-I⁻ at 25° in the light. The complex species were precipitated as the [Pt(en)₂]²⁺ salts. In 1 hr. the amount of iodide in the complex rose to a maximum of 63% of that for complete replacement, after which it steadily decreased. Hydrolysis was therefore competing with substitution to such an extent that the tetraiodoplatinitate was not formed at these concentrations. However, by mixing 25 times more concentrated solutions of chloro- or bromo-platinite with iodide solutions, and diluting with ice-cold water after a few minutes, the complex species obtained was about 90% [PtI₄]²⁻, and hydrolysis in the dark was negligible after 5 min. when measured by the amount of activity in the complex.

Iodoplatinitate-Iodide Exchange.—Half-times for exchange of less than about 30 sec. were observed with 0.005M-complex and 0.02—0.03M-iodide in the dark at 0° and with half-hydrolysed or only slightly hydrolysed forms of the complex. The complex was prepared *in situ* by addition of iodide solution to tetrachloro- or tetrabromo-platinite and the exchange initiated, after attainment of equilibrium, by adding carrier-free ¹³¹I⁻. These rates are faster than expected on the basis of the results reported by Grinberg and his co-workers.¹

Attempted Preparation of Potassium Tetraiodoplatinitate.—Potassium tetraiodoplatinitate does not seem to have been prepared in the solid state although it has been assumed to exist in aqueous solution after treatment of the tetrachloroplatinitate with sufficient excess of iodide.⁹ Such solutions, however, gave no precipitate of a complex iodide on addition of alcohol or acetone. Evaporation of known weights of potassium tetrachloroplatinitate with pure hydrogen iodide, either under an infrared lamp or by freeze-drying in a vacuum, gave a black solid. This was heavier than expected, the proportionate increase in weight being the same by each method. The solid was readily soluble in water, and the solutions gave black precipitates and colourless supernatant solutions on addition of excess of either Cs⁺ or [Pt(en)₂]²⁺ ions. Infrared absorption characteristic of O-H bonds was not observed with the solid, and therefore the excessive weight cannot be attributed to partial five-fold co-ordination of the platinum, as in K₂(H₃O)_nPtI_{4+n} for example. Incorporation of hydrogen iodide in a potassium iodoplatinitate lattice seems unlikely and it is most probable that partial oxidation had occurred. The yield corresponded to a formulation K₂PtI_{4.77} which is in fair agreement with iodide analysis (Found: I, 66.9. Calc. for K₂PtI_{4.77}: I, 68.9%). Iodide exchange with this substance at room temperature in the light, and at 0° in the dark, was fast with 51% of the iodides in the complex followed by no further exchange in 5 min. This is quite close to the 48% fast exchange expected if the substance is a mixture of K₂PtI₆ and K₂PtI₄ in which only the hexaiodoplatinate undergoes fast exchange. However, this agreement is probably fortuitous because (i) the proportion

⁷ Poř and Vaidya, unpublished work.

⁸ Poř and Vaidya, *Nature*, 1959, **184**, 1139.

⁹ Sidgwick, "The Chemical Elements and Their Compounds," Oxford Univ. Press, Oxford, 1950, Vol. II, p. 1605.

of K_2PtI_6 in the mixture is very sensitive to errors in the analysis, (ii) the subsequent slow exchange is not consistent with the rather fast iodoplatinite exchange mentioned above, and (iii) the complex ions are completely precipitated from solution by addition of Cs^+ or $[Pt(en)_2]^{2+}$ ions in contrast with those in $[PtI_6]^{2-}$ - $[PtI_4]^{2-}$ mixtures where the latter is prepared *in situ*. The exact nature of the substance is therefore still unknown.

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