Pulse Radiolysis Studies on Complexes of Iridium

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Pulse irradiation of octahedral complexes $IrCl_6^{3-}$ and $IrCl_6^{2-}$ indicates that the former may be oxidized or reduced and the latter reduced without structural change occurring within a few μs. The electron transfer reaction forms transient iridium(II) from iridium(III). Contrary to photochemical results irradiation does not promote aquation of the complexes in the early stages of reaction. The spectra, rate constants, and extinction coefficients of the discussed species have been determined.

IN a previous publication we discussed changes in the structure of unstable intermediate Pt^{III} species observed in a pulse radiolysis study on aqueous solutions of chloroplatinite and chloroplatinate ions.[1]

The changes could be attributed to rearrangement of the ligand composition in the chloroplatinum(III)-complex depending on its initial structure, *i.e.* on whether it was formed from planar $PtCl_4^{2-}$ or octahedral $PtCl_6^{2-}$.

The numerical data obtained in that work are in remarkably good agreement with those published later by Ghosh-Mazumdar and Hart [2] and our conclusions concerning the stereochemical aspects of the processes occurring are very well in accord with observations by Penkett and Adamson [3] on the flash photolysis of $PtBr_6^{2-}$.

Under these circumstances it seemed desirable to investigate the radiation chemistry of other ions of similar structure and this papers deals with a study of pulse radiolysis of $IrCl_6^{3-}$ and $IrCl_6^{2-}$ solutions.

EXPERIMENTAL

The technique of pulse radiolysis has been described previously.[4] All solutions were prepared using A.R. reagents and triply distilled water. $Na_3IrCl_6,12H_2O$, $(NH_4)_2IrCl_6$, and $Na_2IrCl_6,6H_2O$ were supplied by Johnson, Matthey Ltd. The dose absorbed during the 0·2 μs pulse was usually *ca.* 1200 rad and was measured by KCNS dosimetry.[5] The absorption spectra of the iridium ions were measured with a Unicam SP 1800 spectrophotometer; the reference spectrum of chloroiridate ion was obtained using spectroscopically pure $(NH_4)_2IrCl_6$.

RESULTS AND DISCUSSION

The Absorption Spectra and Properties of $IrCl_6^{3-}$ *and* $IrCl_6^{2-}$.—The structure and properties of $IrCl_6^{3-}$ and $IrCl_6^{2-}$ have been investigated by numerous authors and Jörgensen has discussed the available data in a series of books.

The absorption spectra of aqueous solutions of these ions are presented in Figure 1. Our results are very similar to those by other authors; *e.g.* the extinction coefficients of the characteristic peaks of $IrCl_6^{2-}$, at 418, 434, and 488 nm, have been determined as respectively 2870, 2970, and 3930 l mol^{-1} cm^{-1}, compared with corresponding values 2410, 2560, and 3280 l mol^{-1} cm^{-1} by Jörgensen [6] and 4060 l mol^{-1} cm^{-1} (488 nm peak) by Chang and Garner.[7]

The difference in spectra of $IrCl_6^{2-}$ and $IrCl_6^{3-}$ is very convenient in pulse radiolysis experiments as the former has a characteristic spectrum between 400 and 500 nm with extinction coefficients of the peaks at least 10 times as large as the latter in the same range.

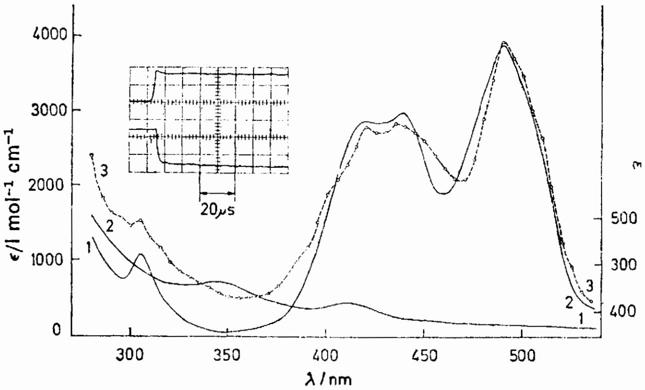

FIGURE 1 Absorption spectra of $IrCl_6^{3-}$ and $IrCl_6^{2-}$ in aqueous solution: 1, unirradiated $IrCl_6^{2-}$; 2, unirradiated $IrCl_6^{3-}$; 3, end of pulse absorption of nitrogen-saturated 0·3 mmol $IrCl_6^{3-}$ solution (1 and 3, left-hand scale; 2, right-hand scale); inset, oscilloscope traces of absorption recorded at 435 nm in nitrogen-saturated aqueous solution of $IrCl_6^{3-}$ (upper trace) and $IrCl_6^{2-}$ (lower trace)

The $IrCl_6^{3-}$ ion is octahedral,[8] stable in HCl solution,[6] and its absorption spectrum was not changed even after boiling in 1 mol NaOH.[9]

Our measurements do not show any difference in the absorption spectra taken in aqueous or HCl solution and the spectra do not change over the period of a few hours. Hence it was possible to irradiate the aqueous solution without stabilizing $IrCl_6^{3-}$ with an addition of HCl, which should be avoided in order to prevent the radiation chemical complications introduced by formation of Cl_2^-, a species likely to oxidize iridium(III).

The $IrCl_6^{2-}$ ion is octahedral as well [8] and is a strong oxidizing agent, being unstable at low HCl concentration. Jorgensen believes that at [HCl] = 0·1 mol l^{-1}

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[1] G. E. Adams, R. K. Broszkiewicz, and B. D. Michael, *Trans. Faraday Soc.*, 1968, **64**, 1256.

[2] A. S. Ghosh-Mazumdar and E. J. Hart, *Internat. J. Radiation Phys. Chem.*, 1969, **1**, 165.

[3] S. A. Penkett and A. W. Adamson, *J. Amer. Chem. Soc.*, 1965, **87**, 2514.

[4] G. E. Adams, J. W. Boag, and B. D. Michael, *Trans. Faraday Soc.*, 1965, **61**, 492.

[5] G. E. Adams, J. W. Boag, and B. D. Michael, *Trans. Faraday Soc.*, 1965, **61**, 1417.

[6] C. K. Jörgensen, *Mol. Phys.*, 1959, **2**, 309.

[7] J. C. Chang and C. S. Garner, *Inorg. Chem.*, 1965, **4**, 209.

[8] C. K. Jörgensen, 'Absorption Spectra and Chemical Bonding in Complexes,' Pergamon, 1962, p. 300.

[9] C. K. Jörgensen, Contract no. DA-91-508-EUC-247 with European Research Office, U.S. Department of the Army, Frankfurt am Main, ASTIA document no. 157158, September 1958.

$IrCl_6^{2-}$ decomposes to form hydroxo-complexes or is reduced to $IrCl_6^{3-}$,[10] and this view has been corroborated by other investigations.[11]

We have noticed the relative instability of $IrCl_6^{2-}$ but found that its decomposition is insignificant over the period of *ca.* 2—3 h after preparation of the solution from the solid salt. Hence it was possible to irradiate aqueous solutions of $IrCl_6^{2-}$ without addition of HCl, the experiments taking far less than 1 h from preparation of the solution to the analysis of the products.

It was observed, however, that the iridium(IV) species obtained by radiation-induced oxidation of $IrCl_6^{3-}$ was extremely unstable and decomposed fully a few minutes after formation.

Iridium(III) *Solutions*.—$IrCl_6^{3-}$ was irradiated in 0·3 mmol aqueous solution, the concentration having been checked to ensure that it was high enough to scavenge all radicals produced during the *ca.* 1200 rad pulse.

In Figure 1, the absorption spectrum determined in the irradiated nitrogen-saturated solution is shown in comparison to that of $IrCl_6^{2-}$ solution prepared from the solid salt. The spectrum is a permanent one, *i.e.* it did not show any decay for the *ca.* 600 μs period of observation. In the inset the oscilloscope traces of nitrogen-saturated solutions of $IrCl_6^{3-}$ and $IrCl_6^{2-}$ are presented.

The absorption was about twice as large in the solution saturated with N_2O than in that saturated with nitrogen.

The observations indicate that iridium(III) is oxidized to iridium(IV) in the reaction

$$IrCl_6^{3-} + OH \longrightarrow IrCl_6^{2-} + OH^- \qquad (1)$$

and that the transfer of an electron does not change either the structure of the complex ion or the identity of the ligands.

When to the N_2- or N_2O-saturated solution of $IrCl_6^{3-}$ 0·1 mol 2-propanol was added, the obtained spectrum did not exhibit any peak attributable to $IrCl_6^{2-}$ but instead a new transient with a maximum at 280 nm was formed. This spectrum is shown in Figure 2. The spectrum has been limited to 320 nm as at longer wavelengths no absorption could be detected and it has been corrected for removal of $IrCl_6^{3-}$.

This indicates that iridium(III) is reduced to iridium(II) by the hydrated electron, hydrogen atom, and organic radical in the reactions:

$$IrCl_6^{3-} + e_{aq}^- \longrightarrow Ir^{2+} \qquad (2)$$

$$IrCl_6^{3-} + H \longrightarrow Ir^{2+} + H^+ \qquad (3)$$

$$IrCl_6^{3-} + R\cdot \longrightarrow Ir^{2+} + R^+ \qquad (4)$$

Iridium(II) disappears rapidly in a second order reaction, probably by dismutation.

$$2Ir^{II} \longrightarrow Ir^{III} + Ir^{I} \qquad (5)$$

However, no absorption formed at the cost of iridium(II) decay has been observed within the wavelength range 260—550 nm. No experimental evidence indicating the fate of that species has been obtained either; *e.g.* in neither of the experiments have traces of any precipitate been observed and whatever is the further scheme of reactions it is not terminated with formation of metallic iridium, unlike the reduction of the platinum complexes.[1,2]

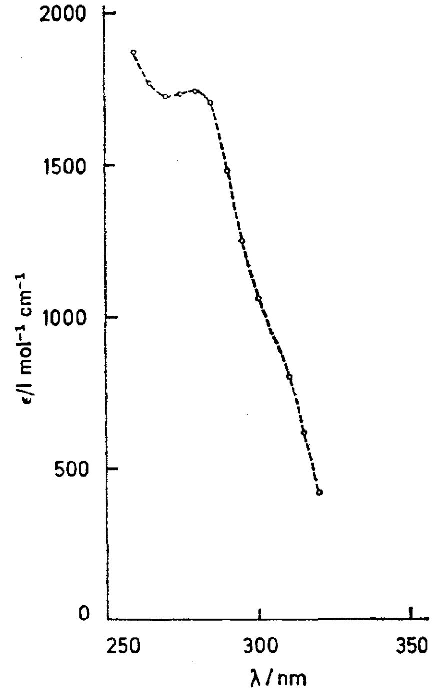

FIGURE 2 End of pulse transient absorption spectrum of nitrogen-saturated 0·3 mmol $IrCl_6^{3-}$ with 0·1 mol 2-propanol

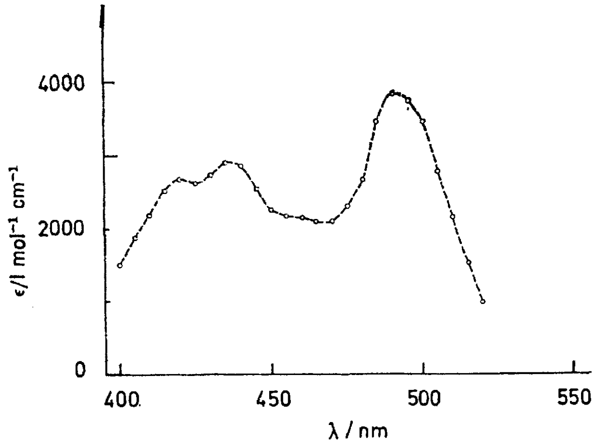

FIGURE 3 End of pulse absorption of nitrogen-saturated 0·15 mmol $IrCl_6^{2-}$ solution. The spectrum shows the decrease of the initial absorption of $IrCl_6^{2-}$

Iridium(IV) *Solutions*.—$IrCl_6^{2-}$ has been irradiated in 0·15 mmol aqueous solution.

Figure 3 shows the absorption spectrum determined in nitrogen-saturated solution. Unlike the case of iridium(III) this spectrum indicates the decrease of the initial absorption. The spectrum is a permanent one and is identical with that of $IrCl_6^{2-}$.

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[10] Ref. 8, p. 267.

[11] D. A. Fine, *J. Inorg. Nuclear Chem.*, 1970, **32**, 2731.

Saturation with N_2O considerably decreases the level of reduction, addition of 1 mmol HCl has no effect and addition of 0·1 mol 2-propanol enhances the reduction. The latter additive has been separately proved not to accelerate the thermal reduction of iridium(IV) to any significant extent.

These results indicate that iridium(IV) is reduced to iridium(III) by the hydrated electron, hydrogen atom, and organic radical in the reactions (6)—(8).

$$IrCl_6^{2-} + e_{aq}^- \longrightarrow IrCl_6^{3-} \tag{6}$$

$$IrCl_6^{2-} + H \longrightarrow IrCl_6^{3-} + H^+ \tag{7}$$

$$IrCl_6^{2-} + R\cdot \longrightarrow IrCl_6^{3-} + R^+ \tag{8}$$

The identity of $IrCl_6^{3-}$ as the reduced form of $IrCl_6^{2-}$ could not be proved in this work directly as, due to the the low extinction coefficients of $IrCl_6^{3-}$, it was not possible to observe its spectrum in the presence of an excess of $IrCl_6^{2-}$.

Rate constants

Matrix	Reaction	peak nm	$10^{-9}k$ l mol^{-1} s^{-1}	Remarks
$IrCl_6^{3-}$ H_2O, t-butyl alcohol	$Ir^{3+} + e_{aq}^- \longrightarrow Ir^{2+}$	280	6·4 ± 0·4	3 × 10^9 (ref. 18)
$IrCl_6^{3-}$ H_2O, t-butyl alcohol	$Ir^{3+} + OH \longrightarrow Ir^{4+}$	434	8·9 ± 0·1	
$IrCl_6^{3-}$ H_2O, isopropyl alcohol	$2Ir^{2+} \longrightarrow Ir^{3+} + Ir^+$ (?)	280	3·3 ± 0·4	$2k$
$IrCl_6^{2-}$ H_2O, t-butyl alcohol	$Ir^{4+} + e_{aq}^- \longrightarrow Ir^{3+}$	434	9·6 ± 0·8	9·3 × 10^9 (ref. 18)
$IrCl_6^{2-}$ $HClO_4$	$Ir^{4+} + H \longrightarrow Ir^{3+}$	434	9·2 ± 0·2	

There is, however, some indirect evidence supporting to an extent the (6)—(8) reaction scheme.

If the phenomena observed when irradiating $IrCl_6^{2-}$ were to be attributed to reactions other than addition of an electron to that structure, the most likely of them would be aquation with or without reduction of iridium(IV).

In a study of $IrCl_6^{2-}$ solutions Sleight and Hare [12] have proved that photolysis at 254 and 360 nm does not initiate reduction to $IrCl_6^{3-}$ but the exchange of chloride by water to produce the aquopentachloroiridate ion, $[Ir(H_2O)Cl_5]^-$.

However, this species has an absorption spectrum quite distinct from $IrCl_6^{2-}$ with peaks at 487, 460, and 450 nm and high extinction coefficients 2345, 3100, and 3320 l mol^{-1} cm^{-1} correspondingly.[13]

As the spectrum shown in Figure 3 clearly does not conform with those data, and other radiation chemical evidence obtained in this work indicates that the actual reaction is that of iridium(IV) reduction, the aquation without reduction can be disregarded under our experimental conditions.

Another possibility is that of simultaneous reduction and aquation of $IrCl_6^{2-}$ to $Ir(H_2O)Cl_5^{2-}$. The latter species has an absorption spectrum consisting of peaks at 347, 405, and 550 nm with extinction coefficients 110, 110, and 12 l mol^{-1} cm^{-1},[13,14] *i.e.* very close to the corresponding coefficients of $IrCl_6^{3-}$ in the wavelength range 400—500 nm, and for the same reason its formation could not be checked. However, our experiments show that reduction is obtained during the pulse and 2—3 μs after, whereas aquation of $IrCl_6^{3-}$ requires a prolonged preparative treatment.[13]

Hence, though $IrCl_6^{2-}$ is known to be reduced under certain conditions to $Ir(H_2O)Cl_5^{2-}$ rather than to $IrCl_6^{3-}$ [15] and that course of reaction cannot be completely ruled out in our case, it is believed that it is unlikely to happen during the pulse and a few μs afterwards and that within that period of time the reaction scheme (6)—(8) is valid.

It should be mentioned that we have not obtained any results indicating oxidation of Ir^{IV} to Ir^{V} or Ir^{VI}, though stable compounds at these valency levels, *e.g.* IrF_6 or $KIrF_6$ have been described.[16]

Rate Constants of Reactions.—The rate constants of the majority of the proposed reactions have been measured and are collected in the Table.

The OH reaction rate constant was measured by a competition technique with t-butyl alcohol, using in calculations the rate constant of OH with t-butyl alcohol 5·2 × 10^8 l mol^{-1} s^{-1}.[17]

The e_{aq}^- rate constants have been followed directly at 600 nm and the values are corrected for salt effect, as described by Anbar and Hart.[18]

To calculate the rate constant of dismutation of Ir^{II}, k_5, the validity of the reaction scheme (2)—(4) has been assumed. Correspondingly, values $G_{OH} = 2{\cdot}9$ and $G_{e_{aq}^-} + G_H = 3{\cdot}7$ have been calculated from reactions (1) or (6) and (7) and the extinction coefficients measured in this work. If all OH's produce 2-hydroxypropyl radicals which in turn reduce Ir^{III} in reaction (4) then the extinction coefficient of Ir^{II}, in its initial form, can be calculated as $\varepsilon^{280} = 1740 \pm 100$ l mol^{-1} cm^{-1}.

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[12] T. P. Sleight and C. R. Hare, *Inorg. Nuclear Chem. Letters*, 1968, **4**, 165.

[13] J. A. Poulson and C. S. Garner, *J. Amer. Chem. Soc.*, 1962, **84**, 2032.

[14] C. K. Jörgensen, *Acta Chem. Scand.*, 1957, **11**, 151.

[15] M. Delèpine, *Bull. Soc. Chim. France*, 1908, [4], **3**, 901.

[16] M. Delèpine, Iridium chapter in 'Nouveau Traité de Chimié Minérale,' ed. P. Pascal, vol. XIX, Masson, Paris, 1958, p. 465.

[17] R. L. Willson, C. L. Greenstock, G. E. Adams, R. Wageman and L. M. Dorfman, *Internat. J. Radiation Phys. Chem.*, 1971, **3**, 211.

[18] M. Anbar and E. J. Hart, 'Radiation Chemistry,' Advances in Chemistry Series 81, Amer. Chem. Soc., Washington, 1968, vol. I, p. 79.

CONCLUSIONS

Results obtained in this work lead to the conclusion that octahedral $IrCl_6^{3-}$ is oxidized by a single electron transfer to octahedral $IrCl_6^{2-}$ and the latter structure is stable within the period of *ca.* 0·5 ms, though its relative instability, when compared with solution of $IrCl_6^{2-}$ prepared from the solid salt, indicates that irradiation produces either an active form of $IrCl_6^{2-}$ of high reactivity towards water, or a system in which this compound is more readily reduced. The nature of relevant processes is under a separate investigation.

$IrCl_6^{3-}$ may be reduced, probably to Ir^{II}, and in this case again the single electron transfer probably does not change the original octahedral structure within a few μs.

$IrCl_6^{2-}$ in aqueous solution is not oxidized by any of the primary radiolytic products, either to Ir^{V} or to Ir^{VI}, but may be reduced to $IrCl_6^{3-}$ without changing the ligand composition within a few μs.

The general conclusion is therefore that the radiation induced oxidation or reduction of octahedral hexachloroiridite and hexachloroiridate does not change those structures within the period of reaction, though they may be the cause of a subsequent mechanism of transformations.

Contrary to the results of illumination with u.v. or visible light [12] irradiation initiates reduction but not aquation of $IrCl_6^{2-}$.

Though the iridium octahedra are well known to dimerize or trimerize by sharing faces, edges, or corners [11,19] even at as low concentration as applied in this work, neither of our spectra conforms with the reported spectra of those polymeric compounds.[11]

This additionally confirms the conclusion that under our experimental conditions the exchange of ligands does not occur, as the polymeric entities of general formula $Ir_n(H_2O)_wO_y(OH)_zCl_6^{(4n-2y-z-6)+}$ are likely to be formed with oxygen or hydroxide bridges between iridium ions.

It seems, therefore, that in spite of aqueous solutions of $IrCl_6^{3-}$ and $IrCl_6^{2-}$ being a rather complicated system the methods of radiation chemistry allow us to collect some experimental evidence on the early stages of the redox reactions and our further work is devoted to investigation of some later stages of transformations occurring during the radiolysis of these systems.

The author is indebted to the International Atomic Energy Agency for financial support of this study, to the British Empire Cancer Campaign for use of the facilities at the Research Unit in Radiobiology, Mount Vernon Hospital, Northwood, where the pulse irradiations were performed, and to Drs. G. E. Adams and R. L. Wilson for many helpful discussions.

[2/2832 *Received*, 18*th December*, 1972]

[19] J. M. Peixoto Cabral, *J. Inorg. Nuclear Chem.*, 1964, **26**, 1657.