Pulse Radiolysis Studies on Stable and Transient Complexes of Platinum

By G. E. Adams,* R. B. Broszkiewicz † and B. D. Michael *

Pulse radiolysis studies on aqueous solutions of platinum complexes reveal several transient spectra. Oxidation of Pt II (as $[PtCl_4]^{2-}$) results in the sequential formation of two short-lived complexes of Pt III, one of which can be formed directly by the reaction between e_{aq}^- and Pt IV ($[PtCl_6]^{2-}$). A short-lived species of Pt I is produced by reduction of Pt II. The relationships between the spectra have been studied as a function of solute concentration, oxygen and N_2O content, and pH. The stereochemistry of the transient species is discussed.

Few publications have appeared on the radiation chemistry of aqueous solutions of platinum complexes. Balandin *et al.*[1] observed the apparent stability of H_2PtCl_6 irradiated either in the solid state or in aqueous solutions. Haissinsky and co-workers [2,3] have shown that Pt II is oxidized to Pt IV, and Pt IV reduced to Pt II, during the stationary-state radiolysis of aqueous solutions.

Pulse radiolysis has been used to study the reactions between e_{aq}^- and platinum complexes and a transient spectrum with peaks at 3000 and 4100 Å, and suggested to be a form of platinum I, has been reported.[4] In this paper, the results of a study of the radiation-induced reduction and oxidation of $[PtCl_4]^{2-}$ and the reduction of $[PtCl_6]^{2-}$ are reported.

EXPERIMENTAL

The general technique of pulse radiolysis has been described.[5-7] All solutions were prepared using A.R. reagents and triply-distilled water. The absorbed dose was usually about 1400 rads and was measured using the transient absorption produced from oxygenated KCNS solution [7] for which the product of the G value and extinction coefficient is known with fair precision.

RESULTS AND DISCUSSION

In aqueous solution, the ions of $[PtCl_4]^{2-}$ and $[PtCl_6]^{2-}$ are planar [8] and octahedral [9] respectively. The absorption spectrum of $[PtCl_4]^{2-}$ shows 6 peaks at 5650, 4760, 3920, 3310, 2640, and 2160 Å with extinction coefficients of 2·6, 15, 59, 64, 250 and $9·58 \times 10^3$ respectively.[10] In this work, the extinction coefficient of the peak at 2160 Å was found to be 10·8 $\times 10^3$ M^{-1} cm^{-1}. The spectrum of $[PtCl_6]^{2-}$ shows peaks near 4530, 3530 and 2620 Å in both water and perchloric acid,[9,10] the extinction coefficients being 50, 490 and $2·45 \times 10^4$ M^{-1} cm^{-1} respectively. However, in view of the spectral overlap, the quantitative estimation of platinum ions is subject to some limitation particularly since ligand-solvent exchange can lead to changes in extinction coefficients.[11,12]

In aqueous solution, exchange of the ligand Cl for H_2O and OH^- occurs, e.g., the species $[PtCl_3H_2O]^-$ and $[PtCl_22H_2O]$ are formed from $[PtCl_4]^{2-}$,[13,14] and

* B.E.C.C. Research Unit in Radiobiology, Mount Vernon Hospital, Northwood, Middlesex, England.

† Institute of Nuclear Research, Department of Radiation Chemistry, Warsaw 91, Poland.

$[PtCl_4 2H_2O]$ from $[PtCl_6]$.[2-15] In a radiation chemical investigation, where both Pt II and Pt IV are present simultaneously, the situation is complicated by the marked catalytic effect of Pt II on ligand exchange in complexes of Pt IV.[16, 17] Intermediate complexes of platinum III are believed to be involved in the ligand exchange processes. The existence of the species $[PtCl_6]^{3-}$, $[PtCl_5]^{2-}$ and $[PtCl_4]^-$ has been postulated in mixtures containing Pt II and Pt IV complexes.[16, 17]

In order to stabilize the ionic species $[PtCl_4]^{2-}$ and $[PtCl_6]^{2-}$ it would seem preferable to carry out experiments in the presence of HCl or chloride ion. However, the radiation chemical complications which would be introduced by the possibility of Cl_2^- formation,[18] particularly in acid solution, generally precluded the use of high concentrations of either HCl or chloride. For most experiments, therefore, only KOH, H_2SO_4 and Na_2SO_4 were used as inorganic additives. There is a small concentration of Cl^- arising from, and in equilibrium with, the $[PtCl_4]^{2-}$. However, except at very low pH, the reactivity of Cl^- for OH radicals [18] is much less than that of the Pt II complex. Therefore, under the conditions of the present work, direct reaction between Cl^- and OH is not a complicating factor.

In all experiments, the solutions containing platinum complexes were irradiated immediately after preparation, in order to minimize the effects of ligand exchange.

PLATINUM II COMPLEXES AT NEUTRAL pH

The transient spectra produced in solutions of K_2PtCl_4, irradiated with a single $0.2\ \mu sec$ electron pulse are shown in fig. 1. All spectra are normalized to the same dose. Between 3×10^{-4} and 10^{-2} M, the OD at 4100 Å was independent of concentration (see fig. 1d(i)). In the N_2-saturated solution (fig. 1a), two absorption maxima at 4500 and 3000-3100 Å are produced during the pulse. The former peak decays rapidly over a period of about 20 μsec and is replaced by another long-lived transient absorption maximum at 4100 Å. The kinetics of the build-up at this wavelength are the same as those of the decay at 4500 Å. During this period, the peak at 3100 Å decays to about 80 % of its initial value.

In N_2O-saturated solutions (fig. 1b), the peaks at 3100, 4100 and 4500 Å are again observed. However, the absorptions at both 4100 and 4500 Å are approximately twice as intense as those observed in N_2O-free solutions. The maximum at 3100 Å is, however, partially suppressed by N_2O.

The peaks at 4100 and 4500 Å, formed in oxygen-saturated solution (fig. 1c) are similar to those produced in nitrogen although the maximum at 3100 Å is smaller. The observations in both O_2 and N_2O solutions suggest that the peaks at 4100 and 4500 Å arise from an OH-induced oxidation of Pt II and represent some form or forms of a Pt III complex :

$$Pt\ II + OH \rightarrow Pt\ III + OH^-. \tag{1}$$

In the presence of N_2O, the absorption due to Pt III is increased :

$$N_2O + e_{aq}^- \rightarrow N_2 + OH^- + OH. \tag{2}$$
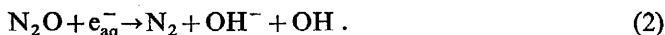
In the oxygen-saturated solution, the oxygen concentration was about four-fold greater than Pt II. We conclude therefore that O_2^- is formed in competition with any reduction process involving Pt I :

$$O_2 + e_{aq}^-\ or\ H \rightarrow O_2^-\ or\ HO_2 \tag{3}$$

$$e_{aq}^- + Pt\ II \rightarrow Pt\ I, \tag{4}$$

and therefore the lack of any effect of O_2 on the magnitude of the absorption at either 4100 or 4500 Å indicates that either O_2^- does not oxidize Pt II, or that the reaction

is very slow. Since the addition of either N_2O or O_2 decreases the initial peak at 3100 Å, one may infer that the species responsible for this absorption is formed by reduction of Pt II by e_{aq}^- and possibly by hydrogen atoms also. k_4 has been measured and is $1·2 \times 10^{10}$ M^{-1} sec^{-1}.[4, 19, 20]

When N_2-saturated solutions containing 0·1 M methanol (fig. 2a) were irradiated, the absorption at 3100 Å was again formed. However, the peaks at 4100 and 4500 Å were completely suppressed thus confirming that both species arise from a reaction

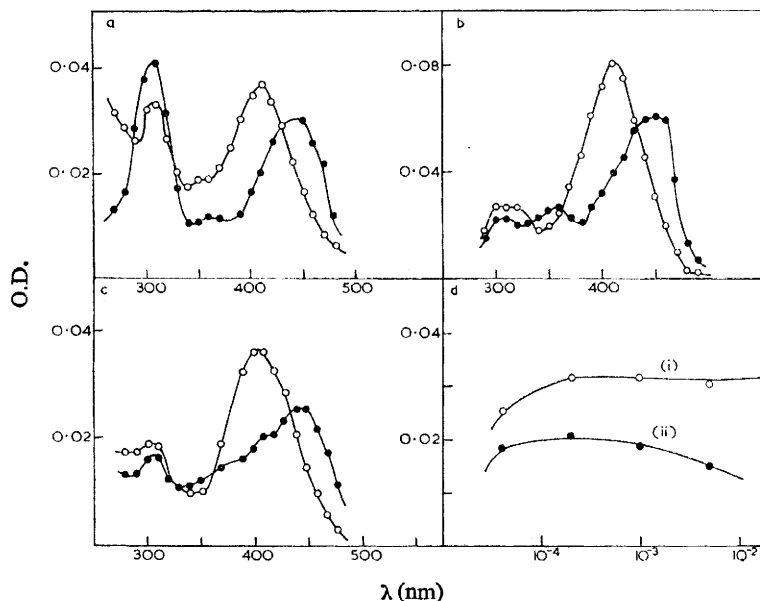FIG. 1a, b, c.—Transient spectra from solutions of Pt II: (a) N_2-saturated, 10^{-3} M Pt II; (b) N_2O-saturated, 10^{-3} M Pt II; (c) O_2-saturated, 3×10^{-3} M Pt II. ●, 1μsec after pulse; ○, 20 μsec after pulse.

FIG. 1d.—Effect of solute concentration on Pt III absorption observed at 4100 Å: (i) Pt II; (ii) Pt IV.

sequence involving OH radicals. Clearly the radical ·CH_2OH produced in reaction (5) does not react rapidly with Pt II:

$$CH_3OH + OH \rightarrow ·CH_2OH + H_2O. \qquad (5)$$

About 15 % of the primary reducing species in irradiated water are hydrogen atoms. It is likely that these species reduce Pt II to Pt I in a reaction analogous to (4) although the data from fig. 1 are not conclusive. In the presence of N_2O (which reacts only slowly with H atoms), the maximum at 3100 Å, corresponding to some form of Pt I, is still appreciable (about 25 %) indicating the involvement of H atoms in the reduction process. Nevertheless, the possible contribution from an absorption tail of the 4500 Å band cannot be ruled out.

Following the pulse radiolysis of Pt II solutions, particularly at high dose, a residue of metallic platinum appears in the irradiation cell. This has been observed during steady-state radiolysis of Pt II.[2, 11] Although this effect presents complications in that metallic platinum catalyzes the thermal reduction of Pt II, it is irrelevant in single pulse experiments where only reactions of the precursors are studied.

Fig. 1a and 1b show that there is a small but significant absorption maximum at or around 3500 Å. It disappears rapidly (ca. 3 μsec) and is not observed in the

presence of either oxygen or methanol. The strong absorption bands at higher and lower wavelengths almost certainly overlap in the region around 3500 Å and, therefore, a quantitative estimation of the true effect of N_2O on this minor absorption peak, could not be made with any precision. Its origin is obscure.

EFFECT OF pH IN Pt II SOLUTIONS

Transient spectra from solutions of K_2PtCl_4 containing (a) 10^{-2} N KOH and (b) 10^{-2} N H_2SO_4 are shown in fig. 2. In both cases, the 4500 Å maximum is not observed although the 4100 Å band, which appears to be formed over two distinct
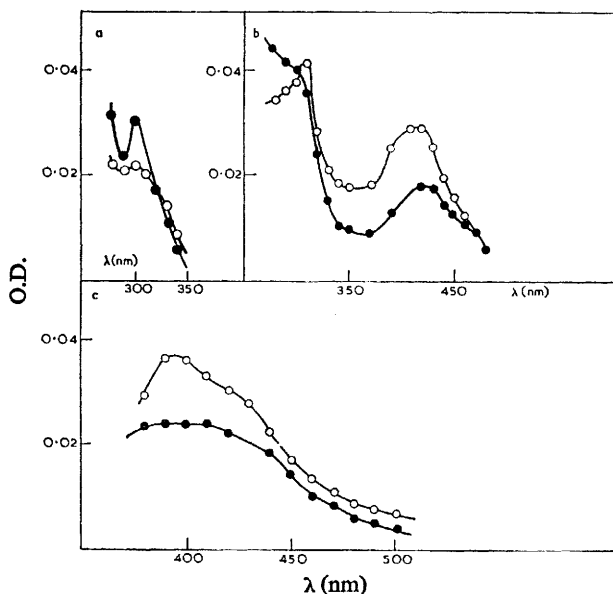

FIG. 2.—Transient spectra from nitrogen saturated Pt II solutions (10^{-3} M): (a) Neutral pH, 10^{-1} M methanol; (b) 10^{-2} N H_2SO_4; (c) 10^{-2} N KOH. ●, 1μsec after pulse; ○, 20 μsec after pulse.

time ranges, is similar to that observed in neutral solution. With 10^{-2} N H_2SO_4 present, the conversion of e_{aq}^- to H• (reaction (6))

$$e_{aq}^- + H_3O^+ \rightarrow H \cdot + H_2O \qquad (6)$$

must take precedence over the reduction of Pt II by e_{aq}^- (reaction (4)) since the concentration of K_2PtCl_4 was only 10^{-3} M. The fact that in acid solution, the intensity of the 3100 Å peak assigned to Pt (I) is similar to that in neutral solution implies that the reduction of Pt II by H atoms must be almost diffusion-controlled:

$$H + Pt\ II \rightarrow Pt\ I + H^+. \qquad (7)$$

Pt IV SOLUTIONS

Transient spectra from irradiated nitrogen-saturated solutions of K_2PtCl_6 at natural pH are shown in fig. 3a. Due to the absorption of 1 mM K_2PtCl_6, it was not possible to record any transient changes in optical density for wavelengths less than 3300 Å. Absorptions above 5500 Å are insignificant.

In the absence of methanol (fig. 3a) an absorption peak at 4100 Å develops over a period of about 20 μsec after the pulse. In the presence of 0·1 M methanol a

similar peak appears over the same time range but the final optical density is about 30 % greater. However, the initial spectrum produced during the pulse is different, particularly in the region around 3600 Å, from that observed in the absence of methanol. The addition of either 10^{-3} KOH or 10^{-4} HCl has no effect on the absorption at 4100 Å, although in N_2O-saturated solution the absorption is decreased by about 60 %, and by 50 % in oxygen-saturated solution. We conclude that the absorption maximum is due to some species of Pt III formed in the reactions,

$$e_{aq}^- + Pt\ IV \rightarrow Pt\ III \tag{8}$$

$$H + Pt\ IV \rightarrow Pt\ III + H^+. \tag{9}$$

In view of the large rate constant of reaction (8) and possibly (9) also, one would not expect electron-scavenging by either N_2O or oxygen to suppress completely the formation of Pt III.
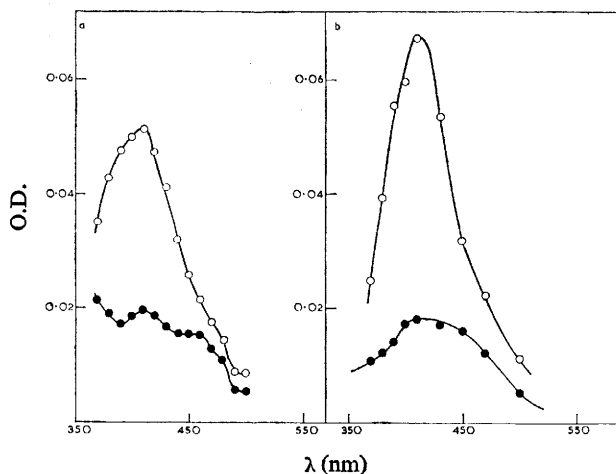

FIG. 3.—Transient spectra from N_2-saturated 10^{-3} M solutions of Pt IV : (a) neutral pH, methanol absent ; (b) neutral pH, 10^{-1} M methanol present. ●, 1 µsec after pulse ; ○, 20 µsec after pulse.

OH scavenging has some effect on the absorption around 3600 Å since in methanol solution the absorption in this region is reduced significantly. The increase of 30 % at 4100 Å in the presence of methanol suggests that reaction (10) may contribute to the overall yield of Pt III :

$$\cdot CH_2OH + Pt\ IV \rightarrow Pt\ III + HCHO + H^+. \tag{10}$$

PROPERTIES OF UNSTABLE SPECIES OF Pt III AND Pt I

The absorption maxima at 4100 and 4500 Å, and possibly a small shoulder or peak at 3500 Å, are assigned to transient Pt III complexes. The kinetics of the decay at 4500 Å over 20 µsec, and the increase, over a similar time range, at 4100 Å in 10^{-3} M N_2-saturated solution of Pt II are both exponential and yield similar time constants. Analysis of several experiments yield a decay constant of $1 \cdot 8 \times 10^5$ sec^{-1}, and a constant for the build-up at 4100 Å of $2 \cdot 0 \times 10^5$ sec^{-1}. The kinetics are unaffected by the presence of nitrous oxide and are independent of ionic strength. The change in the total absorption spectra as a function of time after the pulse is shown in fig. 4. The well-defined isobestic point at 4300 Å provides conclusive evidence that the species absorbing at 4500 Å is the precursor of the species absorbing at 4100 Å. Similar

results were obtained in oxygenated solution. We conclude therefore, that the 4500 Å absorption is produced directly by OH oxidation of Pt II. It has been shown [2] that the reaction between Pt II and H_2O_2 is very slow and under the conditions of the present experiments, the reaction during the pulse of hydrogen peroxide can be ignored.

Unlike the 4500 Å absorption, that observed at 4100 Å can be produced both by oxidation of Pt II and by reduction of Pt IV by e_{aq}^-. The latter reaction is diffusion controlled, and therefore, the product is formed during the pulse. The spectrum of this species, which is probably a precursor of the species absorbing at 4100 Å could not be resolved completely but contributes to the initial absorption from Pt IV solutions shown in fig. 3a. The kinetics of the formation of the 4100 Å peak over the first 20 μsec are exponential, the rate constant being $1\cdot8 \times 10^5$ sec^{-1}.
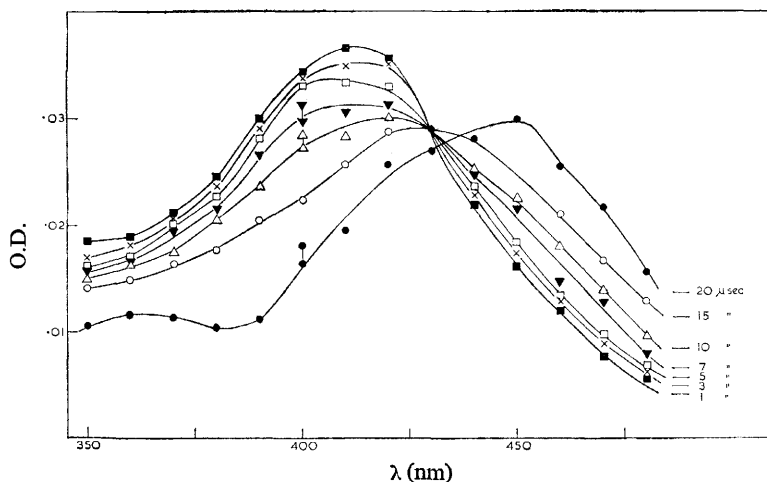

FIG. 4.—Transformation of the Pt III intermediates. Decay of the 4500 Å and growth of the 4100 Å absorption bands.

A transient spectrum with peaks at 3000 and 4150 Å observed during pulse radiolysis of Pt II, has been assigned to a species of Pt I (Baxendale *et al.*).[4, 19] The present work, however, would allow only the assignment of the former peak to Pt I. The absorption decays by first-order kinetics which are independent of ionic strength, indicating that this species does not decay by a simple bimolecular disproportionation process. On the basis of the formation of this species by reduction of Pt II by both e_{aq}^- and H atoms, the extinction coefficient $\varepsilon_{Pt\,I}^{3100}$ is $2\cdot9 \times 10^3$ M^{-1} cm^{-1} in both acid and neutral solution. A G (reducing species) of $3\cdot4$ has been assumed in the calculation.

## STRUCTURES OF TRANSIENT COMPLEXES OF Pt III AND Pt I

In neutral solution, the Pt II complex reacts as a charged entity, i.e., $[Pt\,Cl_4]^{2-}$ or $[Pt\,Cl_3 . H_2O]^-$. The uncharged complex $[Pt\,Cl_2(H_2O)_2]$ is present in trace amounts only. For Pt IV complexes, the structures $[PtCl_6]^{2-}$ and $[PtCl_4(H_2O)_2]$ are present in high proportions. The experimental data relevant to the identification of the transient species are : (i) oxidation of the Pt II complex by OH radicals produces a transient which absorbs at 4500 Å ; (ii) this transient decays by first-order kinetics to produce another transient species which absorbs at 4100 Å ; (iii) The 4500 Å peak is not observed in acid or alkaline solutions ; (iv) reduction of the Pt IV complex

produces a transient species for which the spectrum was not fully resolved; (v) the species produced by Pt IV reduction is transformed into another transient complex whose absorption spectrum is identical to that produced in the slower process following oxidation of Pt II (i.e., the 4100 Å peak); (vi) a transient species with an absorption maximum at 3100 Å is produced by reduction of Pt II by either e_{aq}^- or H atoms.

Oxidation of the Pt II complex can occur by either simple electron transfer to the OH radical or by OH addition to the complex. It is expected that the square planar complex of $[PtCl_4]^{2-}$ would be attacked by OH along the axis perpendicular to the molecular plane resulting in the square pyramidal ion:

$$ (11) $$
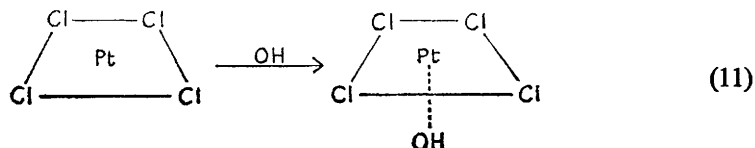
This ion would be unstable and would be converted to the trigonal bipyramid structure where the binding between the ligands and the central ion would be more stable.[20, 21] We therefore assign the transient absorption maximum at 4500 Å to the square pyramidal penta-complex of Pt III and the 4100 Å maximum to the trigonal bipyramid (B):
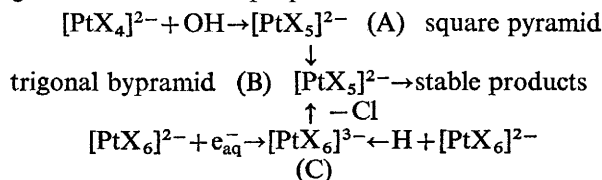

$$ (12) $$
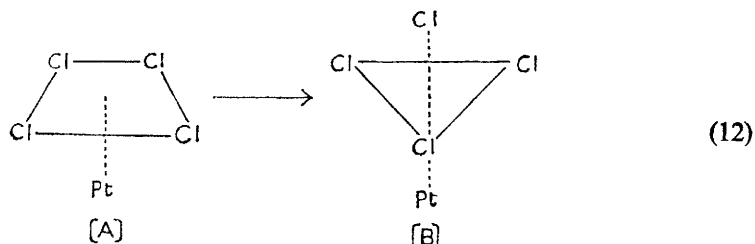
Reduction of Pt IV by e_{aq}^- would proceed initially by electron capture to form the 6 co-ordination complex $[PtCl_6]^{3-}$ (species (C)). We conclude that the 4100 Å absorption produced in this system arises by the dissociation of this entity to give a penta-complex:

$$ [PtCl_6]^{3-} \rightarrow [PtCl_5]^{2-} + Cl^-. \qquad (13) $$
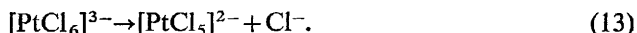
The most stable form of this species would be trigonal-bipyramid,[20, 22] i.e., species (B), hence the final form of the Pt III complex produced by reduction of Pt IV would differ from that formed by oxidation of Pt II only in the ligand composition. However, ligand replacement is accompanied usually by only a small displacement in the absorption maximum, an effect which might be difficult to detect experimentally. It is reasonable to apply the above argument to reactions of the corresponding aquo complexes.

The following reaction scheme is proposed.

$$ [PtX_4]^{2-} + OH \rightarrow [PtX_5]^{2-} \quad (A) \quad \text{square pyramid} $$
$$ \downarrow $$
$$ \text{trigonal bypramid} \quad (B) \quad [PtX_5]^{2-} \rightarrow \text{stable products} $$
$$ \uparrow \; -Cl $$
$$ [PtX_6]^{2-} + e_{aq}^- \rightarrow [PtX_6]^{3-} \leftarrow H + [PtX_6]^{2-} $$
$$ (C) $$

X denotes a ligand of the group Cl^-, OH^- and H_2O. In the last instance, a change in the charge of the complex would be involved.

The mode of decay of the final Pt III complex to form stable end-products is not clear. Pt III complexes in solution undergo an overall disproportionation reaction

$$\text{Pt III} + \text{Pt III} \rightarrow \text{Pt II} + \text{Pt IV}. \tag{14}$$

However, the failure to observe pure second-order kinetics for the decay of Pt III in the present work together with the lack of any effect of ionic strength on the kinetics, implies that the process is more complicated than reaction (14).

The reasons for the effect of acidity and alkalinity on the transient spectra from Pt II solutions are not clear. The 4100 Å absorption is present and reaches its maximum value in a time similar to that observed at neutral pH, although an appreciable proportion of the optical density is attained during the pulse. However, the 4500 Å absorption maximum is not observed. The qualitative differences are true pH effects since alteration of ionic strength, by the addition of inert salts, in no case affected the kinetics in neutral solution.

Square planar structures can be discussed in terms of pseudo-octahedral configurations in which the two vacant positions are occupied by solvent molecules.[22] If such a structure can be stabilized by addition of either OH^- or H_3O^+, it might be expected that the oxidation would proceed not by addition of an OH radical to the complex, but by electron transfer to OH. Thus, the square pyramid intermediate structure might not then be formed although two time-resolved processes are evidently involved.

The optical densities of both species of Pt III (4100 and 4500 Å) formed in irradiated solutions of Pt II are doubled when the solution is saturated with N_2O before irradiation. We therefore equate the G values of the species observed in N_2O-free solutions with the primary yield of OH radicals. Assuming that $G(OH) = 2.8$ in neutral solution, we calculate that $\varepsilon_{Pt\,III}^{4500} = 2.8 \times 10^3 \ M^{-1} \ cm^{-1}$, and $\varepsilon_{Pt\,III}^{4100} = 3.7 \times 10^3 \ M^{-1} \ cm^{-1}$.

We have little information on the structure of the Pt I complex formed by reduction of Pt II by either e_{aq}^- or H atoms. The initial reaction is probably an electron attachment to form the $[PtCl_4]^{3-}$ complex. The decay of the absorption maximum at 3100 Å is first order which would indicate that the initial product decays by transformation of the co-ordination complex into, ultimately, a solvated Pt^+ ion :

$$[PtCl_4]^{3-} \xrightarrow[-3Cl]{H_2O} PtCl\,(H_2O)n \rightarrow Pt^+. \tag{16}$$
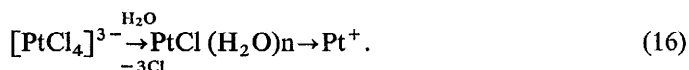
The formation of a metallic residue in the cell after repeated pulsing of the solution supports this mechanism since Pt^+ would be expected to disproportionate :

$$\text{Pt I} + \text{Pt I} \rightarrow Pt° + \text{Pt II}. \tag{17}$$

On this basis the absorption is assigned to the species $PtCl(H_2O)n$.

The present study illustrates the potential value of pulse radiolysis methods in the general field of the structure and physical chemistry of co-ordination complexes. Since short-lived unstable configurations must be involved in redox processes in which changes occur in the co-ordination number, their direct observation and measurement under the realistic conditions of liquid solutions at room temperature is of considerable interest.

[1] A. A. Balandin, V. I. Spitsyn, L. I. Barsova and V. I. Duzhenkow, *Zhur. Fiz. Khim.*, 1959, **33**, 736.

[2] M. Haissinsky, *Radiation Res.*, 1962, **17**, 274.

[3] M. Haissinsky, *J. Chim. Physique*, 1963, **60**, 402.

[4] J. H. Baxendale, E. M. Fielden and J. P. Keene, *Proc. Roy. Soc. A*, 1965, **286**, 320.

[5] E. J. Hart and J. W. Boag, *J. Amer. Chem. Soc.*, 1962, **84**, 4090.

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

[7] G. E. Adams, J. W. Boag and B. D. Michael, *Trans. Faraday Soc.*, 1965, **61**, 1674.

[8] D. P. Mellor, *Chem. Rev.*, 1943, **33**, 137.

[9] C. K. Jörgenson, *Acta Chim. Scand.*, 1965, **10**, 518.

[10] J. Chatt, G. A. Gumlen and L. E. Orgel, *J. Chem. Soc.*, 1958, 486.

[11] R. K. Broszkiewicz, unpublished.

[12] F. Basolo and R. G. Pearson, *Mechanisms of Inorganic Reactions* (J. Wiley & Sons Inc., New York, 1958), pp. 192, 402.

[13] L. F. Grantham, T. S. Ellemen and D. S. Martin, *J. Amer. Chem. Soc.*, 1955, **77**, 2365.

[14] A. A. Grinberg and Yu. N. Kukushkin, *Zhur. Neorg. Khim.*, 1957, **2**, 2360.

[15] H. Remy, *Treatise on Inorganic Chem.* (Elsevier Publ. Co.), 1956, vol. II, p. 349.

[16] R. L. Rich and H. Taube, *J. Amer. Chem. Soc.*, 1954, **76**, 2608.

[17] A. F. Messing, *Diss. Abstr.*, 1958, **18**, 387.

[18] M. Anbar and J. K. Thomas, *J. Physic. Chem.*, 1964, **68**, 3829.

[19] J. H. Baxendale, E. M. Fielden, C. Capellos, J. M. Francis, J. W. Davies, M. Ebert, C. W. Gilbert, J. P. Keene, E. J. Land, A. J. Swallow and J. M. Nosworthy, *Nature*, 1964, **201**, 468.

[20] R. C. Rumfeldt, private communication.

[21] H. M. E. Cardwell, *Chem. and Ind.*, 1955, 422.

[22] F. Basolo, B. D. Stone and R. G. Pearson, *J. Amer. Chem. Soc.*, 1953, **75**, 819.