

Steady-state and Pulse Radiolysis of some Palladium(II) Complexes

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Steady-state and pulse radiolysis studies of three complementary palladium(II) complexes, $[\text{Pd}(\text{bipy})\text{Cl}_2]$, $[\text{Pd}(\text{bipy})(\text{HypO})]\text{Cl}$ and $[\text{Pd}(\text{HypO})_2]$ (bipy = 2,2'-bipyridine, HypO = 4-hydroxy-L-prolinate) have been performed. The site of attack of $e^-(\text{aq})$ and OH^\bullet radical in these complexes and the effect of γ irradiation on the optical activity of the complexes containing HypO has been assessed using optical absorption and circular dichroism techniques. The steady-state γ irradiation results for $[\text{Pd}(\text{bipy})\text{Cl}_2]$ and $[\text{Pd}(\text{bipy})(\text{HypO})]^+$ are significantly different from those of $[\text{Pd}(\text{HypO})_2]$ with both $e^-(\text{aq})$ and OH^\bullet . Precipitation of fine metal palladium particles is observed in the reaction of $e^-(\text{aq})$ with $[\text{Pd}(\text{HypO})_2]$. Formation of a new optically active species is observed in the reaction of OH^\bullet with both $[\text{Pd}(\text{HypO})_2]$ and $[\text{Pd}(\text{bipy})(\text{HypO})]^+$ accompanied by a substantial loss in optical activity of the parent complexes. The substitution of one amino acid ligand in $[\text{Pd}(\text{HypO})_2]$ with bipy leads to a change in the site of attack of $e^-(\text{aq})$ from the metal centre in the binary complex to the bipy ring in the ternary complex. The pulse-radiolysis results support inferences drawn from the steady-state γ -radiolysis investigations.

In the last couple of decades studies of the reactions of the hydrated electron, $e^-(\text{aq})$, and the OH radical together with the development of the pulse-radiolysis technique have led to the accumulation of a large amount of information on unusual valency states of metal ions in aqueous solutions. Use of the hydrated electron, a simple reagent which can undergo either an electron-transfer process or an adduct formation, has made it possible to demonstrate and study a number of new inorganic species in aqueous solution. Studies¹⁻⁶ on transition-metal ions have revealed that the availability of vacant 'd' orbitals facilitates their reduction by $e^-(\text{aq})$. Further, the substitution of co-ordinated H_2O ligands by other ligands significantly affects the reactivity of these complexes. Sometimes the reduced products are well known chemical species, while the existence of some unusual species has been demonstrated for the first time in aqueous solutions. Amino, ethylenediamine, ethylenediamine-tetraacetate, cyano and other complexes of some of the trivalent metal ions of the first transition series react at diffusion-controlled rates ($\approx 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) with the hydrated electron, the difference in any series being attributed to changes in the charge and radii of complexes.⁷ The products of these reactions are the corresponding divalent complexes. The divalent complexes on the other hand react with $e^-(\text{aq})$ at high rates but only some reach the diffusion-controlled limit. The products of these reactions are the monovalent ions. Little information is available about the fate of these monovalent species in the absence of oxidising additives. It is speculated that most probably they dimerise and then disproportionate. The exact mechanism of such processes is still unknown.

The reactions of the OH radical, a strong oxidising agent, with different transition-metal ions have also been widely studied and different mechanisms of oxidation, *viz.* (i) inner-sphere substitution, (ii) hydrogen-atom abstraction and (iii) outer-sphere electron transfer, have been demonstrated. A novel mechanism involving five-co-ordinated trigonal-bipyramidal Pt^{III} has been proposed⁸ for the reaction of square-planar $[\text{PtCl}_4]^{2-}$ with OH^\bullet , while, with $[\text{Co}(\text{NH}_3)_5(\text{py})]^{3+}$ (py = pyridine) this radical induces reduction of the complexed metal ion.⁹ The reactions of OH^\bullet thus offer interesting possibilities.

However, the reactions of $e^-(\text{aq})$ and OH^\bullet with complexes of the second and third transition series have not been investigated as extensively as those of the first. We therefore investigated the

steady-state and pulse radiolysis of aqueous solutions of three complementary binary and ternary complexes.^{10,11} *viz.* $[\text{Pd}(\text{bipy})\text{Cl}_2]$, $[\text{Pd}(\text{bipy})(\text{HypO})]\text{Cl}$ and $[\text{Pd}(\text{HypO})_2]$ where bipy is 2,2'-bipyridine and HypO is 4-hydroxy-L-prolinate which is an optically active and biologically important amino acid. The objective of these studies is to investigate the site of attack of $e^-(\text{aq})$ and OH^\bullet and to monitor the effect of γ irradiation on these systems using optical absorption and circular dichroism (CD) techniques. It is also proposed to assess the role of co-ordinated ligands in stabilising the oxidation state of palladium ions.

Experimental

Synthesis.—The ternary complex was synthesised by a two-step reaction. In the first step the complex $[\text{Pd}(\text{bipy})\text{Cl}_2]$ was precipitated by treating $[\text{Pd}(\text{C}_6\text{H}_5\text{CN})_2\text{Cl}_2]$ prepared as reported¹² with a stoichiometric (1:1) amount of bipy in chloroform. The precipitate was filtered off, washed with chloroform and vacuum dried. In a second step a suspension of $[\text{Pd}(\text{bipy})\text{Cl}_2]$ in water was treated with the amino acid and NaHCO_3 in 1:1:1 molar ratio. On warming with continuous magnetic stirring a yellow solution was obtained. This was filtered and pumped dry to yield $[\text{Pd}(\text{bipy})(\text{HypO})]\text{Cl}$. The complex was purified by repeated extraction in ethanol to remove the traces of NaCl formed as a by-product and then vacuum dried. Crystals were obtained by gradual evaporation of an aqueous solution of the purified complex [Found (Calc. for $\text{C}_{15}\text{H}_{16}\text{ClN}_3\text{O}_3\text{Pd}\cdot 2\text{H}_2\text{O}$): C, 38.95 (38.80); H, 3.90 (4.30); Cl, 7.90 (7.65); N, 8.70 (9.05)%].

The binary derivative $[\text{Pd}(\text{HypO})_2]$ was synthesised by treating PdCl_2 with the amino acid in 1:2 molar ratio in water. The reaction mixture was refluxed for a few hours with magnetic stirring. The resulting yellow solution was concentrated on a water-bath and filtered. Yellow, needle-shaped crystals of the binary complex separated from the clear solution after 1 week. They were washed with acetone and dried in air [Found (Calc. for $\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_6\text{Pd}\cdot 3\text{H}_2\text{O}$): C, 28.65 (28.55); H, 5.40 (5.25); N, 6.80 (6.65)%].

The crystal structures of both these complexes have been reported.^{10,11} Millimolar solutions of the complexes were prepared in deionised 'nanopure' water for these studies. All

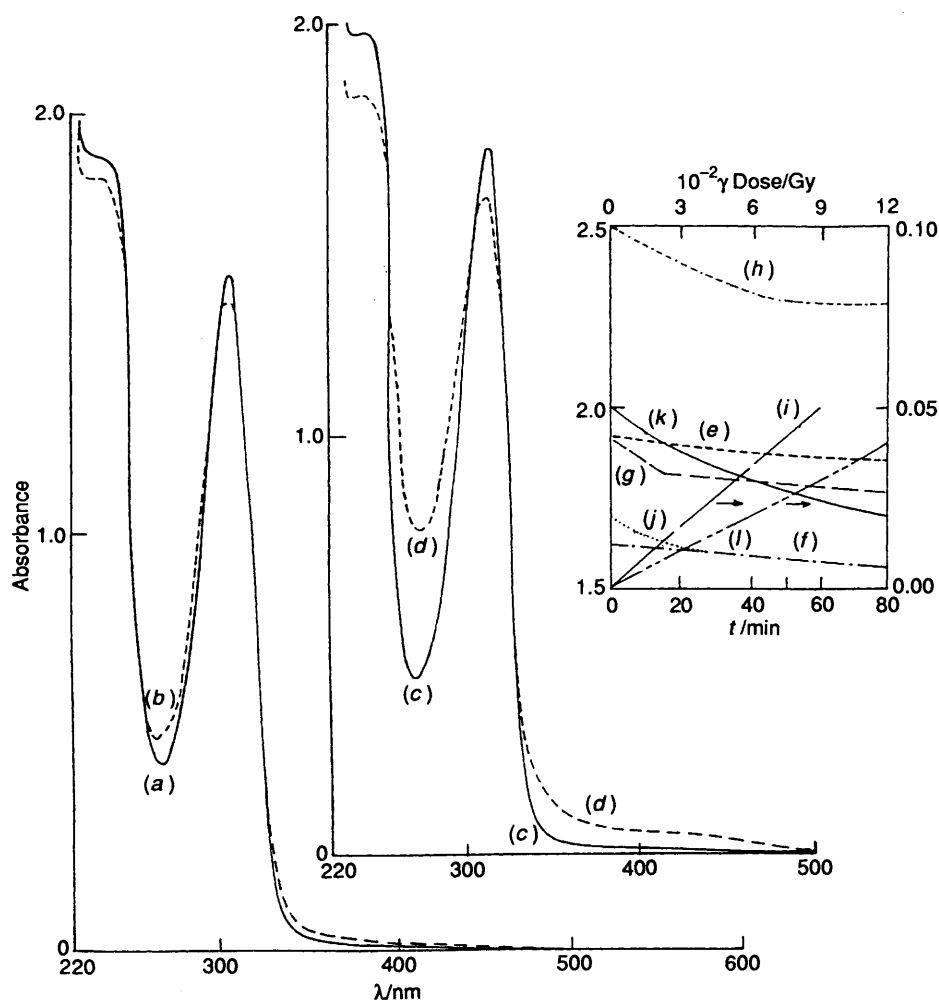
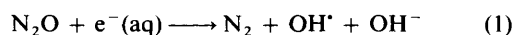


Fig. 1 Steady-state optical absorption spectra of an aqueous solution ($1.9 \times 10^{-4} \text{ mol dm}^{-3}$) of $[\text{Pd}(\text{bipy})(\text{HypO})]^+$ (a) and (c) before γ irradiation, and upon reaction with (b) $e^-(\text{aq})$ and (d) OH^\bullet (after γ irradiation for 80 min). Inset shows variation in absorbance as a function of γ dose: $[\text{Pd}(\text{bipy})(\text{HypO})]^+$ with $e^-(\text{aq})$, at 240 (e) and 308 nm (f), and with OH^\bullet at 400 (i) and 308 nm (j); $[\text{Pd}(\text{bipy})\text{Cl}_2]$ with $e^-(\text{aq})$ at 308 (g) and 240 nm (h) and with OH^\bullet at 308 (k) and 400 nm (l)

other chemicals used were of AnalaR grade purity. Nitrogen and N_2O gases used were of Iolar grade (Indian Oxygen Ltd.).

Irradiation.—Pulse-radiolysis experiments were carried out with high energy ($1.12 \times 10^{-12} \text{ J}$, 50 ns) electron pulses from a linear accelerator.¹³ An aerated aqueous solution of KSCN (10 mmol dm^{-3}) was used to monitor the dose delivered per pulse with $G\varepsilon = 2152 \text{ m}^2 \text{ mol}^{-1}$ for the transient $(\text{SCN})_2^-$ species.¹⁴ The dose delivered per pulse was 16 Gy. The time dependence of the transient absorption was recorded on a storage oscilloscope interfaced to a PC-XT computer for kinetic analysis.¹⁵ The reactions of OH^\bullet were studied in N_2O -saturated solutions where $e^-(\text{aq})$ is quantitatively converted into OH^\bullet ($k_1 = 9.1 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) with $G(\text{OH}^\bullet) = 5.6$ (species per $1.6 \times 10^{-17} \text{ J}$ of energy absorbed) according to reaction (1).



The reaction of $e^-(\text{aq})$ was studied in N_2 -saturated solution containing 0.5 mol dm^{-3} Bu'OH to scavenge the OH^\bullet with $G[e^-(\text{aq})] = 2.7$ according to reaction (2).



For steady-state studies, γ irradiation was carried out using a ^{60}Co gamma source at a dose rate of 15 Gy min^{-1} as determined by a Fricke dosimeter. The error in the measurement of rate constant is within 10%.

Analysis.—The optical absorption spectra of these complexes in aqueous solution (pH 6.0) were recorded at room temperature, before and after γ irradiation, on a Hitachi-330 spectrophotometer. Circular dichroism spectra of the γ -irradiated and non-irradiated aqueous solutions of these complexes were recorded on a Jobin Yvon dichrograph III UVIR using a 1 cm cylindrical quartz cell. The spectra were calibrated using a dioxane solution of isoandrosterone ($25 \text{ mg}/20 \text{ cm}^3$, $\Delta\varepsilon = +0.33 \text{ m}^2 \text{ mol}^{-1}$ at 304 nm) as standard.

Results and Discussion

Reactions with $e^-(\text{aq})$.—(a) *Steady-state γ radiolysis.* (i) *Optical absorption studies.* Fig. 1(a) shows the optical absorption spectrum of an aqueous solution of $[\text{Pd}(\text{bipy})(\text{HypO})]^+$ before γ irradiation. It exhibits two bands at 240 and 308 nm, which correspond to the $\pi-\pi^*$ transition of bipyridine. On γ irradiation the absorption at these two wavelengths decreases with a very small increase in absorption at 260 and 370 nm as can be seen from Fig. 1(b). Fig. 1(e) and 1(f) show the variation of the absorbance as a function of γ dose at 240 and 308 nm respectively. The absorption at 308 nm [*viz.* Fig. 1(f)] decreases linearly, while the decrease at 240 nm was non-linear [*viz.* Fig. 1(e)]. The non-linear decrease may be due to a contribution from some other stable product formed on γ irradiation. The increased absorption at 260 nm also supports this observation. The linear decrease in absorption at 308 nm may be considered as free from interference of other products. Considering this

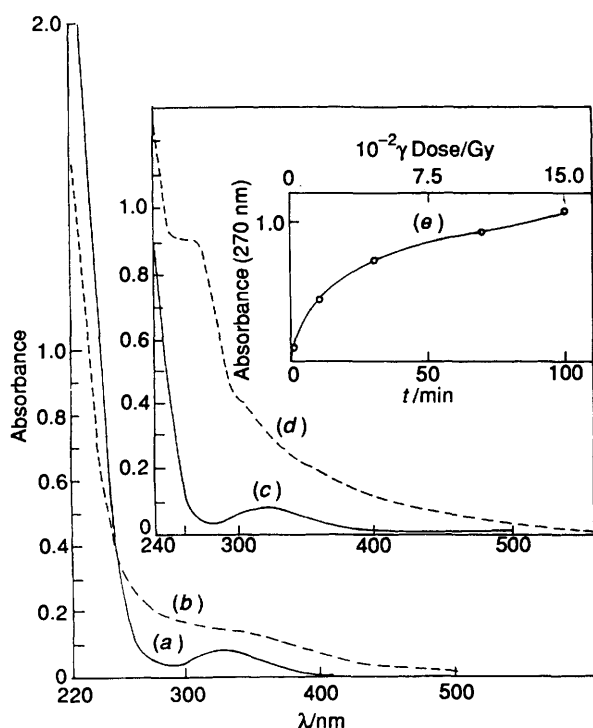


Fig. 2 Steady-state optical absorption spectra of an aqueous solution ($1.7 \times 10^{-4} \text{ mol dm}^{-3}$) of $[\text{Pd}(\text{HypO})_2]$ (a) and (c) before γ irradiation, (b) with $e^-(\text{aq})$ and (d) with OH^- after γ irradiation for 80 min. Inset shows (e) the variation of absorbance at 270 nm as a function of γ dose for OH^- radical reaction

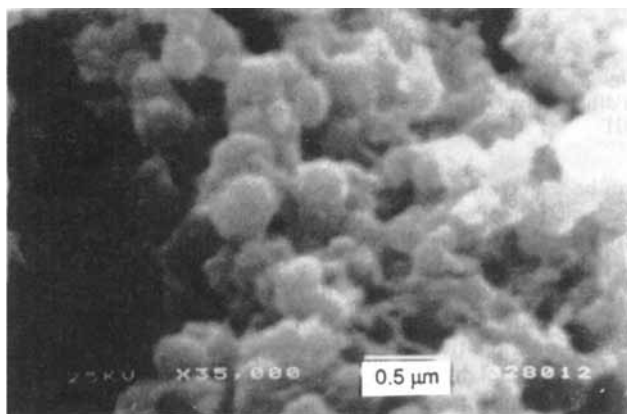


Fig. 3 Scanning electron micrograph ($\times 35\,000$) of fine palladium metal particles precipitated by reaction of $e^-(\text{aq})$ with $[\text{Pd}(\text{HypO})_2]$ during steady-state γ radiolysis

linear decrease to be due to decomposition of the complex on γ irradiation, $G(\text{complex decay})$ was determined to be 0.042.

γ Irradiation of an aqueous solution of $[\text{Pd}(\text{bipy})\text{Cl}_2]$ shows a similar behaviour. Fig. 1(g) and 1(h) show the decrease in absorption at 308 and 240 nm as a function of the γ dose. From the linear decrease in absorbance, $G(\text{complex decay})$ was determined to be 0.1. This is also quite low compared to $G[e^-(\text{aq})]$.

Fig. 2(a) and 2(b) show the optical absorption spectrum of an aqueous solution of $[\text{Pd}(\text{HypO})_2]$ before and after γ irradiation, respectively. This complex shows only one broad band at 320 nm. On γ irradiation an increase in absorption is observed in the region 280–400 nm [Fig. 2(b)]. Owing to the absorption of the complex in the same region, $G(\text{complex decay})$ could not be determined. Fine particles of palladium metal were observed in the irradiated sample. X-Ray diffraction studies of these particles showed their amorphous nature.

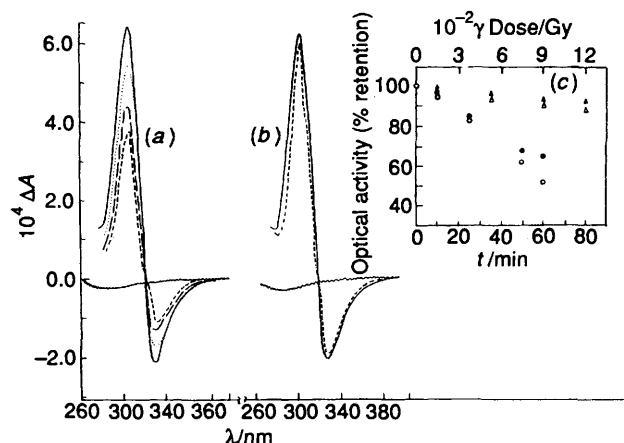


Fig. 4 The CD spectra of an aqueous solution ($1.9 \times 10^{-4} \text{ mol dm}^{-3}$) of $[\text{Pd}(\text{bipy})(\text{HypO})]^+$ before and after steady-state γ radiolysis; (a) with OH^- for different times of γ irradiation; (b) with $e^-(\text{aq})$ at the end of 80 min of γ irradiation; (c) percentage retention of optical activity of bipy ($\pi-\pi^*$) and palladium d-d bands as a function of time of irradiation, (i) d-d (Δ), bipy band (\blacktriangle) with $e^-(\text{aq})$ and (ii) d-d (\circ) and bipy and (\bullet) with OH^-

Scanning electron microscopic investigations suggest the average particle size to be in the range of 1–5 μm as can be seen from Fig. 3 which shows a representative electron micrograph of these fine particles.

(ii) *Site of attack.* The similar optical absorption results obtained on γ irradiation of the aqueous solutions of $[\text{Pd}(\text{bipy})(\text{HypO})]^+$ and $[\text{Pd}(\text{bipy})\text{Cl}_2]$ shows that the $e^-(\text{aq})$ must be reacting with a common site in the two complexes. Further, γ irradiation of an aqueous solution of neat bipyridine showed identical results. This suggests that in these complexes $e^-(\text{aq})$ must be reacting with the bipyridine ring, forming an adduct. However, in the case of $[\text{Pd}(\text{HypO})_2]$ the precipitation of palladium metal particles confirms that the site of $e^-(\text{aq})$ attack is the palladium(II) centre.

(iii) *Circular dichroism studies.* Fig. 4(b) shows the CD spectra of $[\text{Pd}(\text{bipy})(\text{HypO})]^+$ before and after γ irradiation. This complex exhibits two Cotton effects, one small and negative at 328 nm and the other large and positive at 308 nm. The negative effect at 328 nm ($\Delta\epsilon = -0.11 \text{ m}^2 \text{ mol}^{-1}$) is due to the palladium d-d ($d_{xy} \rightarrow d_{x^2-y^2}$) transition of A symmetry (${}^1A_{2g} \leftarrow {}^1A_{1g}$). The intense positive effect ($\Delta\epsilon = +0.34 \text{ m}^2 \text{ mol}^{-1}$) is due to the long-axis polarised intraligand $\pi \rightarrow \pi^*$ (${}^1B_1 \leftarrow {}^1A_1$) transition of bipy which is activated through the vicinal effect of the imino-nitrogen of hydroxyproline which becomes asymmetric on co-ordination. It is of interest that the d-d band of A symmetry is not resolved in the optical absorption spectrum of the complex, as can be seen from Fig. 1(a). The binary complex also exhibits two Cotton effects, one small and positive at 360 nm ($\Delta\epsilon = +0.058 \text{ m}^2 \text{ mol}^{-1}$) and the other large and negative at 314 nm ($\Delta\epsilon = -0.093 \text{ m}^2 \text{ mol}^{-1}$) [Fig. 5(b)]. The positive effect at 360 nm has been assigned to the d-d transition of A symmetry ($d_{xy} \rightarrow d_{x^2-y^2}$) while the negative one at 314 nm has been assigned to the d-d transition ($d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$) of E symmetry (${}^1E_g \leftarrow {}^1A_{1g}$). Here again the advantage of the CD technique over absorption spectroscopy in resolving the overlapping bands is apparent as these two d-d bands are not resolved in the absorption spectrum which shows only a single broad absorption band centred around 320 nm ($\epsilon = 30 \text{ m}^2 \text{ mol}^{-1}$), as can be seen from Fig. 2(a). In the post γ -irradiation studies of the ternary complex the optical activity of the bipy band at 308 nm and that of the d-d band at 328 nm were monitored, while that of both d-d bands was followed for the binary complex. The results of γ irradiation on the optical activity of the ternary complex are shown in Fig. 4(c) while Fig. 5(c) depicts the results obtained for $[\text{Pd}(\text{HypO})_2]$.

For the ternary complex no significant change in optical

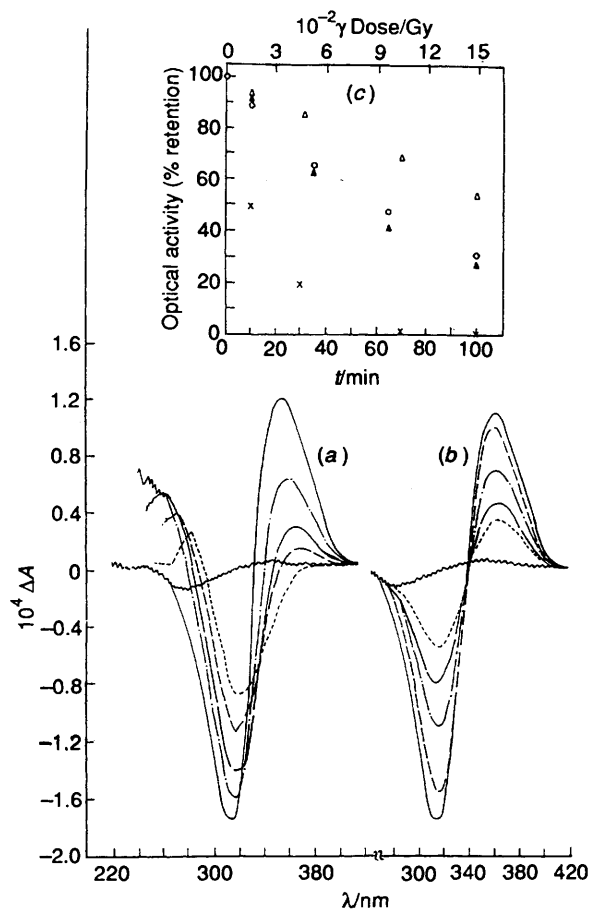


Fig. 5 The CD spectra of an aqueous solution ($1.7 \times 10^{-4} \text{ mol dm}^{-3}$) of $[\text{Pd}(\text{HypO})_2]$ before and after steady-state γ irradiation for different time intervals: (a) with OH^- , (b) with $e^-(\text{aq})$; (c) percentage retention of optical activity of A- and E-symmetry palladium d-d bands, (i) A (\blacktriangle) and E-symmetry band (\circ) with $e^-(\text{aq})$, (ii) A (\times) and E-symmetry band (\triangle) with OH^-

activity is seen even after 80 min of γ irradiation [Fig. 4(c)]. The magnitude of the Cotton effect for both bands remains practically the same, suggesting no significant degradation of the ternary complex. The value of $G(\text{complex decay})$ obtained from CD measurements was found to be 0.24. Since the dichroism measured is free from product interference this value is more reliable than that obtained from optical absorption studies which appears to be effected by product absorption in the region although monitored at very low γ dose. Both these values are, however, still much lower than $G[e^-(\text{aq})] = 2.7$, which suggests that the complex is being regenerated. However, the results for the binary complex $[\text{Pd}(\text{HypO})_2]$ are significantly different and suggest degradation of the complex. The reduction in optical activity of both d-d bands with time is comparable [*viz.* Fig. 5(c)] and indicates a 60% degradation of the complex at the end of 80 min of γ irradiation. The formation of any new optically active species is ruled out. Unlike in the optical absorption method, $G(\text{complex decay})$ in this case could be evaluated from CD measurements as 1.1. This value is understandable since it refers to a two-electron reduction process.

(b) *Pulse-radiolysis studies.* The reaction of $e^-(\text{aq})$ with these complexes was studied by following its decay (700 nm) in the presence of different complex concentrations. The decay becomes faster and shows first order behaviour with respect to the concentration of the complex. Fig. 6(a) and 6(b) show a typical decay of $e^-(\text{aq})$ in the absence and presence of $[\text{Pd}(\text{bipy})(\text{HypO})]^+$, respectively. The pseudo-first-order rate constant (k_{obs}) increased linearly with solute concentration as

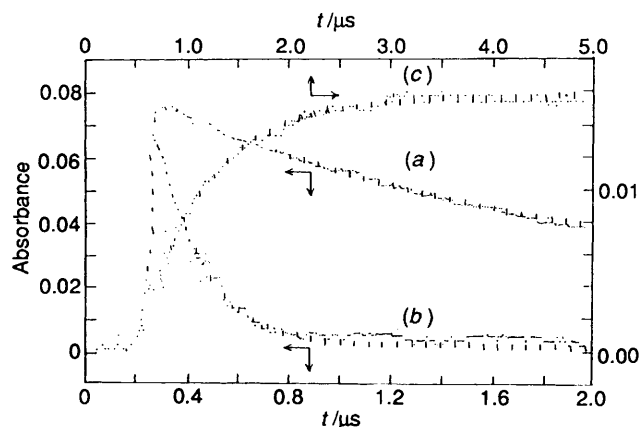


Fig. 6 Absorption vs. time signals for the decay of $e^-(\text{aq})$ (a) in the absence and (b) in the presence of $[\text{Pd}(\text{bipy})(\text{HypO})]^+$ ($1.8 \times 10^{-4} \text{ mol dm}^{-3}$); (c) growth of transient band (345 nm) formed on reaction of OH^- with $[\text{Pd}(\text{bipy})(\text{HypO})]^+$

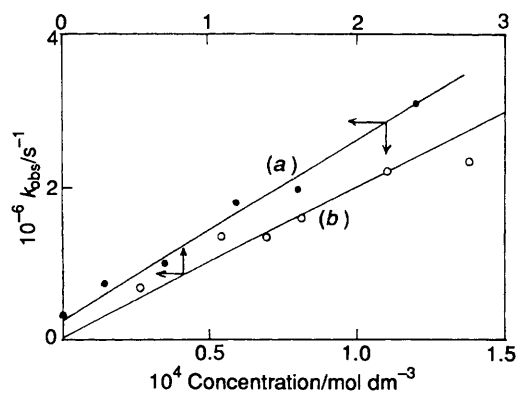


Fig. 7 Variation of the first-order rate constant (k_{obs}) with solute $[\text{Pd}(\text{bipy})(\text{HypO})]^+$ concentration in the reaction of (a) $e^-(\text{aq})$ and (b) OH^-

can be seen from Fig. 7(a). The second order rate constant for the reaction of $e^-(\text{aq})$ with $[\text{Pd}(\text{bipy})(\text{HypO})]^+$ determined from the slope of Fig. 7(a) is $2.4 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The role of the $\text{Bu}^{\bullet}\text{OH}$ radical formed on H-atom abstraction by OH^- was studied independently during pulse radiolysis of an N_2O -saturated aqueous solution of $\text{Bu}^{\bullet}\text{OH}$ (1.0 mol dm^{-3}) containing a relatively very low concentration of the complex ($1.0 \times 10^{-4} \text{ mol dm}^{-3}$). These studies showed the absence of the transient band in the 300–600 nm region suggesting that the radicals produced by radiolysis of $\text{Bu}^{\bullet}\text{OH}$ are unreactive towards the complex.

Time-resolved studies showed the formation of a new band with $\lambda_{\text{max}} = 345 \text{ nm}$ [Fig. 8(a)]. This band was observed to decay by first-order kinetics with $t_{1/2} = 367 \mu\text{s}$. In N_2O -saturated solutions [to scavenge $e^-(\text{aq})$] the transient optical absorption at 340 nm was not observed. This shows that the band is due to the reaction of $e^-(\text{aq})$ with the complex. Under these conditions, the reactivity (rate constant \times concentration) of $e^-(\text{aq})$ with the complex is $5.0 \times 10^6 \text{ s}^{-1}$, which is much higher than its reactivity with itself ($2.5 \times 10^4 \text{ s}^{-1}$). Therefore, all the electrons are reacting with the complex. Thus, the concentration of the transient species ($\lambda_{\text{max}} = 345 \text{ nm}$) could be taken to be equal to that of $e^-(\text{aq})$. The absorption coefficient was determined to be $1.6 \times 10^2 \text{ m}^2 \text{ mol}^{-1}$. The fact that $G(\text{complex decay})$ obtained from both optical absorption and CD measurements in steady-state experiments is found to be much smaller than $G[e^-(\text{aq})]$ implies that the complex is being regenerated from the transient species with time. Pulse-radiolysis studies on an aqueous solution of $[\text{Pd}(\text{bipy})\text{Cl}_2]$ showed similar results [Tables 1, 2 and Fig. 8(b)]. These results also support the earlier conclusion drawn from the steady-state studies that $e^-(\text{aq})$ is reacting with

Table 1 Physical parameters of the transients formed on reaction of $e^-(aq)$ and OH^* with palladium(II) complexes

Complex	Second-order rate constant, $10^{-10}k/dm^3 mol^{-1} s^{-1}$		λ_{max}/nm		$10^{-2}\epsilon_{max}/m^2 mol^{-1}$	
	$e^-(aq)$	OH^*	$e^-(aq)$	OH^*	$e^-(aq)$	OH^*
$[Pd(bipy)(HypO)]^+$	2.4	0.71	345	340	1.6	2.0
$[Pd(bipy)Cl_2]$	2.9	1.1	345	345	1.5	1.3
$[Pd(HypO)_2]$	0.80	0.56	260	275	1.8	3.1

Table 2 Comparison of 'G' values obtained by different techniques and the site of attack of $e^-(aq)$ and OH^*

Complex	$e^-(aq)$			Site of attack	OH^*			Site of attack
	Optical absorption	Circular dichroism	Pulse radiolysis		Optical absorption	Circular dichroism	Pulse radiolysis	
$[Pd(bipy)(HypO)]^+$	0.042	0.24	2.5	bipy	0.30	0.48	4.8	bipy
$[Pd(bipy)Cl_2]$	0.10	<i>a</i>	2.4	bipy	0.16	<i>a</i>	4.5	bipy
$[Pd(HypO)_2]$	<i>b</i>	1.1	2.6	Pd	<i>b</i>	5.6	5.3	Pd

^a Optically inactive. ^b Radiolytic product interference.

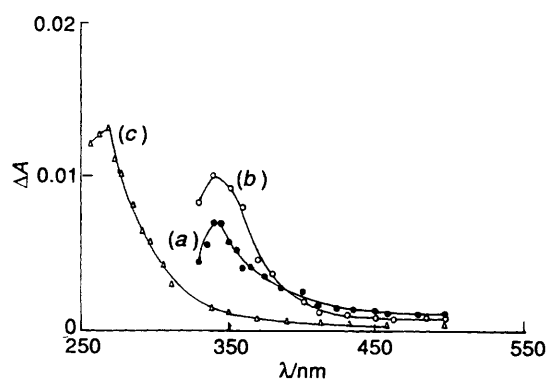


Fig. 8 Transient optical absorption spectra obtained after 1.6 μs of pulse radiolysis of aqueous solutions (N_2 saturated, $[Bu^*OH] = 0.5 mol dm^{-3}$ and $[complex] = 2.0 \times 10^{-4} mol dm^{-3}$) of (a) $[Pd(bipy)(HypO)]^+$, (b) $[Pd(bipy)Cl_2]$ and (c) $[Pd(HypO)_2]$

the bipy ring. The second-order rate constant for the reaction of $e^-(aq)$ with neat bipy is known to be very high ($2.0 \times 10^{10} dm^3 mol^{-1} s^{-1}$), whereas that with aliphatic amino acids is quite low ($\approx 10^7 dm^3 mol^{-1} s^{-1}$).¹⁶ Further, the transient band formed on reaction of $e^-(aq)$ with bipyridine is known¹⁷ to occur at $\lambda_{max} = 365 nm$. In the present case λ_{max} is observed at 345 nm. This shift may be due to the co-ordination with palladium. From these results it is concluded that $e^-(aq)$ is reacting with the bipyridine ring in these complexes, forming an adduct.

However, the reaction of $e^-(aq)$ with $[Pd(HypO)_2]$ shows different results. The second-order rate constant is $8.0 \times 10^9 dm^3 mol^{-1} s^{-1}$ and the transient band occurs at $\lambda_{max} = 260 nm$ [Table 1 and Fig. 8(c)]. Taking the concentration of $e^-(aq)$ to be equal to that of the transient species, the molar absorption coefficient is determined to be $1.8 \times 10^2 m^2 mol^{-1}$. This band decays by second-order kinetics with a rate constant of $1.4 \times 10^8 dm^3 mol^{-1} s^{-1}$. The difference in the decay kinetics and the position of the transient band as compared to what is observed with the other two complexes suggests that the site of attack is different and is the palladium centre in this case, as also inferred from the steady-state results.

Reactions with OH^* Radicals.—(a) Steady-state γ radiolysis.

(i) *Optical absorption studies.* Fig. 1(c) and 1(d) show the optical absorption spectra of aqueous solutions of $[Pd(bipy)(HypO)]^+$ before and after γ irradiation, respectively. On γ irradiation the absorption at 240 and 308 nm decreases and there is an appreciable increase in absorption at 260 and 400 nm [Fig.

1(i)]. The decrease in absorption at 308 nm as a function of γ dose is shown in Fig. 1(j). This is linear initially and levels off at higher doses. Considering the initial decrease in the absorbance as free from interference from other bands, $G(\text{complex decay})$ was determined to be 0.30. The non-linear decrease at longer γ -irradiation time may be due to the formation of other products. The $G(\text{complex decay})$ is much lower than $G(OH^*) = 5.6$ in N_2O -saturated solution.

γ Radiolysis of an aqueous solution of $[Pd(bipy)Cl_2]$ showed similar results [Fig. 1(k) and 1(l)]. From the linear decrease in absorbance of the complex at 308 nm, $G(\text{complex decay})$ was determined to be 0.16. However, γ radiolysis of an aqueous solution of $[Pd(HypO)_2]$ showed significantly different results [Fig. 2(c) and 2(d)]. A new absorption band grew at 270 nm and a broad band in the region 300–400 nm was also observed. Fig. 2(e) shows the increase in absorption at 270 nm as a function of γ dose. These results suggest the formation of a new species. The $G(\text{complex decay})$ could not be determined due to product absorption in the region monitored.

(ii) *Site of attack.* Independent studies on the reaction of OH^* with aqueous solutions of neat bipyridine showed similar results to those observed for $[Pd(bipy)(HypO)]^+$ and $[Pd(bipy)Cl_2]$. This suggests that the radicals are reacting at the bipyridine site of the complex, whereas the site of attack is speculated to be the palladium(II) centre in $[Pd(HypO)_2]$ based on CD results.

(iii) *Circular dichroism studies.* The CD spectra of neat and γ -irradiated ternary complex are shown in Fig. 4(a). For the ternary complex, post γ irradiation shows a significant loss of optical activity ($\approx 40\%$). Fig. 4(c) depicts the quantitative loss of optical activity as a function of irradiation time. The percentage reduction in optical activity of the bipy ($\pi-\pi^*$) band becomes relatively less as compared to that of the palladium d-d band on prolonged γ irradiation. This suggests a systematic degradation of the complex along with the formation of a new optically active species having a Cotton effect in the bipy $\pi-\pi^*$ region. The $G(\text{complex decay})$ was hence determined from the A-symmetry d-d band as 0.48. These results are consistent with the optical absorption studies. However, a significant difference between the two techniques is once again apparent in the sense that, whereas the optical absorption results suggest only the formation of a new species, the CD results go a step further and emphasise that the new species is optically active which in turn implies that the hydroxyproline moiety is intact and attached to palladium. However, the results for $[Pd(HypO)_2]$ are significantly different. Fig. 5(a) depicts the CD spectra of the neat and post γ -irradiated samples, while Fig. 5(c) shows the quantitative loss of optical activity on prolonged γ irradiation.

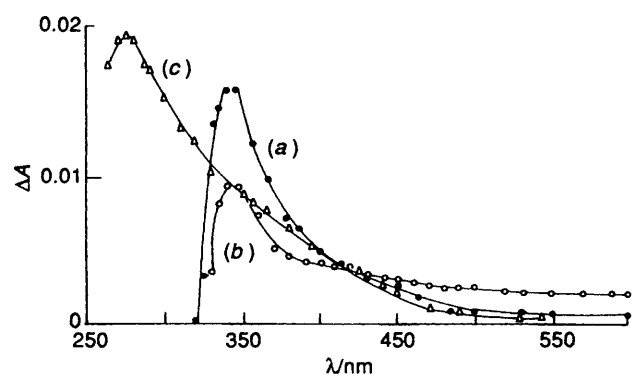


Fig. 9 Transient optical absorption spectra obtained immediately after pulse radiolysis of N_2O -saturated aqueous solutions (2.0×10^{-4} mol dm^{-3}) of (a) $[Pd(bipy)(HypO)]^+$, (b) $[Pd(bipy)Cl_2]$ and (c) $[Pd(HypO)_2]$

Unlike the case of $e^-(aq)$, the loss of optical activity of the d-d bands of A and E symmetry is not comparable. Whereas the optical activity of the A-symmetry band at 360 nm decreases progressively with increasing γ irradiation and vanishes completely at the end of 100 min of irradiation, that of the E-symmetry band at 314 nm shows a reduction of only 50% with band broadening and red shifting. Further, a new band at ≈ 270 nm exhibiting a positive Cotton effect begins to develop on prolonged γ irradiation. These results suggest the formation of a new optically active species, maybe five-co-ordinated, involving a change in oxidation state of palladium (as observed for $[PtCl_4]^{2-}$) and having a Cotton effect in the E-symmetry band region. This also accounts for the broadening, red shifting and the retention of optical activity of this band as compared to the A-symmetry band which vanishes completely. The results thus suggest the site of attack to be the palladium centre. The $G(\text{complex decay})$ determined from the A-symmetry band which is free from product interference was 5.6, which is equal to $G(OH^\cdot)$.

(b) *Pulse-radiolysis studies.* Fig. 9(a) shows the transient optical absorption spectrum obtained on pulse radiolysis of a N_2O -saturated aqueous solution of $[Pd(bipy)(HypO)]^+$. The transient with $\lambda_{max} = 345$ nm is observed to decay by first-order kinetics with $t_{1/2} = 130$ μs . This decay remained independent of dose per pulse (11–24 Gy) confirming its first-order kinetics. In the presence of Bu^1OH (to scavenge OH^\cdot) this transient band was not observed. This suggests that the band is due to the reaction of OH^\cdot with the complex. The corresponding rate constant was determined from formation kinetic studies by monitoring the growth of the band as a function of the solute concentration. The band was observed to grow by first-order kinetics [Fig. 6(c)], the rate constant increasing linearly with solute concentration [Fig. 7(b)]. The second-order rate constant for the reaction was determined to be 7.1×10^9 dm^3 mol^{-1} s^{-1} . The reactivity of OH^\cdot with the complex is 1.4×10^6 s^{-1} , which is much higher than its reactivity with itself (4.6×10^4 s^{-1}). Therefore, all the OH^\cdot radicals can be considered to have reacted with the complex and the concentration of the transient species would be equal to that of the OH^\cdot radicals. The molar absorption coefficient is thus determined to be 2.0×10^2 m^2 mol^{-1} . Pulse-radiolysis studies on the reaction of OH^\cdot with $[Pd(bipy)Cl_2]$ showed similar results [Fig. 9(b)] and the physical parameters are given in Tables 1 and 2. The absorption coefficient for the transient formed was determined on the basis of the complete reaction of OH^\cdot radicals with the complex. Since the nature of the transient formed in the two cases is similar, it must involve reaction of OH^\cdot at a common site which has to be the bipyridine ring. The high reactivity of OH^\cdot radicals with bipyridine¹⁶ and low reactivity with aliphatic amino acids (hydroxyproline) supports this observation. It is reported¹⁸ that OH^\cdot radicals add to the bipyridine ring as well as at the nitrogen site. Addition at nitrogen gives rise to a transient band

with λ_{max} at 260 nm, whereas addition to the bipyridine ring results in a transient band with $\lambda_{max} \approx 340$ –345 nm. In this case therefore the addition of the OH^\cdot radicals to the bipyridine ring is confirmed.

Fig. 9(c) shows the transient optical absorption spectrum obtained on pulse radiolysis of a N_2O -saturated aqueous solution of $[Pd(HypO)_2]$. It exhibits an absorption band with $\lambda_{max} \approx 275$ nm. The second-order rate constant for the reaction of OH^\cdot with this complex is determined to be 5.6×10^9 dm^3 mol^{-1} s^{-1} . In this case the different nature of the transient formed *vis-à-vis* its position and kinetics (Table 1), as compared to those of the other two complexes, suggests that the site of attack of the OH^\cdot is the palladium centre. Besides addition to the complex, OH^\cdot radicals are also known to undergo electron-transfer and hydrogen-abstraction reactions. That they are not undergoing one-electron-transfer reaction is inferred from independent studies with the N_3^\cdot radical (specific one-electron oxidant) obtained from the pulse radiolysis of a N_2O -saturated aqueous solution of N_3^- (1.0×10^{-2} mol dm^{-3}) and $[Pd(bipy)(HypO)]^+$ which failed to produce transient absorption in the region 300–600 nm. Further, the high rate constants for the OH^\cdot radical reaction (10^9 dm^3 mol^{-1} s^{-1}) with these complexes exclude the possibility of H-atom abstraction ($\approx 10^8$ dm^3 mol^{-1} s^{-1}).¹⁶ Therefore, the band observed in the present case must be due to OH^\cdot radical addition at the palladium centre.

Conclusion

The steady-state γ -radiolysis results for the ternary and binary palladium(II) complexes, with both $e^-(aq)$ and OH^\cdot , are significantly different. No substantial loss of optical activity is observed for the reaction of $e^-(aq)$ with $[Pd(bipy)(HypO)]^+$. However, with OH^\cdot there is a significant loss of optical activity and the formation of a new optically active species. Unlike this, the complex $[Pd(HypO)_2]$ shows a substantial loss of optical activity due to the fragmentation of the complex on reaction with both $e^-(aq)$ and OH^\cdot . Formation of fine particles of palladium metal has been observed for this complex due to the reaction of $e^-(aq)$ with the palladium(II) centre and a new optically active species is formed in its reaction with OH^\cdot . Pulse-radiolysis studies confirm the formation of new species due to the reaction of OH^\cdot with all three complexes. The site of attack of both $e^-(aq)$ and OH^\cdot is inferred to be the bipy ring in the complexes $[Pd(bipy)Cl_2]$ and $[Pd(bipy)(HypO)]^+$ whereas it is the palladium(II) centre in $[Pd(HypO)_2]$. Pulse-radiolysis studies adequately support the inferences drawn from steady-state γ radiolysis. The G values evaluated from optical absorption studies, although measured in the low-dose region, still suffer from radiolytic product absorption and lead to erroneous results. In such cases, for optically active complexes, the CD technique offers an alternative for evaluating reliable G values when the radiolytic product is optically inactive or by a suitable choice of Cotton-effect band when the radiolytic product is optically active.

The observation that the substitution of one hydroxyproline ligand in the binary complex by bipy renders the complex stable to reduction by $e^-(aq)$ is interesting. The fact that bipy has vacant π^* orbitals, which can accommodate electrons, may play a vital role in changing the site of $e^-(aq)$ attack from Pd^{II} in $[Pd(HypO)_2]$ to the bipy ring in $[Pd(bipy)(HypO)]^+$. Further investigations on analogous complexes are being carried out to substantiate these inferences.

Acknowledgements

The authors are extremely grateful to the referees for their many fruitful suggestions which have helped in making the manuscript more comprehensive.

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Received 14th December 1992; Paper 2/06610F