# Transient Species in the Reactions of Some Pyridyl Complex Ions with Hydrated Electrons

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The reactions of $e^-_{aq}$ with $Co(bipy)_3{}^{3+}$, $Ru(bipy)_3{}^{2+}$, and $Co(terpy)_2{}^{3+}$ give transient species whose reactivities are consistent with the view that they are radical anions of the pyridyl ligands.

PULSE radiolysis studies of the reactions of the hydrated electron, $e^-_{aq}$, with metal ion co-ordination compounds have given information about a variety of transient intermediates formed in the reduction process.[1] It has been suggested [2] that where such a reduction involves an overall change in spin state of the metal ion, *e.g.*, the change from a low-spin $Co^{III}$ complex to a high-spin $Co^{II}$, the first product might be a transient species having a non-equilibrium spin configuration, *e.g.*, low-spin $Co^{II}$. The reaction of the tris-(2,2′-bipyridyl)cobalt(III) ion, $Co(bipy)_3{}^{3+}$, with $e^-_{aq}$ gives a transient species which is a precursor to the final product $Co(bipy)_3{}^{2+}$, and has been interpreted in this way.[3] Evidence adduced in support was that the life-time of the intermediate is considerably reduced by the presence of known quenching agents for excited states. This might be expected since the $t^6_{2g}e_g$ configuration of the transient low-spin $Co^{II}$ can be considered as an excited state of the $t^5_{2g}e^2_g$ configuration of the high-spin $Co^{II}$.

However, another possibility, which is not at variance with any of the experimental evidence presented so far, is that the intermediate is not a $Co^{II}$ but a $Co^{III}$ species in which the electron resides on the bipyridyl ligand. Such a species, being an aromatic anion, would be expected to react with all the compounds found to be active quenching agents since they are all oxidants. The less active quenching agents used are not good oxidants, *e.g.*, $Na_2SO_4$, $MgSO_4$, or $BaCl_2$, but in view of the high concentrations required to produce any effect further investigation seems desirable.

In the present work we attempt to distinguish between these alternative interpretations.

## EXPERIMENTAL

*Materials.*—Except for those described below all materials were of analytical reagent grade purity and were not treated further before use. Hopkin and Williams G.P.R. grade t-butyl alcohol was recrystallised three times, and the tris-(2,2′-bipyridyl)ruthenium(II) complex, $Ru(bipy)_3{}^{2+}$, obtained as the chloride from G. F. Smith Chemical Co., was purified by precipitation as the perchlorate. The corresponding $Co(bipy)_3{}^{3+}$ and bis-(2,2′,2″-terpyridyl)-cobalt(III) were prepared as the chlorides [4] and purified by three recrystallisations as the perchlorates.

*Techniques.*—All solutions were made up with triply distilled water. Solutions were deaerated by pumping and shaking for γ-radiolysis, and by bubbling with pure argon for pulse radiolysis.

γ-Radiolyses were carried out in cylindrical Pyrex vessels fitted with silica spectrophotometer cells on sidearms for following the progress of reactions by absorption measurement. The apparatus and techniques for pulse radiolysis have been described.[5] For absorption measurements beyond 600 nm the Mullard SPD1 photodiode replaced the photomultiplier. Doses were obtained with the Fricke dosimeter and calculated by use of $G(Fe^{3+}) = 15{\cdot}6$.

The $Co^{II}$ produced in γ-radiolyses of $Co(bipy)_3{}^{3+}$ was estimated by the thiocyanate method.[6]

## RESULTS AND DISCUSSION

*Reactions of* $Co(bipy)_3{}^{3+}$.—*Pulse radiolysis.* We have confirmed Waltz and Pearson's observations [3] that in the reaction (1) a transient intermediate X is produced

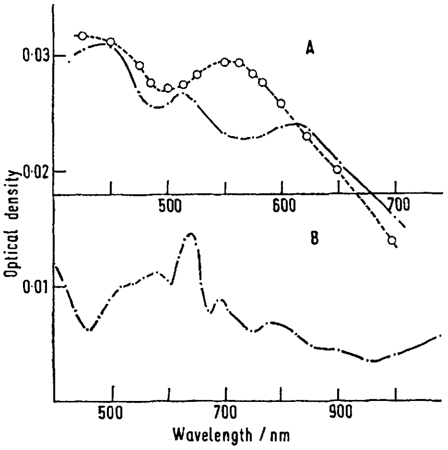

FIGURE 1 Transient spectra on pulse radiolysis of A, $Co(terpy)_2{}^{3+}$; the broken curve refers to immediately after the pulse, and the full curve, which is identical to that for $Co(terpy)_2{}^{2+}$, to 100 μs after the pulse; and B, $Co(bipy)_3{}^{3+}$ immediately after the pulse. Conditions: A, $10^{-4}$M-$Co(terpy)_2{}^{3+}$ and 0·5M-t-butyl alcohol after *ca.* 5 krad electron pulse; B, $10^{-4}$M-$Co(bipy)_3{}^{3+}$ and 0·1M-t-butyl alcohol after *ca.* 3 krad electron pulse

$$e_{aq}{}^- + Co(bipy)_3{}^{3+} \longrightarrow X \longrightarrow Co(bipy)_3{}^{2+} \quad (1)$$

which is a precursor to the final $Co^{II}$ compound. The intermediate has a broad absorption in the visible region (Figure 1) and extends at least as far as 1100 nm. We also confirmed that the species X reacts with $Co(bipy)_3{}^{3+}$ ($k = 8 \times 10^8$ l mol$^{-1}$ s$^{-1}$), with oxygen ($k = 1{\cdot}7 \times 10^9$ l mol$^{-1}$ s$^{-1}$), and with $Cr(CN)_6{}^{3-}$ ($k = 1{\cdot}5 \times 10^9$ l mol$^{-1}$ s$^{-1}$). However, we were unable to observe

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[1] J. H. Baxendale, *Quaderni Ricerca sci.*, 1970, **68**, 43.

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

[3] W. L. Waltz and R. G. Pearson, *J. Phys. Chem.*, 1969, **73**, 1941.

[4] F. H. Burstall and R. S. Nyholm, *J. Chem. Soc.*, 1952, 3570.

[5] J. P. Keene, *J. Sci. Instr.*, 1965, **41**, 493.

[6] E. B. Sandell, 'Colorimetric Determination of Traces of Metals,' Interscience Publishers, New York, 1950, p. 279.

any reaction with $Zn^{2+}$ even at 0·05M although they estimated $k = 2{\cdot}1 \times 10^{7}$ l mol$^{-1}$ s$^{-1}$ using $10^{-3}$M-$Zn^{2+}$ On the other hand we have found that the same transient X is produced in $10^{-4}$M-Co(bipy)$_3^{3+}$ containing 0·05M-$Zn^{2+}$, where from the rate constants of reaction (1) and (2) ($k_2 = 1{\cdot}5 \times 10^{9}$ l mol$^{-1}$ s$^{-1}$) [7] it can be calculated

$$Zn^{2+} + e^{-}_{aq} \longrightarrow Zn^{+} \qquad (2)$$

that almost all $e^{-}_{aq}$ reacts *via* (2). Hence reaction (3) must occur, for which we find $k = 2{\cdot}6 \times 10^{9}$ l mol$^{-1}$ s$^{-1}$.

$$Zn^{+} + Co(bipy)_3^{3+} \longrightarrow Zn^{2+} + X \qquad (3)$$

We also examined the effect of $BaCl_2$, $Na_2SO_4$, and $MgCl_2$ but found that with 0·02M the decay constant of X is only increased about twofold in each case. If X does react with these salts the calculated rate constants are 1·35, 2·0, and $1{\cdot}3 \times 10^{6}$ respectively, which are less by a factor of 3—4 than those obtained by Waltz and Pearson. We suggest that these compounds do not in fact react with X but that their effect is due either to the presence of reducing impurities, or to the kinetic salt effect on the X + Co(bipy)$_3^{2+}$ reaction. An impurity reacting with *k ca.* $10^{9}$ would produce the same effect if present at 0·1% at the concentration used. The kinetic salt effect is in the correct sense since the reaction is between positively charged ions.

*γ-Radiolyses.* It is clear that the nature of the reaction of the intermediate X with the compounds designated by Waltz and Pearson as quenching agents is important, since if X is an electron adduct to the ligand, all such reactions are likely to be reductions, *i.e.*, X will revert to the original $Co^{III}$ compound and the 'quencher' will be reduced. On the other hand a simple deactivation process need not involve such an electron transfer, and if none occurs the final product will be $Co^{II}$. Thus information on the final products, in particular the yield of $Co^{II}$, $G(Co^{II})$, is very relevant. The information can be obtained from γ-radiolyses and we γ-irradiated solutions of Co(bipy)$_3^{3+}$ containing oxygen, $Cr(CN)_6^{3-}$, and $ZnSO_4$, all of which are reported to be quenching agents, measuring $G(Co^{II})$ in each case. All these additives react with $e^{-}_{aq}$, so that we chose concentrations (calculated from the known rate constants [7]) which allow >90% of $e^{-}_{aq}$ to react with Co(bipy)$_3^{3+}$. As the Table shows, in the absence of any additive $G(Co^{II})$ is 2·65 which is the accepted value of $G(e^{-}_{aq})$. Also the solutes previously found very active, $O_2$ and $Cr(CN)_6^{3-}$, give low $G(Co^{II})$. The values obtained however are exactly as calculated from the measured rate constants if there is competition for X between the solutes (behaving as oxidants) and Co(bipy)$_3^{3+}$ itself, *i.e.*, reactions (4) and (5) or (6). We

$$X + Co(bipy)_3^{3+} \longrightarrow Co(bipy)_3^{2+} + Co(bipy)_3^{3+} \qquad (4)$$

$$X + Cr(CN)_6^{3-} \longrightarrow Co(bipy)_3^{3+} + Cr(CN)_6^{4-} \qquad (5)$$

$$X + O_2 \longrightarrow Co(bipy)_3^{3+} + O_2^{-} \qquad (6)$$

also find that $NO_2^{-}$ in the same conditions reduces ($GCo^{II}$) and therefore reacts with X whereas $Zn^{2+}$ is ineffective even at 0·05M. It is also interesting that Ru(bipy)$_3^{2+}$ reduces $G(Co^{II})$ almost to zero and hence reacts with X very rapidly.

Yields of $Co^{II}$ in the γ-radiolysis of Co(bipy)$_3^{3+}$. Neutral solutions of Co(bipy)$_3^{3+}$ containing 0·1M-methanol and the additives listed below. Doses *ca.* 8—50 × $10^{17}$ eV g$^{-1}$

| Additive | Concn. mM | [Co(bipy)$_3^{3+}$] mM | $G(Co^{II})$ [a] | $G(Co^{II})$ | $E°$/V |
|---|---|---|---|---|---|
| None | — | 0·10 | 2·65 | — | −0·02 [b] |
| $O_2$ | 0·25 | 1·00 | 2·60 | 1·40 | −0·19 [c] |
| $Cr(CN)_6^{3-}$ | 0·05 | 0·10 | 2·50 | 1·45 | −1·30 [d] |
| $Zn^{2+}$ | 50 | 0·10 | 2·40 | 2·40 | −2·5 to −3·2 [e] |
| $NO_2^{-}$ | 0·20 | 0·10 | 2·40 | 0·10 | — |
| Ru(bipy)$_3^{2+}$ | 0·05 | 0·50 | 2·40 | 0·20 | — |

[a] $G(CO^{II})_0$ is the value of $G(e^{-}_{aq})$ reacting with Co(bipy)$_3^{3+}$. Calculated from known $e^{-}_{aq}$ rate constants.[7] [b] Calculated [3] for X/Co(bipy)$_3^{3+}$. [c] J. H. Baxendale, M. D. Ward, and P. Wardman, *Trans. Faraday Soc.*, 1971, **67**, 2532. [d] D. A. Johnson, 'Some Thermodynamic Aspects of Inorganic Chemistry,' Cambridge University Press, 1968, p. 144. [e] J. H. Baxendale and R. S. Dixon, *Z. phys. Chem.* (*Frankfurt*), 1964, **43**, 161.

These observations suggest that X is oxidised by $O_2$, $Cr(CN)_6^{3-}$, $NO_2^{-}$, and Ru(bipy)$_3^{2+}$ and reverts to Co(bipy)$_3^{3+}$. Such reactions will only occur if the potentials of the couples involved are favourable with respect to that of X/Co(bipy)$_3^{3+}$. Assuming that X is Co(bipy)$_3^{2+}$ in the low-spin state, Waltz and Pearson [3] calculated $E° = -0{\cdot}02$ V for the latter, and from the values given in the Table it will be seen that the known $E°$ of the reacting species are all well below this.

It seems unlikely therefore that X is the low-spin state of Co(bipy)$_3^{2+}$. It must be a much more potent reducing agent and the suggested alternative, *viz.*, an anion of the bipyridyl ligand, would be expected to satisfy this requirement.

It is interesting that Ru(bipy)$_3^{2+}$ is such an efficient electron acceptor in this context since the corresponding $Ru^{I}$ compound is not known and one surmises that $E°$ of this couple must be very negative. This suggests that the reaction here is an electron transfer to give the anion of the bipyridyl ligand of Ru(bipy)$_3^{2+}$ indicating that such anion formation may be a general feature of bipyridyl complexes. In view of this a radiolysis investigation of Ru(bipy)$_3^{2+}$ was undertaken.

*Reactions of* Ru(bipy)$_3^{2+}$.—*Pulse radiolysis.* In neutral solution in the presence of t-butyl alcohol to remove OH and leave only the reaction (7) of $e^{-}_{aq}$

$$e^{-}_{aq} + Ru(bipy)_3^{2+} \longrightarrow Y \qquad (7)$$

with Ru(bipy)$_3^{2+}$, we have observed a transient species Y with the absorption spectrum shown in Figure 2. If it is assumed that all $e^{-}_{aq}$ reacts and $G(e^{-}_{aq}) = 2{\cdot}7$ then the decadic absorption coefficient for Y at 510 nm is $\varepsilon = 1{\cdot}2 \times 10^{4}$ l mol$^{-1}$ s$^{-1}$. Measurements of the decay of absorption of $e^{-}_{aq}$ at low concentrations of

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[7] M. Anbar and P. Neta, *Internat. J. Appl. Radiation Isotopes*, 1967, **18**, 493.

$Ru(bipy)_3^{2+}$ give $k = 8{\cdot}2 \times 10^{10}$ l mol$^{-1}$ s$^{-1}$ for the reaction.

The same transient absorption is given on the radiolysis of $50\mu$M-$Ru(bipy)_3^{2+}$ + 0·05M-$Zn^{2+}$ + 1·0M-$Bu^tOH$ where, as in the analogous $Co(bipy)_3^{3+}$ system, the first product of the $e^-_{aq}$ reduction must be $Zn^+$ which then reduces $Ru(bipy)_3^{2+}$. We find $k = 2{\cdot}5 \times 10^9$ l mol$^{-1}$ s$^{-1}$ for the reaction (8). The intermediate Y decays rapidly

$$Zn^+ + Ru(bipy)_3^{2+} \longrightarrow Zn^{2+} + Y \qquad (8)$$

by second-order kinetics with $k = 3{\cdot}5 \times 10^8$ l mol$^{-1}$ s$^{-1}$ to another species absorbing as shown in Figure 2. The final change to the permanent products is much slower extending over seconds.

As in the $Co^{III}$ system, the intermediate Y reacts with oxygen ($k = 1{\cdot}8 \times 10^9$ l mol$^{-1}$ s$^{-1}$) and with nitrite ion ($k = 2{\cdot}5 \times 10^7$ l mol$^{-1}$ s$^{-1}$).

In 0·05M-$HClO_4$, where the reducing species is the H atom, a different initial product is formed having peak absorption at 420 nm (Figure 2) compared with 510 nm for the $e^-_{aq}$ reduction. The formation process $Ru^{II}$ + H has $k = 9{\cdot}5 \times 10^9$ l mol$^{-1}$ s$^{-1}$. At 420 nm, $\varepsilon = 1{\cdot}8 \times 10^4$ l mol$^{-1}$ s$^{-1}$ for the primary product which decays by second-order kinetics with $k = 6{\cdot}6 \times 10^8$ l mol$^{-1}$ s$^{-1}$.

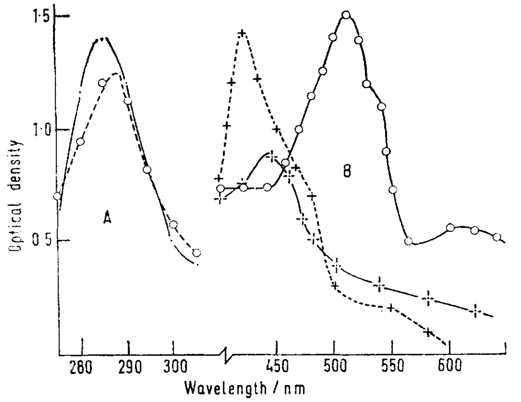

FIGURE 2 Spectra from irradiated $Ru(bipy)_3^{2+}$; A, $10^{-4}$M-$Ru(bipy)_3^{2+}$ and 0·5M-t-butyl alcohol before (full line) and after (broken line) 50 krad γ-irradiation. The spectrum in the visible range is unchanged. B, pulse radiolysis of $Ru(bipy)_3^{2+}$ in neutral and 0·05M-$HClO_4$ solution; the pulse dose is *ca.* 1 krad. Concentration of $Ru^{II}$ is 50 μM in neutral and 20 μM in acid solution; 0·5M-t-butyl alcohol was present in both: broken line, immediate H adduct; full lines, $e^-_{aq}$ adduct: ○, immediate; + after 50 μs. The optical density scale is for A; that for B is ten times smaller

The difference between the products of $e^-_{aq}$ and H reactions suggest that reduction to $Ru^I$ does not occur, but the observations would be consistent with reaction at the ligand to give with $e^-_{aq}$ a bipyridyl radical anion or with H atoms, the monohydrobipyridyl radical.

*γ-Radiolysis.* In neutral solution in the presence of 1·0M-t-butyl alcohol, in contrast with the $Co(bipy)_3^{3+}$ system, we could find no change in the visible absorption spectrum (peak at 450 nm) and only little in the u.v. region even on prolonged γ-radiolysis. The small change in the u.v. spectrum shown in Figure 2 is produced after a dose of *ca.* 50 krad which provides 50% more $e^-_{aq}$ than would be required for the one-electron reduction of the $100\mu$M-$Ru(bipy)_3^{2+}$ present. Hence either the $Ru^I$ product is similar in absorption to the initial compound (which seems improbable) or if the Ru is still present as $Ru^{II}$ another reduced species not involving Ru is formed. Hydrogen is an obvious possibility but we find $G(H_2) = 0{\cdot}8$, which can be accounted for by the molecular hydrogen, $G = 0{\cdot}45$, together with a small amount produced by reaction of part of the hydrogen atoms present ($G = 0{\cdot}6$) with the t-butyl alcohol.

In order to establish that reaction with $Ru(bipy)_3^{2+}$ had indeed occurred we irradiated a $10^{-2}$M solution containing t-butyl alcohol with a dose calculated to allow 20% of the $Ru(bipy)_3^{2+}$ to react with $e^-_{aq}$. The solution was then run through a column of wet silica gel. The coloured Ru compounds were strongly absorbed at the top of the column but could be eluted by concentrated hydrochloric acid with consequent separation of the components. Comparison of the ratio of absorptions at 285 and 450 nm showed that the original $Ru(bipy)_3^{2+}$, for which the ratio is 4·5, is eluted first and is well separated from another coloured compound, presumably the radiolysis product, which has a ratio of 450 to 285 nm absorption of only 2·5.

The small differences in absorption between $Ru(bipy)_3^{2+}$ and the radiolysis product suggest that the latter is still in the $Ru^{II}$ state and any changes are in the bipyridyl ligands. It seems reasonable to suppose that both H atoms and $e^-_{aq}$ adducts to bipyridyl will react by dismutation to give the dihydrobipyridyl and the dianion respectively. This would be a second-order reaction of the intermediate, as is in fact observed. The subsequent slower changes seen in the $e^-_{aq}$ reaction may be reactions of the dianion with water to yield ultimately the dihydrobipyridyl compound.

*Reactions of* $Co(terpy)_2^{3+}$.—These closely parallel those of $Co(bipy)_3^{3+}$. We find that γ-radiolysis of $10^{-4}$M-$Co(terpy)_2^{3+}$ in neutral solution in the presence of 0·5M-t-butyl alcohol gives $Co(terpy)_2^{2+}$ which is identifiable by its absorption spectrum.[8] The measured yield, $G = 2{\cdot}65$, indicates reduction by $e^-_{aq}$.

On pulse radiolysis a transient precursor (Figure 1) is formed before $Co(terpy)_2^{2+}$ with $k = 6{\cdot}5 \times 10^{10}$ l mol$^{-1}$ s$^{-1}$. As in the $Co(bipy)_3^{3+}$ system, the lifetime of this intermediate depends on the concentration of the original $Co^{III}$ compound with which it reacts ($k = 2{\cdot}5 \times 10^8$ l mol$^{-1}$ s$^{-1}$).

However, the precursor cannot be an excited low-spin $Co^{II}$ compound since the ground state of $Co(terpy)_2^{2+}$ is already of low spin.[8]

*Conclusions.*—The above observations suggest that the transient precursors to $Co^{II}$ in the reactions of $e^-_{aq}$ with $Co^{III}$ pyridyl complex ions are electron adducts to the ligand and not excited spin states of the metal.

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[8] R. Hogg and R. G. Wilkins, *J. Chem. Soc.*, 1962, 341.

The reactions of these precursors with additives are explicable in terms of reduction of the additive by a pyridyl anion, but the mechanism whereby they are converted into the Co$^{II}$ product in the absence of additives is not clear. This process apparently requires a reaction with the original Co$^{III}$, and does not proceed by the simple internal transfer of an electron from ligand to metal. We can suggest no reason for this peculiarity.

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