Photochemistry of *cis*-$[Co(en)_2(NO_2)_2]^+$ † in Acetonitrile

P. Natarajan * and A. Radhakrishnan
Department of Inorganic Chemistry, University of Madras, Madras 600 025, Tamil Nadu, India

Photochemistry of the *cis*-$[Co(en)_2(NO_2)_2]^+$ ion in neat acetonitrile exhibits unusual features compared to the excited state processes of the complex ion in aqueous media. In aqueous media excitation of the complex ion in the ligand-to-metal charge-transfer band, $^*(Co{\leftarrow}NO_2)$, produces cobalt(II) ion and the nitrito-linkage isomer. In neat acetonitrile solution excitation of the complex in the same region produces an intermediate cobalt(II) complex co-ordinated to NO_2. Molecular oxygen scavenges the intermediate quantitatively to produce cobalt(II)–oxygen adducts with a rate constant of $(3.5 \pm 0.5) \times 10^5$ dm^3 mol^{-1} s^{-1}. From the amount of oxygen adduct formed, the quantum yield for the intermediate formation on irradiation at 365 nm was found to be 0.3 ± 0.03 while the quantum yield for cobalt(II) formation in deaerated and in air-equilibrated solutions was 0.03 ± 0.006. In the absence of oxygen the photoproduced intermediate leads to the formation of a cobalt(III) complex. The complex ion in neat acetonitrile and in water quenches the excited state of $[Ru(bipy)_3]^{2+}$ (bipy = 2,2'-bipyridine) with similar rate constants ($\sim 9 \times 10^8$ dm^3 mol^{-1} s^{-1}). However, flash photolysis studies show no observable product formation which is attributed to rapid recombination of the products formed in the solvent cage by an electron-transfer quenching process or to a physical quenching process which does not lead to any product formation. Absorption spectral features change markedly in different solvents indicating solvent interaction with the complex. It is suggested that excited state relaxation processes are intimately coupled with the solvent interactions with the complex ion.

Investigations have shown that the solvent medium has a marked effect on the reactivity pattern of excited states.[1-4] Photochemical reactions of Werner type co-ordination compounds are studied primarily in aqueous media since many of these complexes with high charge are only slightly soluble in non-aqueous solvents. In recent years photochemical studies in neat non-aqueous solvents indicate that the excited state processes of co-ordination compounds are affected by the nature of the solvent medium.[5] The predominant excited state reactions of cobalt(III) ammines produce redox decomposition of the metal centre.[6,7] Earlier we have investigated [8] the reactivity of the cobalt(III) ammine complexes in highly viscous solutions containing high polymers and concluded that macroscopic viscosity has no observable effect on the quantum yields for product formation. Investigations in mixed alcohol–water solvents have revealed that change in the solvent environment of the excited state of the ammine complex leads to different product quantum yields.[9-11] In the present study we have investigated the photochemical processes of the complex *cis*-bis(ethylenediamine)dinitrocobalt(III) perchlorate in acetonitrile. Our earlier investigations [12] of the complex ion in aqueous media and in alcohol–water solutions show that the photochemical behaviour follows a pattern similar to that observed for other ammine complexes.

Experimental

The compound *cis*-$[Co(en)_2(NO_2)_2][ClO_4]$ was prepared by a standard procedure.[13] Steady irradiation experiments were carried out using an EIMAC 300 W xenon lamp mounted on an optical bench or a 200 W medium pressure mercury-vapour lamp. Light of a particular wavelength was obtained using appropriate glass and interference filters. Solutions for steady photolysis experiments were deaerated by repeated freeze-thaw cycles. Solutions for the flash photolysis experiments were deaerated, in an all-glass apparatus consisting of a flask connected to the flash photolysis cell, by bubbling with argon for 1 h. After deaeration the solution was transferred from the flask to the flash photolysis cell through the connector in an argon atmosphere and sealed. The flash lamp was xenon filled and the monitoring lamp was a xenon arc lamp. The absorbance of the sample was monitored at different wavelengths using an Oriel monochromator. The energy per flash was *ca.* 250 J and the output from the RCA IP28 photomultiplier tube was digitized and the trace was obtained using an X–Y recorder.

In the photosensitization experiments the lifetime of the excited state of $[^*Ru(bipy)_3Cl_2]$ was measured using a single photon counting set up (Applied Photophysics, London). The lifetime of the emitting state in the presence and in the absence of quenchers was treated by the well known Stern–Volmer relationship.[14] Absorption spectral measurements were carried out in a Cary 219 spectrophotometer. Acetonitrile used in the investigation was of spectro quality (Aldrich) and, once opened, solvent from the sealed container was used for not more than 2 d. Cobalt(II) estimation was carried out by the thiocyanate method.[15] The $[Ru(bipy)_3Cl_2]$ used in this investigation was obtained commercially (Alfa).

Results

Absorption Spectra of *cis*-$[Co(en)_2(NO_2)_2]^+$.—The absorption spectra of the complex ion, *cis*-$[Co(en)_2(NO_2)_2]^+$, in aqueous $HClO_4$ (0.1 mol dm^{-3}) and in neat acetonitrile in the u.v.–visible region are shown in Figure 1. In acetonitrile solution no change in the absorption spectra of the complex was observed for several hours.

Steady Photolysis of *cis*-$[Co(en)_2(NO_2)_2]^+$.—Irradiation of an air-equilibrated acetonitrile solution of the complex using a 330 nm cut-off filter shows significant changes in the absorption spectrum as shown in Figure 2. The dashed line indicates the spectrum of a solution irradiated until there was little change in the spectrum. Irradiation for much longer periods causes a decrease in absorbance in the visible and near-u.v. regions indicating secondary photoreactions. The absorption spectrum of the irradiated solution changes much more

† *cis*-Bis(ethylenediamine)dinitrocobalt(III).

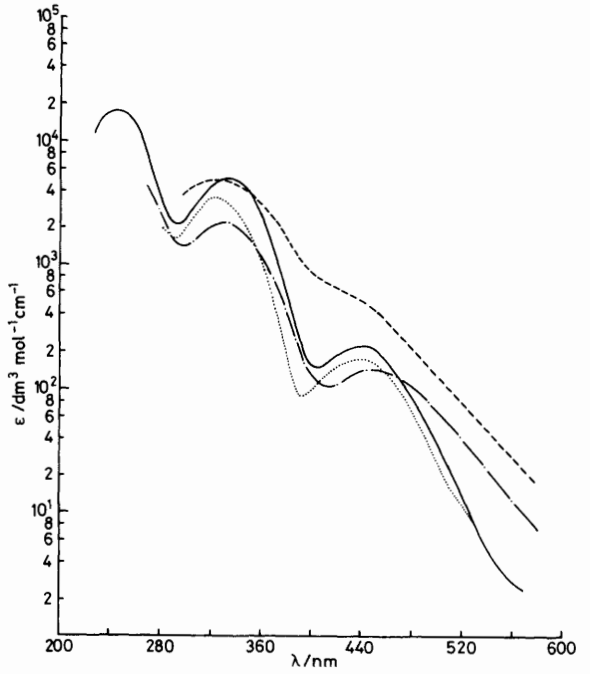


Figure 1. Absorption spectra of *cis*-$[Co(en)_2(NO_2)_2]^+$ in 0.1 mol dm^{-3} $HClO_4$ (····) and acetonitrile (——), the photoproduct (– – –), and *cis*-$[Co(en)_2(NO_2)(H_2O)]^{2+}$ (— · —)

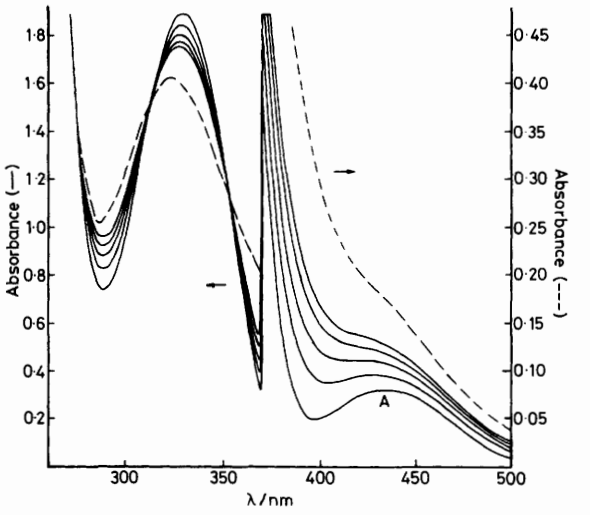


Figure 2. Photolysis of *cis*-$[Co(en)_2(NO_2)_2]^+$ in air-saturated acetonitrile: unirradiated solution (A); after prolonged irradiation (– – – –)

slowly on standing for several hours also indicating thermal decomposition of the product. Irradiation of a thoroughly deaerated solution shows the spectral changes shown in Figure 3. Aeration of this solution does not produce the spectral changes similar to those seen corresponding to solutions irradiated after air equilibration mentioned above. Quantum yields for the product formation in air-equilibrated solutions which were determined spectrophotometrically, knowing the final product spectrum obtained on prolonged irradiation, are shown in Figure 3. The shaded areas indicate the quantum yield for cobalt(II) formation under different conditions.

A deaerated acetonitrile solution of the complex ion after

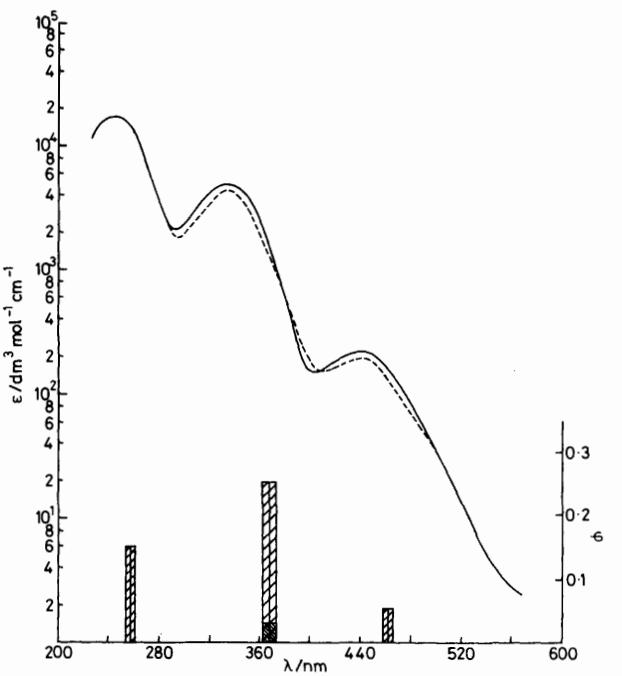


Figure 3. Photolysis of *cis*-$[Co(en)_2(NO_2)_2]^+$ in deaerated acetonitrile: unirradiated solution (——); photolysed solution (– – – –). Quantum yield (φ) for the oxygen adduct formation in the photolysis of air-equilibrated solution (▨); quantum yield (φ) for cobalt(II) on photolysis in deaerated and air-equilibrated solutions (▩)

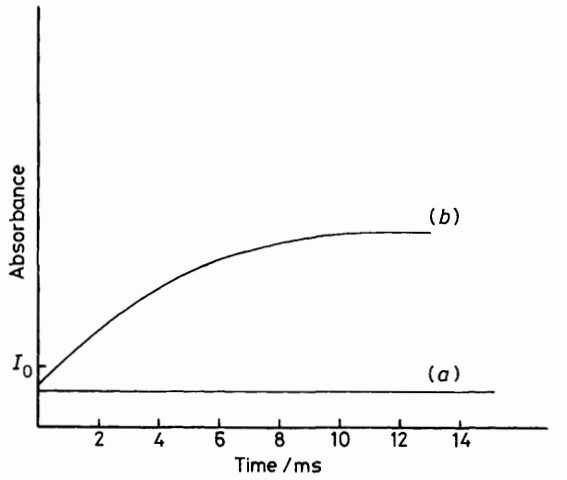


Figure 4. Flash photolysis of *cis*-$[Co(en)_2(NO_2)_2]^+$ in acetonitrile: (*a*) for deaerated solution and (*b*) for air-equilibrated solution. Light on at time = 0 ms. Monitoring wavelength, λ = 400 nm; I_0 = absorbance of unflashed solution

irradiation was evaporated in a vacuum line to remove the solvent completely. The residue was dissolved in deaerated aqueous $HClO_4$ (0.1 mol dm^{-3}) and the spectrum obtained. The spectral features were very similar to those shown in Figure 2 for the *cis*-$[Co(en)_2(NO_2)(H_2O)]^{2+}$ ion. The amount of cobalt(II) present in the latter solution was found to be identical to that found in the acetonitrile solution before evaporation. The quantum yield determined for cobalt(II) ion on irradiation of the complex ion in acetonitrile using 365 nm light was 0.03 ± 0.006.

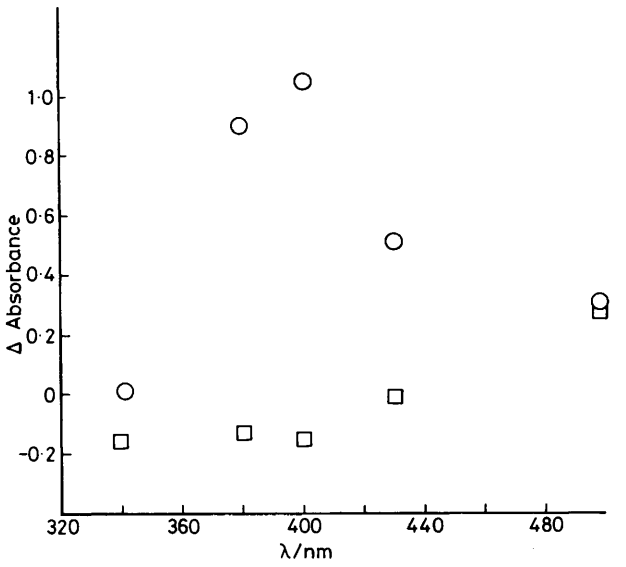


Figure 5. Difference spectra of the product formed in the flash photolysis: air-equilibrated solution (○), deaerated solution (□). The data reported were obtained after a delay of 100 μs

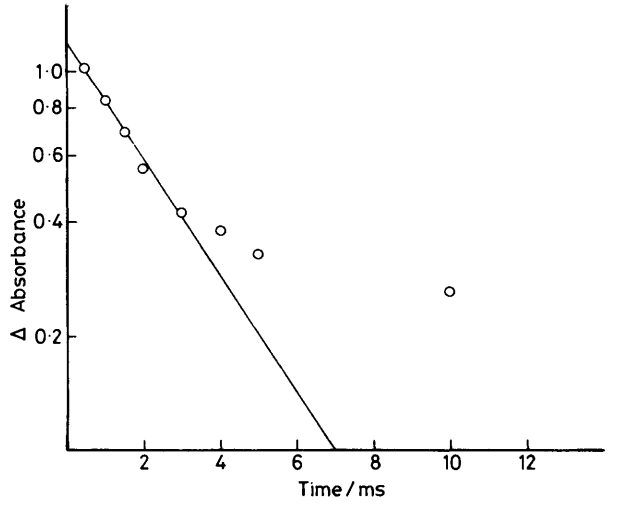


Figure 6. Kinetics of the growth of the transient absorbance in the flash photolysis of *cis*-$[Co(en)_2(NO_2)_2]^+$ in air-equilibrated acetonitrile solution. Monitoring wavelength, λ = 400 nm

Flash Photolysis Studies.—Flash photolysis of a deaerated acetonitrile solution of the complex ion produces no transient species as shown in Figure 4. However, flash photolysis of an air-equilibrated acetonitrile solution of the complex produces the transient species shown in the same Figure. The absorption spectrum of the transient species formed during the flash photolysis of an air-equilibrated solution is shown in Figure 5. The initial rapid portion of the transient growth corresponds to a first-order growth as shown in Figure 6 and the first-order rate constants calculated are shown in the Table for experiments carried out under different conditions.

Photosensitization of cis-$[Co(en)_2(NO_2)_2]^+$ *by* $[*Ru(bipy)_3]^{2+}$.—The lifetime of $[*Ru(bipy)_3]^{2+}$ determined in acetonitrile was 910 ± 25 ns. The decrease in lifetime of $[*Ru(bipy)_3]^{2+}$ due to quenching by *cis*-$[Co(en)_2(NO_2)_2]^+$ in acetonitrile and in aqueous perchloric acid solution was determined. The ratio of the lifetimes τ_0, in the absence of the quencher and τ, in the presence of quencher was plotted as a function of the quencher concentration, [Q], according to the Stern–Volmer equation $\tau_0/\tau = 1 + K_{sv}[Q]$ where $K_{sv} = k_q\tau_0$ (K_{sv} = Stern–Volmer constant). The bimolecular quenching constants, k_q, calculated from such a plot as shown in Figure 7 are $(9.0 \pm 0.5) \times 10^8$ dm^3 mol^{-1} s^{-1} and $(9.3 \pm 0.5) \times 10^8$ dm^3 mol^{-1} s^{-1} in aqueous solution and acetonitrile respectively. A solution of $[Ru(bipy)_3]^{2+}$ (5×10^{-5} mol dm^{-3}) and *cis*-$[Co(en)_2(NO_2)_2]^+$ (3×10^{-3} mol dm^{-3}) in acetonitrile does not produce a transient on flash photolysis; most of the light is absorbed by the $[Ru(bipy)_3]^{2+}$ ion. The same solution on steady irradiation at 450 nm produced no observable product. In aqueous acidic solutions similar experiments show transient bleaching of the solution due to the formation of $[Ru(bipy)_3]^{3+}$ as reported for other cobalt(III) ammine complexes.[16,17]

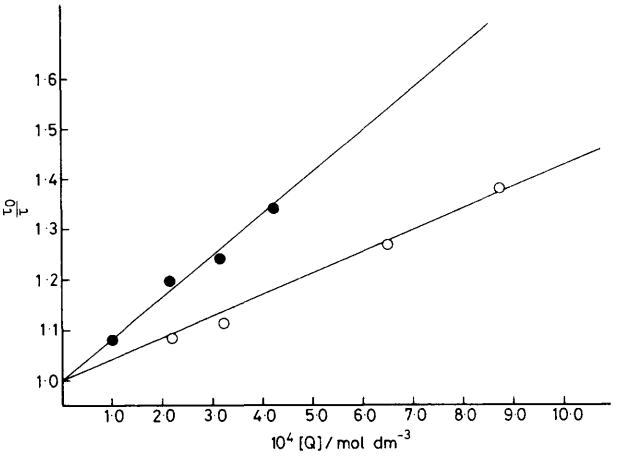


Figure 7. Stern–Volmer plot of quenching of $[*Ru(bipy)_3]^{2+}$ by *cis*-$[Co(en)_2(NO_2)_2]^+$ in water (○) and in acetonitrile (●)

Table. Photolysis of *cis*-$[Co(en)_2(NO_2)_2]^+$ in acetonitrile. Rate constants for the formation of the oxygen adduct

10^4[Complex]/ mol dm^{-3}	λ monitoring/ nm	$10^{-3}k$/s^{-1}	$10^{-5}k'$/ dm^3 mol^{-1} s^{-1} *
0.38	400	0.46	2.9
3.8	500	0.52	3.3
3.8	500	0.58	3.6
0.33	430	0.53	3.3
0.33	340	0.57	3.6

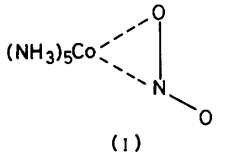
* Calculated by using a concentration of dissolved oxygen = 1.6×10^{-3} mol dm^{-3} (J. F. Cotezee and I. M. Kolthoff, *J. Am. Chem. Soc.*, 1957, **79**, 6110).

Discussion

The spectra of cobalt(III) ammine complexes consist of absorption bands due to ligand-field transitions in the visible region, some of which are symmetry forbidden and some both symmetry and spin forbidden.[6] At high energies charge-transfer ligand-to-metal bands are seen, and excitation in this region results in the formation of the photoredox products. In the case of *cis*-$[Co(en)_2(NO_2)_2]^+$ with the easily oxidisable nitrite ligand, the charge-transfer ligand-to-metal transitions appear at lower energy probably overlapping the *d–d* bands.

The absorption spectral changes shown in Figure 1 when the complex is dissolved in acetonitrile instead of water indicate that the complex ion interacts with the solvent. It is often thought that the changes in the absorption spectra in different solvents are indicative of the presence of charge-transfer to solvent transitions.[6,7] In the current situation the absorption bands of the complex ion are affected in acetonitrile in terms of the intensity and the energy of the transitions. With water as the solvent, interactions between water molecules and the nitrite ligands are rather strong in contrast with the weak interactions of the ligands with acetonitrile. This is consistent with the blue shift of the bands in aqueous solution.[2]

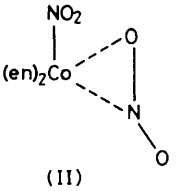
Photoprocesses of cobalt(III) ammine complexes in aqueous solutions do show some characteristics common to the group: (*i*) excitation in the charge-transfer band predominantly results in the photoreduction of the metal centre and (*ii*) excitation in ligand-field bands shows ligand labilization reactions with low quantum yields.[18] When nitrite is present in the complex as one of the ligands along with ammines, cobalt(III) complexes also show the photoinduced nitro→nitrito linkage isomerization upon excitation in the charge-transfer band.[19] It was suggested that a common intermediate formed from the excited state as shown by structure (I) gives rise to cobalt(II) and the linkage isomer. In a later publication[9] it was suggested that an increase in the quantum yield for the linkage isomer and a corresponding decrease in cobalt(II) formation in viscous solvents was evidence for such an intermediate. The photochemistry of *cis*-$[Co(en)_2(NO_2)_2]^+$ [12] in aqueous solution and in mixed alcohol–water solvents shows very strong similarities with the excited state chemistry of $[Co(NH_3)_5(NO_2)]^{2+}$, suggesting that the excited state relaxation processes are governed by similar factors for these complexes.[19]



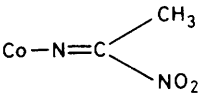
(I)

Excitation of deaerated acetonitrile solutions of *cis*-$[Co(en)_2(NO_2)_2]^+$ in the low energy charge-transfer band produces cobalt(II) with a quantum yield of 0.03 ± 0.005. More information on the photochemical pathways is obtained when molecular oxygen is present in the solution as a scavenger for any reactive species produced. Spectral changes seen in Figure 2 correspond to the product formed between the initial photoproduct and molecular oxygen. The presence of isosbestic points does suggest that oxygen scavenges the photoproduct almost quantitatively. Binuclear cobalt(III) peroxo-complexes with ammine ligands show two closely spaced ligand-to-metal charge-transfer band systems in the region 25 000—33 000 cm^{-1}.[20] The spectrum of the adduct between oxygen and the photoproduct indicates a maximum at 31 700 cm^{-1} with a molar absorptivity of ~5 000 $dm^3\ mol^{-1}\ cm^{-1}$ and a shoulder at 24 400 cm^{-1} with a molar absorptivity of 610 $dm^3\ mol^{-1}\ cm^{-1}$. These two features are very similar to that of other 2 : 1 cobalt : oxygen complexes with the oxygen in the peroxo form.[21] Additionally, the observation that the oxygen adduct does not show any e.s.r. signal in solution at room temperature indicates that the oxygen in the final product is in the peroxo-form and not in the superoxo-form.[22] The quantum yield for the formation of the oxygen adduct indicates that the complex is very photosensitive. In addition, the quantum yield profile indicates that the photoproduct results from the excitation of the band with a maximum around 30 000 cm^{-1}. This band is assigned to the charge-transfer ligand-to-metal transition from the co-ordinated nitro-ligand $*(Co{\leftarrow}NO_2)$. The quantum yield for cobalt(II) on irradiating into this band is an order of magnitude smaller, and it is not clear whether cobalt(II) results from the excited state, $*(Co{\leftarrow}NO_2)$ or from the high-energy $*(Co{\leftarrow}en)$ excited state which has the tail of the band extended to longer wavelengths.

Results of the flash photolysis studies provide further information on the primary photolysis product. Failure to see any transient during the flash photolysis of the complex in deaerated solution indicates that the primary photolysis product is formed within the duration of the flash. In the presence of oxygen the photolysis product reacts with oxygen to form the oxygen co-ordinated complexes. The rate constant determined from the flash photolysis study for the 1 : 1 cobalt and oxygen adduct formation is $(3.5 \pm 0.5) \times 10^5\ dm^3\ mol^{-1}\ s^{-1}$.[23,*] This value is very similar to the values reported for the addition of O_2 to the ammine complexes of cobalt(II).[24] The value reported in the present study is the first estimate on the kinetics of oxygen addition to cobalt(II) complexes in non-aqueous solvents. Cobalt(II) formed in thoroughly deaerated solutions amounts to only a tenth of the oxygen adduct produced in oxygenated solutions. From the rate constant for the oxygenation, the lifetime of the intermediate species is calculated to be longer than milliseconds.[23] The intermediate thus cannot be an excited state of the complex ion. This observation indicates that the intermediate formed is converted to the cobalt(III) complex which on addition of dilute acid produces *cis*-$[Co(en)_2(NO_2)(H_2O)]^{2+}$. The question then is the nature of the primary photolysis product. There are two possible structures for the photoproduced intermediate which could explain the results. The first, structure (II), is an adduct of the cobalt(II) complex and NO_2 bound by a π-type bonding.



(II)



(III)

Oxygen replaces NO_2 to give the oxygen adduct. In the absence of oxygen, solvent replaces NO_2 to give the solvent substituted cobalt(III) complex. Since the linkage isomer does not dissolve in acetonitrile it is presumably not formed from the intermediate. The alternative structure involves a cobalt(II) complex in association with a solvent molecule combined with NO_2 as shown by structure (III).

Adducts formed from NO_2 with acetonitrile are known.[25] Both structures account for the formation of oxygen adducts in aerated solution and formation of a stable cobalt(III) complex in the absence of oxygen. In fact the former structure was suggested as an intermediate in the photolysis of $[Co(NH_3)_5(NO_2)]^{2+}$ by Balzani *et al.*[19] Whether such an intermediate could live over a millisecond is uncertain. On the other hand, similarity in the rate constants for the oxygen adduct formation with the well known rate constants [24] for a cobalt(II) amine–oxygen reaction in water suggests a cobalt(II) complex as an intermediate which is consistent with the latter structure.

Photosensitization of the complex ion by $[*Ru(bipy)_3]^{2+}$ in aqueous solution which results in the formation of the redox products $[Ru(bipy)_3]^{3+}$ and cobalt(II) ion [26] contrasts with the

* The rate constant was calculated knowing the concentration of oxygen in air-saturated acetonitrile to be 1.6×10^{-3} mol dm^{-3} (J. F. Coetzee and I. M. Kolthoff, *J. Am. Chem. Soc.*, 1957, **79**, 6110).

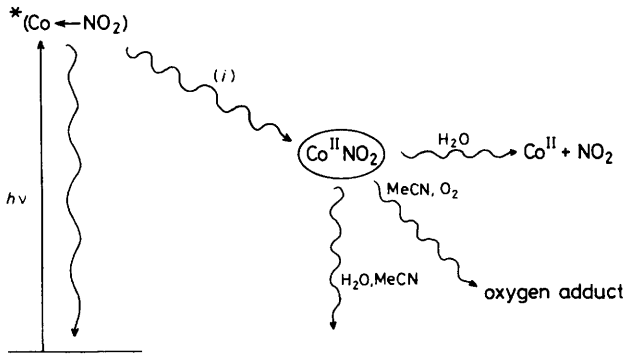


Figure 8. Excited state pathways of *cis*-$[Co(en)_2(NO_2)_2]^+$ in the *(Co←NO_2) charge-transfer state. (*i*) Indicates the relaxation of the initial excited state produced

lack of formation of any kind of products in acetonitrile medium. Sensitization of cobalt(III) ammine complexes by $[*Ru(bipy)_3]^{2+}$ is known to result in the excited state electron transfer to the cobalt(III) centre.[26] In acetonitrile solutions, failure to see any $[Ru(bipy)_3]^{3+}$ ion formation in the flash photolysis experiments does suggest the influence of solvent on the reaction. Failure to see the redox products in the bulk solution indicates a very rapid back electron-transfer process; such rapid back electron-transfer reactions are suggested for the quenching of nitro aromatics by $[*Ru(bipy)_3]^{2+}$.[27] Alternatively, excited state manifolds of the complex ion are perhaps altered in acetonitrile compared to water which results in the physical quenching process deactivating $[*Ru(bipy)_3]^{2+}$.

Excited State Processes in Aqueous and in Acetonitrile Solutions.—Excitation of the complex ion with 365 nm light produces cobalt(II) and the linkage isomer with a total quantum yield of 0.053 in aqueous solution whereas the total photochemical quantum yield in acetonitrile is 0.36 ± 0.04. Thus in acetonitrile nearly 40% of the molecules result in fragmentation whereas in water only about 5% of the excited species undergo decomposition. Flash photolysis studies do not show any recombination between the primary photoproducts to give back the starting materials. Geminate recombination events of course could in principle operate.[28,29] However, even such processes would be more favourable in a less polar solvent such as acetonitrile. It thus appears that there are inherent features in the photochemical processes of the complex ion which involve the solvent environment more strongly.

Various relaxation processes occurring from the excited state of the complex ion are shown in Figure 8. Since the complex does not emit from the excited state even at low temperature it is a formidable task to assign the role of the solvent in the relaxation process of any particular excited state. With the related system $[Co(NH_3)_5(NO_2)]^{2+}$ it was observed that in the solid state only the linkage isomer and not the cobalt(II) complex is produced on photoexcitation.[30] It appears that the excited state, depending upon the environment, goes to produce cobalt(II), the linkage isomer, or any other species. The high quantum yield observed in acetonitrile suggests that the solvent has a role even in the relaxation processes [(*i*) in Figure 8] from the initial excited state produced on excitation. It is possible that the radiationless decay from the charge-transfer excited state to the ground state is decreased in acetonitrile facilitating the formation of the lower lying photoreactive excited state.

Acknowledgements

We thank the Department of Science and Technology, Government of India, for financial support. Part of this work was carried out at the Radiation Laboratory, University of Notre Dame.

References

1 R. M. Noyes, *Prog. React. Kinet.*, 1961, **1**, 128.
2 N. Mataga and T. Kubota, ' Molecular Interactions and Electronic Spectra,' Marcel Dekker, New York, 1970.
3 M. Ottolenghi, *Acc. Chem. Res.*, 1973, **6**, 153.
4 J. F. Endicott, G. J. Ferraudi, and J. R. Barber, *J. Phys. Chem.*, 1975, **79**, 630.
5 M. A. Bergkamp, R. J. Watts, and P. C. Ford, *J. Am. Chem. Soc.*, 1980, **102**, 2627.
6 V. Balzani and V. Carassiti, ' Photochemistry of Coordination Compounds,' Academic Press, New York, 1970.
7 A. W. Adamson and P. D. Fleisauer, ' Concepts of Inorganic Photochemistry,' John Wiley and Sons, New York, 1975.
8 P. Natarajan, *J. Chem. Soc., Chem. Commun.*, 1975, 526.
9 F. Scandola, C. Bartocci, and M. A. Scandola, *J. Am. Chem. Soc.*, 1973, **95**, 7898.
10 J. F. Endicott, in ref. 7.
11 P. Natarajan, *J. Chem. Soc., Dalton Trans.*, 1977, 1400.
12 A. Radhakrishnan and P. Natarajan, *Ind. J. Chem., Sect. A*, 1979, **18**, 165.
13 R. G. Pearson, P. M. Henry, J. G. Bergmann, and F. Basolo, *J. Am. Chem. Soc.*, 1954, **76**, 5920.
14 N. Turro, ' Modern Molecular Photochemistry,' Benjamin-Cummings, New York, 1978.
15 R. E. Kitson, *Anal. Chem.*, 1950, **22**, 664.
16 G. Navon and N. Sutin, *Inorg. Chem.*, 1974, **13**, 2159.
17 W. Bottcher and A. Haim, *J. Am. Chem. Soc.*, 1980, **102**, 1564.
18 R. A. Pribush, C. K. Poon, C. M. Bruce, and A. W. Adamson, *J. Am. Chem. Soc.*, 1974, **96**, 3027.
19 V. Balzani, R. Ballardini, N. Sabbatini, and L. Moggi, *Inorg. Chem.*, 1968, **7**, 1398.
20 A. P. B. Lever and H. B. Gray, *Acc. Chem. Res.*, 1978, **11**, 348.
21 G. McLendon and A. E. Martell, *Coord. Chem. Rev.*, 1976, **19**, 1.
22 R. D. Jones, D. A. Summerville, and F. Basolo, *Chem. Rev.*, 1979, **79**, 139.
23 P. Natarajan, *Inorg. Chim. Acta*, 1980, **45**, L199.
24 R. G. Wilkins, *Adv. Chem. Ser.*, 1971, **100**, 111.
25 ' Nitrogen Tetroxide,' Hercules Co., U.S.A., 1968, p. 6.
26 V. Balzani, I. Moggi, M. Manfrin, F. Bolleta, and G. S. Laurence, *Coord. Chem. Rev.*, 1975, **16**, 321.
27 C. R. Bock, J. A. Connor, A. R. Gutierrez, T. J. Meyer, D. G. Whitten, B. P. Sullivan, and J. K. Nagle, *J. Am. Chem. Soc.*, 1979, **101**, 4815.
28 J. P. Lorand, *Prog. Inorg. Chem.*, 1972, **17**, 207.
29 N. Uri, *Chem. Rev.*, 1952, **50**, 375.
30 B. Adell, *Z. Anorg. Allg. Chem.*, 1955, **279**, 219.

Received 20*th April* 1982; *Paper* 2/657