

Pulse radiolytic studies on *cis*-dichlorobis(1,10-phenanthroline-5,6-dione)Cobalt(III) complex

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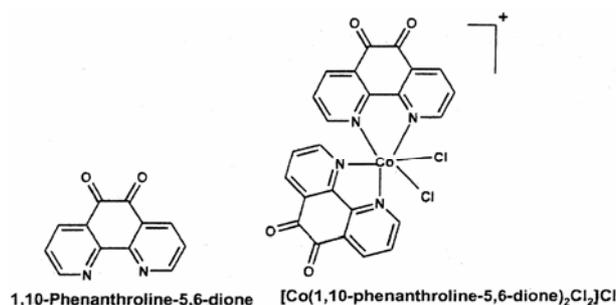
Abstract. Reactions of four reducing radical species namely e_{aq}^- , H-atoms, $(\text{CH}_3)_2\text{COH}^\bullet$ and $^\bullet\text{CO}_2^-$ radicals with $[\text{Co}(\text{III})(\text{phenidione})_2\text{Cl}_2]\text{Cl}$ (complex) have been studied by electron pulse radiolysis. Time resolved transient absorption spectra for all the four species show two peaks which match with those of phenidione anion radical produced by the reaction of e_{aq}^- with phenidione. However, there are some differences in the spectral and kinetic features in the reactions of H-atoms and $^\bullet\text{CO}_2^-$ radicals with the complex which are elaborated. Steady state absorption spectra on irradiation under reducing conditions indicate breakdown of the complex. The anion radical initially produced has fairly long lifetime of few 100 microseconds. Spectral studies show that initial site of attack for electron transfer is the phenidione moiety. Subsequently the electron is transferred to other sites resulting in aquation/decomposition to metal ion. Conductometric studies show that conductance substantially increases on irradiation and could be attributed to aquation/de-ligation of the complex by intramolecular electron transfer.

Keywords. Pulse radiolysis; cobalt(III) complex; 1,10-phenanthroline-5,6-dione; aquation; reactions of radicals; e_{aq}^- , H-atoms, $^\bullet\text{CO}_2^-$ and $(\text{CH}_3)_2\text{COH}^\bullet$.

1. Introduction

Metal-polypyridyl complexes and their redox chemistry have been studied due to variety of their potential applications such as anticancer agents, probes for structural changes in DNA and solar energy utilization. These studies have been carried out mainly on *tris*-polypyridyl complexes of the type $[\text{Ru}(\text{bpy})_3]^{2+}$, $[\text{Ru}(\text{phen})_3]^{2+}$, $[\text{Co}(\text{bpy})_3]^{3+}$ and $[\text{Co}(\text{phen})_3]^{3+}$.^{1–3} As a part of our programme, to study radiation chemical behaviour of complexes having more than one ligand, a series of Co(III) *bis*-polypyridyl complexes⁴ of the type $[\text{Co}(\text{NN})_2\text{Cl}_2]^+$ where NN denotes various polypyridyl ligands, we report here spectral and kinetic properties of the reactions of e_{aq}^- and two other reducing radicals namely dimethyl ketyl and $^\bullet\text{CO}_2^-$ with $[\text{Co}(\text{III})(1,10\text{-phenanthroline-5,6-dione})_2\text{Cl}_2]\text{Cl}$ [henceforth referred to as complex]. The structures of the ligand and complex are depicted in scheme 1. The complex is known to cleave plasmid pBR 322

DNA upon photoirradiation under aerobic conditions.⁵ Hence it is important to understand the free radical/excited state processes occurring in such interactions. Another interest in such complexes having more than one site of electron attack is to understand how the electron initially located at one site migrates to the other. In the complex under investigation added electron can be located on metal as well as the two ligands. Earlier studies on *tris* acetylacetonato Co(III) showed that all the three radical products of water radiolysis, viz. e_{aq}^- , $^\bullet\text{OH}$



Scheme 1.

*For correspondence

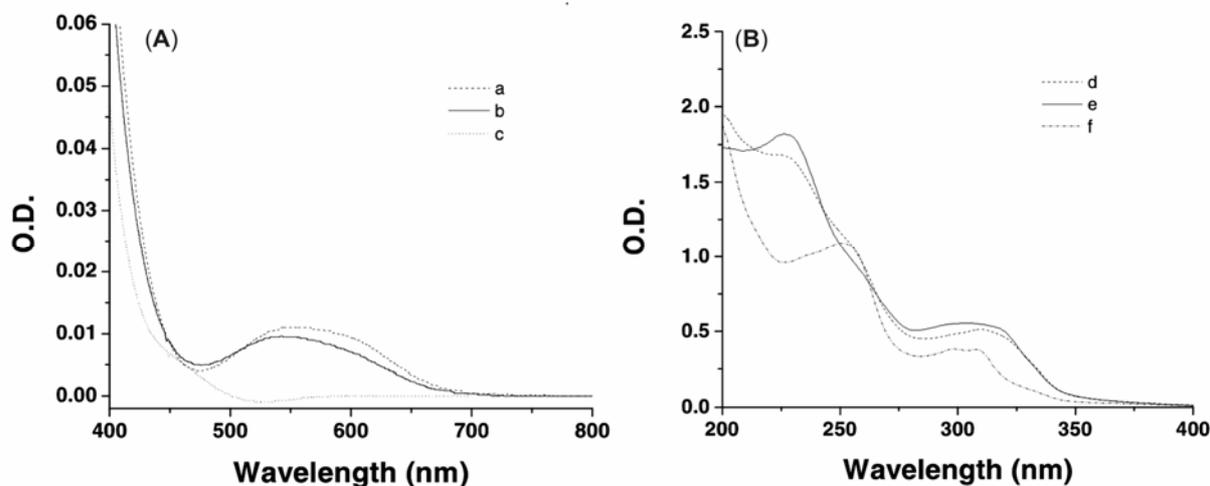


Figure 1. Ground state absorption spectrum of $[\text{Co}(\text{phenanthroline})_2\text{Cl}_2]\text{Cl}$ in water ($2 \times 10^{-4} \text{ mol dm}^{-3}$). **A.** a, $200 \mu\text{M}$ complex, immediately after dissolution, b, $200 \mu\text{M}$ complex, 10 h after dissolution, c, $200 \mu\text{M}$ complex, after irradiation dose 15 Gy, **B.** d, $40 \mu\text{M}$ complex, immediately after dissolution, e, $40 \mu\text{M}$ complex, 10 hrs after dissolution, f, $40 \mu\text{M}$ complex, after irradiation dose 15 Gy.

and H-atoms result in reduction of Co(III) to Co(II).⁶ It is interesting to see in complex containing multiple ligands what is the fate of electron adduct species formed by electron addition. Reduction to Co(II) and intramolecular transfer between the two moieties in the cobalt complexes have also been observed earlier.^{7,8} For comparison reactions of other reducing radicals, viz. H-atoms, $\cdot\text{CO}_2^-$ and dimethyl ketyl radicals have also been studied.

2. Materials and methods

The cobalt complex of 1,10-phenanthroline-5,6-dione (phenanthroline), was synthesized in the laboratory by chlorine oxidation method⁸ and characterized by using standard techniques like UV-Visible, IR, NMR and elemental analysis. Crystal structure of the complex was determined by X-ray diffraction and is reported elsewhere.⁵ The complex is stable towards hydrolysis at least for 10 h as checked by its UV-Visible spectra (figure 1). Experiments were performed on freshly prepared solutions of the complex within ~ 8 h. Optical absorption spectra were recorded using Shimadzu model 1601 UV-Visible spectrophotometer. Conductivities were measured using Equip-tronics model: EQ 664 conductivity meter.

Millipore Milli-Q filtered water was used throughout this work. IOLAR grade N_2 and 99.9% pure N_2O gases were used for deaerating solutions. Reagent grade *t*-butanol, acetone, 2-propanol, sodium for-

mate were used in the present study. Benzophenone (Fluka) was used as received. For reactions with e_{aq}^- complex solutions containing 0.5 mol dm^{-3} of *t*-butanol were saturated with N_2 at neutral pH before carrying out irradiations. For reactions with H-atoms, nitrogen saturated solutions of the complex containing *t*-butanol (0.1 mol dm^{-3}) at pH 1.2 were used. Dimethyl ketyl radicals $[(\text{CH}_3)_2\text{C}\cdot\text{COH}]$ were generated by irradiating N_2O saturated solutions of complex containing 0.1 mol dm^{-3} 2-propanol. For studying $\cdot\text{CO}_2^-$ radical reactions N_2O purged 0.25 mol dm^{-3} formate solutions were used. Qualitative spot tests carried out using nirtoso-R salt show the presence of Co(II) in irradiated solutions.

Pulse radiolysis studies were carried out using facility at National Center for Free Radical Research of University of Pune. The facility is based on 7 MeV linear accelerator (AS and E, HESD USA) giving electron pulses of 10, 20, 50, 100, 200, 400 and 3000 ns duration. Optical absorption detection system is from LUZCHEM Canada, which uses 175 W Xe lamp (Cermax parallel lamp), 1/8 M monochromator (CVI CM 110), photomultiplier (Hamamatsu 7400U-04) and digital oscilloscope (Tektronix TDS 3032 B, 300 MHz, 2.5 GS/s). Acquisition of kinetic and spectral data was achieved by mLFP and superspec software (LUZCHEM) based on Labview platform. Details of pulse radiolysis system are reported.^{4,9,10} The present work was carried out using 50 ns pulses at dose range of 7–12 Gy per pulse for some experiments dose per pulse up to 50 Gy was used. Radiation dose

was measured using KCNS dosimetry taking $G\varepsilon$ for $(\text{SCN})_2^{\bullet-}$ to be $21,522 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ at 480 nm .¹¹

Knowing the values molar extinction coefficients of the complex (ε_c), the absorption values in the transient absorption spectra were corrected using equation A.

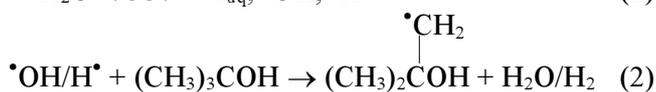
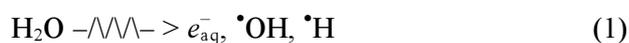
$$\varepsilon_R = \varepsilon_c + 21,522 \times \Delta\text{OD}_R / [\Delta\text{OD}_D \times G e_{\text{aq}}^-], \quad (\text{A})$$

where ε_R and ε_c are the molar extinction coefficients of the transient radical species and the complex respectively at a particular wavelength, ΔOD_D is the optical density of $(\text{SCN})_2^{\bullet-}$ at 480 nm (obtained from KSCN dosimeter solution) and ΔOD_R is the optical density of transient at particular wavelength.

3. Results and discussion

3.1 Reactions of e_{aq}^- with the complex

Radiolysis of water generates hydrated electrons e_{aq}^- , $\bullet\text{OH}$ and H-atoms as primary transient radical species. In the reactions of e_{aq}^- , *t*-butanol (0.5 mol dm^{-3}) is added as scavenger to remove $\bullet\text{OH}$ and H-atoms. The reaction of e_{aq}^- with the complex was studied and absorption spectra before and after radiolysis are shown in figure 1. Typical reactions are depicted in equations 1–3.



As figures 2A and B show, the time resolved transient absorption spectra of the complex anion formed on reaction with e_{aq}^- , which also decays in a few hundred μs . The rate of reaction of e_{aq}^- with complex was determined by decay of e_{aq}^- at 700 nm , and was determined to be $(2.2 \pm 0.2) \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. This rate is diffusion-controlled and comparable with other cobalt(III) complexes.^{4,6,7,12} The spectra (figure 2B) show the absorption peak at 530 nm is split and two new peaks appear at 480 and 560 nm . These may be attributed to the species formed on intramolecular electron transfer within the complex.

Figure 3A shows the decay of complex anion at 530 nm . Since the complex has strong ground state absorption in the region of peak at 340 nm , first order decay constant of $(1.65 \pm 0.2) \times 10^4 \text{ s}^{-1}$ is

evaluated from traces at 560 nm . No effect of complex concentration on the decay rate was seen. The complex anion can decay by (i) aquation (ii) de-ligation (iii) reduction to give Co(II). Reduction to Co(II) has been observed in the case of *tris* acetylacetonato Co (III).⁶ De-ligation has been observed in the case of a Co(II) complex and takes place in millisecond time scale.¹³ Three sites of electron localization exist in the complex studied viz. metal ion, phendione and chloride. UV-Visible spectra of the complex after irradiation indicate (figure 1B) that the complex breaks and de-ligation/aquation occurs.

The time resolved transient absorption spectra of the anion radical of the complex show shifts at $800 \mu\text{s}$, the 520 nm peak splits in to two peaks at 460 nm and at 580 nm . This may be attributed to intramolecular electron transfer within the complex from one moiety to another in the complex. In the dose per pulse $10\text{--}50 \text{ Gy}$ the radical anion decays by first order kinetics with rate constant $1.5 \times 10^4 \text{ s}^{-1}$.

3.2 Reaction of e_{aq}^- with phendione

To see whether the ligand phendione also reacts with e_{aq}^- , some experiments were carried out. The time resolved transient absorption spectra of anion radical of phendione are shown in figure 3 and it matches with the reported one.¹⁴



The rate constant of e_{aq}^- with the ligand determined by us is similar to that of previously obtained.¹⁴ The anion radical of phendione has absorption peaks at 340 and 530 nm , which are also seen in the spectra of the anion radical of the complex studied. The spectral shape and the molar extinction coefficients at these wavelengths also match. Hence it is concluded that the electron is localized in the complex on the phendione moiety. The phendione radical anion decays by first order with a rate constant of $9.4 \times 10^3 \text{ s}^{-1}$. The complex anion decay differs from decay of phendione anion due to mechanistic differences. However, both transients are fairly long lived. Dimethyl ketyl radical and $\bullet\text{CO}_2^-$ also give similar transient absorption spectra obtained on the reaction of e_{aq}^- with the phendione.¹⁴

3.3 Conductivity measurements

If the complex anion radical decays by aquation, chloride ions should be released. To ascertain

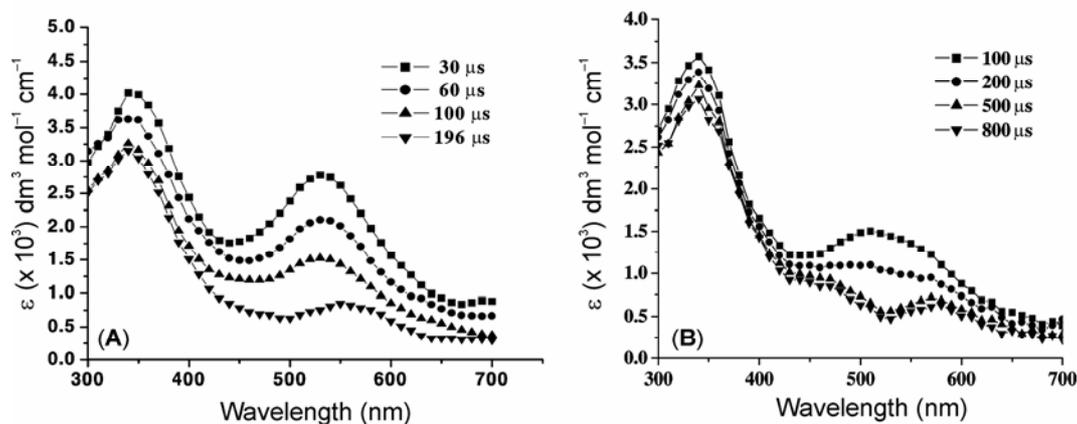


Figure 2. Time resolved corrected transient absorption spectra of anion radical of $[\text{Co}(\text{phenidione})_2\text{Cl}_2]\text{Cl}$, Dose per pulse ~ 10 Gy. $[\text{Complex}]$: 2×10^{-4} mol dm^{-3} ; **A**, 30–196 μs . **B**, 100–800 μs .

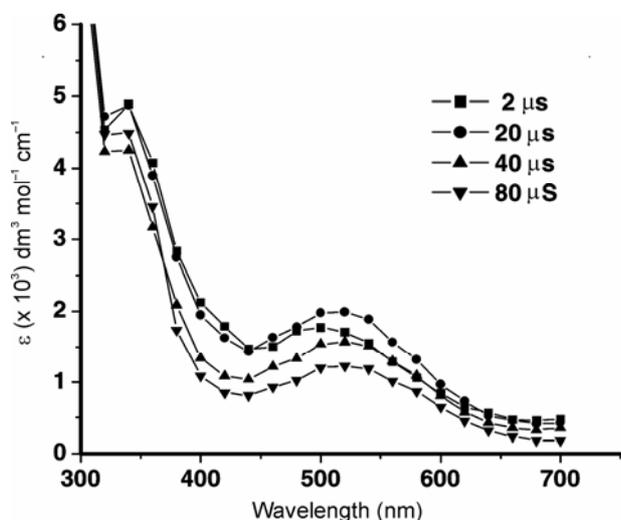
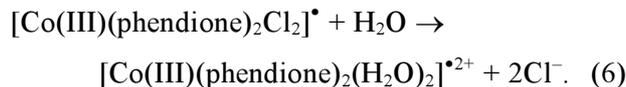
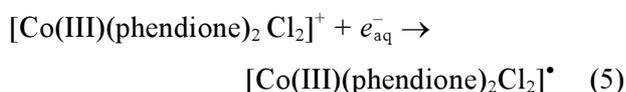
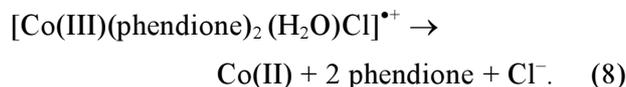
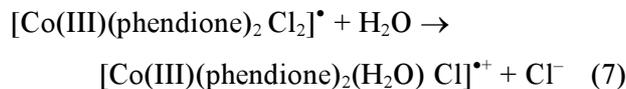


Figure 3. Time resolved transient absorption spectra of anion radical of phenidione. Dose per pulse ~ 10 Gy, $[\text{Phenidione}]$: 2×10^{-4} mol dm^{-3} .

whether such a process results on irradiation, conductivity measurements were carried out. The complex solutions were given a few electron pulses, and conductivities were measured for the unirradiated and irradiated solutions. In the case of the irradiated complex the conductivity almost doubles (table 1), which suggests that the chloride ions are replaced in the complex by water molecules, i.e. aquation takes place. Following reactions can be put forth to explain both aquation and de-ligation:

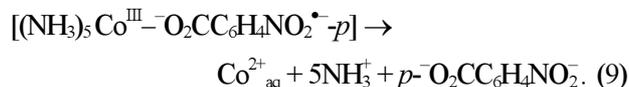


Release of one chloride ion also may be possible (reaction 7), which might result in the reduction of $\text{Co}(\text{III})$ to $\text{Co}(\text{II})$.

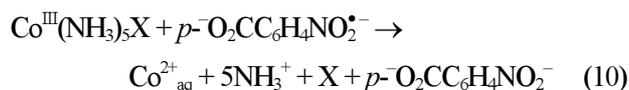


Qualitative spot tests carried out using nirtoso-R salt show the presence of $\text{Co}(\text{II})$ in irradiated solutions.¹⁵

Intramolecular electron transfer reactions have been previously observed in a $\text{Co}(\text{III})$ complex⁷ and the rate of following intramolecular electron transfer reaction was measured to be $k = 2.6 \times 10^3$ s^{-1} .



These rates are slower or equal to the rates of the analogous intermolecular reactions of the type¹⁶



($X = \text{NH}_3$ or $-\text{O}_2\text{CC}_6\text{H}_5$), $k = (0.12 \pm 0.04) \times 10^{-6}$ $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ for $X = \text{NH}_3$ and $k = (0.21 \pm 0.05) \times 10^{-6}$ $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ for $-\text{O}_2\text{CC}_6\text{H}_5$.

Table 1. Conductivity measurements before and after irradiation in milli mhos.

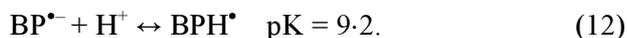
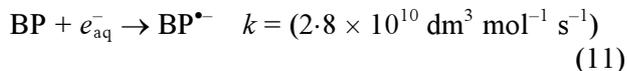
Complexes	Before irradiation*	After irradiation
[Co(1,10-phenanthroline-5,6-dione) ₂ Cl ₂]Cl without BP	0.227	0.484
[Co(1,10-phenanthroline-5,6-dione) ₂ Cl ₂]Cl with BP	0.210	0.242

Dose: 10 Gy, pH: 6.2 [complex] = 2×10^{-4} mol dm⁻³ [benzophenone(BP)] = 5×10^{-5} mol dm⁻³

*Immediately after dissolution

3.4 Effect of benzophenone

The anion radical formed on reaction with e_{aq}^- has transient absorption peaks at 340 and 530 nm (figure 2) and decays by first order process with a rate constant of 1.6×10^4 s⁻¹, probably undergoes intramolecular electron transfer. Hence it is seen that the intramolecular electron transfer in the complex radical anion is fairly a slow process. Benzophenone (BP) was used as a scavenger (concentrations of complex and BP: 2×10^{-4} and 5×10^{-5} mol dm⁻³ respectively) to observe effect of electron scavenger on the radiolytic process. Benzophenone reacts with e_{aq}^- at diffusion-controlled rate constant to give BP^{•-} anion and BP^{•-} exists as ketyl (BPH^{•-}) radical in acidic conditions.⁷



On the basis of competition kinetics since the rates of electron reaction with BP and complex are almost equal, about 25% of e_{aq}^- generated would react with BP. However, conductivity results show better protection of the complex. In experiments with BP, it is seen that conductivity does not change significantly after irradiation. This observation points to the reduction of radiation damage to the complex in the presence of BP. Some results on this aspect would be presented in our next communication.

3.5 Reactions of H-atoms with the complex

H-atoms are selectively generated in the irradiated aqueous solutions at pH < 3 as follows:

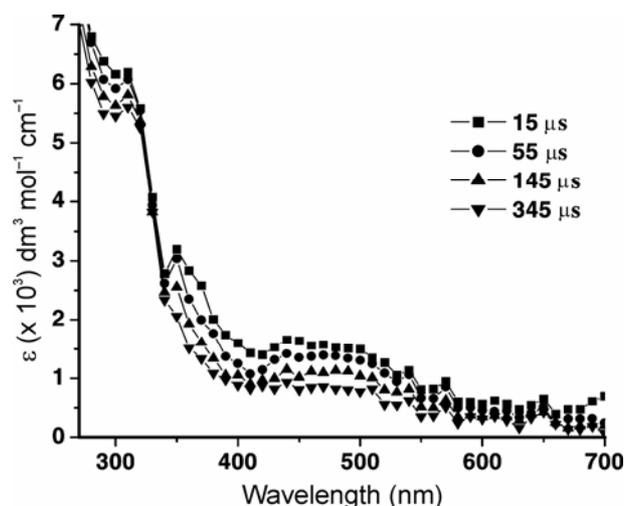
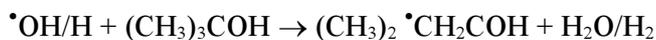
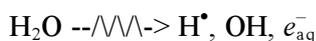


Figure 4. Time resolved transient absorption spectra obtained in the reaction of H-atom with [Co(phenanthroline)₂Cl₂]Cl, Dose per pulse 12 Gy [complex]: 2×10^{-4} mol dm⁻³.

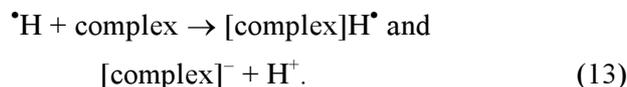


Figure 4 shows the time resolved transient spectra obtained on the reaction of H-atoms with the complex. The rate constant for the reaction of H-atom with the complex is evaluated to be $(3.5 \pm 0.3) \times 10^9$ dm³ mol⁻¹ s⁻¹ (lifetime ~ 1.3 μs) from the growth of 440 nm peak. This is about 5 times lower than that of the reaction of complex with e_{aq}^- . In this reaction, absorption peak is observed at 340 nm, and is attributed to H-atom addition to the phenanthroline moiety. The species decay by first order rate of $(6.1 \pm 0.2) \times 10^3$ s⁻¹. The kinetics of decay differs from that is seen in the reaction with e_{aq}^- . The adduct eventually gives cobalt (II) in the course of time (>1 ms). The difference in decays of two peaks at 340 and 500 nm shows that two species exist which are attributed to (i) H-atom adduct, (ii) other generated by electron transfer from H-atom to give Complex anion radical. As a rough estimate $\sim 35\%$ H-atoms to give anion radical by electron transfer.

Table 2. Rate constant for the reaction of e_{aq}^- , $\bullet\text{H}$, $(\text{CH}_3)_2\bullet\text{COH}$ and $\text{CO}_2^{\bullet-}$ radicals with $[\text{Co}(1,10\text{-phenanthroline-5,6-dione})_2\text{Cl}_2]\text{Cl}$ complex.

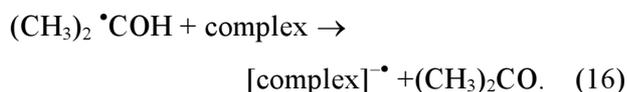
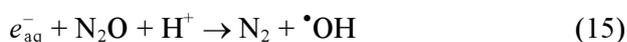
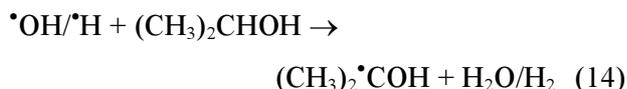
Reaction	Rate constant
$[\text{Co}(1,10\text{-phenanthroline-5,6-dione})_2\text{Cl}_2]\text{Cl} + e_{\text{aq}}^-$, pH = 6.2	$(2.2 \pm 0.2) \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
$[\text{Co}(1,10\text{-phenanthroline-5,6-dione})_2\text{Cl}_2]\text{Cl}$ decay of the radical anion, pH = 6.2	$(1.65 \pm 0.2) \times 10^4 \text{ s}^{-1}$
$[\text{Co}(1,10\text{-phenanthroline-5,6-dione})_2\text{Cl}_2]\text{Cl} + (\text{CH}_3)_2\bullet\text{COH}$	$(1.2 \pm 0.1) \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
$[\text{Co}(1,10\text{-phenanthroline-5,6-dione})_2\text{Cl}_2]\text{Cl} + \text{CO}_2^{\bullet-}$	$(2.3 \pm 0.2) \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
$[\text{Co}(1,10\text{-phenanthroline-5,6-dione})_2\text{Cl}_2]\text{Cl} + \bullet\text{H}$	$(3.5 \pm 0.3) \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
1,10-phenanthroline-5,6-dione + e_{aq}^- , pH = 6.2	$(3.2 \times 0.2) \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1*}$
	$(3.0 \pm 0.2) \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1**}$

*Value from reference¹⁴. **This work

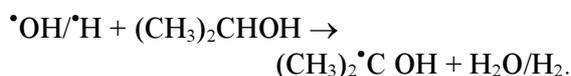
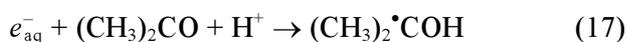
3.6 Reactions of dimethyl ketyl radical with the complex

Dimethyl ketyl radical is strong one electron reducing species ($E_0^1 = -1.4 \text{ V}$ vs NHE) and was produced in this work in two ways.

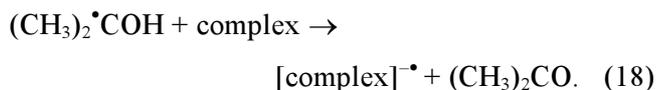
(i) In N_2O saturated solutions of 0.1 mol dm^{-3} 2-propanol, both H-atoms and $\bullet\text{OH}$ radicals react with 2-propanol to give dimethyl ketyl radicals.¹⁷



(ii) In mixed aqueous organic solvent (1 mol dm^{-3} each of acetone and 2-propanol) dimethylketyl radical¹⁷ is produced as follows:



In both the systems the $(\text{CH}_3)_2\bullet\text{C OH}$ radicals react with complex to reduce it.



The time resolved transient spectra obtained on the reaction of dimethyl ketyl radicals with the complex using both the methods of their generation are iden-

tical with that obtained in the reaction of e_{aq}^- with the complex (figure 2). The rate constant for the reaction of dimethyl ketyl radical with the complex is evaluated to be $(1.2 \pm 0.1) \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (lifetime $\sim 4 \mu\text{S}$) from the growth of 530 nm peak. The 530 nm peak decays slowly by first order rate of $(7.8 \pm 0.2) \times 10^3 \text{ s}^{-1}$.

No effect of 2-propanol concentration was seen on the transient absorption spectra and kinetics.

3.7 Reactions of $\bullet\text{CO}_2^-$ radical with the complex

The $\bullet\text{CO}_2^-$ radical ($E_0 = -1.9 \text{ V}$ vs NHE) is generated in N_2O saturated formate ion solutions ($0.1\text{--}0.25 \text{ mol dm}^{-3}$) as follows:



Figure 5 shows the time resolved transient spectra obtained on the reaction of e_{aq}^- , $\bullet\text{CO}_2^-$ radicals with the complex. The rate constant for the reaction of $\bullet\text{CO}_2^-$ radicals with the complex is evaluated to be $(2.3 \pm 0.2) \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ from the growth of 530 nm peak. The species decay by first order rate of $(9.3 \pm 0.2) \times 10^3 \text{ s}^{-1}$.

It is seen from the figure that absorption at $\sim 380 \text{ nm}$ increases as at 300 and 530 nm decreases. To ascertain the effect of formate ion concentration on this peak, the formate concentration was changed from 0.1 to 0.25 mol dm^{-3} . This resulted in increase of transient absorption at 380 nm as at 530 nm decreased. This is attributed to the replacement of chloride ligand by formate ions during the course of reduction.

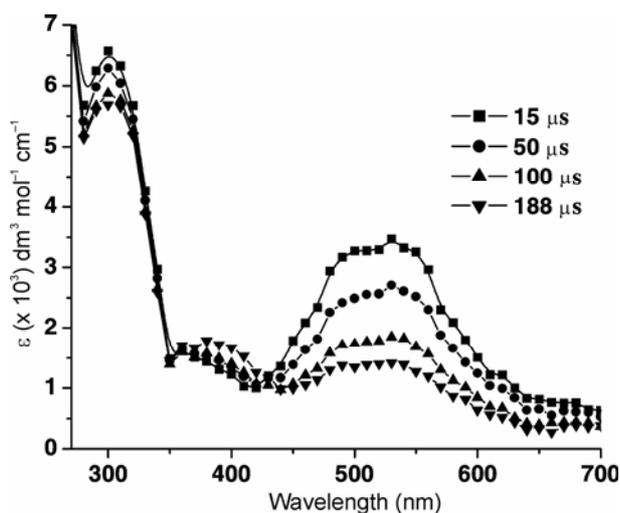


Figure 5. Time resolved transient absorption spectra obtained in the reaction of $\cdot\text{CO}_2^-$ radical with $[\text{Co}(\text{phendione})_2\text{Cl}_2]\text{Cl}$ complex. Dose per pulse ~ 12 Gy. $[\text{complex}]$: 2×10^{-4} mol dm^{-3} .

Similar radical insertion reactions have been observed in Co(III) aquo-ammonia complexes where $\cdot\text{CH}_3$, acetate radicals replace H_2O to generate Co-carbon σ -bond.¹⁸ Brezniak and Hoffman¹⁹ have estimated the half life for ligand replacement in $[\text{Co}(\text{NH}_3)_5\text{CO}_2^-]$ complex to be ~ 2 μs and half life for dissociation for all the NH_3 groups to be ~ 500 μs . In the present case we find that lifetime for ligand replacement, i.e. Cl^- by formate ions, is ~ 200 μs . While that for dissociation of phendione groups was well above 10 ms. This fact could be attributed to the stronger ligand field offered by phendione ligand as against weaker ligand ammonia. Hence breakdown of the complex is delayed. Since water and 2-propanol are weaker ligands than Cl^- , replacement by solvent does not result in spectral shift.

4. Conclusion

Reaction of four reducing free radical species namely e_{aq}^- , H-atoms, Dimethyl ketyl radicals and $\cdot\text{CO}_2^-$ with $[\text{Co}(\text{III})(\text{phendione})_2\text{Cl}_2]\text{Cl}$ complex has been studied by electron pulse radiolysis. Rate constants of these species with the complex have been determined to be $(2.2 \pm 0.2) \times 10^{10}$, $(3.5 \pm 0.3) \times 10^9$, $(1.2 \pm 0.1) \times 10^9$, $(2.3 \pm 0.2) \times 10^9$ $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ respectively. Time resolved transient absorption spectra show two peaks at 340 and 530 nm, which match with those of phendione anion radical. Steady

state absorption spectra on irradiation indicates breakdown of the complex. The complex anion radical decays by first order with a rate constant of $(1.65 \pm 0.2) \times 10^4 \text{ s}^{-1}$. H-atom reaction with the complex shows both electron transfer and addition reactions. The electron from the complex anion radical could be scavenged by benzophenone thus protecting the complex. Conductometric studies show that conductance increases on irradiations and could be attributed to aquation/de-ligation of the complex. In the presence of benzophenone conductance of the irradiated solutions does not significantly increase indicating protection of the complex. This shows that benzophenone may be able to intercept the intramolecular electron transfer leading to aquation/de-ligation of the complex on irradiation. The ligand replacement process and release of Cl^- ions seems to take place in a few 100 μs time scale as seen from the results with ion $\cdot\text{CO}_2^-$ radical reaction while the breakup of the complex into ligand and Co(II) takes place in the time scale of several ms.

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References

1. Erkkila K E, Odom D T and Barton J K 1999 *Chem. Rev.* **99** 2777
2. Sigman D S, Mazumdar A and Perrin D M 1993 *Chem. Rev.* **93** 2295
3. Grätzel M 2005 *Inorg. Chem.* **44** 6841
4. Ghosh S, Kawade V A, Sapre A V and Kumbhar A S 2008 *Ind. J. Chem.* **A47** 690
5. Ghosh S, Barve A C, Kumbhar A A, Kumbhar A S, Puranik V G, Datar P A, Sonawane U B and Joshi R R 2006 *J. Inorg. Biochem.* **100** 331
6. Rama Rao K V S, Shastri L V and Shankar J 1970 *Radiation Effects* **2** 193
7. Hayon E, Ibata T, Lichtin N N and Simic M 1972 *J. Phys. Chem.* **76** 2072
8. Hoffman M Z and Simic M 1972 *J. Am. Chem. Soc.* **94** 1757
9. Pramod G, Prasanthkumar K P, Mohan H, Manoj V M, Manoj P, Suresh C H and Aravindkumar C T 2006 *J. Phys. Chem.* **A110** 11517

10. Yadav P, Kulkarni M S, Shridhonkar M and Rao B S M 2007 *Curr. Sci.* **92** 599
11. Fielden E M 1982 *The study of fast processes and transient species by electron pulse radiolysis* (eds) J H Baxendale and F Busi (Riedel, Dodrecht: Holland) pp. 59–62
12. Waltz W L and Pearson R G 1969 *J. Phys. Chem.* **73** 941
13. Funston A M, McFadyen W D and Tregloan P A 2002 *Dalton Trans.* 2053
14. Bao H, Navaratnam S, Parsons B J and Phillips G O 1995 *Radiat. Phys. Chem.* **46** 545
15. Mendham J, Denney R C, Barnes J D and Thomas M J K 2002 *Vogel's textbook of quantitative chemical analysis* (New Delhi, India: Pearson Education Ltd) 6th edn, p. 658
16. Cohen H and Meyerstein D 1975 *J. Chem. Soc. Dalton Trans.* **23** 2477
17. Buxton G V, Greenstock C L, Helman W P and Ross A B 1988 *J. Phys. Chem. Ref. Data* **17** 513
18. Shanam N, Masarwa A, Matana Y, Cohen H and Meyerstein D 2002 *Eur. J. Inorg. Chem.* 87
19. Breznik N V and Hoffman M Z 1979 *Inorg. Chem.* **18** 2935