Studies on Azido Complexes of Cobalt. Part-III : Photochemical Studies

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The effect of viscosity, concentration and pH on the photochemical reduction of Co(III) to Co(II) on irradiation with light of 254, 313, 365 nm have been investigated for complexes of the type $[CoL_2(N_3)_2]^{+1}$ (L = ethylene diamine, 2,2'-bipyridyl, 1,10-phenanthroline, biguanide) and also for *cis*- and *trans*-$[Co(en)_2(NO_2)(H_2O)]^{2+}$. Results show that for a particular exciting light $\phi_{Co^{2+}}$ is affected only by the viscosity of the photolytic medium and is independent of the concentration of the complex, and pH. It has also been observed that for *cis*- and *trans*-$[Co(en)_2(N_3)_2]ClO_4$ the redox quantum yield goes through a maximum and the ϕ_{redox} vs wave length profile is almost parallel to the contour of the uv absorption spectra.

Investigations show that the *bis*azido complexes on excitation in the charge transfer spectral region in nonaqueous media undergo photodecomposition without the formation of Co(II).

THE role of viscosity of the solvent medium on the quantum yields of Co(II) formation has received some attention as an aid towards understanding the mechanism of photoreduction. Such studies have been restricted mainly to the acidopentammine-cobalt(III) complexes of the type $[Co(NH_3)_5X]^{2+}$[1,2] where X = Cl⁻, NCS⁻, Br⁻, N_3^-, NO_2^-. One of the objects of the present investigation is to extend such studies to *bis*azido ethylenediamine complexes of Co(III) and to the pair consisting of *cis*- and *trans*-$[Co(en)_2(NO_2)(H_2O)]^{2+}$.

Studies on the variation of quantum yield as a function of wave length are of great significance in the understanding of the reactivities of the excited states[3-5]. With this objective the redox quantum yields of *cis*- and *trans*-$[Co(en)_2(N_3)_2]ClO_4$ has been studied at various wave lengths corresponding to the LMCT bands.

Investigations on the photolysis of azido complexes have been carried out in nonaqueous media partly as an extension of our previous work[6] dealing with the effect of solvents on the spectra of these complexes, and partly to circumvent the difficulties associated with the limited solubilities in water of complexes of the type $[CoL_2(N_3)_2]^+$ with L = 1,10-phenanthroline (phen), biguanide (bigH), 2,2'-bipyridyl (bipy).

Experimental

The compounds *cis*- and *trans*-$[Co(en)_2(N_3)_2]ClO_4$, *trans*-$[Co(bipy)_2(N_3)_2]N_3.2H_2O$ and *trans*-$[Co(phen)_2(N_3)_2]N_3$ were prepared by the methods given in the literature[7,8].

Cis- and *trans*-$[Co(bigH)_2(N_3)_2]ClO_4.H_2O$ have been prepared by reacting saturated aqueous solutions of *cis*[9]- and *trans*[9]-$[Co(bigH)_2(N_3)_2]N_3.H_2O$ with solid sodium perchlorate, cooling and recrystallising from water.

Cobalt was estimated gravimetrically by converting a known weight of the complex into anhydrous cobalt sulphate. ClO_4^- was estimated by titrating the acid liberated by passing a known volume of the standard solution of the complex through a column of Amberlite IR-120 in the H⁺ form. The results of the analysis of these compounds are given below : *Trans*-$[Co(bigH)_2(N_3)_2]ClO_4.H_2O$. Found : Co, 12.93 ; ClO_4^-, 21.50 ; H_2O, 3.82. Calcd. : Co, 12.74 ; ClO_4^-, 21.52 ; H_2O, 3.89%. *Cis*-$[Co(bigH)_2(N_3)_2]ClO_4.H_2O$. Found : Co, 12.28 ; ClO_4^-, 21.28 ; H_2O, 3.90. Calcd. : Co, 12.74 ; ClO_4^-, 21.52 ; H_2O, 3.89%.

The solution for photolysis were prepared with the above compounds by dissolving the solid in NaOAc/HOAc buffers of pH 3.42, 4.05 and 5.2.

Cis- and *trans*-$[Co(en)_2(H_2O)(NO_2)]^{2+}$ were prepared by quantitative hydrolysis[10,11] of *cis*-$[Co(en)_2(NO_2)_2]NO_3$ and *trans*-$[Co(en)_2(NO_2)(Cl)]ClO_4$ but they were not isolated in the solid state. To get solutions of different pH the hydrolysis of the *trans*-isomer was carried out with NaOAc/HOAc buffers. Since complete hydrolysis of *cis*-$[Co(en)_2(NO_2)_2]NO_3$ occurs in a solvent medium with a nitric acid concentration of $4 \times 10^{-3} M$[10], ionic strength of 3.5 (adjusted by adding sodium nitrate), pH variation studies were not done with this compound.

The photolysis of trans-[Co(bipy)₂(N₃)₂]N₃·2H₂O was carried out in a mixture of ethanol and NaOAc/HOAc buffer consisting of 50% by volume of ethanol. The photolysis of trans-[Co(phen)₂(N₃)₂]N₃ was carried out in a mixture of methanol and NaOAc/AcOH buffer consisting of varying proportions of methanol by volume (4% to 50%).

It is found that the compounds are stable in solutions under such conditions for several hr. For varying viscosity, glycerol-water (buffer solution) were prepared with different amounts of glycerol. Viscosities of these mixtures were determined by an Ostwald viscometer and some values were taken from literature[12]. The pH of these solutions were measured by a Elico pH-meter (Model L 1-10).

Photolysis was carried out in quartz cells of 1 cm path length at 30°. 365 and 313 nm wavelength of radiation were isolated from a medium pressure mercury vapour lamp with appropriate filters[13,14] and 254 nm radiation from a 110 watt low pressure mercury vapour lamp, (M/s Thermal Syndicate, model T/M5759A). 302 nm and 334 nm radiations were isolated from a super pressure mercury vapour lamp (HBO 100 watt) with the help of a high radiance monochromator of Applied Photophysics Limited.

Ferrioxalate actionometry[15] was used in determining the output of the lamp. Co²⁺ formed by photoreduction was estimated colorimetrically[16] at 625 nm from previously prepared calibration graph. A Varian Techtron Series 635 recording spectrophotometer, a Beckman spectrophotometer model D. U. and Cary-17D spectrophotometer were used to obtain spectra of solutions before and after irradiation. Quantum yields of Co²⁺ formation were calculated using the relation

$$\phi_{Co^{2+}} = \frac{\text{No. of molecules of Co}^{2+}\text{ formed per sec.}}{\text{No. of quanta incident per sec} \times (1-T/100)}$$

where T is the percent transmission of the photolysing solution.

Results and Discussion

The spectra of all the complexes in different solvents remain unchanged for a period of six hours in the dark and thus the possibility of any thermal reaction is ruled out.

All these azido complexes have well defined absorption bands in the uv region (Fig. 1). The effects of solvents on the absorption spectra were discussed in a previous communication[6]. The wavelengths used for irradiation were well within the absorption bands of the complexes. Band assignments based on literature reports and our investigations are given in Table 1. Quantum yield data are given in Table 2.
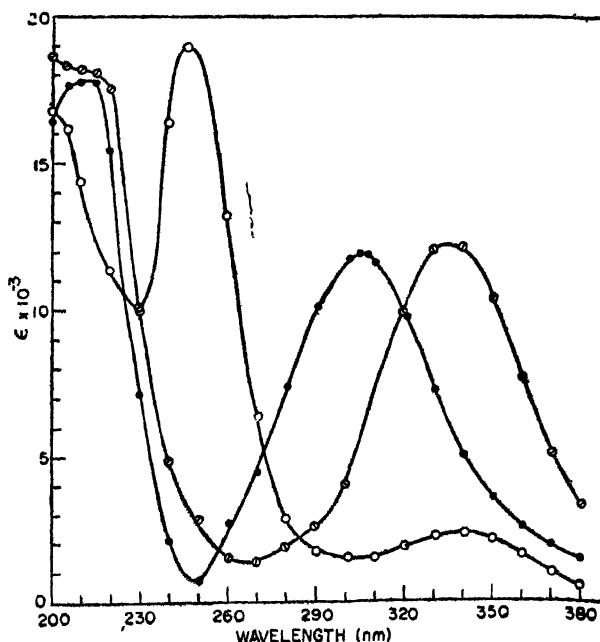

Fig. 1. Absorption spectra in aqueous perchloric acid (pH=4.05).
○—trans-[Co(en)₂(NO₂)(H₂O)]ClO₄
●—cis-[Co(en)₂(N₃)₂]ClO₄
⊘—trans-[Co(en)₂(N₃)₂]ClO₄

TABLE 1

Compounds	Solvent	uv peaks nm	Nature of the band
trans[Co(en)₂(N₃)₂]ClO₄[b]	Aqueous pH=4.05	337*	*N₃→Co[1'³³]
cis[Co(en)₂(N₃)₂]ClO₄[b]	,,	304*	*N₃→Co[1'³³]
trans[Co(bigH)₂(N₃)₂]ClO₄.H₂O[a]	,,	272[c], 354****	****(¹A₁g→¹T₁g)³³
cis[Co(bigH)₂(N₃)₂]ClO₄.H₂O[a]	,,	Shoulder band[c] 270-296 nm	
trans[Co(en)₂(NO₂)(H₂O)]ClO₄[b]	,,	338**, 248[c]	**d-d transition³⁴
trans[Co(Dipy)₂(N₃)₂]N₃.2H₂O[b]	50% ethanol NaOAc/HOAc	333*, 302***, 244***	***Intraligand π→π* transition³⁵'³⁶ *N₃→Co³⁵
trans Co(phen)₂(N₃)₂]N₃[b]	4% methanol NaOAc/HOAc	357*, 275***	***Intraligand π→π* transition³⁷ *N₃→Co³⁸

b = Reported from literature ; a = Present study ; c = Not characterised.

TABLE 2—VARIATION OF $\phi_{Co^{2+}}$ WITH WAVE LENGTH OF EXCITING RADIATION AND VISCOSITY OF THE PHOTOLYTIC MEDIUM

Medium	Viscosity centipoise[a]	Exciting light nm	$\phi_{Co^{2+}}$ of the compound		
			$trans[Co(en)_2(N_3)_2]ClO_4$	$cis[Co(en)_2(N_3)_2]ClO_4$	$trans[Co(en)_2(NO_2)(H_2O)]_{ClO_4}^{Cl}$
Aqueous pH 4.05	0.80	365	0.095	0.068	0.146
		334	0.184	—	—
		313	0.162	0.164	0.084
		302	—	0.189	—
		254	0.090	0.068	0.048
Aqueous pH 3.42	0.80	365	0.092	0.066	0.141
		313	0.162	0.160	0.085
		254	0.090	0.069	0.048
30% glycerol[b] pH 4.05	1.92	365	0.072	0.055	0.084
		313	0.123	0.120	0.069
		254	0.077	0.051	0.033
56% glycerol[b] pH 4.05	5.10	365	0.052	0.047	0.053
		313	0 097	0.060	0.030
		254	0.052	0.042	0.026
92% glycerol[b] pH 4.05	110	365	×	×	0.029
		313	0.046	0.037	×
		254	×	×	×
Ethylene[c] glycol	13.50	365	0.042	0.030	—

The value of $\phi_{Co^{2+}}$ in cis-Co(en)$_2$(NO$_2$)(H$_2$O)](NO$_3$)$_2$ at 365 nm and at pH 4.00 at 30° = 0.030.

— Quantum yield not determined ;   a—values determined experimentally ;   b—composition in wt. percent.
  × No reduction ,   c—obtained from literature[13].

For all the complexes investigated it has been found that $\phi_{Co^{2+}}$ always decreases on increasing the viscosity of the aqueous acidic solvent medium (by the addition of glycerol) irrespective of the wavelength. This is consistent with previous studies on acidopentammine-Co(III) complexes[1,2]. For [Co(NH$_3$)$_5$(NO$_2$)]$^{2+}$, $\phi_{Co^{2+}}$ at 365 and 254 nm was found to decrease[1,2] with the increase in the viscosity of the solvent medium with a simultaneous increase in the quantum yield of linkage isomerism. Previous studies indicate that the nitro-nitrito isomerism takes place even in the solid state on irradiation with uv light[17], on heating[18], and on prolonged exposure to sunlight[19]. We are unable to explore the possibility of linkage isomerism for $trans$-[Co(en)$_2$(NO$_2$)(H$_2$O)]$^{2+}$ as the nitrito isomer of this complex is not known. As we could not isolate $trans$-[Co(en)$_2$(NO$_2$)(H$_2$O)]$^{2+}$ in the solid state, we irradiated solid $trans$-[Co(en)$_2$(NO$_2$)Cl]$^+$ (by the hydrolysis of which the aquo-complex is prepared) directly as well as dispersed in nujol at 365 and 313 nm and did not find any evidence of linkage isomerism from the analysis of the ir spectra[20] of the irradiated and unirradiated compound.

The primary product on irradiation of the pentammine azido Co(III) in the CTTM region is radical pairs in the solvent cage. Some of these undergo recombination. Photo redox and photo substitution products result from the fragmentation of the radical pairs that escape the solvent cage. Hence, it appears that in the sequence of steps leading to the formation of the end products from primary radical pair, the one involving the diffusing apart of radical pairs is hindered by increasing the viscosity of the solvent medium resulting in a decrease of $\phi_{Co^{2+}}$. Since we did not observe any significant change in band maxima or band intensity in glycerol-water mixtures of cis- and $trans$-[Co(en)$_2$-(N$_3$)$_2$]ClO$_4$ it appears that viscosity effects are free from any complicating features as was observed[5] for [Co(NH$_3$)$_5$Br]$^{2+}$.

There is no clear cut trend in the magnitude of the quantum yields of photoreduction of cis and $trans$ isomers. For instance, it is known that $\phi_{Co^{2+}}$ ($trans$) $<$ $\phi_{Co^{2+}}$ (cis) for cis and $trans$ [Co(en)$_2$(H$_2$O)-Cl]$^{2+}$[21] and $\phi_{Co^{2+}}$ ($trans$) $>$ $\phi_{Co^{2+}}$ (cis) for cis- and $trans$-[Co(en)$_2$F$_2$]$^+$[22] and [Co(en)$_2$Cl$_2$]$^+$[21]. The nature of the products are also known to be dependent on the wave length of irradiation. For all the compounds investigated by us it has been found that ϕ_{redox} for the $trans$ is always greater than that of the cis for all the wave lengths. For the pair cis- and $trans$-[Co(en)$_2$(N$_3$)$_2$]ClO$_4$, ϕ_{redox} is almost equal for irradiation with 313 nm. This behaviour of the bis-azido complexes is similar to the bis-dichloro and -difluoro complexes and is expected since azide is a pseudo halogen.

With cis- and $trans$-[Co(en)$_2$(N$_3$)$_2$]ClO$_4$ the redox quantum yield, $\phi_{Co^{2+}}$, has been determined at various wave lengths ranging from 254-366 nm. Quantum yield data (Table 2 and Fig. 2) indicate that there is a reduction of quantum yield at higher energies (at 254 nm) and that for both the compounds the redox quantum yield goes through a

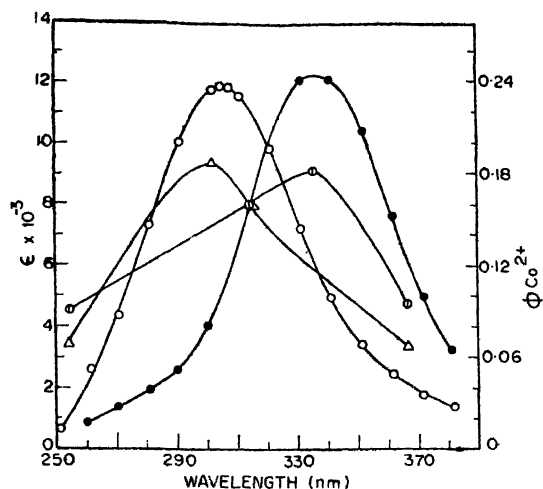maximum and the quantum yield vs wave length profile is almost parallel to the near uv absorption bands (Fig. 2).

Fig. 2. Absorption spectra and quantum yield (reduction) profile of (A) cis-[Co(en)$_2$(N$_3$)$_2$]ClO$_4$, (B) trans-[Co(en)$_2$(N$_3$)$_2$]ClO$_4$.
O—Absorption spectra of (A)
●—Absorption spectra of (B)
△—$\phi_{Co^{2+}}$ of (A)
◑—$\phi_{Co^{2+}}$ of (B)

Fig. 3. Absorption spectra of trans-[Co(en)$_2$(N$_3$)$_2$]ClO$_4$ in aqueous perchloric acid (pH = 4.05).

Such a decrease of quantum yield at lower wavelengths has been reported[23,24] for [Co(NH$_3$)$_5$N$_3$]$^{2+}$ with $\phi_{Co^{2+}}$ = 0.20 and 0.44 at 254 and 370 nm, respectively. $\phi_{Co^{2+}}$ for the pentammino azido complex has also been found to be dependent on both time and intensity of irradiation[23]. This lower value of ϕ_{redox} at higher energy for the pentammine azido complex and its dependance on time and intensity of irradiation has been explained by Endicott and Hoffman[23] to be due to the formation of [Co(NH$_3$)$_4$(N$_3$)H$_2$O]$^{2+}$ at the initial stages of the reaction. We irradiated cis and trans bisazido complexes, as also the other compounds mentioned in this work, at different concentrations and for different times, but noticed no change in the value of $\phi_{Co^{2+}}$. ϕ_{redox} was also found to be independent of pH. The complete near uv absorption spectra of both these geometrical isomers were recorded before and after irradiation. With 366 and 313 nm radiations the only discernible change was a fall in the intensity of the existing band (Figs. 3 and 4). With 254 nm radiation, a new band appeared around 240 nm with a sharp decrease of the 338 nm band for the trans- (304 nm band for the cis-) isomer. Though it seems from the spectral data that total photo effect is maximum at 254 nm, the photo redox quantum yield ($\phi_{Co^{2+}}$) is lower compared to that of 313 nm. In the present work we did not determine the aquated products. We concentrated only on photo-redox processes. Sharp decrease of the 338 nm bands for the trans- (304 nm band for the cis-) isomer suggest that probably the photo aquation of N$_3^-$ ligand is the other route of the photoprocess and that the yield of this aquation process is higher at 254 nm compared to other excit-
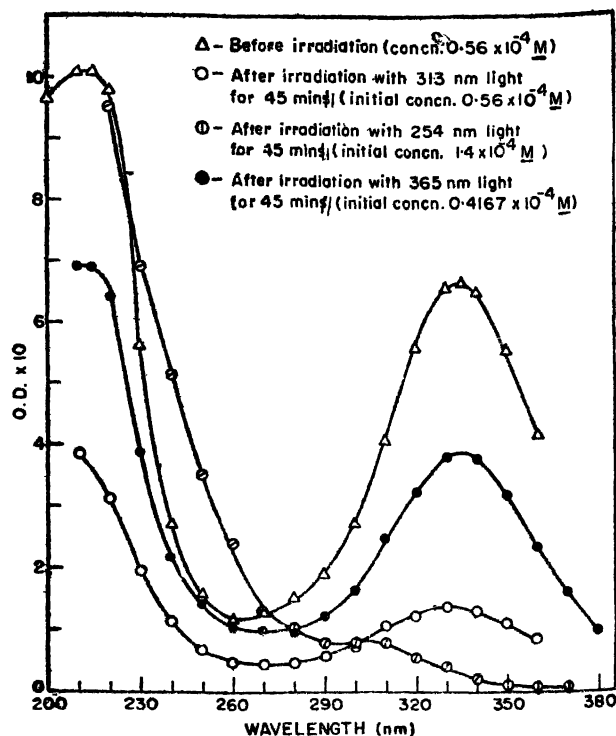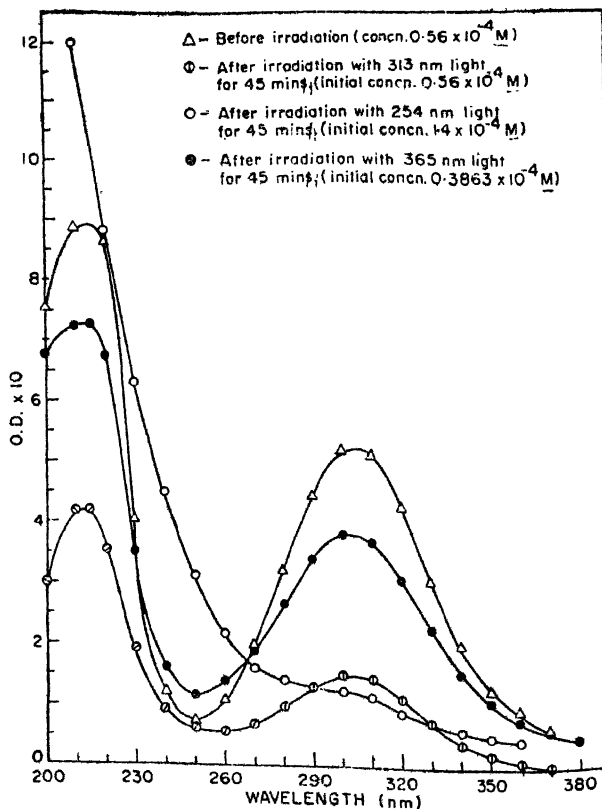

Fig. 4. Absorption spectra of cis-[Co(en)$_2$(N$_3$)$_2$]ClO$_4$ in aqueous perchloric acid (pH = 4.05).

ing wave lengths. The similarity in the contour of the absorption spectra and the redox quantum yield vs wave length profile for the cis and trans bisazido complexes is uncommon for cobalt complexes. However, such a behaviour has been observed[25] for the complex Fe(HEDTA)OH$_2$.

The deep uv spectra of the cis and trans bisazido complexes reveal the presence of a high intensity band at ~ 225 nm (Fig. 1) of considerable width. Internal transitions of the azide anion are reported[26] to be at 188 and 232 nm. One way therefore is to regard the band at 225 nm as an intraligand transition shifted on complexation. A low quantum yield for 254 nm is expected, if this wave length falls within the envelope of an intraligand band. Inner filter effects due to the presence of cobaltous perchlorate in the irradiated solutions need not be considered as the perchlorate anion has an absorption[26] at 178 nm and cobaltous perchlorate in aqueous solution[27] has negligibly low molar absorbances at 198 and 250 nm.

Since the azide ion has a π system of its own, we may regard the near uv absorption band for both these complexes ($\lambda_{max} = 338$ nm for trans and $\lambda_{max} = 304$ nm for cis) to be solely of the CTTM type but composite in nature, involving transitions from different π molecular orbitals of the azide ion to the e_g orbital of Co(III). The region of the broad absorption bands close to 254 nm may correspond to a photochemically unreactive component of the charge transfer band. Alternatively there may exist a photochemically unreactive excited state which becomes populated by inter system crossing on irradiation at 254 nm. This unreactive excited state is at a higher energy than λ_{max} and at a lower energy than 254 nm. Hence we observe that from λ_{max} to 366 nm, the quantum yield profile shows the usual behaviour, that of increasing redox, quantum yield with increasing energy of irradiation.

Irradiation of trans- [Co(bipy)$_2$(N$_3$)$_2$]N$_3$.2H$_2$O, trans-[Co(phen)$_2$(N$_3$)$_2$]N$_3$, cis- and trans-[Co(bigH)$_2$-(N$_3$)$_2$]ClO$_4$.H$_2$O with 365, 313 and 254 nm in alcohol-water mixtures indicates no photoreduction. Trans-[Co(bipy)$_2$(N$_3$)$_2$]N$_3$.2H$_2$O is the only exception. On prolonged irradiation (~ 4 hr) with 254 nm in methanol-water solvent photoreduction is observed with $\phi_{Co^{2+}} \sim 3 \times 10^{-4}$. However, all these compounds undergo photochemical reaction other than photoreduction since the spectra of irradiated and unirradiated solution show considerable differences. A representative example is given in Fig. 5.

We irradiated cis- and trans-[Co(en)$_2$(N$_3$)$_2$]ClO$_4$ and trans- [Co(en)$_2$N$_3$Cl]ClO$_4$ in DMSO at 313 and 365 nm but could not detect any Co(II) in the irradiated solution. In this respect the photoreactivity in aqueous medium is different from that in DMSO. However, for the complexes cis- and trans-[Co(en)$_2$Cl$_2$]$^+$, Co(II) has been observed both in aqueous[28] and in DMSO medium[29].

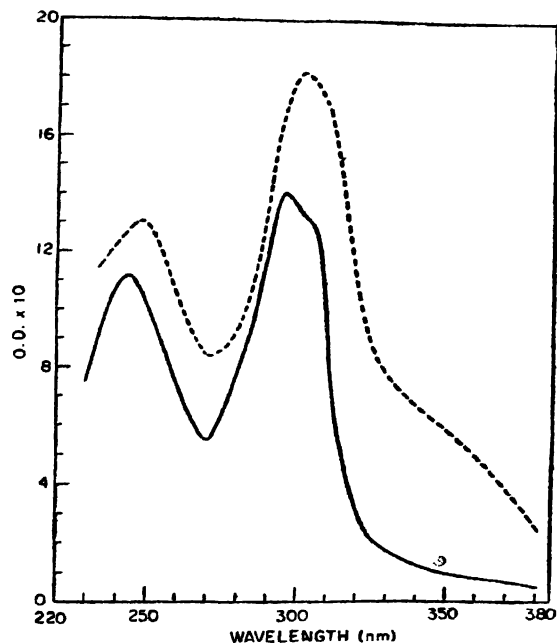It is also known[30] that on prolonged exposure to sun light in DMSO solution cis- and trans-[Co-

Fig. 5. Absorption spectra of trans-[Co(bipy)$_2$(N$_3$)$_2$]N$_3$.2H$_2$O in 50% ethanol. — — — — —Before irradiation (conc. $5.624 \times 10^{-4} M$). — — — — After irradiation with 365 nm light for 90 min (initial conc. $5.624 \times 10^{-4} M$).

(en)$_2$Cl$_2$]$^+$ produces a solution containing the species [Co(en)$_2$DMSO Cl]$^{2+}$, which can be isolated and has a characteristic absorption spectra. We are unable to isolate any new compound from the irradiated solution, but found that a new band around 490 nm can be detected by plotting the difference spectra of the irradiated and unirradiated solutions of trans-[Co(en)$_2$(N$_3$)$_2$]ClO$_4$ in DMSO. Such a new band cannot be detected after irradiation in aqueous perchloric acid media.

From these observations it appears that excited state precursors are different in aqueous and non-aqueous media. Specific substrate solvent interactions are capable of conferring some stability to the radical pairs, resulting in the formation of an excited charge-transfer state, which could populate a ligand field excited state by inter system crossing. Such excited state dynamics would result in a photoactive state in nonaqueous media which is different, from that in the aqueous medium.

For a better understanding of the role of solvent on the photochemistry of the substrate it is desirable to investigate the role of polarity and size of solvent molecules in nonaqueous medium. The disadvantage of using mixed aqueous solvents lies in the fact that Co(III) complexes are preferentially solvated by water molecules so that the microscopic environment of the substrate is not affected in mixed solvents.

Acknowledgement

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