*Journal of Organometallic Chemistry*, 349 (1988) 235–243
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

# Photochemical and thermal behaviour of isocyanide complexes

## VI *. Photochemistry of isocyanide ruthenium(II) complexes

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(Received December 17th, 1987)

## Abstract

Irradiation of $[Ru(CNCH_3)_6]^{2+}$ at 254 nm induced release of $CNCH_3$ and formation of the monosolvated cation $[Ru(CNCH_3)_5(NCCH_3)]^{2+}$ in acetonitrile and of the dimeric cation $[Ru_2(CNCH_3)_{10}]^{4+}$ in $H_2O$ and in $CH_2Cl_2$. The photochemical products were isolated as tetrafluoroborate salts and characterized by elemental analysis, conductivity measurements, and $^1H$ NMR, UV and IR spectroscopy. The dimeric cation $[Ru_2(CNCH_3)_{10}]^{4+}$ was photochemically stable, but reacted thermally with acetonitrile to give the mixed complex $[Ru(CNCH_3)_5(NCCH_3)]^{2+}$, which underwent conversion into the dimeric species when irradiated in an inert solvent. The overall quantum yields of the photoprocesses were determined under various experimental conditions. The results are consistent with a mechanism in which the primary photochemical step consists in a dissociation of the starting complex into a free molecule of $CNCH_3$ (or $NCCH_3$) and a pentacoordinate intermediate, which undergoes fast thermal reactions to give the final products.

## Introduction

Early investigations of the photochemical behaviour of isocyanide $Fe^{II}$ complexes revealed that the irradiation caused heterolytic fission of the Fe–C bond, leading to formation of a pentacoordinate intermediate and release of isocyanide. In inert solvents no net chemical reaction occurred, whereas in coordinating solvents, as water or acetonitrile, photosolvation took place. In water [1–4] a progressive photoaquation, giving the $[Fe(H_2O)_6]^{2+}$ ion, took place through photochemical and secondary thermal processes. In acetonitrile [5–8], a solvent molecule coordinated to

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* For parts I–V see refs. 5–8.

0022-328X/88/$03.50

the sixth position of the pentacoordinate intermediate to form acetonitrile-substituted compounds, which were thermally stable but photosensitive. Thus, it was possible to obtain photochemically the isolable mono- and bis-acetonitrile substituted $Fe^{II}$ complexes, the acetonitrile of which can be replaced easily with various ligands to give complexes with mixed ligands.

With the aim of providing information about the photochemical behaviour of analogous complexes of heavier $d^6$ ions, we have studied the hexatris(methylisocyanide)ruthenium(II) tetrafluoroborate. We did this because, in spite of the interest in photophysical aspects of the ruthenium complexes, little information about their photochemical behaviour has been reported.

## Experimental

### *Preparation of compounds*

$[Ru(CNCH_3)_6][BF_4]_2$ was prepared [9] by treating $K_4Ru(CN)_6$ (2.4 g) with $(CH_3)_2SO_4$ (90 ml). The mixture was stirred at 95 °C under reflux for 6 h and filtered hot. The filtered solution was set aside, loosely covered, at room temperature for 12 days, then extracted with water. The product was precipitated from the concentrated extract by addition of saturated aqueous $NaBF_4$, filtered off, and recrystallized from methanol. Mol. wt. calculated 521. Found (by osmometry in $CHCl_3$) 540. Analysis. Found: C, 27.70; H, 3.51; N, 15.98. $C_{12}H_{18}B_2F_8N_6Ru$ calcd.: C, 27.67; H, 3.48; N, 16.13%. $(\Lambda_0-\Lambda)/\sqrt{c}(H_2O)$, 230 ($\Lambda$, equivalent conductivity, $ohm^{-1}$ $cm^2$ $eq^{-1}$; $c$, equivalent concentration), 25 °C. $^1H$ NMR ($CD_2Cl_2$, 80 MHz, 22 °C), 3.56 ppm. UV ($H_2O$ $\lambda_{max}$, 230 nm ($\epsilon$ 2900), 25 °C. IR (KBr): $\nu(CN)$ 2241 $cm^{-1}$.

$[Ru_2(CNCH_3)_{10}][BF_4]_4$ was obtained by irradiating at 254 nm a $5\times10^{-3}$ $M$ solution of $[Ru(CNCH_3)_6][BF_4]_2$ in $CH_2Cl_2$ in a quartz vessel (250 ml) with nitrogen bubbling through the solution. When reaction was complete, n-hexane (ca. 100 ml) was added to initiate precipitation, the solution was concentrated to ca. 300 ml under vacuum, and the colourless microcrystals that separated were filtered off and washed with hexane. Mol. wt. calculated for $[Ru_2(CNCH_3)_{10}][BF_4]_4$ 960. Found ($CHCl_3$) by osmometry 960. Anal. Found: C, 25.20; H, 3.30; B, 4.35; F, 31.77; N, 14.51; Ru, 20.80. $C_{20}H_{30}B_4F_{16}N_{10}Ru_2$ calcd.: C, 25.03; H, 3.15; B, 4.50; F, 31.67; N, 14.59; Ru, 21.06%. $(\Lambda_0-\Lambda)/\sqrt{c}$ ($H_2O$), 580, 25 °C. $^1H$ NMR ($CD_2Cl_2$, 80 MHz, 22 °C) 3.59; 3.47 ppm. UV ($H_2O$) $\lambda_{max}$, 282 nm ($\epsilon$ 4450), 25 °C. IR (KBr): $\nu(CN)$ 2230; 2280 $cm^{-1}$, $\mu_{eff}$ 3.5 BM.

$[Ru(CNCH_3)_5(NCCH_3)][BF_4]_2$ was prepared by mixing a concentrated solution of $[Ru_2(CNCH_3)_{10}][BF_4]_4$ in $CH_2Cl_2$ (ca. $10^{-2}$ $M$) with an equal volume of acetonitrile. After 24 h n-hexane was added to initiate precipitation and the solution was concentrated slowly under vacuum to ca. 2/3 of the initial volume. The precipitate was filtered off and washed with hexane. Mol. wt. calculated for $[Ru(CNCH_3)_5(NCCH_3)][BF_4]_2$, 521. Found by osmometry 540. Analysis. Found: C, 27.78; H, 3.60; B, 3.96; F, 29.01; N, 15.98; Ru, 19.20. $C_{12}H_{18}B_2F_8N_6Ru$ calcd.: C, 27.67; H, 3.48; B, 4.22; F, 29.17; N, 16.13; Ru, 19.40%. $(\Lambda_0-\Lambda)/\sqrt{c}$ ($H_2O$) 220, 25 °C. $^1H$ NMR ($CD_2Cl_2$, 80 MHz, 22 °C), 2.41; 3.53; 3.60 ppm. UV ($H_2O$), $\lambda_{max}$, 251 nm ($\epsilon$2200), 25 °C. IR (KBr): $\nu(CN)$ 2230; 2280 $cm^{-1}$; $\nu(NC)$ 2320 $cm^{-1}$. $\mu_{eff}$ 2.5 BM.

### *Apparatus and procedures*

Normal equipment was used for the irradiation. The 254 nm radiation was supplied from a Rayonet photochemical reactor equipped with four or two 24 W lamps. The intensity was of the order of $10^{-6}$ Einstein $\text{min}^{-1}$. The $^1$H NMR, UV, and IR spectra were recorded by use of the apparatus previously described [6].

The quantum yields were calculated in all cases in terms of disappearance of the irradiated complex and were determined in the temperature range 15–55 °C with $0.2 \times 10^{-3}$ to $2 \times 10^{-3}$ $M$ solutions deareated by prolonged nitrogen bubbling. The spectra of the solutions were recorded after various times of irradiation. The fraction of the light absorbed was corrected for absorption by the photochemical products.

## Results and discussion

At room temperature in the dark the cation $[\text{Ru(CNCH}_3)_6]^{2+}$ was inert in the solvents used, namely $CH_3CN$, $H_2O$, and $CH_2Cl_2$. The UV spectrum was almost unaffected by the solvent; in $H_2O$ it exhibits an intraligand (IL) band at about 200 nm ($\epsilon$ 47500), and a shoulder about 230 nm ($\epsilon$ 2900) due to metal to ligand charge transition (MLCT) partially overlapped by the higher IL band. No ligand field (LF) band was detectable and the absorption was negligible above ca. 300 nm. (These spectral features means that only 254 nm radiation can be used in the photochemical investigation).

The irradiation caused release of isocyanide and formation of a stable photoproduct; the photoreaction proceeded in one step until there had been complete conversion of the starting compound into new species, $[\text{Ru}_2(\text{CNCH}_3)_{10}]^{4+}$ in $H_2O$ and $CH_2Cl_2$ and $[\text{Ru(CNCH}_3)_5(\text{NCCH}_3)]^{2+}$ in $CH_3CN$.

*Irradiation in $CH_2Cl_2$ and $H_2O$.* Upon irradiation of solutions of $[\text{Ru(CNCH}_3)_6]^{2+}$ in these solvents the UV spectrum was shifted towards longer wavelengths with an isosbestic point at 252 nm and appearance of a new symmetric band at 282 nm (Fig. 1). The photoreaction proceeded to complete conversion of the starting compound without detectable side reactions.

The isolated photoproduct was identified as a dimeric ruthenium species by molecular weight and elemental analysis. The formula which fits best with these data is $[\text{Ru}_2(\text{CNCH}_3)_{10}][\text{BF}_4]_4$. The chemical physical data are also consistent with this formula. The equivalent conductivities of various aqueous solutions were determined; the value of $K$ (580) (as given by the Onsager equation $\Lambda_0 - \Lambda = K\sqrt{c}$ [10]) was very close to that found for $K_4Fe(CN)_6$, and so we concluded that the photoproduct is a uni-tetravalent electrolyte. The $^1$H NMR spectra exhibited two peaks, arising from the two non-equivalent groups of MeNC ligands at 3.59 and at 3.47 ppm, the first much more intense than the second.

The IR spectra show a split $\nu$(CN) band at 2230–2280 $\text{cm}^{-1}$. In the UV spectra the band attributable to MLCT appeared at longer wavelength ($\lambda$ 282 nm; $\epsilon$ 4450), indicating that the $Ru_2$ unit to ligand transition requires less energy. An X-ray study of the structure of the dimer is in progress. At present only limited information about it can be given. Two structures are possible: the two units $[\text{Ru(CNCH}_3)_5]^{2+}$ can be held together either (a) by $CNCH_3$ bridging ligands with or without metal–metal bonding, or (b) by a metal–metal bond without bridging ligands.

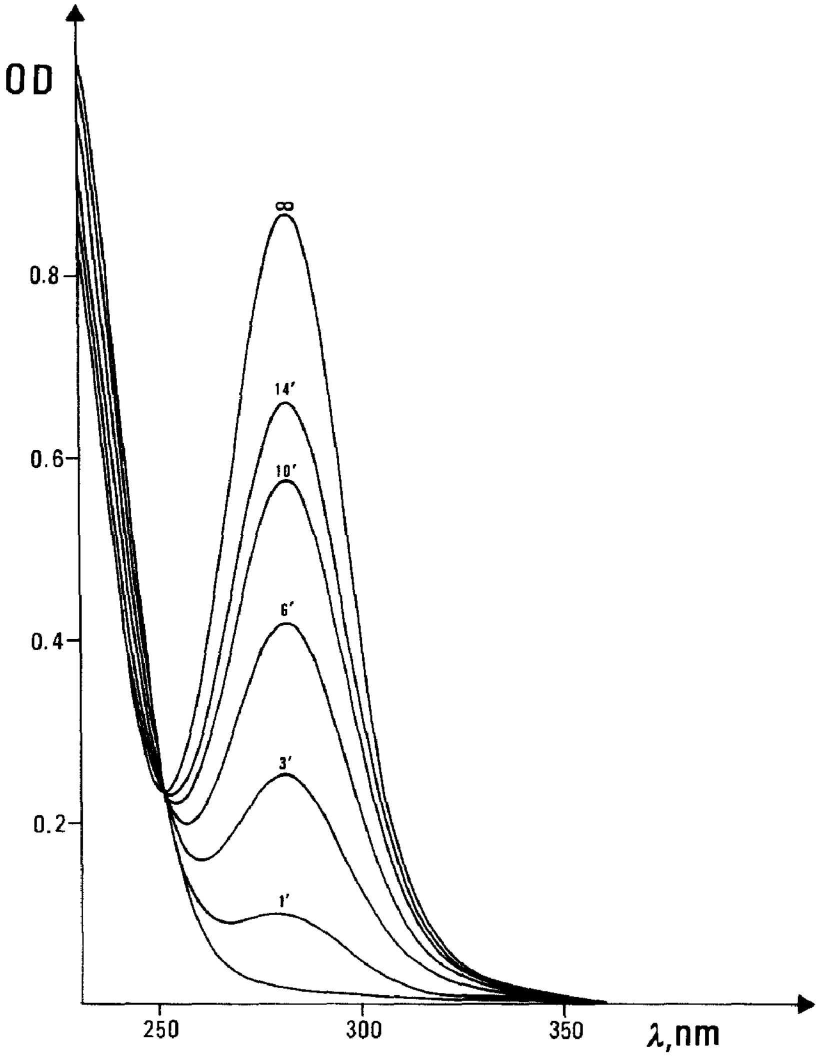

Fig. 1. Photochemical formation of binuclear complex $[Ru_2(CNCH_3)_{10}]^{4+}$ for irradiation of $[Ru(CNCH_3)_6]^{2+}$ in $CH_2Cl_2$ at 254 nm; the numbers refer to the irradiation times.

The infrared spectra of the dimer indicated only the presence of terminal isocyanide ligands; there was no band at about 1640 $cm^{-1}$ that would be expected for bridging isocyanide whereas none of the spectral features were inconsistent with the second formulation. A plausible ground state electronic configuration for the $Ru_2^{4+}$ unit is $\sigma^2\ \pi^4\ \delta^2\ \delta^{\star 2}\ \pi^{\star 2}$. For this configuration a triplet spin system, arising from the two singly-occupied degenerate orbitals $\pi^{\star 2}$, and a net bond order of 2 between the Ru atoms are expected, and both features were observed. The dimer is paramagnetic with $\mu_{eff}$ 3.5 BM. Its reactions are analogous to those of binuclear complexes with multiple metal–metal bonds, which react readily with added ligands to give mononuclear complexes with six coordinated ligands. The Ru dimer is attacked by free isocyanide with regeneration of the starting compound, and by various ligands with nitrogen or phosphorus donor atoms to form new mixed complexes. In particular the mixed cation $[Ru(CNCH_3)_5(NCCH_3)]^{2+}$ was pre-

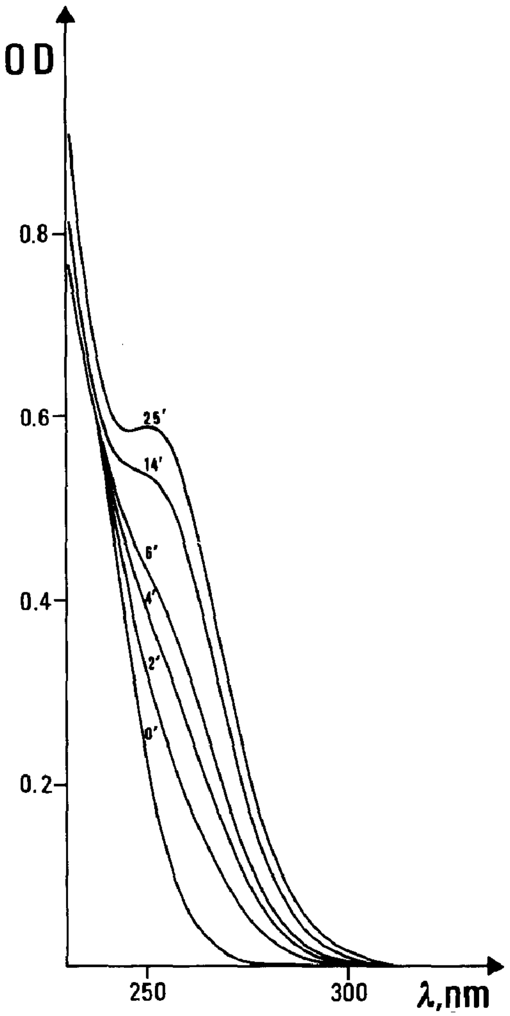

Fig. 2. Photochemical formation of $[Ru(CNCH_3)_5(NCCH_3)]^{2+}$ for irradiation of $[Ru(CNCH_3)_6]^{2+}$ in acetonitrile at 254 nm; the numbers refer to the irradiation times.

pared, and isolated as the tetrafluoroborate salt, and found to be identical with that obtained by irradiation of $[Ru(CNCH_3)_6]^{2+}$ in $CH_3CN$ as described below.

*Irradiation in acetonitrile.* Upon irradiation of acetonitrile solutions of $[Ru(CNCH_3)_6]^{2+}$ the UV spectrum shifted towards longer wavelengths and a shoulder appeared at about 250 nm (Fig. 2). The initial isosbestic point at 237 nm was not maintained after some time because of absorption by side products formed by the released isocyanide. The product, isolated as its fluoroborate salt, had the same molecular weight and elemental analysis as the starting compound. It was soluble and thermally stable in water and in other organic solvents; upon addition of isocyanide it converted into the initial $[Ru(CNCH_3)_6]^{2+}$. The equivalent conductivities at various concentrations indicated that the photoproduct is a uni-bivalent electrolyte. These results indicate that no redox process had occurred, only a photosolvation; the spectral characteristics pointed to a monoacetonitrile-substituted compound. The $^1H$ NMR spectra showed three significant peaks; a peak at 2.41 ppm is attributable to the methyl protons of the coordinate acetonitrile, that at

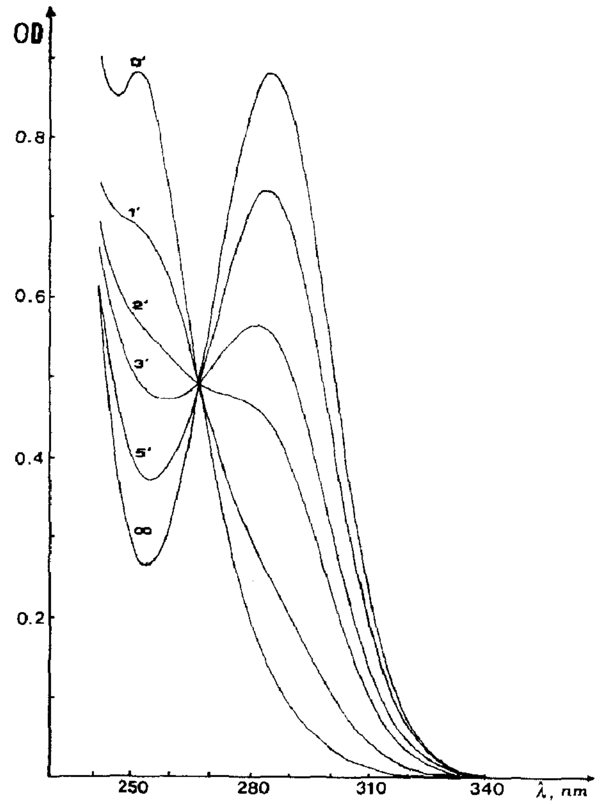

Fig. 3. Photochemical formation of binuclear complex $[Ru_2(CNCH_3)_{10}]^{4+}$ for irradiation of $[Ru(CNCH_3)_5(NCCH_3)]^{2+}$ in $CH_2Cl_2$ at 254 nm; the numbers refer to the irradiation times.

3.60 ppm to the in plane isocyanide molecules *cis* to the acetonitrile, and the peak of the lower intensity at 3.53 ppm is due to the protons of the isocyanide in an axial position *trans* to the acetonitrile. The IR spectra showed a split $\nu(CN)$ isocyanide band at 2230–2280 $cm^{-1}$, along with a new single $\nu(NC)$ band at 2320 $cm^{-1}$ attributable to the acetonitrile ligand. In the UV spectra the shift of the MLCT band to longer wavelength (λ 251 nm, $\epsilon$ 2200), as found for analogous compounds, confirmed that there had been replacement of $CNCH_3$ by the ligand $NCCH_3$ in an octahedral symmetry distorted towards a tetragonal one.

The compound is paramagnetic with $\mu_{eff}$ 2.5 BM and so a ground triplet state is likely. It is thermally stable even in the presence of free ligands, but upon irradiation in water or in $CH_2Cl_2$ it is completely converted into the Ru dimer described above (Fig. 3).

*Photochemical kinetics.* The overall quantum yields of the photoreactions $[Ru(CNCH_3)_6]^{2+} \rightarrow [Ru(CNCH_3)_{10}]^{4+}$, $[Ru(CNCH_3)_5(NCCH_3]^{2+} \rightarrow [Ru_2(CNCH_3)_{10}]^{4+}$, $[Ru(CNCH_3)_6]^{2+} \rightarrow [Ru(CNCH_3)_5(NCCH_3)]^{2+}$,

$$\phi = \frac{-d[\text{irradiated complex}]}{I\,dt} = \frac{d[\text{final photoproduct}]}{I\,dt}$$

(where $I = (Nh\nu/V) \times F$

$Nh\nu$ = light intensity; $F$ = fraction of the light absorbed by complex, $V$ = solution volume in liters) indicated respectively by as $\phi_D$, $\phi'_D$ and $\phi_M$, were determined at

Table 1

Overall quantum yields

| | Solvent | Temperature (°C) | | | | |
|---|---|---|---|---|---|---|
| | | 15 | 25 | 35 | 45 | 55 |
| $\phi_D$ | $H_2O$ | 0.22 | 0.28 | 0.32 | 0.35 | 0.38 |
| | $CH_2Cl_2$ | 0.27 | 0.33 | 0.37 | – | – |
| $\phi'_D$ | $H_2O$ | 0.11 | 0.16 | 0.18 | 0.22 | 0.24 |
| | $CH_2Cl_2$ | 0.14 | 0.18 | 0.22 | – | – |
| $\phi_M$ | $NCCH_3$ | 0.74 | 0.75 | 0.76 | – | 0.75 |

254 nm for solutions in the concentration range $0.2 \times 10^{-3}$ to $2 \times 10^{-3}$ *M* at various temperature (15–55 °C). The values of $\phi_D$ and $\phi'_D$ (Table 1), obtained for short irradiation (< 10% transformation) were independent of the initial concentration, but they increased with the temperature. Furthermore these values fell slightly as the photoreaction proceeded, the effect being more evident at the higher concentrations. Some experiments carried out in the presence of small amounts of $CNCH_3$ or $NCCH_3$ suggested that this effect can be attributed to mass law retardation by the free ligand. The value of $\phi_M$ (Table 1) was independent of concentration, irradiation time, and temperature. The results are consistent with the mechanism summarized in the scheme below (Fig. 4). The sequence of the steps leading to the dimer from the initial $[Ru(CNCH_3)_6]^{2+}$ is

$$[Ru(CNCH_3)_6]^{2+} \xrightarrow{h\nu,\varphi} [Ru(CNCH_3)_5]^{2+} + CNCH_3 \tag{1}$$

$$[Ru(CNCH_3)_5]^{2+} + CNCH_3 \xrightarrow{k_1} Ru(CNCH_3)_6{}^{2+} \tag{2}$$

$$[Ru(CNCH_3)_5]^{2+} + [Ru(CNCH_3)_5]^{2+} \xrightarrow{k_2} [Ru_2(CNCH_3)_{10}]^{4+} \tag{3}$$

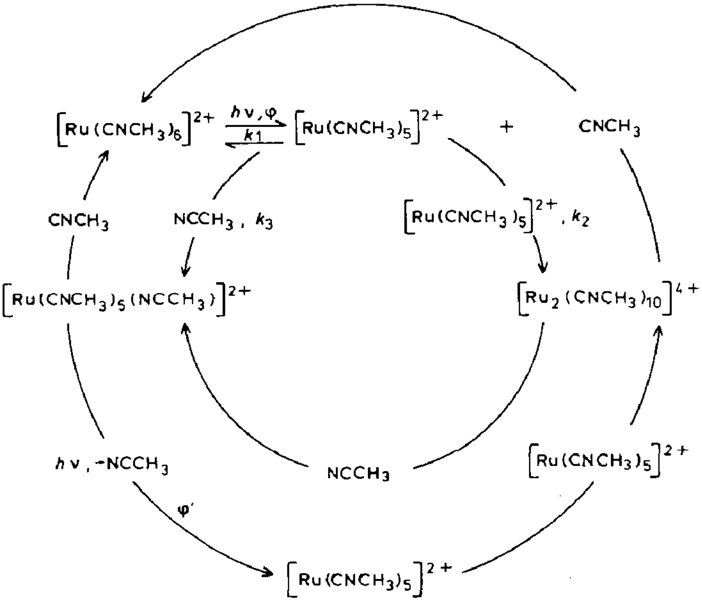

Fig. 4. Photochemical mechanism scheme.

The rate of disappearance of the starting compound is given by eq. 4:

$$-\frac{\mathrm{d}\left[\left[\mathrm{Ru(CNCH_3)_6}\right]^{2+}\right]}{\mathrm{d}t}=\varphi I-k_1\left[\left[\mathrm{Ru(CNCH_3)_5}\right]^{2+}\right]\left[\mathrm{CNCH_3}\right] \tag{4}$$

$$\frac{\mathrm{d}\left[\left[\mathrm{Ru(CNCH_3)_5}\right]^{2+}\right]}{\mathrm{d}t}=\varphi I-k_1\left[\left[\mathrm{Ru(CNCH_3)_5}\right]^{2+}\right]\left[\mathrm{CNCH_3}\right]-k_2\left[\left[\mathrm{Ru(CNCH_3)_5}\right]^{2+}\right]^2 \tag{5}$$

For short times of irradiation it can be roughly assumed that $[\mathrm{CNCH_3}] \approx [[\mathrm{Ru(CNCH_3)_5}]^{2+}]$, and so equations 4 and 5 become respectively:

$$-\frac{\mathrm{d}\left[\left[\mathrm{Ru(CNCH_3)_6}\right]^{2+}\right]}{\mathrm{d}t}=\varphi I-k_1\left[\left[\mathrm{Ru(CNCH_3)_5}\right]^{2+}\right]^2 \tag{4$'$}$$

$$\frac{\mathrm{d}\left[\left[\mathrm{Ru(CNCH_3)_5}\right]^{2+}\right]}{\mathrm{d}t}=\varphi I-k_1\left[\left[\mathrm{Ru(CNCH_3)_5}\right]^{2+}\right]^2-k_2\left[\left[\mathrm{Ru(CNCH_3)_5}\right]^{2+}\right]^2 \tag{5$'$}$$

By application of the steady state approximation for $[[\mathrm{Ru(CNCH_3)_5}]^{2+}]$, equation 4′ becomes

$$-\frac{\mathrm{d}\left[\left[\mathrm{Ru(CNCH_3)_6}\right]^{2+}\right]}{\mathrm{d}t}=\varphi I\frac{k_2}{k_1+k_2} \tag{6}$$

Thus $\phi_\mathrm{D}=\varphi\frac{k_2}{k_1+k_2}$ (7)

The observed increase of $\phi_\mathrm{D}$ with the temperature is a consequence of the expected variation of the kinetic constants ($k_1$ and $k_2$) with temperature.

The formation of the dimer from $[\mathrm{Ru(CNCH_3)_5(NCCH_3)}]^{2+}$ occurs through the following steps:

$$\left[\mathrm{Ru(CNCH_3)_5(NCCH_3)}\right]^{2+}\xrightarrow{h\nu,\varphi'}\left[\mathrm{Ru(CNCH_3)_5}\right]^{2+}+\mathrm{NCCH_3} \tag{8}$$

$$\left[\mathrm{Ru(CNCH_3)_5}\right]^{2+}+\mathrm{NCCH_3}\xrightarrow{k_3}\left[\mathrm{Ru(CNCH_3)_5(NCCH_3)}\right]^{2+} \tag{9}$$

$$\left[\mathrm{Ru(CNCH_3)_5}\right]^{2+}+\left[\mathrm{Ru(CNCH_3)_5}\right]^{2+}\xrightarrow{k_2}\left[\mathrm{Ru_2(CNCH_3)_{10}}\right]^{4+} \tag{3}$$

A kinetic treatment analogous to that above gives, for short times of irradiation:

$$\phi'_\mathrm{D}=\varphi'\frac{k_2}{k_2+k_3} \tag{10}$$

The observed increase of $\phi'_\mathrm{D}$ with the temperature is consistent with equation 10.

In irradiation of $[\mathrm{Ru(CNCH_3)_6}]^{2+}$ in $\mathrm{NCCH_3}$, steps 1 and 9 are involved and steps 2 and 3 are negligible, since $[\mathrm{NCCH_3}] \gg [[\mathrm{Ru(CNCH_3)_5}]^{2+}]$ and $[\mathrm{NCCH_3}] \gg [\mathrm{CNCH_3}]$.

In this case equation 11 appears:

$$-\frac{\mathrm{d}\left[\left[\mathrm{Ru(CNCH_3)_6}\right]^{2+}\right]}{\mathrm{d}t}=\varphi I \tag{11}$$

It follows that the experimental quantum yield $\phi_M$ is equal to the primary quantum yield $\varphi$, and is expected to be higher than $\phi_D$ and independent of kinetic factors such as temperature and concentration.

We conclude that the photochemical formation of the binuclear complex $[Ru_2(CNCH_3)_{10}]^{4+}$ upon irradiation of $[Ru(CNCH_3)_6]^{2+}$ or $[Ru(CNCH_3)_5(NCCH_3)]^{2+}$ is the result of an initial photodissociation of the starting complex into a free ligand ($CNCH_3$ or $NCCH_3$, respectively) and a pentacoordinate intermediate that undergoes two fast competing reactions involving attack by the released ligand or by another pentacoordinate intermediate. Clearly in acetonitrile, a coordinating solvent, only the ligand attack occurs. The fact that the $\phi'_D$ is lower than $\phi_D$ indicates that the attack of $NCCH_3$ is faster than that of the $CNCH_3$ ($k_3 > k_1$).

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