

Short Communication

Hydrated electron formation from photoexcited $[\text{Ru}(\text{CN})_6]^{4-}$ and $[\text{W}(\text{CN})_8]^{4-}$ ions

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Introduction

The photolytic production of hydrated electrons from aqueous solutions of various transition metal cyanide complexes has been reported using the flash photolysis technique as well as steady illumination at 253.7 nm [1, 2]. The dependence of the quantum yield of e_{aq}^- formation on the exciting wavelength has been investigated for the $[\text{Fe}(\text{CN})_6]^{4-}$ ion and the $[\text{Mo}(\text{CN})_8]^{4-}$ ion in aqueous solution [3 - 5] and in alkaline glasses at 77 K [6, 7].

In the case of the $[\text{Fe}(\text{CN})_6]^{4-}$ ion in aqueous solution and in 10 M NaOH glasses [3, 6] it has been shown that the photoelectron formation process is a prominent one at wavelengths below 300 nm. Above 313 nm the hydrated electron was found to be insignificant and the photoaquation process was enhanced. In aqueous solutions of $[\text{Fe}(\text{CN})_6]^{4-}$ a maximum value of 0.89 for $\phi(e_{\text{aq}}^-)$ was obtained at 228.8 nm and 214 nm, while the value obtained for the quantum yield at 313 nm was 0.1.

In the case of $[\text{Mo}(\text{CN})_8]^{4-}$ in aqueous solutions [5] a value of $\phi(e_{\text{aq}}^-) = 0.29$ at 254 nm and lower wavelengths was reported. The yield at 313 nm was 0.11. Above 313 nm the electron formation limiting quantum yield was insignificant both in aqueous solutions [5] and in 10 M NaOH glasses at 77 K [7].

In the case of $[\text{Fe}(\text{CN})_6]^{4-}$ [3, 4] it was suggested that the CTTS state can be reached both by direct excitation at around 270 nm or by internal conversion from the excited states: ${}^1A_{1g} \rightarrow {}^1T_{2g}$ at 270 nm and ${}^1A_{1g} \rightarrow {}^1T_{1u}$ at 218 nm. In the case of $[\text{Mo}(\text{CN})_8]^{4-}$ it was suggested [5] that the electrons are being formed mainly through the CTTS excited state at around 265 nm which may be reached either by direct excitation or by passage through the CT transition.

In the present investigation the dependence of photoelectron formation in aqueous solution on the wavelength was investigated for two other cyano complex ions: $[\text{Ru}(\text{CN})_6]^{4-}$ and $[\text{W}(\text{CN})_8]^{4-}$. A general mechanism is suggested for the process of the e_{aq}^- formation from transition metal multicharge ionic complexes.

Experimental

Materials

$K_4[Ru(CN)_6] \cdot 3H_2O$ was obtained commercially (Alfa Inorganics Inc.) and was used as pure substance. $K_4[W(CN)_8] \cdot 2H_2O$ was synthesized according to the procedure given by E. A. Heintz [8]. Solutions were prepared using triple distilled water. The N_2O gas was a Matheson product used for medical purposes and was used after purification from oxygen.

Preparation of samples

Solutions ($1 \times 10^{-3}M$) of $[Ru(CN)_6]^{4-}$ and $[W(CN)_8]^{4-}$ in triple distilled water were used for the illumination experiments. Solutions were de-aerated and equilibrated with N_2O (500 - 600 mmHg of N_2O) as described previously [3], and the e_{aq}^- yields were determined from the N_2 pressure obtained by reaction of the e_{aq}^- and N_2O .

Light sources

228.8 nm and 253.7 nm. The light sources, filters and actinometry [9] were described previously [3]. The light intensity for the 228.8 nm wavelength was 6×10^{-6} einstein dm^{-3} . The light intensity for 253.7 nm was 4.6×10^{-6} einstein dm^{-3} .

265 nm, 313 nm and 365 nm. The light source for these wavelengths was a high pressure 125 W Mercury Discharge Type MBL/D (Thorn). For the 265 nm illumination an interference filter (Baird Atomics) that peaked at 265 nm with a peak transmittance of 6.5% was used. Actinometry was done as described previously [3, 9]. The light intensity at 265 nm was 2.3×10^{-6} einstein dm^{-3} . For the 313 nm illuminations an interference filter (Baird Atomics) that peaked at 313 nm with a bandwidth at half-peak transmittance of 280 Å and a peak transmittance of 8% was used. The light intensity was 1.2×10^{-5} einstein dm^{-3} . The 365 nm was obtained using a combination of a Corning Glass 7 - 37 filter and a Yena W1 glass filter. The bandwidth at half peak was 460 Å. The dose rate was 3.8×10^{-5} einstein dm^{-3} . Actinometry for the wavelengths 265 nm, 313 nm and 365 nm was as described previously [3, 9].

Results and discussion

The photoelectron formation quantum yields were determined from the N_2 pressure, obtained as a result of the electron scavenging by N_2O [3]. The dependence of the e_{aq}^- limiting quantum yields on the wavelengths for $[Ru(CN)_6]^{4-}$ and $[W(CN)_8]^{4-}$ are given in Tables 1 and 2, respectively. The dependence of the limiting quantum yield of the e_{aq}^- formation on the wavelength was similar for the $[Ru(CN)_6]^{4-}$ and the $[W(CN)_8]^{4-}$ ions.

As can be seen from the tables, the limiting quantum yields $\phi(e_{aq}^-)$ reach the value of 0.50 at 228.8 nm for the $[Ru(CN)_6]^{4-}$ ion and a value of 0.46 at 228.8 nm for the $[W(CN)_8]^{4-}$ ion. In both cases the values of the limiting quantum yields decrease with the wavelength, reaching a value of 0.076 at

TABLE 1

Quantum yields as function of wavelength for $[\text{Ru}(\text{CN})_6]^{4-}$

λ (nm)	Concentration of $[\text{Ru}(\text{CN})_6]^{4-}$ (M)	$\phi(\text{N}_2) = \phi(\text{e}_{\text{aq}}^-)$
228.8	10^{-4}	0.50
228.8	10^{-3}	0.48
253.7	10^{-2}	0.36
265	10^{-2}	0.37
313	10^{-2}	0.076
365	10^{-2}	0.013

TABLE 2

Quantum yields as function of wavelength for $[\text{W}(\text{CN})_8]^{4-}$

λ (nm)	Concentration of $[\text{W}(\text{CN})_8]^{4-}$ (M)	$\phi(\text{N}_2) = \phi(\text{e}_{\text{aq}}^-)$
228.8	10^{-4}	0.46
228.8	10^{-3}	0.45
253.7	10^{-3}	0.34
265	10^{-3}	0.38
313	10^{-3}	0.093
365	10^{-3}	0.011

313 nm for the $[\text{Ru}(\text{CN})_6]^{4-}$ ion and a value of 0.093 at 313 nm for the $[\text{W}(\text{CN})_8]^{4-}$ ion. Above 313 nm hydrated electron formation is insignificant. At 365 nm the yield was almost zero for both ions.

In the case of the $[\text{Ru}(\text{CN})_6]^{4-}$ ion, according to Gray and Beach [10] there is a ligand field transition from the ground state $^1A_{1g}$ to the excited state $^1T_{1g}$ at 322.5 nm. There are two CT transitions from $^1A_{1g}$ to $^1T_{1u}$ at 206.0 nm and from $^1A_{1g}$ to $^1T_{1u}$ at 190.2 nm. Gittel and Shirom [11] have shown through the investigations of environmental effects the existence of a CTTS transition at the 230 - 270 nm region of the $[\text{Ru}(\text{CN})_6]^{4-}$ spectrum.

In the case of the $[\text{W}(\text{CN})_8]^{4-}$ ion, according to Perumareddi *et al.* [12] several ligand field transitions are expected. The two lowest d-d transitions are from the ground state 1A_1 to 1B_1 at 370.3 nm and from 1A_1 to 1E at 303.1 nm. Two CT transitions exist at 273.7 nm and 249.0 nm.

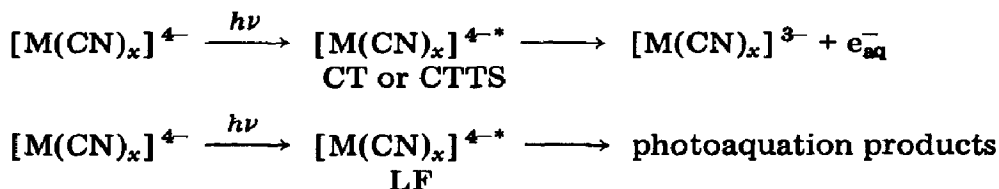
The present work indicates that, both for the $[\text{Ru}(\text{CN})_6]^{4-}$ and the $[\text{W}(\text{CN})_8]^{4-}$ ions, photoelectrons are being formed as a result of illumination at the CTTS and the CT transition region similar to the cases of the $[\text{Fe}(\text{CN})_6]^{4-}$ [3, 4] and $[\text{Mo}(\text{CN})_8]^{4-}$ ions [5]. The ligand field d-d absorption bands do not lead to photoelectron production for the four metal cyano complexes.

In the cases of $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Mo}(\text{CN})_8]^{4-}$ and $[\text{W}(\text{CN})_8]^{4-}$ [2, 4, 13 - 19] a photoaquation reaction was reported for the ligand field transition

region illumination. Photoaquation was reported also for $[\text{Ru}(\text{CN})_6]^{4-}$ [20].

It may be concluded that, for the illumination of the four cyano complexes $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Mo}(\text{CN})_6]^{4-}$, $[\text{Ru}(\text{CN})_6]^{4-}$ and $[\text{W}(\text{CN})_6]^{4-}$, the main source for the electron formation is the CTTS and CT transition region. It is suggested that the CTTS state can be reached either directly or by internal conversion from CT transitions, but cannot be reached through excitation into the lower d-d transitions. In some cases electrons may also be formed directly from CT excited states.

The general mechanism suggested for the photochemical reactions occurring for the cyanocomplex ions can be described by the scheme



- 1 W. L. Waltz and A. W. Adamson, *J. Chem. Phys.*, 73 (1969) 4250.
- 2 W. L. Waltz, A. W. Adamson and P. D. Fleischauer, *J. Am. Chem. Soc.*, 89 (1967) 3923.
- 3 V. Balzani and V. Carassiti, *Photochemistry of Coordination Compounds*, Academic Press, London, 1970.
- 4 M. Shirom and G. Stein, *J. Chem. Phys.*, 55 (1971) 3372.
- 5 M. Shirom and G. Stein, *J. Chem. Phys.*, 55 (1971) 3379.
- 6 M. Shirom and Y. Siderer, *J. Chem. Phys.*, 57 (1972) 1013.
- 7 M. Shirom and M. Weiss, *J. Chem. Phys.*, 56 (1972) 3170.
- 8 M. Shirom and Y. Siderer, *J. Chem. Phys.*, 58 (1973) 1250.
- 9 E. A. Heintz, *Inorg. Synth.*, 7 (1963) 142.
- 10 E. J. Bowen, *Chemical Action of Light*, 2nd edn., Oxford Univ. Press, London, 1946.
- 11 H. B. Gray and M. A. Beach, *J. Am. Chem. Soc.*, 85 (1963) 2922.
- 12 C. Guttel and M. Shirom, *J. Photochem.*, 1 (1972/73) 197.
- 13 J. R. Perumareddi, A. D. Liehr and A. W. Adamson, *J. Am. Chem. Soc.*, 85 (1963) 249.
- 14 A. W. Adamson, W. L. Waltz, E. Zinato, D. W. Watts, P. D. Fleischauer and R. D. Lindholm, *Chem. Rev.*, 68 (1968) 541.
- 15 A. G. MacDiarmid and N. F. Hall, *J. Am. Chem. Soc.* 75 (1953) 5204.
- 16 S. Asperger, I. Murati and D. Pavlovic, *J. Chem. Soc.*, (1960) 730.
- 17 V. Carassiti and V. Balzani, *Ann. Chim. (Rome)* 50 (1960) 630.
- 18 A. Jakob, A. Kosinska-Samotus and Z. Stasicka, *Rocz. Chem.*, 36 (1962) 611.
- 19 A. W. Adamson and A. H. Sporer, *J. Am. Chem. Soc.*, 80 (1958) 3865.
- 20 V. Balzani, M. F. Marfin and L. Moggi, *Inorg. Chem.*, 8 (1969) 47.
- 21 G. Emschwiller, *C. R. Acad. Sci.*, 248 (1959) 959.