Laser Flash Photolysis Study of the Charge-transfer Photochemistry of Octacyanomolybdate(V) and Octacyanotungstate(V) Ions

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Laser flash photolysis (at 249 nm) of $[M^V(CN)_8]^{3-}$ (M = Mo or W) in water and methanol produces an intense absorption ($\lambda_{max.}$ 410 nm) decaying by first-order kinetics with a long lifetime ($\tau \sim 5$ ms in H_2O at 293 K). The transient lifetime is profoundly shortened (by orders of magnitude) on adding hydrogen ion and/or electrolytes, in a manner suggesting cation-, but not anion-, specificity, and implying ion pairing in the accelerated deactivation process. The transient is assigned to an ion-paired radical-pair configuration, *viz.* $\{[M^{IV}(CN)_7(\dot{C}N)]^{3-}, M_x^+\}$ ($M_x^+ = H^+, Li^+, Na^+, K^+, Cs^+, NH_4^+, NEt_4^+$, or Ca^{2+}), which decays to the final product $[M^{IV}(CN)_8]^{4-}$. Detailed analysis by computer-fitting of the accelerative effects of different cations gave values for the absolute decay rate constant, k_0, the specific decay rate constants, k_{M_x}, and the association constants, K_{M_x}, which decrease in the sequences: $Cs^+ > H^+ > Ca^{2+} > K^+ > NH_4^+ > Na^+ > Li^+ > NEt_4^+$ and $NEt_4^+ > H^+ > Ca^{2+} > Li^+ > Na^+ > NH_4^+ > K^+ > Cs^+$ for k_{M_x} and K_{M_x} respectively.

The photochemistry of tungsten(V) and molybdenum(V) octacyanides has been investigated by several research groups.[1-6] The one-electron photoreduction of octacyanotungstate(V) has been interpreted previously in terms of an intermolecular redox process [equation (1), c.t.t.m. = charge transfer to metal],[1-3]

$$[W(CN)_8]^{3-} + H_2O \xrightarrow[\text{c.t.t.m.}]{h\nu} [W(CN)_8]^{4-} + H^+ + {}^{\bullet}OH \quad (1)$$

with a quantum yield of *ca.* 0.8 over a wide pH range.[3] The charge-transfer (c.t.) photochemistry of octacyanomolybdate(V) is more ambiguous. The early papers of Carassiti and Balzani[1] suggested a similar mechanism, but the work of Gray and Spence[4] and Stasicka and co-workers[5] suggests an intramolecular process (2) with a different sequence of reactions

$$[Mo(CN)_8]^{3-} \xrightarrow[\text{c.t.t.m.}]{h\nu} [Mo(CN)_7]^{3-} + {}^{\bullet}CN \quad (2)$$

leading to the formation of $[Mo(CN)_8]^{4-}$. Spin-trapping experiments provided additional evidence for the operation of a free-radical mechanism involving: (*i*) ${}^{\bullet}OH$ radicals from $[M(CN)_8]^{3-}$ (M = Mo or W) in aqueous solutions,[7,8] (*ii*) ${}^{\bullet}OCH_3$ and ${}^{\bullet}CN$ radicals from $[Mo(CN)_8]^{3-}$ in methanolic solution[9] (although the assignment of the spin adduct attributed to the ${}^{\bullet}CN$ radical remains unclear[10]), and (*iii*) ${}^{\bullet}CN$ radicals from $[Mo(CN)_8]^{3-}$ in CH_2Cl_2 solution.[10] It was also found that a competing dissociation process of small efficiency, equation (3), occurs following c.t. excitation.[8,9]

$$[M(CN)_8]^{3-} \xrightarrow[\text{c.t.t.m.}]{h\nu} [M(CN)_7]^{2-} + CN^- \quad (3)$$

In the present study the photoreduction of $[W(CN)_8]^{3-}$ has been found to proceed through a long lived intermediate ($\tau \sim 5$ ms in H_2O) with an absorbance maximum at 410 nm that decays into $[W(CN)_8]^{4-}$. Moreover, we have found laser flash photolysis (249 nm) of $[Mo(CN)_8]^{3-}$ to produce a similar transient species of comparable behaviour which was not observed in a previous flash photolysis study.[5] This paper describes the spectra and unusual kinetic behaviour of these transient species and suggests a mechanism involving the ion-paired radical-pair species $\{[M^{IV}(CN)_7(\dot{C}N)]^{3-}, M_x^+\}$ as the critical intermediate.

Experimental

Materials.—The preparations of solid $K_3[W(CN)_8]\cdot1.5H_2O$ and $H_3[W(CN)_8]$ in solution have been described previously.[2,11] A solution of $K_3[Mo(CN)_8]$ was obtained by the literature method.[12] The purity of the complexes was checked spectrophotometrically (i.r. and/or u.v.–visible spectra). Buffer and electrolyte solutions were prepared from reagents of AnalaR grade. Merck Uvasol CH_3OH, CH_3CN and D_2O (Merck n.m.r. solvent) were used without further purification. Water was distilled four times altogether, with the third distillation from alkaline $KMnO_4$.

Equipment and Procedures.—Preliminary flash photolysis experiments were performed using a conventional flash photolysis apparatus described elsewhere.[13] An oxygen photoflash lamp with a flash energy of *ca.* 400 J was used. In these experiments a Schott (Jena) BG 9 filter was used for cutting off radiation with $\tilde{\nu} > 31\,0000$ cm^{-1}. The radiation from the spectroflash between 45 000 and 13 000 cm^{-1} was recorded. The shortest delay time used was 20 µs. The flash photolysis experiments were carried out in solutions deoxygenated by bubbling with purified N_2 for 1 h before each experiment. The measurements were carried out at room temperature with both 5×10^{-5} mol dm^{-3} and 2×10^{-3} mol dm^{-3} aqueous solutions of $H_3[W(CN)_8]$ and $K_3[W(CN)_8]$, the potassium salt solutions at pH 7.0 and 13.0.

The kinetics of decay of the transient intermediate were determined using excimer (Kr/F_2) laser flash photolysis equipment described before,[14] which delivers 15 ns pulses of 249 nm radiation of 150—200 mJ energy. The photolysis experiments were carried out in solutions deoxygenated by bubbling with argon for 15 min before each experiment. Measurements were carried out with solutions of $K_3[W(CN)_8]$ (8.00×10^{-4} mol dm^{-3}) and of $K_3[Mo(CN)_8]$ (8.96×10^{-4} mol dm^{-3}) at room temperature.

The profiles of the transient absorption bands were obtained by monitoring end-of-pulse absorptions at wavenumbers in the range 27 000—22 000 cm^{-1} (370—450 nm). The decay of the transient was monitored at 410 nm. Data analysis and computer fitting procedures were as given previously.[15]

The effect of pH on the rate constant of decay was determined as follows. (*i*) In buffer solutions at an ionic strength 0.2 mol dm^{-3} adjusted with KCl. The buffer solutions of pH ranges 1—2 and 6—13 were prepared according to Bates.[16] In the pH range 3—5, CH_3CO_2H-NH_3(aq.) buffer solutions were used. The pH of solutions was checked with a calibrated Pye Unicam model PW 9410 digital pH-meter. (*ii*) In perchlorate media, varying the hydrogen-ion concentration from 1×10^{-4} to 0.1 mol dm^{-3} with a constant concentration of ClO_4^-, equal to 0.1 mol dm^{-3}, obtained by addition of $NaClO_4$.

The effects of added electrolytes on the rate constant of decay of the transient in water were determined for CsCl, KCl, NaCl, $NaClO_4$, NaF, LiCl, NH_4Cl, NEt_4Cl, and $CaCl_2$ for $[W(CN)_8]^{3-}$ and for KCl for $[Mo(CN)_8]^{3-}$. The concentrations of electrolytes were in the range 1×10^{-4}—0.4 mol dm^{-3} where the ionic strength was allowed to vary simply as a function of concentration of added electrolyte.

The effects of solvent on the decay of the transient were determined in deaerated H_2O, D_2O, and CH_3OH media for $[W(CN)_8]^{3-}$.

The effect of oxygen on the decay of the transient was determined in aerated aqueous and methanolic solutions of $[W(CN)_8]^{3-}$.

The effects of added salt and polar solvents on the absorption spectrum of $K_3[W(CN)_8]$ were investigated for 4×10^{-4} mol dm^{-3} solutions in H_2O, CH_3OH, and CH_3CN media and in aqueous KCl, CsCl, and NEt_4Cl (all at 0.45 mol dm^{-3}). Electronic spectra were obtained by means of a Specord u.v.–visible (Zeiss, Jena) spectrophotometer.

Calculations.—Kinetic data were interpreted assuming the simple scheme, equations (4) and (5), involving ion-pair

$$A \xrightarrow{k_0} \text{product} \qquad (4)$$

$$A + B \overset{K_B}{\rightleftharpoons} (A,B) \xrightarrow{k_B} \text{product} \qquad (5)$$

formation between the multinegatively charged species A and cation B (the charges are omitted for simplicity).

The approximation was made that the first reversible step in equation (5) is much more rapid than the second irreversible step. This gives the rate law,[17] equation (6), in which [B] represents the total concentration of cation B, equal to the sum of the concentrations of the counter cation, $[B]_0$, and of the added cation, $[B]_{add}$. The values of k_0, k_B, and K_B were determined by fitting equation (6) as a function of k_0, k_B, and K_B to the experimental plots of $k_{obs.}$ *vs.* [B].

$$k_{obs.} = \frac{k_0 + k_B K_B[B]}{1 + K_B[B]} \qquad (6)$$

For solutions containing counter cation B and added cation C an additional reaction is involved [equation (7) and (8)]. Values

$$A + C \overset{K_C}{\rightleftharpoons} (A,C) \xrightarrow{k_C} \text{product} \qquad (7)$$

$$k_{obs.} = \frac{k_0 + k_B K_B[B]_0 + k_C K_C[C]_{add}}{1 + K_B[B]_0 + K_C[C]_{add}} \qquad (8)$$

of k_0, k_C, and K_C were determined by fitting equation (8) as a function of k_0, k_C, and K_C to the experimental plots of $k_{obs.}$ *vs.* $[C]_{add}$. Values of k_B and K_B used in these calculations were those determined according to equation (6). For solutions containing counter cation B, added cation C, and added hydrogen ion H, equations (9) and (10) must be considered. Values of k_0, k_H, and

$$A + H \overset{K_H}{\rightleftharpoons} (A,H) \xrightarrow{k_H} \text{product} \qquad (9)$$

$$k_{obs.} = \frac{k_0 + k_B K_B[B]_0 + k_C K_C[C]_{add} + k_H K_H[H]_{add}}{1 + K_B[B]_0 + K_C[C]_{add} + K_H[H]_{add}} \qquad (10)$$

K_H were determined by fitting equation (10) as a function of k_0, k_H, and K_H to the experimental plot of $k_{obs.}$ *vs.* $[H]_{add}$. The values of k_B, K_B and k_C, K_C were those determined according to equations (6) and (8), respectively. For the determination of the association constants K_B, K_C, K_H and the decay rate constants k_0, k_B, k_C, k_H a least-squares minimization procedure was applied.*

Results

Environmental Effects on the Electronic Absorption Spectrum of $[W(CN)_8]^{3-}$.—The spectra of $[W(CN)_8]^{3-}$ in H_2O, CH_3OH, CH_3CN, and aqueous KCl (0.45 mol dm^{-3}) are presented in Figure 1 and the values of $\tilde{\nu}_{max.}$ and $\varepsilon_{max.}$ in various media are listed in Table 1. The dominant features of the spectra are transitions at 242, 255, and 357 nm, which are very likely c.t.t.m. in nature.[18] A simplified scheme indicating the excited states of complexes $[M(CN)_8]^{3-}$ of approximate D_{4d} symmetry, based on the SCCC (self-consistent charge and configuration) molecular orbital (m.o.) calculations of Gołebiewski and Kowalski,[18] is presented in Figure 2.

Sensitivity to the medium environment is common for c.t.t.m. transitions.[19] In the case of $[W(CN)_8]^{3-}$ this is manifested mainly in intensity changes of all three distinct bands (a, c, and d) with rather small shifts of the band maxima. The transition b, existing in the region 36 000—31 000 cm^{-1}, is also perturbed in intensity by the media employed.

Flash Photolysis of $[W(CN)_8]^{3-}$ *and* $[Mo(CN)_8]^{3-}$ *Ions.*—Some typical spectra produced by broad-band ($\lambda > 320$ nm) μs flash irradiation (mainly $1^2E_1 \longleftarrow {}^2A_1$ excitation) of $[W(CN)_8]^{3-}$ in aqueous solution are presented in Figure 3. A novel, transient absorption band was observed at *ca.* 400 nm, a wavelength unaffected by the pH of solution. The decay of this relatively long-lived transient intermediate was accompanied by the formation of $[W(CN)_8]^{4-}$ ($\lambda_{max.}$ 430 nm) and $[W^{IV}O_2(CN)_7]^{3-}$ ($\lambda_{max.}$ 535 nm); the latter is supposed to be the product of a photosubstitution pathway.[8]

Figure 4 shows the spectra obtained on 249-nm laser flash photolysis (l.f.p.) ($2^2E_1 \longleftarrow {}^2A_1$ excitation) of $[W(CN)_8]^{3-}$ solutions. In aqueous solution the transient intermediate was characterized by $\lambda_{max.}$ at 410 nm. In methanol a similar spectrum was observed although $\lambda_{max.}$ was slightly blue-shifted (to 400 nm). When acetonitrile was employed as the solvent no transient absorption was generally observed. The only result of l.f.p. of $[W(CN)_8]^{3-}$ in CH_3CN was a general increase in intensity in the region of absorption of the starting material. Addition of water or methanol to the acetonitrile even at concentrations of only 5% (v/v) resulted in the appearance of the transient absorption typical of the pure hydroxylic solvent.

L.f.p. of $[Mo(CN)_8]^{3-}$ in aqueous solution produced a similar transient intermediate with $\lambda_{max.}$ at 410 nm (Figure 4). In both cases the only observable final products under these particular experimental conditions were the octacyanometalates(IV).

Kinetics of 410-nm *Transient Absorption Decay and Influence of Solvent.*—The kinetics of the decay of the transient absorption at $\lambda_{max.}$ 410 nm produced on l.f.p. were strictly first order for 3—4 half-lives.

The rate constant of the W-transient intermediate was found to be dependent on the solvent employed as shown in

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* Minuit (D506), CERN Library Programs, with a CYBER 72 computer.

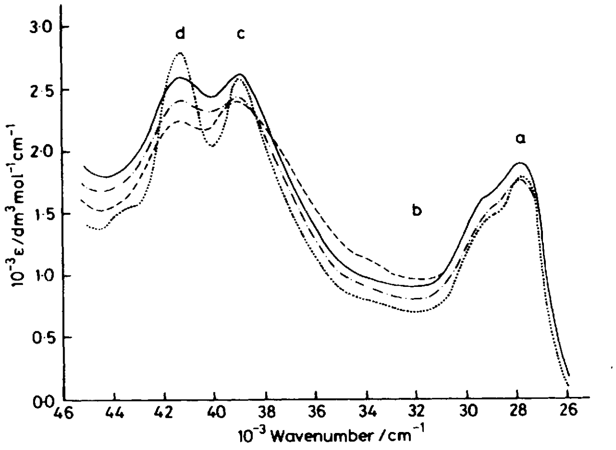

Figure 1. Electronic absorption spectra of $K_3[W(CN)_8]$ in H_2O (——), 0.45 mol dm^{-3} KCl (— · —), CH_3OH (- - -), and CH_3CN (· · · ·)

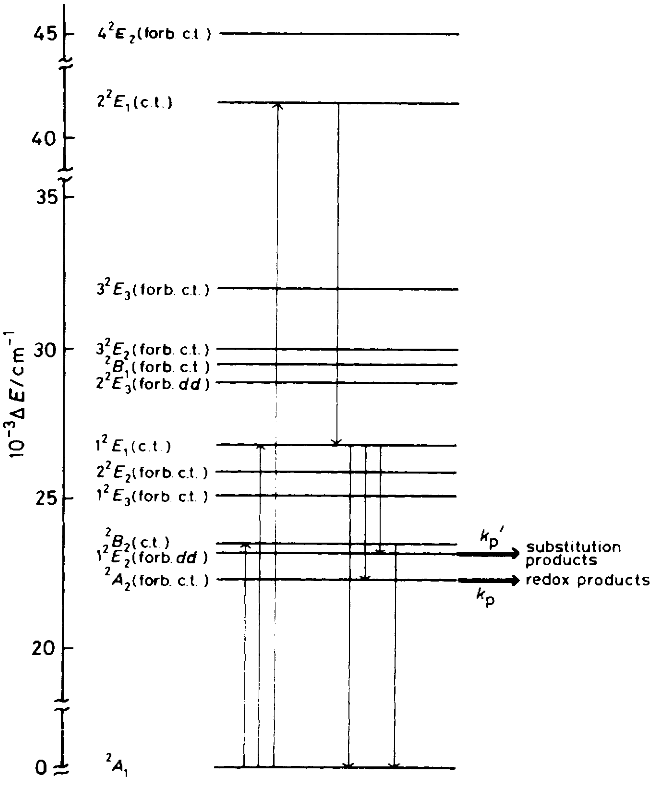

Figure 2. A simplified scheme indicating the excited states of d^1 octacyanides and symmetry-allowed dipole transitions (based on calculations of Gołebiewski and Kowalski[18]) (forb. = forbidden)

Table 1. Environmental effects on electronic absorption spectra of $K_3[W(CN)_8]$ in solution

Medium	$10^{-3}\tilde{\nu}/cm^{-1}(10^{-3}\varepsilon/dm^3 mol^{-1} cm^{-1})$
H_2O	41.3 (2.59), 39.1 (2.60), 27.8 (1.91)
H_2O[a]	41.5 (2.39), 39.2 (2.49), 28.2 (1.76)
KCl[b]	41.2 (2.41), 39.0 (2.44), 27.9 (1.75)
CsCl[b]	41.0 (2.57), 39.2 (2.59), 27.8 (1.74)
NEt_4Cl[b]	41.0 (2.73), 39.0 (2.68), 27.8 (1.74)
CH_3OH	41.4 (2.23), 39.0 (2.40), 27.8 (1.93)
CH_3CN	41.3 (2.78), 39.0 (2.58), 27.8 (1.79)

[a] Ref. 11. [b] At 0.45 mol dm^{-3}.

Table 2. Effect of solvent on the rate of decay of the W-transient produced on l.f.p.

Solvent	$k_{obs.}$[a]/s^{-1}	$k_{obs.}$[b]/s^{-1}
H_2O	184	534
D_2O	39	—
CH_3OH	11	2.18×10^3

[a] Deaerated solutions. [b] Aerated solutions.

Table 3. Effects of acidity and calcium cation on the rate of decay of the W-transient produced on l.f.p.

	$k_{obs.}/s^{-1}$	
[Cation[a]]/mol dm^{-3}	$HClO_4$[b]	$CaCl_2$
1×10^{-4}	3.62×10^3	358.5
2.5×10^{-4}	4.69×10^3	—
5×10^{-4}	5.25×10^3	531.1
1×10^{-3}	7.32×10^3	638.3
2.5×10^{-3}	6.80×10^3	—
5×10^{-3}	8.76×10^3	1.79×10^3
1×10^{-2}	1.55×10^4	3.81×10^3
2.5×10^{-2}	2.84×10^4	6.70×10^3
5×10^{-2}	7.22×10^4	1.75×10^4
0.1	1.25×10^5	2.72×10^4
k_0/s^{-1}	43.0 ± 6.1	57.4 ± 8.7
$K_{M_x}/dm^3 mol^{-1}$	5.53 ± 1.37	4.38 ± 1.09
k_{M_x}/s^{-1}	$(3.02 \pm 0.14) \times 10^5$	$(8.41 \pm 0.52) \times 10^4$

[a] H^+ or Ca^{2+}. [b] At I = 0.1 mol dm^{-3} adjusted with $NaClO_4$.

Table 2. The values of $k_{obs.}$ decrease in the order $H_2O > D_2O > CH_3OH$. Oxygen was also found to affect the rate constant of the W-transient species; $k_{obs.}$ increases markedly in the presence of oxygen, especially in methanol, thus changing the order of the rate constants: $k_{obs.}$ in $H_2O < k_{obs.}$ in CH_3OH.

Effect of pH *on the Decay Rate Constant of the* 410-nm *Transient*.—The effect of pH on $k_{obs.}$ for $[W(CN)_8]^{3-}$ and $[Mo(CN)_8]^{3-}$ is shown in Figures 5 and 6, respectively. In the case of $[W(CN)_8]^{3-}$, $k_{obs.}$ rises sharply at low pH values, falls to a plateau region between pH 4 and 7, and then rises slightly to another plateau region between pH 9 and 13.

For $[Mo(CN)_8]^{3-}$ the values of $k_{obs.}$ rise both at low and high pH values. The reason why this complex shows a large scatter of $k_{obs.}$ values in neutral and alkaline media is not apparent.

Effect of Electrolytes on the Decay Rate Constant of the 410-nm *Transient*.—Added electrolytes were found to increase the rate constant of the transient decay profoundly, as summarised in Tables 3—6 while plots of log $k_{obs.}$ *versus* log [salt] are shown in Figures 7—9. Clearly, specific cation effects are operating. It can also be seen that changing the anions does not significantly affect the values of $k_{obs.}$ (Table 5 and Figure 8). Experiments undertaken using $[Mo(CN)_8]^{3-}$ show the same type of relationship as $[W(CN)_8]^{3-}$ (Table 6 and Figure 9).

The effect of added salts upon the reaction rate is generally accommodated according to the relation $k_{obs.} = k_0 + k_s$[salt].

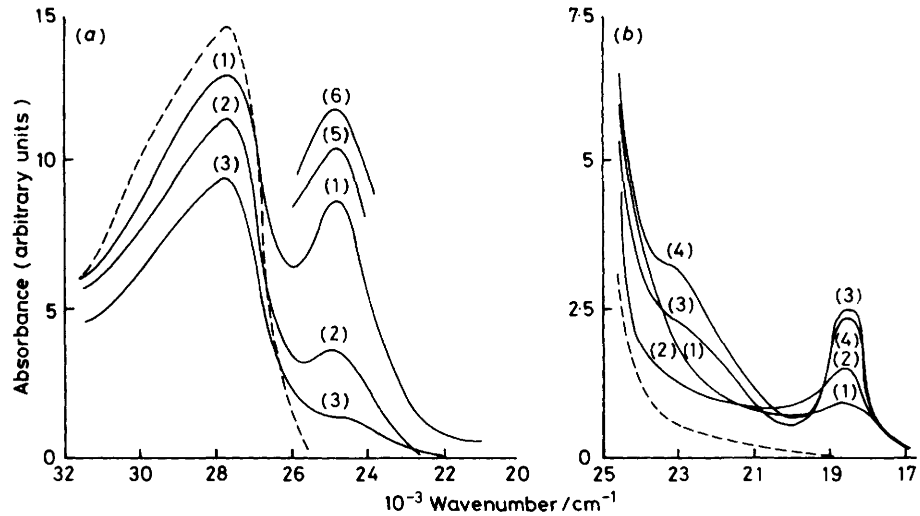

Figure 3. Flash photolysis spectra of $H_3[W(CN)_8]$ [5×10^{-5} mol dm^{-3} (*a*) and 2×10^{-3} mol dm^{-3} (*b*)] in aqueous solutions following μs flash ($\lambda > 320$ nm) at delay times: (1) 30 μs, (2) 30 ms, (3) 30 s, and (4) 300 s. Curves (5) and (6) correspond to a 5×10^{-5} mol dm^{-3} solution of $K_3[W(CN)_8]$ at pH 7.0 and 13.0 respectively, at a delay time of 20 μs. The dashed line indicates unirradiated $H_3[W(CN)_8]$

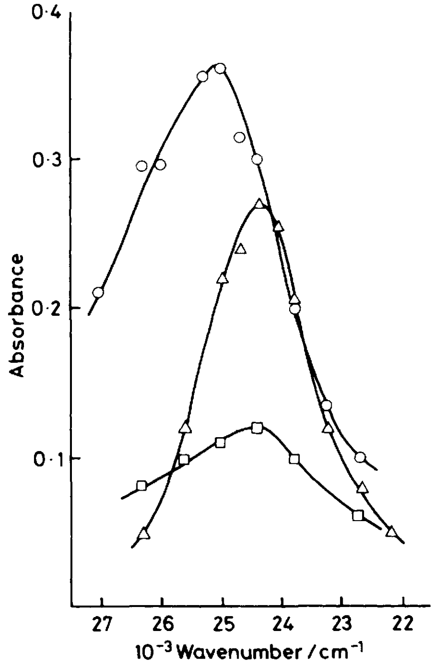

Figure 4. Profiles of the transient absorption band produced on l.f.p. of $[M(CN)_8]^{3-}$: W-transient in H_2O (○) and in CH_3OH (△); Mo-transient in H_2O (□) (spectra do not reflect the relative molar absorption coefficients)

However, the relationships obtained in our system between $k_{obs.}$ and the concentrations of added salts deviated significantly and positively from such simple linearity. The specific effect of the cation could be explained by assuming a close-contact ion pair between the transient intermediate and the cation. The association constants of the transient with the cation M_x, K_{M_x}, and the decay rate constants of the free transient, k_0, and its ion-pair, k_{M_x}, were determined as described in the Experimental section assuming the simplest model of monoassociation. The average value of the decay rate constant k_0 for the non-ion-paired transient was 39 ± 24 s^{-1} for all the systems employed.

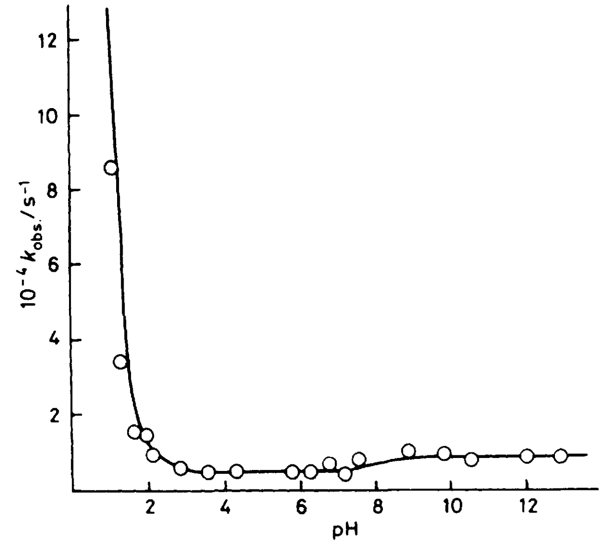

Figure 5. Dependence of $k_{obs.}$ on pH of the W-transient in l.f.p. at $I = 0.2$ mol dm^{-3}

The values of k_{M_x} and K_{M_x} obtained are presented in Tables 3—6 and the resulting theoretical plots of log $k_{calc.}$ *vs.* log [cation] (solid lines) are shown in Figures 7—9. The values of the decay rate constants, k_{M_x}, of the monovalent cations, decrease in the following sequence $Cs^+ > H^+ > K^+ > NH_4^+ > Na^+ > Li^+ > NEt_4^+$, whereas the values of the association constants, K_{M_x}, increase approximately in the same order with only a change in the position of H^+, *i.e.* $Cs^+ < K^+ < NH_4^+ < Na^+ < Li^+ < H^+ < NEt_4^+$. By replacing the monovalent cation (K^+) with the corresponding divalent cation (Ca^{2+}) k_{M_x} and K_{M_x} were greatly increased (Table 3 and Table 6). That the anion has no significant effect on the values of K_{M_x} and k_{M_x} is seen from the solid line in Figure 8 which represents log $k_{calc.}$ *vs.* log [Na^+], where $k_{calc.}$ was obtained by averaging values of K_{M_x} and k_{M_x} for all the Na^+ salts investigated. Identical values of the association constants K_{M_x} for the K^+ cation were obtained for the W- and Mo-transient intermediates (Table 6) indicating that the values

Table 4. Effect of electrolytes on the rate of decay of the W-transient produced on l.f.p.

	$k_{obs.}/s^{-1}$			
[Salt]/mol dm^{-3}	CsCl	NH_4Cl	LiCl	NEt_4Cl
1 × 10^{-4}	157.1	148.8	290.2	141.4
5 × 10^{-4}	267.3	286.2	300.5	211.2
1 × 10^{-3}	275.4	319.8	297.0	248.7
5 × 10^{-3}	805.65	424.9	375.75	515.2
1 × 10^{-2}	1.30 × 10^3	637.6	510.46	775.2
2.5 × 10^{-2}	4.63 × 10^3	1.08 × 10^3	897.82	1.96 × 10^3
5 × 10^{-2}	9.04 × 10^3	1.75 × 10^3	1.46 × 10^3	2.70 × 10^3
0.1	1.91 × 10^4	4.51 × 10^3	1.80 × 10^3	3.33 × 10^3
0.2	2.94 × 10^4	7.70 × 10^3	3.50 × 10^3	3.87 × 10^3
0.4	4.90 × 10^4	1.11 × 10^4	4.97 × 10^3	5.74 × 10^3
k_0/s^{-1}	9.2 ± 6.2	40.5 ± 5.8	81.3 ± 6.5	8.0 ± 5.9
$K_{M_x}/dm^3\ mol^{-1}$	0.23 ± 0.09	1.17 ± 0.42	4.02 ± 0.88	13.46 ± 1.76
k_{M_x}/s^{-1}	(6.24 ± 0.06) × 10^5	(3.55 ± 0.23) × 10^4	(7.16 ± 0.62) × 10^3	(5.95 ± 0.41) × 10^3

Table 5. Effect of sodium salts on the rate of decay of the W-transient produced on l.f.p.

	$k_{obs.}/s^{-1}$		
[Salt]/mol dm^{-3}	NaCl	$NaClO_4$	NaF
1 × 10^{-4}	142.2	194.2	243.0
5 × 10^{-4}	164.1	195.1	287.1
1 × 10^{-3}	217.7	417.1	278.6
5 × 10^{-3}	308.8	474.1	395.2
1 × 10^{-2}	362.5	366.6	584.0
2.5 × 10^{-2}	694.6	560.4	719.2
5 × 10^{-2}	1.05 × 10^3	1.27 × 10^3	1.49 × 10^3
0.1	2.04 × 10^3	3.09 × 10^3	1.72 × 10^3
0.2	3.34 × 10^3	4.42 × 10^3	4.29 × 10^3
0.4	6.36 × 10^3	—	—
0.5	—	5.00 × 10^3	—
k_0/s^{-1}	11.2 ± 6.2	43.0 ± 6.1	56.4 ± 13.1
$K_{M_x}/dm^3\ mol^{-1}$	1.22 ± 0.49	1.84 ± 0.30	1.14 ± 0.48
k_{M_x}/s^{-1}	(1.76 ± 0.12) × 10^4	(1.16 ± 0.04) × 10^4	(2.07 ± 0.12) × 10^4

of k_{M_x} are principally responsible for the different rates of decay of the transient.

Discussion

The general mechanism proposed for the photoreduction of $[W(CN)_8]^{3-}$ in aqueous and methanolic solution is presented in the Scheme.

In solutions of very polar solvents the highly charged $[W(CN)_8]^{3-}$ ion must be considered to be both strongly associated with cations and solvated. The ground-state acid dissociation constants of $H_4[W(CN)_8]$ and $H_3[W(CN)_8]$[11] and the association constants of $[M(CN)_8]^{n-}$ (n = 3 or 4) with some monovalent[20] and polyvalent cations[6] have been reported previously. Many more data on ion-pair formation are available for Fe^{II}– and Fe^{III}–cyanide complexes of the same charge.[21] The effect of ion pairing of $[W(CN)_8]^{3-}$ with some monovalent cations (Figure 1 and Table 1) arises without significant changes in the energy of the excited states, producing only a variation in the intensity of the bands. This behaviour can be expected for purely electrostatic association which does not result in a change in the electronic structure of the complex. Much more remarkable are the shifts of the c.t. transition on going from $K_3[W(CN)_8]$ to $H_3[W(CN)_8]$ in solution, which can be attributed to stronger interactions of the hydrogen ion with the complex anion compared to that of the potassium cation. We suppose also that the ion-pairing effect is dominant in non-aqueous solvents (CH_3OH, CH_3CN) and obscures the solvent dependence of the c.t. transitions since the lower dielectric constants of CH_3OH and CH_3CN would be expected to increase the amount of ion pairing.

Table 6. Effect of KCl on the rate of decay of the W- and Mo-transients produced on l.f.p.

	$k_{obs.}/s^{-1}$	
[KCl]/mol dm^{-3}	$[W(CN)_8]^{3-}$	$[Mo(CN)_8]^{3-}$
1 × 10^{-4}	205.3	129.5
5 × 10^{-4}	207.9	144.3
1 × 10^{-3}	331.8	211.3
5 × 10^{-3}	704.3	397.9
1 × 10^{-2}	724.8	684.6
2.5 × 10^{-2}	1.82 × 10^3	789.0
5 × 10^{-2}	3.87 × 10^3	1.24 × 10^3
0.1	5.39 × 10^3	2.00 × 10^3
0.2	8.97 × 10^3	3.95 × 10^3
0.4	2.42 × 10^4	—
0.45	—	1.35 × 10^4
k_0/s^{-1}	40.1 ± 13.0	78.9 ± 6.8
$K_{M_x}/dm^3\ mol^{-1}$	1.03 ± 0.33	1.03 ± 0.29
k_{M_x}/s^{-1}	(6.33 ± 0.42) × 10^4	(2.80 ± 0.98) × 10^4

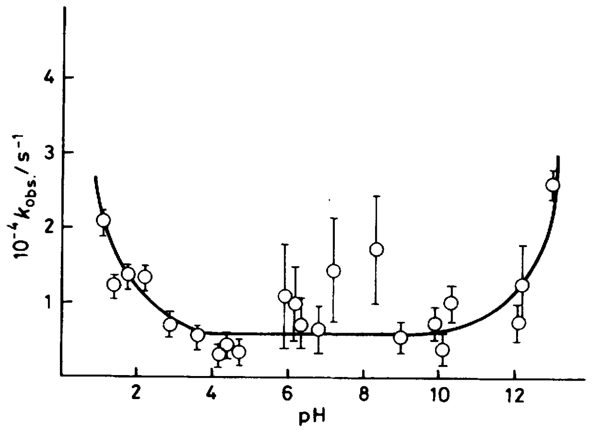

Figure 6. Dependence of $k_{obs.}$ on pH for the Mo-transient in l.f.p. at I = 0.2 mol dm^{-3}

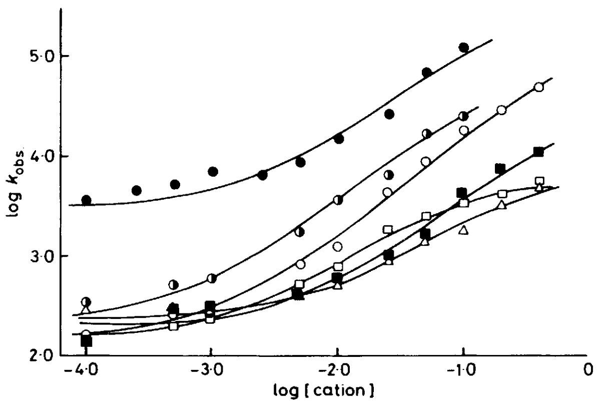

Figure 7. Plots of log $k_{obs.}$ *vs.* log [cation] for the W-transient (l.f.p.) in aqueous solution. (●), $CaCl_2$ (◑), CsCl (○), NH_4Cl (■), LiCl (△) and NEt_4Cl (□). Solid lines are theoretical curves (*cf.* text)

Irradiation of both $[W(CN)_8]^{3-}$ and the ground-state ion pair $\{[W(CN)_8]^{3-}, M_x^+\}$ with $\lambda > 320$ nm (mostly 355 nm) or 249 nm light involves excitation to their high-energy c.t.t.m. states; 1^2E_1 and 2^2E_1, respectively (Figure 2).[*] Observation of the same transient (Figures 3 and 4) strongly suggests that the same, probably lowest energy, symmetry forbidden excited state, $^2A_2$, or a high vibrational level of the ground state is reactive. Such a state appears to be efficiently populated by the irradiation of absorption bands above its threshold as indicated by the high quantum yields of $[W(CN)_8]^{4-}$ formation.[3]

The Franck–Condon states (1^2E_1, 2^2E_1) reached in the initial excitation should be regarded as containing eight fractionally oxidized ligands and having ground-state association and solvation.[19] As the system moves along the photoreaction co-ordinate the excited system relaxes until the thermally equilibrated primary photoproduct is formed. It can be regarded as a solvent trapped radical pair species, $[W^{IV}(CN)_7(\dot{C}N)]^{3-}$, and its ion pair or 'outer-sphere' complex $\{[W^{IV}(CN)_7(\dot{C}N)]^{3-}, M_x^+\}$. In such a case the medium environment must ultimately relax to the association and solvation appropriate to the radical pair product.

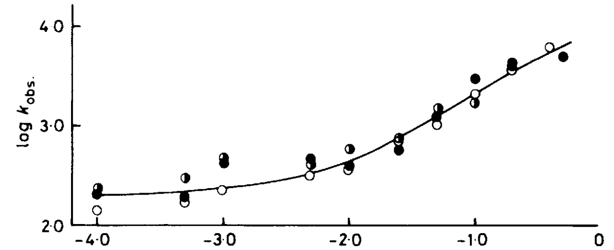

Figure 8. Plots of log $k_{obs.}$ *vs.* log [Na$^+$] for the W-transient (l.f.p.) in aqueous NaCl (○), $NaClO_4$ (●), and NaF (◑); solid line is the theoretical curve (*cf.* text)

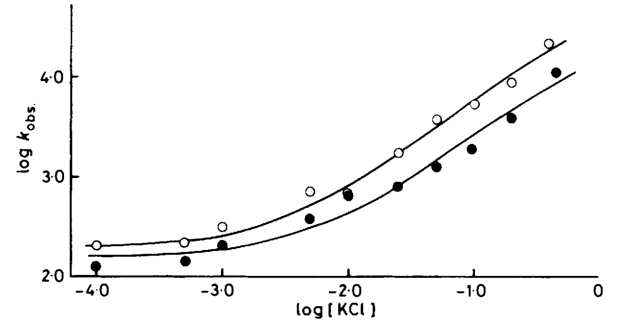

Figure 9. Plots of log $k_{obs.}$ *vs.* log [KCl] for the W-transient (○) and Mo-transient (●) on l.f.p. of aqueous solutions

We suggest that the $[W(CN)_8]^{4-}$ ion and $^{\bullet}OH$ radical [equation (1) and Scheme] stem from a process in which the electron-deficient ligand extracts an electron (or possibly a hydrogen atom) from an adjacent solvent molecule. The active role of the solvent, which strongly affects the rate of electron transfer (*cf.* Table 2) may be understood by considering a kinetic barrier due to a specific solvation with a preferential solvation by H_2O. The effect of oxygen (Table 2) suggests that decay of the radical complex originates from its interaction with O_2, possibly by reoxidation of the W^{IV} centre or, if the radical complex is viewed as an excited state, by simple deactivation.

In order to interpret the sensitivity of the decay rate constant to the nature and concentration of the cations present, it was necessary to assume that the reactive species is an ion pair between the radical pair and the cation. A key feature in considering the ion pair and its role is that the decay rate constants not only increase with increasing H^+ and salt concentration but do so with sigmoidal-shaped curves and specificity towards the cation concerned. Competitive ion pairing between $[W^{IV}(CN)_7(\dot{C}N)]^{3-}$ and K^+ and other M_x^+ ions, equation (11), can provide a satisfactory explanation of the

$$\begin{tikzcd}
{[W^{IV}(CN)_7(\dot{C}N)]^{3-} + K^+} \arrow[r, shift left, "K_K"] \arrow[d, shift left, "+ M_x^+"] & {\{[(W^{IV}(CN)_7(\dot{C}N)]^{3-}, K^+\}} \arrow[l, shift left] \arrow[d, "H_2O", "k_K"'] \\
{\{[W^{IV}(CN)_7(\dot{C}N)]^{3-}, M_x^+\}} \arrow[u, shift left, "K_{M_x}"] \arrow[r, "k_{M_x}"] & {\{[W(CN)_8]^{4-}, K^+ \text{ or } M_x^+\} + {}^{\bullet}OH + H^+}
\end{tikzcd} \qquad (11)$$

pattern observed in Figures 7—9. The relative ion-pairing tendencies vary roughly inversely with the ionic radius of the cation as expected for simple electrostatic interaction. It is

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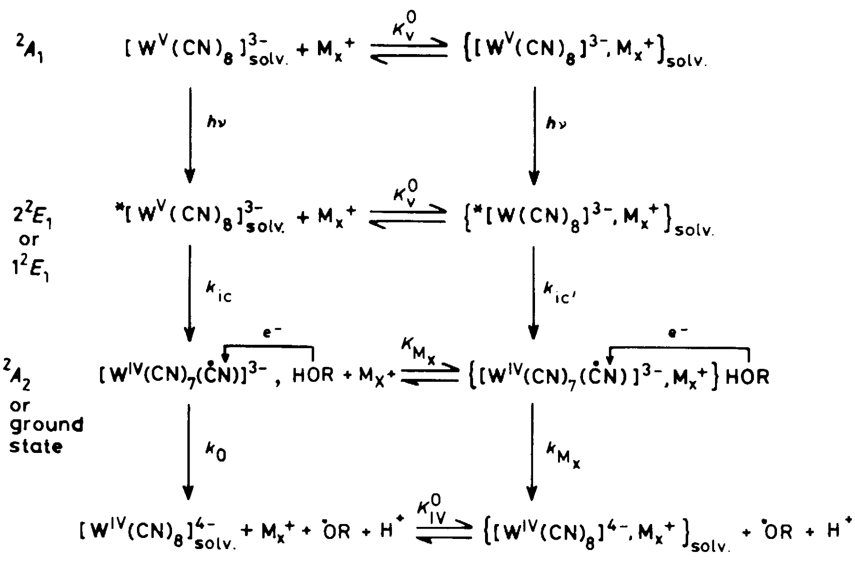
[*] While the structure of $[W(CN)_8]^{3-}$ cannot be definitely assigned, we assume the antiprismatic arrangement found for the solid sodium salt[22] and predicted as more stable from SCCC m.o. calculations.[23]



Scheme. R = H or CH_3, $k_{M_x} \gg k_0$; k_{ic} and $k_{ic'}$ are rate constants for internal conversion

interesting, however, that values of $k_{obs.}$ and k_{M_x} increase with decreasing values of the association constants K_{M_x} in the same direction as the increasing electronic polarizability of the cations. It appears therefore that the cations participate in the transfer of an electron, possibly acting as an electron conducting bridge. The departure of the large NEt_4^+ cation from this interpretation (a high value of the association constant coupled to a small value of the rate constant) may result from the participation of hydrogen bonding between the terminal methyl group of the cation and the N atoms of the cyanide ligand, as well as from the poor ability of the substituted ammonium ion to act as a relay species.

The exceptional effectiveness of hydrogen ion as the catalyst for the decay of the transient is due to a combination of the large association constants together with the unusual reactivity of the species $\{[W^{IV}(CN)_7(\dot{C}N)]^{3-}, H^+\}$.

Flash photolysis of $[Mo(CN)_8]^{3-}$ in aqueous solution ($\lambda > 320$ nm) produces a strongly absorbing transient, the spectra and identification of which have been discussed previously by Stasicka and co-workers.[5] We have found, however, l.f.p. at 249 nm produces a different, strongly absorbing species the spectrum and reactivity of which are similar to the tungsten species. Thus, we suppose that the photoredox path leading to the formation of $[Mo(CN)_8]^{4-}$ is the same as for the tungsten system (Scheme). It also explains the spin-trapping experiments resulting in the formation of OH radicals.[7] We suggest that the products observed[5] previously, namely red heptacyano-complexes, CN^-, and $(CN)_2$ may result from competitive substitutional photochemistry (Figure 2) with subsequent redox reactions.

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