

Ligand Field Photolysis of $[\text{Cr}(\text{CN})_6]^{3-}$ in Acetonitrile

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The photochemistry of hexacyanochromate(III) has been widely studied [1–3]. Photosolvolytic was found to be the main reaction path in aqueous, dimethylformamide (dmf) and dimethylsulfoxide solutions. A preliminary flash experiment has led to the suggestion that a photoredox reaction occurs as well [4]. In a recent study [5] the photochemical production of CrO_4^{2-} ions from $[\text{Cr}(\text{CN})_6]^{3-}$ was found to proceed in alkaline aqueous solution upon irradiation within the charge transfer region. To extend such studies to non-aqueous solutions, we have chosen acetonitrile as the solvent, on account of its high transparency in the UV region. In this paper we report our results on irradiation into the ligand field bands as a basis for the understanding of the more complex charge transfer photoreaction.

Experimental

Potassium hexacyanochromate(III) was prepared according to Bigelow [6] and then converted to the tetrabutylammonium salt [7]. Acetonitrile (MeCN) (Merck, Uvasol) was used as provided. Absorption spectra were recorded on a Cary 14 spectrophotometer. Quantum yields were determined in an apparatus described before [8]. The photochemical conversions were followed spectrophotometrically using 25 differential absorptivities in the range of 360 to 600 nm, as obtained on the basis of the CN^- release. Cyanide was determined potentiometrically. Irradiated solutions were diluted 1:9 with 0.1 N aqueous NaOH. Excess of water was necessary to prevent damage to the CN-sensitive electrode (Orion 94-06-00).

Results and Discussion

The spectral changes upon irradiation at 366 nm were similar to those reported for aqueous [9] and

dmf solutions [10] (Fig. 1). This result indicates photosolvolytic. Neither primary nor secondary thermal reactions could be observed at room temperature, up to several days after irradiation. On prolonged exposure, particularly to polychromatic light, the absorption increased at longer wavelengths in accordance with further photolysis.

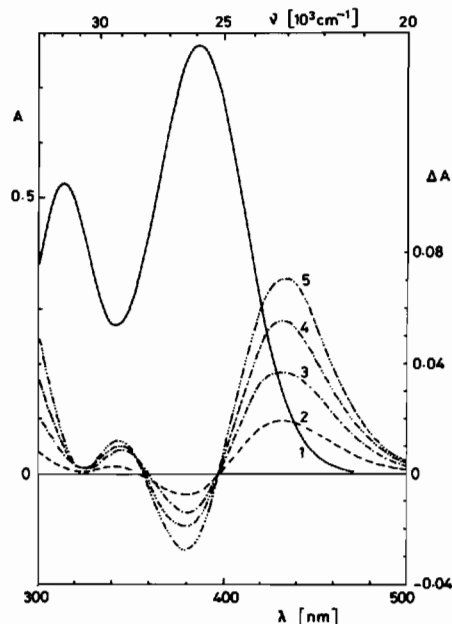


Fig. 1. Spectral changes upon 366 nm irradiation of 0.01 M $[\text{Cr}(\text{CN})_6]^{3-}$ in acetonitrile. Curve 1 (left scale) represents the spectrum of the unirradiated complex, curves 2 to 5 (right scale) are differential spectra, recorded for 3, 6, 9, and 12 min of exposure with 2.2, 4.6, 6.2, and 7.3% conversion, respectively.

The absorption spectrum of the reaction product $[\text{Cr}(\text{CN})_5\text{MeCN}]^{2-}$ was obtained from the spectral changes in combination with the potentiometric cyanide determination. The spectrum shows two moderately weak bands at 23.6×10^3 ($\epsilon = 107$) and 28.6×10^3 cm^{-1} ($\epsilon = 44$) and three more intense bands at 36.9×10^3 ($\epsilon = 6.3 \times 10^3$), 39.7×10^3 ($\epsilon = 1.8 \times 10^3$), and 44.8×10^3 cm^{-1} ($\epsilon = 5.8 \times 10^3$). Figure 2 compares the calculated spectrum with that of $[\text{Cr}(\text{CN})_5\text{H}_2\text{O}]^{2-}$. In agreement with the slightly higher ligand field strength and the smaller electron repulsion parameter of acetonitrile with respect to water [11], the long wavelength ligand field band is slightly blue shifted, while the second ligand field band shows a pronounced bathochromic shift. In the charge transfer region the first absorption (LMCT) lies at longer wavelength than that in $[\text{Cr}(\text{CN})_6]^{3-}$.

The quantum yields for the photolysis in acetonitrile are presented in Table I. They turned out to

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TABLE I. Photosolvolytic Quantum Yields of $[\text{Cr}(\text{CN})_6]^{3-}$ at 366 nm.

Solvent	Temperature [°C]	Time of exposure [min]	Quantum yield	$\phi_{t \rightarrow 0}^a$
MeCN	25	3	0.0421	0.043 ± 0.002
		6	0.0411	
		9	0.0401	
	15	3	0.0426	
		6	0.0417	
		9	0.0405	
dmf [10]	25		0.08	
H ₂ O [1]			0.10 to 0.15 ^b	

^aQuantum yield extrapolated to zero exposure time. ^bDepending on pH.

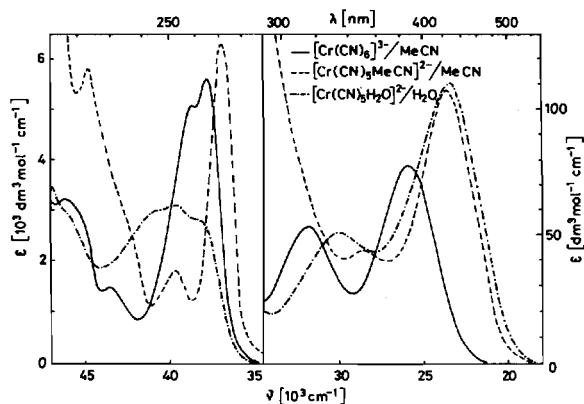


Fig. 2. Electronic absorption spectra of some cyano complexes of chromium(III).

be smaller than those in water and dmf. In the case of the corresponding cobalt complex the experimental evidence is controversial. Nakamura *et al.* [12] reported almost the same quantum yield for the photosolvolytic of $[\text{Co}(\text{CN})_6]^{3-}$ in acetonitrile ($\phi = 0.28$) as in water ($\phi = 0.32$). Wong and Kirk [13] found smaller quantum yields in acetonitrile–water mixtures than in neat water. $[\text{Cr}(\text{CN})_6]^{3-}$ and $[\text{Co}(\text{CN})_6]^{3-}$ reacted in parallel in glycerol–water mixtures [14]. In the latter case, mainly photoaquation was observed. The decrease in quantum yield found on increasing glycerol concentration was probably caused by the more effective cage recombination at the higher viscosities. For the reaction in acetonitrile a viscosity effect can be ruled out, because viscosity effects appear to be unimportant below a critical value [15]; moreover, acetonitrile is more fluid than water or dimethylsulfoxide.

The photolysis quantum yield of $[\text{Cr}(\text{NCS})_6]^{3-}$ is insensitive to the change of solvent ($\phi_{\text{MeCN}} = 0.37$; $\phi_{\text{H}_2\text{O}} = 0.33$ [16]), while the quantum yield of $[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^-$ is reduced in acetonitrile

with respect to water ($\phi_{\text{MeCN}} = 0.16$; $\phi_{\text{H}_2\text{O}} = 0.29$ [16]). The difference to $[\text{Cr}(\text{NCS})_6]^{3-}$ was interpreted in terms of different life times of the photoactive states. If the photoactive state survives several encounters, it may 'seek' a reactive solvent molecule [17] and the quantum yield will not depend on the solvent. If, on the other hand, the photoactive state is short lived, only static effects can be operative [18]. Thus only those molecules in the first solvation shell will be able to coordinate. For the $[\text{Cr}(\text{CN})_6]^{3-}$ complex, this explanation is in line with the observed solvatochromic effect [19].

Another interpretation based on Vanqickenborne and Ceulemans' [20] conception is also conceivable. Thus, the first step would be dissociation of one of the CN^- ligands, followed by isomerisation and nucleophilic attack of a solvent molecule. The dissociative character of the first step would be consistent with a weakening of the Cr–CN bond in the LF excited states, as was calculated by the SINDO method [21], as well as with the positive activation volume found by Angermann *et al.* [14]. According to this conception, the last step depends on the nucleophilic properties of the solvent. It should be responsible for the solvent dependence of the quantum yield. Due to the strong destabilization of the excited quartet state of $[\text{Cr}(\text{CN})_6]^{3-}$, the formation of the new bond must be finished within the time scale of a few vibrations. Hence, the weaker coordinating properties of acetonitrile reduce the quantum yield with respect to water and dimethylformamide.

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