Inorganica Chimica Acta, 37 (1979) L471–L472
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Photocatalytic Systems. XXXIII.* Photoreactions of Octacyano Molybdate(V) in Nonaqueous Solution Studied by ESR Spin Trapping

D. REHOREK, J. SALVETTER, A. HANTSCHMANN, H. HENNIG**

Department of Chemistry, Karl Marx University, DDR-701 Leipzig, Liebigstrasse 18, G.D.R.

Z. STASICKA and A. CHODKOWSKA

Department of Chemistry, Jagiellonian University, Krakow, Poland

Received June 22, 1979

Although octacyano molybdate(V) complexes have been known to be photosensitive for more than fifty years [1], there have yet remained some different opinions regarding the nature of primary reaction pathways. Thus, oxidation of water leading to molecular oxygen was found by Carassiti *et al.* [2–4], whereas other workers [5, 6] were able to detect cyanogen formed by reaction of cyano free radicals. Therefore either outer-sphere oxidation of the solvent (1) or inner-sphere oxidation of coordinated cyano ligand (2) were assumed to be the primary steps of photoreaction:

$$\mathrm{Mo(CN)_8^{3-} + H_2O \xrightarrow{h\nu} Mo(CN)_8^{4-} + H^+ + {}^{\bullet}OH} \qquad (1)$$

$$\mathrm{Mo(CN)_8^{3-} \xrightarrow{h\nu} Mo(CN)_7^{3-} + {}^{\bullet}CN} \qquad (2)$$

Heptacyano complexes formed according to (2) will undergo further reactions giving molybdate(VI), cyanide ions and $\mathrm{Mo(CN)_8^{4-}}$ as stable final products [7].

Unfortunately, none of the short-lived paramagnetic species proposed in the above reactions has been hitherto detected by ESR owing to their low stationary concentrations. On the other hand, we have shown recently [8] that photolytically formed cyano radicals may be trapped by phenyl N-t-butyl nitrone in organic solvents in concentrations sufficient for ESR detection.

It is the purpose of this paper to give some ESR evidence for paramagnetic intermediates in photolysis of octacyano molybdate(V) complexes in methanol solution in order to support any of the mechanisms given above (1, 2).

Experimental

Octacyano molybdate(V) solutions used were prepared by dissolving $\mathrm{K_4Mo(CN)_8 \cdot 2H_2O}$ in methanol/methylene chloride (1:1 v/v) with the aid of crown-ether (18-crown-6), followed by air-oxidation.

$\mathrm{K_4Mo(CN)_8 \cdot 2H_2O}$ [9], nitrosodurene [10] and phenyl N-t-butyl nitrone [11] were prepared by methods described in the literature. Commercially available 18-crown-6 (Merck) was used.

ESR spectra were recorded at room temperature using a JEOL JES-3BQ spectrometer working in X-band. Irradiations were performed directly within the ESR cavity by a high-pressure mercury lamp HBO-200 (VEB Narva, Berlin) equipped with glass filters to prevent heating of the samples.

Results and Discussion

The ESR spectrum of air-oxidized $\mathrm{Mo(CN)_8^{4-}}$ is represented in Fig. 1. ESR parameters given in Table I are close to those reported for $\mathrm{Mo(CN)_8^{3-}}$ in aqueous solution [12]. After short irradiation into the intense charge-transfer bands near 365 nm a sharp decrease in signal intensity of $\mathrm{Mo(CN)_8^{3-}}$ (complex *1*) is observed. ESR spectra of two new Mo(V) complexes (*2*, *3*; see Fig. 2) were detectable. These intermediates differed markedly by their stability: whereas complex *3* could be detected under continuous irradiation only, complex *2* was sufficiently stable to be observed after stopping irradiation.

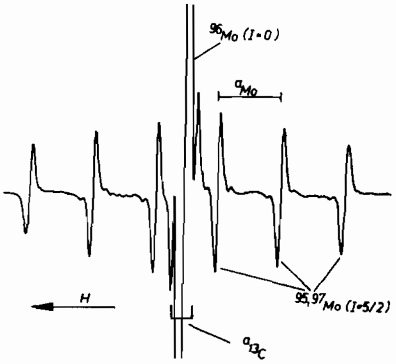


Fig. 1. ESR spectrum of $\mathrm{Mo(CN)_8^{3-}}$ formed by air-oxidation of $\mathrm{K_4Mo(CN)_8}$ in methanol/methylene chloride at 298 K.

Concentration of complex *2* was found to increase with increasing concentration of $\mathrm{Mo(CN)_8^{4-}}$ which is normally present in air-oxidized solutions of $\mathrm{K_4Mo(CN)_8}$/crown-ether. No complex *2* was found in irradiated frozen solution. Therefore it was concluded that complex *2* will be formed by reaction of

---

*Part XXXII: D. Rehorek, *Z. Chem.*, in press.

**Author to whom correspondence should be addressed.

TABLE I. Paramagnetic Species Detected during Irradiation of $Mo(CN)_8^{3-}$ in Methanol/Methylene Chloride (T = 298 K).

No.	Species	ESR Parameters
1	$Mo(CN)_8^{3-}$	$g_0 = 1.9911 \pm 0.0005$ $a_{Mo} = 3.27 \pm 0.03$ mT $a_C = 1.13 \pm 0.01$ mT
2	$(CN)_7MoCNMo(CN)_7^{6-}$	$g_0 = 1.9790 \pm 0.0008$ $a_{Mo} = 3.65 \pm 0.05$ mT
3	$Mo(CN)_7^{2-}$	$g_0 = 1.9908 \pm 0.0010$ $a_{Mo} = 3.75 \pm 0.07$ mT
4	$D\text{-}N(O^{\bullet})Mo(CN)_7^{2-}$[a]	$g_0 = 1.9823 \pm 0.0005$ $a_{Mo} = 3.56 \pm 0.02$ mT $a_N = 0.38 \pm 0.02$ mT
5	$D\text{-}N(O^{\bullet})CH_2OH$	$g_0 = 2.0059 \pm 0.0005$ $a_N = 1.38 \pm 0.02$ mT $a_H = 0.81 \pm 0.02$ mT (2H)
6	$PBN\text{-}OCH_3$[b]	$g_0 = 2.0060 \pm 0.0005$ $a_N = 1.42 \pm 0.02$ mT $aH = 0.27 \pm 0.02$ mT
7	PBN-CN[b]	$g_0 = 2.0059 \pm 0.0005$ $a_N^1 = 1.46 \pm 0.03$ mT $a_N^2 = 0.16 \pm 0.03$ mT $a_H = 0.49 \pm 0.02$ mT

[a] D = 2,3,5,6-Tetramethyl phenyl. [b] Spin adduct to phenyl N-t-butyl nitrone.

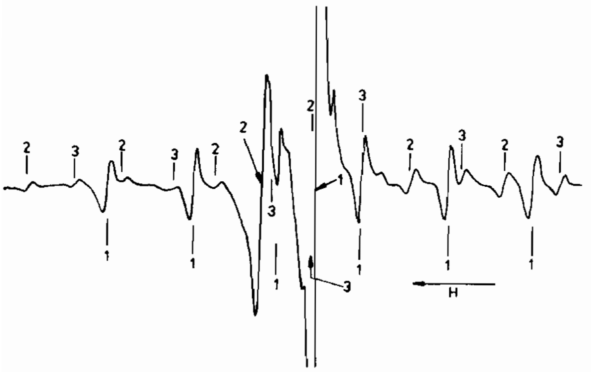
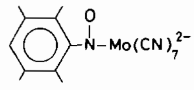


Fig. 2. ESR spectrum of shortly (5 s) irradiated $Mo(CN)_8^{3-}$ (*1*); *2*, $(CN)_7(MoCNMo(CN)_7^{6-}$; *3*, $Mo(CN)_7^{2-}$. ^{96}Mo signals (I = 0) are indicated by arrows.

any coordinatively unsaturated Mo(V) complex with $Mo(CN)_8^{4-}$ as formulated in Eq. (4). Species *3* may be tentatively assigned to $Mo(CN)_7^{2-}$ strongly supported by our spin trapping experiments.

In the presence of high concentrations of nitrosodurene (total concentration *ca.* 0.1 mol l^{-1}) neither complex *2* nor *3* were detectable during irradiation of $Mo(CN)_8^{3-}$. Instead of them a new species (*4*; see Table I) which exhibits a hyperfine structure from one interacting Mo and one nitrogen was present. *4* was assigned to the spin adduct of $Mo(CN)_7^{2-}$ to nitrosodurene.



4

Spin adducts of hydroxymethyl radicals ($^{\bullet}CH_2OH$, *5*) additionally could be detected. Using phenyl N-t-butyl nitrone as a spin trap $^{\bullet}OCH_3$ radicals (*6*) were trapped at room temperature. On lowering the temperature to about 200 K spin adducts of cyano radicals to phenyl N-t-butyl nitrone were detectable. The hyperfine coupling constants (see Table I) well agree with those given by Mao and Kevan [13].

It should be noted that species similar to complex *2* were also found in the absence of crown-ether using ethylene glycol as a solvent.

From these results the following scheme may be derived.

$$\underset{1}{Mo(CN)_8^{3-}} \xrightarrow[h\nu]{CH_3OH} \begin{cases} Mo(CN)_8^{4-} + H^+ + {}^{\bullet}OCH_3 & (3a) \\ Mo(CN)_7^{3-} + {}^{\bullet}CN & (3b) \\ \underset{3}{Mo(CN)_7^{2-}} + CN^- & (3c) \end{cases}$$

$$Mo(CN)_7^{2-} + Mo(CN)_8^{4-} \longrightarrow \underset{2}{(CN)_7MoCNMo(CN)_7^{6-}} \quad (4)$$

$${}^{\bullet}OCH_3 + CH_3OH \longrightarrow CH_3OH + {}^{\bullet}CH_2OH \quad (5)$$

Obviously both outer-sphere and inner-sphere redox processes (3a, 3b) as well as substitution reactions (3c) have to be considered as primary photoreactions of $Mo(CN)_8^{3-}$ in methanol solution.

References

1 W. R. Brucknall and W. Wardlow, *J. Chem. Soc.*, 2981 (1927).
2 V. Balzani and V. Carassiti, 'Photochemistry of Coordination Compounds', London–New York, 1970, p. 12.
3 L. Moggi, F. Bolletta, V. Balzani and F. Scandola, *J. Inorg. Nucl. Chem., 28,* 2589 (1966).
4 V. Carassiti and V. Balzani, *Ann. Chim. (Rome), 52,* 432 (1962).
5 G. W. Gray and T. J. Spence, *Inorg. Chem., 10,* 2751 (1971).
6 Z. Stasicka and H. Bulska, *Rocz. Chem., 48,* 389 (1974).
7 Z. Stasicka, *Rocz. Chem., 47,* 485 (1973).
8 D. Rehorek, *Z. Chem.*, in press.
9 N. H. Furman and C. O. Miller, *Inorg. Synth., 3,* 160 (1950).
10 L. I. Smith and F. L. Taylor, *J. Am. Chem. Soc., 57,* 2370, 2460 (1935).
11 W. Rundel, 'Houben/Weyl, Methoden der organischen Chemie', Georg-Thieme-Verlag, Stuttgart, 1968, Bd. X/4.
12 B. R. McGarvey, *Inorg. Chem., 5,* 476 (1966).
13 S. W. Mao and L. Kevan, *J. Phys. Chem., 80,* 2330 (1976).