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Photocatalytic Systems. XXVII.* On the Detection of Paramagnetic Intermediates formed during the Photolysis of Potassium Dichromate in Propan-1-ol

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Solutions of dichromate in water/alcohol mixtures are known to be photosensitive [1]. Depending on the pH and the total Cr^{VI} concentration, different Cr^{VI} species are formed [2]. However, Kläning [3] has shown that the formation of chromic esters of the type $ROCrO_3^-$ is responsible for the photoreaction regardless of whether dichromate or chromate are used as Cr^{VI} source. Neither free radicals nor Cr^V could be detected in low-temperature photolysis of frozen alcoholic chromate solutions [4] suggesting the first step being a two-electron transfer from alcohol to Cr^{VI} forming aldehydes (or ketones) and Cr^{IV}. Contrary to these results, we have found recently [5] that in the absence of water the mechanism is different from that observed in water/alcohol mixtures. In the photolysis of K_2CrO_4 in pure alcohols, evidence for both two-electron and one-electron transfer giving Cr^{IV} and Cr^V in the first step, respectively, was obtained.

In order to get some information about the photochemical oxidation of alcohols by the dichromate ion, we have investigated the photolysis of $K_2Cr_2O_7$ crown-ether complex in propan-1-ol.

Experimental

Solutions containing $K_2Cr_2O_7$ in a concentration of *ca.* 3 X 10^{-3} *M* were obtained by dissolving $K_2Cr_2O_7$ in propan-1-ol in the presence of a threefold excess of 18-crown-6. Nitrosodurene dissolved in CH_2Cl_2 and phenyl N-tert-butyl nitrone, respectively, were added in the spin trapping experiments. All samples were deaerated with streams of nitrogen before use.

ESR spectra were recorded either at room temperature or at *ca.* 100 K using a JES-3BQ (Jeol) spectrometer. Continuous irradiations were performed directly within the cavity of the ESR spectrometer using a high-pressure Hg lamp HBO-200 (VEB Narva, Berlin). To prevent heating, a water filter was arranged between irradiation source and sample.

TABLE I. ESR Parameters of Paramagnetic Species Formed in Photolysis of $K_2Cr_2O_7$ in Propan-1-ol.

Species	T (K)	g value	Hyperfine Splitting[a]
Cr^V(A)	295	1.968 ± 0.001	a_{Cr} = 1.395 ± 0.010
Cr^V(B)	295	1.979 ± 0.001	not observed
Cr^V(B)	100	g_1 = 1.990 ± 0.003 g_2 = 1.982 ± 0.005 g_3 = 1.972 ± 0.003	not observed
Cr^V, Cr^V [b]	100	1.995 ± 0.010	D = 2.59 ± 0.03[c]
$\cdot CH_2CH_3$[d]	295	2.0059 ± 0.0005	a_N = 1.42 ± 0.02 a_H = 1.20 ± 0.02 (2H)
$C_2H_5 \cdot \dot{C}HOH$[d]	295	2.0058 ± 0.0005	a_N = 1.49 ± 0.02 a_H = 0.29 ± 0.02 (1H)
CE[d,e]	295	2.0059 ± 0.0005	a_N = 1.35 ± 0.02 a_H = 0.85 ± 0.02 (1H)
$C_3H_7O\cdot$[f]	295	2.0058 ± 0.0005	a_N = 1.43 ± 0.02 a_H = 0.25 ± 0.02 (1H)

[a] Hyperfine coupling constants given in mT; in parentheses: number of interacting protons. [b] Radical pair. [c] Dipolar interaction term. [d] Spin adducts to nitrosodurene: $\text{Dur}-\overset{\overset{\bullet}{O}}{\overset{|}{N}}-\text{R}$. [e] Crown-ether radical $\overline{-(CH_2CH_2O)_5-CH_2\dot{C}HO-}$. [f] Spin adduct to phenyl N-tert-butyl nitrone: $C_6H_5-\overset{R}{\overset{|}{C}}H-\overset{\overset{\bullet}{O}}{\overset{|}{N}}-C_4H_9$.

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*Part XXVI; D. Rehorek, R. Wagener, T. Jarzynowski, and Z. Stasicka, *Z. Chem.*, in press.

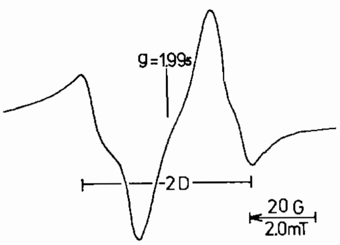

Fig. 1. ESR spectrum of a $\overline{CrO_3^-\cdot\ \bullet CrCo_3^-}$ radical pair formed during the photolysis at 100 K.

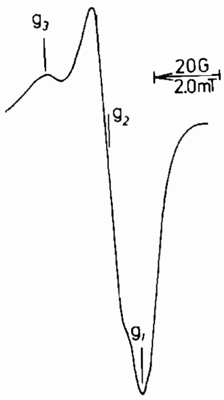

Fig. 2. ESR spectrum of Cr^V (B) recorded at 100 K.

Results and Discussion

No ESR signals were obtained from freshly prepared samples stored in the dark. In liquid solution, a strong ESR signal due to a Cr^V species (complex A, see Table I) appeared immediately after irradiation. Moreover, small amounts of a second Cr^V species have been detected (complex B), but its concentration reached only about 5% of the former one. The ESR parameters of the Cr^V species given in Table I are very close to those observed in the photolysis of K_2CrO_4 [5].

In order to answer the question whether the photoactive species in the photolysis of dichromate and chromate are the same or not, we have also photolysed frozen solutions of dichromate. A rather intense ESR signal with a fine structure due to dipolar interaction of two unpaired electrons has been detected at 100 K (see Fig. 1). Obviously, this spectrum may be attributed to a radical pair. The low g value indicates that the spectrum may be ascribed to a pair of Cr^V species rather than do an organic radical pair. This is supported by the fact that after warming and freezing the sample again, the spectrum of the radical pair disappeared and a new one represented in Fig. 2 was detected. The same spectrum could be obtained after freezing liquid solutions containing essentially Cr^V (B) which were prepared by thermal reaction of K_2CrO_4 in propan-1-ol under mild conditions [5].

No radicals could be detected in samples irradiated at 100 K. Since the absorption spectrum of $K_2Cr_2O_7$ in propan-1-ol solution exhibits a shoulder at the long-wavelength part of the absorption band in the visible region which is not seen in aqueous solution, the formation of dichromic esters of the type $ROCr_2O_6^-$ is likely. Using nitrosodurene and phenyl N-tert-butyl nitrone as spin traps, free radicals ($\cdot CH_2CH_3$, $C_2H_5\cdot\dot{C}HOH$, $C_3H_7O\cdot$, and crown-ether radical, see Table I) could be detected in photolysed liquid solutions. Although the mechanism seems to be rather complicated and has not been clarified in all details yet, the following reaction pathways may be of some importance:

$$C_3H_7OCr_2O_6^- \xrightarrow{h\nu}$$

$$C_2H_5CHO + H^+ + {}^-OCr^{IV}(O)\text{–}O\text{–}Cr^{VI}(O)_2O^- \qquad (1)$$

$${}^-OCr^{IV}(O)\text{–}O\text{–}Cr^{VI}(O)_2O^-$$

$$\longrightarrow Cr^{IV} + CrO_4^{2-} \qquad (2a)$$

$$\longrightarrow \underset{\text{radical pair}}{\overline{CrO_3^-\cdot\ \ \cdot CrO_3^-}} \qquad (2b)$$

$$\overline{CrO_3^-\cdot\ \ \cdot CrO_3^-} \longrightarrow 2CrO_3^-\cdot \qquad (3)$$

$$CrO_3^- + C_3H_7OH \longrightarrow \underset{\text{complex B}}{C_3H_7OCrO_3^{2-}} + H^+ \qquad (4)$$

$$Cr^{IV} + Cr^{VI} \longrightarrow 2\ Cr^V\ (\text{complex A}) \qquad (5)$$

$$Cr^{IV} + C_3H_7OH \longrightarrow Cr^{III} + C_3H_7O\cdot \qquad (6)$$

Dissociation of the mixed valence dimeric chromium complex formed in reaction (1) giving Cr^{IV} and Cr^{VI} (2a) competes with intramolecular electron transfer which leads to a Cr^V radical pair (2b). In view of the results published by Vanquickenborne *et al.* [6], the reaction of primary formed $CrO_3^-\cdot$ species with alcohol (4) seems to be very probable. In frozen solution, reaction (2b) should be favoured, whereas at higher temperatures Cr^{IV} and Cr^{VI} can escape. Propoxy radicals ($C_3H_7O\cdot$) are formed by thermal reaction of Cr^{IV} with propan-1-ol. As we have shown in [5], these radicals can form $C_2H_5\text{-}\dot{C}HOH$, $\cdot CH_2CH_3$, and $\overline{(CH_2CH_2O)_5\text{–}CH_2\dot{C}HO}$ either by isomerization, fragmentation or hydrogen abstraction at the crown ether, respectively. Additional

Cr^V (B) complex is obtained from reaction of hydroxy propyl radicals ($C_3H_7\dot{C}HOH$) with CrVI, whereas Cr^V (A) is formed by disproportionation of Cr^{IV} and Cr^{VI} (5) [5].

Unfortunately, no information can be obtained regarding the structure of Cr^V (A) complex. Nevertheless, the evidence given here strongly suggests different primary processes being present in the photolysis of $K_2Cr_2O_7$ and K_2CrO_4, respectively.

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