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EPR Study on Dichromate–Dithizone Interaction in Nonaqueous Medium

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The dichromate–dithizone interaction in organic media is studied in detail at different reaction conditions. Using the EPR method it was found that the Cr(VI) reduction proceeds through different reaction mechanisms depending on the dichromate–dithizone concentration ratio. At low dithizone concentrations the redox process goes on through two consecutive two-electron steps. In the course of the Cr(VI) reduction a relatively stable Cr(V)–dithizone complex is formed, denoted as $Cr^V(2)$*. At higher dithizone concentrations the Cr(VI) reduction to Cr(V) proceeds via one-electron transfer resulting in parallel free radical and Cr(V) formation. In this case another Cr(V) complex is formed denoted as* $Cr^V(1)$*. It was shown that the* $Cr^V(1)$ *further reduction proceeds through a two-electron process. The reaction mechanism including one-electron reduction of Cr(VI) to Cr(V) is observed for the first time.*

Introduction

Recently we have studied the solvent effect on the mechanism of dichromate reduction with dithizone in nonaqueous medium [1]. By means of EPR spectroscopy it was established that at a molar ratio [Dithizone] : [Cr(VI)] = 3:1 two Cr(V) complexes are formed, denoted as $Cr^V(1)$ and $Cr^V(2)$. The EPR signal of $Cr^V(1)$ is a singlet, while that of $Cr^V(2)$ shows 5-component superhyperfine structure (shfs). It was shown that some of the solvents studied participate in the redox process reducing Cr(VI) to Cr(IV), the process being photochemical. Solvents capable of reducing Cr(VI) and leading to the formation of Cr(V) are dimethylformamide (DMF), dimethylsulfoxide (DMSO) and hexamethylphosphortriamide (HMPA). No free radical formation both at room temperature and at ~70 K was observed in the course of the Cr(VI)–dithizone interaction under these conditions. It was found that the $Cr^V(1)$ concentration was significantly lower than that of $Cr^V(2)$ and its signal could be observed only at the begining of the reaction. The following reaction scheme was proposed for the process studied:

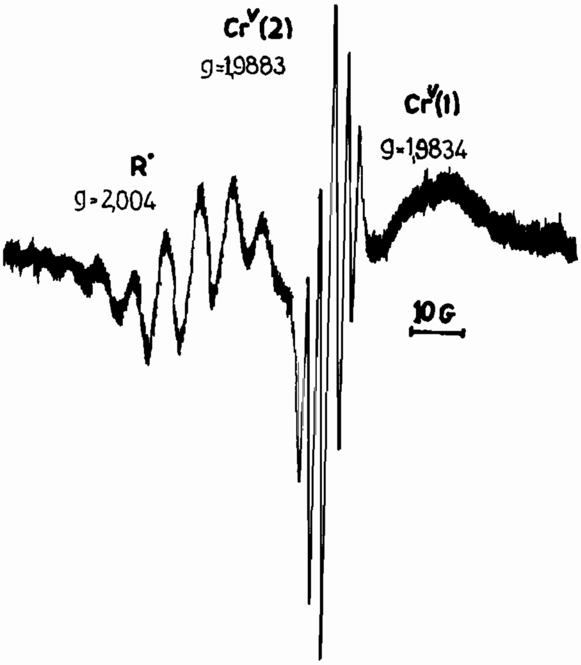


Fig. 1. EPR spectrum of the system $K_2Cr_2O_7$–Dithizone–DMF at 20 °C. Molar ratio [Dtz] : [Cr(VI)] = 8:1.

SCHEME I

$$\mathrm{Cr(VI)} + \mathrm{S} \xrightarrow{h\nu} \mathrm{Cr(IV)} + \mathrm{P_1} \qquad (1)$$

$$\mathrm{Cr(IV)} + \mathrm{Cr(VI)} \longrightarrow 2\,\mathrm{Cr(V)} \qquad (2)$$

$$\mathrm{Cr(V)} + \mathrm{Dtz} \rightleftharpoons \mathrm{Cr^V(Dtz)_2} \equiv \mathrm{Cr^V(2)} \qquad (3)$$

$$\mathrm{Cr^V(Dtz)_2} \longrightarrow \mathrm{Cr(III)} + \mathrm{P_2} \qquad (4)$$

(Dtz ≡ dithizone; S ≡ solvent; P ≡ oxidation products)

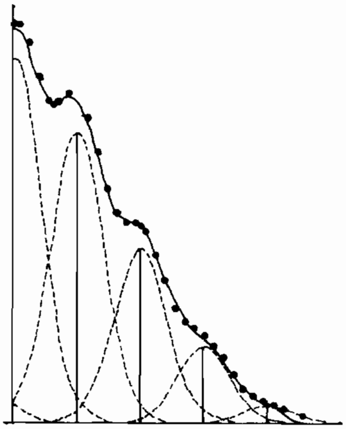


Fig. 2. EPR spectrum of the free radical (g = 2.004, a = 2.6 Oe) in DMF at 20 °C (integrated curve). —— observed spectrum, ... simulated spectrum.

However, on changing the reaction conditions, namely on increasing the ligand concentration ([Dtz] : [Cr(VI)] > 6) three different EPR signals with g-values 2.004, 1.9883, 1.9834 respectively are observed in the EPR spectrum of the system (Fig. 1). Attempts were made to identify these paramagnetic species and the kinetics and mechanism of their formation and decay were studied in order to obtain additional information on the mechanism of the overall redox process between dichromate and dithizone in organic medium. The solvents DMF, DMSO, HMPA and acetonitrile (An) were used for the purpose.

Experimental

The formation and decay of the paramagnetic species in the course of the dichromate reduction were studied using the EPR method. Potassium dichromate (0.0168 g) and dithizone (0.230 g) were dissolved in 2.00 ml organic solvent, the ratio [Dtz] : [Cr(VI)] being 8:1. The reaction was carried out in a thermostated reaction vessel at 60 °C. The experimental technique used is already described in detail [1–3]. Diphenylpicryl hydrazile (DPPH) (g = 2,0036) and oriented ruby crystal (g = 2,4) were used as standards to determine the concentrations of the paramagnetic species.

Materials and Apparatus

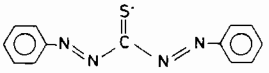
All the reagents used were of AR grade. Dithizone and potassium dichromate were used as finely ground powder, the latter being dried for two hours at 110 °C. The solvents used were distilled under low pressure and stored over molecular sieves. An was distilled over P_2O_5.

The EPR spectra were obtained on a standard X-band EPR spectrometer. A 100 W Xe-point source lamp was used in the photochemical experiments.

Results and Discussion

As was mentioned above three EPR signals are observed in the spectrum of the system $K_2Cr_2O_7$–dithizone in DMF, DMSO and HMPA solutions, dithizone being in moderate excess (Fig. 1). Two of them were identified as due to the $Cr^V(1)$ and $Cr^V(2)$ complexes (g values 1.9834 and 1.9883 respectively). The third one is due most probably to a free radical (g = 2.004). At room temperature its spectrum shows 9-component partially resolved hfs. In order to determine the relative intensity ratio of the individual components the spectrum was simulated as described in the literature [4] for additional hyperfine interaction with four equivalent ^{14}N (I = 1). On Fig. 2 the experimental and simulated spectra are shown. The obtained individual component ratio 0.8:4:9:15:19:15:9:4:0.8 is in good agreement with the theoretical 1:4:9:16:19:16:9:4:1 ratio.

An analogous EPR spectrum with exactly the same g value and hfs was observed when dithizone was oxidized with $(NH_4)_2S_2O_8$ in DMF solution. This fact proves the assumption that the signal is due to a free radical obtained from dithizone most probably with the following structure:



The structure of the $Cr^V(2)$ complex with dithizone has been already discussed [1, 5]. As the EPR signal of $Cr^V(1)$ is a singlet line no definite conclusions about the $Cr^V(1)$ complex structure could be drawn.

The EPR investigations on the dithizone–$K_2Cr_2O_7$ interaction in DMF, DMSO and HMPA at various molar ratios of the reagents showed that the formation of the intermediate paramagnetic species under study depends strongly on the reaction conditions. As was proved before [1] at low excess of the ligand ([Dtz] : [Cr(VI)] < 6) only $Cr^V(1)$ and $Cr^V(2)$ are formed, the latter being the predominant Cr(V) species in the system. On increasing the dithizone concentration in the reaction system (6 < [Dtz] : [Cr(VI)] < 10) The $Cr^V(1)$ concentration increased too and at the same time the EPR signal due to the free radical appeared in the spectrum. At greater excess of the ligand ([Dtz] : [Cr(VI)] > 10) only the signals due to $Cr^V(1)$ and the free radical are observed.

The kinetics of formation and decay of the three paramagnetic species in DMF was followed at a molar ratio [Dtz] : [Cr(VI)] = 8:1 and the results obtained

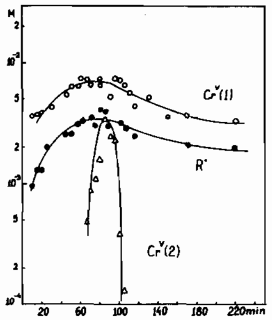


Fig. 3. Kinetics of $Cr^V(1)$, $Cr^V(2)$ and free radical formation and decay in DMF at 60 °C. Molar ratio [Dtz] : [Cr(VI) = 8:1.

are shown in Fig. 3. It can be seen that the $Cr^V(2)$ kinetic curve proceeds through a sharp maximum, while at lower concentrations of dithizone the complex $Cr^V(2)$ proved to be kinetically rather stable [1]. Under these conditions the $Cr^V(1)$ concentration is higher than that of $Cr^V(2)$ and its kinetic curve is analogous to that of the free radical.

The irradiation of the reaction solution with xenon lamp showed no influence on the $Cr^V(1)$ and the free radical formation in contrast to $Cr^V(2)$ [1].

In order to obtain additional information on the mechanism of the process attempts were made to isolate the Cr(III) complex formed as a final reaction product. It was found that at the molar ratio [Dtz] : [Cr(VI)] = 2:1 the Cr(III) complex obtained is a brownish-black residue insoluble both in high and low polar solvents. At the molar ratio [Dtz] : [Cr(VI)] = 10:1 another Cr(III) complex is formed which is soluble in organic solvents and all attempts to isolate it from the reaction mixture failed. These results show that two different Cr(III) complexes are formed as final reaction products depending on the reagents concentration ratio in the system. As Cr(III) complexes are known to be kinetically inert it should be expected that Cr(III) species formed in the course of Cr(VI) reduction would include in its coordination sphere some oxidation products of the ligands coordinated to the initial species – Cr(VI) and Cr(V). Similar results for coordination of the reaction products to Cr(III) have been already reported for other reactions [2, 6]. For that reason it might be concluded that the two different Cr(III) complexes formed at different reaction conditions result from different Cr(V) intermediates, indicating that the redox process really proceeds through two parallel reaction pathways.

As was already shown, at low excess of the ligand Scheme I (reactions (1)–(4)) is operating [1], while at larger excess of the ligand another mechanism is valid involving formation of free radical.

One of the possible reaction schemes for the case is that suggested by Roček [7]:

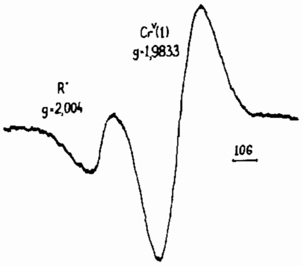


Fig. 4. EPR spectrum of the system $K_2Cr_2O_7$–Dithizone–An at 20 °C.

SCHEME II

$$\mathrm{Cr(VI)} + \mathrm{Dtz} \longrightarrow \mathrm{Cr(IV)} + P_6 \qquad (5)$$

$$\mathrm{Cr(IV)} + \mathrm{Dtz} \longrightarrow \mathrm{Cr(III)} + R^{\bullet} \qquad (6)$$

$$\mathrm{Cr(VI)} + R^{\bullet} \longrightarrow \mathrm{Cr^V(1)} + P_4 \qquad (7)$$

$$\mathrm{Cr^V(1)} + \mathrm{Dtz} \longrightarrow \mathrm{Cr(III)} + P_5 \qquad (8)$$

(Dtz ≡ Dithizone; P ≡ Oxidation products; $R^{\bullet}$ ≡ Free radical)

In order to check this possibility the process (7) was studied separately. For the purpose the free radicals were generated in relatively high concentration (Dithizone was oxidized by $(NH_4)_2S_2O_8$ in DMF solution) and then $K_2Cr_2O_7$ was added to it. According to Scheme II interaction between the free radical and Cr(VI) should take place (process (7)) resulting in $Cr^V(1)$ formation giving rise to its EPR signal. However, the EPR data obtained showed that after addition of $K_2Cr_2O_7$ fast decay of the free radical and no Cr(V) formation was observed. Therefore the validity of Scheme II for the process studied should be ruled out. The free radical however, could be formed as a result of Cr(VI) reduction by dithizone via one-electron step:

$$\mathrm{Cr(VI)} + \mathrm{Dtz} \longrightarrow \mathrm{Cr^V(1)} + R^{\bullet} \qquad (9)$$

A strong support for such assumption could be found in the fact that the kinetic curves for the formation of $Cr^V(1)$ and the free radical are analogous.

Since in the one-electron redox interaction between Cr(VI) and dithizone (process (9)) no reducing solvent is involved it should be expected to proceed even in such solvents. This offers another possibility for checking the validity of the mechanism suggested. For that reason the Cr(VI)–dithizone interaction was studied in An as the latter cannot reduce Cr(VI) to Cr(III).

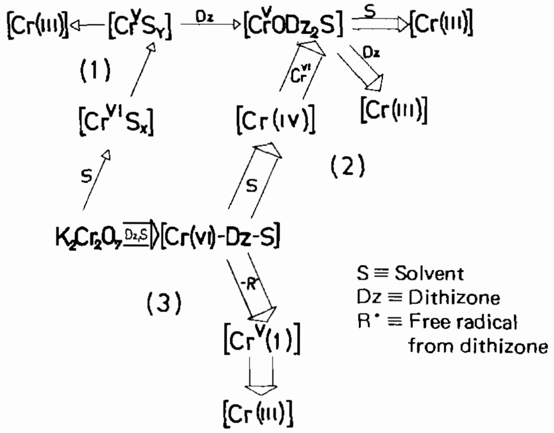
The results obtained showed that in An solution the Cr(VI)–dithizone interaction proceeds though with much lower rate and only $Cr^V(1)$ and the free radical are formed (Fig. 4).

On the basis of all experimental data it can be concluded that at large excess of the ligand and in non-reducing solvents $Cr^V(1)$ is formed together with the free radical as a result of one-electron reduction of Cr(VI) according to equation (9). Such mechanism of one-electron reduction of Cr(VI) to Cr(V) is observed for the first time.

In the next step of the redox process $Cr^V(1)$ is reduced to Cr(III) most probably via a two-electron mechanism:

$$Cr^V(1) + Dtz \longrightarrow Cr(III) + P \qquad (10)$$

Summarizing the results discussed in the present and previous [1] papers the following reaction scheme for the $K_2Cr_2O_7$ reduction with dithizone in DMF, DMSO, HMPA and An is proposed:



The reaction scheme proposed includes three reaction paths for the Cr(VI) reduction. In the absence of dithizone the Cr(VI) reduction to Cr(V) proceeds only through the reaction path (1). In the presence of dithizone the reduction of Cr(VI) goes on with much higher rate, the reaction mechanism depending significantly on the reagents concentration ratio. At the molar ratio [Dtz] : [Cr(VI)] < 4 the reaction path (2) is the predominant one, connected with two consecutive two-electron steps. Increasing the [Dtz] : [Cr(VI)] ratio the reaction path (3) is also realized, being the main pathway of the Cr(VI) reduction at a molar ratio [Dtz] : [Cr(VI)] > 6. In this case a one-electron redox step leads to the reduction of Cr(VI) to Cr(V), connected with the formation of free radical from dithizone.

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