Cr(V) Complex Species with Crown Ethers

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Cr(V) complex formation was studied with a series of crown ethers in the course of $K_2Cr_2O_7$ reduction in nonaqueous media in darkness and on irradiation. In the dark only one type of Cr(V) complex with the ligands studied was formed, the Cr(V)–18-Crown-6 being the most stable. On irradiation several other Cr(V) species were also formed. The structure of the Cr(V) complexes is discussed.

Introduction

Stabilization of unusual oxidation states of some metal ions (silver(II), uranium(V)) was achieved using crown ethers as ligands [1, 2]. Recently some new data on Cr(V) complex formation with a macrocyclic N_4-ligand were reported [3]. The aim of the present work was to study the possibility for stabilization of Cr(V) through complex formation with O-containing crown ethers, as well as the structure of the complexes formed. The corresponding complexes were obtained as intermediates during the reduction of Cr(VI) by the same ligands.

Experimental

The reduction of Cr(VI) with 12-Crown-4,15-Crown-5, 18-Crown-6, Dibenzo-18-Crown-6 was studied. The Cr(V) complex formation was followed by means of an EPR method, the corresponding g-values being measured using DPPH as a standard. As we have already shown [4, 5], Cr(V) formation and decay are photosensitive processes, so that both the dark and photochemical reactions were studied. The kinetics of the reactions were investigated as described previously [4] at a molar ratio [Cr(VI)] : [Crown ether] of 1:5.

Materials and Apparatus

All reagents used were of AR grade.

The initial Cr(V) compounds Na_3CrO_4 and $[pyH]^+[Cr^VOCl_4]^-$ (py ≡ pyridine) were synthesized as described in the literature [6, 7]. Acetonitrile (An) was dried by distillation over P_2O_5 and hexamethylphosphortriamide (HMPA) was kept above molecular sieves 4A.

The measurements were made on a standard X-band EPR spectrometer and on a spectrometer ERS-220 (GDR).

The photochemical experiments were carried out at irradiation with a 100 w point-source Xenon lamp under standard conditions.

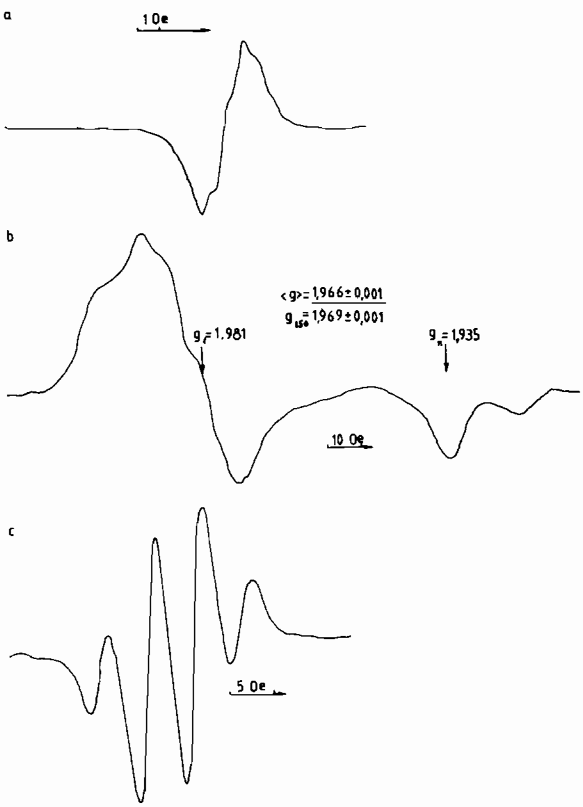

Fig. 1. EPR spectra of the systems: a) Cr^V(1)–15-Crown-5 and Cr^V(1)–18-Crown-6 at 20 °C; b) Cr^VOCl_4–18-Crown-6 at –170 °C; c) $Cr_2O_7^{2-}$–15-Crown-5 after long irradiation at 20 °C.

TABLE I. EPR Data for the Cr(V) Complexes Obtained with the Crown Ethers.

Ligand	$K_2Cr_2O_7$ solv. HMPA	$[pyH]^+[Cr^VOCl_4]^-$ solv. An	Na_3CrO_4 solv. HMPA
	$Cr^V(1)^{a,b}$ 1.9776 ± 0.0006		$Cr^V(1)^{a,b}$ 1.9781 ± 0.0004
		$Cr^V(2)^{a,b}$ 1.969 ± 0.001	
18-Crown-6		$Cr^V(3)^{a,b}$ 1.9803 ± 0.0003	
	$Cr^V(4)^b$ 1.971 ± 0.001		
	$Cr^V(5)^b$ 1.9672 ± 0.0006		
	$Cr^V(6)^b$ 1.967 (broad)		
	$Cr^V(1)^{a,b}$ 1.9777 ± 0.0006		
		$Cr^V(2)^{a,b}$ 1.969 ± 0.001	
Dibenzo-18-Crown-6	$Cr^V(4)^b$ 1.9708 ± 0.0008		insoluble
	$Cr^V(5)^b$ 1.9672 ± 0.0005		
	$Cr^V(6)^b$ 1.967 (broad)		
	$Cr^V(1)^{a,b}$ 1.9779 ± 0.0006		$Cr^V(1)^{a,b}$ 1.9777 ± 0.0006
		$Cr^V(2)^{a,b}$ 1.9686 ± 0.0004	
15-Crown-5		$Cr^V(3)^{a,b}$ 1.9806 ± 0.0004	
	$Cr^V(4)^b$ 1.971 ± 0.001		
	$Cr^V(5)^b$ 1.9672 ± 0.0006		
	$Cr^V(6)^b$ 1.967 (broad)		
	$Cr^V(1)^{a,b}$ 1.978 ± 0.001		
12-Crown-4		$Cr^V(2)^{a,b}$ 1.9684 ± 0.0004	insoluble
		$Cr^V(3)^{a,b}$ 1.9806 ± 0.0004	

[a] Dark reaction. [b] Photochemical reaction.

Results and Discussion

Dark Reactions

The kinetics of Cr(V) formation was studied in the course of $K_2Cr_2O_7$ reduction in darkness with 12-Crown-4, 15-Crown-5, 18-Crown-6 and Dibenzo-18-Crown-6 in organic solvents (An or HMPA) in the temperature range −170–+60 °C. Under these conditions one Cr(V) complex was formed, denoted as $Cr^V(1)$.

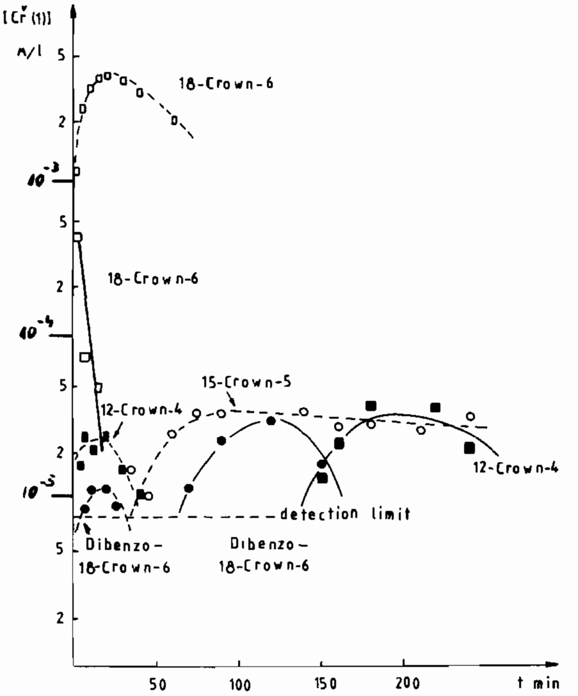

Fig. 2. Kinetic data for $Cr^V(1)$ formation with the crown ethers at 20 °C in acetonitrile. ----- dark reactions, —— photochemical reactions.

The EPR signal of $Cr^V(1)$–12-Crown-4 is a singlet line, while the signals of all $Cr^V(1)$ complexes show 5-component hyperfine structure (hfs) ($A = 0.5 \pm 0.1$ Oe) (Fig. 1a). The corresponding g-values determined are given in Table I and the kinetic data in Fig. 2.

The highest Cr(V) concentration is observed in the case of 18-Crown-6. This might be due either to the higher solubility of $K_2Cr_2O_7$ in 18-Crown-6, the latter being the best complexation agent for K^+ [8], or to the fact that the ligand offers the best geometrical conditions for complexation with the $Cr^V{=}O$ unit. In order to discriminate between these two possibilities we have studied the Cr(V) complex formation of Na_3CrO_4 with the crown ethers mentioned above. In saturated solutions of Na_3CrO_4 in HMPA the highest Cr(V) concentration was again observed with 18-Crown-6, although the most suitable complexation agent for Na^+ is 15-Crown-5 [8]. These data show that 18-Crown-6 stabilizes most effectively Cr(V).

Dibenzo-18-Crown-6 in contrast to 18-Crown-6 shows the lowest ability for complexation with Cr(V) (see Fig. 2), most probably for steric reasons. In the case of 18-Crown-6 the six O-atoms are coplanar, while the structure of Dibenzo-18-Crown-6 is distorted.

It was found that the same $Cr^V(1)$ complexes with the ligands studied were obtained when Na_3CrO_4 was used instead of $K_2Cr_2O_7$. In the case of $[pyH]^+$-$[CrOCl_4]^-$–Crown ether interaction, however, two new Cr(V) complexes were formed, denoted as $Cr^V(2)$ and $Cr^V(3)$ (see Table I).

Photochemical Reactions

The irradiation of the system Cr(VI)–Crown ether with visible light leads to the formation of several new Cr(V) complexes, denoted as $Cr^V(4)$, $Cr^V(5)$, *etc.* (see Table I).

The kinetic data obtained upon irradiation show that in these conditions the concentration of $Cr^V(1)$ complexes with 18-Crown-6 and 15-Crown-5 is rather low (with the latter ligand being under the detection minimum). On the contrary, the corresponding $Cr^V(1)$ concentrations with Dibenzo-18-Crown-6 and 12-Crown-4 are a little higher than those in the dark reactions (see Fig. 2). The photochemically formed $Cr^V(4)$, $Cr^V(5)$, *etc.* are kinetically unstable and can only be detected in the reaction mixture during irradiation. In the dark they disappear very quickly (3–5 min). The kinetic data show that in the course of the irradiation only the $Cr^V(5)$ concentration increases, while those of $Cr^V(1)$, $Cr^V(4)$ and $Cr^V(6)$ decrease.

As a strong oxidant $K_2Cr_2O_7$ might produce a number of oxidation products – alcohols, aldehydes, carboxylic acids, *etc.* which also could coordinate to Cr(V). In order to check this possibility we have studied the reactions between Cr(V) compounds and the same crowns, comparing the results with those for the system $K_2Cr_2O_7$–crown ethers. The data obtained with saturated solutions of Na_3CrO_4 in HMPA and $[pyH]^+[Cr^VOCl_4]^-$ in An are represented in Table I.

It should be emphasized that on irradiation $Cr^V(1)$ is formed again only when $K_2Cr_2O_7$ or Na_3CrO_4 is used, while in the case of $[pyH]^+[Cr^VOCl_4]^-$ only the complexes $Cr^V(2)$ and $Cr^V(3)$ are formed.

$Cr^V(1)$ Structure

At room temperature all $Cr^V(1)$ complexes except $Cr^V(1)$–12-Crown-4 show a 5-component EPR signal with g-value of 1.978 ± 0.001, which does not change with the crown ether and the solvent used (see Tables I and II). The same $Cr^V(1)$ species are formed in the course of Na_3CrO_4–crown ether reaction.

The data thus obtained indicate that the solvent does not participate in the coordination sphere of $Cr^V(1)$. Hence, it seems that the most probable structure for these complexes is the pyramidal one, with the crown oxygens in the equatorial plane and the oxygen from the $Cr^V{=}O$ unit in an axial position. Such a structure was observed for the Cr(V) complexes with many other ligands [4, 7, 10]. The partially resolved 5-component hfs indicates that only

TABLE II. G-Factors of $Cr^V(1)$ Complexes in Different Solvents.

Solvent	g-value	Donor Number DN [9]
Formamide (FA)	1.9787 ± 0.0004	~40
Dimethylsulfoxide (DMSO)	1.9783 ± 0.0003	29.8
Acetonitrile (An)	1.9789 ± 0.0004	14.1
Hexamethylphosphortriamide (HMPA)	1.9784 ± 0.0006	38.3
Without solvent[a]	1.9777 ± 0.0006	–

[a]The spectrum was obtained at 40 °C dissolving the $K_2Cr_2O_7$ in the molten ligand (m.p. 37–39 °C).

four H-atoms from the crown ether molecule are present in the Cr(V) vicinity.

$Cr^V(2)$ Structure

It was established that $Cr^V(2)$ complexes are formed only in the course of the substrates reaction with $[pyH]^+[Cr^VOCl_4]^-$ but not with $K_2Cr_2O_7$ or Na_3CrO_4. This fact might be assigned to the presence of Cl^- in the complexes. In order to check this assumption HCl was added to the $Cr^V(1)$–15-Crown-5 solution. Under these conditions the $Cr^V(2)$ signal appears immediately in the EPR spectrum, thus proving the Cl^- presence in the inner coordination sphere of $Cr^V(2)$.

The EPR spectrum of the frozen $[Cr^VOCl_4]^-$–18-Crown-6 system (–170 °C) shows an axial anisotropy of the g-value (Fig. 1b). Therefore it might be assumed that in $Cr^V(2)$ complexes the crown ether is in the equatorial plane, Cl^- being located along the z-axis opposite to the Cr=O unit.

The concentrations of the other Cr(V) complexes formed in the course of the photochemical reduction of Cr(VI) were very low, so that it was impossible to obtain information concerning their structure. It seems likely that these Cr(V) species include oxidation products of the crown ethers. Thus, after long irradiation of the system $[Cr_2O_7^{2-}]$–15-Crown-5 in DMSO an EPR signal with g-value 1.9743 ± 0.0005 was observed. The latter shows 4-component hfs (A = 4.9 ± 0.4 Oe) due to 3 almost equivalent ^1H ($I = \frac{1}{2}$) (Fig. 1c). Evidently a 15-Crown-5 oxidation product (aldehyde) is coordinated to Cr(V). We have already observed the formation of similar Cr(V) complexes with aldehyde in the $Cr^V(2)$ coordination sphere [4].

On the other hand it was proved [11] that solvents such as HMPA, DMSO, DMF, FA, *etc.* can reduce Cr(VI) to Cr(V), which then can complex with the ligands present in the system. Other solvents (An, C_6H_6, $CHCl_3$, *etc.*) which are not able to reduce Cr(VI) serve only as a reaction medium. Therefore we have studied the Cr(VI) reduction with the crown ethers in solvents of both types, An and HMPA. The fact that we did not observe any solvent effect either in the kinetics of Cr(V) formation or in the g-values of the Cr(V) complexes obtained shows that the solvents do not participate directly either in the redox or coordination processes of crown ethers with Cr(VI) and Cr(V).

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