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CHROMIUM(V) COORDINATION CHEMISTRY

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CONTENTS

A. INTRODUCTION

Particular interest has been shown regarding the intermediate oxidation states of chromium, Cr(V) and Cr(IV), and especially on their role in the process of Cr(VI) reduction [1–3]. Their formation as intermediates was predicted long ago [4] but because of their high reactivity and low kinetic stability no direct evidence for their existence was available for a long time. Only in the last two decades and using the EPR method, was the formation of Cr(V) and Cr(IV) in the course of Cr(VI) reduction experimentally proven.

During the past few years the formation of Cr(V) complex species in biochemical systems has also been observed [5,6].

Firstly Kon [7,8] and Garifianov and Usacheva [9] used EPR to study some Cr(V) complexes both at liquid nitrogen and room temperatures. Later Garifianov [10] showed that using EPR it is possible not only to identify Cr(V) complexes but also to study their structure without preliminary

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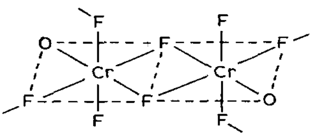
isolation and purification. During the last 10–15 years numerous Cr(V) complexes have been identified and studied. Part of the corresponding EPR data has already been briefly reviewed [11–13] but no comprehensive review of all data obtained for Cr(V) coordination chemistry has been available up to now. In the present review an attempt is made to summarize the data reported for Cr(V) coordination compounds, their mechanism of formation and decay in the course of Cr(VI) reduction.

B. Cr(V) COORDINATION COMPOUNDS: STRUCTURE AND BONDING

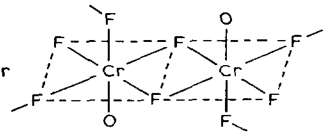
The only binary compound of Cr(V) known is CrF_5 [14,15]. The oxofluoride $CrOF_3$ [16] and the corresponding oxochloride [17] are also described in the literature as solid compounds. In the presence of traces of water hydrolysis and disproportionation take place, leading to the formation of Cr(VI) and Cr(III).

Green et al. [16b] have synthesized $CrOF_3$ via reaction of ClF and CrO_3 at 0 °C and thoroughly studied its structure and properties. The magnetic moment (1.82 BM at 17 °C) is consistent with that of a Cr(V) species (d^1 system). On the basis of IR and Raman spectral data a polymeric structure is suggested for the solid state (I) with terminal Cr–O bonds and extensive halide bridging.



I

or



I′

In a recent paper [18] precise data for the UV–vis, IR, EPR and mass spectra of $CrOCl_3$ are reported. The EPR singlet line ($g = 1.989 \pm 0.002$) confirmed the existence of the Cr(V) oxidation state. A polymeric structure in the solid state, similar to that of $CrOF_3$ is proposed for $CrOCl_3$.

(i) *Chromate(V) ion,* CrO_4^{3-}

Bailey and Symons [19] obtained the chromate(V) ion in strong KOH solution and recorded its electronic spectrum in the visible and UV region, where two broad bands at 265 ± 5 nm ($\epsilon = 250 \pm 50$) and at 355 ± 5 nm ($\epsilon = 500 \pm 50$) were found. The authors have shown that CrO_4^{3-} is stable only in the presence of a large excess of KOH. On increasing the acidity of the solution a fast disproportionation process takes place

$$3\ \mathrm{Cr(V)} \rightarrow 2\ \mathrm{Cr(VI)} + \mathrm{Cr(III)} \qquad (1)$$

Recently Niki and Leitinen [20] confirmed the formation of CrO_4^{3-} as a stable species in a strong alkaline medium.

A number of alkaline, alkaline-earth, rare-earth and lanthanide metal salts of chromate(V) of the types M'_3CrO_4, $M''_3(CrO_4)_2$ and $M'''CrO_4$ have been synthesized and their properties studied [21–24]. The salts are solid hygroscopic compounds undergoing simultaneously hydrolysis and disproportionation in the presence of water. The magnetic susceptibility of these chromates(V) has been measured and the magnetic moments found correspond to one unpaired electron ($\mu_{eff} \sim 1.7$ BM) [21,24].

Carrington et al. [25] have studied the EPR spectrum of CrO_4^{3-} in frozen solution (20 K). A very broad and temperature dependent singlet line was observed with an anisotropic g-value ($g_{\parallel} = 1.98$ and $g_{\perp} = 1.97$). At higher temperature the signal broadens significantly and disappears at $T > 90$ K. This fact is a strong indication for a tetrahedral structure of CrO_4^{3-}, the lower excited states of which are close to the ground state. For that reason the spin-lattice relaxation times are short and therefore the absorption lines are broad and detectable only at low temperature [25].

The electronic structure of CrO_4^{3-} is discussed in a series of papers [26–37]. The electronic spectral data are also consistent with a distorted tetrahedral structure with a D_{2d} symmetry, the d^1 electron populating mainly the d_{z^2} orbital. Some new data on preparation, symmetry and magnetic properties of K_3CrO_4 are reported by Ziegler et al. [35]. In a recent paper [37] critical discussion on the interpretation of CrO_4^{3-} electronic spectral data is provided on the basis of a more precise spectrum obtained for CrO_4^{3-} doped in $Sr_5(PO_4)_3Cl$ crystals at 4 K. The set of bands in the range 10000–17000 cm^{-1} corresponds to ligand field transitions. The Td ligand field parameter Δ is determined to be 13500 cm^{-1}. It is concluded that the ground state is $^2E_{z^2}$.

Besides the metal salts of CrO_4^{3-} a number of chromium(V) complexes are also known. All these complexes show narrow EPR signals even at room temperature. Usually they are observed as intermediates in the course of Cr(VI) reduction with different organic and inorganic substrates. These complexes easily undergo either disproportionation (eqn. (1)) or internal redox reaction, the chromium(V) oxidizing the coordinated ligand

$$Cr^{V}L_n \rightarrow Cr^{III}L_m + P \tag{2}$$

where P is the oxidation product of L. For this reason the $Cr^{V}L_n$ complexes are regarded as "kinetically unstable" species.

In many cases attempts to isolate the Cr(V) complexes from the reaction mixture failed and they were studied only in solution mainly using the EPR method.

The first complexes of this type were studied by Gray and co-workers

[38,39], Kon [7,8] and Garifianov [9]. The significant reduction of the EPR line width of these complexes compared with that of CrO_4^{3-} ion is due to an extreme deviation from cubic symmetry. As a result the spin-lattice relaxation time increases and detection of the corresponding EPR signals is possible at room temperature. The deviation from cubic symmetry is due to the presence of $[Cr{=}O]^{3+}$ as a structural unit [8,38,39] giving rise to a strong axial component in microcrystalline field symmetry as in the case of VO^{2+} and MoO^{3+} [39]. In fact some of the authors denote them as complexes of chromyl(V) ion, CrO^{3+} [10,25,38–41].

(ii) Oxohalo complexes of Cr(V), $CrOX_4^-$ and $CrOX_5^{2-}$

The first species of this type, namely M_2CrOCl_5 and $[CrOCl_4]^-HR^+$ ($M = K^+$, Rb^+, Cs^+ or NH_4^+; R = pyridinium, quinolinium or tetramethylammonium ion) were obtained by Weinland et al. in 1905–1907 by reducing CrO_3 with dry HCl [42,43]. Much later $KCrOF_4$ and $AgCrOF_4$ were synthesized [44,45] from the corresponding dichromates and BF_3 and from $CrOF_3$ and KF in anhydrous HF [16b].

Using the EPR method Garifianov [46,47] has shown that both oxochloro and oxofluoro complexes of Cr(V) can be obtained simply by dissolving CrO_3 in the corresponding acid.

During the last 10–20 years a number of oxochloro and oxofluoro complexes have been obtained and their structure, chemical, magnetic and spectral properties studied [8,16b,38–41,46–63]. In a recent paper [62] crystal structure data (unit cell parameters) are reported together with summarized IR data. The red complexes obtained ($K_2[CrOCl_5]$, $Rb_2[CrOCl_5]$ and $Cs_2[CrOCl_5]$) are photosensitive. The complexes $K_2[CrOCl_5]$ and $Rb_2[CrOCl_5]$ proved to be orthorhombic, while $Cs_2[CrOCl_5]$ is cubic [51,62]. The $\nu_{Cr=O}$ stretching mode occurs in the range 980–933 cm^{-1} and the δ(Cr–O) bending mode (rocking) occurs at 240–215 cm^{-1}. The ν_{Cr-Cl} stretching modes appear at 370–320 cm^{-1}, while the bending modes lie at 200–160 cm^{-1} [62].

Some mixed complexes have also been prepared, such as $CsCrO(AB)Cl_3$ (AB = anions of tartaric, hydroxymalonic or malic acids [41]), $CrO(bipy)Cl_3$ and $CrO(phen)Cl_3$ [55a,b] and $CrOF_{4-n}Cl_n$ ($n = 0$–4) [54]. In the last paper the higher thermodynamic stability of $CrOF_4^-$ compared with $CrOCl_4^-$ was mentioned.

Many attempts to obtain the corresponding oxo, bromo and oxoiodo complexes failed [41,46] and it was assumed that Cr(VI) was reduced by HBr directly to Cr(III) [64]. Nevertheless, the synthesis of $[CrOBr_5]^{2-} \cdot H_2bipy^{2+}$ was reported later [65] by reduction of $K_2Cr_2O_7$ with hydrobromic acid saturated with HBr at temperatures below 0 °C. Oxobromo complexes of

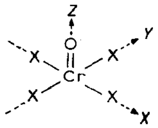
Cr(V) with pyridinium, quinolinium, 2,2′-bipyridinium and 1,10-phenanthroline were also prepared [66]. For a similar purpose some adducts of chromyl(VI) chloride with N-heterocyclic base have been reduced with an HBr solution at low temperature ($T < 0\,^{\circ}C$). However, the existence of oxobromo complexes of Cr(V) is still disputable. According to Seddon and Thomas [58,59] the compound considered to be $[CrOBr_5]^{2-}[H_2bipy]^{2+}$ [65] is in fact a mixture with a high content of "perbromide".

The complex salts of Cr(V) mentioned above are coloured compounds, relatively stable at room temperature if stored in a dry inert atmosphere. Even traces of moisture lead to the disproportionation process (eqn. (1)). In this respect a report for the stabilizing effect of water in the formation of oxobromo complexes in the course of Cr(VI) reduction with HBr [65] seems rather surprising.

The complexes already discussed were identified as Cr(V) species (d^1 configuration) using magnetic susceptibility measurements. Their magnetic moments ($\mu_{eff} \sim 1.60$–2.00) correspond to the spin only value (1.73 BM). Most of these data have been summarized by Ziebarth and Selbin [41] and Seddon and Thomas [58,59].

The EPR spectra of $CrOCl_5^{2-}$, $CrOCl_4^-$, $CrOF_5^{2-}$ and $CrOF_4^-$ have been studied and interpreted by different authors [8,40,41,46,47,53,54,63,67–71]. The spectra consist of a strong narrow line showing hyperfine structure of four lines due to ^{53}Cr ($I = 3/2$) [11,12]. The EPR parameters of CrO^{3+} complexes should be very similar to those of VO^{2+} complexes [12]. The latest EPR data obtained by Garner et al. [71] showed unambiguously that the complexes thought to be $CrOCl_5^{2-}$ [40,41,53,67] were in fact $CrOCl_4^-$. The same authors have also shown the proper conditions for $CrOCl_5^{2-}$ formation and report the corresponding g values: 1.988 ± 0.001 for $CrOCl_4^-$ and 1.970 ± 0.001 for $CrOCl_5^{2-}$.

After the pioneering investigations of Gray et al. [38,39] on the structure of CrO^{3+} species, numerous data have been obtained [8,41,47,48,50,57,58, 61,70] consistent with a C_{4v} symmetry for the complexes (structure **II**).



II

The four halogen ions in the xy plane are equivalent and the Cr=O bond is notably short [8,38,39,47,70]. The existence of a Cr=O bond was proven by means of IR spectroscopy, $\nu_{Cr=O}$ being in the range 1050–900 cm^{-1} [8,41,50–56]. The IR data obtained have been summarized [41,58,62] together with a critical analysis thereof [58].

The available EPR and IR spectral data indicate the existence of two types of CrO^{3+} complexes, namely $CrOX_4^-$ and $CrOX_5^{2-}$ [50,60,71]. When the halogen ions are present in excess, they coordinate to $CrOX_4^-$ at the vacant axial site in the inner coordination sphere of Cr(V) giving rise to a new EPR signal and a new $\nu_{Cr=O}$ band in the corresponding spectra.

The electronic structure of these complexes is discussed in a series of papers [38,39,50,53,71–74]. The first molecular scheme was proposed by Gray et al. [38,39] based on electronic and EPR spectral data and semiempirical MO calculations. The following *d*-orbital sequence was assumed: $d_{xy}(b_2) < d_{xz,yz}(e) < d_{x^2-y^2}(b_1) < d_{z^2}(a_1)$, the unpaired electron populating the d_{xy} orbital. The first two absorption bands are due to the *d–d* transitions: $d_{xy} \rightarrow d_{xz,yz}$ and $d_{xy} \rightarrow d_{x^2-y^2}$. These assignments were generally accepted [11,50] till recently when Garner et al. [58,71–74] performed detailed electronic and EPR single crystal investigations on $[(C_6H_5)_4As]^+[CrOCl_4]^-$ and ab initio MO calculations for the ground and excited states of CrO^{3+} complexes. The results obtained confirmed the earlier prediction [38,39,50] that the unpaired electron occupies the d_{xy} orbital, which is essentially a chromium atomic orbital. However, their data indicate that the two absorption bands with the lowest energy at 13000 cm^{-1} and 18000 cm^{-1} should be assigned to the $d_{xy} \rightarrow d_{xz,yz}$ and $Cr \rightarrow O_{(\pi)} \rightarrow CrO_{(\sigma^*)}$ transitions respectively. For this reason it is concluded that since the EPR spectral data have been interpreted [11] on the basis of the assumptions made by Gray et al. [38,39] these interpretations might be erroneous [72,73]. Garner et al. [71] proposed a molecular orbital scheme for $[CrOCl_4]^-$ assuming square-pyramidal geometry and a critical review on the MO coefficients used was published.

Recently [75,76] MO calculations for the transition energies of $CrOCl_5^{2-}$, $CrOF_5^{2-}$ and $CrOCl_4^-$ were reported. The lowest energy absorption is confirmed to be mainly the $d_{xy} \rightarrow d_{xz,yz}$ transition. However, the second absorption and the two higher energy bands are assigned to halogen-to-metal CT transitions. A comparison between calculated values and the experimental data available for electronic excitation energies is given.

Calculations of M–O bond covalency in the oxochloro complexes of Cr(V) were also performed [77], based on EPR data.

Dioxodichlorochromates(V) have also been prepared and their magnetic moments, IR and EPR spectra studied [78]. The data obtained indicate dimeric and polymeric structures for these compounds.

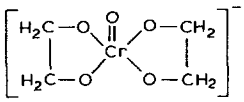
(iii) Cr(V) complexes of alcohols, phenols and thiols

Garifianov [9] first mentioned complex formation between Cr(V) and glycerol when chromates and dichromates were dissolved in glycerol. Cr(V) formation was observed by means of EPR. Later, complexation of Cr(V) with 2-propanol [79a,b], a series of diols and polyethylene glycols [80–89], some phenols [90–92] and thiols [91–95] was also established in the course of their oxidation with chromates. These complexes were only studied in solution and have not been isolated as pure complex salts, the only exception being the oxochromium(V) complex with perfluoropinacol [85].

In contrast to the other diols mentioned above, pinacol and its derivative perfluoropinacol form rather stable (with respect to further reduction) chromium(V) complexes [85–89]. The problem of the kinetic stability of Cr(V) complexes will be discussed below.

The EPR spectrum of the Cr(V)–ethylene glycol complex has been studied in detail [80,81,84,96,97]. The EPR signal shows a 9-component super hyperfine structure due to the eight equivalent protons. A structure with C_{2v} symmetry was proposed (III) analogous to that of oxohalo complexes of Cr(V).

Similar structures were proposed for Cr(V) complexes with dithioethylene glycol [94], 1,2-propanediol, 1,3-, 1,4- and 2,3-butanediol, pinacol, hexylene glycol [82,83,86–88] and perfluoropinacol [85] (**III'**). The EPR spectra of these complexes show no super hyperfine structure due to protons.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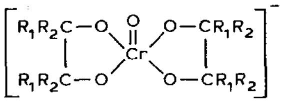
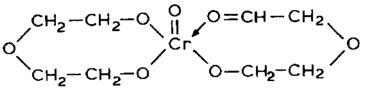

III'

The visible spectrum of the Cr(V)–ethylene glycol complex [98] shows a weak band at 602 nm ($\epsilon = 140 \pm 15$) due to a *d–d* transition. The corresponding Cr(III) complex absorbs at 595 nm.

It was established using the EPR method that in the course of the di- and triethylene glycol oxidation by Cr(VI) two different types of Cr(V) complexes were formed, denoted as $Cr^V(1)$ and $Cr^V(2)$ [86,88]. The EPR signals show 8-component super hyperfine structure due to seven equivalent (or almost equivalent) protons. On the basis of the EPR spectral data available structure **IV**, similar to that of the Cr(V)–ethylene glycol complex, was proposed for $Cr^V(2)$ complexes with di- and triethylene glycol [86,88].

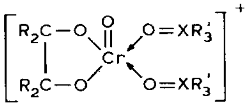
The main difference between $Cr^V(2)$ in this case and the analogous complex with ethylene glycol is that the $Cr^V(2)$ complex includes in its coordination sphere one molecule of the oxidation product (aldehyde) together with a molecule of the substrate.

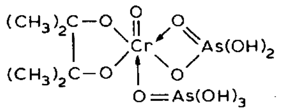
The absence of super hyperfine structure in the EPR spectra of $Cr^V(1)$ complexes does not permit any definite conclusions about their composition and structure [86,88] to be made.



IV

Some mixed Cr(V) complexes with diols (ethylene glycol or pinacol) and phosphine oxide, arsine oxide and arsenic acid have also been described [99] and the following structures proposed (**V**, **VI**):





(X ≡ P, As; R ≡ H, CH_3 ; R'≡ Et, Ph)

V

VI

The authors [99] have shown that phosphine and arsine oxides alone do not stabilize Cr(V); in the absence of diol no kinetically stable Cr(V) complex is formed, while with excess diol only the formation of the known Cr(V)–diol complexes was observed.

Kinetic data obtained for Cr(V) complex formation with different diols [88] showed a marked influence of the ligand structure on the process of complexation. The ligands most suitable for complexation with Cr(V) are those forming five-membered chelate rings (ethylene glycol, 1,2-propylene glycol, pinacol, oxalic acid). Further increase of the chelate ring size significantly decreases the tendency for complexation with chromium(V).

The nature of the Cr(VI) compound used as an oxidant also affects Cr(V) complex formation [87,88].

The electronic structure and bonding in CrO^{3+} complexes with ethylene glycol [96,97], 1,2-propylene glycol [97] and perfluoropinacol [89] have been discussed on the basis of EPR and electronic spectral data. It seems that the unpaired electron occupies the $d_{x^2-y^2}$ orbital [96]. In all cases a high degree of σ and π covalency in the xy plane was observed. On the basis of EPR data it is concluded that considerable distortion in the xy plane is realized for Cr(V)–perfluoropinacol [89].

During the last 10–15 years some Cr(V)–diol complexes have been used as dynamically polarized proton targets in high energy experiments [83,96,100,101]. The most suitable target materials are those in which a high degree of proton polarization is obtained combined with a high proton content. Among the compounds used for this purpose the Cr(V)–ethylene glycol complex seems to be one of the best [83].

An attempt has been made to study the mechanism of spin density transfer in the Cr(V)–ethylene glycol complex [100].

(iv) Miscellaneous Cr(V) complexes

Using EPR the formation of Cr(V) complexes with other types of ligands (mono- and polydentate) containing O-, N- and S-donor atoms was also studied [7,8,90,95,102–123]. However, the concentration of Cr(V) complexes obtained with these ligands is much lower (two orders of magnitude or even more) than in the case of the Cr(V)–diol complexes [114].

In the course of the Cr(VI)–ligand interaction, Cr(V) is formed and takes part further both in coordination and redox processes

$$\mathrm{Cr(VI)} + \mathrm{L} \xrightarrow{k_1} \mathrm{Cr(V)} + \mathrm{P} \tag{3}$$

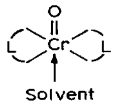
$$\mathrm{Cr(V)} + n\mathrm{L} \rightleftharpoons \mathrm{Cr^{V}L}_n \tag{4}$$

$$\mathrm{Cr^{V}L}_n \xrightarrow{k_2} \mathrm{Cr^{III}L}_m + \mathrm{P} \tag{5}$$

where P is the oxidized product of L.

In cases where the rate of process (3) and the equilibrium constant K of process (4) are high enough, the corresponding EPR signal could be observed. The term "kinetically stable complex" might be used to denote such complexes. In all other cases, when the rate of Cr(V) formation is negligible or the corresponding Cr(V) complex is not thermodynamically stable, or the rate of Cr(V) decay is higher than that of its formation ($k_2 > k_1$), no EPR signal could be observed.

The direct interaction between the ligand and some stable chromium(V) compounds, e.g. Na_3CrO_4, $[pyH]^+[CrOCl_4]^-$, etc., was also studied [90,114,123]. In this case Cr(V) also participates both in coordination and redox processes. All the complexes thus obtained also exhibit the characteristic narrow EPR signals even at room temperature, suggesting the presence of a CrO^{3+} structural unit in them. On this basis most of the systems possibly possess a tetragonal pyramidal structure (III). With a free coordination site in the position *trans* to the O atom these molecules are capable of coordinating a solvent molecule [123] such as dimethylformamide (DMF), dimethyl-

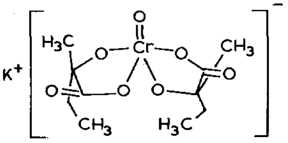


VII

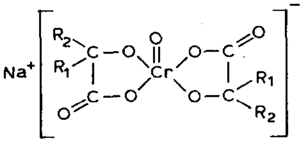
sulfoxide (DMSO), hexamethylphosphotriamide (HMPA), pyridine (py) (**VII**) thus stabilizing the Cr(V) complexes [118,119,123].

In the EPR spectra of Cr(V)–dithizone [107], Cr(V)–*o*-aminobenzoic acid and Cr(V)–*o*-aminothiophenol [113] super hyperfine structure due to ^{14}N with 5 and 9 lines respectively, has been observed.

The EPR data for Cr(V)–crown ether complexes [122] showed a pyramidal structure with the presence of 4 hydrogen atoms in the Cr(V) moiety (5-component super hyperfine structure), no data for solvent coordination being found. Upon irradiation several other short lived Cr(V) species were observed, including most probably some oxidation products of the crown ethers in their inner-coordination sphere. None of these complexes was isolated from the reaction mixture as a stable Cr(V) compound but the potassium bis(2-hydroxy-2-methylbutyrato)oxochromate(V) (**VIII**) [116] as well as the analogous Cr(V) complexes with a series of tertiary α-hydroxy acids with general formula $Na[OCr(O_2COCR_1R_2)_2]$ (**IX**) [117] were obtained and isolated.



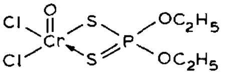
VIII



IX

These complexes proved to be water- and air-stable Cr(V) species and were identified by means of UV, IR, X-ray diffraction, magnetochemical and EPR measurements ($\mu_{eff} = 2.05$ BM, $g = 1.9780 \pm 0.0005$ for the first complex) [116]. C_2 symmetry is assumed for these complexes, the structure being intermediate between square-pyramidal and trigonal bipyramidal.

The structure of the Cr(V)–diethyldithiophosphate complex (**X**) has been discussed [124] where a four-membered chelate ring is formed and conclusions were drawn about π-bonding therein.



X

The experimental data show that the best complexation agents for Cr(V) are O-containing ligands. However, some N- and S-containing ligands, such as ethylene diamine, 8-mercaptoquinoline, dithizone, diethyldithiophosphates, etc., also form kinetically and thermodynamically stable complexes. The experimental data obtained indicate better complexation of Cr(V) with monothio-β-diketones compared with the corresponding β-diketones [95]. Similarly 8-hydroxyquinoline quickly reduces Cr(V) to Cr(III), while 8-mercaptoquinoline forms kinetically stable complexes with Cr(V) [90]. Significantly high concentrations of Cr(V)–dithizone complex were obtained (up to 70% of the total Cr in the system [119]).

Summarizing these data it can be concluded that the best ligands for stabilization of the Cr(V) oxidation state are the diols. Among them the best complexation agents are the 1,2-dihydroxy derivatives forming five membered chelate rings. Most of the complexes synthesized with diols, carboxylic acids and polyphenols form five- and six-membered chelate rings [90,95,114,123] although complexes with seven membered and four-membered rings have also been obtained with some ligands (maleic, citraconic and itaconic acids or diethyldithiophosphate respectively) [114,123].

If one of the OH groups of the ligand is engaged in esterification, the complexation ability of the ligand is strongly decreased as shown in the example of salicylic acid and its methyl ester [90].

The kinetic stability of the chromium(V) complexes formed depends not only on the ligand structure, i.e. on the thermodynamic stability of the complex, but also on the reducing ability of the ligand. Ligands with a low oxidation potential and proper kinetic behaviour for a fast reduction are not capable of stabilizing Cr(V) even when the structure is appropriate. Such ligands reduce Cr(V) rapidly to Cr(III) as is the case with *o*-aminophenol, 8-hydroxyquinoline, thioglycolic acid, toluene-3,4-dithiol, etc. [90,95,114,119]. During the last few years Groves et al. have obtained some Cr(V) complexes with porphyrins by oxidation of the corresponding Cr(III) complexes [5,125,126]. The Cr(V) oxidation state was again detected by means of EPR (g values of 1.982 and 1.987), the signals observed showing super hyperfine structure of 9 lines due to four N ($I = 1$) [5,127]; magnetochemical measurements gave μ_{eff} as 2.05 ± 0.2 [125,126]. Structural investigations have shown the presence of the $Cr^{V}{=}O$ structural unit and a pyramidal structure was suggested for the complexes. Strong π-bond formation between chromium and the axial oxygen atom is assumed to destabilize the d_{xz} and d_{yz} metal orbitals and hence the unpaired electron must occupy the d_{xy} orbital. The oxoporphyrinatochromium(V) complex is capable of hydroxylating and epoxydizing hydrocarbons under catalytic and stoichiometric conditions due to exchange of its oxoligand [126,127].

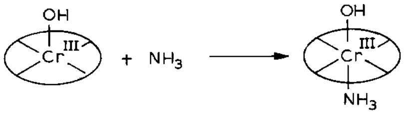
In contrast to Cr(V) complexes with the other types of ligand discussed above and especially to the Cr(V) complexes with O-containing crown ethers [122] these porphyrin complexes are remarkably stable and can be isolated and purified.

Similarly $[Cr^{V}O(\text{salen})]^{+}$ (salen = N,N'-ethylene-bis(salicylideneamine)) was obtained via oxidation of $[Cr^{III}(\text{salen})(H_2O)_2]^{+}$, isolated by precipitation with halogenides and its structure and catalytic properties studied [128]. Electronic, IR, EPR and X-ray crystal structure data are reported. The complex can participate in an efficient oxygen atom transfer both to alkenes and phosphines and is of interest in the development of new catalytic systems.

Another interesting new type of Cr(V) complex was synthesized recently by several groups: Arshankow and Poznjak [129], Buchler et al. [130] and Groves et al. [131]. Its structure is also pyramidal with coordination number five but $Cr{=}O^{3+}$ is replaced by the structural unit $Cr{\equiv}N^{2+}$. The complexes are obtained through photochemical [129,131] oxidation of the corresponding Cr(III)–azide–L complexes according to the reaction [129]

$$L\text{-}Cr^{3+}\text{-}N_3^- \xrightarrow{h\nu} [L\text{-}Cr^{V}\text{-}N^{3-}] + N_2 \qquad (6)$$

or by hypochlorite oxidation of $Cr^{III}(OH)L$ (L = porphyrin) in the presence of ammonia [130]. The following reaction scheme is proposed [130]



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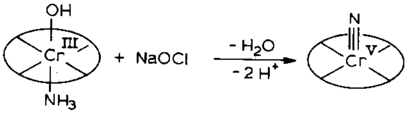


(8)

The nitrido Cr(V) species are quite stable and their EPR, UV– vis and IR spectra [129–131] as well as their crystal structure [131] have been studied in detail. The EPR spectra observed are typical for Cr(V) species (g values = ca. 1.98) exhibiting well resolved ^{14}N super hyperfine splitting. The EPR data show that the axial N-atom is magnetically equivalent to the equatorial ones. The detailed EPR and ENDOR study [130] shows strong spin localization in the d_{xy} orbital and almost no spin localization in the d_{z^2} orbital.

The $\nu_{Cr\equiv N}$ band is observed in the range 1020–1010 cm^{-1} [129–131]. For the nitrido(5,10,15,20-tetra-*p*-tolylporphyrinato)chromium(V) the molecular structure was determined and indicated a chromium–nitrogen distance of 1.565 Å. The chromium atom is 0.42 Å above the mean plane of the pyrrole nitrogens [131].

Cr(V) complexes with coordination number 6 and distorted octahedral structure without Cr=O or Cr≡N structural units are also known. These are complexes with *cis*-1,2-ditrifluoromethylethylene-1,2-dithiolate ($g = 1.9941 \pm 0.0003$) [132], *cis*-1,2-diphenylethylene-1,2-dithiolate ($g = 1.996 \pm 0.003$) [133] and *o*-aminothiophenol and *N*-methyl-*o*-aminothiophenol ($g = 1.987 \pm 0.002$) [134].

During the last few years the toxicity and carcinogenicity of Cr(VI) compounds have been unambiguously proven [135,136]. As Cr(VI) is readily reduced by biological reductants some authors were inspired to study the metabolism of chromate and dichromate in biological tissues [137] and in rat liver microsomes in the presence of NADPH [6a]. Cr(V) complex formation in the course of Cr(VI) reduction with a series of ribonucleotides [6b] was also studied. In all cases EPR signals typical for Cr(V) species ($g \sim 1.98$) were observed and the complexes formed are thought to be carcinogenic [6a,137].

C. MECHANISM OF CHROMIUM(V) FORMATION AND DECAY IN THE COURSE OF CHROMIUM(VI) REDUCTION

(i) Chromium(VI) reduction by metal ions

Numerous studies have been provided on Cr(VI) reduction by different metal ions: Fe(II), V(IV), V(III), Np(V), Ir(III), Cr(II), Mo(IV) [2,138–147] in water medium, most of them having already been reviewed in detail by Espenson [2]. It is generally accepted that in such systems reduction proceeds via three consecutive one-electron steps

$$\mathrm{Cr(VI)} + \mathrm{M}^{n+} \rightarrow \mathrm{Cr(V)} + \mathrm{M}^{(n+1)+} \tag{9}$$

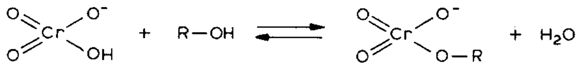
$$\mathrm{Cr(V)} + \mathrm{M}^{n+} \rightarrow \mathrm{Cr(IV)} + \mathrm{M}^{(n+1)+} \tag{10}$$

$$\mathrm{Cr(IV)} + \mathrm{M}^{n+} \rightarrow \mathrm{Cr(III)} + \mathrm{M}^{(n+1)+} \tag{11}$$

On the basis of kinetic data it was concluded that reaction [10] is rate-limiting, connected with a change both in structure and coordination number. The coordination number 4 and a tetrahedral structure is most often characteristic of chromium(V) as is also the case with chromium(VI), while chromium(IV) and chromium(III) exhibit coordination number 6 and an octahedral structure. No direct experimental evidence is available, however, for the formation of Cr(V) in the course of Cr(VI) reduction by metal ions.

(ii) Chromium(VI) reduction by organic substrates

The first systematic investigation into the mechanism of Cr(VI) reduction with organic substrates was provided by Westheimer [4]. Studying the Cr(VI) reduction in water-acidic medium he suggested that the first step of Cr(VI) reduction is an ester formation between the chromate and the substrate, which is in fact a complexation of Cr(VI) by the substrate S



(12)

or

$$\mathrm{Cr(VI)} + \mathrm{S} \rightleftharpoons [\mathrm{Cr}^{\mathrm{VI}}\text{-}\mathrm{S}]$$

Later the Cr(VI) complex formation was confirmed spectrophotometrically for many organic [84,86–88,114,148–154] and inorganic [155–167] substrates. Kläning and Symons [168] have studied the complexation of chromates with different alcohols and have shown that complex formation is connected with the appearance of a new band ($\lambda = 450$ nm) in the visible spectrum, assigned to a charge transfer from oxygen to chromium.

It should be noted, however, that the Cr(VI) reduction might also proceed in systems where no $\mathrm{Cr}^{\mathrm{VI}}$–S formation takes place. Thus oxidation of many hydrocarbons and ethers by Cr(VI) can proceed although no evidence for any complex formation has been found [1].

In 1949 Watanabe and Westheimer [169], on the grounds of kinetic data, assumed that when alcohols are oxidized with Cr(VI), Cr(V) and Cr(IV) species are formed as intermediates. During the last 20 years this suggestion has been experimentally proven. By means mainly of EPR the formation of Cr(V) both in water and organic media was proven unambiguously [79a,b,81,84,86–88,109–112,116–122]. Some experimental evidence for Cr(IV) formation in the reaction course is also available [170–175].

Systematic investigations into the mechanism of Cr(VI) oxidation in acidic-water media were provided using most frequently the oxidation of 2-propanol as a model reaction [1,4]. On the basis of numerous kinetic data, Watanabe and Westheimer proposed the following reaction scheme [4,169]

$$\mathrm{Cr(VI)} + \mathrm{S} \rightarrow \mathrm{Cr(IV)} + \mathrm{P} \tag{13}$$

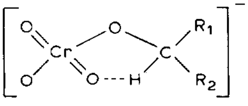
$$\mathrm{Cr(IV)} + \mathrm{Cr(VI)} \rightarrow 2\ \mathrm{Cr(V)}\ \text{fast} \tag{14}$$

$$\mathrm{Cr(V)} + \mathrm{S} \rightarrow \mathrm{Cr(III)} + \mathrm{P} \tag{15}$$

where S is the substrate and P its oxidation product.

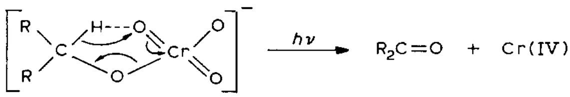
In 1919 Plotnikov and later Morton [176] observed that Cr(VI) reduction by alcohols is photosensitive. This fact allowed Kläning and Symons [148,171,173] and Bontchev and co-workers [86] to study the consecutive steps of the photochemical reaction in isolation (at −190 °C) and to obtain experimental data concerning its mechanism.

Kläning and Symons [148,171] have shown that the photoreduction of Cr(VI) proceeds via a two-electron transfer in the framework of the complex [Cr(VI)–alcohol]. A cyclic structure **XI** was assumed for the latter stabilized by H-bond formation. The much lower oxidation rate of t-butanol [171] is in agreement with this assumption.

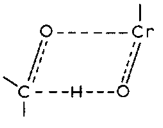


XI

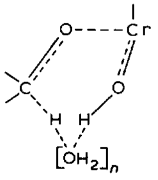
The EPR data obtained for the system at 77 K showed that no Cr(V) nor radical formation were observed. At the same time a blue colour developed on irradiation, which is associated with a Cr(IV) species. It was assumed that H-atom transfer takes place leading to ketone and Cr(IV) formation [171]



This suggestion is also in agreement with the experimental data obtained by studying the kinetic isotopic effect [177–181]. Using deuterated substrates a significant isotopic effect was observed showing that the rate limiting step of the overall reaction is the breaking of the C–H bond. Kwart and Nickle [181,182] have studied the temperature dependence of the kinetic isotopic effect and suggested a cyclic symmetric planar structure **XII** for the normal alcohols and asymmetric transition state **XIII** for the sterically hindered alcohols *.



XII



XIII

(16)

The Watanabe–Westheimer mechanism is also accepted for the oxidation of some other substrates [157,160,164,167,183–186].

The validity of this reaction scheme for the Cr(VI) dark and photochemical reduction by diols [84,86–88] was proven unambiguously when the process was carried out in the absence of any solvent. By means of the

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* According to this assumption the H-transfer in the case of sterically hindered alcohols can be realized only in the presence of hydroxyl-containing solvents [181].

induced polymerization and the EPR method it was shown that no radicals are formed during the redox process. The EPR and kinetic data for Cr(V) formation and decay showed that the first redox step of the diol oxidation in a non-aqueous medium is a two-electron transfer leading to Cr(IV) formation. This reacts further with Cr(VI) [86], resulting in Cr(V) formation. The latter, stabilized through complex formation with the diol was detected and monitored experimentally by means of EPR. Its reduction to Cr(III) seems also to be a two-electron transfer [84,86–88]. Using partially and totally deuterated ethylene glycols [187], Cr(VI)–ester formation as a precursor in the redox reaction was also proven together with the realization of the redox steps via H transfer, equivalent to a two-electron transfer.

Numerous experimental data, however, are available showing free radical formation in some other redox systems containing Cr(VI) [188–193]. Their appearance is a result of one-electron redox steps realized in the course of the overall Cr(VI) reduction. In order to explain these experimental facts Roček proposed another reaction scheme including both one- and two-electron processes [188,194]

$$\mathrm{Cr(VI)} + \mathrm{S} \rightarrow \mathrm{Cr(IV)} + \mathrm{P}_6 \tag{17}$$

$$\mathrm{Cr(IV)} + \mathrm{S} \rightarrow \mathrm{Cr(III)} + \mathrm{R}^{\cdot} \tag{18}$$

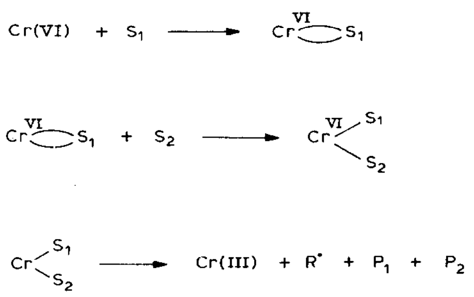
$$\mathrm{Cr(VI)} + \mathrm{R}^{\cdot} \rightarrow \mathrm{Cr(V)} + \mathrm{P}_4 \tag{19}$$

$$\mathrm{Cr(V)} + \mathrm{S} \rightarrow \mathrm{Cr(III)} + \mathrm{P}_5 \tag{20}$$

where $\mathrm{R}^{\cdot}$ is a free radical, S the substrate, and P_i are oxidation products of different chromium species.

This mechanism is widely accepted for the oxidation of aldehydes, primary, secondary and tertiary alcohols in water-acidic medium by Cr(VI) [109,110,152,173,185,186,189,190,192–205]. The numerous mechanistic studies, however, do not show direct evidence for the fate of the intermediates (free radicals, Cr(IV) and Cr(V) species) and the sequence of their formation. In order to obtain additional information on the mechanism and reactivity of the Cr(IV) and Cr(V) species Cr(VI) oxidation in water-acidic medium in the presence of some transition metal ions (V(IV, Ce(III)) [196,197,206–210] was studied. The authors succeeded in studying the Cr(IV) oxidation separately, as on the basis of experimental evidence, and with the conditions studied, Cr(VI) and Cr(V) do not react with the substrate. The kinetic data indicate the significant difference in the oxidative action of Cr(IV) and Cr(V) in water medium. Chromium(IV) is supposed to be highly effective in oxidation processes connected with C–C cleavage, while Cr(V) is believed to be responsible mainly for breaking of C–H bonds [191,196,197].

Studying the co-oxidation of alcohols and oxalic acid (or some hydroxy acids) in water-acidic medium, Hasan and Roček postulated a three-electron mechanism [198,211–225]



(21)

(22)

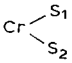
(23)

$$Cr(VI) + R^{\bullet} \rightarrow Cr(V) + P_1 \tag{24}$$

$$Cr(V) + S_1 \rightarrow Cr(III) + P_1 \tag{25}$$

$$Cr(V) + S_2 \rightarrow Cr(III) + P_2 \tag{26}$$

where S_1 = oxalic acid or α-hydroxy acid; S_2 = alcohol; $R^{\bullet}$ = oxalic acid radical and P_1, P_2 = oxidation products.

On the basis of kinetic isotopic effect data it was proven that the rate-limiting step of the overall reaction is C–H bond cleavage (eqn. (23)) [198,219,225]. We consider, however, that this mechanism is still disputable as no direct evidence has been obtained both for the formation of the ternary complex  and especially for the simultaneous three-electron transfer in the rate-limiting step.

Some other reaction schemes have been proposed for the mechanism of chromium(VI) reduction. On the basis of kinetic data only, Haight et al. [109] proposed a reaction scheme similar to that of Watanabe and Westheimer (cf. eqns. (13)–(15)).

$$Cr(VI) + S \rightarrow Cr(IV) + P \tag{27}$$

$$2\ Cr(IV) \rightarrow Cr(V) + Cr(III) \tag{28}$$

$$Cr(V) + S \rightarrow Cr(III) + P \tag{29}$$

The only difference from eqns. (13)–(15) is that Cr(V) is supposed to be formed as a result of Cr(IV) disproportionation (reaction (27)) instead of a Cr(VI)–Cr(IV) reaction. The latter is considered to be thermodynamically unfavourable in contrast to Cr(IV) disproportionation [152]. This assumption, however, seems unlikely as it has already been shown and will be discussed further, that Cr(VI)–Cr(IV) interaction proceeds with a very high rate even at low temperatures and in darkness [86,175]. Reaction (28) could prevail only at quite high concentrations of Cr(IV) that can be scarcely realized in the presence of unreacted Cr(VI). Possibly this contradiction is the reason that the scheme is thought to operate only for the oxidation in water medium of a restricted number of substrates such as hydrazine [183,226] or hydroxylamine [227] known to act as two-electron reductants [183,225] and of certain other substrates [228–230].

In the course of Cr(VI) reduction two consecutive two-electron transfers take place according to other authors [231,232] leading to the formation of Cr(II) as follows

$$\mathrm{Cr(VI)} + \mathrm{S} \rightarrow \mathrm{Cr(IV)} + \mathrm{P} \tag{30}$$

$$\mathrm{Cr(IV)} + \mathrm{S} \rightarrow \mathrm{Cr(II)} + \mathrm{P} \tag{31}$$

Cr(II) is a strong reducing agent and is oxidized immediately either by atmospheric oxygen [231]

$$\mathrm{Cr(II)} \xrightarrow{\mathrm{O_2}} \mathrm{Cr(III)} \tag{32}$$

or by unreacted Cr(IV) [232]

$$\mathrm{Cr(II)} + \mathrm{Cr(IV)} \rightarrow \mathrm{Cr(V)} + \mathrm{Cr(III)} \tag{33}$$

$$\mathrm{Cr(V)} + \mathrm{S} \rightarrow \mathrm{Cr(III)} + \mathrm{P} \tag{34}$$

Wiberg and co-workers [111,172] had proposed another reaction scheme (eqns. (35)–(38)) for the oxidation of aryl amines in acetic acid solution including only one-electron steps

$$\mathrm{Cr(VI)} + \mathrm{S} \rightarrow \mathrm{Cr(V)} + \mathrm{R^{\bullet}} \tag{35}$$

$$\mathrm{Cr(VI)} + \mathrm{R^{\bullet}} \rightarrow \mathrm{Cr(V)} + \mathrm{P} \tag{36}$$

$$\mathrm{Cr(V)} + \mathrm{S} \rightarrow \mathrm{Cr(IV)} + \mathrm{R^{\bullet}} \tag{37}$$

$$\mathrm{Cr(V)} + \mathrm{R^{\bullet}} \rightarrow \mathrm{Cr(IV)} + \mathrm{P} \tag{38}$$

where S is the substrate and $\mathrm{R^{\bullet}}$ the free radical.

According to these speculations and based again on kinetic data alone, Cr(IV) thus formed is stable and does not participate further in redox reactions. This reaction scheme is accepted for thiocarbamide oxidation with Cr(VI) [233] and for chromyl acetate reduction with alkylaromatic compounds in acetic anhydride medium [234]. Although the formation of Cr(V) *

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* Most probably the EPR signal observed [234] is due to a Cr(V)–acetic acid complex as its g-value ($g = 1.971$) is almost the same as that reported by Kon [8] ($g = 1.965 \pm 0.003$).

and free radicals have been proven by means of EPR [111,233,234] and induced polymerization [233] this reaction mechanism is still debatable.

It is evident that the mechanism of Cr(VI) reduction depends strongly both on the nature of the substrate and the reaction medium. The oxidation of 2-propanol and of cyclobutanol in water-acidic medium has been interpreted both in terms of the Watanabe and Westheimer (eqns. (13)–(15)) [4,148,178] and Roček (eqns. (17)–(20)) [173,192,195] reaction schemes. The same is valid for the oxalic acid oxidation in water medium. On the basis of kinetic data only Roček has proposed two different mechanisms depending on the reaction conditions: at high Cr(VI) concentration in strongly acidic medium steps (17)–(20) operate [110,152], while at lower Cr(VI) concentration and in less acidic medium the three-electron mechanism (eqns. (21)–(26)) is preferred [213,216]. Numerous other experimental data are available concerning the influence of the reaction medium on the Cr(VI) reduction mechanism. It is proven that the rate of oxidation with Cr(VI) depends both on the acidity [235] and on the nature of the acid [155,157,236–241]. The effect of the anionic part is connected mainly with their tendency for complexation with CrO_4^{2-}. The following sequence was found for the oxidation ability of such complex species [186,237]: $H_2CrPO_7 < HCrClO_3 < H_2CrSO_7 < HCrClO_7 < HCrNO_6$.

No experimental data have been available until now concerning the mechanism of action of the anions mentioned above. As far as they do not undergo oxidation it seems likely that they facilitate the introduction of the substrate into the inner coordination sphere of Cr(VI), i.e. act as catalysts for the substitution reaction.

A catalytic effect upon the oxidation with Cr(VI) is also shown by a series of complexing agents such as picolinic acid [204,205], EDTA and other polyvalent acids [242], 2,2′-bipyridyl and 1,10-phenanthroline [184,243–245]. Pyridine exhibits no catalytic effect [235,244,245] in these processes. In these cases the mechanism of their catalytic action is again unclear. It is supposed, however, that they stabilize some of the intermediate oxidation states of chromium [204,205].

The nature of the reaction medium strongly affects the process of Cr(VI) reduction. Studies concerning this process in non-aqueous solvents [84,86–88,118,119,121,175,234,246,247] or in mixed water-organic media [184,190,193,195,235] indicated a strong influence of the organic solvent both on the mechanism and the reaction rate of the redox reaction. The same conclusions can be drawn from the data available for the standard redox potentials in water-acidic and organic media (see Table 1).

Investigations of the mechanism of Cr(VI) reaction with dithizone, thio-β-diketones and some other ligands in organic media [95,118–121,175] have also shown a strong solvent effect. Reduction proceeds and only Cr(V) complexes are formed in solvents with high donor ability, such as DMF, DMSO, HMPA, etc., and not in acetonitrile (An) or in nitrobenzene (NB) [95,119,120]. The photochemical reduction of Cr(VI) with a series of pure solvents in a liquid phase and in a rigid glass matrix was studied using EPR in the absence of any other substrate [174]. Solvents with a high donor ability are capable of reducing Cr(VI) whose photochemical reduction by the solvent proceeds via two consecutive two-electron steps (Watanabe and Westheimer scheme, reactions (13)–(15)). The formation of a Cr(IV) precursor to that of Cr(V) was proven by EPR [174]. Such a redox process with participation of the solvent can play a very important role in systems where the ligand present cannot reduce Cr(VI) with sufficient rate, but can only coordinate and thus stabilize the intermediate Cr(V) [120,123].

A strong solvent effect was observed for the stereospecific epoxidation of alkenes with some Cr(VI) complexes [248]. The active species is an oxochromium(V) complex whose existence was proven by EPR. It is supposed to be formed via two consecutive one-electron oxidation steps with participation of the solvent (Solv)

$$\mathrm{Cr(VI)} + \mathrm{Solv} \rightarrow \mathrm{Cr(V)} + \mathrm{Solv}^{+\cdot} \tag{39}$$

$$\mathrm{Cr(VI)} + \mathrm{Solv}^{+\cdot} \rightarrow \mathrm{Cr(V)} + \mathrm{P} \tag{40}$$

No free radical formation was observed, however, and hence the two-electron reduction Cr(VI) → Cr(IV) followed by the Cr(VI) + Cr(IV) reaction resulting in Cr(V) formation seems more likely.

Interesting results were obtained studying the mechanism of dichromate–dithizone interaction in organic media. Three reaction paths [118,119,123] are possible depending on the nature of the solvent and the Cr(VI): dithizone concentration ratio (see eqn. (41)). Using EPR it was found that in solvents with a high donor ability (DMSO, DMF, HMPA, etc.) and at low dithizone concentrations, the redox process proceeds via two

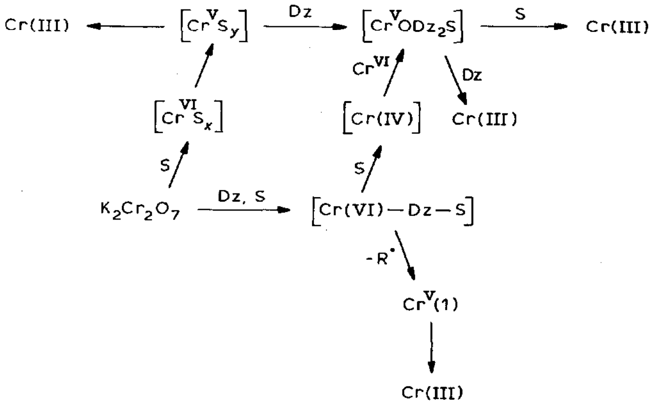
TABLE 1

Standard redox potentials of different chromium couples

Reaction medium	Redox couple	E^0 (V)	Ref.
Acidic (pH = 0)	$\mathrm{Cr^{VI}/Cr^{III}}$	1.36	167, 228
Acidic (pH = 0)	$\mathrm{Cr^{V}/Cr^{III}}$	$\geqslant 1.75$	167, 228
Acidic (pH = 0)	$\mathrm{Cr^{IV}/Cr^{III}}$	> 1.75	167, 228
Acetonitrile (An)	$\mathrm{Cr^{VI}/Cr^{III}}$	1.632	247
Acetic anhydride (Ac_2O)	$\mathrm{Cr^{VI}/Cr^{III}}$	1.381	247
Acetone (Ac)	$\mathrm{Cr^{VI}/Cr^{III}}$	1.094	247

consecutive two-electron steps (eqns. (13)–(15)). In the course of the Cr(VI) reduction a relatively stable Cr(V) complex is formed, containing two molecules of the substrate and a solvent molecule in the first coordination sphere (**VII**) [123]. The kinetic stability of this complex depends on the nature of the solvent *. According to the kinetic data the following order for the stabilizing effect of the solvent was found [123]: HMPA > DMSO > DMF > > MAA ⩾ TMP > > FA.

At higher dithizone concentration, the first reaction step is a one-electron transfer resulting in parallel formation of a free radical and Cr(V). In this case another Cr(V) complex was formed, whose further reduction is realized through a two-electron transfer. A reaction mechanism including a direct one-electron reduction of Cr(VI) to Cr(V) has been proven experimentally for the first time.



(41)

where S = solvent; Dz = dithizone and R˙ = free radical obtained from dithizone.

The mechanism of the Cr(VI)–oxalic acid interaction in water-acidic medium is still disputed. Three different reaction schemes have been proposed: Roček discriminates two different mechanisms depending on the reaction conditions [110,152,213,216] and the reaction scheme of Haight [109] has also been suggested for the same system.

Another reaction mechanism was proven to be valid for the photochemical oxidation of oxalic acid in a non-aqueous medium [175]

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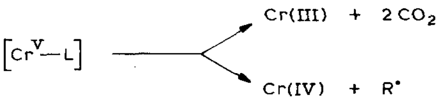
* Many other experimental data are available concerning the role of the solvent in Cr(VI) reduction and its stabilizing effect on the Cr(V) complexes with different ligands [119,120,123].

$$[\mathrm{Cr^{VI}}\text{–}\mathrm{L}] \rightarrow \mathrm{Cr(IV)} + 2\,\mathrm{CO_2} \tag{42}$$

$$\mathrm{Cr(VI)} + \mathrm{Cr(IV)} \rightarrow 2\,\mathrm{Cr(V)} \tag{43}$$

$$\mathrm{Cr(V)} + \mathrm{L} \rightarrow \mathrm{Cr^{V}}\text{–}\mathrm{L} \tag{44}$$



(45)

(46)

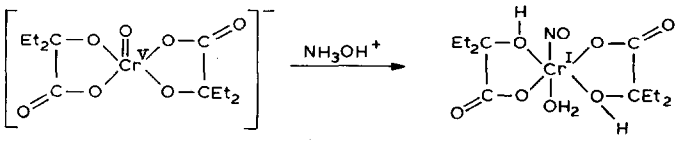
$$\mathrm{Cr(VI)} + \mathrm{R^{\bullet}} \rightarrow \mathrm{Cr(V)} + \mathrm{CO_2} \tag{47}$$

The formation of Cr(IV) as a result of a two-electron transfer and its interaction with the initial Cr(VI) giving rise to Cr(V) (processes (42) and (43)) was directly proven using EPR. Further, studying the process of Cr(V) reduction to Cr(III) in isolation (the Cr(V)–oxalic acid complex was obtained from $[\mathrm{pyH}]^+[\mathrm{Cr^VOCl_4}]^-$) the formation of free radicals and Cr(III) was experimentally proven as a result of parallel reactions [175].

During the last three years, the reduction of the stable complex bis(2-ethyl-2-hydroxylbutyrato)oxochromate(V) (synthesized first by Krumpolc and Roček [117]) was studied with hydrazine and hydroxylamine [249,250]. In both cases formation of a $\mathrm{Cr^V}$–N–R (R = hydrazinium or hydroxylaminium group) precursor complex is assumed. Further, hydrazine is converted to N_2 by two consecutive two-electron steps [249]

$$\mathrm{N_2H_4} \xrightarrow[-2\mathrm{H}^+\,-2e]{\mathrm{Cr(V)}} \mathrm{N_2H_2} \xrightarrow[-2\mathrm{H}^+\,-2e]{\mathrm{Cr(V)}} \mathrm{N_2}$$

while the oxidation of hydroxylamine is supposed to be a one-step four electron transfer leading to the formation of a Cr(I) complex [250]

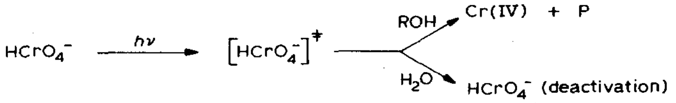


(48)

Summarizing all the data reviewed, the mechanism of Cr(VI) reduction and the oxidation capacity of Cr(VI), Cr(V) and Cr(IV) depend strongly on the nature both of the substrate and the reaction medium. These results might also be used for synthetic purposes. During the last ten years some authors have varied the reaction conditions to achieve selective oxidation of some alcohols to the corresponding aldehydes [251–254].

D. PHOTOCHEMISTRY OF Cr(VI) REDUCTION

Cr(VI) oxidation of alcohols is photosensitive [255]. The first systematic investigation of the photochemical oxidation of alcohols with $K_2Cr_2O_7$ in water medium was provided by Bowen et al. [256–259] who supposed that the $HCrO_4^-$ ions are the photoactive species. These authors showed that the quantum yield of the reaction is independent of temperature (in the range 0–60 °C), of $K_2Cr_2O_7$ concentration and of the wavelength (in the range 366–436 nm). On the other hand, the yield depends both on the concentration of the alcohol and pH. In the absence of alcohol the dichromate solutions do not show any sensitivity. The quantum yield of the process was found to be two $HCrO_4^-$ ions per quantum of absorbed light. On the basis of these experimental data Bowen and Chatwin [259] have proposed two reaction paths for the primary photochemical reactions; firstly



$$HCrO_4^- \xrightarrow{h\nu} [HCrO_4^-]^* \begin{cases} \xrightarrow{ROH} Cr(IV) + P \\ \xrightarrow{H_2O} HCrO_4^- \text{ (deactivation)} \end{cases}$$

(49)

and secondly

$$(HCrO_4^-)(ROH) \xrightarrow{h\nu} Cr(IV) + P \qquad (50)$$

$$(HCrO_4^-)(H_2O) \xrightarrow{h\nu} HCrO_4^- \text{(deactivation)} \qquad (51)$$

In order to explain the high quantum yield of the reaction and its dependence on the hydrogen ion concentration the following scheme (eqns. (52)–(54)) for the secondary reactions was proposed

$$2\ Cr(IV) \rightarrow Cr(V) + Cr(III) \qquad (52)$$

$$Cr(IV) + Cr(VI) \xrightarrow{H^+} 2\ Cr(V) \qquad (53)$$

$$Cr(V) + ROH \rightarrow Cr(III) + P \qquad (54)$$

Weber and Asperger [260] studying the photochemical $Cr_2O_7^{2-}$ oxidation of glycerol in acidic and neutral water media have proposed another reaction mechanism for the photochemical oxidation. It is based on their observation that $Cr_2O_7^{2-}$ solutions exhibit a higher photosensitivity in comparison with CrO_4^{2-} and hence $Cr_2O_7^{2-}$ was supposed to be the photoactive species. It should be noted, however, that the alternative assumption for [$Cr_2O_7^{2-}$–alcohol] being the photoactive species could also be in agreement with this experimental fact.

The profound studies of Kläning and Symons [148,171] on the photochemical oxidation of 2-propanol in rigid glasses have shown that the primary photochemical reaction proceeds according to eqns. (50) and (51) resulting in Cr(IV) formation [171]. They have also shown that the electronic spectrum of the photoactive species Cr(VI)–alcohol is similar to that of $HCrO_4^-$ [261] whose bands at 270 nm and 360 nm are due to p- and π-charge transfer from oxygen to chromium. It was shown that light with wavelength corresponding to these bands is effective in the photochemical oxidation of 2-propanol [171].

The dependence of the quantum yield on different reaction conditions was studied [255] and found to depend on the alcohol and $HCrO_4^-$ concentrations, acidity, intensity and wavelength of the light used for irradiation.

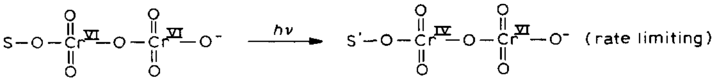
Recently Kläning reinvestigated the process of photochemical oxidation of 2-propanol by $HCrO_4^-$ in water medium [173]. Using flash-photolysis and an EPR technique combined with a spin trap and quantum yield measurements at low light intensity he has confirmed the formation of Cr(IV) in the primary process. The mechanism of the subsequent reaction involving Cr(IV) is discussed.

The mechanism of K_2CrO_4 photoreduction with alcohol was also studied in the presence of crown ethers [262,263]. The authors have estimated again that the primary photochemical reaction is the Cr(VI) reduction to Cr(IV) [263]. In the course of the subsequent dark reactions, Cr(V) complexes and free radicals are formed.

The photochemistry of the oxidation of several diols with chromates and dichromates in non-aqueous medium was also studied [86–88,98,114]. The experiments have confirmed that the process of Cr(VI) reduction to Cr(IV) is photosensitive [86–88]. The spectral sensitivity was also investigated and it was found that the maximum reaction rate is obtained at irradiation with wavelength 450 nm ($\phi = 0.46$) [86]. The reduction of Cr(V) to Cr(III) (reaction (15)) is also photosensitive. In this case UV light with $\lambda = 270$ nm was shown to be the most effective [86]. The maxima in the spectral sensitivity of both reactions correspond to the charge transfer bands of the complexes Cr(VI)–diol and Cr(V)–diol [86,114].

Studying the interaction of some organic solvents [175] and oxalic acid [121] with Cr(VI) and Cr(V), the processes Cr(VI) → Cr(IV) and Cr(V) → Cr(III) are shown to be photochemical steps.

The experiments at low temperature have proven unambiguously that Cr(V) formation results from the Cr(VI) + Cr(IV) interaction [86,121]. This dark reaction proceeds with a high rate in liquid phase. Investigation of frozen solutions of $Cr_2O_7^{2-}$–S and CrO_4^{2-}–S in isolation have shown that in the first system the Cr(VI) + Cr(IV) is realized in the framework of the complex $Cr_2O_7^{2-}$–S [86,121] as follows



$$\mathrm{S{-}O{-}\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{Cr^{VI}}}}}{-}O{-}\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{Cr^{VI}}}}}{-}O^{-} \xrightarrow{h\nu} S'{-}O{-}\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{Cr^{IV}}}}}{-}O{-}\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{Cr^{VI}}}}}{-}O^{-}}\ \text{(rate limiting)} \tag{55}$$

$$\mathrm{S'{-}O{-}\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{Cr^{IV}}}}}{-}O{-}\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{Cr^{VI}}}}}{-}O^{-} \longrightarrow 2\,Cr(V) + P}\ \text{(fast)} \tag{56}$$

where S stands for the substrate; S′ for an intermediate reaction product; P for the final reaction product [86,121].

Irradiation of the frozen solution containing $Cr_2O_7^{2-}$–S leads to Cr(V) formation in contrast to the CrO_4^{2-}–S system [86,121] where in the rigid glass the Cr(IV) species once formed in the first photochemical act cannot react further with another Cr(VI). After melting, the dark reaction (14) proceeds very rapidly and an intense EPR signal for Cr(V) is obtained only after the appearence of the liquid phase. These experimental data are in accordance with earlier observations [260] for a higher rate of $Cr_2O_7^{2-}$ photoreduction in comparison with that of CrO_4^{2-}.

The photochemical reduction of Cr(VI) in gelatine and other polymer materials with respect to its application in photography has been studied [264]. By means of EPR it was shown that in the dark reaction stable Cr(V) species are formed, while upon irradiation simultaneously Cr(V) and free radicals are present in the system. The mechanism of Cr(V) formation is discussed and both intermediates are assumed to result from one-electron transfer

$$\mathrm{Cr(VI)\cdots RH \xrightarrow{h\nu} Cr(V) + \dot{R}\overset{\cdot+}{H}} \tag{57}$$

E. CONCLUSIONS

The variety of information summarized in the present review shows that the formation of chromium(V) through reduction of chromium(VI) in solutions depends strongly on the reacting species–Cr(VI) compound and the substrate, and on the reaction media. The concentration ratio $C_{\mathrm{Cr(VI)}} : C_{\mathrm{S}}$, and the temperature are also parameters that in some cases can determine the reaction pathway.

REFERENCES

1 K.B. Wiberg, Oxidation in Organic Chemistry, Part A, Academic Press, New York, 1965.
2 J.H. Espensen, Acc. Chem. Res., 3 (1970) 347.
3 J.K. Beattie and G.P. Haight, Progr. Inorg. Chem., 17 (1972) 93.

4 F.H. Westheimer, Chem. Rev., 45 (1949) 419.
5 J.T. Groves and R.C. Haushalter, J. Chem. Soc., Chem. Commun., (1981) 1165.
6 (a) K. Wetterhahn Jennette, J. Am. Chem. Soc., 104 (1982) 874.
(b) D.M.L. Goodgame, P.B. Hayman and D.E. Hathway, Polyhedron, 1 (1982) 497.
7 H. Kon, Bull. Chem. Soc. Jpn., 35 (1962) 2054.
8 H. Kon, J. Inorg. Nucl. Chem., 25 (1963) 933.
9 N.S. Garifianov and N.F. Usacheva, Dokl. Akad. Nauk SSSR, 145 (1962) 565 (in Russian).
10 N.S. Garifianov, in B.M. Kozyrev (Ed.), Radiospectroscopy, Nauka, Moscow, 1973, p. 5.
11 B.A. Goodman and J.B. Raynor, Adv. Inorg. Chem. Radiochem., 13 (1970) 136.
12 H.A. Kuska and M.T. Rogers, Electron Spin Resonance of First Row Transition Metal Complex Ions, Interscience, New York, 1968.
13 S.A. Altshuler and B.M. Kozyrev, Electron Spin Resonance of Transition Metal Compounds, Nauka, Moscow, 1972 (in Russian).
14 A.J. Edwards, Proc. Chem. Soc., (1963) 205.
15 O. Glemser, H. Roesky and K.H. Hellberg, Angew. Chem. Int. Ed. Engl.), 2 (1966) 266.
16 (a) F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, Third Edn., Interscience, New York, 1972, p. 830.
(b) P.J. Green, B.M. Johnson, T.M. Loehr and G.L. Gard, Inorg. Chem., 21 (1982) 3562.
17 R.B. Johannesen and H.L. Krauss, Chem. Ber., 97 (1964) 2094.
18 W. Levason, J.S. Ogden and A.J. Rest, J. Chem. Soc., Dalton Trans., (1980) 419.
19 N. Bailey and M.C.R. Symons, J. Chem. Soc., (1957) 203.
20 K. Niki and H.A. Laitinen, J. Inorg. Nucl. Chem., 37 (1975) 91.
21 R. Scholder and H. Schwarz, Z. Anorg. Chem., 326 (1963) 1, 11.
22 H. Schwarz, Z. Anorg. Allg. Chem., 322 (1963) 1, 15, 129, 137, 323 (1963) 275.
23 G. Meyer, D. Paus and R. Hoppe, Z. Anorg. Allg. Chem., 408 (1974) 15.
24 A. Roy and K. Nag, J. Inorg. Nucl. Chem., 40 (1978) 1501.
25 A. Carrington, D.J.E. Ingram, D. Schonland and M. Symons, J. Chem. Soc., (1956) 4710.
26 B.R. McGarvey, in R.L. Carlin (Ed.), Transition Metal Chemistry, Vol. 3, Dekker, New York, 1966.
27 E. Banks, M. Greenblatt and B.R. McGarvey, J. Chem. Phys., 47 (1967) 3772.
28 E. Banks, M. Greenblatt and S. Holt, J. Chem. Phys., 49 (1968) 1431.
29 C. Simo, E. Banks and S.L. Holt, Inorg. Chem., 9 (1970) 183.
30 E. Banks, M. Greenblatt and B.R. McGarvey, J. Solid State Chem., 3 (1971) 208.
31 L. Di Sipio, L. Oleari and P. Day, J. Chem. Soc., Faraday Trans. 2, 68 (1972) 1032.
32 J.B. Milstein, J. Ackerman, S.L. Holt and B.R. McGarvey, Inorg. Chem., 11 (1972) 1178.
33 M. Greenblatt and J.M. Pifer, J. Chem. Phys., 66 (1976) 559.
34 R. Olazcuaga, J.-M. Reau, G. Le Flem and P. Hagenmuller, Z. Anorg. Allg. Chem., 412 (1975) 271.
35 T. Ziegler, A. Rauk and E.J. Baerends, Chem. Phys., 16 (1976) 209.
36 M. Greenblatt, J.H. Pifer and E. Banks, J. Chem. Phys., 66 (1977) 559.
37 R. Borromei, L. Oleari and P. Day, J. Chem. Soc., Faraday Trans. 2, 75 (1979) 401.
38 H.B. Gray and C.R. Hare, Inorg. Chem., 1 (1962) 363.
39 C.R. Hare, I. Bernal and H.B. Gray, Inorg. Chem., 1 (1962) 831.
40 H. Kon and N.E. Sharpless, J. Chem. Phys., 42 (1965) 906.
41 O.V. Ziebarth and J. Selbin, J. Inorg. Nucl. Chem., 32 (1970) 849.
42 R.F. Weinland and W. Fridrich, Ber., 38 (1905) 3784.
43 R.F. Weinland and M. Fiederer, Ber., 40 (1907) 2090.
44 A.G. Sharpe and A.A. Woolf, J. Chem. Soc., (1951) 798.

45 H.C. Clark and Y.N. Sadans, Can. J. Chem., 42 (1964) 702.
46 N.S. Garifianov, Dokl. Akad. Nauk SSSR, 155 (1964) 385 (in Russian).
47 N.S. Garifianov, S.E. Kamenev and I.V. Ovchinnikov, Zh. Phys. Khim., 43 (1969) 1091 (in Russian).
48 D. Brown, J. Chem. Soc., (1964) 4944.
49 R.J.H. Clark, Spectrochim. Acta, 21 (1965) 955.
50 I.P. Lipatova and E.I. Semjenova, Teor. Exp. Khim., 2 (1966) 279.
51 E. Wendling, Bull. Soc. Chim. Fr., (1967) 5.
52 E. Wendling and R. Rohmer, Bull. Soc. Chim. Fr., (1967) 8.
53 L.A. Dalton, R.D. Bereman and C.H. Brubaker, Jr., Inorg. Chem., 8 (1969) 2477.
54 I.N. Marov, T.I. Abramova and A.N. Ermakov, Zh. Neorg. Khim., 15 (1970) 2383 (in Russian).
55 (a) S. Sarker and J.P. Singh, J. Chem. Soc., Chem. Commun., (1974) 509.
(b) D.A. Edwards and S.C. Jennison, Transition Met. Chem., 6 (1981) 235.
56 M. Majumder and R.K. Mukhopadhyay, Indian J. Chem., 11 (1973) 183.
57 M.N. Najumder and A.B. Mitra, J. Indian Chem. Soc., 52 (1975) 670.
58 K.R. Seddon and V.H. Thomas, Inorg. Chim. Acta, 20 (1976) L37.
59 K.R. Seddon and V.H. Thomas, J. Chem. Soc., Dalton Trans. (1977) 2195.
60 B. Gahan, D.C. Garner, L.H. Hill, F.E. Mabbs, K.D. Hargrave and A.T. McPhall, J. Chem. Soc., Dalton Trans. (1977) 1726.
61 K.R. Seddon and V.H. Thomas, Inorg. Chem., 17 (1978) 749.
62 J.E. Fergusson, A.M. Greenaway and B.K. Penfold, Inorg. Chim. Acta, 71 (1983) 29.
63 H.K. Saha, S.K. Ghosh and T.K. Ray Chaudhuri, Indian J. Chem., 22A (1983) 346.
64 F. Pettilon, M.T. Youinou and J.E. Guerchois, C.R. Acad. Sci., Ser. C, 268 (1969) 615.
65 A.K. Banerjee and N. Banerjee, Inorg. Chem., 15 (1976) 488.
66 M.N. Majumder and A.K. Saha, J. Inorg. Nucl. Chem., 38 (1976) 1374.
67 H. Kon and N.N. Sharpless, J. Chem. Phys., 43 (1965) 1081.
68 S.L. Verbeek and P.E. Cornaz, Rec. Trav. Chim. Pays-Bas, 86 (1967) 209.
69 R.S. Abdrachmanov, N.S. Garifianov and E.I. Semjenova, Zh. Strukt. Khim., 9 (1968) 530.
70 R.T. Manoharan and M.T. Rogers, J. Chem. Phys., 49 (1968) 5510.
71 C.D. Garner, I.H. Hillier, F.E. Mabbs, C. Taylor and M.F. Guest, J. Chem. Soc., Dalton Trans., (1976) 2258.
72 C.D. Garner, I.H. Hillier, F.E. Mabbs and M.F. Guest, Chem. Phys. Lett., 32 (1975) 224.
73 C.D. Garner, I.H. Hillier, J. Kendrick and F.E. Mabbs, Nature (London), 258 (1975) 138.
74 C.D. Garner, J. Kendrick, P. Lambert, F.E. Mabbs and I.H. Hillier, Inorg. Chem., 15 (1976) 1287.
75 S. Sakaki, M. Mishikawa, N. Tauru, T. Yamashita and A. Ohyoshi, J. Inorg. Nucl. Chem., 41 (1979) 673.
76 J. Weber and C.D. Garner, Inorg. Chem., 19 (1980) 2206.
77 V.I. Muraviev, N.B. Unusov and I.V. Ovchinnikov, Zh. Phys. Khim., 48 (1974) 1600 (in Russian).
78 E.K. Mooney and K.R. Seddon, Transition Met. Chem., 2 (1977) 215.
79 (a) K.B. Wiberg and H. Schäfer, J. Am. Chem. Soc., 89 (1967) 455.
(b) K.B. Wiberg and H. Schäfer, J. Am. Chem. Soc., 91 (1969) 933.
80 V.N. Fedotov, Zh. Eksp. Teor. Fiz., 53 (1967) 1982 (in Russian).
81 N.S. Garifianov, B.M. Kozyrev and V.N. Fedotov, Dokl. Akad. Nauk SSSR, 178 (1968) 808.

82 Z.U. Usmanov and A.V. Iliasov, Zh. Strukt. Khim., 13 (1972) 728 (in Russian).
83 W. de Boer, Nucl. Instrum. Methods, 107 (1973) 99.
84 P.R. Bontchev, A. Malinovski, M. Mitewa and K. Kabassanov, Inorg. Chim. Acta, 6 (1972) 499.
85 C.J. Willis, J. Chem. Soc., Chem. Commun., (1972) 944.
86 M. Mitewa, A. Malinovski, P.R. Bontchev and K. Kabassanov, Inorg. Chim. Acta, 8 (1974) 17.
87 P.R. Bontchev, M. Mitewa, K. Kabassanov and A. Malinovski, Inorg. Nucl. Chem. Lett., 11 (1975) 799.
88 M. Mitewa, P.R. Bontchev, A. Malinovski and K. Kabassanov, C.R. Acad. Bulg. Sci., 29 (1976) 81.
89 P.F. Bramman, Tr. Lund, J.B. Raynor and C.J. Willis, J. Chem. Soc., Dalton Trans., (1975) 45.
90 M. Mitewa, P.R. Bontchev and V. Bojinov, Inorg. Nucl. Chem. Lett., 8 (1972) 51.
91 A.M. Galeev and G.A. Tchmutova, Izv. Akad. Nauk SSSR, Ser. Khim., (1974) 715.
92 A.M. Galeev and Z.I. Usmanov, Zh. Strukt. Khim., 17 (1976) 731 (in Russian).
93 E.I. Steifel, R. Eisenberg, R.C. Rosenberg and H.B. Gray, J. Am. Chem. Soc., 88 (1966) 2956.
94 N.S. Garifianov, Dokl. Akad. Nauk SSSR, 190 (1970) 1368.
95 M. Mitewa, P.R. Bontchev, K. Kabassanov, G. Petrov, P. Russev and M. Natzkova, C.R. Acad. Bulg. Sci., 31 (1978) 1437.
96 C.J. Winscom, Mol. Phys., 28 (1974) 1579.
97 E.G. Derouane and Tr. Ouhadi, Chem. Phys. Lett., 31 (1975) 70.
98 P.R. Bontchev, G. Georgiev, P. Russev, M. Mitewa and K. Stamenov, C.R. Acad. Bulg. Sci., 32 (1974) 775.
99 A.M. Galeev, N.A. Chadaev, A.Sh. Muchtarov and A.V. Iliasov, Zh. Strukt. Khim., 15 (1974) 927 (in Russian).
100 H. Glättly, M. Odehnal, I. Ezratty, A. Malinovski and A. Abragam, Phys. Rev. Lett. Sect. A, 29 (1969) 250.
101 A. Mazaike, H. Glättly, I. Ezratty and A. Malinovski, Phys. Rev. Lett. Sect. A, 30 (1969) 63.
102 V.I. Muraviev, I.V. Ovchinnikov and N.B. Unusov, Izv. Akad. Nauk SSSR, Ser. Khim., (1976) 1696.
103 H.C. Mishra and M.C.R. Symons, J. Chem. Soc., (1963) 4490.
104 N.S. Garifianov, S.E. Kamenev and I.V. Ovchinnikov, Teor. Exp. Khim., 3 (1967) 661 (in Russian).
105 R.S. Abdrachmanov, N.S. Garifianov and E.K. Semjenova, Zh. Neorg. Khim., 13 (1968) 2442 (in Russian).
106 I.N. Marov, T.I. Abramova and A.N. Ermakov, Zh. Neorg. Khim., 14 (1969) 2416 (in Russian).
107 N.S. Garifianov, Zh. Strukt. Khim., 12 (1971) 170.
108 N.S. Garifianov, A.V. Iliasov, B.M. Kozyrev and Z.I. Usmanov, Dokl. Akad. Nauk SSR, 198 (1971) 868.
109 G.P. Haight, Jr., T.J. Huang and B.Z. Shakhashiri, J. Inorg. Nucl. Chem., 33 (1971) 2169.
110 V. Srinivasan and J. Roček, J. Am. Chem. Soc., 96 (1974) 127.
111 K.B. Wiberg and G. Szeimies, J. Am. Chem. Soc., 96 (1974) 1889.
112 G.P. Haight, Jr., T.J. Huang and H. Platt, J. Am. Chem. Soc., 96 (1974) 3137.
113 L.N. Duglaev and Z.I. Usmanov, Zh. Strukt. Khim., 16 (1975) 312 (in Russian).
114 M. Mitewa, Ph.D. Thesis, University of Sofia, 1975.

115 M. Krumpolc and J. Roček, J. Am. Chem. Soc., 98 (1976) 872.
116 M. Krumpolc, B.G. De Boer and J. Roček, J. Am. Chem. Soc., 100 (1978) 145.
117 M. Krumpolc and J. Roček, J. Am. Chem. Soc., 101 (1979) 3206.
118 P. Russev, P.R. Bontchev, M. Mitewa and A. Malinovski, Inorg. Chim. Acta, 34 (1979) 103.
119 P.R. Bontchev, M. Mitewa, P. Russev, G. Petrov, A. Malinovski and K. Kabassanov, J. Inorg. Nucl. Chem., 41 (1979) 1451.
120 P. Russev, P.R. Bontchev, M. Mitewa and H. Mäller, J. Prakt. Chem., 322 (1980) 705.
121 P. Russev, M. Mitewa and P.R. Bontchev, J. Inorg. Nucl. Chem., 43 (1981) 35.
122 M. Mitewa, P. Russev, P.R. Bontchev, K. Kabassanov and A. Malinovski, Inorg. Chim. Acta, 70 (1983) 179.
123 P. Russev, Ph.D. Thesis, Sofia University, 1981.
124 I.F. Gaynulin, in B.M. Kozyrev (Ed.), Radiospectroscopy, Nauka, Moscow, 1973, p. 76.
125 J.T. Groves and W.J. Kruper, Jr., J. Am. Chem. Soc., 101 (1979) 7613.
126 J.T. Groves, W.J. Kruper, T.E. Nemo and R.S. Myers, J. Mol. Catal., 7 (1980) 169.
127 Y. Matsuda, S. Yamada and Y. Murakami, Inorg. Chim. Acta, 44 (1980) L309.
128 Th.L. Siddall, N. Miyaura, J.C. Huffman and J.K. Kochi, J. Chem. Soc., Chem. Commun., (1983) 1185.
129 S.I. Arshankow and A.L. Pozniak, Z. Anorg. Allg. Chem., 481 (1981) 201.
130 J.W. Buchler, C. Dreher, K.-L. Lay, A. Raap and K. Gersonde, Inorg. Chem., 22 (1983) 879.
131 J.T. Groves, T. Takahashi and W. Butler, Inorg. Chem., 22 (1983) 884.
132 A. Davison, N. Edelstein, R.H. Holm and A.H. Maki, J. Am. Chem. Soc., 86 (1964) 2799.
133 J.H. Waters, R. Williams, H.B. Gray, G.N. Schrauzer and H.W. Finck, J. Am. Chem. Soc., 86 (1964) 4198.
134 I.F. Gaynulin, N.S. Garifianov and V.V. Trachevskii, Izv. Acad. Nauk SSSR, Ser. Khim., 10 (1969) 2176.
135 J.M. Davis, Lancet, (1978) 384.
136 A. Furst, M. Schlauder and D.P. Sasmore, Cancer Res., 36 (1976) 1779.
137 P.L. Gutierrez, T. Sarna and H.M. Swartz, Phys. Med. Biol., 21 (1976) 949.
138 J.H. Espenson and E.L. King, J. Am. Chem. Soc., 85 (1963) 3328.
139 J.H. Espenson, J. Am. Chem. Soc., 86 (1964) 1883, 5101.
140 J.H. Espenson, J. Am. Chem. Soc., 92 (1970) 1880.
141 K. Davis and J.H. Espenson, J. Am. Chem. Soc., 92 (1970) 1884.
142 K.L. Bridges, S.K. Mukherjee and G. Gordon, Inorg. Chem., 11 (1972) 2494.
143 J.C. Sullivan, J. Am. Chem. Soc., 87 (1963) 1495.
144 J.P. Birk, J. Am. Chem. Soc., 91 (1969) 3189.
145 J.P. Birk and J.W. Gasievski, Inorg. Chem., 10 (1971) 1586.
146 J.C. Kenny and D.W. Carlyle, Inorg. Chem., 12 (1973) 1952.
147 G.F. McKnight and G.P. Haight, Inorg. Chem., 12 (1973) 1619.
148 U.K. Kläning and M.C.R. Symons, Proc. Chem. Soc., (1959) 95.
149 U.K. Kläning and M.C.R. Symons, J. Chem. Soc., (1960) 977.
150 K.B. Wiberg and H. Schäfer, J. Am. Chem. Soc., 91 (1969) 927.
151 J. Roček and S.A. Riehl, J. Am. Chem. Soc., 88 (1966) 4749.
152 F. Hasan and J. Roček, Tetrahedron, 30 (1974) 21.
153 J.P. McCann and A. McAuley, J. Chem. Soc., Dalton Trans., (1975) 783.
154 Y. Hojo, Y. Sugiura and H. Tanaka, J. Inorg. Nucl. Chem., 39 (1977) 1859.
155 G.P. Haight, D. Richardson and N. Coburn, Inorg. Chem., 3 (1964) 1777.

156 G.P. Haight, E. Perchonock, F. Emmeneger and G. Gordon, J. Am. Chem. Soc., 87 (1965) 3835.
157 G.P. Haight, M. Rose and J. Preer, J. Am. Chem. Soc., 90 (1968) 4809.
158 G.P. Haight, Jr., F. Snentowski, M. Rose and C. Heller, J. Am. Chem. Soc., 90 (1968) 6324.
159 I. Baldea and C. Niag, Inorg. Chem., 7 (1968) 1232.
160 J.N. Cooper, J. Phys. Chem., 74 (1970) 955.
161 M.I. Edmonds, K.E. Howlett and B.L. Wedzicha, J. Chem. Soc. A, (1970) 2866.
162 D.A. Durham, L. Dozsa and M.T. Beck, J. Inorg. Nucl. Chem., 33 (1971) 2971.
163 K.I. Muirhead and G.P. Haight, Inorg. Chem., 12 (1973) 1116.
164 U. Muralikrishna and K.V. Bapanaiah, Z. Phys. Chem. (Leipzig), 255 (1974) 16.
165 K.K. Sen Gupta, J.K. Chahladar and A.K. Chatterjee, J. Inorg. Nucl. Chem., 35 (1973) 901.
166 K.K. Sen Gupta, A.K. Chatterjee and S.P. Moulik, Bull. Chem. Soc. Jpn., 43 (1970) 3841.
167 K.K. Sen Gupta, Sh. Sen Gupta and H.R. Chatterjee, J. Inorg. Nucl. Chem., 38 (1976) 549.
168 U.K. Kläning and M.C.R. Symons, J. Chem. Soc., (1961) 3204.
169 W. Watanabe and F.H. Westheimer, J. Chem. Phys., 17 (1949) 61.
170 (a) E. Punger and J. Trompler, J. Inorg. Nucl. Chem., 5 (1957) 123.
(b) E. Pungor and J. Trompler, J. Inorg. Nucl. Chem., 7 (1958) 412.
171 U.K. Kläning and M.C.R. Symons, J. Chem. Soc., (1960) 977.
172 K.B. Wiberg and P.A. Lepse, J. Am. Chem. Soc., 86 (1964) 2612.
173 U.K. Kläning, J. Chem. Soc., Faraday Trans. 1, 73 (1977) 434.
174 P. Russev, M. Mitewa, P.R. Bontchev and A. Malinovski, C.R. Acad. Bulg. Sci., 33 (1980) 519.
175 P. Russev, P.R. Bontchev, M. Mitewa and A. Malinovski, Inorg. Nucl. Chem. Lett., 16 (1980) 121.
176 V. Balzani and V. Carassity, Photochemistry of Coordination Compounds, Academic Press, London, 1970, p. 113.
177 F.H. Westheimer and N. Nicolaides, J. Am. Chem. Soc., 71 (1949) 25.
178 F. Westheimer, F. Holloway and M. Cohen, J. Am. Chem. Soc., 73 (1951) 65.
179 S.D. Paul and D.G. Pradham, Indian J. Chem., 9 (1971) 835.
180 V.M. Sadagopa Ramanujam and N. Venkatasubramanian, Indian J. Chem., 13 (1975) 285.
181 H. Kwart and J.H. Nickle, J. Am. Chem. Soc., 95 (1973) 3394.
182 H. Kwart and J.H. Nickle, J. Am. Chem. Soc., 98 (1976) 2881.
183 M.T. Beck and D.A. Durham, J. Inorg. Nucl. Chem., 32 (1970) 1971.
184 P.S. Radhakrishnamurty and T.C. Behera, Indian J. Chem., 9 (1971) 41.
185 D.S. Jha and G.V. Bakore, J. Indian Chem. Soc., 48 (1971) 645.
186 K.K. Sen Gupta and J.K. Chakladar, J. Chem. Soc., Perkin Trans. 2, (1973) 929.
187 M. Mitewa, P.R. Bontchev, K. Kabassanov and A. Malinovski, Inorg. Nucl. Chem. Lett., 11 (1975) 793.
188 R. Stewart, Oxidation Mechanisms: Application to Organic Chemistry, W.A. Benjamin, New York, 1964, p. 38.
189 W.A. Mosher and G.L. Driscoll, J. Am. Chem. Soc., 90 (1968) 4189.
190 P.M. Nave and W.S. Trahanovsky, J. Am. Chem. Soc., 92 (1970) 1120.
191 P.M. Nave and W.S. Trahanovsky, J. Am. Chem. Soc., 93 (1971) 4536.
192 M. Rahman and J. Roček, J. Am. Chem. Soc. 93 (1971) 5462.

193 S.T. Nandibewood and J.R. Raji, J. Indian Chem. Soc., 55 (1978) 1284.
194 J. Roček and A.E. Radkowsky, J. Am. Chem. Soc., 90 (1968) 2986.
195 K.B. Wiberg and S.K. Mukherjee, J. Am. Chem. Soc., 93 (1971) 2543.
196 K. Meyer and J. Roček, J. Am. Chem. Soc., 94 (1972) 1209.
197 J. Roček and A.E. Radkowsky, J. Am. Chem. Soc., 95 (1973) 7123.
198 F. Hasan and J. Roček, J. Am. Chem. Soc., 96 (1974) 534.
199 K.B. Wiberg and S.K. Mukherjee, J. Am. Chem. Soc., 96 (1974) 1884.
200 P. Müller and J. Roček, J. Am. Chem. Soc., 96 (1974) 2836.
201 K.B. Wiberg and S.K. Mukherjee, J. Am. Chem. Soc., 96 (1974) 6647.
202 F. Hasan and J. Roček, J. Am. Chem. Soc., 97 (1975) 1444.
203 A.M. Martinez, G.E. Cushmac and J. Roček, J. Am. Chem. Soc., 97 (1975) 6502.
204 T.-Y. Peng and J. Roček, J. Am. Chem. Soc., 98 (1976) 1026.
205 J. Roček and T.-Y. Peng, J. Am. Chem. Soc., 99 (1977) 7622.
206 M.P. Doyle, R.J. Swedo and J. Roček, J. Am. Chem. Soc., 92 (1970) 7599.
207 M. Rahman and J. Roček, J. Am. Chem. Soc., 93 (1971) 5455.
208 M.P. Doyle, R.J. Swedo and J. Roček, J. Am. Chem. Soc., 95 (1973) 8352.
209 J. Roček and Chiu-Sheung Ng, J. Am. Chem. Soc., 96 (1974) 1522.
210 J. Roček and Chiu-Sheung Ng, J. Am. Chem. Soc., 96 (1974) 2840.
211 F. Hasan and J. Roček, J. Am. Chem. Soc., 94 (1972) 3181.
212 F. Hasan and J. Roček, J. Am. Chem. Soc., 94 (1972) 8946.
213 F. Hasan and J. Roček, J. Am. Chem. Soc., 94 (1972) 9073.
214 F. Hasan and J. Roček, J. Org. Chem., 38 (1973) 3812.
215 F. Hasan and J. Roček, J. Am. Chem. Soc., 95 (1973) 5421.
216 F. Hasan and J. Roček, J. Org. Chem., 39 (1974) 2612.
217 F. Hasan and J. Roček, J. Am. Chem. Soc., 96 (1974) 6802.
218 F. Hasan and J. Roček, J. Am. Chem. Soc., 97 (1975) 3762.
219 F. Hasan and J. Roček, J. Am. Chem. Soc., 98 (1976) 6574.
220 M. Krumpolc and J. Roček, J. Am. Chem. Soc., 99 (1977) 137.
221 S. Ramesh, J. Roček and D.A. Schoeller, J. Phys. Chem., 82 (1978) 2751.
222 K.G. Srinivasan and J. Roček, J. Am. Chem. Soc., 100 (1978) 2789.
223 D. Ip and J. Roček, J. Org. Chem., 44 (1979) 312.
224 S.N. Mahapatro, M. Krumpolc and J. Roček, J. Am. Chem. Soc., 102 (1980) 3799.
225 S. Ramesh, S.N. Mahapatro, J.H. Liu and J. Roček, J. Am. Chem. Soc., 103 (1981) 5172.
226 J.N. Cooper, G.N. Standt, M.L. Smalzer, L.M. Settzo and G.P. Haight, Inorg. Chem., 12 (1973) 2075.
227 R.A. Scott, G.P. Haight Jr. and J.N. Cooper, J. Am. Chem. Soc., 96 (1974) 4136.
228 K.C. Sharma, R.C. Rai and B.S. Rajput, J. Indian Chem. Soc., 48 (1971) 625.
229 K.K. Sen Gupta and J.K. Chakladar, J. Chem. Soc., Dalton Trans., (1974) 222.
230 G.N. Salaita, J. Inorg. Nucl. Chem., 38 (1976) 1653.
231 K.K. Sen Gupta and A.K. Chatterjee, Z. Phys. Chem. (Frankfurt am Main), 75 (1971) 15.
232 R. Gopalan and K. Subbarayan, J. Indian Chem. Soc., 56 (1979) 669.
233 M.A. Olatunji and A. McAuley, J. Chem. Soc., Dalton Trans. (1975) 682.
234 F. Freeman, C.R. Armstead, M.G. Essig, E.M. Karchefski, C.J. Kojima, V.C. Manopoli and A.H. Wickman, J. Chem. Soc., Chem. Commun., (1980) 65.
235 S.K. Tandon, K.K. Banerjji and G.V. Bakore, Indian J. Chem., 9 (1971) 677.
236 M. Cohen and F.H. Westheimer, J. Am. Chem. Soc., 74 (1952) 4387.
237 D.G. Lee and R. Stewart, J. Am. Chem. Soc., 86 (1964) 3051.
238 K.H. Heckner and K.H. Grupe, Z. Phys. Chem. (Leipzig), 242 (1969) 255.

239 P.V. Subba Rao and P. Kamannarayana, Z. Phys. Chem. (Leipzig), 248 (1971) 267.
240 P.V. Subba Rao, Z. Phys. Chem. (Frankfurt am Main), 78 (1972) 219.
241 P.V. Subba Rao, K.S. Murty and R.V.S. Murty, Z. Phys. Chem. (Leipzig), 258 (1977) 407.
242 M.T. Beck and D.A. Durham, J. Inorg. Nucl. Chem., 33 (1971) 461.
243 (a) S.V. Anantakrishnan and H. Jayaraman, Indian J. Chem., 2 (1964) 91.
(b) S.V. Anantakrishnan and H. Jayaraman, Indian J. Chem., 2 (1964) 146.
244 N. Venkatasubramaman and S. Sundaram, J. Inorg. Nucl. Chem., 31 (1969) 1761.
245 S.V. Anantakrishnan and H. Jayaraman, Indian J. Chem., 8 (1970) 423.
246 M. Mitowa, P.R. Bontchev, K. Kabassanov and M. Natzkova, Commun. Dept. Chem. Bulg. Acad. Sci., 12 (1979) 68.
247 T. Takeya, E. Kotani and S. Tobinaga, J. Chem. Soc., Chem. Commun., (1983) 98.
248 N. Miyaura and J.K. Kochi, J. Am. Chem. Soc., 105 (1983) 2368.
249 V.S. Srinivasan and E.S. Gould, Inorg. Chem., 20 (1981) 3176.
250 N. Rajasekar, R. Subramanian and E.S. Gould, Inorg. Chem., 21 (1982) 4110.
251 Y. Shyamsunder Rao and R. Filler, J. Org. Chem., 39 (1974) 3304.
252 K.E. Harding, L.M. May and K.F. Dick, J. Org. Chem., 40 (1975) 1664.
253 G. Cardillo, M. Orena and S. Sandri, J. Chem. Soc., Chem. Commun., (1976) 190.
254 J.S. Filippo Jr. and Ch.-I. Chern, J. Org. Chem., 42 (1977) 2182.
255 V. Balzani and V. Carassity, Photochemistry of Coordination Compounds, Academic Press, London, 1970, p. 113.
256 E.J. Bowen and C.W. Bunn, J. Chem. Soc., (1927) 2353.
257 E.J. Bowen and E.T. Yarnold, J. Chem. Soc., (1929) 1648.
258 E.J. Bowen, T.A. Peacocke and E.R. Wellburn, J. Chem. Soc., (1931) 1866.
259 E.J. Bowen and J.E. Chatwin, J. Chem. Soc., (1932) 2081.
260 K. Weber and S. Asperger, J. Chem. Soc., (1948) 2119.
261 U.K. Kläning and M.C.R. Symons, J. Chem. Soc., (1961) 3204.
262 D. Rehorek and R. Wagener, Inorg. Chim. Acta, 33 (1979) L129.
263 D. Rehorek and R. Wagener, J. Prakt. Chem., 321 (1979) 466.
264 V.P. Sherstjuk, O.A. Lialotzkay and L.E. Mazur, Teor. Eksp. Khim., 18 (1982) 243 (in Russian).