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ESR Study on Chromium(V) Complexes formed in the Process of Photochemical Oxidation of Diethylene Glycol by Dichromate

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The oxidation of diethylene glycol with $K_2Cr_2O_7$ was studied in pseudo first-order conditions, the diol being in a large excess. The first stage of the reaction is the formation of non-cyclic monoester of $Cr_2O_7^{2-}$ with the diol, in which a photochemical redox process takes place leading to a complex of $Cr^{(V)}$, denoted as $Cr^{V}(1)$. This complex can be stabilized only at low temperatures; at room temperature it changes into another $Cr^{(V)}$ complex, denoted as $Cr^{V}(2)$. The ESR parameters of the complexes $Cr^{V}(1)$ and $Cr^{V}(2)$ permit some information to be obtained about their composition and structure. The last stage of the reaction which is also a photosensitive one, proceeds on in the complex $Cr^{V}(2)$, leading to the final reaction products – $Cr^{(III)}$ and a carboxylic acid. The spectral sensitivity of the photochemical processes was studied and compared with the absorption spectra of the initial and transition species. The quantum yield of the first photochemical reaction – the formation of $Cr^{(V)}$ – was found to be 0.46. The consecutive stages of the reaction are discussed in detail, some of them being experimentally studied in separation. A scheme for the reaction mechanism is proposed.

Introduction

The oxidation of different reducing agents by $Cr^{(VI)}$ usually proceeds on with the formation of $Cr^{(III)}$ as a final state of chromium(VI) reduction. Because of the low probability for a onestep tri-electron transfer, the formation of $Cr^{(IV)}$ and $Cr^{(V)}$ as intermediate species was assumed to take place. Some kinetic data that support the idea for the formation of such oxidation states in the reaction course have been reported by many authors,[1] but direct experimental evidences for the formation of intermediate chromium(V) species have been obtained only in the last years.[2–5]

In a previous work published recently[5] we have studied the mechanism of ethylene glycol oxidation by dichromate and have established the formation of intermediate $Cr^{(V)}$ complex with the substrate. The formation of such complexes was found to proceed also between Na_3CrO_4 and many nitrogen-, oxygen- and sulphur-containing ligands.[6] Some of these complexes can be used as dinamically polarized proton targets for high energy experiments[7,8] and for that reason an increased interest is recently observed in this field.

The aim of the present work was to proceed on the investigations on the $Cr^{(V)}$ complexes formed during the reduction of $Cr^{(VI)}$, using diethylene glycol as a reaction substrate and $K_2Cr_2O_7$ as an oxidant.

Experimental

Methods

The experimental method used in the investigations was the ESR method, as $Cr^{(V)}$ compounds are paramagnetic species (electron configuration d^1) with a well defined ESR signal. Electronic and vibrational spectra were also used for identification of some products in the reaction course.

The reaction was studied in pseudo first-order conditions ($C_{Diet}:C_{K_2Cr_2O_7} = 143:1$) when the whole amount of dichromate added is easily dissolved in diethylene glycol. The samples were measured together with DPPH as a standard and the concentration of the paramagnetic species calculated by a double integration of the derivative curves. Corrections were made for the different g-factors and spin values of the paramagnetic chromium species and the standard sample.

Materials and Apparatus

The reagents used in the investigations were of AR grade. Diethylene glycol was dried over anhydrous Na_2SO_4. Potassium dichromate was dried for two hours at 110° and used as a finally ground powder.

The standard chromium(V) compound, Na_3CrO_4, was synthetized according to the procedure proposed by Scholder and Schwarz.[9] It was obtained with 100% yield, stored in a dry nitrogen atmosphere and used without any further purification.

The ESR investigations were carried out with a standard X-band ESR spectrometer. The vibrational spectra were obtained on a spectrometer IR–10, Carl Zeiss, Jena, and those in the visible and UV region on recording spectrometer Specord UV–VIS, Carl Zeiss.

Results

Reaction Kinetics

The oxidation of diethylene glycol by $K_2Cr_2O_7$ shows a high photosensitivity. At room temperature the reaction proceeds on with a measurable rate only at light, while in darkness it is very slow. For that reason the reaction kinetics was studied in the following way. The reagents were mixed in darkness, transferred in a capillary tube in the resonator of the ESR spectrometer, where the sample was irradiated by a 100w xenon point-source lamp and the concentrations ot the paramagnetic chromium species monitored with time.

In such conditions three ESR signals were observed to appear, two ot them due to $Cr^{(V)}$ complexes and the third one to the final product of $Cr^{(VI)}$ reduction, a complex of chromium(III). The complex of $Cr^{(V)}$, denoted as $Cr^{v}(1)$, shows a singlet ESR line. The second, more intensive ESR signal, due to another complex of $Cr^{(V)}$, was denoted as $Cr^{v}(2)$. This signal shows a resolved hyperfine structure with eight components. At the final stage of the reaction, when the $Cr^{(III)}$ concentration becomes relatively high, a broad singlet line also appears with a line width ΔH varying from 300 to 400 Oe. Its line width strongly depends on the viscosity of the system that affects the correlation time τ_c and hence the spin–lattice relaxation time. A typical kinetic curves for the three paramagnetic species formed in the reaction system is shown on Figure 1.

It can be seen from Figure 1 that after a relatively short period the $Cr^{v}(2)$ concentration becomes about 10 times higher than that of $Cr^{v}(1)$. The concentrations of both Cr(V) species proceed through a maximum and then decrease while the concentration of chromium(III) increases untill the complete conversion of $Cr^{(VI)}$ to $Cr^{(III)}$.

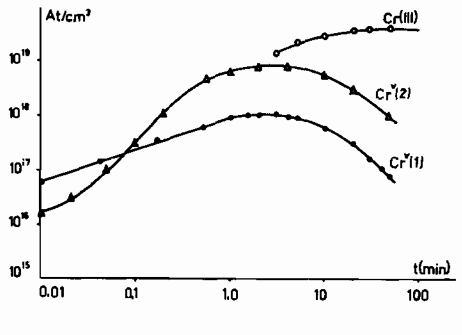

Figure 1. Typical kinetic curves for the formation of the three paramagnetic species. Room temperature, irradiation with a xenon lamp without filters.

The kinetic curve shown on Figure 1 was obtained at room temperature. Experiments carried out at 77° K have shown that in these conditions only $Cr^{v}(1)$ is obtained, $Cr^{v}(2)$ being formed only at higher temperatures from $Cr^{v}(1)$.

ESR Data for $Cr^{v}(1)$

The ESR spectrum of $Cr^{v}(1)$ at room temperature shown on Figure 2 represents a singlet line with the following parameters: $g_{iso} = 1.9780 \pm 0.0005$ and $\Delta H = 2.7$ Oe (peak–to–peak separation of the derivative). When the reaction mixture is irradiated for 1 hour by 100w xenon lamp at 77° K it shows the ESR spectrum given on Figure 3. This is a typical spectrum of a polycristalline sample having an axial symmetry. The analysis of the spectrum gave the following values: $g_{//} = 1.944 \pm 0.003$ and $g_{\perp} = 1.992 \pm 0.002$. Accepting the validity of the relation $<g> = \frac{1}{3}(2g_{\perp} + g_{//})$, the mean value of the g-tensor $<g> = 1.976 \pm 0.003$ was obtained. The average $<g>$ value, calculated from the anisotropic parts of the g-tensor at 77° K is in a good agreement with the isotropic value g_{iso}, given above. Since these two values are identical to within the limits of the experimental error, it seems that both signals are due to one and the same complex, namely $Cr^{v}(1)$.

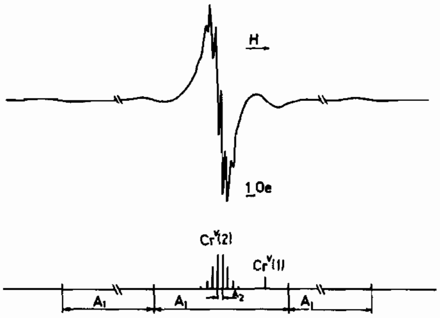

Figure 2. ESR spectra of the two $Cr^{(V)}$ complexes at room temperature.

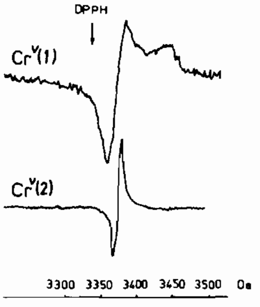

Figure 3. ESR spectra of the two $Cr^{(V)}$ complexes at 77° K.

When the temperature is increased in darkness over 77° K the signals shown on Figure 3 remain unchanged untill the melting-point of the frozen solution is reached. With the appearance of the liquid phase the ESR spectrum changes and becomes identical with that shown on Figure 2 with an intensity ratio $Cr^{v}(2) : Cr^{v}(1) = 10:1$. Hence the conversion of $Cr^{v}(1)$ to $Cr^{v}(2)$ is not a photochemical process.

ESR Data for $Cr^{v}(2)$

The ESR spectrum of $Cr^{v}(2)$ at room temperature and in dilute solution (Figure 2) shows a hyperfine structure of eight narrow lines with an intensity distribution approximately the same as the binominal one, 1:7:21:35:35:21:7:1. The integrated derivative curve and the calculated best fit are shown on Figure 4.

The spectrum was calculated using the following parameters: eight lorentzian components with binominal intensity distribution, a hyperfine constant $A_2 = 0.61$ Oe and line-width of the individual components $\Delta H_{pp} = 0.45$ Oe.

A four-component hyperfine structure was also observed (Figure 2) due to the ^{53}Cr isotope with a natural abundance of 9.5 per cent. Such hfs was found only in the case of $Cr^{v}(2)$. These lines do not provide additional hyperfine splitting.

Therefore the liquid-solution spectrum of the $Cr^{v}(2)$ complex can be described by the spin Hamiltonian: $H = g\beta\ HS + A_1I_1S\ /A_2I_2S$ where $S = {}^1/_2$, $g = 1.9809 \pm 0.0005$, A_1 is the hfs constant for ^{53}Cr with $I_1 = {}^3/_2$, equal to 16,2 Oe, A_2 the constant for additional hfs from 7 equivalent protons with $I_2 = {}^7/_2$, equal to 0.61 Oe.

At 77° K an unique, almost isotropic line was observed (Figure 3) with the same g-factor and unresolved hyperfine structure. Despite the slight assymmetry of the spectrum, the g-tensor is almost isotropic within the limits of the line-width (12 Oe). The difference $\Delta g = g_{//} - g_{\perp}$, must be less than 3×10^{-3}. Therefore the complex $Cr^{v}(2)$ has a structure that includes 7 equivalent (or almost equivalent) protons in the neighbourhood of $Cr^{(V)}$.

A similar signal with hyperfine structure corresponding to eight equivalent protons was observed firstly in the course of ethylene glycol oxidation with $Cr^{(VI)}$ by Garifyanof[3] and studied in detail by the authors.[5] The g-tensor isotropy in this case was assigned to the high symmetry of the complex with the four oxygen atoms and $Cr^{(V)}$ being in one plane, and the Cr=O bond perpendicular to this plane. In order to explain the isotropy of the g-factor an additional assumption was made for the validity of the relations $4\delta \approx \Delta$ and $\beta^2 \approx \gamma^2$ where δ and Δ are the splitting parameters between the energy levels in the ^2D-term, β and γ the MO parameters. The narrowness of the observed ESR lines was attributed to the McConnell mechanism when the spin–spin and the spin–lattice relaxation times are very long due to the small value of Δg and the zero value of the quantum number I for the even chromium isotopes.

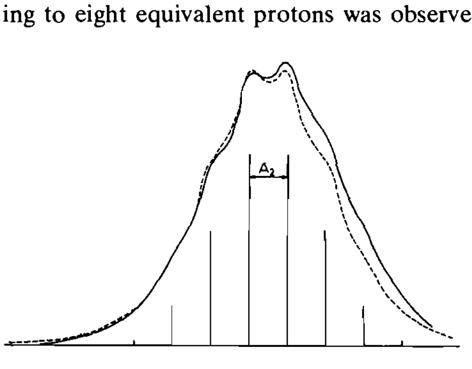

Figure 4. Hyperfine structure in $Cr^{v}(2)$. Full line observed; dashed line calculated best fit.

Comparing these results with the experimental data here reported it can be calculated that the complex $Cr^{v}(2)$ is very similar to the complex of $Cr^{(V)}$ with ethylene glycol. Both g-tensors are identical to within the limit of the experimental error*, suggesting analogous electronic structure of both complexes. The hyperfine coupling constants are also comparable giving further exidence for the similarity of the structure of the complexes.

No other paramagnetic species were found in the reaction system neither at irradiation nor in darkness at nitrogen and at room temperature.

Photosensitivity of the Reaction

The formation of $Cr^{v}(1)$ proceeds on with a measurable rate only at irradiation. The special sensitivity of the $Cr^{(V)}$ formation was studied using a xenon lamp and a set of interference filters. Samples of the reaction mixture prepared in darkness, were irradiated for 25 minutes at room temperature and the $Cr^{(V)}$ concentration measured. In this initial period of the reaction the intensity of $Cr^{v}(2)$ signal is about 10 times higher than that of $Cr^{v}(1)$ and their ratio is practically constant. For that reason the concentration of $Cr^{v}(2)$ formed for a fixed time of irradiation was used as a measure of the reaction rate. Corrections were made for the spectral characteristic of the lamp and the transmittance of the filters. The data thus obtained given on Figure 5, curve a, show that a maximal rate of $Cr^{v}(2)$ formation occurs for a wavelength $\lambda \approx 450$ nm. As the conversion of $Cr^{v}(1)$ into $Cr^{v}(2)$ is not a photochemical process, it is clear that in fact the rate of $Cr^{v}(1)$ formation is maximal at this length.

The quantum yield of the $Cr^{v}(2)$ formation was also determined at 450 nm. The light intensity was measured by a calibrated thermocouple. Corrections were made for the geometry of the sample (cylindrical tube). The quantity of $Cr^{v}(2)$ formed was measured by a double

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* Recently we have obtained a more accurate value for the g-tensor of the complex $Cr^{(V)}$–ethylene glycol: $g = 1.9809 \pm 0.0005$.

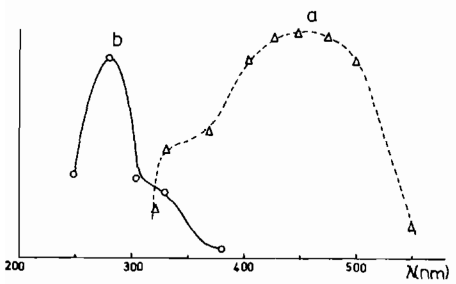


Figure 5. Spectral sensitivity of the $Cr^{(V)}$ formation and decay. (a) Rate of $Cr^{(V)}$ formation; (b) rate of $Cr^{(V)}$ decay. The rates are not in scale and are represented in arbitrary units.

integration of the ESR curve; DPPH sample was used as a reference. The average value for the quantum yield formed from five measurements is 0.46 molecules per quantum of light.

It is noteworthy that after the mixing of the reagents – $K_2Cr_2O_7$ and diethylene glycol – a new band in the optical absorption spectrum at 450 nm is observed (Figure 6), that disappears at the end of the reaction. According to Kläning and Symons[10] this is a charge-transfer band, typical for the complexes of $Cr^{(VI)}$ with alcohols, that corresponds to a transition from oxygen to chromium. Therefore, the photosensitivity of the $Cr^{v}(1)$ formation is due to the absorption of photons by the complex $Cr^{(VI)}$–substrate that leads to an electron-transfer process in the complex.

Similar investigations were carried out in order to estimate the spectral sensitivity of the next redox stage of the reaction – the reduction of $Cr^{(V)}$ to $Cr^{(III)}$.

Samples of the reaction mixture were irradiated with a xenon lamp for 20 minutes, when small amounts only of unreacted $Cr^{(VI)}$ are present in the system (see Figure 1) and the $Cr^{v}(2)$ concentration decreases at further illumination. The samples were then again irradiated by light from a narrow spectral range (interference filters) and the decrease of the $Cr^{v}(2)$ concentration followed with time. The plot of the $\log Cr^{v}(2)$ vs time was found to be linear and the slope of this line was used as a measure of the $Cr^{(V)}$ reduction rate. The results given on Figure 6, curve b, show that the reduction of $Cr^{(V)}$ proceeds with a maximal rate when light with $\lambda \approx 270$ nm was used.

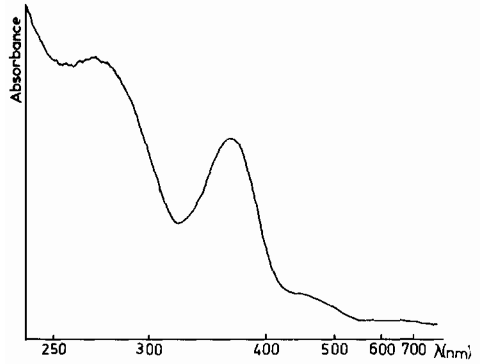


Figure 6. Absorption spectrum of the dichromate–diethylene glycol mixture.

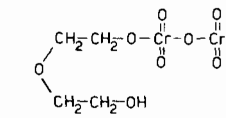
The absorption spectrum in the UV region in these conditions shows two bands at 270 and 365 nm. The same bands are also present in the $Cr^{(VI)}$–diethylene glycol complex. As no other bands were found to appear in the reaction system spectra it seems possible that the corresponding bands of the $Cr^{v}(2)$ complex lie in the same spectral region as those of $[Cr^{(VI)}$–Diet]. Hence, the photosensitivity of the $Cr^{(V)}$ reduction could be ascribed to absorption of light in the 270 nm band.

Intermediate and Final Reaction Products

After the mixing of the reagents a new absorption band appears in the UV spectra of the reaction solution usually assigned to an ester formation between $Cr^{(VI)}$ and the diol.[10] This process could be regarded also as a complex formation with diol entering the coordination sphere of chromium(VI). The formation of such complex as a first stage of the process was also confirmed by the IR spectra of the system. After the mixing of the reagents the bands at 1080 and 1135 cm^{-1} due to the δ(C–O) vibration of alcoholic and ether bands[11] are broadened which also indicates the complex formation process.

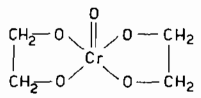
The ester formed in the reaction conditions is not extracted by organic solvents with low polarity as benzene or n-heptane, which extract quantitatively neutral cyclic esters of $Cr^{(VI)}$ with diols.[12] This fact indicates to the formation of charged ester which is possible only if monoester of dichromate is formed.

Experiments with ion-exchange resins have confirmed this assumption – the complex is sorbed by anion-exchange resin (Wofatit L–150) thus indicating that non-cyclic monoester of diethylene glycol of the type



is formed in the process.

The ESR data obtained for the complex $Cr^{v}(2)$ (the g-tensor, the hyperfine coupling constant, and the line width) are very similar to the same parameters found for the complex $Cr^{(V)}$–ethylene glycol[5] which has the structure

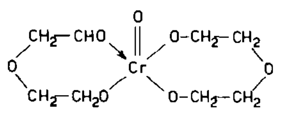


This fact indicates a very close similarity in the structure of both complexes. In the same time the analysis of the ESR data for $Cr^{v}(2)$ has shown the presence of 7 protons in the surroundings of $Cr^{(V)}$. Such structure can arise only if one molecule of the first reaction product – an aldehyde – is coordinated around $Cr^{(V)}$ together with the substrate.

Another important problem concerning the complex $Cr^{v}(2)$ is whether the ether oxygen of the substrate molecule participates in complex formation processes with $Cr^{(V)}$ or not. On the ground of the lower basicity of the ether oxygen atom compared with that of the oxygen atom in the alcoholic groups it seems that coordination of the substrate via ether oxygen could be scarcely expected. However, in order to study such a possibility the reduction of $K_2Cr_2O_7$ was carried out by methyl and ethyl esters of ethylene glycol. The experiments with these substrates have shown that complex formation between $Cr^{(V)}$ and the methyl ester takes place only in a negligible extent and with ethyl ester no complex formation was observed at all.

These results show that with a bulky groups bonded to the ether oxygen its participation in complex formation processes with chromium(V) is prevented most probably because of a steric hindrance. On the other hand it follows from these results that in the complexes with $Cr^{(V)}$ the diols act as bidentate ligands. If one of the hydroxy groups is blocked by etherification the monoether acts as a monodentate ligands which could not stabilize chromium(V) in a complex. Analogous results have been yet found when a large number of ligands were studied with respect of their tendency for coordination with $Cr^{(V)}$.[6]

All the experimental data and considerations stated above show that the most probable structure of the complex $Cr^{v}(2)$ is the following one:



The absence of hyperfine structure of the ESR spectrum ot the complex $Cr^{v}(1)$ does not permit to make more definite conclusions about the composition of that complex. The difference between the ESR parameters of $Cr^{v}(1)$ and $Cr^{v}(2)$ however indicates that these complexes differ in composition and structure.

It was found that the final reaction products obtained as a result of $Cr^{(VI)}$ reduction by diethylene glycol are chromium(III) and carboxylic acid. After the end of the reaction the products were distilled at low pressure (~ 40 mm Hg). The IR spectrum of the distilate has shown only the presence of diethylene glycol and water. In the IR spectrum of the solid residue two new bands at 1380 and 1610 cm^{-1} were observed. The same bands were also found to appear with increasing intensity in samples taken from the reaction mixture during the course of the reaction. According, to the literature data[13] these two bands were assigned to the symmetric and asymmetric valent vibrations of coorinated carboxy-group.

No indications were found for the presence of other products formed as a result of breaking of C–O group, i.e. as a result of a cleavage of the diethylene glycol molecule.

Aldehyde was not detected in the reaction system by means of IR spectra, because of the low concentration of the intermediate species in the reaction system. We failed to prove its formation using also electronic spectra in the range 250–310 nm, where weak bands could be observed as a result of $n \rightarrow \pi^*$ transitions due to nonconjugated C=O groups.[14] This is probably due to the low intensity of the band as well as its overlapping with the corresponding band of $Cr_2O_7^{2-}$.

There exists also a possibility that the oxidation of the intermediate aldehyde to carboxylic acid could proceed on with the participation of the air oxygen. Experiments, when the reaction was carried out in a pure nitrogen atmosphere did not show any difference in the reaction kinetics nor in the amount of the carboxylic acid formed and therefore this assumption should be rejected.

Discussion

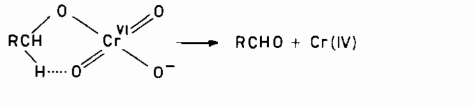
The data stated above permit to obtain a valuable information on the steps of the process and their sequence in the reaction course.

The first step in the reagents interaction is the formation of a non-cyclic monoester of diethylene glycol with dichromate. The presence of such monoester in the reaction system was proved by means of absorption UV and IR spectra, and its charge estimated by extraction and ion-exchange experiments. The formation of esters was considered by Westheimer[15] as a first necessary step in the oxidation of alcohols by $Cr^{(VI)}$ and such esters were really found in many cases.[16]

The next step of the overall interaction is a redox process or processes that take place in the complex, leading to the intermediate valent state chromium(V). Two possibilities exist for the formation of $Cr^{(V)}$ on that stage of the process.

(a) Chromium(V) might be formed as a result of one-electron transfer between the substrate and $Cr^{(VI)}$ together with free radicals from the substrate. Our experiments have shown, that $Cr^{(V)}$ is formed in relatively high concentrations even at 77° K and no organic radicals have been found in spite of the fact that their recombination at nitrogen temperature could not proceed in a high extent. It has been already shown that when primary and secondary alcohols are oxidized by one-electron oxidants as Ce^{4+}, the formation of the corresponding free radicals can be easily estimated by means of ESR at 77° K.[17] On the ground of these considerations we think that the possibility for one-electron mechanism of $Cr^{(V)}$ formation must be eliminated from further discussions.

(b) The oxidation can proceed through a two-electron mechanism with the formation of aldehyde and $Cr^{(IV)}$:



(1)

The two electron mechanism of the first redox step of alcohol oxidation by $Cr^{(VI)}$ is now considered to be valid at least in most cases. It should be emphasized that in this case the reduction of $Cr^{(VI)}$ is a photochemical process, connected with absorption of light in the charge-transfer band of the dichromate monoester of diethylene glycol. Two different schemes were proposed further for the formation of $Cr^{(V)}$ from $Cr^{(IV)}$, by Watanabe–Westheimer,[18]

$$Cr^{(IV)} + Cr^{(VI)} \rightarrow 2Cr^{(V)} \qquad (2)$$

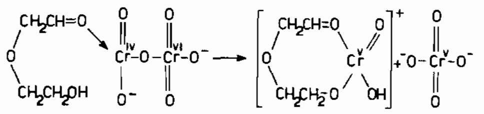
and by Roček[19]

$$RCHOH + Cr^{(IV)} \rightarrow R_2\dot{C}OH + Cr^{(III)} \qquad (3)$$

$$R_2\dot{C}OH + Cr^{(VI)} \rightarrow R_2C{=}O + Cr^{(V)} \qquad (4)$$

In the previous work[5] we have proposed an experimental criterion for distinguishing between both mechanisms and have found that the Watanabe–Westheimer mechanism is operating in the reaction of ethylene glycol oxidation by $K_2Cr_2O_7$. The same criterion together with the absence of free radicals in the reaction system even at 77° have shown that in the present case $Cr^{(V)}$ is also formed according to the scheme (2).

The rate of the $Cr^{(V)}$ formation is high enough even at low concentration of $Cr_2O_7^{2-}$ and at 77° K, when the ion mobility is very low and the possibility for a collision between $Cr^{(IV)}$ and $Cr^{(VI)}$ is practically negligible. However, if the first two-electron step has as a result the reduction of one of both $Cr^{(VI)}$ in $Cr_2O_7^{2-}$, the interaction(2) could be realized between $Cr^{(IV)}$ and $Cr^{(VI)}$ still being linked by oxygen in the transition complex.



(5)

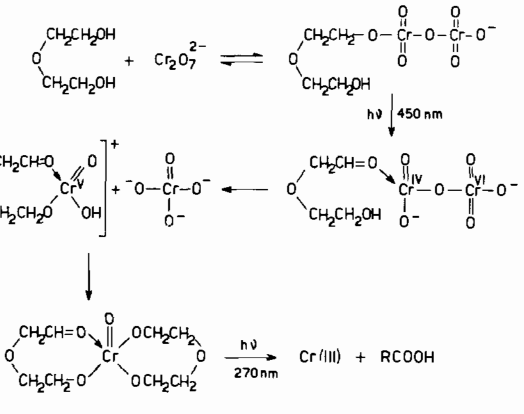
A strong evidence in favour of this assumption was obtained when $K_2Cr_2O_7$ was replaced by K_2CrO_4. In this case when the frequency of the $Cr^{(IV)}$–$Cr^{(VI)}$ collisions is high enough (at room temperature) the reaction proceeds on with nearly the same rate as with $Cr_2O_7^{2-}$. If however the CrO_4^{2-}–diethylene glycol mixture was irradiated at 77° K no $Cr^{(V)}$ formation was observed while with $Cr_2O_7^{2-}$ chromium(V) complex formation proceeds on even at nitrogen temperature. When CrO_4^{2-} is used however $Cr^{(IV)}$ is still formed and accumulated in the system at irradation as it was demonstrated by the following experiment. The chromate–diethylene glycol system was irradiated by a xenon lamp at 77° K for 2 hours, no $Cr^{(V)}$ signal being observed in these conditions. Then the frozen reaction solution was melted in darkness. An intensive $Cr^{(V)}$ signals, due to $Cr^{v}(1)$ and $Cr^{v}(2)$, arised immediately when the melting point of the system was reached.

These considerations show, that the chromium(V) complex firstly formed according to (5) corresponds to the complex denoted as $Cr^{v}(1)$. As it is formed from the tetrahedral $Cr^{(VI)}$ it might be expected for $Cr^{v}(1)$ to represent a distorted tetrahedron. Such assumption is in accordance with the ESR data showing anisotropy of the g-tensor, due to distortion of the structure. In any case the exact composition and structure of the complex $Cr^{v}(1)$ is still not firmly estimated and the formula written above (eq. 5) should be regarded only as one of the most probable structures.

The next reaction step is the conversion of the firstly formed distorted $Cr^{v}(1)$ complex stable only at nitrogen temperatures into the complex $Cr^{v}(2)$ with a higher symmetry, which can be kept in darkness for several days even at room temperature. The process is not a photochemical one and takes place only in a liquid phase, when the substrate molecule can be included in the coordination sphere of $Cr^{(V)}$.

The final step in the $Cr^{(VI)}$ reduction to $Cr^{(III)}$ is the redox process that proceeds in $Cr^{v}(2)$, leading to the formation of $Cr^{(III)}$ and carboxylic acid. This stage of the reaction is also a photochemical process. Chromium(III) and the carboxylic acid are formed in a reaction stage, where both reagents are previously bonded together. Taking into account the fact that $Cr^{(III)}$ forms inert complexes (d^3 configuration) it is clear why after the end of the reaction $Cr^{(III)}$ is found bonded in a complex with the reaction product and not with the substrate, present in a much larger amounts in the system.

The reaction mechanism here discussed can be summarized in the following scheme:



The oxidation of diethylene glycol by dichromate shows some marked differences from the analogous process with ethylene glycol. Firstly, the oxidation of diethylene glycol is much more sensitive to light than that of ethylene glycol. Secondly, when ethylene glycol is oxidized by $K_2Cr_2O_7$ the final reaction product is aldehyde, and $Cr^{(V)}$ forms complexes with the substrate only, while in the case of diethylene glycol the final reaction product is carboxylic acid and $Cr^{(V)}$ can be stabilized only if the intermediate product, aldehyde, is coordinated to $Cr^{(V)}$.

This was confirmed by studying the interaction of Na_3CrO_4 with diethylene glycol. No complex including only the substrate molecules into the coordination sphere of $Cr^{(V)}$ was found. The same ESR spectrum as when $K_2Cr_2O_7$ is used as an oxidant was obtained with the characteristic lines only of $Cr^v(1)$ and $Cr^v(2)$. This result accounts well for the fact that when CrO_4^{3-} is formed in the process of $Cr^v(1)$ formation no other signals were found to appear in the ESR spectrum.

References

1 K.B. Wiberg, "Oxidation in Organic Chemistry", Academic Press, New York (1965).
2 H. Kon, *J. Inorg. Nucl. Chem.*, *25*, 933 (1963).
3 N.S. Garifyanov, B.M. Kozyrev, and V.N. Fedotov, *Doklady Academii Nauk. USSR*, *178*, 808 (1968).
4 K.B. Wiberg and H. Schäfer, *J. Am. Chem. Soc.*, *91*, 933 (1969).
5 P.R. Bontchev, A. Malinovski, M. Mitewa, and K. Kabassanov, *Inorg. Chim. Acta*, *6*, 499 (1972).
6 M. Mitewa, P.R. Bontchev, and V. Bojinov, *Inorg. Nucl. Chem. Letters*, *8*, 51 (1972).
7 A. Mazaike, H. Glättli, I. Ezratty, and A. Malinovski, *Phys. Letters*, *30A*, 63 (1969).
8 W. de Boer, *Nucl. Instr. and Methods*, 107, 99 (1973).
9 R. Scholder and H. Schwarz, *Z. Anorg. Allg. Chem.*, *326*, 1 (1963).
10 U.K. Kläning and M.C.R. Symons, *J. Chem. Soc.*, 3204 (1961).
11 L.J. Bellamy, "The Infra-Red Spectra of Complex Molecules", Moscow, Isdatelstvo Inostranoy Literaturi (1963) p. 137, 165 (in Russian).
12 F. Westheimer, F. Holloway, and M. Cohen, *J. Am. Chem. Soc.*, 73, 65 (1951).
13 See ref. 11, p. 232
14 C.N.R. Rao, "Ultra-Violet and Visible Spectroscopy", Butterworths, London (1961) p. 17.
15 See ref. 1, p. 161.
16 K.B. Wiberg and H. Schäfer, *J. Am. Chem. Soc.*, *91*, 927 (1969).
17 D. Greatorex and T.J. Kemp, *Trans. Faraday Soc.*, *67*, 56 (1971).
18 W. Watanabe and F.H. Westheimer, *J. Chem. Phys.*, *17*, 61 (1949).
19 J. Roček and A.E. Radkowsky, *J. Am. Chem. Soc.*, *90*, 2986 (1968).