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Intermediate Chromium(V) Complex Species and their Role in the Process of Chromium(VI) Reduction by Ethylene Glycol

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The interaction of ethylene glycol with potassium dichromate is studied at 80° in pseudo first-order conditions by ESR method, monitoring the formation of Cr^V and Cr^{III}. The formation of Cr^V complex with ethylene glycol was observed and its kinetics studied. The kinetic data show, that Cr^V is produced as a result of the reaction $Cr^{IV}+Cr^{VI}\rightarrow 2Cr^V$. Water has a strong influence on the reaction as in its presence the process $3Cr^V\rightarrow 2Cr^{VI}+Cr^{III}$ takes place. If the reaction is carried out at a low pressure and water formed in the reaction course removed, the current Cr^V concentration i srelatively high and the Cr^V complex with ethylene glycol stabilized for several days at room temperature. The final products of ethylene glycol oxidation are water and glycol aldehyde, no cleavage reaction being found to proceed in these conditions.

Introduction

Recently an increased interest is observed on the investigations on dynamically polarized proton targets for high energy experiments. One of the most suitable target of this type is chromium(V)-ethylene glycol complex with the highest degree of polarization obtained up to now.[1,2]

The formation of such a complex was established several years ago[3] as an intermediate in the interaction of ethylene glycol with Cr^{VI} but the chemical reactions vs. leading to its formation were not studied at all. This problem, however, is of great importance because the efficiency of the target depends on the $[Cr^V]:[Cr^{III}]$ ratio in the system.[4] Best results can be obtained, therefore, if we know the reaction mechanism and can carry out the reaction on conditions where a maximal value of this ratio could be obtained.

The oxidation of ethylene glycol by chromic acid has been studied only in water acidic solutions.[5,6] It was shown that the substrate oxidation proceeds in two parallel pathways: a) by the removal of hydrogen atom alpha to the OH group and b) by the cleavage of the C–C bond. Chromium(V) has not been found as an intermediate in this case, formaldehyde, formic acid, glyoxal, glycolic aldehyde and oxalic acid being the reaction products.

There are no reasons, however, to consider that the same reaction scheme can be applied for the reaction between $K_2Cr_2O_7$ and ethylene glycol without any other solvent or acid present, when the formation of Cr^V-ethylene glycol complex has been observed. On the contrary, Wiberg has pointed out[7] that in the oxidation of organic substrates by Cr^{VI} the change in the reaction conditions and particularly of the reaction medium could strongly affect the mechanism because of the significant difference in the reactivity of Cr^{VI} and Cr^V, supposed to be an intermediate in such reactions.

For these reasons the present investigation deals with the mechanism of the reaction between potassium dichromate and ethylene glycol in the absence of any other substances that could participate as reactants or solvents in the reaction.

Experimental Section

Kinetic Method. The ethylene glycol oxidation was studied at 80° in pseudo first-order conditions, $[Etgly]:[K_2Cr_2O_7] = 26$. The ESR method was used to follow the reaction kinetics, monitoring the concentration of the paramagnetic complexes of Cr^V and Cr^{III}.

In all the experiments finely ground $K_2Cr_2O_7$ (1.0 g) was added to ethylene glycol (10.0 ml) in a thermostated reaction vessel fitted with a magnetic stitter. Dichromate dissolves easily for 1-2 minutes with the formation of orange-brown homogeneous solution, which then slowly changes to greenish-brown and finally to bluish-green. Samples were taken out of the vessel in glass capillary tubes and measured on a ESR spectrometer in the X-band.

The formation of intermediate Cr^V species was established by the appearance of a well-defined signal in the reaction course with g-value about 1.98 and line width varrying from 3 to 36 Oe at room tempe-

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[1] H. Glättli, M. Odehnal, I. Ezratty, A. Malinovski and A. Abragam, *Phys. Leatters, 29A*, 250 (1969).

[2] A. Mazaike, H. Glättli, I. Ezratty, and A. Malinovski, *Phys. Letters, 30A*, 63 (1969).

[3] N.S. Garifyanov, B.M. Kozyrev, and V.N. Fedotov, *Doklady Academii Nauk. SSSR, 178*, 808 (1968).

[4] W. G. Williams and L. J. Thomas, *Rutherf. Lab. Reports*, 213, (1971).

[5] A.C. Chatterji and S.K. Mukherjee, *Z. phys. Chem.*, *207*, 372 (1957).

[6] A.C. Chatterji and S.K. Mukherjee, *ibid.*, *288*, 166 (1965).

[7] K.B. Wiberg and H. Schäfer, *J. Am. Chem. Soc.*, *91*, 933 (1969).

rature (Figure 1). This singlet can be resolved—in very dilute solutions the ESR spectrum consists of nine narrow lines from the eight hydrogens of the Cr^V complex and shows a four-component hyperfine structure from the isotope ^{53}Cr.

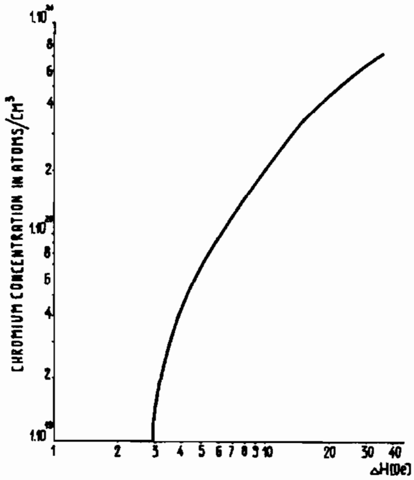

Figure 1. ESR Line Width (p.t.p. in the derivative curve) vs. Absolute Concentration of Cr^V in atoms. cm^{-3}.

Chromium(III) shows a very broad singlet analogous to that obtained by Levanon and Charbinsky[8] with the same g-factor as Cr^V. The line width varries in the reaction course from 350 to 400 Oe probably due to the increasing viscosity in the system.

The samples were measured together with DPPH as a standard and the concentrations of the paramagnetic species were calculated by a double integration of the derivative curves. A correction was made for the different g-factors and spin values of the paramagnetic chromium species and the standard sample. The calculated final Cr^{III} concentration was found to be about 8% higher than the total chromium concentration in the solution. This is probably due to the dielectric constant of ethylene glycol and some geomeric factors not taken into account.

Materials. All the reagents used were of AR grade. Ethylene glycol was dried for 10 days over anhydrous Na_2SO_4 and distilled at 12 mm Hg. Very finely ground $K_2Cr_2O_7$ was used, dried for two hours at 110°.

The glycolic aldehyde used for comparison in the spectral investigations was synthetized according to Fenton and Jackson.[9] The product was separated from the iron salts used in the synthesis by extraction with dioxan. The latter was then removed by heating to 40° at 12 mm Hg, the residue being a mixture of glycolic aldehyde and ethylene glycol.

The standard chromium(V) compound we have used, Na_3CrO_4, was synthetized according to Scholder and Schwarz.[10] It was obtained with 100% yield and used without any further purification. Because of its instability in the presence of oxygen and traces of water it was stored in a dry nitrogen atmosphere.

Optical Spectra. Electronic spectra in the visible and UV region were obtained on a spectrometer Specord UV-VIS, Carl Zeiss Jena and infrared spectra—on a spectrometer IR-10, Carl Zeiss Jena.

Results

Kinetic Data. The ESR data have shown that while the Cr^{III} concentration increases in the reaction course the concentration of the Cr^V complex proceeds through a maximum (Figure 2). It is noteworthy that the current concentration of this complex is too high—at 80° in the maximum it corresponds nearly to 50% of the total chromium concentration.

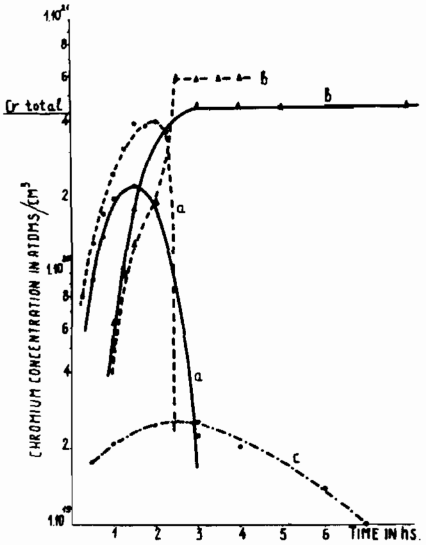

Figure 2. Reaction Kinetics at 80°. Full lines — in the presence of water formed in the reaction: a) Cr^V concentration b) Cr^{III} concentration. Dashed lines — water removed: a) Cr^V concentration b) Cr^{III} concentration. Curve c: Cr^V concentration in the presence of 20 vol.% water added initially.

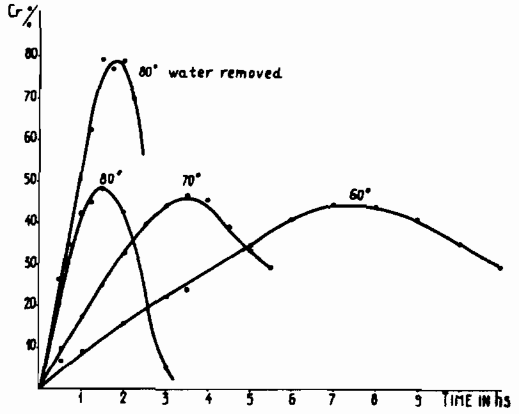

Figure 3. Time Dependence of Cr^V Concentration for Different Temperatures. The concentration of Cr^V is given in percents according to the total chromium concentration.

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(8) H. Levanon and S. Charbinsky, *J. Chem. Phys.*, *53*, 3056 (1970).
(9) H.J.H. Fenton and H. Jackson, *J. Chem. Soc.*, *75*, 1 (1899).
(10) R. Scholder and H. Schwarz, *Z. anorg. allg. Chem.*, *326*, 1 (1963).

At lower temperatures the maximum becomes broader but the maximal concentration of the Cr^V complex decreases in a small extent only (Figure 3). That means that at lower temperatures the complex could be established as a stable species for a relatively long period. Experiments with samples heated at 80° for 1½ hours (corresponding to t_{max}) and then sharply cooled to room temperature showed high concentration of the complex for several days. Analogous results were obtained also with the same complex prepared from Na_3CrO_4 and ethylene glycol.

Water was found to exhibit a strong influence on the reaction kinetics. When water formed as a reaction product remains in the system, a dispropotionation process takes place

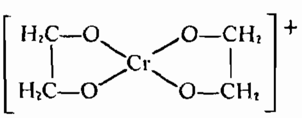
$$3Cr^{V} \rightarrow 2Cr^{VI} + Cr^{III} \qquad (1)$$

which regenerates partly Cr^{VI} on account of Cr^{V}.[11]

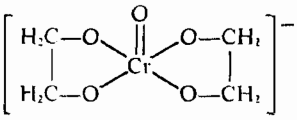
If the reaction is carried out at lower pressure (12 mm Hg) and water is pumped out during the reaction course a higher maximal $[Cr^V]$ — value is observed (Figure 2).

The role of water was proved by experiment when 2 ml H_2O were added initially to the reaction mixture, the amount of $K_2Cr_2O_7$ also being increased correspondingly in order to keep the initial Cr^{VI} concentration the same. In this case the maximal Cr^V concentration is about 10 times lower but after the maximum it decreases slower than in the absence of water (Figure 2c).

Identification of the Intermediate Cr^V Complex. The fact that the ESR spectrum of the Cr^V intermediate consists of nine lines shows that it is bonded in a complex having eight equivalent hydrogen atoms in it. Two possible structures could account for this spectrum:



A



B

The structure B keeping one double bond $Cr=O$ seems more probable but it contradicts to the idea for Cr^V having a coordination number of 4. The IR spectra, namely the frequency corresponding to $Cr=O$, could not be used satisfactorily because of the two bands at 860 and 880 cm^{-1} due to CH_2 rocking vibration $\delta(CH)$ which practically coincides with $\nu_{Cr=O}$.

The opposite charges of A and B offer another possibility for discriminating between these structures. Using ion-exchange resins we have found that the paramagnetic Cr^V complex is negatively charged and therefore the structure B is to be prefered.

This result is in accordance with the idea developed by Kon.[12] This author considers that oxygen in the CrO^{3+} unit causes a sufficiently large perturbation of the microcrystalline field that makes possible the observation of relatively narrow line in the ESR spectra of Cr^V complexes.

Dissolving Na_3CrO_4 in ethylene glycol at room temperature we have obtained Cr^V-ethylene glycol complex with the same ESR spectrum as that obtained in the reaction system.

No other ESR signals due to paramagnetic intermediates such as Cr^{IV} or organic radicals were found in the reaction solution in the course of the process.

Identification of the Final Reaction Products. It was found that the only product of ethylene glycol oxidation in the reaction conditions we have used is glycolic aldehyde.

After the end of the reaction when Cr^{VI} is completely reduced to Cr^{III} the reaction mixture was distilled at 12 mm Hg. and two fractions were obtained: a) at $t° < 100°$ and b) $100° < t° < 180°$. The fraction a) consists mainly of water and some ethylene glycol, while b) contains ethylene glycol and glycolic aldehyde. The latter was identified by the hydrazone formed with 2,4-dinitrophenylhydrazine[13] (m.p. 155-157°, after recrystalization from EtOH 153-155°).

Analogous results were obtained when the reaction system was treated after the completion of the reaction with 1 ml conc. $HCl + 20$ ml H_2O, heated to boiling and the vapours passed through 2,4-dinitrophenylhydrazine solution, No other aldeyde products (*e.g.* glyoxal) were found with the hydrazone reaction used.

The melting point of the corresponding hydrazone formed by formaldehyde is very near to that obtained by glycolic aldehyde and small amounts of HCHO could be missed. For that reason we studied also the electronic and vibration spectra of glycolic aldehyde and compared them with those of the reaction solution.

We have found that in the UV-region glycolic aldehyde shows a symmetric absorption band at 267 nm which we assigned to $n \rightarrow \pi^*$ transition. This band was found in the spectrum of the fraction b) and with a very low intensity in the fraction a). It was also found in the residue after the distillation of both these fractions. For this purpose the solid dark-green residue was dissolved in conc. CH_3COOH and treated with anion exchange resin Wofatit L-150 in order to remove Cr^{III}. Sodium hydroxide 0.5 N was used as an eluent and the transmittance of these eluates studied in the UV-region.

No other bands in the range 250-380 nm were found that could be due to formaldehyde, glyoxal, oxalic or formic acids.

Infrared spectra were also used for identification of the product. In the progress of the reaction a new band with increasing intensity appears at 1652 cm^{-1}. Using the fingerprint method we have found that this band must be assigned to a valent $C=O$ vibration in glycolic aldehyde. The lowering of this frequency which in aldehyde usually appears at about 1720-1740 cm^{-1} could be ascribed to the presence of HO-group in alpha position and the formation of intramolecular chelate system.

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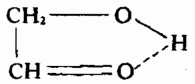
(11) N. Bailey and M.C.R. Symons, *J. Chem. Soc.*, 203 (1957).

(12) H. Kon, *Bull. Chem. Soc. Japan*, 35, 2054 (1962).

(13) H. Collatz and C. Neuberg, *Biochem. Z.*, 255, 29 (1932).



Other compounds with similar structure and low C=O frequency are known in the literature.[14]

After the end of the reaction when Cr^{III} is the only chromium species present it was found as a complex with the reaction product—glycolic aldehyde. As a result of the coordination $\nu_{C=O}$ is lowered from 1652 cm^{-1} to 1610 cm^{-1}. Analogous band is found also to appear in the range 1570-1660 cm^{-1} in the spectra of other metal chelate complexes with two oxygen donors.[15-17]

The band at 1610 cm^{-1} appears and increases in intensity in the course of the process. It was found also in the IR spectrum of the residue obtained after distillation of the reaction mixture at 180° and 12 nm Hg, when pracically no ethylene glycol remains. The residue was dissolved in conc. CH_3COOH and sorbed on anion exchange resin Wofatit L-150. The alkaline eluate (0.5 N NaOH used as eluent) after evaporation to drynes shows only the band at 1652 cm^{-1}, due to the free glycolic aldehyde.

The IR spectra of systems containing Cr^{V} and ethylene glycol show the presence of a new band at 1310 cm^{-1}. Krimm, Liang and Sutherland[18] have suggested that OH in-plane deformation frequency δ(OH) in an associated alcohol molecule interacts with δ-(CH) giving rise to two mixed vibrations with corresponding absorption bands near 1330 cm^{-1} and 1410 cm^{-1}. It may be assumed therefore that the band at 1310 cm^{-1} appears as a result of the complexation process between the diol molecule and Cr^{V}.* Miyake[19] has also observed similar band at 1307 cm^{-1} in the IR spectra of ethylene glycol complexes with Ni^{II} and Co^{II}.

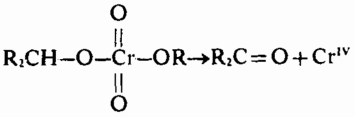
It should be mentioned that the band at 1310 cm^{-1} appears also in the IR spectrum of the reaction mixture after the end of the reaction but with a much lower intensity. Most probably here it is due to a complexation between Cr^{III} and the reaction product glycolic aldehyde.

In spite of the fact that HCHO was not found as a reaction product it seems possible that small amounts of eventually formed HCHO could be missed because of its volatility when samples were taken out of the reaction vessel. For that reason a run was carried out at 12 mm Hg not taking any samples from the mixture and connecting a liquid air cooled trap between the reaction vessel and the pump. The condensate (1.0 ml) contained only water and traces of ethylene glycol, no other products being found in it.

Discussion

It was proposed first by Westheimer[20] and proved by Wiberg[21] that the first stage in primary and secondary alcohol oxidation by Cr^{VI} is a fast formation of esters that might be regarded also as Cr^{VI} complexes. The fact that $K_2Cr_2O_7$ dissolves very readily in ethylene glycol with the formation of homogeneous orange-brown solution seems also to be due to such a complexation especially taking into acocunt the possibility for a chelate formation with ethylene glycol.

As to the first oxidation step of the process we have no data that contradict to the well-known reaction scheme for alcohol oxidation[21] which includes the formation of Cr^{IV} as an intermediate in the Cr^{VI} reduction.



$$R_2CH-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{Cr}}-OR \rightarrow R_2C=O+Cr^{IV}$$

Two different opinions exist, however, for the further fate of Cr^{IV} and the mechanism of Cr^{V} formation. Watanabe and Westheimer[22] put forward the idea that Cr^{IV} reacts with Cr^{VI} to produce Cr^{V} which is reduced further by the substrate with the formation of the final chromium species Cr^{III}:

$$Cr^{IV}+Cr^{VI}\rightarrow 2Cr^{V} \quad (3)$$

$$Cr^{V}+R_2CH-OH\rightarrow R_2C=O+Cr^{III} \quad (4)$$

According to Roček[23] Cr^{IV} oxidizes the substrate to a free radical which then reacts with Cr^{VI} to aldehyde and Cr^{V}:

$$R_2CHOH+Cr^{IV}\rightarrow R_2\dot{C}OH+Cr^{III} \quad (5)$$

$$R_2\dot{C}OH+Cr^{VI}\rightarrow R_2C=O+Cr^{V} \quad (6)$$

$$R_2CHOH+Cr^{V}\rightarrow R_2C=O+Cr^{III} \quad (7)$$

Our kinetic data offer a possibility for a reliable discrimination between these two schemes. If Watanabe-Westheimer mechanism is really operating, it follows from (3) and (4) that the condition $[Cr^{V}]>[Cr^{III}]$ is to be fulfilled before the maximum in the Cr^{V} concentration.

On the other hand if the Roček scheme is realized in the case, the reverse should be expected, *i.e.* $[Cr^{III}]>[Cr^{V}]$.

The experimental results show that for any moment in the period before the maximal $[Cr^{V}]$ is obtained, Cr^{V} is present always in larger concentrations then Cr^{III} *i.e.* $[Cr^{V}]:[Cr^{III}]>1$ and hence Watanabe-Westheimer mechanism for the Cr^{V} production is valid in the case (Figure 4).

The fact that we did not detect any formaldehyde amongst the reaction products shows that no cleavage reaction proceeds in the reaction conditions used.

(*) It was practically impossible to find any change in the absorption near 1400 cm^{-1} because of the series of intensive lines in the range 1340-1480 cm^{-1} due to ethylene glycol.

(14) L.J. Bellami and L. Beecher, *J. Chem. Soc.*, 4487 (1954).

(15) L.J. Bellami and R.F. Branch, *J. Chem. Soc.*, 4491 (1954).

(16) L.J. Bellami, G.S. Spicer and J.D. Strickland, *J. Chem. Soc.*, 4653, (1952).

(17) K. Nakamoto, P. McCarthy, and B. Miniatas, *Spectrochim. Acta, 21*, 379 (1965).

(18) S. Krimm, C.Y. Liang, and G. Sutherland, *J. Chem. Phys.*, 25, 778 (1956).

(19) A. Miyake, *Bull. Chem. Soc. Japan*, 32, 1381 (1959).

(20) K.B. Wiberg, Oxidation in Organic Chemistry. New York: Academic Press, 161 (1965).

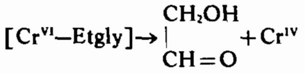
(21) K.B. Wiberg and H. Schäfer, *J. Am. Chem. Soc.*, *91*, 927 (1969).

(22) W. Watanabe and F.H. Westheimer, *J. Chem. Phys.*, *17*, 61 (1949).

(23) J. Roček and A. E. Radkowsky, *J. A. Chem. Soc.*, *90*, 2986 (1968).

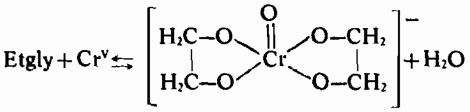
Therefore, the mechanism of the process can be represented as follows:

$$\text{Etgly} + \text{Cr}^{VI} \rightleftarrows [\text{Cr}^{VI}\text{–Etgly}] + H_2O \qquad (8)$$



$$[\text{Cr}^{VI}\text{–Etgly}] \rightarrow \begin{matrix} CH_2OH \\ | \\ CH{=}O \end{matrix} + \text{Cr}^{IV} \qquad (9)$$

$$\text{Cr}^{IV} + \text{Cr}^{VI} \rightarrow 2\text{Cr}^{V} \qquad (10)$$



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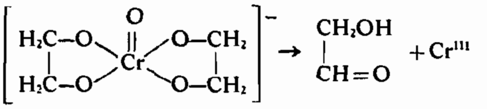

(12)

It seems interesting that Cr^{III} was found after the end of the reaction as a complex with the reaction product, glycolic aldehyde, and not with ethylene glycol, a ligand with a better donor properties, present in a large excess. Chromium(III) is formed, however, as a result of the redox reaction (12) taking place in the Cr^{V}-ethylene glycol complex and therefore both products are bonded together at the moment of their formation. On the other hand, because of its d^3 configuration Cr^{III} forms inert complexes and substitution of aldehyde by ethylene glycol could not be easily realized. Even when the reaction mixture after the end of the reaction is distilled and heated to 180° such a substitution does not proceed and Cr^{III} remains in the residue as a complex with glycolic aldehyde.

It is evident from Figure 4 that when water is pumped out of the system the $[\text{Cr}^{V}]:[\text{Cr}^{III}]$ ratio is increased. This fact was used in experiments carried out at Saclay in May, 1971, for dynamic nuclear polarization of Cr^{V}-Etgly targets obtained in this way. Better results were really found with such targets, than with the ordinary ones, when water was not removed from the system.

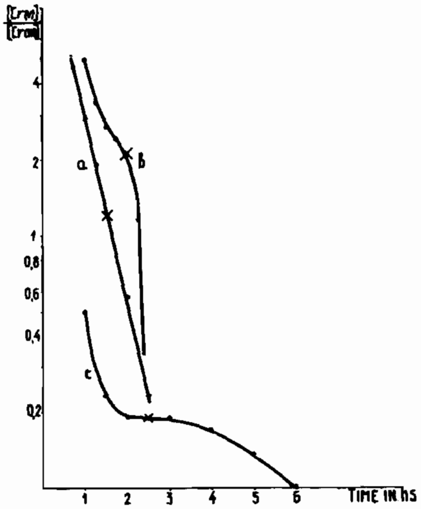

Figure 4. The $[\text{Cr}^{V}]:[\text{Cr}^{III}]$ Ratio for Different Reaction Conditions: a) water foremd in the reaction course present b) water removed by pumping out at 12 mm Hg c) 20 vol.% water added initially. The position of the maximum of the Cr^{V} concentration is shown with a cross on every curve.

The kinetics of oxidation of some other diols as di-, tri- and tetraethylene glycol, 1,3- and 1,4-butylene glycols, etc. by chromates was also studied and the work on the identification of the products is in progress. The oxidation reactions show a very high sensibility to light. The results of these investigations will be published in a short time.