

Kinetics of the reduction of oxalic acid by Cr(II) ions

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The results of kinetic study of the reduction of oxalic acid by chromium(II) ions in aqueous perchloric acid solution are described. The final product of this reaction is glycolic acid and some complexes consisting of Cr(III) and oxalic acid, which are formed by the catalytic effect of Cr(II) ions. The redox reaction is of second order with respect to the concentration of Cr(II) ions and its rate conspicuously increases with the decreasing concentration of hydrogen ions. The effect of chelate-forming reagents on the stoichiometry and reaction rate was also studied.

The presumable reaction mechanism is discussed on the basis of kinetic data obtained from the time dependence of polarographic limiting diffusion currents of Cr(II) ions.

The solutions of chromium(II) ions reduce some organic molecules [1–10]. If the oxidation agent contains an atom which can be a potential donor, the reduced form of the oxidation agent or at least a part of it is usually fastened in the coordination sphere of the primary Cr(III) ion formed. That is in operation just in the case of the reaction of oxalic acid with Cr(II) ions [4]. Thus the kinetic investigation of this reaction with the view of specifying the really reacting particles has been desirable and is the subject matter of this paper.

Experimental

The solution of Cr(II) ions was prepared by dissolving metallic chromium of 99.999% purity (Koch—Light) in 1 M-HClO₄ solution. Before dissolving, chromium was activated in 6 M-HCl for 5 minutes. All solutions with which Cr(II) ions came into contact were deprived of atmospheric oxygen by bubbling through nitrogen, appropriate for electric discharge lamp industry, which was purified by passing through the solutions of Cr(II) ions. The following anal. grade chemicals were used without further purification: oxalic acid (Lachema), perchloric acid (Apolda), sodium perchlorate (Fluka), disodium salt of ethylenediaminetetraacetic acid (Lachema), and sodium pyrophosphate (Lachema). Glyoxylic acid was in the form of 90% aqueous solution and glycolic acid was of chemical grade. The solutions were prepared by using distilled water.

The experiments with ion exchangers were made to identify the Cr(III) products of redox reaction. A column filled with Dowex 50W-X2, 200–400 mesh in H⁺ form was used. The length of column was 8 cm, its diameter 1 cm. The spectra of reaction products were recorded with a Specord (Zeiss, Jena) spectrophotometer. The polarographic measurements were made with an OH-102 (Radelkis) polarograph. The Kalousek vessel adapted for thermostating with water was used as a reaction vessel. The standard

calomel electrode was applied as a reference electrode while the dropping mercury electrode (drop time 4 s, flow rate 1.85 mg s⁻¹, mercury column height 64 cm) served as a measuring electrode. The temperature control of reaction system was accurate to $\pm 0.1^\circ\text{C}$. The complete removal of oxygen as well as mixing of reaction system was achieved by bubbling through purified nitrogen.

The detection of glycolic acid was carried out by chromatography on MN 300 cellulose layer. The solvent system contained *n*-propanol and 25% ammonia (6 : 4). The detection was made with the reagent consisting of bromocresol green, bromophenol blue, and potassium permanganate solution. The R_F values of the standards were: oxalic acid 0.25, glyoxylic acid 0.25–0.30, glycolic acid 0.50, and perchloric acid 0.70.

The kinetics of oxalic acid reduction with chromium(II) ions in the aqueous perchloric acid solution was investigated polarographically by recording the temporal dependence of anodic limiting diffusion current of Cr(II) ions at the potential of -0.1 V against standard calomel electrode (SCE). It was verified that the limiting current of Cr(II) ions had the diffusion character. It did not change with time in the absence of oxalic acid. At the potential of -0.1 V against SCE none of all reacting substances or products but the Cr(II) ions make the current increase. On the basis of the experiments carried out with a sufficient excess of oxalic acid the rate constants were evaluated according to the kinetic equation of the second-order reaction

$$\frac{1}{i} - \frac{1}{i_0} = \frac{k_{\text{obs}}}{\alpha} t, \quad (1)$$

where i_0 and i are the heights of the limiting diffusion current of Cr(II) ions at the beginning of reaction and at the time t , respectively. The slope of the linear relationship $1/i = f(t)$ multiplied by the constant of the diffusion current of Cr(II) ions α gives the value of the rate constant k_{obs} which corresponds to a pseudo second-order reaction. The course of the reaction was usually followed for two half-life periods. The presented values of rate constants are an average of at least 3 measurements. The accuracy of individual determination of the rate constant is $\pm 7\%$.

Results

Stoichiometry

The preliminary experiments indicated that the redox reaction of Cr(II) ions with oxalic acid was very rapid at the concentration of hydrogen ions lower than 0.1 M and at the concentrations of reactants about 10^{-2} M. The stoichiometry of the reaction was established at $[\text{H}^+] = 0.1$ M and 25°C while the ionic strength regulated with sodium perchlorate was equal to 1.1. It was observed that in a solution originally containing both Cr(II) ions and oxalic acid in 2×10^{-2} M concentration the consumption of Cr(II) ions was 28% for $t = 1$ min., 32% for $t = 16$ min., 35% for $t = 32$ min., 37% for $t = 48$ min. and afterwards it did not practically change any more. In a solution containing oxalic acid in 4×10^{-2} M and Cr(II) ions in 2×10^{-2} M concentration the consumption of Cr(II) ions amounted to 69% after 48 minutes. The 95% consumption of Cr(II) ions could be observed in a solution containing oxalic acid in 6×10^{-2} M and Cr(II) ions in 2×10^{-2} M concentration. These results show clearly that the expected stoichiometry 4 moles of Cr(II) ions to 1 mole of oxalic acid has not been obtained under given conditions because the formation of the complexes consisting of Cr(III) ions and oxalic acid occurs and this process is catalyzed by Cr(II) ions. The consumption of Cr(II) ions in the reaction with oxalic acid may be raised by adding some complex-

-forming agents into the solution. An addition of 1.8×10^{-2} M-EDTA into the 1.8×10^{-2} M solution of Cr(II) ions effects an instantaneous colour change to slight violet-red. After adding 1.8×10^{-2} M oxalic acid the colour becomes markedly deeper and the consumption of Cr(II) ions reaches 80% in 30 minutes. The increase in the EDTA concentration to 3.6×10^{-2} M under equal conditions effects the concentration of Cr(II) to fall to zero in 5 minutes. If the EDTA concentration continues increasing, the reduction of EDTA with chromium(II) ions starts to be effective. The influence of pyrophosphate is still more expressive. Provided pyrophosphate, oxalic acid, and Cr(II) ions are present each in 1.8×10^{-2} M concentration in the solution, the concentration of Cr(II) ions decreases immediately to zero. The 2.7×10^{-2} M solution of pyrophosphate is able to cause the drop of the concentration of chromium(II) ions to zero in a 9×10^{-3} M solution of oxalic acid in which Cr(II) ions have originally been present in 1.8×10^{-2} M concentration.

The hexaaquochromic ions are not the reaction product even in the absence of chelate-forming agents. It follows from the experiments with ion exchangers because it is possible to eluate the complexes of Cr(III) ions from a column filled with catex even with the 0.1 M solution of HClO_4 . That is also confirmed by the absence of the polarographic cathodic wave with $E_{1/2} = -0.98$ V against SCE which belongs to the hexaaquochromic ions in 1 M solution of HClO_4 . In the cathodic part of the polarogram of reaction products no wave occurs up to -1.3 V against SCE. The spectrophotometric investigation of the reaction shows an increase in absorbance in the visible spectral region and a colour change from bright blue colour of Cr(II) ions to grey-blue. The absorbance of reaction products is in the region of about 390 nm much higher than that which should correspond to hexaaquochromic ions. In the presence of EDTA or pyrophosphate ions the spectra of products are in a good agreement with the spectra of the Cr(III) complexes involving the above chelate-forming agents.

To determine the character of organic products of the redox reaction between Cr(II) ions and oxalic acid, 5 ml of the 0.6 M solution of Cr(II) in 1 M- HClO_4 and 10 ml of the 1 M solution of oxalic acid were allowed to react at 25°C. After one week the chromatographic analysis on cellulose layer was carried out. This period of time is sufficient for the system to get into the state of thermodynamic equilibrium. Under given conditions it means that other ligands coordinated to Cr(III) complexes are replaced by oxalate ions because oxalic acid used in excess forms more stable complexes with Cr(III) ions than other ligands, which must be considered. The results showed that glycolic acid was the final product of the redox reaction. The unconsumed oxalic acid present in excess was also detected. But no other organic compounds which could be products of the reaction were observed on chromatograms.

Kinetics

The reaction order with respect to the concentration of Cr(II) ions in excess oxalic acid was determined by the integral method using the time dependence of the anodic limiting current of Cr(II) ions. The linear character of the relationship $1/i = f(t)$ gives evidence that the reaction is of second order with respect to the concentration of Cr(II) ions (Fig. 1). The linear relationship

$$\log k_{\text{obs}} = f(\log [\text{oxalic acid}]) \quad (2)$$

was used for the determination of its slope, oxalic acid being present in sufficient excess. Thus it was found that the slope of this straight line equals 2.91 at 25°C for $[\text{H}^+] = 0.4$ M and ionic strength $\mu = 1$. That indicates the third reaction order with respect to the concentration of oxalic acid. A variation of the concentration of hydrogen ions showed

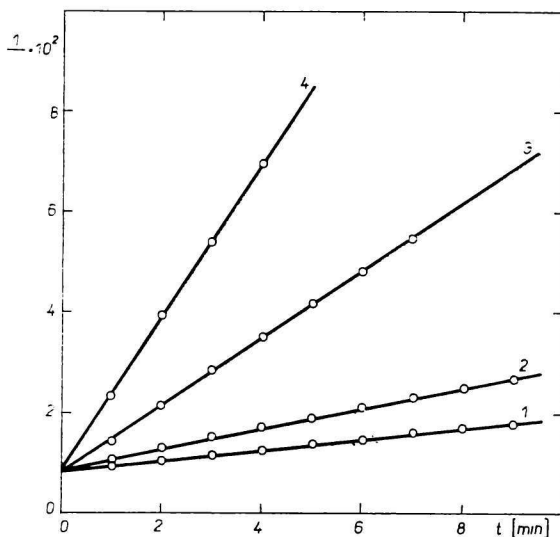


Fig. 1. Reaction of Cr(II) ions with oxalic acid. Evidence of the second-order reaction with respect to the concentration of Cr(II) ions.

2×10^{-3} M-Cr(II), 0.4 M-HClO₄, temperature 25°C, ionic strength 1. Concentration of oxalic acid: 1. 0.08 M; 2. 0.1 M; 3. 0.15 M; 4. 0.2 M.

Table 1

Effect of hydrogen ion concentration and temperature on the measured rate constant of the reaction of Cr(II) ions with oxalic acid

t [°C]	[H ⁺]	k_{obs} [l mol ⁻¹ s ⁻¹]
15	0.21	21.00
15	0.31	8.31
15	0.41	2.31
15	0.61	0.82
25	0.21	20.1
25	0.31	5.65
25	0.40	2.01
25	0.51	1.16
25	0.81	0.26
40	0.21	13.1
40	0.31	4.16
40	0.41	1.78
40	0.61	0.52
40	0.81	0.26

2×10^{-3} M Cr(II), 10^{-1} M oxalic acid, ionic strength 1.

that the rate equation had to involve a term which should express the indirect dependence of the reaction rate on hydrogen ion concentration (Table 1). The plots of the dependence of the observed rate constant on $[\text{H}^+]^{-3}$ are straight lines which go practically through the origin for all temperatures of the measurements. The rate law for the redox reaction between Cr(II) ions and oxalic acid thus assumes the form

$$-\frac{d[\text{Cr(II)}]}{dt} = \left(k_0 + \frac{k_1}{[\text{H}^+]^3} \right) [\text{Cr(II)}]^2 [\text{H}_2\text{Ox}]^3 \quad (3)$$

The value of k_0 approaches zero and $k_1 = 1.90 \times 10^2 \text{ l mol}^{-1} \text{ s}^{-1}$, $1.68 \times 10^2 \text{ l mol}^{-1} \text{ s}^{-1}$ and $1.24 \times 10^2 \text{ l mol}^{-1} \text{ s}^{-1}$ for the temperatures of 15, 25, and 40°C, respectively. As it follows from the data in Table 1, the rate of redox reaction decreases with increasing temperature at all hydrogen ion concentrations studied. This effect was investigated more thoroughly in the 0.41 M solution of HClO_4 where the reaction proceeds at a rate allowing to use a larger temperature interval. By using the linear relationship $\log k_{\text{obs}} = f(1/T)$, it was found that the apparent activation energy $E^\ddagger = -4.6 \pm 0.8 \text{ kcal mol}^{-1}$ for the ionic strength $\mu = 1$.

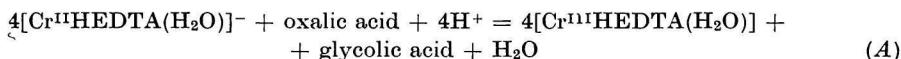
The change in ionic strength from 0.32 to 1.02 for $[\text{H}^+] = 0.32 \text{ M}$ has no effect on the reaction rate what may mean that at least one reacting particle has no electric charge. To evade the contribution of migration of the Cr(II) ions in their polarographic investigation, it was not possible to study the effect of the ionic strength on the reaction rate in the region where the Brönsted-Bjerrum equation is exactly valid. EDTA and pyrophosphate influence the rate of the redox reaction between Cr(II) ions and oxalic acid, too. EDTA in $1.8 \times 10^{-2} \text{ M}$ concentration brings about an increase in the reaction rate by 60% and the solution of pyrophosphate of equal concentration even by 124%. But the reaction remains of the second order with respect to chromium(II) ions.

Since glycolic acid is the final reaction product in the redox reaction between Cr(II) ions and oxalic acid, it may be assumed that the reduction of one carboxylic group of oxalic acid goes through aldehydic group and glyoxylic acid is therefore the supposed intermediate. The study of the reduction of glyoxylic acid with Cr(II) ions in the aqueous perchloric acid solution was carried out in order to verify this assumption. The measurements showed that the reaction was too fast to be measured by the used method at 20°C in 1 M- or 0.01 M- HClO_4 solutions in the case of about 10^{-4} M concentrations of reactants. Provided the overall order of the reaction equals two, it means that the rate constant of this reaction is greater than $10^2 \text{ l mol}^{-1} \text{ s}^{-1}$. The stoichiometric ratio of two moles of Cr(II) ions to one mole of glyoxylic acid was determined by polarometric titration. The analysis of organic products by chromatography on cellulose layer gave evidence that glycolic acid was the organic product of the redox reaction. The absorption spectrum of the reaction products in 1 M- HClO_4 shows maxima at 412 and 574 nm which, together with the behaviour of inorganic products on a column filled with Dowex 50W-X2, confirm that hexaquo chromic ions are the primary product of the redox reaction. The absence of $\text{Cr}_{\text{aq}}^{3+}$ ions as products in the reduction of oxalic acid with Cr(II) ions does not, however, exclude the possibility that the reaction proceeds through glyoxylic acid because the anation of oxalic acid with $\text{Cr}_{\text{aq}}^{3+}$ ions is rapid in the presence of Cr(II) ions [19] and all experiments were made in excess oxalic acid.

Discussion

The solution of Cr(II) ions prepared by dissolving metallic chromium in perchloric acid contains a small amount (less than 5%) of Cr(III) ions as impurities. After adding EDTA or pyrophosphate into such a solution, the formation of the Cr(II) complex with chelate-forming agent and on the other hand the transfer of EDTA or pyrophosphate into the

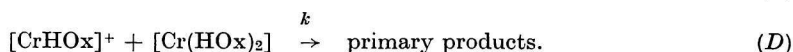
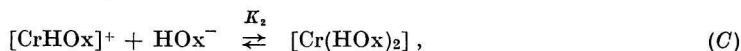
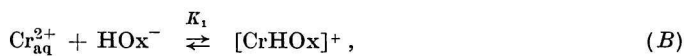
coordination sphere of Cr(III) present as impurity occurs. These reactions are rapid and take place during mixing [11]. The concentration of the Cr(III)–EDTA complex thus formed is equal to the original concentration of Cr(III) ions. The Cr(III)–EDTA complex is in the form of $[\text{Cr}^{\text{III}}\text{HEDTA}(\text{H}_2\text{O})]$ and conjugated base $[\text{Cr}^{\text{III}}\text{EDTA}(\text{H}_2\text{O})]^-$. For the dissociation of the first stage pK_A equals 3.1 and the equilibrium is established rapidly [12]. Both the forms have absorption maxima at 390 and 540 nm with the absorption coefficients 113 and $167 \text{ l mol}^{-1} \text{ cm}^{-1}$ for the form dominant in the given medium [11]. The formation constant of the $[\text{Cr}^{\text{II}}\text{EDTA}(\text{H}_2\text{O})]^{2-}$ complex is $10^{13.6}$ while the association constant of formation of the protonated $[\text{Cr}^{\text{II}}\text{HEDTA}(\text{H}_2\text{O})]^-$ complex equals 10^3 [13]. The shape of the spectrum of $[\text{Cr}^{\text{II}}\text{EDTA}(\text{H}_2\text{O})]^{2-}$ ($\epsilon_{\text{max}} = 15 \text{ l mol}^{-1} \text{ cm}^{-1}$ at 740 nm) is similar to that of the spectrum of $\text{Cr}_{\text{aq}}^{2+}$ ions and in the presence of Cr(III)–EDTA complexes the contribution of the absorbance of Cr(II) ions is negligible. The Cr(II) and Cr(III) complexes with EDTA contain one molecule of water in their first coordination sphere [13, 14]. The experimental results suggest that in the presence of sufficient amount of EDTA the reduction of oxalic acid with Cr(II) ions should proceed under given conditions according to the following overall stoichiometric equation



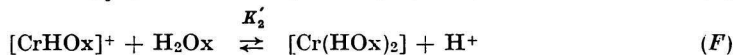
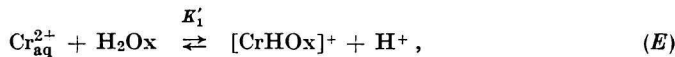
The Cr(II)–EDTA ions are stronger reduction agents than hexaaquochromic ions. That follows from a comparison of standard redox potentials [15]. According to the theory of Marcus [16, 17] the rate of the reactions with electron transfer increases with free reaction enthalpy. Most reactions of Cr(II) ions proceed by inner-sphere mechanism [18]. The possibility of outer-sphere mechanism in the redox reactions of the Cr(II)–EDTA ions [11] as well as of the inner-sphere mechanism [15] has been discussed recently. It is, however, probable that a favourable change in free enthalpy also contributes to the rate of the redox reactions, which proceed by inner-sphere mechanism.

In the absence of chelate-forming agents the consumption of oxalic acid in the reaction with Cr(II) ions is substantially greater than it follows from expected stoichiometry. That means that oxalic acid is consumed not only in the redox reaction but also in a substitution reaction with the oxidation product of Cr(II) ions catalyzed by Cr(II) ions. It is known that the anation of hexaaquochromic ions with oxalic acid is catalyzed by Cr(II) ions and is very rapid [19]. Cr(II) ions play a similar part in the aequation of $[\text{Cr}^{\text{III}}(\text{Ox})_3]^{3-}$, which is essentially slower as well as in *trans-cis* isomerization of chromium bis-oxalate. The fact that the formation of the Cr(III)-oxalate complexes is effective in the reaction of Cr(II) ions with oxalic acid is in agreement with the paper of Milburn and Taube [4].

The dependence of the rate constant on hydrogen ion concentration may be interpreted by the mechanism involving a fast equilibrium reaction in which protons are produced. This mechanism is effective before the rate-determining step. The hydrolysis of $\text{Cr}_{\text{aq}}^{2+}$ ions in acid solutions is negligible [21] and the dissociation of oxalic acid is the step in which hydrogen ions are produced. The kinetic results conform with the following reaction scheme



The equilibrium in reactions (B) and (C) is established rapidly because of the substitution lability of Cr(II) ions. The mechanism suggested is in agreement with the experimentally determined rate law on condition that the values of K_1 and K_2 are not too high. Kinetically it is not possible to distinguish the above mechanism from the mechanism in which the dissociation of proton takes place after the complex of $\text{Cr}_{\text{aq}}^{2+}$ with oxalic acid has been formed



with the same rate-determining step (D).

The numerical values of equilibrium constants of the complexes of Cr(II) with oxalic acid should be known in order that we might be able to calculate the rate constant k and activation parameters of the rate-determining step. Reactions of the type (B), (C) and (E), (F) usually show negative reaction enthalpies. Since the experimentally established activation energy is composed of the heat effects of reactions (B), (C) or (E), (F) and the activation energy of reaction (D) (the dissociation constant of oxalic acid does not practically change in the temperature interval used), its negative value is not too surprising.

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