

A KINETIC STUDY OF THE REDUCTION OF MALEIC AND FUMARIC ACID BY CHROMIUM(II) IONS

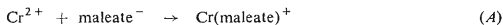
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A kinetic study was made of the reduction of maleic and fumaric acid by chromium(II) ions in aqueous perchloric acid. The products of the redox reaction are hexaaquochromium(III) and tetraaquisuccinatochromium(III) ions. The reactions are first order both in chromium(II) ions and in the oxidizing agent. With fumaric acid as oxidizing agent the rate equation contains term which expresses inverse dependence of reaction rate on the concentration of hydrogen ions. Activation parameters for both reactions are reported. The kinetic data, obtained polarographically, are discussed in terms of the mechanism of the reactions.

The reduction of maleic and fumaric acid by chromium(II) ions in the acidic¹ as well as the ammonia² medium yields succinic acid as the final product. A qualitative study of the reduction of maleic and fumaric acid and their diesters in perchloric acid medium was performed by Malliaris and Katakis³ who employed matrix analysis of spectrophotometric data. The rate determining



step suggested by these authors for the reduction of maleic acid (Eq. (A)) is at variance with the mechanism proposed by Castro, Stephens and Mojé⁴ on the basis of the study of the reduction of diesters of both acids. The latter authors assume that the formation of a chelate is fast equilibrium reaction, rate determining step being the attack of another Cr(II) ion on the Cr(II)-olefin complex. In the case of diethyl ester of maleic acid, the observed rate equation agrees, however, with the proposed mechanism only under assumption of a high ratio of initial concentration of Cr(II) ions to that of the diester.

We believed that a detailed kinetic study of redox reactions between Cr(II) ions and maleic or fumaric acid, which is the subject of the present study, could provide valuable information concerning the mechanism of mutual interaction and further that it could be useful in connection with the importance of the systems with conjugated double bonds, which serve as bridge groups in the activated complex in the reduction of Co(III) and Cr(III) complexes by Cr(II) ions.

EXPERIMENTAL

Chemicals. The following chemicals of analytical purity were used without further purification: maleic acid (Fluka A.G.), fumaric acid (Lachema), succinic acid (Carlo Erba), sodium per-

chlorate (Fluka), perchloric acid (Apolda), sodium chloride and hydrochloric acid (Lachema). Diethyl ether and methanol (both of analytical purity) were fractionated. All solutions were prepared using distilled water. A solution of chromium(II) was obtained by dissolving metallic chromium (99.999% purity, Koch-Light), activated by 6M-HCl for 5 minutes, in 2M-HClO₄. The HClO₄-solution was freed from atmospheric oxygen by passing through nitrogen (for electric bulbs) which was purified by bubbling through Cr(II) solutions.

Analysis. The analysis of organic products was made on Perkin-Elmer, Model F-11, gas chromatograph, using column filled with 7% poly(ethylene glycol succinate) on Chromosorb W 60/80 and the column temperature 110°C. The organic acids were extracted from the reaction mixture with ether, then converted by anhydrous methanol acidified by HCl to corresponding methyl esters which were determined chromatographically. The methylation was carried out at 90°C for 24 h. The Cr(III) complexes were analysed by means of chromatography on ion exchange resins. The two columns, filled with Dowex 50W-X 2 (200–400 mesh) in the H⁺ form, were used. The one was 6 cm long and 1 cm across, the other was 8 cm long and 0.5 cm across. The spectra of individual fractions were recorded on Perkin-Elmer 450 spectrophotometer. Some kinetic measurements were followed on MOM 202 spectrophotometer (Hungary).

Kinetics. Polarographic measurements were carried out on OH-102 recording polarograph (Radelkis). The reaction vessel was that designed by Kalousek and was equipped with jacket for outside heating by constant temperature water. The reference electrode was standard calomel electrode, the indication electrode was mercury dropping electrode with the time of drops 4 seconds and the flow rate 1.85 mg s⁻¹. The reaction temperature was maintained constant within 0.1°C. The perfect removal of oxygen and the efficient stirring of the reaction mixture were accomplished by bubbling the purified nitrogen through. The kinetics of the reduction of maleic and fumaric acid by Cr(II) ions in HClO₄ medium was followed polarographically, by recording the time dependence of anodic limiting diffusion current of Cr(II) ions at the potential of -0.1 V relative to normal calomel electrode (N.C.E.). It was found that the height of limiting diffusion current of Cr(II) ions is directly proportional to their concentration and does not change with time in the absence of maleic or fumaric acid. At the potential -0.1 V vs N.C.E. only Cr(II) ions are responsible for current increase. In experiments in which a sufficient excess of the oxidizing agent was used the rate constants were calculated according to first order kinetic equation (1), where i_0 and i are the heights of the limiting diffusion current of Cr(II) ions at time $t = 0$ and t , respectively. The value of rate constant k_M equals to the product of the rate constant of the second order reaction, k_B , and the oxidizing agent concentration, providing that the reaction order in the oxidizing agent is one. In experiments in which stoichiometric amounts of the reagents were used, rate constants were determined graphically, using the dependence of $1/i = f(t)$. The reaction was usually followed two half-times. The values of rate constants are averaged values of at least three measurements. The rate constants in individual runs were determined with relative error of $\pm 7\%$.

$$\log(i_0/i) = (k_M/2.3) t. \quad (1)$$

RESULTS

Reduction of Maleic Acid

Polarography. Polarographic method enabled us to follow simultaneously both the reactants and the Cr(III) complexes formed in HClO₄ medium. Chromium(II) ions give anodic wave with $E_{1/2} = -0.36$ V, maleic acid yields cathodic wave with $E_{1/2} =$

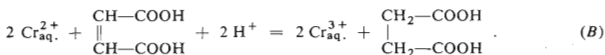
= -0.67 V and $E_{1/2}$ of $\text{Cr}_{\text{aq}}^{3+}$ = -0.98 V (all in 1M-HClO_4 against N.C.E.). When Cr(II) ions are added to a solution of maleic acid in 1M-HClO_4 freed from oxygen, besides the wave with $E_{1/2}$ = -0.98 V the new wave appears with the half-wave potential $E_{1/2}$ = -0.84 V. This wave increases during the reaction by the rate which equals to that of increase of the wave of hexaaquochromium(III) ions, until all the reducing agent is consumed. We have started from the assumption that during the redox reaction half-wave potentials of the formed Cr(III) complexes do not change. After completion of a comparatively fast redox reaction (reaction time was usually 5–10 minutes) the wave of $E_{1/2}$ = -0.84 V slowly decreases, which is accompanied by simultaneous increase of the height of the wave with $E_{1/2}$ = -0.98 V. After sufficient period of time (at 25°C c. one week, at 70°C after c. 3 h) only the wave corresponding to hexaaquochromium(III) ions can be observed on polarogram. With derivative connexion it is possible to follow the decrease of the peaks of maleic acid and chromium(II) ions and the increase of the peaks with maxima -0.84 V and -0.98 V vs N.C.E. in the course of the redox reaction.

Spectrophotometry. After mixing the reactants in 1M-HClO_4 , the absorbance in visible region increases. The bright blue solution of chromium(II) ions turns to the dark red, and after the redox reaction is completed the absorption curve has maxima at 410 nm and 520 nm. Then the absorbance begins to decrease slowly and the colour of the solution gradually changes to violet-blue. The position of the first maximum does not change with time, while the second maximum shifts finally to 572 nm. After sufficient period of time the spectrum resembles that of hexaaquochromium(III) ions.

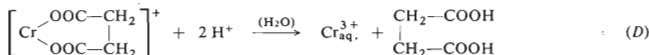
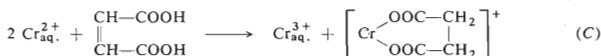
Gas chromatography. When excess of maleic acid is reacted with chromium(II) ions in 1M-HClO_4 , instantly after the completion of the redox reaction no organic products, except unreacted maleic acid, can be detected in the reaction mixture. If chromium(II) ions are used in excess, no organic product can be found. After standing the reaction mixture for sufficient period of time, with excess of maleic acid the products contain succinic acid and unconsumed maleic acid, with excess of chromium(II) ions the mixture contains only succinic acid and less than 1% of fumaric acid.

Experiments on ion exchangers. The analysis of reaction mixture instantly after the completion of the redox reaction showed that the reaction product are two chromium(III) complexes. The red complex can be eluted already by 0.2M-HClO_4 . The rate by which it is eluted by 0.5 and 1M-HClO_4 corresponds to the +1 charged complex. Its half-wave potential is -0.84 V vs N.C.E. (in 1M-HClO_4). Its absorption spectrum shows maxima at 410 nm (ϵ $63 \text{ l mol}^{-1} \text{ cm}^{-1}$) and 520 nm (ϵ $41 \text{ l mol}^{-1} \cdot \text{cm}^{-1}$). The blue complex is eluted by the rate corresponding to the +3 charged complex. Its half-wave potential is -0.98 V vs N.C.E. (in 1M-HClO_4). When the reaction mixture after the redox reaction is allowed to stand for sufficient period

of time, the blue complex of Cr(III) is the final reaction product. The fraction which cannot be eluted by 2M-HClO₄, consisting probably of binuclear Cr(III) complexes, is small. On the basis of experimental results it can be concluded that the overall stoichiometry of the reaction is



The reaction proceeds obviously in two steps. The first is comparatively fast redox reaction (Eq. (C)), the second one is slow hydrolysis of the succinate complex of Cr(III) (Eq. (D)).



Kinetics of the redox reaction. The reaction order in Cr(II) ions in the presence of the excess of maleic acid was determined by integral method, from the time dependence of limiting anodic diffusion current of Cr(II) ions. The linear form of the dependence (2) proves that the reaction is first order in Cr(II) ions (Fig. 1). From the dependence (3) it follows that the slope of the straight line equals to 1.3 at 1M concentration of hydrogen ions. From the experiments in which stoichiometric amounts of the reagents were used, overall order of the reaction $n = 2$ was determined by half-life method. The resultant rate equation has the form (4).

$$\log \frac{i_0}{i} = f(t), \quad (2)$$

$$\log k_M = f(\log [\text{maleic acid}]), \quad (3)$$

$$-\frac{d[\text{Cr}^{2+}]}{dt} = k_B[\text{Cr}^{2+}] \cdot [\text{maleic acid}]. \quad (4)$$

We have found that the reaction rate does not depend on the hydrogen ion concentration within the range of HClO₄ concentration, 0.04–0.1M at ionic strength 1 (adjusted by NaClO₄). At temperatures 293, 308 and 323K the values of the pseudo-first order rate constants k_M were successively $8.06 \cdot 10^{-3}$, $8.75 \cdot 10^{-3}$ and $10.3 \cdot 10^{-3} \text{ s}^{-1}$. The initial Cr(II) and maleic acid concentrations were respectively 10^{-3}M and $5 \cdot 10^{-2}\text{M}$. The concentration of hydrogen ions was 1M and ionic strength was 1. From the calculated values of $k_B = k_M/[\text{maleic acid}]$ the following activation para-

eters were obtained by means of Eyring equation: $\Delta H^\ddagger = 0.9 \pm 0.6 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -58.5 \pm 2 \text{ cal deg}^{-1} \text{ mol}^{-1}$. The chloride ions concentration 0.9M, similarly as the change of ionic strength from 0.1 to 1.8 at $[\text{H}^+] = 0.1\text{M}$ and 25°C have small effect on reaction rate. Rate constant decreased by 15% at the above change of ionic strength.

Kinetics of hydrolysis of the succinate complex of Cr(III). After separation on Dowex the solution of $\text{Cr}(\text{succinate})^+$ in 1M-HClO_4 was placed in a temperature controlled bath and the reaction was followed at temperatures 50, 60 and 70°C . Using spectrophotometric method we have followed the dependence of absorbance on time at the wavelength 410 nm, which is identical with the absorption curve maximum whose position does not change with time. The rate constants were determined from the relation (5)

$$\log \left(\frac{A_0 - A_\infty}{A_t - A_\infty} \right) = \frac{k}{2.3} \cdot t, \quad (5)$$

where A_0 and A_t is the absorbance read at times $t = 0$ and t , respectively, and A_∞ is the absorbance read when the solution was heated to 70°C for 3 h and when the position of the second maximum reached 572 nm. The observed linear dependence proves that the reaction is first order in 1M-HClO_4 . Activation parameters, determined in the same way as in the preceding section, were $\Delta H^\ddagger = 23.7 \pm 0.4 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -4.6 \pm 1.5 \text{ cal deg}^{-1} \text{ mol}^{-1}$. The effect of hydrogen ion concentration on reaction rate has not been studied in detail. It has been observed, however, that the reaction is catalysed by H^+ ions. The extrapolated value of rate constant for temperature 25°C , $k = 2.6 \cdot 10^{-6} \text{ s}^{-1}$ in 1M-HClO_4 , indicates that hydrolysis of the $\text{Cr}(\text{succinate})^+$ complex at room temperature is sufficiently slow.

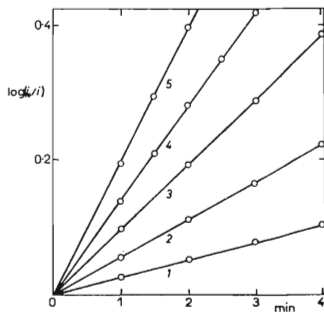


FIG. 1

Evidence for First Order in Cr(II) Ions in Their Reaction with Maleic Acid

10^{-3}M-Cr(II) , 1M-HClO_4 , maleic acid conc.: 1 0.01M; 2 0.02M; 3 0.03M; 4 0.04M; 5 0.05M; temperature 25°C .

Reduction of Fumaric Acid

Because of the lower solubility of fumaric acid in water we have not been able to carry out all the experiments as with the Cr(II) ions-maleic acid system. Nevertheless, the results speak for the similarity of both systems.

Experiments on ion exchangers. The analysis of inorganic products of the redox reaction between Cr(II) ions and fumaric acid in 1M-HClO₄ showed that the red Cr(III) complex is eluted by 0.5M-HClO₄ by the rate which corresponds to the +1 charged complex. The blue complex of Cr(III) is eluted by the rate corresponding to the +3 charged complex. The half-wave potential of the red complex was -0.84 V against N.C.E. and that of the blue one was -0.98 V against N.C.E. in 1M-HClO₄. After hydrolysis the only inorganic products present in the reaction mixture were hexaquo chromium(III) ions.

Gas chromatography. Only unreacted fumaric acid was found when the redox reaction was carried out in the excess of fumaric acid. When Cr(II) ions were used in excess, no free organic acid was formed. When fumaric acid was reacted with excess of Cr(II) ions at 70°C for 3 h, the dark red reaction mixture turned to blue solution and succinic acid was the sole product. Polarographically determined stoichiometry of the reaction is



and, similarly as in the case of maleic acid, the redox reaction is followed by hydrolysis of the Cr(III) succinate complex.

Kinetics of the redox reaction. The reaction order in Cr(II) ions was determined in the presence of an excess of fumaric acid from the dependence of anodic diffusion current of Cr(II) ions on time by integral method (Eq. (2)). The linear dependence within the region of $[\text{H}^+] = 0.04 - 1 \text{M}$ at temperatures 50 and 70°C proves that the reaction is of the first order in Cr(II) ions. The slope of the straight line (Eq. (3)) is 1.2 at $[\text{H}^+] = 1 \text{M}$. The dependence of rate constant on hydrogen ion concentration showed that rate equation has to include the term which expresses inverse dependence of reaction rate on $[\text{H}^+]$ (Eq. (6)),

$$-\frac{d[\text{Cr}^{2+}]}{dt} = \left(k_0 + \frac{k'_D}{[\text{H}^+]} \right) [\text{Cr}^{2+}] \cdot [\text{fumaric acid}], \quad (6)$$

where $k_0 = 3.30 \cdot 10^{-3} \pm 3 \cdot 10^{-4} \text{ l mol}^{-1} \text{ s}^{-1}$, $k'_D = 2.03 \cdot 10^{-3} \pm 1.5 \cdot 10^{-4} \text{ s}^{-1}$ at 50°C and ionic strength 1 (adjusted by NaClO₄). The concentration term for fumaric acid expresses total concentration of the oxidizing agent. Rate constant k_0 at 70°C is $4.02 \pm 0.3 \cdot 10^{-3} \text{ l mol}^{-1} \text{ s}^{-1}$ and k'_D is $2.17 \pm 0.15 \cdot 10^{-3} \text{ s}^{-1}$. These values were obtained from data listed in Table I. The effect of ionic strength is more

TABLE I

The Effect of Hydrogen Ion Concentration and Temperature on Pseudo-First Order Rate Constant for the Reaction of Cr(II) Ions with Fumaric Acid

10^{-3} M Cr(II) , $5 \cdot 10^{-2} \text{ M fumaric acid}$, ionic strength 1.

$T, \text{ K}$	$[\text{H}^+], \text{ M}$	$k_M \cdot 10^3, \text{ s}^{-1}$	$T, \text{ K}$	$[\text{H}^+], \text{ M}$	$k_M \cdot 10^3, \text{ s}^{-1}$
323	0.04	2.75	343	0.03	3.77
323	0.05	2.15	343	0.04	2.88
323	0.08	1.41	343	0.06	1.96
323	0.14	0.93	343	0.21	1.15
323	0.44	0.38	343	0.21	0.69
343	0.02	5.66			

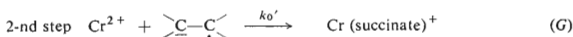
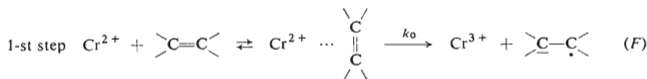
pronounced than in the reaction of maleic acid. From the dependence

$$\log k_M = f\left(\frac{\sqrt{\mu}}{1 + \sqrt{\mu}}\right), \quad (7)$$

which is roughly linear within the 0.06–1 ionic strength region at 0.06M hydrogen ion concentration, the slope of the straight line was found to be -0.6 .

DISCUSSION

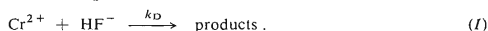
During the reduction of maleic acid and fumaric acid by chromium(II) ions binuclear Cr(III) complexes are not formed. As stoichiometry of the reaction requires 2 mol of Cr(II) per 1 mol of the unsaturated acid, the reaction being first order both in Cr(II) ions and in the oxidizing agent, the reaction involves two one-electron steps. The mechanism which agrees with experimental results can be depicted in the following way:



where $k'_0 \gg k_0$. An analogous mechanism was suggested for the reaction of Cr^{2+} ions with $\text{S}_2\text{O}_8^{2-}$ ions⁵, which proceeds *via* radicals and in which the ratio of the formed hexaquo chromium(III) ions to CrSO_4^+ ions equals to 1. The formation

of Cr^{3+} ions is explained or by the possibility of the occurrence of outer-sphere mechanism either hydrogen transfer. Reaction (G) cannot be rate determining since it is known that the interaction of Cr^{2+} with the radical is very fast, which is caused by the character of substitution labile Cr^{2+} ions. The reaction of another Cr^{2+} ion with the radical inhibits polymerization of the unreacted olefin. Similarly, the reduction of hydroxylamine by chromium(II) ions, though proceeding *via* NH_2 radicals, does not yield hydrazine⁶. In favour of the suggested mechanism speaks also the fact that diethyl esters of maleic and fumaric acids react with Cr^{2+} ions faster than do free acids⁴. The formation of the chelate with Cr^{2+} ions is inhibited in the case of the diesters and fumaric acid by steric factors. On the other hand, in the reduction of N-oxides by chromium(II) ions the reaction rate increases with increasing stability of the formed radical. For instance, dimethylaniline N-oxide reacts more rapidly than trimethylamine N-oxide, the latter being reduced faster than hydroxylamine⁶.

The dependence of rate constants on reciprocal value of hydrogen ion concentration, which in the case of fumaric acid is nearly linear, can be explained by the mechanism which involves fast reaction producing protons and preceding the rate determining step. The extent of hydrolysis of Cr^{2+} ions in acidic solutions is negligible⁷ and the rates of many redox reactions of Cr^{2+} ions do not depend on hydrogen ion concentration. The dissociation of fumaric acid is therefore the step which produces protons. Kinetic results can be explained by the system of two parallel reactions:



The major form of the oxidizing agent in the studied region of hydrogen ion concentrations is undissociated fumaric acid (H_2F) and the experimental parameter k_D' equals therefore to $k_D \cdot K$. Based on known value of dissociation constant of fumaric acid at 25°C ($K = 9.57 \cdot 10^{-4} \text{ mol l}^{-1}$) and assuming that at 50°C the value of the constant would be by 10% lower and at 70°C by further 10% lower, we have determined $k_D = 2.36 \pm 0.2 \text{ l mol}^{-1} \text{ s}^{-1}$ for 50°C and $2.82 \pm 0.2 \text{ l mol}^{-1} \text{ s}^{-1}$ for 70°C. These results enabled us to estimate activation parameters for the reaction path involving dissociated fumaric acid, $\Delta H^\ddagger = 1.4 \pm 0.8 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -53.5 \pm 3 \text{ cal deg}^{-1} \text{ mol}^{-1}$, and for that involving the undissociated acid, $\Delta H^\ddagger = 1.5 \pm 0.8 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -65.1 \pm 3 \text{ cal deg}^{-1} \text{ mol}^{-1}$, at ionic strength 1. The k_D to k_0 ratio is approximately 700.

Gould and Taube⁸ explains the inverse dependence of reaction rate on hydrogen ion concentration, observed in the reduction of Co(III) complexes of dicarboxylic acids by chromium(II) ions, by the reaction path in which the complex has the remote carboxylic group ionized. The rate constant for this path is around 10^3 greater than for the reaction with the nonionized group. One of the factors which are responsible for rate increase in the case of the dissociated acid is the

negative charge residing on carboxylic group. However, this cannot be the sole one, since in the case of maleic acid the reaction rate does not depend on hydrogen ion concentration, indicating that dissociated acid reacts in the rate which is comparable with, or even slower than that of the reaction of undissociated acid. Similar magnitude of activation parameters for maleic and fumaric acid, as well as for k_D path in the case of fumaric acid, supports the assumption that all three cases have the same mechanism of reduction.

In a study of the reduction of maleic and fumaric acid and their diesters by V^{2+} ions it was reported that free acids as well as monoesters are reduced smoothly, while diesters are not⁹. This indicates the necessity, but also sufficiency, of one free carboxylic group and the different mechanism from that by which the reduction by chromium(II) ions proceeds.

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