The Mechanism of Reduction of Maleic Acid by Chromous Ion

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The reduction of maleic acid by chromous ion in acid solution is studied. A less systematic study is also made of the reduction of fumaric acid and the maleic and fumaric diethyl esters. A matrix analysis of the spectrophotometric data gives information on the number of species formed and the relations between them. On the basis of this analysis and chromatographic and kinetic data, a simple mechanism for the main path of the reaction is proposed and discussed.

Examples of reduction of both the carbon–carbon double bond and the carbon–oxygen double bond by chromous and vanadous ions have been given in a number of cases in acid,[2] aqueous ammonia,[3] and ethanol media.[4] The reduction yields either monomolecular products by transfer of two electrons, or bimolecular products by dimerization of the free radicals formed by one-electron transfer. Maleic and fumaric acids, in particular, on heating with an excess of chromous ion give succinic acid.[5] A more detailed investigation, however, of this reaction seems desirable, especially in view of recent discoveries[6] on the importance of systems with conjugated double bonds when acting as bridging groups in the activated complex in the reduction of Co(III) complexes by chromous, vanadous, and europous ions. The behavior of these ligand systems has been correlated to their reducibility,[7] and a knowledge of the mechanism of their reduction in the absence of the Co(III) center seems useful.

Experimental

Chromous perchlorate was prepared by reduction of chromic perchlorate with amalgamated zinc. The preparation of the Cr^{2+} solution and the reaction were carried out in an inert gas atmosphere. All reagents were of analytical grade. Water was distilled from acid dichromate, alkaline permanganate, and finally with nothing added to it.

The chromatographic separations were done on a DX-50 column in an inert gas atmosphere.

The organic acids were recovered from the solution by repeated ether extraction after boiling with pyrophosphate to destroy the complexes. They were identified by their melting points and infrared spectra. Visible and ultraviolet spectra were taken with a Cary 14 spectrophotometer.

In a series of kinetic runs, unreacted Cr^{2+} was quenched by H_2O_2 and its concentration determined by comparing the increase in absorption at 570 mμ to a standard curve. There is no evidence that the peroxide induces incorporation of maleic acid into the chromium coordination sphere, beyond that resulting from the direct reaction. The spectrum of the products of oxidation of Cr^{2+} by H_2O_2 does not seem to be affected by the presence of maleic acid. This conclusion is also supported by the fact that the analysis of the spectrophotometric data described below gives for the Cr^{2+} concentration the same results obtained with the H_2O_2 method.

The possibility of hydrolysis of the esters was tested by titration with standard alkali.

The difference between the number of species and the relations between their concentrations at the various stages of the reaction was determined by matrix analysis of the spectrophotometric data.[8] The method is particularly useful in cases where separation (i.e., by ion exchange) is not desirable, either because it is too slow and the reaction continuous, or because new reactions are induced during the separation, complicating the results. The method does not require knowledge of the extinction coefficients.

The matrix analysis was done as follows. The matrix D of the optical densities is set up for each kinetic run. The rows of D refer to different wave lengths, the columns to different times and hence different concentrations of colored reacting species and products. The rank of D gives the number of linearly independent concentrations, and, therefore, the difference between the number of species and the number of relations between them. The determination of the rank was done with the aid of a digital computer. The method is described in detail elsewhere.[9] It is based on the Gauss process of elimination.[10] In every step of the process the rank is diminished by one, until a matrix $\bar{Q}_m$ is obtained, where m is the number of steps, having all its elements absolutely smaller than the elements of the corresponding error matrix. $\bar{Q}_m$ then can be considered as being zero. Therefore, rank $\bar{Q}_m = 0$, and since the rank is diminished by one in each step, rank $D = m$.

Results

The development of the reaction is illustrated in Figure 1, where the absorption at selected wave lengths near the peaks is given. It is seen that there is a relatively fast reaction, during which the optical density increases, followed by a slow reaction resulting in a decrease in optical density The maximum absorption

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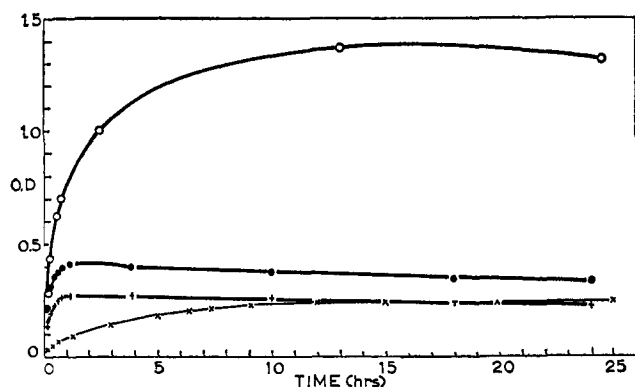(10) E. Bodewig, "Matrix Calculus," North Holland Publishing Co., Amsterdam, 1959.

Figure 1. Typical examples of the change with time of the absorption in various reaction mixtures in 1 M $HClO_4$ and 10-cm. path (room temperature): $+$, $(Cr^{2+})_0 = 1.11$ mM, (maleic acid)$_0$ = 8.88 mM at 550 mμ; ●, the same at 400 mμ; O, $(Cr^{2+})_0 = 3.33$ mM, (maleic ester)$_0$ = 6.66 mM at 400 mμ; $\times$, $(Cr^{2+})_0 = 1.11$ mM, (fumaric acid)$_0$ = 8.88 mM at 415 mμ.

Figure 2. Second-order plot of the reaction between maleic acid and chromous ion at 1 M $HClO_4$, at 20°0: $(Cr^{2+})_0 = 1.64$ mM, (maleic acid)$_0$ = 5.06 mM. The concentrations were obtained by quenching the Cr^{2+} with H_2O_2 (open circles) or calculated from spectrophotometric data (closed circles). The rate constant, estimated from the slope, is 0.088 l. mole^{-1} sec.$^{-1}$.

is reached faster in the case of maleic acid than in the case of fumaric acid or maleic ester. The visible spectrum of the maleic acid reaction mixture in 1 M $HClO_4$ has two maxima, at 414 and 540 mμ. The wave length of the first maximum does not depend on the reaction time, whereas the wave length of the second maximum does. At the first phases of the reaction, the long wavelength maximum stays at 540 mμ, but after the peak absorption has been exceeded, it is shifted to longer wave lengths tending eventually, after a few days, to values near 570 mμ. At lower acidity (0.05 M $HClO_4$) both maxima are displaced toward longer wave lengths.

Fumaric acid reaction mixtures in 1 M $HClO_4$ give a peak at 413 mμ, which does not shift with time. The wave length of the second maximum, which immediately after mixing lies near the end of the red side of the spectrum, decreases with time, tending toward 570 mμ.

Maleic ester reaction mixtures in 1 M $HClO_4$ immediately upon mixing give a maximum at 416 mμ, which is soon shifted to 414 mμ where it remains for a few days and then decreases again. The second maximum at 566 mμ shifts at first to shorter wave lengths until after a few days when it starts to increase again. Maxima at 409 and 575 mμ were observed with a reaction mixture containing initially 6.66 mM ester and 3.33 mM Cr^{2+} at 22°, a few days after mixing.

Succinic and unreacted maleic or fumaric acids were identified after the completion of the reaction. Isomerization of maleic to fumaric acid or vice versa was not observed. No attempt was made to determine quantitatively the organic products.

The best kinetics for the Cr^{2+} concentration vs. time data at constant acidity are first order in both the maleic acid and the chromous ion (Figure 2), with stoichiometry for the over-all reaction of two chromous ions to one maleic acid. One set of points in Figure 2 was obtained on the basis of the determination of Cr^{2+} by H_2O_2. The other set was obtained using the corresponding spectrophotometric data and assuming that two chromous ions reduce one molecule of maleic acid, forming the red intermediate and Cr_{aq}^{3+} monomer. The extinction coefficients of the red intermediate are given in Figure 3. For the extinction coefficients of the Cr_{aq}^{3+} monomer, the values given by Laswick and
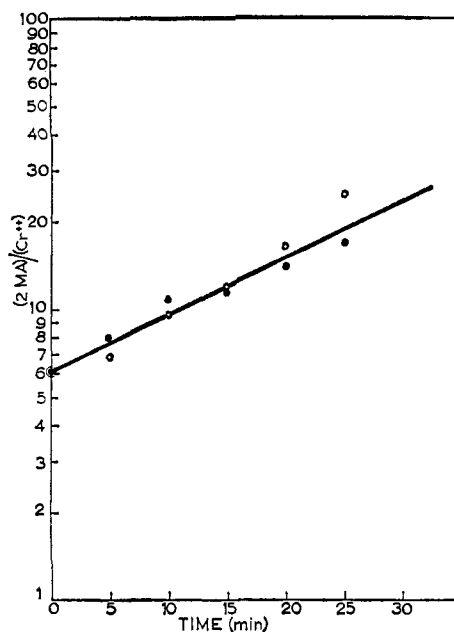
Plane[11] were used. On the basis of these assumptions we also estimate that the maximum concentration of the red intermediate, as well as of Cr_{aq}^{3+}, which is to be compared to half the initial concentration of Cr^{2+} (0.82 mM), is 0.826 mM. For the maleic acid data in Figure 1 we obtain a value of 0.54 mM for the maximum concentration of the intermediate, as compared to 0.55 for half the initial chromous ion concentration. Similar calculations made at various wave lengths differ between them by less than 2%.

Figure 4 is a first-order plot of the kinetic data on the decomposition of the red product which is eluted first from the ion-exchange column. The calculation of the concentration of the red product at various times was made using the formula

$$(R)_t = \frac{A_t - A_\infty}{\epsilon_R - \epsilon_P}$$

where A_t and A_∞ are the absorbancies at times t and ∞, respectively, and ϵ_R and ϵ_P are the extinction coefficients of the reactant and product, respectively. A_∞ and ϵ_P were obtained from the spectra of the boiled solutions. A possible, relatively small deviation of these values from the real ones does not affect the first-order fit, changing only the slope of the straight line.

A reaction mixture 8 mM in maleic acid and 2 mM in Cr^{2+} was sealed in vacuo and analyzed for gaseous products after 1 month. No gases were detected; hence any possibility of reaction of Cr^{2+} with H^+, catalyzed by the organic acid, can be excluded.

In the reactions with the maleic or fumaric diethyl esters the titrations at various times after mixing gave no indication of change in the hydrogen ion concentration.

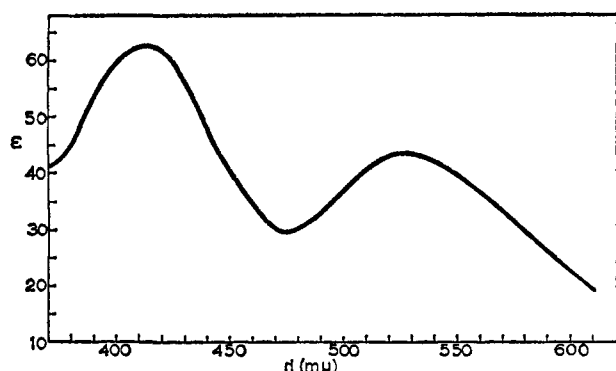(11) J. A. Laswick and R. A. Plane, J. Am. Chem. Soc., 81, 3564 (1959).

Figure 3. Spectrum of the red product of the reaction of Cr^{2+} with maleic acid, separated by ion exchange.
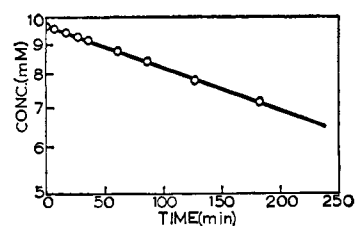

Figure 4. First-order decomposition of the red product of the reaction of Cr^{2+} with maleic acid in 1 M $HClO_4$ at 31° (point after 46.5 hr., not shown in the figure, falls on the extension of the line).

The results of the matrix analysis of the spectrophotometric data are summarized in Table I. The order of the matrices used was between 4 × 4 and 9 × 9. Runs 1 through 14 are with maleic acid, the rest as indicated in the table. Region A is the region of increasing optical densities, region B of decreasing. All solutions were 1 M in $HClO_4$. The temperature was 31° except for runs 4, 18, and 19, which were at 22°. In the runs where more than one matrix was set up, all had the same rank.

In the ion-exchange experiments, the continuation of the reaction on the resin complicates the results. The different colored fractions in the maleic acid reaction mixtures appear, nevertheless, to be two in region A and three in region B.

Table I. Ranks of the Absorption Matrices

Run no.	No. of matrices	Initial conditions Cr^{2+}, mM	Organic compd., mM	Region	Assumed % error[a]	Rank within assumed error
1	1	0.59	9.44	A	0.2	1
2	1	1.11	8.88	A	1	1
3	2	2.0	8.0	A	2	1
4	1	3.29	6.5	A	1	1
5	1	3.33	6.66	A	0.5	1
6	2	5.0	5.0	A	1	1
7	1	25.0	25.0	A	0.5	1
8	2	Columns corresponding to various init. concn. at a specified time after mixing		A	1	1
9	2	0.36	9.64	B	2	2
10	2	1.11	8.88	B	1	2
11	1	2.5	2.5	B	2	2
12	1	5.0	5.0	B	2	2
13	1	25.0	25.0	B	2	2
14	1	25.0	25.0	b	2	2
15	2	Red product of the reaction of maleic acid with Cr^{2+}		B	2	2
16	1	Same as run 15 with one column replaced by the column of the boiled solution		B	2	⩾2
17	1	1.11 (fumaric acid)	8.88	A	2	1
18	1	3.33 (maleic ester)	6.66	A	2	⩾2
19	1	3.33 (maleic ester)	6.66	B	2	⩾2
20	1	Columns corresponding to various init. concn. at times where the hydrolysis of the red product in the maleic acid–Cr^{2+} reaction mixtures is nearly complete			2	1

[a] In the spectrophotometric measurements. [b] Open to the air 63 min. after mixing.

Discussion

The matrix analysis of the spectrophotometric data for the reaction of maleic acid with Cr^{2+} indicates that in region A there are n colored species and $n - 1$ relations between them. This conclusion is also consistent with the behavior of the absorption maxima during the course of the reaction. In view of the ion-exchange observations, n seems to be equal to 2. We must therefore be dealing with two colored products formed in constant ratio. A simple mechanism for the main path of the initial stage (region A) of the reaction, under the conditions used, is represented by the reactions

$$Cr^{2+} + MH^- \longrightarrow Cr(MH)^+ \qquad (1)$$

$$Cr^{2+} + Cr(MH)^+ + H^+ \longrightarrow Cr(SA)^+ + Cr_{aq}^{3+} \qquad (2)$$
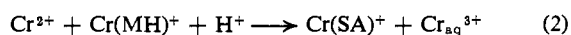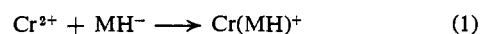
where MH^- stands for the maleate ion and $Cr(MH)^+$ and $Cr(SA)^+$ are complexes of maleic and succinic acids to be specified further. In order to account for the observations, reaction 1 has to be the rate-determining step and the intermediate $Cr(MH)^+$ must be present only in steady-state amounts. The mechanism would anticipate a disappearance of Cr^{2+} first order in chromous ion and maleic acid, as was indeed observed.

The detailed dependence on hydrogen ion concentration was not investigated. It was observed, however, that the reaction is slower at lower acidity.

The products of reaction 2 are separate rather than associated in the form of a binuclear species. The easiness by which the highly absorbing red complex produced in reaction 2 is eluted from the ion-exchange column provides additional support to the view that a multicharged binuclear species is not formed. On the basis of the above evidence, we are inclined to suggest that both $Cr(MH)^+$ and $Cr(SA)^+$ have chelate structures. In the intermediate formed in reaction 1, there is no carbonyl group available for further attack by a second chromous ion, both being joined to the metal center. Regarding the formal charge on chromium in the complex $Cr(MH)^+$, the present experiments provide no evidence to distinguish between a Cr(IV) complex of

succinic acid and a Cr(III) complex of the organic free radical.

In region B the main reaction has been completed and the observed change in absorption can be attributed to the hydrolysis of the red complex. The chromatographic experiments indicate that there are three species in region B. In this region the ranks of the optical density matrices become two. One linear relationship between the concentrations of these species is, therefore, still holding. A very likely explanation is that the hydrolysis involves, as a first step, the change from the chelated succinate complex to the monodentate form. In that case the linear relationship existing between the three species present is the constant ratio between the concentration of the Cr_{aq}^{3+} and the sum of the concentrations of the two forms of the succinate complex. Run 14, where the reaction mixture was exposed to the air after all Cr^{2+} had been consumed, also gives a matrix of rank two. After the hydrolysis has been completed (run 20) the rank becomes again one, because there are only two linearly dependent concentrations.

The rank of the matrix for fumaric acid in region A is also one. A mechanism similar to the one proposed for maleic acid, with a slower rate-determining step, is also proposed for fumaric acid. In the maleic ester, chelation, even after the formation of the free radical, is inhibited and the mechanism seems to be different. If a formally similar mechanism to the one proposed for the acid is also adopted for the ester, it has to be assumed that the intermediate formed in reaction 1 is less reactive toward Cr^{2+} than the corresponding intermediate formed with the acid, accumulating and giving, in region A, matrices of rank two. This hypothesis is consistent with runs 18 and 19 of Table I, although a more complicated process cannot be excluded. Hydrolysis, in particular, cannot be excluded. The fact that hydrogen ion concentration does not seem to change during the reaction may simply mean that the amount of H^+ consumed in the reduction of the double bond equals the amount of H^+ formed in the hydrolysis.

If the mechanism proposed for the reduction of maleic acid by chromous ion is accepted, it is not surprising that no isomerization to fumaric acid was observed. In the cases where activation for isomerization takes place,[6] evidence has been presented that an intermediate is formed containing both the oxidizing and reducing metal ions, directly bonded to the organic ligand.

The Reaction of Metal Carbonyls and Amines. I. Iron Carbonyl with Piperidine and n-Butylamine. The Initial Stages of the Reaction[1,2]

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The reaction between $Fe(CO)_5$ and amines was studied with particular attention to the n-butylamine and piperidine systems. Three different iron carbonyl species, I–III, have been observed, appearing successively in time in the reaction mixture at room temperature. The infrared bands arising from modes in these species appear about 100 $cm.^{-1}$ lower than the $Fe(CO)_5$ values, indicating the presence of negative charge on the iron carbonyl moiety, but they do not correspond to the values from the known polynuclear carbonylferrates. II is ionic; I is either an ion of low conductivity in piperidine solutions or is nonionic. While the evidence is less certain, III appears to be nonionic. I is formed almost instantaneously in the pure amines but its formation may be reversed to $Fe(CO)_5$ and amine by the addition of nonpolar solvents. I was identified as $Fe(CO)_3(NHC_5H_{10})_3$ in the case of piperidine. Its structure and bonding are considered. II was found to be $HFe(CO)_4^-$ and the other species formed with it were identified. III is postulated to be $Fe(CO)_4(NHC_5H_{10})$. The reaction paths by which these species are formed are considered.

It has been proposed that $Fe(CO)_5$ disproportionates into $Fe(CO)_6^{2+}$ and $Fe(CO)_4^{2-}$ in various amines such as piperidine.[4] Two infrared bands, 2016 and 1898 $cm.^{-1}$, were observed for such solutions and were assigned to the first and second ions, respectively. A substance analyzed as $Fe(CO)_5 \cdot 3C_5H_{10}NH$ was obtained from the reaction of $Fe(CO)_5$ and piperidine at liquid nitrogen temperatures and viewed as a loose association of the reagents which gave the spectrum of unmodified $Fe(CO)_5$ and piperidine when dissolved in cyclohexane or ether.[5] It was proposed that the "adduct," when dissolved in piperidine, was converted

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