orbital into the higher energy unfilled MO of **17**, represented in **19**, and not into the lower energy occupied MO, **20**. We would encourage synthetic efforts directed toward derivatives of species **12**. We would also like to direct the reader to some similarly inspired work by Ashe[40] on the ability of phosphorus to transmit conjugation.

Acknowledgment. We are grateful to J. Swenson for some calculations, and to the National Institutes of Health for a postdoctoral fellowship to D. B. B. and for the support of this work at Cornell through Grant No. GM 13468.

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Reaction of Aqueous Vanadium(II) Ions with Maleic Acid, Fumaric Acid, and Derivatives. II. Kinetics of Reduction and Isomerization

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Abstract: Kinetic data on the reduction by V_{aq}^{2+} of maleic, fumaric, citraconic, and chloromaleic acids as well as methyl maleate were found to fit the general rate expression $R = (k_a[A] + k_b[A][H^+] + k_c[A]^2 + k_d[A]^2[H^+])[V_{aq}^{2+}]^2$, where R is the rate and [A] the concentration of the organic acid. With the half-ester, the rate law contains a term inverse in hydrogen ion concentration. In the isomerization of maleic to fumaric acid, caused by vanadium(II) ion, there are two terms in the rate law, one independent of and the other inverse in [H^+], both first order in maleic acid and vanadium(II) ion. The empirically determined rate constants, activation energies, etc., are interpreted on the basis of a mechanism which combines complex ion formation, reduction, and isomerization.

It has already been shown[1] that the reduction by V_{aq}^{2+} of maleic acid, fumaric acid, and some of their derivatives, require two vanadium(II) ions for each molecule of unsaturated acid, V(II) being oxidized to V(III). The only products detected were those corresponding to this stoichiometry; they were therefore formed by an overall two-electron transfer process.

In the present paper we determine the empirical rate laws for the reduction under a variety of conditions in order to obtain information about the main paths leading eventually to reduction and the composition of the activated complexes involved. We also tried to follow in more detail the various stages of the reaction as well as the sequence of these stages. The two-electron change seems to break down into distinct steps that can be subject to independent experimental investigation.

One of the steps of the overall reaction is the complex ion formation equilibrium. Evidence already presented[1] indicates that the equilibrium established between V_{aq}^{2+} and the organic acids studied may be related to electron transfer from V_{aq}^{2+} to the system of the conjugated double bonds. It seems likely that complex formation is the first step in the interaction and that it is essential for the subsequent reactions. Complex formation provides the necessary preliminary placement of the reactants in space, in relative positions favorable for further reaction. In this paper we attempt to clarify this point further and also broaden the experimental basis for the study of the other stages of the interaction between V_{aq}^{2+} and the conjugated dibasic acids.

One of the consequences of this interaction is isomerization of maleic acid to fumaric acid, catalyzed by vanadium(II) ion. Preliminary results[2] indicate that complex formation may be important in this respect too. We here compare the kinetics of reduction to the kinetics of isomerization.

Experimental Section

Most of the experimental techniques used here have already been described.[1]

The progress of the reaction was in most cases followed spectrophotometrically using a Cary 14. The mixing of the reactants was done direct in the spectrophotometer cells.

The extinction coefficients of V_{aq}^{2+} and V_{aq}^{3+} used[3] agree with those reported by Gordon and Tewari.[4] The extinction coefficients of the complexes forming in the system depend on hydrogen ion concentration. Measurements at two or more wavelengths are necessary in order to determine the concentrations of all the vanadium species present. Appropriate wavelengths for most cases were 400 and 510 mμ. The extinction coefficients of V_{aq}^{2+} and V_{aq}^{3+} at 510 mμ have essentially the same value and any change in absorbance at this wavelength is practically due to the change in the concentration of the complex.

Results

1. Reduction of Maleic Acid (HM). In the hydrogen ion concentration range from 0.43 to 2.0 M the two complexes between V_{aq}^{2+} and maleic acid have comparable concentrations.[1] Two series of kinetic runs were made in this acid range, one with a large excess of maleic acid and the other with a large excess of V_{aq}^{2+}.

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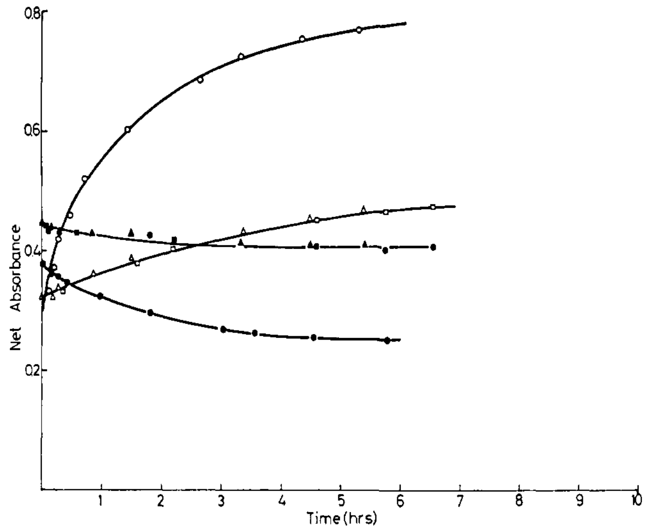

Figure 1. Typical spectrophotometric data in the reaction of V_{aq}^{2+} with excess maleic acid: $[V^{2+}]_0 = 0.01$ *M*, $[HM]_0 = 0.156$ *M*, $[HClO_4] = 1.8$ *M*, $[NaClO_4] = 0.19$ *M*, 23°; ○, 400 mμ; ●, 510 mμ. Pseudo-second-order rate constant calculated from these data, 0.023 ± 0.0004 l. mol^{-1} sec^{-1}. Spectrophotometric data for two kinetic runs at different ionic strengths: $[V_{aq}^{2+}]_0 = 0.013$ *M*, [HM] = 0.029 *M*, $[HClO_4] = 0.375$ *M*; △, ▲, $[NaClO_4] = 1.7$ *M*, and □, ■, no $NaClO_4$ added, at 400 and 510 mμ, respectively.

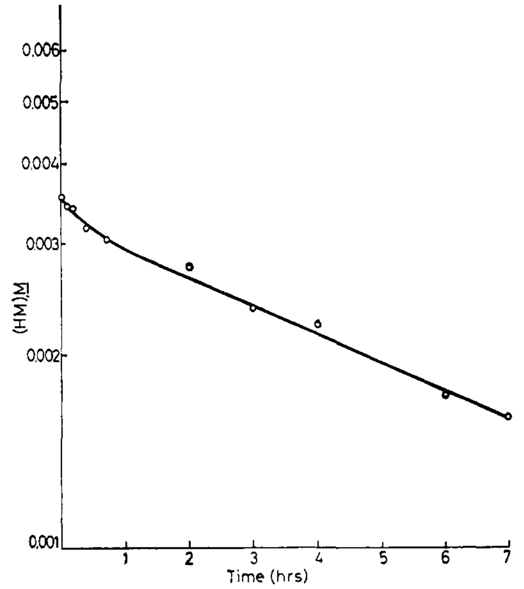

Figure 2. Variation of maleic acid concentration with time in a solution containing $[V^{2+}]_0 = 0.066$ *M*, $[HM]_0 = 0.0036$ *M*, $[HClO_4] = 1.8$ *M*, and $[NaClO_4] = 0.19$ *M* at 23°.

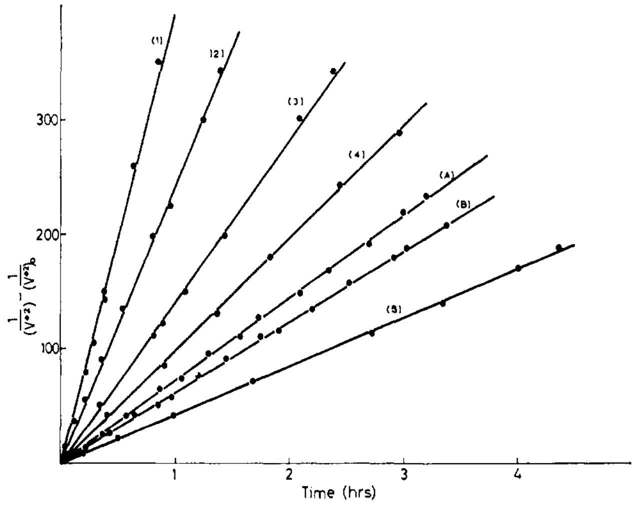

Figure 3. Variation of $1/[V^{2+}] - 1/[V^{2+}]_0$ with time in a solution containing $[V^{2+}]_0 = 0.01$ *M*, $[HClO_4] = 2$ *M*, and [HM] = 0.30, 0.25, 0.20, 0.156, and 0.10 *M* for runs 1, 2, 3, 4, and 5, respectively. Effect of chloride: $[V_{aq}^{2+}]_0 = 0.01$ *M*; [HM] = 0.156 *M*; $[NaClO_4] = 1.15$ *M*; (A), [HCl] = 0.85 *M*; (B), $[HClO_4] = 0.85$ *M*.

Figure 1 is typical of spectrophotometric results obtained with excess maleic acid. From data of this type, by plotting $(1/[V_{aq}^{2+}] - 1/[V_{aq}^{2+}]_0)$ *vs.* time, we find that the reaction rate has a term second order in $[V_{aq}^{2+}]$. At the end of the reaction in the mixture of Figure 1, 4.6% of maleic acid has been isomerized to fumaric acid. Isomerization in this case, cannot, therefore, have an appreciable effect on the kinetics of reduction.

With a large excess of V_{aq}^{2+} the reaction rate was found to have two first-order branches. A semilogarithm plot of [HM] *vs.* time is shown in Figure 2. [HM] was calculated from the amount of V(III) formed during the reaction. A polarographic analysis of the reaction mixture long before the reaction was over showed that maleic acid had been completely isomerized to fumaric acid. The data obtained in a more detailed investigation of the initial period of the reaction under these conditions, before appreciable accumulation of fumaric, fit a first-order expression with respect to maleic acid. The method used in these experiments for the determination of the organic acid does not distinguish between maleic and fumaric acids. The first-order behavior late in the reaction can, therefore, be attributed to a first-order dependence on fumaric acid.

In another series of runs we determined the order with respect to maleic acid by varying its concentration but keeping it always in excess over $[V_{aq}^{2+}]$. The results are shown in Figure 3. A plot of the slopes of the straight lines of Figure 3 against [HM] does not give a straight line, whereas a similar plot against $[HM]^2$ does give a straight line passing through the origin. It follows that, under the conditions of these experiments, the reaction is second order in maleic acid. In series of runs with 0.01 *M* V_{aq}^{2+}, 2 *M* $HClO_4$, and varying concentrations of maleic acid, we find the value 1.09 ± 0.06 for the fourth-order rate constant (second order in [V(II)] and second order in maleic acid).

The hydrogen ion concentration dependence from 0.43 to 2.0 *M* [H$^+$] was obtained with excess maleic acid at $\mu = 2.0$ (made up with $NaClO_4$) and 23°. The observed second-order rate constant with respect to (V_{aq}^{2+}) is a linear function of the hydrogen ion concentration. In a mixture containing initially 0.01 *M* V_{aq}^{2+} and 0.156 *M* maleic acid, the straight line describing the hydrogen ion dependence is given by the empirical equation

$$k_{HM} = 0.0102 + 0.0096[H^+] \text{ l. mol}^{-1} \text{ sec}^{-1} \quad (A)$$

with an overall error of about 5%.

The coefficients in this expression contain the maleic acid concentration, which can be considered to remain constant in the course of the reaction. Change of ionic strength in the range from 0.375 to 2.0 has no effect within the same hydrogen ion concentration interval. This lack of an ionic strength effect is illustrated in Figure 1.

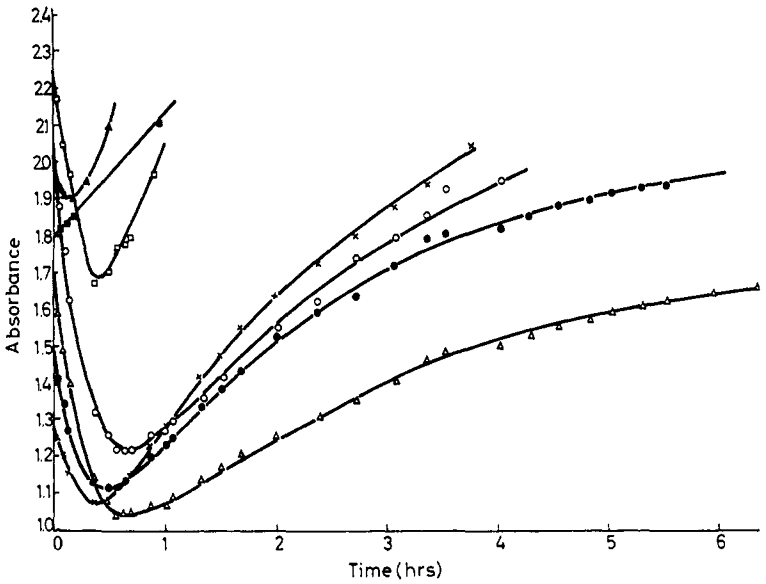

Figure 4. Variation of absorbance with time, at low hydrogen ion concentrations. Reaction mixture contained initially 0.01 M V^{2+}, 0.1 M sodium maleate, and 0.015 M $HClO_4$ (pH 2.7); 5-cm cell; 23°; wavelengths (mμ) ■, 380; ▲, 400; □, 450; ○, 490; △, 520; ●, 560; ×, 580.

With excess vanadium(II) (0.036 M) the initial pseudo-first-order rate constant as a function of the hydrogen ion concentration is given by the expression

$$k_{HM}' \times 10^5 \cong 2.34 + 1.82[H^+] \text{ sec}^{-1} \qquad (B)$$

This expression was obtained with solutions having initially a tenfold excess of vanadium(II) ion over maleic acid, at 23°. The hydrogen ion concentration was varied from 0.8 to 1.9 M. The coefficients contain the initial vanadium(II) concentration which is assumed to remain constant. The measurements involve small differences in absorbance and the values obtained can only be considered as approximate.

At lower hydrogen ion concentrations the situation becomes considerably more complicated. The data in Figure 4 were obtained with a mixture having a pH of 2.7. During the course of the reaction the pH was found to remain constant. The most striking observation in Figure 4 is that the absorbance in most wavelengths goes through minima that have not been observed at higher [H+]. An observation that may be relevant to this is that with V_{aq}^{3+} in a mixture otherwise identical with that of Figure 4 a slow steady increase in absorbance is observed with time, even though no net oxidation to V(IV) was detected. A similar increase in absorbance was not observed at higher acidities. This kind of behavior cannot be simply explained on the basis of complex formation and oxidation by the organic acid of vanadium(II). It may rather indicate that the vanadium(III) formed in the redox reaction undergoes further slow reactions at low H^+ concentrations, *e.g.*, complex formation or dimerization, resulting in delayed increase of the total absorbance. A term in the rate law for the reduction of the organic acid by V(II) inverse in hydrogen ion concentration is expected to become dominant at low acidity. However, the unresolved complications at these acidities make it difficult to decide whether there is indeed such a term and we have not attempted to make a more detailed investigation under these conditions.

A rate of reduction in a mixture containing 0.026 M V_{aq}^{2+}, 0.071 M HM, and 1 M $HClO_4$ did not seem to be affected by V_{aq}^{3+} (0.026 M).

Chloride ion was found to accelerate the rate of reduction (Figure 3). The effect of 0.83 M HCl in a mixture containing 0.01 M V_{aq}^{2+}, 0.002 M V_{aq}^{3+}, 0.156 M HM, 0.02 M $HClO_4$, and 1.15 M $NaClO_4$ was to increase the pseudo-second-order rate constant by about 14.5%. It is interesting that Cl^- under these conditions causes a decrease in complex ion formation. This was observed spectrophotometrically and was confirmed by determining the equilibrium constant by the method of Sakellaridis.[1] Thus, in a reaction mixture containing 1.14 M Cl^- the equilibrium constant for complex formation was found to be 1.46, while in the absence of Cl^-, at the same acidity and ionic strength, we found the value 2.96. In view of the fact that under these conditions there is no ionic strength effect, the effect of chloride must be specific. In order to test this hypothesis further with another anion, the pseudo-second-order rate constant of a mixture containing 0.008 M V_{aq}^{2+}, 0.143 M HM, and 1.26 M $HClO_4$ was compared to a similar mixture in which part of the $HClO_4$ was replaced by H_2SO_4 (0.97 M). The rate constant of the second mixture is estimated to be higher by about 70%.

The temperature dependence (Figure 5) of the second-order rate constant in excess maleic acid ($[V_{aq}^{2+}]$ = 0.01 M, [HM] = 0.156 M) gives an activation energy of 6.05 ± 0.3 kcal mol^{-1} at 1.05 M $HClO_4$, and 7.86 ± 0.4 kcal mol^{-1} at 0.59 M $HClO_4$, 0.46 M $NaClO_4$. In the temperature range from 7 to 39°, the Arrhenius equation is obeyed.

2. Reduction of Fumaric Acid (HF). The reduction of fumaric acid by V_{aq}^{2+} is somewhat simpler because there is no interference from isomerization. With excess fumaric acid the data fit a second-order rate law with respect to V_{aq}^{2+}. In excess V_{aq}^{2+} the reaction seems to be first order in fumaric acid during its initial stages; there is some deviation, however, at longer times. Experiments with varying concentrations of excess fumaric acid, similar to those performed with maleic are excluded because of the limited solubility of fumaric. It can be stated, however, that the rate law does not consist of a single term second order in $[V_{aq}^{2+}]$ and first order in fumaric acid, even when the hydrogen ion concentration is kept constant. Table I gives the rate constants calculated on the assumption of a single term. There are two pairs of runs in this table, one with excess furmaric acid, the other with excess vanadium ion, at two acid concentrations. Apparent values of k_{calcd} vary with $[V_{aq}^{2+}]$; the rate law is thus not a simple one.

Table I. Calculated Rate Constants in the Reaction between Fumaric Acid and V_{aq}^{2+} at 23°

$[V^{2+}]$, *M*	[HF], *M*	$[HClO_4]$, *M*	$[NaClO_4]$, *M*	k_{calcd}, $l.^2\ mol^{-2}\ sec^{-1}$
0.011	0.036	0.90	0	0.0138
0.011	0.036	0.72	0.18	0.0123
0.072	0.0036	0.90	0	0.0083
0.072	0.0036	0.72	0.18	0.0073

The dependence on hydrogen ion concentration with excess fumaric acid is linear. In a solution containing 0.01 *M* V_{aq}^{2+} and 0.036 *M* fumaric at 23°, $\mu = 0.9$, and small conversion ratios, the straight line of the hydrogen ion dependence is given by the empirical equation

$$k_{HF} = 0.00019 + 0.00032[H^+]\ l.\ mol^{-1}\ sec^{-1} \quad (C)$$

with an overall error of about 5%. The numerical coefficients in this expression include the concentration of fumaric acid.

The determination of the activation energy in the case of fumaric acid (Figure 5) involves a large error because it is based on small differences in absorbance. Nevertheless, in solutions containing 0.01 *M* V_{aq}^{2+} and 0.36 *M* HF the Arrhenius equation is obeyed over the temperature range from 7 to 39°. Under these conditions the activation energy is estimated to be 10 ± 1 kcal mol^{-1} at 0.59 *M* $HClO_4$ and 11 ± 1 kcal mol^{-1} at 0.88 *M* $HClO_4$.

3. Reduction of Derivatives of Maleic and Fumaric Acids. The behavior of citraconic (methylmaleic) acid is similar to that of maleic acid. To minimize complications from the *cis*-to-*trans* isomerization, all kinetic experiments reported here were done with a large excess of citraconic acid (HC). Under these conditions the rate was found to be second order in $[V_{aq}^{2+}]$, the magnitude of the rate constant being considerably smaller than the corresponding rate constant for maleic acid.

The dependence on hydrogen ion concentration for a particular run done at 23°, $\mu = 2.0$, and with initial concentrations $[V_{aq}^{2+}] = 0.01$, $[HC] = 0.156$ *M*, is given by the empirical equation

$$k_{HC} = 0.0014 + 0.0043[H^+]\ l.\ mol^{-1}\ sec^{-1} \quad (D)$$

Mesaconic (methylfumaric) acid was not reduced at 23° to any detectable extent over a period of a few days. The low solubility of mesaconic acid in water precludes the possibility of a detailed study.

Itaconic acid does not even form a spectrophotometrically detectable complex with V_{aq}^{2+}.

Chloromaleic acid is reduced faster than maleic acid, the rate being also pseudo second order in $[V_{aq}^{2+}]$ when excess organic acid is used. A comparison of the rates of maleic, citraconic, and chloromaleic acids, measured under similar conditions, is given in Table II, which contains the apparent rate constants in solutions 0.01 *M* in V_{aq}^{2+}, 1.81 *M* in $HClO_4$, 0.19 *M* in $NaClO_4$, and 0.156 *M* in the corresponding organic acid.

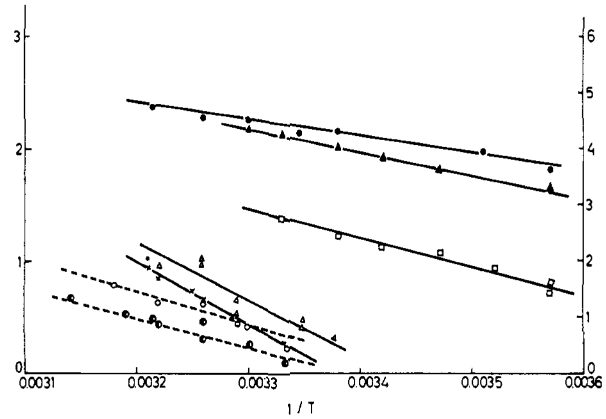

Figure 5. Temperature dependence of the reaction rates. Pseudo-second-order rate constants (l. mol^{-1} hr^{-1}) of the reduction of maleic acid as a function of temperature: $[V_{aq}^{2+}]_0 = 0.01$ *M*; [HM] = 0.156 *M*; ●, $[HClO_4] = 1$ *M*; ▲, $[HClO_4] = 0.6$ *M*; $[NaClO_4] = 0.4$ *M* (right scale). Pseudo-second-order rate constants (l. mol^{-1} hr^{-1}) of the reduction of methyl maleate as a function of temperature: □, $[V_{aq}^{2+}]_0 = 0.01$ *M*, [MM] = 0.156 *M*, $[HClO_4] = 0.2$ *M*, $[NaClO_4] = 0.156$ *M* (right scale). Pseudo-second-order rate constants (l. mol^{-1} hr^{-1}) of the reduction of fumaric acid as a function of temperature: $[V_{aq}^{2+}]_0 = 0.01$ *M*; [HF] = 0.036 *M*; △, $[HClO_4] = 0.88$ *M*; ×, $[HClO_4] = 0.59$ *M*; $[NaClO_4] = 0.29$ *M* (left scale). Pseudo-first-order rate constants (hr^{-1}) of the isomerization of maleic acid as a function of temperature: $[V_{aq}^{2+}]_0 = 0.01$ *M*; [HM] = 0.156 *M*; ◐, $[HClO_4] = 1$ *M*; ○, $(HClO_4) = 0.6$ *M*; $[NaClO_4] = 0.4$ *M* (left scale).

Table II. Comparison of Apparent Rate Constants[a] of Maleic Acid and Derivatives

	Apparent rate constant, l. mol^{-1} sec^{-1}
Maleic acid	0.027
Citraconic acid	0.009
Chloromaleic acid	0.277

[a] Pseudo-second-order rate constant with respect to vanadium(II), obtained with organic acid in excess. Solutions were initially 0.01 *M* in V_{aq}^{2+}, 1.81 *M* in $HClO_4$, 0.19 *M* in $NaClO_4$, and 0.156 *M* in the organic acid.

No evidence for reduction or isomerization of the dimethyl ester of maleic acid was found; the half-ester (MM) is, however, reduced at a convenient rate under the conditions of our experiments. Only runs at low hydrogen ion concentrations were done with methyl maleate, in order to avoid hydrolysis. In a mixture containing 0.01 *M* V_{aq}^{2+}, 0.156 *M* half-ester, 0.016 *M* $HClO_4$, and 0.156 *M* $NaClO_4$ at 23°, the pseudo-second-order rate constant in V(II) was found to be 0.0034 ± 0.0001 l. mol^{-1} sec^{-1}. Addition of acetic acid has very little influence on this rate constant: 2 *M* acetic acid causes a change to 0.0037 ± 0.0001 l. mol^{-1} sec^{-1}. Experiments with the half-ester in excess at different concentrations show that there is a term in the rate law second order in the half-ester (Figure 6). In series of runs with 0.01 *M* V_{aq}^{2+}, 0.055 *M* $HClO_4$, 0.356 *M*

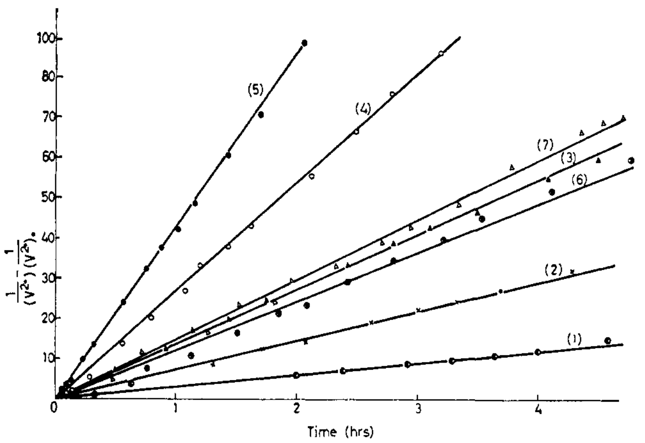

Figure 6. Dependence of the rate of reduction of methyl maleate on the concentration of MM in solutions containing $[V_{aq}^{2+}]_0 = 0.01$ *M*, $[HClO_4] = 0.055$ *M*, $[NaClO_4] = 0.356$ *M*, and [MM] = 0.089, 0.156, 0.222, 0.289, and 0.356 *M* for runs 1, 2, 3, 4, and 5, respectively. Effect of hydrogen ion concentration on the reduction of methyl maleate in solutions containing $[V_{aq}^{2+}]_0 = 0.01$ *M*, [MM] = 0.156 *M*, $[NaClO_4] = 0.356$ *M*, and $[HClO_4] = 0.055$, 0.039, and 0.021 *M*, for runs 2, 6, and 7, respectively.

$NaClO_4$, and varying concentrations of methyl maleate (but always in excess) (Figure 6) we find the value 0.092 ± 0.002 l. mol^{-1} sec^{-1} for the second-order rate constant with respect to the half-ester.

Within the range of conditions investigated the dependence on hydrogen ion concentration is somewhat more complicated than with maleic acid. Thus, the pseudo-second-order rate constant with respect to V_{aq}^{2+} in the last series of runs at 0.156 *M* methyl maleate (0.055 *M* $HClO_4$) is 0.002, whereas at 0.016 *M* $HClO_4$ we obtained the value 0.0034. The rate law seems therefore to have a term inverse in $[H^+]$. This conclusion is also confirmed by a series of runs with 0.01 *M* V_{aq}^{2+}, 0.156 *M* methyl maleate, 0.411 *M* $NaClO_4$ + $HClO_4$, and varying ratios of $HClO_4$ to $NaClO_4$ (Figure 6). With hydrogen ion concentrations 0.021, 0.039, and 0.055 *M*, we obtain the pseudo-second-order constants 0.0043 ± 0.0003, 0.0034 ± 0.0002, and 0.0019 ± 0.0000 l. mol^{-1} sec^{-1}, respectively. These values are not linear in $[H^+]$ but clearly indicate an inverse dependence on hydrogen ion concentration. Minima in absorbance similar to the ones observed with maleic acid at low acid concentrations were not observed with the half-ester.

From 7 to 39° the Arrhenius equation is obeyed by the half-ester, and the activation energy with 0.01 *M* V_{aq}^{2+}, 0.156 *M* half-ester, 0.204 *M* $HClO_4$, and 0.156 *M* $NaClO_4$ was found to be 10.16 ± 0.44 kcal mol^{-1} (Figure 5).

4. Isomerization. At constant ionic strength and acid concentration, and in excess maleic acid, the rate of isomerization depends on the instantaneous V_{aq}^{2+} concentration, which is obtained by integrating the empirical equation

$$-\frac{d[V^{2+}]}{dt} = k_{red}[V_{aq}^{2+}]^2$$

Assuming for the isomerization itself a first-order dependence on the V_{aq}^{2+} concentration, we obtain the integrated expression

$$[HF] = \frac{k_{isom}}{k_{red}} \ln [1 + k_{red} [V_{aq}^{2+}]_0 t]$$

which describes in a satisfactory way our experimental data. The rate constants and activation energies given below are based on this expression. Both k_{isom} and k_{red} contain the mleic acid concentration, which is assumed to remain constant. The above expression is therefore valid only in excess maleic acid and for small conversion ratios.

In solutions containing initially 0.01 *M* V_{aq}^{2+} and 0.156 *M* maleic acid at 0.5 *M* ($HClO_4$), $\mu = 2.0$ and 23°, the experimentally determined pseudo-first-order rate constant for isomerization was found to have the value $k_{isom} = (2.1 \pm 0.2) \times 10^{-4}$ sec^{-1}. Under these conditions, variation of the acid concentration from 0.5 to 1.2 *M* ($HClO_4$) has an effect, significantly outside experimental error, which is illustrated in Figure 5. As has already been reported,[2] the rate constant of isomerization depends inversely on hydrogen ion concentration. The activation energies of the two paths, the acid-dependent one and the acid-independent, do not differ very much from each other. The overall activation energies were determined between 23 and 45°, in solutions containing initially 0.01 *M* V_{aq}^{2+} and 0.156 *M* HM, at $\mu = 1$ (Figure 5). They were found to have the values 5.2 ± 0.2 and 5.9 ± 0.3 kcal mol^{-1} at 1 and 0.6 *M* H^+, respectively. The activation energy at lower hydrogen ion concentration is a little higher than the one at higher acid concentration. Over the limited range of conditions studied, the data fit fairly well the Arrhenius plot. It must be recalled that the overall activation energy for reduction also increases with decreasing (H^+), but always remains higher than that for isomerization. Thus, it was found[2] that in excess maleic acid, at 0.058 *M* H^+, increase in temperature accelerates the process with the higher activation energy, namely the reduction, more than it accelerates isomerization, as expected from the Arrhenius equation.

At low acid concentrations we also observe a marked dependence on ionic strength. Thus, in a solution 0.1 *M* in V_{aq}^{2+}, 0.156 *M* in maleic acid, and 0.015 *M* in $HClO_4$ (pH 1.4), at 23°, the concentration (*M*) of fumaric acid formed after all vanadium(II) ion has been consumed is given by the empirical equation

$$[HF]_{final} = 0.06 + 0.02[NaClO_4]$$

The sodium perchlorate concentration was varied between zero and 1.3 *M*.

5. Rate Laws. The data for all organic acids studied seem to fit the following general rate expression

$$R = (k_a[A] + k_b[H^+][A] + k_c[A]^2 + k_d[H^+][A]^2)[V^{2+}]^2 \quad (E)$$

where A is the conjugated organic acid and *R* the rate of reduction by vanadium(II). Each of the terms in this rate law has been established directly. Thus for maleic acid, the first two terms follow from empirical eq B and the last two terms from empirical eq A. In addition, in some cases cross checking is also possible. For example, in 2 *M* $HClO_4$ we calculate from eq A the value of 1.2 ± 0.06 for the overall fourth-order rate constant in excess maleic acid. Within experimental error this value agrees with the value 1.09 ± 0.06 found in the independent experiments at different excesses of maleic acid. For fumaric acid, eq C and Table I also support the rate law E. The last two terms in (E) were also directly verified in the case of citraconic acid (eq D). Finally, Figure 6 shows the overall fourth-order dependence in the case of methyl maleate.

The rate law may also contain another term inverse in hydrogen ion concentration, which, however, was not identified, except in the case of the half-ester (Figure 6).

Values for some of the rate constants for maleic, fumaric, and citraconic acids, estimated from the experimental data on the basis of the above rate law, are given in Table III.

Table III. Constants in the Rate Laws for the Reduction of Maleic, Fumaric, and Citraconic Acids (23°)

	Maleic acid	Fumaric acid	Citraconic acid
k_a	~0.018	0.003	
k_b	~0.014	0.005	
k_c	0.420	0.100	0.059
k_d	0.393	0.044	0.178

The upper or lower limits of the activation energies of some of the terms in (E) are estimated from the experimentally determined activation energies using the general formula for the average

$$E_{\text{obsd}} \cong \langle E \rangle_{\text{av}} = \frac{kE + k'E'[\text{H}^+]}{k + k'[\text{H}^+]}$$

E and E' being the activation energies of two parallel processes, and k and k' the corresponding rate constants at a given temperature.

For the upper limit of the Arrhenius activation energy for the acid-dependent path in excess maleic acid, we obtain the estimate of 4.5 kcal. The corresponding lower limit for the acid-independent path is 10 kcal. The magnitude of the error is larger in the case of fumaric acid and makes estimates of even the upper and lower limits less reliable. The observed activation energies in excess fumaric acid indicate, however, that both the acid-independent and acid-dependent paths have activation energies of 10 kcal.

In the rate law for the *cis–trans* isomerization of maleic acid, two terms can be clearly identified. They both are first order in V(II) and maleic acid, but one has also an inverse dependence on hydrogen ion.

Discussion

Complex ion formation, reduction, and isomerization can be related to each other through the mechanism

$$\text{V}_{\text{aq}}{}^{2+} + \text{HM} \underset{}{\overset{K_1}{\rightleftarrows}} \text{VMH}^{2+} \tag{1}$$

$$\text{V}_{\text{aq}}{}^{2+} + \text{M}^- \underset{}{\overset{K_2}{\rightleftarrows}} \text{VM}^{+} \tag{2}$$

$$\text{VMH}^{2+} + \text{V}_{\text{aq}}{}^{2+} + \text{H}^+ \xrightarrow{k_3} 2\text{V}_{\text{aq}}{}^{3+} + \text{S}^- \tag{3}$$

$$\text{VMH}^{2+} + \text{VMH}^{2+} + \text{H}^+ \xrightarrow{k_4} 2\text{V}_{\text{aq}}{}^{3+} + \text{S}^- + \text{HM} \tag{4}$$

$$\text{VM}^{+} + \text{V}_{\text{aq}}{}^{2+} + \text{H}^+ \xrightarrow{k_5} 2\text{V}_{\text{aq}}{}^{3+} + \text{S}^- \tag{5}$$

$$\text{VM}^{+} + \text{VM}^{+} + \text{H}^+ \xrightarrow{k_6} 2\text{V}_{\text{aq}}{}^{3+} + \text{S}^- + \text{M}^- \tag{6}$$

$$\text{VMH}^{2+} \xrightarrow{k_7} \text{V}_{\text{aq}}{}^{2+} + \text{HF} \tag{7}$$

$$\text{VM}^{+} \xrightarrow{k_8} \text{V}_{\text{aq}}{}^{2+} + \text{F}^- \tag{8}$$

M^-, F^-, and S^- stand for the maleate, fumarate, and succinate ions, respectively.

Qualitative comparison of the observed rates (Table II) of the various acids studied indicates a connection between observed rate constants and complex formation equilibrium constants. At any rate, the mechanism can give a self-consistent explanation to all the results reported in this paper. Fast complex formation seems to provide the first intermediate step in the complex, multibody encounter necessary for the reaction. The establishment of this equilibrium is probably related to the π acceptor and donor properties of the organic acids used and $\text{V}_{\text{aq}}{}^{2+}$, respectively. The data available for the corresponding reactions of Cr(II) are not detailed enough to permit a direct comparison to be made with V(II). Nevertheless, the existing information suggests that although there are similarities, there are also interesting differences which can be partly attributed to the different donor characteristics of $\text{Cr}_{\text{aq}}{}^{2+}$ (σ electron donor). Thus, in the reaction of $\text{Cr}_{\text{aq}}{}^{2+}$ with maleic acid, a term in the rate law first order in $\text{Cr}_{\text{aq}}{}^{2+}$ and first order in maleic acid was clearly established.[5] In the reduction of dimethyl maleate with Cr(II) in dimethylformamide–water mixtures[6] the first-order term is also clearly identified. However, the first-order dependence on Cr(II) of the rate constant of this reaction depends on the ratio of $[\text{Cr(II)}]_0$ to [diethyl maleate]$_0$, suggesting that there is also a term in the rate law second order in [Cr(II)]. Under the conditions of the experiments reported in ref 6, the term second order in [Cr(II)] seems to be the predominant one when diethyl fumarate is the oxidant.

The mechanism has been written schematically for maleic acid. Similar reactions can be written for the other organic acids, except that reactions 7 and 8 are omitted with the *trans* acids. A reaction between two VM^+'s could give a term inverse in H^+, which was only observed with the half-ester. The equilibrium between succinate (S) and succinic acid (HS) is, of course, established rapidly. The same is true for the other acids.

The positions of the protons involved in the reactions cannot be inferred from the present results. It is pointed out, however, that the observed exchange with the solvent,[2] of the double-bond hydrogen, indicates that at least one proton is at some stage of the reaction attached to a carbon atom at the double bond and induces its activation. It must be noted also that the form of the hydrogen ion dependence of the reduction suggests that there are paths where hydrogen ion is necessary in the activation process. Eventually, of course, the double bond is hydrogenated and the overall stoichiometry requires two protons. Experiments on the exchange now underway could clarify better the changes taking place at the site of the double bond itself.

If we associate the acid-dependent terms (reactions 3 and 4) and the acid-independent terms (reactions 5 and 6) with equilibria 1 and 2, respectively, using the known values of $K_1 = 0.21$ and $K_2 = 64$ for maleic acid[1] and the rate constants from Table III, we can calculate k_3, k_4, k_5, and k_6. Thus $k_3 = k_b/K_1 = 6.7 \times 10^{-2}$, $k_4 = k_d/K_1{}^2 = 8.9$, $k_5 = k_a/K_2 = 2.8 \times 10^{-4}$, and $k_6 = k_c/K_1K_2 = 3.1 \times 10^{-2}$. It is noted that $k_3 < k_4$ and $k_5 <$

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(5) A. Malliaris and D. Katakis, *J. Amer. Chem. Soc.*, **87**, 3077 (1965).

(6) C. E. Castro, R. D. Stephens, and S. Mojé, *ibid.*, **88**, 4964 (1966).

k_6. Reactions between the corresponding complexes are faster than reactions between one such complex and vanadium(II), perhaps because the complexes are closer to formation of an ion-radical intermediate. It is also indicated that under the conditions of our experiments hydrogen ion enhances the specific rate. This is also reflected in the activation energies in excess maleic acid. Chloride and sulfate also accelerate the reactions. The proton on the complex ion seems to eventually facilitate the transfer of the electron, possibly by improving the conjugation, as suggested in a similar case by Taube.[7]

Equilibrium constants for fumaric acid are not available, but as a rough approximation the data in ref 1 suggest values close to those for maleic acid. If we use these values we get, for fumaric acid, rate constants which are a little smaller than the corresponding ones of maleic acid. However, with regard to their relative values, they show the same trends, except that k_4 and k_6 have comparable values. This behavior is also consistent with the results on the activation energies. With smaller values for K_1 and K_2 the agreement between fumaric and maleic acids is improving.

The isomerization is described by eq 7 and 8, which give the zero-order terms and those which are inverse in $[H^+]$, respectively. Taking into account the equilibrium constants for the two complexes involved in these reactions, we estimate from the experimental data that the specific rate for reaction 7 is two or three orders of magnitude higher than that for 8. This difference is due to the frequency factors rather than to activation energies and can be attributed to small differences in the geometry of the two activated complexes.

The experiments with the ester and the half-ester show that one free carboxyl group is necessary but also sufficient for reaction with V(II) to take place in the conjugated systems studied. It must be recalled[5,6] that Cr(II) reacts readily with the corresponding diethyl esters, which is another important difference from V(II). The fact that the half-ester undergoes reaction with V(II), whereas the ester does not, makes rather unlikely the possibility of an attack on the remote end of the complexed organic molecule. Regarding the geometry of the activated complexes in reactions 4 and 6, some significance should also be attached to the fact that dimer is not formed.

Inasmuch as the "reducibility" of the organic acid is expected to be the main factor controlling the rates of reductions investigated in this paper, it is rather surprising that some rate constants for the reduction of maleic acid by V_{aq}^{2+}, as well as the activation energy for the third term in the corresponding rate law, differ so little from those of fumaric. This can be contrasted to the results with the Co(III) complexes of these acids; the rate of reduction of Co(III) through maleate is faster by more than two orders of magnitude than through fumarate.[8-10] Reducibility of course, must still play an important role and this is also demonstrated by comparing maleic to citraconic acid (Table III), but the evidence seems to suggest that it is not the only important factor operating. These remarks bring into focus the fact that the attached metal ion in the first step of the reduction has a serious effect on the electron acceptor properties of the organic molecule and that "reducibility" is modified by the specific environment in which the ligand finds itself. In the interaction with V_{aq}^{2+}, the advantage over fumaric acid offered by maleic acid by the availability of lower lying electron acceptor orbitals is partially offset by another factor which seems to be related to the occupied rather than the unoccupied orbitals and to the donor rather than the acceptor properties of the organic molecule. It possibly involves displacement of the electronic cloud toward the positive center to an extent related to the oxidizing power of this center. Qualitatively, it is roughly the same factor that operates in making attachment of a proton on fumarate easier than on maleate, as it is evidenced by the corresponding pK values. Thus, although the reducibility of the free ligand favors maleate, attachment of a positive charge favors fumarate. With positive ions such as V_{aq}^{2+} the two factors tend to balance each other. If the positive ion is, however, a good oxidizing agent, additional stability gained by its electron affinity largely removes the disadvantage of maleate over fumarate and the reducibility of the free ligand becomes the dominant factor. This seems to be the case with the corresponding complexes of Co(III). Finally, the same factor may also be operating in the reduction of the isonicotinamide complexes of Co(III) and Cr(III), which are believed to involve electron transfer to the ligand.[11] The Co(III) complex was found to react with Cr_{aq}^{2+} by about one order of magnitude faster than the Cr(III) complex.

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