Reaction of Aqueous Vanadous Ions with Maleic Acid, Fumaric Acid, and Derivatives. I. Complex Formation and Stoichiometry of the Reduction[1a]

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Abstract: There are four aspects of the interaction between aqueous vanadous ion and maleic acid, fumaric acid, or their derivatives: complex formation equilibrium, reduction of the carbon–carbon double bond, *cis–trans* isomerization, and exchange of the double bond hydrogens. This paper reports data on the fast equilibrium established between V_{aq}^{2+} and these acids, and on the overall stoichiometry of the reduction. The latter is found to be two vanadous ions for each molecule of the organic acid reduced, under all conditions investigated. The only products of reduction found are succinic acid from maleic and fumaric acids and the corresponding hydrogenated compounds from the derivatives. Detailed study of the complex formation between V_{aq}^{2+} and maleic acid indicates the presence of two complexes with formation constants $K_1 = 0.21$ and $K_2 = 64$ at 23°, both having a 1:1 ratio of vanadium to maleic acid. Formation of the first of these complexes is independent of hydrogen ion concentration, but formation of the second shows inverse dependence on hydrogen ion concentration. Accordingly, the spectrum in the visible region depends strongly on hydrogen ion concentration. Ionic strength affects the equilibrium only at low acidity. The formation of the first complex does not depend on temperature in the range from 7 to 45°, indicating a negligible standard enthalpy of formation, and $\Delta S° = -3.2 \pm 1$ cal mol^{-1} deg^{-1}. The observations on the V_{aq}^{2+}–maleic acid system are compared to similar, although less detailed, observations made with the other compounds used, and some conclusions are drawn about the factors determining complex formation and the form of these complexes.

Early studies[2,3] of the interaction of reducing metal ions with a series of organic molecules having double or triple bonds revealed one of the aspects of this interaction, namely the reduction of some of the double or triple bonds. The products of this reduction can be either monomolecular, by transfer of two electrons, or bimolecular, by dimerization of the one-electron transfer intermediates.

Recent studies in this laboratory[4] showed that reduction is only one of the consequences of the interaction. In the case of the V_{aq}^{2+}–maleic acid system three more aspects were found, namely, complex ion formation, *cis* to *trans* isomerization, and exchange of the double bond hydrogens with the hydrogens of the solvent. The choice of reactants made is, of course, essential in demonstrating all these aspects. Only reduction has been reported, with chromous ion as the reducing agent in ammonia[5] and acid[6] media. The interaction of the investigated organic molecules with reducing metal ions is expected to be closely related to their role in the electron transfer process when used as ligands.[7]

This paper constitutes a report on the complex ion formation between V_{aq}^{2+} and maleic acid, fumaric acid, or their derivatives. Also reported are observations on the stoichiometry of the reduction. The kinetics of the reduction will be reported in a separate paper. Preliminary information on the isomerization and the exchange has already been reported.[4]

Experimental Section

Solutions of Vanadous Ion. Vanadium(II) perchlorate solutions were prepared by electrolytic reduction of V_2O_5 suspended in a perchloric acid medium, on a mercury pool cathode. This method can only be used at relatively high acidities. At low acid concentrations V_2O_5 is reduced only incompletely, forming a black precipitate which cannot be reduced further to V_{aq}^{2+}. The complication, however, can be avoided by electrolyzing the soluble pervanadic acid, obtained by treating V_2O_5 with hydrogen peroxide in acid solution. The voltage during the electrolysis was 10 V and the current density ranged from 3.2 to 13 mA/cm^2, depending upon the $HClO_4$ concentration.

The solutions of V_{aq}^{2+} were kept under an atmosphere of argon and at a temperature of $\sim$2°, in order to avoid oxidation by air and $HClO_4$.

The acid content of the V_{aq}^{2+} solutions was measured by titration with alkali using a pH meter.

Other Materials. All reagents used were of analytical grade. Mesaconic acid was prepared by heating citraconic anhydride with a solution of HNO_3, following the method of Shriner, *et al.*[8] Sodium methylmaleate was prepared by a modification[9] of a method proposed by Pekkarinen.[10] A solution of sodium methoxide is added dropwise to a solution of maleic anhydride in methanol, and the product is obtained by precipitating with acetone after removal of the methanol by distillation. The product is purified by dissolving in a 1:1 methanol–methyl ethyl ketone mixture, condensing, and adding an excess of methyl ethyl ketone. The ester obtained by recrystallizing twice had mp 149–150°. At hydrogen ion concentrations below 0.02 *M*, at room temperature, the ester is not hydrolyzed to any detectable extent.

Determination of Vanadium in Solution. The concentrations of V_{aq}^{2+} and V_{aq}^{3+} were measured spectrophotometrically. The extinction coefficients for V_{aq}^{2+}, V_{aq}^{3+}, and VO^{2+} [11] determined in the present work agree with those reported by Gordon and Tewari.[12]

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[1] (a) Part of this work was taken from the Doctor of Engineering thesis submitted by E. Vrachnou-Astra to the Technical University of Athens, 1968; (b) author to whom correspondence should be addressed.

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Vanadous ion was also measured by titration with a deaerated solution of Fe(III). Since the oxidation of V(II) to V(III) by Fe(III) is much faster than the oxidation of V(III) to V(IV),[13,14] it is possible to titrate V(II) before V(III) starts becoming oxidized, provided that vanadium does not find itself in an environment of a large excess of Fe(III). The titration is performed by adding the Fe(III) solution to the V(II) solution, and the end point determined potentiometrically. It was found by spectrophotometric examination at the end of the titration that V(IV) is not formed. Total vanadium was determined by oxidation to V(V) by the exact amount of $KMnO_4$ needed, and titration with 0.1 N $FeSO_4$.[15]

Polarographic Measurements. The concentrations of the organic acids in the reaction mixtures were measured polarographically using a Metrohm AG Herisau rapid polarograph. The polarographic determinations were preceded by an ion exchange separation of the organic acids from vanadium, using Dowex 50WX2; the organic acids are recovered quantitatively by eluting with 1 M $HClO_4$. This treatment was found to be sufficient for the complete dissociation of the unstable complexes formed between vanadium and the organic acids.

Maleic and fumaric acids were determined polarographically in 1 M ammonium chloride buffer at a pH 8.2, following the method of Warshowsky, *et al.*[16] Citraconic and mesaconic acids were determined in a buffer containing 0.04 M HCl and 0.5 M NH_4Cl, following the method of Novak.[17]

Gas Chromatography. Strongly acidic reaction mixtures were passed over acidic Dowex 50WX2 and eluted with 2 M $HClO_4$ to decompose any vanadium complexes. The solution of organic acids obtained was neutralized with KOH, the $KClO_4$ filtered out, and the remaining solution evaporated to dryness at 30° in a rotating evaporator. The organic acids are then dissolved again in methanol, and after removal of some additional $KClO_4$, which precipitates out, they are treated with a solution of BF_3 in ether. The esterification is completed over a period of a few hours.

A butane diol-succinate column is used for the gas chromatographic analysis of the esters obtained by the above procedure, following the method of Mazliak and Salsac.[18]

Thin Layer and Paper Chromatography. The samples were treated the same way as in the gas-chromatographic analysis, except for the esterification, which is not needed in this case. The solvent used in the thin layer chromatography was benzol-methanol-acetic acid (45:8:4).[19] The solvent used for paper chromatography was ethyl formate-98% formic acid-water (12:5:3, v/v).[20]

Results

(1) Study of the Complex between V_{aq}^{2+} and Maleic Acid (HM). Immediately upon mixing V_{aq}^{2+} with the solution of the organic acid in an all glass apparatus under a strong stream of argon, an increase in absorbance is observed. This "zero-time" increase in visible light absorption is attributed to a fast complex ion formation between V_{aq}^{2+} and the corresponding acids, and can be distinguished clearly from the much slower changes occurring in cases where V_{aq}^{2+} is oxidized by the organic acid. No attempt was made to measure the rate of complex formation, but it is expected to be related to the substitution properties of V_{aq}^{2+}. The complex or complexes between V_{aq}^{2+} and maleic acid are sufficiently stable to be subject to a detailed investigation at acidities higher than $\sim$0.3 M. Under conditions similar to those used with bivalent vanadium V_{aq}^{3+} does not give a measurable change in absorbance.

(a) Stoichiometry and Formation Constants of the V_{aq}^{2+}–HM Complexes. The ratio between vanadium and maleic acid in the complex was determined by the methods of Bent and French[21] and of Vosburgh and Cooper.[22] The method of Bent and French for unstable complexes is based on the relation

$$\log A_mB_n = m \log A + n \log B - \log K$$

which is obtained by taking the logarithm of the mass action expression. Plotting log A_mB_n *vs.* log A at constant B or *vs.* log B at constant A gives m and n,r espectively. The same is true if, instead of concentrations, differences in absorbance are used.

Two series of experiments were performed, one keeping V_{aq}^{2+} constant and varying HM, the other keeping HM constant and varying V_{aq}^{2+}. The plots of the logarithms of the varying concentrations against the logarithms of the increase in absorbance at 560 mμ gave straight lines in both cases, with slopes very nearly one. This shows that the ratio between vanadium and maleic acid in the complex, at least under the conditions at which the data were obtained, is 1:1.

The method of Vosburgh and Cooper is a generalization of the method of continuous variations.[23] The plot of the difference in absorbance as a function of the composition of the solution has a maximum or minimum, and the composition of the mixture at this point is simply related to the ratio of the two complexing species in the complex. Figure 1 shows the results of the application of this method to the V_{aq}^{2+}–HM system. The experiments consisted in mixing x ml of a 0.038 M maleic acid solution with $(10 - x)$ ml of a V_{aq}^{2+} solution of the same molar concentration. Plots of the increase in absorbance due to complex formation, measured at four different wavelengths, against the composition gave curves with maxima corresponding to a ratio 1:1 between the reactants. Similar results are obtained if the medium is changed from 0.2 M $HClO_4$, 0.55 M $NaClO_4$ to 0.042 M $HClO_4$, 1.96 M $NaClO_4$. In all these cases no colored complex with composition other than 1:1 seems to be present.

The equilibrium constants for complex formation were determined using the method of Sakellaridis.[24] Series of samples were prepared, containing x ml of a V_{aq}^{2+} solution of concentration A, and $(10 - x)$ ml of a maleic acid solution of concentration fA, f being an integer. Plots of the increase in absorbance against the composition were made. Using the compositions x, x' of the mixtures corresponding to the same increase in absorbance, the equilibrium constant of the complex can be calculated by solving the system

$$K_m = \frac{(A(1 - x) - Z)(fxA - Z)}{Z}$$

$$Z = \frac{[1 - (x + x')]fA}{f - 1}$$

$$K_m' = \frac{(V_{aq}^{2+})(HM)}{(V^{II} - HM)} = \frac{1}{K_m}$$

where Z is the concentration of the complex, x and x' represent the volume of the V_{aq}^{2+} solution contained in the mixtures with the same increase in absorbance, and K_m is the equilibrium constant.

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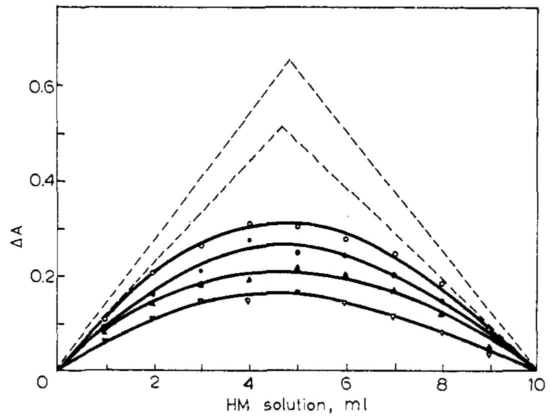


Figure 1. Plot of the differences in absorbance (ΔA) between mixtures of V_{aq}^{2+} and HM and the corresponding values, had no complex been formed, *vs.* the composition of the mixture. The curves, from top to bottom, correspond to 450, 400, 510, and 560 mμ. x ml of 0.037 M maleic acid solution is mixed with $(10 - x)$ ml of 0.037 M V^{2+} solution, both solutions containing 0.042 M $HClO_4$, 1.958 M $NaClO_4$; 10-cm cell, 23°.

By using this method, $K_{m'}$ could be calculated with an error of ~5%. Table I shows the results of four series of experiments.

Table I. Equilibrium Constants of the V_{aq}^{2+}–Maleic Acid Complex[a]

A, M	f	[$HClO_4$], M	[$NaClO_4$], M	K_m'
0.038	3	0.375	0.375	0.495 ± 0.025
0.037	5	0.375	0.375	0.471 ± 0.022
0.037	6	0.042	1.96	0.288 ± 0.014
0.037	9	1.806	0.19	4.679 ± 0.234

[a] Temperature 23°.

(b) Spectrum of the V_{aq}^{2+}–HM Complex and Effect of [H^+] and Ionic Strength. Hydrogen ion concentration has a large effect on the complex formation equilibrium between V_{aq}^{2+} and HM. At higher hydrogen ion concentration the difference in absorbance due to complex formation becomes smaller. A study of the visible spectrum of the complex at different hydrogen ion concentrations gave the results shown in Figure 2. The appearance of the spectrum changes considerably at low [H^+]. Addition of $HClO_4$ to a mixture of V_{aq}^{2+} and maleic acid with low [H^+] causes a change in the spectrum to that corresponding to the higher acidity.

At relatively high hydrogen ion concentration (0.375 M $HClO_4$) variation of the ionic strength from 0.375 to 2.0 had no measurable effect on the equilibrium. At lower acidities, however, there is a considerable effect of the ionic strength (Table II), although the qualitative features of the spectrum remain essentially unchanged (Figure 2). Study of the complex between V_{aq}^{2+} and maleic acid at hydrogen ion concentrations lower than those reported in Figure 2 is complicated by the dissociation of maleic acid and the hydrolysis of V(II).

Calculation of the extinction coefficients of the complexes at different acidities is inaccurate because it involves division by the difference of two numbers of comparable magnitude; but just to give an idea of the order of magnitude, it is mentioned that ϵ at 510 mμ was found to be ~14 and ~24 at 0.375 M and 0.042 M $HClO_4$, respectively. At 1.806 M $HClO_4$, the extinction coefficients were found to be ~40 at 510 mμ and ~35 at 400 mμ. The absorption of the complex at 510 mμ is particularly useful because the extinction coefficients of V_{aq}^{2+} and V_{aq}^{3+} at this wavelength are approximately the same, and any increase in absorbance is due to the complex alone.

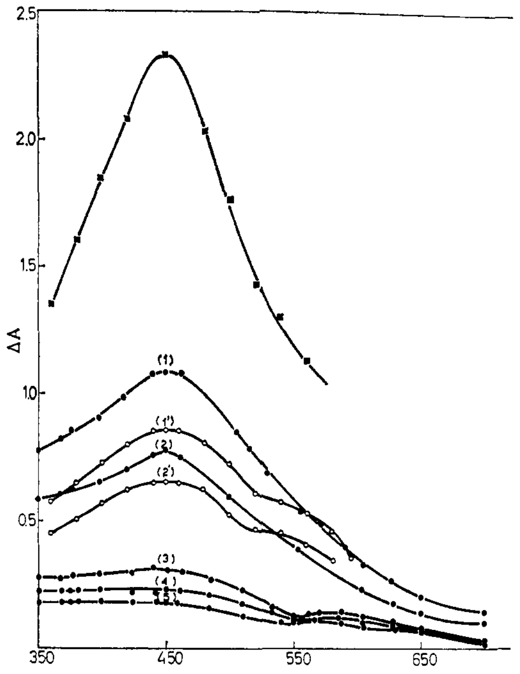


Figure 2. Difference in absorbance (ΔA) due to complex formation between V_{aq}^{2+} and maleic acid as a function of wavelength and hydrogen ion concentration. Closed circles: [V^{2+}] = 0.009 M, [HM] = 0.156 M, [$HClO_4$] + [$NaClO_4$] = 2 M. Hydrogen ion concentration: (1) 0.042, (2) 0.091, (3) 0.434, (4) 0.826, (5) 1.806 M. Open circles: [V^{2+}] = 0.01 M, [HM] = 0.156 M, [$HClO_4$] = 0.014 M; (1') no $NaClO_4$ added, (2') 1.714 M $NaClO_4$ added. Squares: [V^{2+}] = 0.011 M, [HM] = 0.156 M, [NaOH] = 0.156 M, [$HClO_4$] = 0.0161 M, pH of the mixture 2.7.

Table II. Dependence of Zero-Time Absorbance at 450 mμ on [$NaClO_4$][a]

Initial absorbance	[$NaClO_4$], M
0.94	0.00
0.84	0.07
0.80	0.10
0.77	0.20
0.76	0.39
0.74	0.58
0.72	0.95
0.72	1.35

[a] All mixtures had [V^{2+}] = 0.01 M, [HM] = 0.156 M, and [$HClO_4$] = 0.014 M; 10-cm cells, 23°.

(c) Effect of Chloride Ion and Temperature. The concentration of the complex was found to decrease in the presence of chloride ion. Application of the method of Sakellaridis at 0.83 M H^+, $\mu = 2$, 23°, in the presence of 1.14 M Cl^- gave a value of K_m' which is double the value obtained under similar conditions in the absence of Cl^-. The most probable explanation of this effect is that chloride ion causes a decrease in the available vanadous ion, chiefly through formation of the

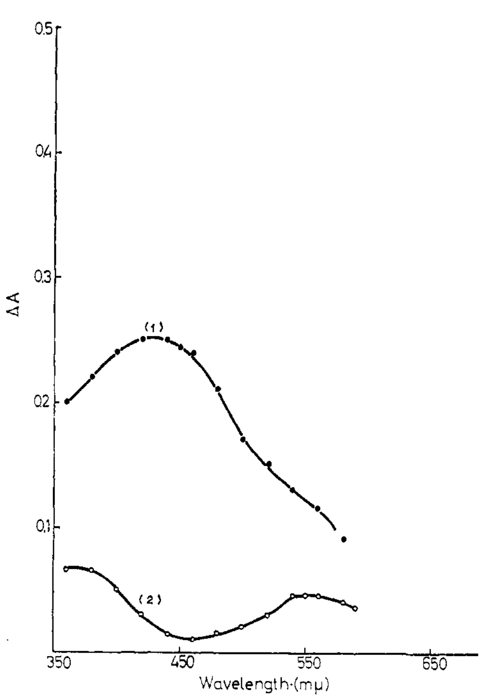


Figure 3. Difference in absorbance (ΔA) due to complex formation between V_{aq}^{2+} and fumaric acid and between V_{aq}^{2+} and the maleic monomethyl ester as a function of wavelength. (1) $[V^{2+}] = 0.011$ *M*, [HF] = 0.045 *M*, $[HClO_4] = 0.021$ *M*, 10-cm cell. (2) $[V^{2+}] = 0.011$ *M*, [sodium methyl maleate] = 0.156 *M*, $[HCLO_4] = 0.016$ *M*, $[NaClO_4] = 0.156$ *M*, 5-cm cell.

corresponding chloro complex. Making the assumption that the chloro complex does not complex further with maleic acid, it is estimated from these data that its formation constant is 0.87, with an uncertainty of ~5%.

At 1 *M* H^+ there seems to be no effect of temperature on K_m, in the range from 7 to 45°.

(d) Matrix Rank Analysis of the Spectral Data. The difference between the number of colored species and the linear relations between their concentrations at the time of mixing of the reactants was determined by matrix rank analysis of the spectrophotometric data, using a computer.[25] Calculations were performed for a number of reaction mixtures containing the same V_{aq}^{2+} and HM concentrations (0.01 *M* V^{2+}, 0.156 *M* HM), but varying H^+ concentrations (0.042, 0.091, 0.433, 0.826, and 1.806 *M*). The ionic strength was kept constant at 2.0 by making up with $NaClO_4$

The number of linearly independent colored species was found to be two. One of them must be V_{aq}^{2+}, so, if there is more than one colored complex in the solution, a linear relation between their concentrations must exist.

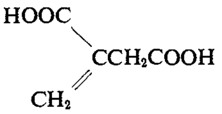
(2) Complex Formation with Other Acids and Esters. (a) Fumaric Acid. A complex is also formed between fumaric acid and V_{aq}^{2+} of comparable stability to that formed with maleic acid. Its detailed study, however, is difficult because of the limited solubility of fumaric acid. The spectra obtained with fumaric acid are similar to those for maleic acid (Figure 3), and there is again a change in appearance of the spectrum in going from high to low concentrations of hydrogen ion. The lowest $[H^+]$ tried with fumaric acid was ~0.02 *M* $HClO_4$; at lower acidities a precipitate is formed.

(b) Sodium Methyl Maleate. The complex with the half-ester of maleic acid is considerably less stable than that with maleic acid. At relatively high acidity the spectra obtained by mixing V_{aq}^{2+} and solutions of sodium methyl maleate bear qualitative resemblance to the corresponding spectra with maleic and fumaric acids. At lower acidities, however, significant differences are observed, as illustrated in Figure 3. The absorption with maximum around 450 mμ dissappears. In the case of maleic and fumaric acids the absorption maximum around 550 mμ appears as a shoulder on the much stronger 450-mμ peak. With the half-ester, the 550-mμ peak is affected much less (if at all) than the 450-mμ peak, becoming more pronounced at 0.016 *M* $HClO_4$. At even lower acidities (pH 3.6), absorption over the whole spectral range seems to increase, but the 550-mμ peak levels off and the absorption appears to have been shifted to wavelengths in the near-ultraviolet.

The dimethyl ester of maleic acid does not seem to form a complex with V_{aq}^{2+}, nor does it oxidize V_{aq}^{2+}.

(c) Substituted Maleic and Fumaric Acids. Citraconic (methylmaleic) and maleic acids behave similarly. A colored complex is formed with both upon mixing of the reactants, but the citraconic acid complex is less stable than that of maleic acid. The behavior of mesaconic (methylfumaric) acid with respect to complex formation is similar to that of fumaric acid.

Itaconic acid, which is an isomer of citraconic and mesaconic acids, but does not have a system of conjugated double bonds, does not seem to react at all.



$$HOOC-C(=CH_2)CH_2COOH$$

Chloromaleic acid, on the other hand, forms a complex with V_{aq}^{2+} which is more stable than that of maleic acid.

(3) Stoichiometry of the Reduction of Maleic Acid by V_{aq}^{2+}. A series of measurements was made in order to establish the stoichiometry of the reduction of maleic acid by V_{aq}^{2+} under a variety of conditions. In all cases V_{aq}^{2+} is oxidized to V_{aq}^{3+}; under the conditions of our experiments, higher oxidation states of vanadium were not found. The only reduction product found was succinic acid. The identification was done by ir, melting point, gas chromatography, thin layer and paper chromatography, and polarography. Systematic efforts, in particular, to find dimerization products such as butanetetracarboxylic acid or products of reduction of the carboxyl groups gave negative results; no such products were found over the whole range of conditions (concentrations of reactants, acidity, etc.) covered by this work. From the product analysis, therefore, it seems quite certain that the stoichiometry is two vanadous ions for each molecule of maleic acid reduced, in an overall two-electron change. This conclusion is also supported by quantitative analysis of all reactants and products of the reaction by various combinations of the analytical techniques already described.

(4) Stoichiometry of the Reduction of the Other Acids by V_{aq}^{2+}. Fumaric, citraconic, and chloromaleic acids, as well as the monomethyl ester of maleic acid, are all reduced by V_{aq}^{2+} in aqueous acid solutions, the result being hydrogenation of the double bond. The stoichi-

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ometry in all these cases is also two vanadous ions for one molecule of the organic acid.

Mesaconic (methylfumaric) acid was not reduced at 23° over a period of a few days. Since this reaction is expected to be slower than that of fumaric acid, and since the reaction of fumaric acid itself is rather slow, the failure to observe reaction with mesaconic acid should not come as a surprise. At any rate, the existence of an appreciable interaction is indicated by the observed complex ion formation. With itaconic acid, the situation seems to be different. No measurable interaction of any kind is recorded, even with a large excess of the acid.

Discussion

The discussion in this paper will be confined to the aspects of the data pertaining to the complex ion formation itself and to the stoichiometry of the reduction. The data also have implications of a more general nature with regard to the interaction between V_{aq}^{2+} and the organic acids investigated.

The stoichiometry of the reduction shows that the overall reaction is

$$2V_{aq}^{2+} + HO_2CR{=}CHCO_2H \longrightarrow 2V_{aq}^{3+} + HO_2CCHRCH_2CO_2H$$

Under the conditions of our experiments, secondary paths leading to other reduction products do not seem to be important.

Regarding the formation of the complexes, it has been established that their stoichiometry is 1:1 with respect to the vanadium and the organic acid. Moreover there is strong spectroscopic evidence that the organic acids enter the first coordination sphere of vanadium and that the complex formed is stabilized by charge transfer from the metal ion to the ligand. The observed effect of chloride ion is consistent with this idea. The fact that trivalent and divalent vanadium do not form complexes under the same conditions can be attributed to the electron donor properties of the latter. The absence of a temperature effect in the region where the acid independent complex between V_{aq}^{2+} and maleic acid predominates indicates that the standard enthalpy change is close to zero. Taking into account the experimental error in the determination of K_1, the upper limit for the absolute value of $\Delta S_{298}^{\circ} = -3.2 \pm 1$ cal deg^{-1} mol^{-1}.

As indicated by the absence of reaction with the dimethyl ester, availability of at least one carboxyl group is necessary for complex formation.

The dependence on hydrogen ion concentration indicates that, at least in the case of maleic acid, which was studied in detail, there is more than one complex connected by acid–base equilibria. The matrix rank analysis calculations corroborate this conclusion. The data can be explained if it is assumed that there are two complexes formed between V_{aq}^{2+} and maleic acid, one independent of the hydrogen ion concentration and the other depending on the inverse of [H$^+$]. These two complexes have considerably different spectra. The complex formation equilibria can be represented schematically

$$V_{aq}^{2+} + HM \overset{K_1}{\rightleftarrows} VMH^{2+} \qquad \text{(I)}$$

$$V_{aq}^{2+} + M \overset{K_2}{\rightleftarrows} VM^{+} \qquad \text{(II)}$$

VMH^{2+} and VM^+ being related to each other by the equilibrium

$$VMH^{2+} \overset{K_3}{\rightleftarrows} VM^{+} + H^{+} \qquad \text{(III)}$$

where $K_3 = K_2K_a/K_1$, and K_a is the first dissociation constant of maleic acid.

Using eq 6 (Appendix) and the value 1.2×10^{-2} for K_a, we calculate from the first three entries in Table I the values 0.21 and 64 for K_1 and K_2, respectively. The uncertainty in these values is about 5%. Using these values we estimate K_m for the last entry in Table I to be 4.75, which is within experimental error of the measured value. The effect of ionic strength, in the range where the data of Table I were obtained, is negligible.

Attachment of a hydrogen ion to the carboxyl group adjacent to vanadium improves the conjugation of the metal ion–maleic acid system[26] and is probably a significant factor in improving the stability of both complexes. This would then imply that the hydrogen ion in the second complex is removed from the carboxyl group remote to vanadium. The importance of conjugation is also indicated by the fact that in the case of itaconic acid, where the advantage of conjugation is not present, there is neither complex formation nor reduction. The ionic strength effect observed at low acidities probably influences equilibrium 2, for example by ion pair formation. This hypothesis is also supported by the fact that the second complex does not seem to be formed in the case of the half-ester.

The similarity between the spectra obtained with maleic and fumaric acids, the low extinction coefficients, and the hydrogen ion dependence are among the arguments that can be used to rule out chelation, under the conditions of the present experiments.

Another factor that seems to be important regarding the stability of the complexes formed is the reducibility of the organic acid. The trend within the series investigated seems to be that the easier it is to reduce the molecule, the more stable are the complexes formed, although the similarity between maleic and fumaric acids certainly indicates that "reducibility" is not the only factor involved. It is also interesting, although perhaps not unexpected, that hydrogen ion on the remote end or chlorine on the double bond carbon improves the stability of the complex relative to CH_3, presumably by attracting the V_{aq}^{2+} electron through the conjugated system.

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Appendix

The method used to determine equilibrium constants[24] was developed for one complex only. Its use therefore for the equilibrium between V_{aq}^{2+} and maleic acid must be justified. First, an appropriate generalization is considered, and then it is applied to the special case of two complexes.

Consider a system containing i forms ($i = 1, 2, 3$, etc.) of a substance A and j forms ($j = 1, 2, 3$, etc.) of a sub-

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(26) D. K. Sebera and H. Taube, *J. Amer. Chem. Soc.*, **83**, 1785 (1961).

stance B, the molar concentrations a_r, b_r, respectively, being related by

$$a_r = k_r a_1 \quad (r = 1, 2, \ldots, i) \tag{1}$$

$$b_r = l_r b_1 \; (r = 1, 2, \ldots, j) \tag{2}$$

These different forms of A and B, combined, give n complexes, the molar concentrations of which are related by

$$c_r = m_r c_1 \quad (r = 1, 2, \ldots, n) \tag{3}$$

The linear relation (eq 3) assumed to exist between the concentrations of the various complexes imposes a restriction on the composition of the complexes considered.

K_m is defined by the relation

$$K_m = \frac{\sum\limits_n c_n}{\sum\limits_i a_i \sum\limits_j b_j} \tag{4}$$

Using eq 1, 2, and 3 with 4 gives

$$K_m = \frac{c_1}{a_1 b_1} \frac{\sum\limits_{r=1}^{n} m_r}{\sum\limits_{r=1}^{i} k_r \sum\limits_{r=1}^{j} l_r} \tag{5}$$

In eq 5 c_1/a_1b_1 is the inverse of the instability constant of complex c_1; the remaining terms on the right side are generally functions of the instability constants of the various complexes and also of various experimental parameters such as hydrogen ion concentration, ionic strength, etc. These experimental parameters remain constant during the determination of the equilibrium constants by the modified method of continuous variations.[24] The maximum or minimum of an additive property of the system, such as the absorbance, corresponds to the maximum or minimum of the concentration of each of the complexes at the given conditions and hence of their sum, also. This is a direct consequence of the assumed linear relations (eq 3) between the concentrations of the complexes. Moreover, with the assumptions made, there is a one to one correspondence between the sum of the concentrations of the complexes and the measured property, *i.e.*, two points having the same value of the property must also correspond to the same value of the sum of the concentrations of the complexes. K_m (eq 4) can, therefore, be determined by the method of Sakellaridis; it is the measured equilibrium constant. Determining K_m as a function of the experimental parameters mentioned above, numerical coefficients directly related to the equilibria between complexes can be found.

In order to apply these general considerations to the case of $V_{aq}{}^{2+}$ + maleic acid we examine the dependence of K_m on one parameter only, namely the hydrogen ion concentration, the other parameters assumed to remain constant. Then in the case of the two complexes of eq I and II, from eq 5

$$K_m\left(1 + \frac{K_a}{[H^+]}\right) = K_1 + K_a K_2 \frac{1}{[H^+]} \tag{6}$$

Ligand Substitution Catalysis *via* Hard Acid–Hard Base Interaction

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Abstract: Spectrophotometric and potentiometric methods have been used to obtain quantitative rate data which show that certain cations accelerate the hydrolytic displacement of fluoride from a variety of anionic fluoro complexes. Typical hard acids, such as Be(II), Al(III), Zr(IV), and Th(IV), catalyze the hydrolysis of $AsF_5(OH)^-$, PF_6^-, BF_4^-, and AsF_6^-. The extent of catalysis varies with the catalyst: total fluoride ratio, the pH of the hydrolysis media, and the stability of the catalyst ion–fluoro complex. Catalyzed hydrolyses are first order in substrate only when the ratio of catalyst to substrate is large. Direct interaction between bound fluoride and the catalyst ion rather than promotion of an acid catalyzed reaction is shown by the extensive hydrolysis of PF_6^- and AsF_6^- under conditions of acidity (pH 2) where the uncatalyzed hydrolysis has a half-life of several months. These results show that the hard and soft acid–base theory can be used to select catalysts for replacement of ligands by basing the selection on the hard or soft nature of the ligand to be replaced.

The hard and soft acid–base theory[1] has contributed significantly to the understanding of acid–base interactions and has become a useful tool for predicting the acid–base behavior of species in many types of reaction. Previously[2] it has been shown that soft acids can catalyze the replacement of soft bases present as ligands within the coordination sphere of a metal. The objective of the present study was to determine the validity of the generalization of this phenomenon to systems of hard acids and hard bases. Specifically the authors wished to determine if hard acids *in general* were able to catalyze the hydrolytic displacement of complexed fluoride. The hydrogen ion catalysis of

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(1) R. G. Pearson, *J. Amer. Chem. Soc.*, 85, 3533 (1963).

(2) (a) C. Bifano and R. G. Linck, *Inorg. Chem.*, 7, 908 (1968), and references therein; (b) S. P. Tanner and W. C. E. Higginson, *J. Chem. Soc., A*, 1164 (1969).