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## The Vanadyl-Tartaric Acid System at Low pH. Equilibrium Quotients and Complexation Kinetics<sup>1</sup>

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A study by optical and pH methods indicates that the species present in solutions of vanadyl ( $\text{VO}^{2+}$ ) ion and tartaric acid ( $\text{H}_2\text{T}$ ) below pH 2 can be formulated as 1:1 and 1:2 complexes of the types VOT and  $\text{VOT}_2^{2-}$ . The formation constants so determined are  $K_1 = (\text{VOT})(\text{H}^+)/(\text{VO}^{2+})(\text{HT}^-) = 12.5$  and  $K_2 = (\text{VOT}_2^{2-})(\text{H}^+)/(\text{VOT})(\text{HT}^-) = 2.0$  at 25° and ionic strength 0.25  $M$ . Temperature-jump and pressure-jump relaxation methods were used to study the reactions of tartaric acid and bitartrate anion with vanadyl ion. An initial-rate stopped-flow study was used to corroborate the rate constant for the formation of a 1:1 complex. Relaxation methods determine the forward rate constant for the reaction  $\text{VO}^{2+} + \text{HT}^- \rightleftharpoons \text{VOT} + \text{H}^+$  to be  $170 M^{-1} \text{sec}^{-1} \pm 20\%$ . The rate constant determined by initial-rate stopped-flow methods is  $185 M^{-1} \text{sec}^{-1}$ , the two values agreeing within experimental error. The forward rate constant for the reaction  $\text{VOT} + \text{HT}^- \rightleftharpoons \text{VOT}_2^{2-} + \text{H}^+$  is  $277 M^{-1} \text{sec}^{-1} \pm 10\%$ . The rate constants for fully protonated tartaric acid are much smaller and were unable to be determined. The value determined for the rate of formation of the 1:1 complex, which is low relative to that expected for normal substitution (*i.e.*, that value equal to the product of the ion-pairing constant and the water-exchange rate on vanadyl), indicates that the rate-determining step in the reaction is the chelation process itself. Rather than being due to steric restrictions, this shift in rate-determining step is viewed as arising from protonation of the ligand binding site.

The most recent examination of the vanadyl-tartrate system established the existence of a unique dimeric structure in aqueous solution above pH 5 by electron spin resonance spectra.<sup>2</sup> This structure was also established in the solid state by a crystal structure determination.<sup>3</sup> For a time this conclusion was disputed,<sup>4</sup> however, those same workers later found similar evidence for the dimer.<sup>5</sup>

Titration curves of mixtures of both *d*-tartaric acid and *l*-tartaric acid with vanadyl indicate that below pH 5 only mononuclear species are present.<sup>2</sup> This fact was substantiated by the pH dependence of the optical spectra. The identities of the mononuclear species below this pH were not determined. However, the existence of species other than 1:1 monomers was established.

There is a general lack of stability constant data on tartrate complexes. It is probably for this reason that the kinetics of these reactions has been studied so little. The first object, therefore, of this study is to obtain equilibrium data on vanadyl-tartrate solutions in acid media below pH 2, leading to a determination of the complex stability constants. This information forms the basis of the second part of the study, namely, vanadyl-tartrate complexation rate constant determination by temperature-jump, pressure-jump, and stopped-flow techniques.

### Experimental Section

The reagents used in the following experiments were  $\text{VOSO}_4 \cdot 2\text{H}_2\text{O}$  (Fisher purified reagent), *d*-tartaric acid (Baker Analyzed

reagent), and  $\text{Ba}(\text{NO}_3)_2$  (Fisher Certified reagent). Belmont Springs distilled water was used throughout.

To avoid the problem of sulfate interaction with vanadyl, barium nitrate was used to precipitate quantitatively the sulfate as  $\text{BaSO}_4$ . The resulting solution of vanadyl nitrate was then analyzed for vanadyl by EDTA complexometric titration using  $\text{MgSO}_4$  back-titration to an Eriochrome Black T end point. The titrations were run in  $\text{NH}_3\text{-NH}_4\text{Cl}$  pH 10 buffered solutions. Ascorbic acid was added as a reducing agent. From the calculated concentrations, the extinction coefficients could be obtained from the measured optical density. The values obtained agreed with the literature values.<sup>6</sup> From this point, analysis of the prepared vanadyl solution was carried out spectrophotometrically. It should be noted that the  $\text{VO}^{2+}$  band extending into the red region was pH independent. The band extending into the ultraviolet region showed a small variation of optical density with pH. This is most probably due to the appearance of hydroxovanadyl,  $\text{VOOH}^+$ . This species is absent in solutions equal to or greater than 0.02  $M$  in acid.<sup>7</sup>

Since  $\text{VO}^{2+}$  is air oxidized, the solutions were prepared immediately prior to use. In the acidic solutions used in the temperature-jump experiments, oxidation of prepared vanadyl solutions was not noted for at least 1 day.

All solutions were made up to approximately the same ionic strength,  $\mu \approx 0.25 M$ . This unusually high ionic strength was necessitated by the fact that the reaction was followed directly (no indicator was coupled to the reaction) and rather large concentrations of metal had to be used to see any effect at all.  $\text{KNO}_3$  was used to adjust the ionic strength. Experiments were also done by arbitrary addition of salt. No variation of relaxation time was experimentally measurable. The pH of all solutions was adjusted by dropwise addition of  $\text{NaOH}$  or  $\text{HNO}_3$ . The relative pH accuracy is  $\pm 0.02$  pH unit, and the temperature is  $25 \pm 1^\circ$ .

The optical density measurements were made on a Beckman DU-2 spectrophotometer. The pH readings were made on a Corning Model 12 pH meter. To convert from measured pH to hydrogen ion concentration, the activity coefficient,  $\gamma$ , of hydrogen ion was calculated using the Davies equation<sup>8</sup>

$$\log \gamma_{\pm} = -0.5 z_+ z_- \left( \frac{\sqrt{\mu}}{1 + \sqrt{\mu}} - 0.2\mu \right)$$

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(2) R. E. Tapscott and R. L. Belford, *Inorg. Chem.*, **6**, 735 (1967).

(3) J. G. Forrest and C. K. Prout, *J. Chem. Soc., A*, 132 (1967).

(4) R. H. Dunhill and T. D. Smith, *ibid.*, **A**, 2189 (1968).

(5) R. H. Dunhill and M. C. R. Symons, *Mol. Phys.*, **15**, 105 (1968).

(6) S. C. Furman and C. S. Garner, *J. Am. Chem. Soc.*, **72**, 1785 (1950).

(7) G. Jones and W. A. Ray, *ibid.*, **66**, 1571 (1944).

(8) C. W. Davies, *J. Chem. Soc.*, 2093 (1938).

where  $z_{+,-}$  is ionic charge. In all cases, the pH mentioned hereafter refers to concentration, not activity. The activity coefficient of a cation is largely determined by the anions in solution, not depending markedly on the nature of the other cations.<sup>9</sup> In these experiments,  $\text{NO}_3^-$  is the principal anionic species. The solutions were therefore treated as being solutions of  $\text{HNO}_3$  of the appropriate ionic strength. The Davies equation is accurate for these 1:1 systems to better than 8% at an ionic strength as high as 0.5 *M*.

Experiments were attempted over a considerably larger pH range than is reported in Table III. As the pH is raised, the amplitude of the effects decreases, ultimately becoming too small to measure accurately. At lower pH, the effects become so long that the temperature no longer remains constant during the relaxation process. All traces were plotted semilogarithmically to ensure exponentiality. An on-line Fabritek Instrument computer was used to analyze several of the reaction traces. In all cases the curves proved to be simple exponentials. The reported  $1/\tau$  ( $\tau$  is relaxation time) is taken as the average of several traces. The relative error in the measurement of the relaxation spectra is  $\pm 10\%$ . This is less than the standard error later reported for some of the rate constants as these depend on additional factors. Pressure-jump experiments verified the measured relaxation times obtained by temperature jump for some solutions.

The data from the stopped-flow initial-rate studies were plotted, and an average value of the initial slope was taken from at least five traces.

### Stability Quotients

The stability quotients of the vanadyl-tartaric acid system were determined by the use of both optical and pH methods. Although the structural studies of Belford and coworkers indicate that two protons are released on complexation, this has not been assumed in this determination. The initial method followed that used by Furman and Garner<sup>10</sup> in their determination of the stability constant of the vanadyl-thiocyanate system. Assume only one complex is present, at concentration *c*, and the absorbances of the complex and of  $\text{VO}^{2+}$ , these being the only absorbing species, obey Beer's law. With *a* being the initial concentration of vanadyl, *b* the initial concentration of tartaric acid, and *K* their association constant, the following relation holds when  $c^2 \ll ab$

$$\frac{ab}{A - a\epsilon_{\text{VO}^{2+}}} = \frac{a + b}{\Delta\epsilon} + \frac{1}{K\Delta\epsilon} \quad (1)$$

where  $\Delta\epsilon$  is the difference in the absorption coefficients of complex ( $\epsilon_{\text{ex}}$ ) and  $\text{VO}^{2+}$ , and *A* is the measured absorbance.

A plot of  $ab/(A - a\epsilon_{\text{VO}^{2+}})$  vs. (*a* + *b*) is then a straight line, the slope of which is  $1/K\Delta\epsilon$ . This method allows a determination of both  $\epsilon_{\text{ex}}$  and *K* since everything else in eq 1 is known.<sup>11</sup> In the case of tartaric acid, experiments were done at one pH to determine the stability constant *K*. As defined, *K* is only an apparent constant since no account has been taken of the number of protons released. The variation of *K* with pH could then be used to determine the number of protons ionized on complexation.

Experiments were done at two wavelengths. At

(9) J. N. Newton, "Ionic Equilibrium," Addison-Wesley Publishing Co., Inc., Reading, Mass., 1964, Chapter 12.

(10) S. C. Furman and C. S. Garner, *J. Am. Chem. Soc.*, **73**, 4528 (1951).

(11) F. J. C. Rossotti and H. Rossotti, "The Determination of Stability Constants," McGraw-Hill Book Co., Inc., New York, N. Y., 1961, p 276.

580 nm, near linearity could be obtained. At 350 nm, no linear correlation was apparent. This lack of linearity indicated the presence of complexes in addition to the postulated 1:1 complex.

This problem was discussed by Kruh<sup>12</sup> in a paper dealing with discrepancies in two different determinations of the stability constants of the copper halide complexes. If a second complex,  $\text{ML}_2$ , is present in addition to the postulated species, ML, linearity may still be obtained in a plot of  $ab/(A - a\epsilon_{\text{VO}^{2+}})$  vs. (*a* + *b*) under the conditions  $K_2/K_1 \leq 1/4$  and  $\epsilon_1 \leq \epsilon_2 \leq 2\epsilon_1$ , where subscript 1 refers to ML and subscript 2 to  $\text{ML}_2$ . In this case the slope and intercept are not given by eq 1 but are functions of the extinction coefficients and stability constants for the second complex as well.

As a second complex was indicated by the plots of eq 1, further experiments were done to determine the absorption coefficients of the species ML and  $\text{ML}_2$  and the charge of the complex. Since complexation occurs by the release of at least one carboxyl proton, the reaction can be displaced to the right by raising the pH. Solutions were prepared of high metal-to-ligand ratios and high pH to determine the absorption coefficient of the species ML. The reaction was assumed to be displaced essentially completely to the right when no further change of absorbance occurred on addition of base. Solutions were also prepared of high ligand-to-metal ratios to determine the absorption coefficient of  $\text{ML}_2$ . The presence of a second complex was immediately indicated as the solution thus prepared was green, not blue typical of the other prepared solutions. The absorption coefficients so determined at 580 and 350 nm are given in Table I.

TABLE I  
ABSORPTION COEFFICIENTS OF THE VANADYL TARTRATES<sup>a</sup>

$\lambda$ , nm	$\epsilon_{\text{VO}^{2+}}$	$\epsilon_{\text{VO}^+}$	$\epsilon_{\text{VO}_2^{2-}}$
580	4.3	10	20
350	1	12	50

<sup>a</sup> Absorption coefficients are in  $M^{-1} \text{cm}^{-1}$ .

In order to determine the number of protons ionized on complexation, the following experiments were performed. Solutions of vanadyl nitrate and tartaric acid were prepared of equal hydrogen ion concentration. Upon mixing the solutions, any change in hydrogen ion concentration is then directly attributable to the formation of complex. The amount of complex formed can be approximately obtained from the change in absorbance on mixing. Comparison of optical and pH experiments indicates that the complexation is accompanied by the release of two protons: ML is therefore neutral;  $\text{ML}_2$  is doubly negative.

Most recently a study has appeared in which the release of three protons on complexation is indicated.<sup>13</sup> The authors were not aware of the work of Belford and coworkers and assumed, in part, that tartaric acid could act as a quadridentate ligand as previously

(12) R. Kruh, *J. Am. Chem. Soc.*, **76**, 4865 (1954).

(13) K. Lal and R. P. Agarwal, *J. Indian Chem. Soc.*, **46**, 49 (1969).

TABLE II  
 $\Delta[\text{H}^+]$  ON MIXING VANADYL AND TARTARIC ACID SOLUTIONS<sup>a</sup>

[VO <sup>2+</sup> ] <sub>0</sub>	[H <sub>2</sub> T] <sub>0</sub>	[H <sup>+</sup> ] <sub>0</sub>	[H <sup>+</sup> ] <sub>final</sub>	$A_{350}$		$\Delta[\text{H}^+]$	[VO <sup>2+</sup> ]	[VOT]	[VOT <sub>2</sub> <sup>2-</sup> ]
				Initial	Final				
0.0365	0.0428	0.0275	0.0442	0.158	0.201	0.0167	0.0285	0.0077	0.0003
0.0370	0.0435	0.0138	0.0372	0.159	0.220	0.0234	0.0264	0.0100	0.0006

<sup>a</sup> All concentrations are molar. Subscript 0 denotes initial concentration.

 TABLE III  
 EXPERIMENTAL AND CALCULATED VALUES OF ABSORBANCE<sup>a</sup>

Soln no.	[VO <sup>2+</sup> ]	[VOT]	[VOT <sub>2</sub> <sup>2-</sup> ]	Exptl		Calcd		$\Delta/A_{350}(\text{exptl})$	$\Delta/A_{350}(\text{exptl})$
				$A_{350}$	$A_{380}$	$A_{350}$	$A_{380}$		
1	0.0580	0.0116	0.0004	0.388	0.245	0.373	0.217	-0.04	-0.11
2	0.0636	0.0063	0.0001	0.335	0.126	0.338	0.145	+0.01	+0.15
3	0.0337	0.0316	0.0047	0.580	0.660	0.555	0.648	-0.04	-0.02
4	0.0484	0.0203	0.0014	0.450	0.392	0.439	0.362	-0.02	-0.08
5	0.0219	0.0130	0.0012	0.243	0.210	0.248	0.238	+0.02	+0.13
6	0.0152	0.0189	0.0038	0.321	0.405	0.330	0.432	+0.03	+0.07
7	0.0465	0.0219	0.0016	0.482	0.440	0.451	0.390	-0.06	-0.11
8	0.0567	0.0128	0.0005	0.383	0.242	0.382	0.236	0.00	-0.02
9	0.0111	0.0029	0.0001	0.075	0.056	0.079	0.051	+0.05	-0.09
10	0.0660	0.0061	0.0001	0.347	0.125	0.347	0.144	0.00	+0.15
11	0.0605	0.0112	0.0003	0.388	0.215	0.378	0.210	-0.03	-0.02
12	0.0285	0.0077	0.0003	0.201	0.127	0.206	0.136	+0.02	+0.07
13	0.0264	0.0100	0.0006	0.220	0.152	0.226	0.176	+0.03	+0.16
								Av 0.03	Av 0.09

<sup>a</sup> All concentrations are molar.  $K_1 = (\text{VOT})(\text{H}^+)/(\text{VO}^{2+})(\text{HT}^-) = 12.5$ ;  $K_2 = (\text{VOT}_2^{2-})(\text{H}^+)/(\text{VOT})(\text{HT}^-) = 2.0$ .

proposed by Jørgensen.<sup>14</sup> Their conclusion seems inconsistent with the malic acid (HOOCCH<sub>2</sub>CHOH-COOH) study contained in the same paper for which only two protons are found to be released on complexation. In a kinetic study of nickel-tartrate and nickel-malate complexation,<sup>15</sup> it was assumed that coordination of the hydroxyl function did not lead to proton release.

The absorption coefficients of Table I and the results of the pH mixing experiments, Table II, are then used to obtain  $K_1$  and  $K_2$  by calculating the best fit of the absorbancies of the solutions presented in Table III, where  $K_1$  and  $K_2$  so obtained are presented. At 580 nm, the average error in fitting calculated and observed optical densities is 3%. At 350 nm, the average error is somewhat larger, 9%. The largest error in these experiments is in the determination of pH. Small errors in pH would cause greater errors at 350 nm where  $\epsilon_2 \simeq 4\epsilon_1$  than at 580 nm where  $\epsilon_2 \simeq 2\epsilon_1$ .

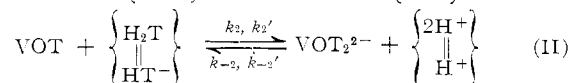
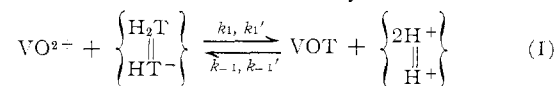
It must be pointed out that no account of the possible acid dissociation of the complexes has been taken. At such low pH, this seems a reasonable assumption especially in view of the fact that the bor-tartrate complex is less acidic than bitartrate as has been shown experimentally.<sup>16</sup> Also, from the reported hydrolysis constants for vanadyl determined by Rossotti and Rossotti,<sup>17</sup> no species such as VOOH<sup>+</sup> were proposed.

There have been few other determinations of stability constants of vanadyl complexes with  $\alpha$ -hydroxy car-

boxylates. A study appeared by Martell and co-workers<sup>18</sup> in which stability constants were measured for the complexes with salicylic acid, sulfosalicylic acid, and other ligands which were not  $\alpha$ -hydroxy carboxylic acids. In these cases, 2 mol of proton is produced per mole of metal chelate formed. Indeed, this, and all previous evidence on vanadyl complexes, supports the contention that, in general, the phenolic and alcoholic hydrogens of ligands are easily displaced by the vanadium(IV) provided the ligand forms a chelate.<sup>19</sup>

### The Relaxation Time for Vanadyl Tartrate Complexation

From the preceding equilibrium study, the following reactions can be used to describe the system



The unprimed rate constants refer to the reaction of H<sub>2</sub>T; the primed, to the reactions of HT<sup>-</sup>. In these equations the reaction of the ambident HT<sup>-</sup> to produce an anionic species has been neglected. Whether this is a good assumption will be discussed later. As in a similar boric acid study,<sup>20</sup> the tartaric acid protolytic step is assumed to be very fast. ( $K_a = [\text{H}^+][\text{HT}^-]/[\text{H}_2\text{T}] = 1.28 \times 10^{-3}$ .<sup>21</sup>) Under this assumption, this set of reactions possesses two relaxation times. Therefore

$$(1/\tau)^2 - (a_{11} + a_{22})(1/\tau) + (a_{11}a_{22} - a_{21}a_{12}) = 0 \quad (2)$$

(14) C. K. Jørgensen, *Acta Chem. Scand.*, **11**, 73 (1957).  
 (15) H. Hoffmann and U. Nickel, *Ber. Bunsenges. Physik. Chem.*, **72**, 1096 (1968).  
 (16) L. I. Katzin and E. Gulyas, *J. Am. Chem. Soc.*, **88**, 5209 (1966).  
 (17) F. J. C. Rossotti, and H. S. Rossotti, *Acta Chem. Scand.*, **9**, 1177 (1955).

(18) G. E. Mont and A. E. Martell, *J. Am. Chem. Soc.*, **88**, 1387 (1966).  
 (19) J. Selbin, *Chem. Rev.*, **65**, 153 (1965).  
 (20) K. Kustin and R. Pizer, *J. Am. Chem. Soc.*, **91**, 317 (1969).  
 (21) V. Frei, *Collection Czech. Chem. Commun.*, **30**, 1402 (1965).

where the  $a_{ij}$  terms are known functions of the rate and equilibrium constants,<sup>22</sup> and the two relaxation times are given by the positive and negative roots of this quadratic equation.

### Kinetic Results and Treatment of Data

**Relaxation Experiments.**—The equilibrium concentrations of the species in solution were calculated on the basis of the equilibrium quotients previously determined. An iterative Newton-Raphson computer program was used to calculate the concentrations presented in Table III. An IBM 1130 computer was used in all computations.

The equilibrium concentrations, the equilibrium quotients, and the relaxation times of the experimental solutions then constitute the input data for a non-linear least-squares routine.<sup>23</sup> From this analysis one obtains a set of "best fit" rate constants, which determine the coefficients of the polynomial in  $1/\tau$ , namely, eq 2. The result of the best fit of calculated and experimental values of  $1/\tau$  is presented in Table IV.

TABLE IV  
RELAXATION TIMES FOR VANADYL-TARTRATE SOLUTIONS

Soln no. <sup>a</sup>	$\tau$ , sec		$[\text{H}^+]$ , M
	Exptl	Calcd	
1	0.66	0.50	0.0758
2	0.75	0.61	0.0758
3	0.12	0.13	0.0269
4	0.20	0.19	0.0269
5	0.28	0.20	0.0269
6	0.17	0.15	0.0269
7	0.21	0.13	0.0447
8	0.41	0.60	0.0447

<sup>a</sup> Solution numbers refer to Table III.

The program finds the best values of the four forward rate constants. The reverse constants are, of course, determined by the equilibrium quotients. The initial best fit for the four-parameter equation led to positive values for  $k_1'$  and  $k_2'$  and small negative values for  $k_1$  and  $k_2$ . The latter rate constants were then arbitrarily set equal to zero and the best fit obtained for  $k_1'$  and  $k_2'$ . This treatment led to the values  $k_1' = 170 \text{ M}^{-1} \text{ sec}^{-1}$  with a standard error of  $\pm 34 \text{ M}^{-1} \text{ sec}^{-1}$  and  $k_2' = 277 \text{ M}^{-1} \text{ sec}^{-1}$  with a standard error  $\pm 25 \text{ M}^{-1} \text{ sec}^{-1}$ . These standard errors of  $\pm 20$  and  $\pm 10\%$ , respectively, were by far the best fit obtainable.

In these cases,  $1/\tau$  is a function of the rate constants for both complexations. An inspection of the matrix for the reaction indicates that the system becomes uncoupled only when  $[\text{VO}^{2+}] \gg [\text{VOT}]$ . (In this case the term  $a_{21}$  would become very small.) Simply having the concentration of  $\text{VOT}_2^{2-}$  be small is not sufficient to consider the observed relaxation time to be a function of the first complexation only. The equilibrium data in Table III indicate that the system is coupled.

**Stopped-Flow.**—The principal advantage of the method of initial rates is that the stability constant of

the system is not required. The assumption is made that the initial portion of the reaction trace is solely due to formation of the first complex, the back-reaction and second complexation reaction not being important. The expression for the rate of appearance of the complex, VOT, under these assumptions is then

$$\frac{d[\text{VOT}]}{dt} = k_1'[\text{VO}^{2+}][\text{HT}^-] \quad (3)$$

from which it follows that

$$k_1' = \left( \frac{dA}{dt} \right) / (\Delta\epsilon[\text{VO}^{2+}][\text{HT}^-]) \quad (4)$$

From consideration of the relaxation results in which  $k_1$  was found to be small, eq 3 was written only in terms of reaction of  $\text{VO}^{2+}$  with  $\text{HT}^-$ .

The overall absorbance change was measured by mixing the solutions together and measuring the new absorbance spectrophotometrically. The slope was then taken from a plot of the oscilloscope trace. A sample is given in Figure 1. The  $\text{VO}^{2+}$  and  $\text{HT}^-$

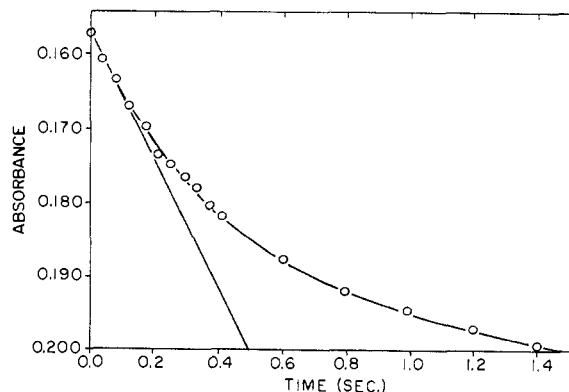


Figure 1.—Stopped-flow initial-rate reaction plot. Conditions:  $[\text{VO}^{2+}]_0 = 0.0375 \text{ M}$ ,  $[\text{H}_2\text{T}]_0 = 0.0430 \text{ M}$ ,  $[\text{H}^+]_0 = 0.0269 \text{ M}$ ,  $\mu = 0.25 \text{ M}$ ,  $25^\circ$ . Circles represent data points obtained from oscillographic trace. The curved line represents a "best fit" of these points, the straight line being the slope at zero time.

concentrations are the initial concentrations;  $\Delta\epsilon$  is known from Table I.

Experiments were done at two different initial hydrogen ion concentrations,  $[\text{H}^+] = 0.0269$  and  $0.0135 \text{ M}$ . In the more acidic solution, reaction was complete in approximately 1.5 sec. In the other, reaction was complete in approximately 1 sec.

At  $[\text{H}^+] = 0.0269 \text{ M}$ ,  $k_1'$  as determined from eq 4 was  $190 \text{ M}^{-1} \text{ sec}^{-1}$ . At  $[\text{H}^+] = 0.0135 \text{ M}$ ,  $k_1'$  was determined to be  $182 \text{ M}^{-1} \text{ sec}^{-1}$ . As the error in these experiments is at least  $\pm 20\%$ , no hydrogen ion dependence is experimentally measurable. This rate constant easily agrees within experimental error with that determined by relaxation methods and is independent of any uncertainties in stability constants.

### Discussion

Crystal structures of vanadyl complexes with bidentate ligands show that the ligands occupy the equatorial positions of the first coordination sphere

(22) G. G. Hammes and J. I. Steinfeld, *J. Am. Chem. Soc.*, **84**, 4639 (1962).

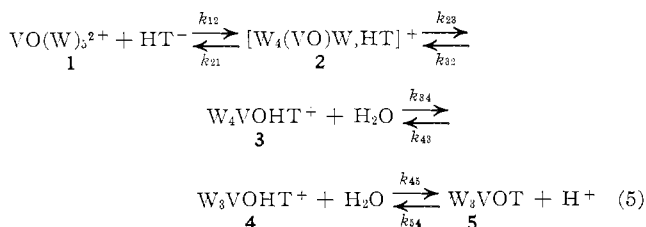
(23) We wish to thank Mr. A. Gottlieb for adapting the nonlinear least-squares program (AGNLS) for use on the IBM 1130.

of the metal ion. This structure has been shown for both the tartrate<sup>3</sup> and acetylacetonate<sup>24</sup> complexes. The structures in these cases are pyramidal, the plane of the coordinated ligands being below the vanadium. In these structures only a weak coordination of a sixth (axial) ligand is possible. This geometry has also been indicated in aqueous solution by electron spin resonance experiments.<sup>2</sup> Coordination of a bidentate ligand through one equatorial and the axial position has never been indicated or observed.

In determining the rate of elimination of coordinated water molecules from the inner coordination sphere of vanadyl, Wüthrich and Connick<sup>25</sup> also noted the great difference between axial and equatorial sites on vanadyl. They determined the water-exchange rate for the equatorial waters to be 500 sec<sup>-1</sup> at 25°. Their data indicate that the rate of exchange from the axial position must be at least a factor of 10<sup>6</sup> greater.

The water-exchange rate from the equatorial position is much slower than that previously observed for other labile bivalent first-row transition metal ions.<sup>26</sup> This indicates that the vanadyl can be formally regarded as being composed of a V<sup>4+</sup> and O<sup>2-</sup>; *i.e.*, the bound waters appear to experience a considerably higher positive charge than +2.

For  $\alpha$ -hydroxy acids, the overall complexation reaction can be described as a four-step process. The first is the diffusion-controlled formation of an ion pair. The second step involves the release of a water molecule from the inner coordination sphere of the metal followed by coordination of one of the ligand sites. The third step involves release of a second water molecule from the inner coordination sphere of the metal and coordination of the second ligand site to form a five-membered chelate ring. The release of the hydroxyl proton of the tartaric acid has been included as a fourth step. The detailed mechanism is formulated as follows (where W  $\equiv$  H<sub>2</sub>O)



The overall equilibrium quotient for such a system is given by

$$K = (k_{12}k_{23}k_{34}k_{45}) / (k_{21}k_{32}k_{43}k_{54})$$

$k_{12}/k_{21}$  is referred to as the ion-pairing constant,  $K_{ip}$ . If the rate-determining step in this sequence is the release of the first water molecule from the inner coordination sphere of the metal, the overall forward rate constant would then be  $k_1' = K_{ip}k_{23}$ , where  $k_{23}$  is the previously

determined rate constant for water release<sup>27,28</sup> found to be equal to 500 sec<sup>-1</sup>.

The ion-pairing constant,  $K_{ip}$ , requires discussion. Identical expressions for the ion-pairing constant were independently derived by Eigen<sup>29</sup> and Fuoss.<sup>30</sup> In each case the models were based on assumptions that the solvent is a continuum and the ions are rigid spheres of radius  $a/2$ , where  $a$  is the distance of closest approach of the charged particles. The ligand quite obviously does not conform to this model. In this case, even the central metal does not meet the criteria for the application of the model. With modifications, it has been applied to obviously nonspherical bidentate ligands. For VO<sup>2+</sup>, at the least, a steric factor must be applied to take into account the occupied axial site. This would tend to decrease the calculated  $K_{ip}$ . However, the charge of the central metal atom would most certainly have to be taken as greater than +2.

The calculated values of  $K_{ip}$  for 2:1 and 3:1 electrolytes are 2 and 5 M<sup>-1</sup>, respectively,<sup>22</sup> the distance of closest approach being picked as 5 Å. It seems fairly certain that  $k_1'$  calculated from this model would then have a value >10<sup>3</sup> M<sup>-1</sup> sec<sup>-1</sup>, clearly greater than experimentally observed.

If the detailed mechanism is instead treated from the following point of view, a different expression for  $k_1'$  can be derived. Assuming that the ion pairing is very fast and state **3** is in a steady state ( $d[\mathbf{3}]/dt = 0$ ),<sup>22</sup> the resulting expression for the overall forward rate constant is

$$k_1' = K_{ip}k_{23} \left( \frac{k_{34}}{k_{32} + k_{34}} \right)$$

The value obtained above for  $K_{ip}k_{23}$  implies, if this mechanism is correct, that  $k_{32} > k_{34}$ . The rate-determining step is then the closing of the chelate ring itself.

A previously reported departure from normal substitution kinetics leading to a change in rate-determining step was ascribed to sterically restricted ring closure.<sup>31</sup> It should be clear that, although both a shift in rate-determining step and limiting ring closure are now being postulated, the effect is viewed as arising from protonation of the ligand-binding site, rather than unfavorable ring geometry. In fact, a similar result obtained by Hoffmann and Nickel<sup>15</sup> in their study of the nickel-tartrate system has also been interpreted this way. In this case, however, the fit of their pressure-jump data indicated that the hydroxyl proton was still present in the complex.

It cannot be concluded from this study that fully protonated H<sub>2</sub>T does not complex with VO<sup>2+</sup>. If this reaction also proceeded as in the detailed mechanism, the change in ion-pairing constant must be taken

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(31) K. Kustin, R. F. Pasternack, and E. M. Weinstock, *ibid.*, **88**, 4601 (1966).

(24) R. P. Dodge, D. H. Templeton, and A. Zalkin, *J. Chem. Phys.*, **35**, 55 (1961).

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into account. As before,  $k_{23}$  is  $500 \text{ sec}^{-1}$ ; however,  $K_{ip}$  for a neutral uncharged species is about  $0.1 M^{-1}$ . From the HT<sup>-</sup> result, taking  $k_{34}/(k_{32} + k_{34}) \approx 0.1$ , an upper limit for  $k_1$  of  $5 M^{-1} \text{ sec}^{-1}$  can be obtained. Whether this rate constant is in fact equal to zero cannot be definitely concluded from the experiments. This experimentally determined low value for  $k_1$  is the reason the reaction of ambident bitartrate to produce an anionic complex was neglected in the relaxation expression.

The same model may be applied to the complexation of a second ligand molecule. Relative to the first complexation, competing factors are operative. The water-exchange rate of the remaining equatorial waters is considerably enhanced.<sup>32</sup> This effect has been interpreted in the case of  $\text{VO}^{2+}$  solely on electrostatic grounds wherein the negatively charged coordinating group of the ligand neutralizes in part the high positive charge, leading to labilization of the remaining waters. In the case of vanadyl, two orders of magnitude may be involved. However, the ion-pairing constant is also affected. The complex VOT is neutral, leading to a much lower  $K_{ip}$  from electrostatic considerations. There are also fewer binding sites and unfavorable steric requirements, which lower  $K_{ip}$ .

(32) K. Wüthrich and R. E. Connick, *Inorg. Chem.*, **7**, 1377 (1968).

From the considerations above, we see that an *a priori* calculation of the relative rates of the first and second complexations is not possible. In the latter case, the value of  $k_2'$  experimentally determined from relaxation methods is  $277 M^{-1} \text{ sec}^{-1}$ , reflecting a compromise of the competing trends. The value of  $k_1'$  was confirmed by the initial rate stopped-flow experiments, the interpretation of which does not depend on the stability constant. The value of  $k_2'$  (although its standard error is smaller) is directly dependent on the equilibrium quotients.

Since all of the experiments were performed at  $\text{pH} \leq 1.85$ , the hydroxovanadyl species,  $\text{VOOH}^+$ , was not postulated in the overall mechanism. The coordinated hydroxyl would lead to an increase in the rate *via* a labilization of the remaining waters as described above. This path was not included on the basis of the work of Rossotti and Rossotti<sup>17</sup> and that of Jones and Ray.<sup>7</sup> In the vanadyl complexation studies by, for example, Wendt and Schlund,<sup>33</sup> this pathway was included. The work in this case was done in the  $\text{pH}$  range 3–5. Extrapolation of their data to lower  $\text{pH}$  indicates that pathways incorporating hydroxy species are unimportant at the acidities of this study.

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## Vanadyl(IV)-Monothio- $\beta$ -diketone Complexes. I. Square-Pyramidal Compounds

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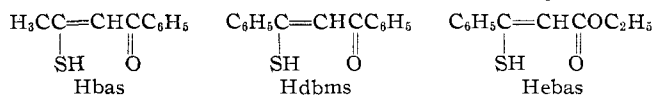
Three vanadyl(IV) complexes of monothio- $\beta$ -diketones,  $\text{RC}(\text{SH})=\text{CHCOR}'$  ( $\text{R} = \text{C}_6\text{H}_5$ ,  $\text{R}' = \text{C}_6\text{H}_5$ ,  $\text{C}_2\text{H}_5\text{O}$ ;  $\text{R} = \text{CH}_3$ ,  $\text{R}' = \text{C}_6\text{H}_5$ ), have been prepared and characterized by infrared, electron spin resonance, and optical spectral studies as well as by the usual analytical methods. The complexes are monomeric and appear to be square pyramidal. The behavior of the complexes in a variety of solvents indicates that solvent effects are comparable to those previously observed for vanadyl(IV)  $\beta$ -diketones. Some qualitative conclusions about the nature of the bonding in these complexes have been reached and some spectral assignments are discussed.

### Introduction

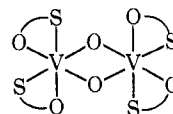
Although vanadyl(IV) complexes have been the objects of many studies,<sup>1,2</sup> there still is not a large body of information pertaining to any but compounds with V–O or V–N bonds. Accordingly, we have undertaken an investigation of vanadyl(IV) compounds involving second-period donor atoms, with emphasis on sulfur.<sup>3,4</sup>

In view of recent developments in the coordination chemistry of monothio- $\beta$ -diketones,<sup>5</sup> it seemed partic-

ularly worthwhile to investigate vanadyl(IV) complexes of such ligands in detail. The ligands used in this work and our abbreviations for these ligands are



Livingstone<sup>6</sup> has reported a dimeric complex formed from a fluorinated monothio- $\beta$ -diketone and  $\text{VO}^{2+}$ , for which the following structure was proposed



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