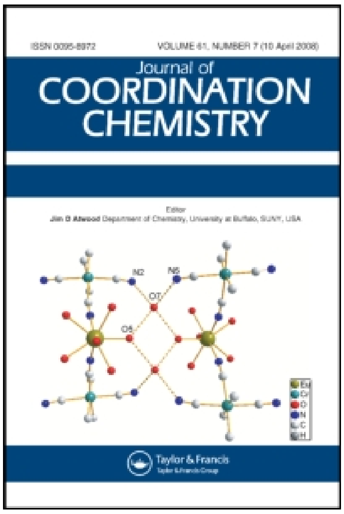

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

EQUILIBRIA OF VANADYL(IV) TARTRATES IN AQUEOUS SOLUTION ABOVE pH 7

Richard M. Holland[a]; Robert E. Tapscott[a]
[a] Department of Chemistry, The University of New Mexico, Albuquerque, NM

To cite this Article Holland, Richard M. and Tapscott, Robert E.(1981) 'EQUILIBRIA OF VANADYL(IV) TARTRATES IN AQUEOUS SOLUTION ABOVE pH 7', Journal of Coordination Chemistry, 11: 1, 17 — 26
To link to this Article: DOI: 10.1080/00958978108080661
URL: http://dx.doi.org/10.1080/00958978108080661

J. Coord. Chem., 1981, Vol. 11, pp. 17–26
0095-8972/81/1101-0017$06.50/0

EQUILIBRIA OF VANADYL(IV) TARTRATES IN AQUEOUS SOLUTION ABOVE pH 7

RICHARD M. HOLLAND and ROBERT E. TAPSCOTT

Contribution from the Department of Chemistry, The University of New Mexico, Albuquerque, NM 87131

(*Received July 8, 1980*)

In aqueous solution at pH ∿8, the reaction of binuclear vanadyl(IV) tartrate(4–), $(VO)_2(C_4H_2O_6)_2^{4-}$, with excess tartrate(2–) ligand gives the mononuclear complex, $VO(C_4H_3O_6)_2^{4-}$. Spectral evidence indicates that the product has a *trans* coordination by two ionized hydroxyl oxygen atoms and structures are proposed. At ionic strengths of 1.00 M (3.00 M) at 298°K, stoichiometric equilibrium constants of $0.34 \pm 0.02\ M^{-1}$ ($0.8 \pm 0.2\ M^{-1}$) and $0.054 \pm 0.002\ M^{-1}$ ($0.07 \pm 0.01\ M^{-1}$) have been determined for the binuclear-mononuclear reactions in, respectively, the active system, $(VO)_2(d\text{-}C_4H_2O_6)_2^{4-} + 2d\text{-}C_4H_4O_6^{2-} \rightleftarrows 2VO(d\text{-}C_4H_3O_6)_2^{4-}$, and the racemic system, $(VO)_2(d\text{-}C_4H_2O_6)(l\text{-}C_4H_2O_6)^{4-} + 2dl\text{-}C_4H_4O_6^{2-} \rightleftarrows 2VO(dl\text{-}C_4H_3O_6)_2^{4-}$. From these experimentally determined equilibrium constants, the equilibrium constant for the interconversion of the active and racemic binuclear complexes has been derived for two different assumptions of the monomeric isomer distribution in the racemic system. Assuming stereospecific formation of $VO(d\text{-}C_4H_3O_6)_2^{4-}$ and $VO(l\text{-}C_4H_3O_6)_2^{4-}$ in the racemic system, an equilibrium constant of ∿8 is calculated for the reaction $1/2(VO)_2(d\text{-}C_4H_2O_6)_2^{4-} + 1/2(VO)_2(l\text{-}C_4H_2O_6)_2^{4-} \rightleftarrows (VO)_2(d\text{-}C_4H_2O_6)(l\text{-}C_4H_2O_6)^{4-}$. A value of ∿28 is calculated for this equilibrium constant assuming that the binuclear-mononuclear racemic reaction exhibits no stereoselectivity. That these values bracket reported values determined potentiometrically and estimated from calorimetric data indicates that the binuclear-mononuclear reaction is stereoselective but not stereospecific.

INTRODUCTION

In aqueous solution between pH ∿7 and pH ∿10, vanadyl(IV) ion coordinates with optically active or racemic tartaric acid, forming 2:2 binuclear complexes containing the tartrato(4–) ligand, $C_4H_2O_6^{4-}$, from which both the hydroxyl and carboxyl protons have been ionized.[1] With active tartaric acid, the complexes $(VO)_2(d\text{-}C_4H_2O_6)_2^{4-}$ or $(VO)_2(l\text{-}C_4H_2O_6)_2^{4-}$, containing two ligands of the same enantiomeric form, are obtained. In the presence of racemic tartaric acid, the complex $(VO)_2(d\text{-}C_4H_2O_6)(l\text{-}C_4H_2O_6)^{4-}$ is formed. From these solutions, solid salts having the general formula $M_4[(VO)_2(C_4H_2O_6)_2] \cdot xH_2O$, where "M" denotes a univalent cation, can be obtained. These salts contain the same principal species present in the aqueous solutions.[1] Crystal structures have been reported for three of these solids – $(NH_4)_4[(VO)_2(d\text{-}C_4H_2O_6)_2] \cdot 2H_2O$,[2] $[N(C_2H_5)_4]_4[(VO)_2(d\text{-}C_4H_2O_6)(l\text{-}C_4H_2O_6)] \cdot 8H_2O$,[3] and $Na_4[(VO)_2(d\text{-}C_4H_2O_6)(l\text{-}C_4H_2O_6)] \cdot 12H_2O$.[4]

In aqueous solution, the vanadyl(IV) racemic binuclear complex is more stable than the active species. From potentiometric titration studies, an equilibrium constant of 16 has been determined for the reaction $1/2(VO)_2(d\text{-}C_4H_2O_6)_2^{4-} + 1/2(VO)_2(l\text{-}C_4H_2O_6)_2^{4-} \rightleftarrows (VO)_2(d\text{-}C_4H_2O_6)(l\text{-}C_4H_2O_6)^{4-}$ in aqueous solution at 25°C and $\mu = 0.1$ M (KNO_3).[5] This value is in reasonably good agreement with the value of 24 estimated from a ΔH of -1.46 kcal mol^{-1} determined calorimetrically and an assumed ΔS of -1.38 cal mol^{-1} °K^{-1} due only to ligand mixing.[6]

The stereochemistry of tartrate-bridged binuclear complexes has been reviewed[7] and a detailed analysis of the geometric and entropy factors influencing the relative stabilities of the possible isomers has been reported.[8] From the results presented in the latter paper cited, we may propose that the better staggering of the tartrate group in the racemic complex, along with an entropy contribution due to ligand mixing, gives a greater stability to the $(VO)_2(d\text{-}C_4H_2O_6)(l\text{-}C_4H_2O_6)^{4-}$ isomer. The present paper reports the results of further experimental studies on the solution thermodynamics of racemic and active vanadyl(IV) tartrate complexes above pH 7. All equilibrium constants discussed herein are stoichiometric equilibrium constants.

EXPERIMENTAL

Materials

Tetrasodium di-μ-*d*-tartrato(4-)-bis(oxovanadate(IV)) 6-hydrate, tetrasodium di-μ-*l*-tartrato(4-)-bis(oxovanadate(IV)) 6-hydrate, and tetrasodium *μ-d*-tartrato-(4-)-*μ-l*-tartrato(4-)-bis(oxovanadate(IV)) 12-hydrate[9] were prepared by a previously described method.[1] The salts were recrystallized three times and stored in a tightly capped container to prevent loss of water of crystallization, to which these compounds are susceptible.[1,4] *Anal.* Calcd. for $Na_4[(VO)_2(d\text{-}C_4H_2O_6)_2]\cdot 6H_2O$: C, 15.44; H, 2.58; V, 16.28. Found: C, 15.43; H, 2.45; V, 16.08. Found for $Na_4[(VO)_2(l\text{-}C_4H_2O_6)_2]\cdot 6H_2O$: C, 15.54; H, 2.53; V, 16.13. Calcd. for $Na_4[(VO)_2(d\text{-}C_4H_2O_5)(l\text{-}C_4H_2O_6)]\cdot 12H_2O$: C, 13.09; H, 3.84; V, 13.88. Found: C, 12.99; H, 3.78; V, 13.70.

Baker AR sodium *d*-tartrate 2-hydrate was used as obtained. *Anal.* Calcd. for $Na_2C_4H_4O_6\cdot 2H_2O$: H_2O, 15.66. Found: H_2O, 15.56. Reported[10]: $[\alpha]_D^{20}$ ($c = 0.257$ g ml^{-1}), +8.48°. Found: $[\alpha]_D^{24}$, +8.48°. Sodium *l*-tartrate 2-hydrate was prepared from Aldrich *l*-tartaric acid and sodium hydroxide. *Anal.* Calcd. for $Na_2C_4H_4O_6\cdot 2H_2O$: H_2O, 15.66; C, 20.88; H, 3.50. Found: H_2O, 15.63; C, 20.96; H, 3.81; $[\alpha]_D^{23}$, -8.52°.

Fisher sodium perchlorate 1-hydrate and GFS lithium perchlorate 3-hydrate were employed as added electrolytes. The sodium perchlorate was analyzed for water and the masses required to prepare solutions were calculated accordingly. The stock solution of lithium perchlorate was prepared, filtered, and analyzed by evaporating the solution *in vacuo* with heat and weighing the residue (assumed to be $LiClO_4$). In some cases, carefully analyzed, recrystallized lithium perchlorate was directly weighed out for use.

In our initial studies, pH was not controlled. Solutions were prepared by dissolution of weighed amounts of the sodium vanadyl(IV) tartrate salts. The pH values of these solutions were in the range 7.5 to 8.5; however, the pH values were not recorded since the binuclear tartrate(4-) complexes are stable only in an unbuffered pH region.[1] Individual pH values would, therefore be highly suspect.

In later studies, the pH was controlled using mixtures of dabco (1,4-diazabicyclo[2.2.2]octane, Aldrich Chemical Co.) and its acid perchlorate salt as buffers. Dabco was recrystallized, twice sublimed, and allowed to dry over $CaCl_2$ for several days to give a free flowing, powdery material. *Anal.* Calcd. for $N_2C_6H_{12}$: C, 64.24; H, 10.78; N, 24.98. Found: C, 63.79; H, 11.09; N, 25.12. The purified dabco was partially neutralized with dilute perchloric acid to give a pH of 6.5 and the water was allowed to evaporate *in vacuo* to give a viscous solution. Crystals obtained on cooling were filtered off and dried over $CaCl_2$ to give an anhydrous white powder. *Anal.* Calcd. for $HN_2C_6H_{12}ClO_4$: C, 33.89; H, 6.16; N, 13.17; ClO_4, 46.77. Found: C, 33.84; H, 6.30; N, 12.99; ClO_4, 46.4. Caution! Though this material does not appear to be shock sensitive and melts without detonation, organic perchlorate salts are known to be unstable and should be handled with care in small amounts. The acid perchlorate salt of dabco will decompose vigorously in a flame. That little or no spectral change occurs upon addition of the dabco buffers to vanadyl(IV) tartrate solutions indicates no significant interaction between dabco and vanadyl(IV). This was not true for other buffers which were tried.

Optical Spectra

Spectra of the vanadyl(IV) tartrate salts in aqueous solutions containing varying amounts of excess ligand were recorded. Sodium *d*-tartrate was added to the solutions of sodium vanadyl(IV) *d*-tartrate and an equimolar mixture of sodium *d*- and *l*-tartrate was added to the solutions of sodium vanadyl(IV) *dl*-tartrate. These spectra were used to calculate equilibrium constants for the binuclear-mononuclear reactions discussed in this paper.

Three problems were encountered in selecting conditions for the spectral measurements.

1) At concentrations of V(IV) below 0.005 M, the effects of oxidation of the vanadyl(IV) complexes by traces of oxygen could not be neglected.

2) At V(IV) concentrations above ∿0.1 M the spectral changes effected by reasonable amounts of added ligand were insufficient to obtain reliable values for the equilibrium constants.

3) The high charges on the complexes and the necessity of adding large excesses of ligand caused large variations in the ionic strength in the absence of added electrolyte.

In the studies on unbuffered systems, concentrations of V(IV) from 0.005 to 0.050 M for the racemic complex and 0.01 to 0.10 M for the active complex were employed. Three ionic strength conditions were used for the active system – 2.00 M sodium perchlorate media with no attempt to hold the ionic strength constant, constant ionic strength 3.00 M using lithium perchlorate, and constant 3.00 M sodium ion using sodium perchlorate. The first two ionic strength conditions as well as constant ionic strength 1.00 M using lithium perchlorate were used for the racemic system.

In the buffered studies, V(IV) concentrations of

0.005 to 0.050 M were used with the ionic strength maintained constant at 1.00 with $LiClO_4$. Dabco and dabco acid perchlorate concentrations of 0.004 M and 0.036 M and of 0.125 M and 0.02 M were used to maintain pH 8.0 and 8.7 respectively.

The spectra were determined with monochromatic sample illumination over the region 1300 to 300 nm using a Cary Model 14R spectrophotometer. A lead sulfide detector was used above 700 nm and a photomultiplier tube, at lower wavelengths. Water at $298.1 \pm 0.1°K$ was circulated through the cell holder. A baseline was determined for each series of spectra. Absorbances which had been corrected for baseline were reproducible to ±0.004 absorbance units.

The aqueous solutions of the vanadyl(IV) tartrate salts were susceptible to oxidation by dissolved oxygen.[11] Oxidation was always accompanied by the appearance of an intense spectral band in the region 300–400 nm. Preliminary spectral studies on solutions prepared from nitrogen-purged and oxygen-purged water showed that

1) the oxidation was rapid (at pH $\sim$8, the dissolved oxygen appeared to be depleted within a few seconds),
2) the susceptibility to oxidation increased with increasing pH, and
3) the addition of excess tartrate decreased the spectral change accompanying the oxidation (apparently by buffering the solution so that the release of protons during the oxidation did not change the pH to as great an extent) but did not significantly affect the oxidation rate.

In a previous paper,[1] variation of aqueous solution spectra of the vanadyl(IV) tartrates with changes in concentration was interpreted as evidence for a dimer-monomer equilibrium. The concentration dependence of these previously reported spectra was apparently due to traces of hydroxy species and oxidation products. In the present studies, solutions prepared air-free with small amounts of added tartrate ligand to suppress formation of hydroxy species showed little spectral dependence on concentration.

Air-free solutions for the spectral studies were prepared using volumetric flasks having septum-stoppered side arms for withdrawal of samples. These flasks were attached to an apparatus which allowed nitrogen-flushing, the addition of nitrogen-purged water, and the addition of known volumes of nitrogen-purged lithium perchlorate solution. Sodium vanadyl(IV) tartrate, sodium tartrate, and, for some studies, sodium perchlorate, dabco, and dabco hydrogen perchlorate were weighed into the volumetric flask. The system was flushed for approximately one-half hour with Baker "Ultra Pure" nitrogen which had been bubbled through chromous chloride solution to remove any traces of oxygen and then through water. Water, and, in some cases, lithium perchlorate solution were added, and the mixture was stirred magnetically to effect dissolution. After diluting to volume, a sample was withdrawn with a nitrogen-flushed gas-tight syringe and transferred to a nitrogen-purged absorption cell. The spectrum was recorded after allowing five minutes for temperature equilibration. Each spectrum was run on a freshly prepared solution. A maximum of twenty minutes elapsed between the preparation of the solution and the spectral determination. Under these conditions, we could detect no indication of oxidation except for solutions with $[V(IV)] < 0.005$ M.

Calculations

The University of New Mexico IBM 360 computer was used to carry out the equilibrium constant calculations, using procedures described later in this paper.

RESULTS

Binuclear-Mononuclear Equilibria

The addition of excess ligand to solutions of the active and racemic dimeric complexes effects changes in the optical spectra. Figures 1 and 2 show the spectra observed for sodium vanadyl(IV) *d*-tartrate with added sodium *d*-tartrate ligand and for sodium vanadyl(IV) *dl*-tartrate with added equimolar sodium *d*- and *l*-tartrate. The presence of a distinct isosbestic point at 831 nm in the spectra of the active solutions indicates that there are only two absorbing species in this wavelength region. Isosbestic points in the racemic spectra are less easily determined owing to large regions of essentially no spectral change.

We propose that the addition of excess ligand to solutions of the binuclear vanadyl(IV) tartrate complexes causes formation of tetranegative mononuclear complexes containing two tartrate(3-) ligands. The reactions and corresponding stoichiometric equilibrium constant expressions are given in Eqs. (1)–(4).[12] Eqs. (1) and (2) obviously apply equally to the enantiomeric *l*-tartrate system. The isomeric composition of the product in Eqs. (3) and (4) is not specified. The exact form of the equilibrium constant expression for the racemic reaction depends on the distribution of product isomers (*vide infra*).

$$V_2(d\text{-}T)_2^{4-} + 2d\text{-}TH_2^{2-} \rightleftarrows 2V(d\text{-}TH)_2^{4-} \qquad (1)$$

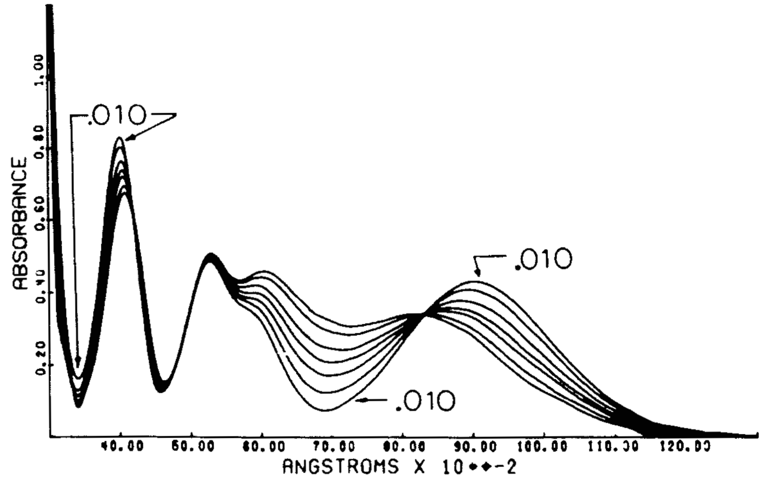

FIGURE 1 Optical spectra of sodium vanadyl(IV) *d*-tartrate ([V(IV)] = 0.02 M) in 2.0 M sodium perchlorate for concentrations of 0.010, 0.050, 0.100, 0.150, 0.200, 0.300, and 0.400 M in added sodium *d*-tartrate. Cell path length = 1.00 cm.

$$K_1 = \frac{[\mathrm{V}(d\text{-TH})_2^{4-}]^2}{[\mathrm{V}_2(d\text{-T})_2^{4-}]\,[d\text{-TH}_2^{2-}]^2} \tag{2}$$

$$\mathrm{V}_2(d\text{-T})\,(l\text{-T})^{4-} + 2dl\text{-TH}_2^{2-} \rightleftarrows 2\mathrm{V(TH)}_2^{4-} \tag{3}$$

$$K_2 = \frac{[\mathrm{V(TH)}_2^{4-}]^2}{[\mathrm{V}_2(d\text{-T})(l\text{-T})^{4-}]\,[dl\text{-TH}_2^{2-}]^2} \tag{4}$$

The following evidence supports the existence of these proposed reactions.

1) That the spectral changes are effected by added tartrate indicates that the number of ligands per metal ion increases. The observed spectral changes are not due to the buffering action of the added ligand since the changes do not even remotely resemble those caused by addition of acid or base to solutions of the vanadyl(IV) tartrates.

2) Spectral evidence, discussed later, indicates that the coordination sphere of the product complex contains two ionized hydroxyl oxygen atoms and two ionized carboxyl oxygen atoms with a *trans* coordination. The structure of a 1:2 vanadyl(IV) α-hydroxycarboxylate with such a geometry has been reported.[13]

3) The experimental equilibrium constants based

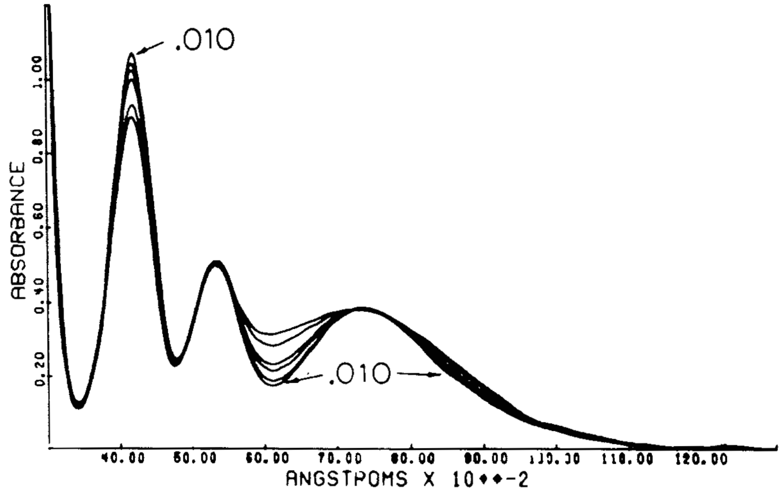

FIGURE 2 Optical spectra of sodium vanadyl(IV) *dl*-tartrate ([V(IV)] = 0.02 M) in 2.0 M sodium perchlorate for concentrations of 0.010, 0.050, 0.100, 0.150, 0.300, and 0.400 M in added tartrate ligand. An equimolar mixture of sodium *d*-tartrate and sodium *l*-tartrate was employed. Cell path length = 1.00 cm.

on the proposed equilibria do not show any significant trends with the total vanadium concentration.

4) The values calculated for the equilibrium constant for the interconversion of active and racemic binuclear complexes from the binuclear-mononuclear equilibrium constants are approximately equal to these determined potentiometrically[5] and predicted from calorimetric data and from reasonable assumptions of the entropy contribution.[6]

The spectral changes resulting from the addition of excess ligand to solutions of the vanadyl(IV) tartrates can be used to calculate values for the binuclear-mononuclear equilibrium constants, K_1 and K_2. The following procedure is used. The spectral absorbances, A, per unit cell-path length are related to the extinction coefficients, ϵ_b and ϵ_m, and to the concentrations, B and M, of the binuclear and mononuclear complexes by Equation (5).

$$A = B\epsilon_b + M\epsilon_m \tag{5}$$

From the stoichiometry of reactions 1 and 3, we find that $B = B_0 - 1/2M$ and $L = L_0 - M$, where L is the free ligand concentration and B_0 and L_0 are, respectively, the initial binuclear complex concentration and the concentration of added ligand. Using these relations, we rewrite Eqs. (5) and (2) or (4) to give the following expressions.

$$A = (B_0 - 1/2M)\,\epsilon_b + M\epsilon_m \tag{6}$$

$$K = \frac{M^2}{(B_0 - 1/2M)(L_0 - M)^2} \tag{7}$$

In Eq. (7), $K = K_1$ for the active system and $K = K_2$ for the racemic system. In our analysis, we assume that all monomeric isomers in the racemic solutions have identical extinction coefficients – an assumption which is justified later.

Eqs. (6) and (7) contain four unknowns – the mononuclear and binuclear complex extinction coefficients (ϵ_m and ϵ_b), the equilibrium constant (K), and the concentration of the mononuclear species (M). The last unknown may be eliminated by combining these two equations. Values of ϵ_b taken from spectra with no added tartrate are unreliable owing to the presence of small but variable amounts of other species. In the absence of added tartrate, spectra of vanadyl(IV) tartrate solutions do not strictly exhibit a Beer's Law concentration dependence. Comparison of the spectral changes effected by concentration variation with those caused by addition of base indicates that the contaminants are hydroxy species. Addition of small amounts of excess tartrate decreases markedly this interference; however, the spectra are then affected by the presence of some monomer. Extrapolation of absorbances to zero concentration of added tartrate has been tried, but our results indicate that a better fit to the absorbance data can be obtained by treating the extinction coefficient of the binuclear complex as one of the variables to be determined. Essentially the same results are given by calculations in which these extinction coefficients are obtained

1) from spectra of solutions with small concentrations of added tartrate,

2) by extrapolation to zero added tartrate concentration, and

3) from a direct fit of the spectral data using ϵ_b as a third variable.

Wavelengths have been selected to give maximum absorbance changes for changes in added tartrate and values of ϵ_b, ϵ_m and K which minimize the squared deviations between the calculated and experimental absorbances as a function of ligand added have been determined. Identical minima are found both by a grid search technique[14] using the program GRID4[15] and by a simplex method. The results are presented in Table I.

The average deviation between the calculated and experimental absorbances is less than 0.05 absorbance unit in every case. The shallow minima found for the error-square-sum function cause the relatively large scatter observed in the values calculated for the equilibrium constants. That minimizations started from several points always give the same values of ϵ_b, ϵ_m, and K indicates that there is only one true minimum. Buffering appears to significantly improve the scatter; however, the very limited pH variation data indicate that the equilibrium constants are pH independent between pH 8.0 and pH 8.7. Attempts to buffer at pH values above this region led to poor fits between observed and calculated spectral absorbances, apparently owing to interferences by hydroxy species. The values of K decrease somewhat with ionic strength, a not unexpected trend for a reaction in which there is the formation of species with a higher charge. For this reason we consider the results where ionic strength was not maintained constant (data sets 1–4 and 8 in Table I) to be less reliable. Using the results of the constant ionic strength experiments, we assign values of 0.34 ± 0.02 and $0.8 \pm 0.2\ \mathrm{M}^{-1}$ to K_1 at $\mu = 1.00$ and 3.00 M. Values of 0.054 ± 0.002 and $0.07 \pm 0.01\ \mathrm{M}^{-1}$ are assigned to K_2 at $\mu = 1.00$ and 3.00 M. The values for

TABLE I
Binuclear-mononuclear complex stoichiometric equilibrium constants at 298°K

Data Set[a]	[V(IV)],[b]M	Media	K,[c]M^{-1}	μ,[d]M
Active System, $K = K_1$				
1	0.02	2.00 M $NaClO_4$	0.70(.04)	2.1–3.2
2	0.04	2.00 M $NaClO_4$	0.54(.09)	2.4–3.2
3	0.01	2.00 M $NaClO_4$	0.59(.15)	2.1–2.4
	0.02	2.00 M $NaClO_4$	0.53(.32)	2.1–2.4
4	0.01	3.00 M in Na^+ ($NaClO_4$)	0.78(.01)	3.1–3.3
	0.02	3.00 M in Na^+ ($NaClO_4$)	0.80(.01)	3.1–3.3
	0.04	3.00 M in Na^+ ($NaClO_4$)	0.96(.09)	3.2–3.4
5	0.025	$LiClO_4$	0.95(.28)	3.00
	0.10	$LiClO_4$	0.68(.19)	3.00
6	0.05–0.20	Buffered pH = 8.0; $LiClO_4$	0.319(.014)	1.00
7	0.050–0.20	Buffered pH = 8.7; $LiClO_4$	0.352(.012)	1.00
Racemic System, $K = K_2$				
8	0.02	2.00 M $NaClO_4$	0.089(.014)	2.1–3.2
9	0.025	Ionic strength 3.00 M ($LiClO_4$)	0.074(.010)	3.00
10	0.05–0.20	$LiClO_4$	0.046(.007)	1.00
11	0.05–0.20	Buffered, pH = 8.0; $LiClO_4$	0.055(.001)	1.00

[a]Data Set 1: L_0 (concentrations of ligand added) = 0.025, 0.050, 0.075, 0.100, 0.150, 0.200, 0.300, 0.400 M; λ (wavelengths) = 600, 650, 675, 700, 725, 900, 925 nm. Data Set 2: L_0 = .050, .100, .150, .200, .300, .400 M; λ = 600, 650, 675, 700, 725, 900, 925 nm. Data Set 3: L_0 = .015 to .100 M in increments of .005 M; λ = 900 and 700 nm. Determinations of absorbances at 700 nm were made with both lead sulfide and photomultiplier tube detectors giving two sets of absorbances at this wavelength. Data Set 4: L_0 = .050, .100, .150, .200, .250 M; λ = 900 and 700 nm. Data Set 5: L_0 = .100 to .500 M in increments of 0.050 M; λ = 590, 600, 610, 630, 640, 650, 670, 690, 710, 730, 750, 770, 880, 900, 920, 940, 960, 980, 1000 nm. Data Sets 6, 7, 10, 11: L_0 = .005, .010, .025, .035, .050 M; [V(IV)] = .050, .100, .125, .150, .200; λ = 610 to 750 nm in increments of 10 nm for runs 6 and 7 and λ = 600 to 690 nm in increments of 10 nm for runs 10 and 11. Data Set 8: L_0 = .025, .050, .075, .100, .150, .200, .300, .400 M; λ = 575, 600, 625, 650, 675 nm. Data Set 9: L_0 = .100 to .500 M in increments of 0.50 M; λ = 590, 600, 610, 620, 630, 640, 650 nm. [b]Total vanadium concentration. [c]Average values for all wavelengths used with average deviations in parentheses. [d]Ionic strength range for each series of solutions used.

ionic strength 3.00 M are for unbuffered reactions while those for ionic strength 1.00 M are for buffered reactions. Note that these values are determined from results of runs with $LiClO_4$ added electrolyte only. The reliabilities given with these figures are conservatively estimated from the average deviations of the measured values.

In order to better characterize the products of the binuclear-mononuclear reactions, spectra of the mononuclear complexes have been synthesized by calculating the monomer extinction coefficients over the spectral range 300 to 1300 nm. Data taken from the spectra illustrated in Figures 2 and 3 and values of $K_1 = 0.7\ M^{-1}$ and $K_2 = 0.09\ M^{-1}$ (determined for systems under these conditions) have been employed in these computations. The calculations are made by taking all pairs of absorbances at each wavelength, applying Equations (6) and (7) to solve for ϵ_b and ϵ_m, and averaging the values of ϵ_m. It is not possible to carry out a direct least-squares analysis for the extinction coefficient at each wavelength owing to rounding errors in the computer. The calculated values of ϵ_m have been used to generate spectra of the monomeric products of the two systems for a cell path length of 1.00 cm and a V(IV) concentration of 0.02 M. The calculated absorbance values, fit with a cubic spline for clarity, are shown in Figures 3 and 4.

The spectra calculated for the mononuclear products of the reactions of active and racemic vanadyl(IV) binuclear tartrates with excess ligand are remarkably similar. Although there is a small difference in the extinction coefficients of the highest energy bands calculated for the two spectra, these bands appear in the spectral region most likely to be affected by oxidation. Since only a $V(d\text{-}TH)_2^{4-}$ diastereoisomer is possible for the mononuclear product in the active system and since the calculated spectra for the two systems are virtually identical, we feel that our assumption that all of the products in the racemic system have the same spectral properties is justified.

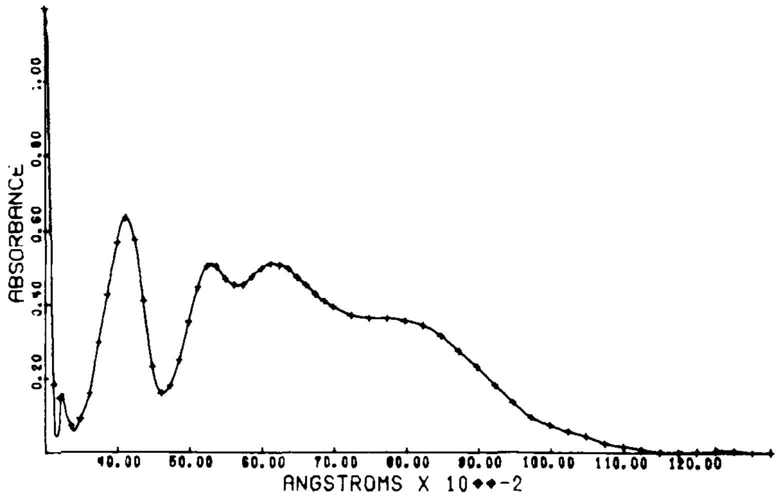

FIGURE 3 Computed spectrum for the product formed by the reaction of vanadyl(IV) *d*-tartrate with sodium *d*-tartrate in 2.0 M sodium perchlorate. Values of 0.7 M^{-1} and 0.02 M were used respectively for K_1 and [V(IV)]. Cell path length = 1.00 cm. The peak at ∿ 3200 Å is probably generated by the cubic spline fitting procedure.

The synthesized spectra closely resemble those determined for several vanadyl(IV) α-hydroxycarboxylates in aqueous solution above pH 7 (Table II). The origins of the spectral bands in α-hydroxycarboxylate complexes of vanadyl(IV) have been discussed elsewhere[16-18] and will not be discussed here except for the following remarks. At room temperature, solution spectra of most vanadyl(IV) complexes contain, at most, three bands in the visible region.[19] However, alkaline solutions of the α-hydroxycarboxylates, with the exception of *cis*-coordinated vanadyl(IV) *dl*-tartrate,[1] exhibit four spectral bands in this region.[17] The appearance of four bands in the spectra of this group of complexes has been ascribed to a reduced symmetry of the ligand field by *trans* coordination of two strongly bound, ionized hydroxyl oxygen atoms.[16,18] If this is the case, most vanadyl(IV) α-hydroxycarboxylates have a primarily *trans* coordination geometry.[13,20] Since the computed monomer spectra resemble those

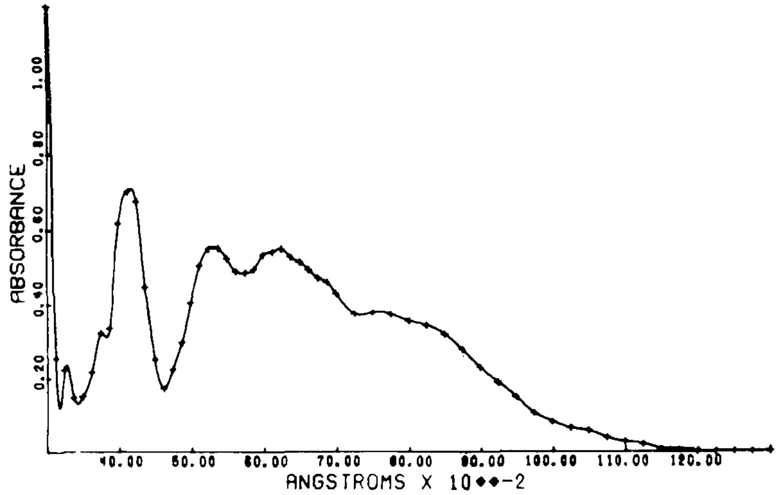

FIGURE 4 Computed spectrum for the product formed by the reaction of vanadyl(IV) *dl*-tartrate with sodium *dl*-tartrate in 2.0 M sodium perchlorate. Values of 0.09 M^{-1} and 0.02 M were used respectively for K_2 and [V(IV)]. Cell path length = 1.00 cm. The features at ∿3200 and ∿3700 Å are probably generated by the cubic spline fitting procedure.

TABLE II
Spectral bands observed in optical spectra of vanadyl(IV) α-hydroxycarboxylates in aqueous solution[a]

Compound	pH	λ,nm(ε,l mol^{-1} cm^{-1})				Ref.
		I	IIA	IIB	III	
Vanadyl(IV) *dl*-tartrate[b]	∿8	737(25.4)	536(25.4)		421(52.9)	16
Vanadyl(IV) *d*-tartrate[b]	∿8	902(22.6)	590(22.4)[c]	533(27.7)	399(46.4)	16
Vanadyl(IV) benzilate[d]	8.5	847(31)	599(26)	541(27)	417(36)	18
Vanadyl(IV) mandelate	8.5	826	599	535	413	18
Vanadyl(IV) lactate[e]	>7	813	599	529	407	17
Vanadyl(IV) malate[e]	>7	815	608	530	410	17
Product, active system[f]	∿8	775(18.0)[c]	615(25.4)	531(25.4)	413(31.7)	this work
Product racemic system[f]	∿8	756(18.8)	623(26.4)	532(27.6)	418(36.3)	this work

[a] [V(IV)] = 0.04 M unless otherwise noted. The spectral bands are numbered from the lowest energy in the optical region using the numbering system given in ref. 16. [b] 0.04 M in excess tartrate. [c] This band appears as a shoulder and, therefore, the band maximum is difficult to locate precisely. [d] 0.16 M in excess benzilate. [e] Concentration was not reported. A two-fold excess of ligand was present. [f] The band maxima were taken from the spectra calculated for a solution 0.2 M in V(IV) using a cubic spline fit. See Figures 3 and 4.

of other vanadyl(IV) α-hydroxycarboxylate complexes, the monomers are apparently also *trans*. Our results are compatible with the structures shown in Figure 5 for the two possible monomeric diastereoisomers.

The values for K_1 and K_2 are remarkably small. It is difficult to see why the binuclear complexes are so stable towards the addition ligand. Though the structures indicated for the mononuclear complexes (Figure 5) imply a higher entropy for the mononuclear complex than for the binuclear, the change in number of species in the reactions given in Eqs. (1) and (3) and the unknown changes in solvation entropy make any conclusion about the entropy contributions to the binuclear-mononuclear reactions impossible. The calorimetric studies[6] of the binuclear-binuclear heats of reaction show that an endothermic side reaction occurs in the presence of excess ligand. Assuming that this is the formation of the mononuclear species discussed here, we can use our equilibrium constant of 0.054 M^{-1} for the racemic system at μ = 1.00 M ($LiClO_4$) and the calorimetric data[6] collected under similar conditions to estimate a value of ΔH = +3 kcal mol^{-1} for the reaction of Eq. (3). This indicates that the stability of the binuclear complexes relative to the mononuclear species is enthalpic in origin.

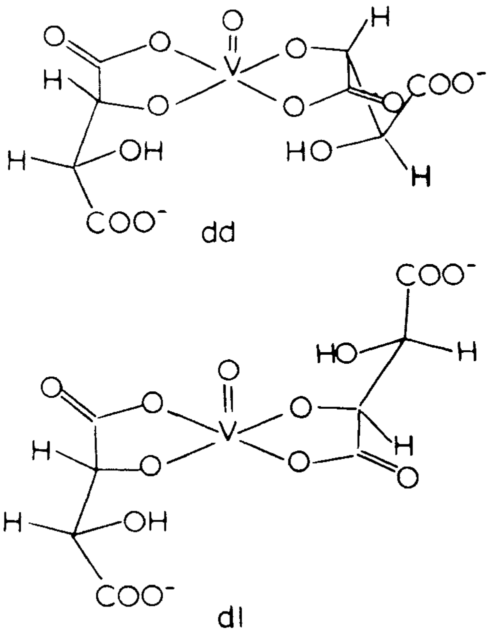

FIGURE 5 Structures indicated for monomeric complexes formed by the reactions of the vanadyl(IV) tartrates with excess ligand.

We wish to demonstrate another, somewhat less precise, method for calculating binuclear-mononuclear reaction equilibrium constants. Since the spectra synthesized for the monomers indicate that the products formed in the active and racemic systems have the same spectral properties, we can employ the computer program GRID4 to determine values of K_1 and K_2 which minimize the sum of the squared deviations between the calculated values of ϵ_m for the active and racemic monomeric products. Spectra data collected for the two systems under the same conditions of ionic strength, total metal ion concentration, and ligand concentration range have been employed in such calculations. The results, presented in Table III, show that the values obtained for the equilibrium constants are somewhat depend-

TABLE III

Dimer-monomer equilibrium constants at 298° K calculated by minimizing the squared deviations between the computed mononuclear complex extinction coefficients for the active and racemic systems[a]

Media	[V(IV)],[b] M	K_1,M^{-1}	K_2,M^{-1}
2.00 M $NaClO_4$[c]	0.020	0.77	0.088
		0.84	0.100
		0.56	0.094
ionic strength 3.00 M ($LiClO_4$)[d]	0.020	0.57	0.057

[a]No average deviations can be given since data for all wavelengths were employed simultaneously. [b]Total vanadium concentrations. [c]λ (wavelengths) = 575, 587.5, 600, 612.5, 625, 637.5, 650, 662.5 nm. The first set of values were calculated from spectra for L_0 (concentrations of ligand added) = 0.010, 0.025, 0.050, 0.075, 0.100, 0.150, 0.200, 0.300, 0.400 M. The second and third sets of values were calculated respectively with data for L_0 = 0.200 M eliminated and with data for L_0 = 0.200 and 0.010 M eliminated. [d]λ = 590, 600, 610, 620, 630, 640, 650 nm. L_0 = 0.500, 0.450, 0.400, 0.350, 0.300, 0.250, 0.200, 0.150, 0.100 M.

ent on the particular data used since elimination of selected spectral data gives slightly different results. On the other hand, the values obtained by this method are very close to those calculated for the same media by directly fitting the separate spectral data for the two systems (Table I).

Binuclear-Binuclear Equilibria

In aqueous solution, the enantiomeric vanadyl(IV) tartrate dimers react spontaneously to form the racemic dimer.[1] The reaction equation and equilibrium constant are given in Eq. (8) and (9).

$$1/2V_2(d\text{-T})_2^{4-} + 1/2V_2(l\text{-T})_2^{4-} \rightleftarrows V_2(d\text{-T})(l\text{-T})^{4-} \qquad (8)$$

$$K_3 = \frac{[V_2(d\text{-T})(l\text{-T})^{4-}]}{[V_2(d\text{-T})_2^{4-}]^{1/2}[V_2(l\text{-T})_2^{4-}]^{1/2}} \qquad (9)$$

The equilibrium constant for the interconversion of active and racemic binuclear complexes, K_3, can be related to the experimental binuclear-mononuclear equilibrium constants, K_1 and K_2, if the exact isomer distribution obtained in the reaction of racemic dimer with excess ligand were known. There are three limiting cases for this reaction:

1) the stereospecific formation of $V(d\text{-TH})(l\text{-TH})^{4-}$ mononuclear species,

2) the stereospecific formation of an equimolar mixture of $V(d\text{-TH})_2^{4-}$ and $V(l\text{-TH})_2^{4-}$ diastereomers, and

3) the nonstereoselective formation of all possible isomers, whose relative concentrations are governed totally by statistical factors.

Of course, none of these limiting cases may apply, *e.g.*, there may be some stereoselectivity but not total stereospecificity.

The reaction among the mononuclear products in the racemic system can be expressed by Eq. (10) with the distribution of isomers being determined by the equilibrium constant K_4.

$$1/2V(d\text{-TH})_2^{4-} + 1/2V(l\text{-TH})_2^{4-} \rightleftarrows V(d\text{-TH})(l\text{-TH})^{4-} \qquad (10)$$

$$K_4 = \frac{[V(d\text{-TH})(l\text{-TH})^{4-}]}{[V(d\text{-TH})_2^{4-}]^{1/2}[V(l\text{-TH})_2^{4-}]^{1/2}} \qquad (11)$$

From Eqs. (2), (4), (9) and (11) it is easy to show that the binuclear-binuclear equilibrium constant can be related to the ratio of the binuclear-mononuclear constants.

$$K_3 = K_1(2 + K_4)^2/4K_2 \qquad (12)$$

Although spectral differences between diastereoisomeric mononuclear species are likely to be small, we feel that the striking similarity between the calculated spectra for the products of the reactions of active and racemic dimers with excess ligand allows us to rule out the first limiting case as a possibility. For this case, the products of the active and racemic systems would be totally different. For limiting case 2, where the reaction is totally stereospecific to form only active dimers, $K_4 = 0$ and $K_3 = K_1/K_2$. For limiting case 3, the distribution of products is purely statistical so that $[V(d\text{-TH})_2^{4-}] = [V(l\text{-TH})_2^{4-}] = 1/2[V(d\text{-TH})(l\text{-TH})^{4-}]$, $K_4 = 2$, and $K_3 = 4K_1/K_2$.

One would expect little dependence of K_3 on ionic strength since the reactants and products of the binuclear-binuclear reaction have the same charge and essentially the same size and shape. Values of K_1 and K_2 calculated from data collected under the same conditions of ionic strength are expected to give the same value for K_3 even though the dimer-monomer equilibrium constants themselves may vary. Using ratios of dimer-monomer equilibrium constants determined under the same conditions, we calculate values (with accuracies conservatively estimated from the average deviations of K_1 and K_2) for K_3 of 8 ± 2 (data sets 1,8), 13 ± 6 (5,9), and 6 ± 1 (6,11) if limiting case 2 holds. The respective values if case 3 holds are 31 ± 8, 51 ± 24, and 23 ± 4. The average of the K_3 values weighted by the reciprocal of the estimated accuracies are 8 and 28 for the two limiting cases.

That the K_3 values determined potentiometrically[5] and predicted from calorimetric data[6] lie between the values derived for the two cases considered indicates that neither limiting case holds for the racemic binuclear-mononuclear reaction. The reaction is stereoselective but not stereospecific with the active products present in greater abundance. In fact, if we can employ the value of $K_3 = 16$, determined under conditions different from ours,[5] we can use our results and Equation (12) to show that $K_4 \sim 0.8$ which would correspond to a percent stereoselectivity of $\sim$40%, where the percent stereoselectivity is defined as [(conc. active – conc. racemic)/(total conc)] x 100.

ACKNOWLEDGEMENT

Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Research Allocations Committee of the University of New Mexico for support of this work.

REFERENCES AND NOTES

1. R. E. Tapscott and R. L. Belford, *Inorg. Chem.*, 6, 735 (1967).
2. J. G. Forrest and C. K. Prout, *J. Chem. Soc. A*, 1312 (1967).
3. R. B. Ortega, C. F. Campana, and R. E. Tapscott, *Acta Cryst., B36*, 1786 (1980).
4. R. E. Tapscott, R. L. Belford, and I. C. Paul, *Inorg. Chem.*, 7, 356 (1968).
5. L. D. Pettit and J. L. M. Swash, *J. Chem. Soc. Dalton*, 286 (1978).
6. R. E. Tapscott, L. D. Hansen, and E. A. Lewis, *J. Inorg. Nucl. Chem.*, 37, 2517 (1975).
7. R. E. Tapscott, R. L. Belford, and I. C. Paul, *Coord. Chem. Rev.*, 4, 323 (1969).
8. R. E. Tapscott, *Inorg. Chim. Acta*, 10, 183 (1974).
9. For simplicity, these compounds will designated, respectively, as sodium vanadyl(IV) *d*-tartrate, sodium vanadyl(IV) *l*-tartrate, and sodium vanadyl(IV) *dl*-tartrate.
10. T. M. Lowry and P. C. Austin, *Phil. Trans. Roy. Soc. London A*, **222**, 249 (1922).
11. R. D. Gillard and R. A. Wiggins, *J. Chem. Soc. Dalton*, 125 (1973).
12. Throughout the remainder of this paper, "$V_2(d\text{-}T)_2^{4-}$", "$V_2(l\text{-}T)_2^{4-}$", and "$V_2(d\text{-}T)(l\text{-}T)^{4-}$" specify binuclear vanadyl(IV) complexes containing, respectively two bridging *d*-tartrato(4-) ligands, two bridging *l*-tartrato(4-) ligands, and one bridging ligand of each enantiomer. Mononuclear diastereomers containing one vanadyl(IV) ion and two tartrato(3-) ligands will be written as "$V(d\text{-}TH)_2^{4-}$", "$V(l\text{-}TH)_2^{4-}$", and "$V(d\text{-}TH)(l\text{-}TH)^{4-}$". The dinegative tartrate ion is indicated by "TH_2^{2-}".
13. N. D. Chasteen, R. L. Belford, and I. C. Paul, *Inorg. Chem.*, 8, 408 (1969).
14. J. G. Becsey, L. Berke, and J. R. Callan, *J. Chem. Educ.*, 45, 728 (1968).
15. J. G. Becsey, Report ARL 68–0111, Aerospace Research Laboratories, Office of Aerospace Research, Wright-Patterson Air Force Base, Ohio.
16. R. E. Tapscott, Ph.D. Dissertation, University of Illinois, Urbana (1970).
17. J. Selbin and L. Morpurgo, *J. Inorg. Nucl. Chem.*, 27, 673 (1965).
18. N. D. Chasteen, Ph.D. Dissertation, University of Illinois, Urbana (1970).
19. J. Selbin, *Coord. Chem. Rev.*, 1, 293 (1966).
20. This statement seems to be particularly true when there are large substituents at the carbinol carbon. N. D. Chasteen and M. W. Hanna, *J. Phys. Chem.*, 76, 3951 (1972).