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Kinetics of Vanadyl Complexation and the Reactivity of Hydroxovanadyl

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The kinetics of vanadyl complex formation with vanillomandelic, mandelic, and thiolactic acids was studied at 25 °C and ionic strength 0.5 M (KNO_3) by temperature jump. The complex stability constant for thiolactic acid with vanadyl was determined by utilizing the Bjerrum titration technique. Due to the unavailability of acid-dissociation constants for the α-hydroxyl groups, the complex stability constants for vanillomandelic and mandelic acids with vanadyl could not be directly determined by the Bjerrum method. For all three ligand systems an iterative procedure was carried out in which apparent forward and reverse rate constants for the complexation reaction were used to calculate the complex stability constant. The stability constants, $K_c = [VOL][H^+]/[VO^{2+}][HL^-]$, obtained were $(4.45 \pm 0.37) \times 10^{-3}$, $(6.14 \pm 0.33) \times 10^{-3}$, and $(1.79 \pm 0.06) \times 10^{-2}$ for the VO^{2+}–vanillomandelic acid, VO^{2+}–mandelic acid, and VO^{2+}–thiolactic acid complexes, respectively. Vanadyl complexation with all three ligands occurred with the loss of two protons, indicating bidentate chelation. Inclusion of the $VOOH^+$ species in the overall reaction scheme led to rate constants consistent with a dissociative (Eigen) mechanism. For the vanillomandelic, mandelic, and thiolactic acid systems (ligand = HL^-), the VO^{2+} complex formation rate constants obtained were $(1.13 \pm 0.07) \times 10^3$, $(1.09 \pm 0.06) \times 10^3$, and $(6.76 \pm 0.19) \times 10^2$ $M^{-1}\,s^{-1}$, respectively; and those determined for $VOOH^+$ complex formation were $(4.17 \pm 0.20) \times 10^4$, $(5.86 \pm 0.25) \times 10^4$, and $(7.93 \pm 0.14) \times 10^4$ $M^{-1}\,s^{-1}$, respectively. Reanalysis of the relaxation data of earlier vanadyl studies reporting high VO^{2+} complexation rate constants resulted in lower values.

Introduction

Many complexes of oxovanadium(IV) are known to exist in aqueous solution.[1] Yet there have been relatively few investigations of the kinetics of VO^{2+} complex formation.[2] Moreover, a broad range of metal complex formation rate constants has resulted from these studies in which techniques such as pressure jump,[3-5] temperature jump,[6-9] and stopped flow[7,8] were used. In all these studies, oxovanadium(IV) substitution was considered to proceed by a dissociative mechanism where the rate is independent of ligand characteristics and is determined rather by the loss of a water molecule from the inner-sphere coordination shell.

The first-order vanadyl–water exchange rate constant has been determined by NMR methods.[10] To be consistent with the NMR results and the dissociative mechanism, a number of investigators, finding larger than expected second-order rate constants, were prompted to make somewhat unusual interpretations of their kinetics results. The present study was therefore undertaken in an attempt to resolve the wide range of VO^{2+}–ligand complex formation rate constants as well as to gain further insight into the complexation characteristics of oxovanadium(IV).

The ligands used in this investigation were mandelic acid, vanillomandelic acid (VMA, a metabolite of noradrenaline), and thiolactic acid. Due to the high formal charge (4+) on vanadium, the vanadyl ion is stable only in acidic media[1] (pH 0–4) where complexation by many common basic ligands cannot occur. Thus, the low pK_a's and the chelating ability of the α-alcoholic or α-thiol groups of the aforementioned ligands allowed VO^{2+} complexation experiments to be done at low pHs.

To obtain unambiguous complexation data, we performed temperature-jump studies under conditions of excess metal to ligand concentration ratios in the pH range 3.0–4.5. It was also necessary to carry out equilibrium studies as no stability constants were available for the complexes formed. In this paper, we report the kinetics and equilibria of VO^{2+}–mandelic, VO^{2+}–vanillomandelic, and VO^{2+}–thiolactic acid complex formation.

Experimental Section

Stock solutions of oxovanadium(IV) were prepared by dissolving Fisher reagent grade $VOSO_4{\cdot}2H_2O$ in doubly distilled water. The sulfate ions were subsequently removed with $Ba(NO_3)_2$ (Fisher certified reagent) by quantitative precipitation as $BaSO_4$. The resulting vanadyl nitrate solution was then analyzed for total V(IV) by titration with EDTA.

The ligands vanillomandelic acid obtained from Sigma Chemical Co., mandelic acid from J. T. Baker Chemical Co., and thiolactic acid from Aldrich Chemical Co. were used without further purification. Indicators used were methyl orange and methyl red, both from Eastman Industries. All solutions were prepared with doubly distilled water. Concentrations of ligand stock solutions were determined by titration with standard NaOH.

Hydrogen ion concentrations were adjusted by dropwise addition of NaOH and HNO_3. Constant ionic strength (μ = 0.5 M) was maintained for sample solutions with the addition of KNO_3 (Fisher Certified reagent). pH measurements, taken on an Orion research digital ionalyzer, Model 801A, were converted to H^+ concentrations by dividing the measured hydrogen activity by $\gamma_\pm = 0.692$ obtained from the Davies[11] equation.

Spectral analysis was carried out on a Beckman Model 25 spectrophotometer. Relaxation experiments were performed at 25 ± 0.1 °C with a temperature-jump apparatus previously described.[12] Data was either collected as photographs of stored oscilloscope traces or recorded digitally on Texas Instruments 733ASR terminal magnetic cassette tapes by a Biomation 610B transient recorder equipped with a Datacap Model B103 interface. Rate constant and mechanistic analyses were performed through the use of a PDP-10 computer system.

Equilibrium studies were done by using a 100-mL capped double-walled cell. Solutions were thermostated at 25 ± 0.1 °C by circulating constant-temperature water through the double wall. All titrations were done under argon.

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(6) Kustin, K.; Hurwitz, P. *J. Phys. Chem.* **1967**, *71*, 324.

(7) Tomiyasu, H.; Dreyer, K.; Gordon, G. *Inorg. Chem.* **1972**, *11*, 2409.

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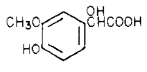
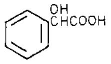
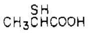
Table I. Equilibrium Data

ligands	pK_{a_1} [a]	pK_{a_1} [b]	pK_{a_2} [b]	K_c [c]	K_c [a]
vanillomandelic acid	3.39 ± 0.04	3.42[d]		$(4.45 \pm 0.37) \times 10^{-3}$	
mandelic acid	3.35 ± 0.03	3.40[d]		$(6.14 \pm 0.33) \times 10^{-3}$	
thiolactic acid	3.55 ± 0.04	3.54[e]	10.00[e]	$(1.79 \pm 0.06) \times 10^{-2}$	$(2.21 \pm 0.53) \times 10^{-2}$

indicator	K_{In} [f]	indicator	K_{In} [f]
methyl orange	3.47×10^{-4}	methyl red	1.00×10^{-5}

[a] Determined by Bjerrum titration. [b] Published value. [c] Determined from k_f/k_r. $K_c = [VOL][H^+]/[VO^{2+}][HL^-]$. [d] Klingenberg, J. J.; Knecht, D. S.; Harrington, A. E.; Meyer, R. L. *J. Chem. Eng. Data* 1973, *23*, 327. [e] Martell, A. E.; Smith, R. M. "Critical Stability Constants"; Plenum Press: New York, 1977; Vol. 3. [f] $K_{In} = [H^+][In^-]/[HIn]$; values obtained from: Kolthoff, I. M. *J. Phys. Chem.* 1930, *34*, 1466.

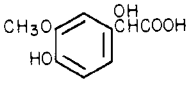
Table II. Relaxation Data[a] for VO^{2+} Complexation with Vanillomandelic, Mandelic, and Thiolactic Acids at 25 °C and $\mu = 0.5$ M

ligand	pH	$10^2[VO^{2+}]_0$,[b] M	$10^2[HL^-]_0$, M	$10^{-2}(1/\tau_{obsd})$, s^{-1}	$10B$	10^3C
	3.53	5.00	0.50	3.31	2.60	0.61
	3.45	5.00	1.00	3.68	3.01	0.58
	3.51	6.50	1.00	4.35	3.42	0.77
vanillomandelic acid	3.50	8.00	1.00	4.50	3.92	0.86
	3.82	5.00	0.50	3.28	2.32	1.05
	3.79	5.00	1.00	3.42	2.64	1.12
	3.80	6.50	1.00	4.00	3.14	1.38
	3.74	8.00	1.00	4.56	3.66	1.40
	3.30	5.00	0.50	2.94	2.51	0.35
	3.30	8.00	0.50	3.49	3.21	0.45
	3.38	8.00	1.00	4.23	3.67	0.61
mandelic acid	3.48	3.00	0.50	2.26	1.77	0.37
	3.50	5.00	1.00	3.29	2.61	0.58
	3.46	8.00	1.00	4.48	3.61	0.72
	3.68	3.00	0.50	2.27	1.62	0.54
	3.72	5.00	0.50	2.73	2.18	0.79
	3.75	5.00	1.00	3.00	2.46	0.95
	3.69	8.00	1.00	4.52	3.43	1.17
 $CH_3\overset{SH}{C}HCOOH$	2.99	3.00	1.74	1.17	1.67	0.11
	3.06	5.00	0.87	1.33	1.85	0.15
thiolactic acid	2.94	5.00	1.74	1.56	2.21	0.13
	3.04	8.00	0.87	1.77	2.44	0.19
	3.19	3.00	1.74	1.20	1.52	0.16
	3.19	5.00	1.74	1.69	2.12	0.23
	3.25	5.00	4.35	1.75	2.19	0.27
	3.18	8.00	0.87	2.02	2.53	0.27
	3.49	1.00	0.17	0.43	0.49	0.11
	3.51	2.00	1.74	0.83	0.99	0.23
	3.48	5.00	0.87	1.52	1.86	0.39

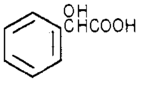
[a] The values of τ_{obsd} were obtained by averaging at least five experimental values. The deviations were less than 10% in these averaged relaxation times. [b] The subscript refers to total stoichiometric concentration.

Equilibrium Studies

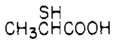
Potentiometric titrations were performed to determine the extent of complex formation between VO^{2+} and the ligands whose structures are shown.



vanillomandelic acid



mandelic acid



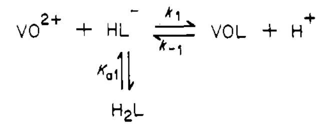
$CH_3\overset{SH}{C}HCOOH$

thiolactic acid

The ligands were initially titrated in the absence of metal ion. The pK_a's of the protons first dissociated (assigned to the carboxylic group) were determined by the Bjerrum method.[13] The results obtained were in close agreement with published values[14] and are given in Table I.

With the addition of vanadyl ion to the ligand solutions, the titration data showed the loss of two protons from each ligand upon complexation. For all three ligands, the first proton is lost from the carboxylic group. In the case of the second proton, dissociation is from the thiol group in the thiolactic acid and from the α-hydroxyl group in vanillomandelic and mandelic acids. Due to the unavailability of dissociation constants for the α-hydroxyl groups, the complex stability constants for vanillomandelic and mandelic acids with vanadyl could not be directly determined by the Bjerrum method. Thus, for these ligand systems an iterative procedure was carried out where initial guess stability constants were used in the determination of the equilibrium concentrations. Upon determination of the apparent forward (k_f) and reverse (k_r) rate constants for ML formation (see Appendix), a calculated stability constant, K_c(calcd) = k_f/k_r, was determined and subsequently used to calculate a new set of equilibrium concentrations. This procedure was continued until guess and calculated stability constants converged. For the thiolactic acid system both the Bjerrum technique and the iterative procedure were used in the determination of the complex stability constant. The final results are given in Table I with other relevant equilibria data.

Scheme I



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[13] Bjerrum, J. "Metal Ammine Formation in Aqueous Solution"; P. Haase: Copenhagen, 1957.

[14] Klingenberg, J. J.; Knecht, D. S.; Harrington, A. E.; Meyer, R. L. *J. Chem. Eng. Data* **1978**, *23*, 327.

Table III. Rate Constants of Vanadyl Complexation at 25 °C

		Scheme II			
		VO^{-2}			
ligand	Scheme I $10^{-3}k_1$, $M^{-1}\ s^{-1}$	k_1, $M^{-1}\ s^{-1}$	k_{-1}, $M^{-1}\ s^{-1}$	$VOOH^+$ $10^{-4}k'_1$, $M^{-1}\ s^{-1}$	k'_1/k_1
vanillomandelic acid	3.11 ± 0.26	$(1.13 \pm 0.07) \times 10^3$	2.54×10^5	4.17 ± 0.20	3.69 × 10
mandelic acid	3.07 ± 0.18	$(1.09 \pm 0.06) \times 10^3$	1.78×10^5	5.86 ± 0.25	5.38 × 10
thiolactic acid	1.72 ± 0.11	$(6.76 \pm 0.19) \times 10^2$	3.78×10^4	7.93 ± 0.14	1.17×10^2

Kinetics Studies

For metal–ligand complex systems that conform to a dissociative mechanism[15]

$$k_1 = k_{H_2O}K_{ip} \tag{1}$$

where k_1 is the complex formation rate constant, k_{H_2O} is the water-exchange rate constant for the metal ion, and K_{ip} is the ion-pair formation constant. The value of k_{H_2O} for VO^{2+} has been found to be $5 \times 10^2\ s^{-1}$.[10] The ion-pair formation constant can be theoretically calculated by using the Eigen–Fuoss equation;[16] for a (2+, 1−) interaction, K_{ip} is equal to 2 M^{-1}.[17] Many studies[2] have shown this value to prevail as an upper limit for (2+, 1−) systems.

The observed relaxation data for vanadyl complexation with vanillomandelic, mandelic, and thiolactic acids are given in Table II. Initial analysis of the relaxation data was carried out by utilizing Scheme I.

The relaxation expression for Scheme I can be written as in eq 2 where τ is the relaxation time. The α and β (eq 3 and

$$\frac{1}{\tau[H^+]} = k_1\left(\frac{\dfrac{[VO^{2+}]}{\alpha} + [HL^-]}{[H^+]}\right) + k_{-1} \tag{2}$$

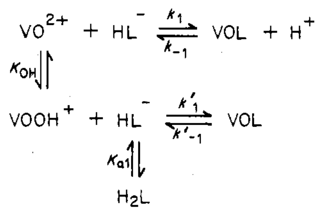
$$\alpha = 1 + \frac{[H^+]}{K_{a1}} - \frac{\beta[HL^-]}{K_{a1}} \tag{3}$$

$$\beta = \frac{1 + \dfrac{2[H^+]}{K_{a1}}}{1 + \dfrac{2[HL^-]}{K_{a1}} + \dfrac{[In^-]}{K_{In} + [H^+]}} \tag{4}$$

4) terms arise from the contributions of the rapidly established ligand and indicator protolytic equilibria to the overall relaxation, all concentrations refer to final equilibrium conditions. A plot of $1/\tau[H^+]$ vs. $([VO^{2+}]/\alpha + [HL^-])/[H^+]$ results in a straight line with a slope equal to k_1. Values of k_1 for the three ligand systems cover the range of $(1.72–3.11) \times 10^3\ M^{-1}\ s^{-1}$ (Table III). With these forward rate constants, values of K_{ip} were determined by using eq 1 and were found to be greater than the calculated value of 2 M^{-1}.

Obtaining higher rate constants than expected for vanadyl complexation suggested that the hydroxovanadyl species, $VOOH^+$, was involved in the overall reaction scheme. The presence of a coordinated hydroxyl group would labilize the remaining water molecules on the vanadyl ion and thus increase the overall rate of complex formation. In addition, the inclusion of the $VOOH^+$ reaction path is further supported by the fact that this study was done in the pH range 3.0–4.5 where the interaction of the $VOOH^+$ species cannot be neglected. The reaction scheme, which is analogous to one proposed for the formation of the Ni(II)–salicylate monocomplex at neutral pHs,[18] is given by Scheme II.

Scheme II



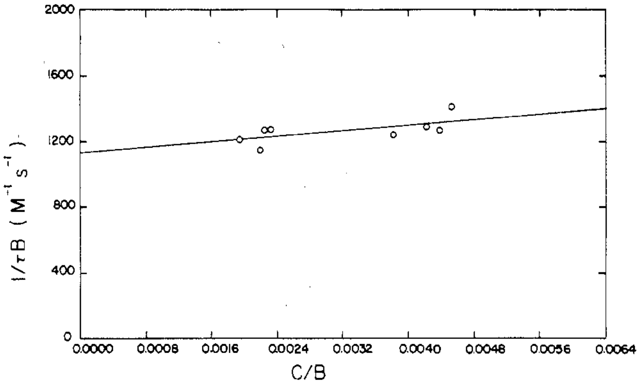


Figure 1. Plot of $1/\tau B$ vs. C/B for VO^{2+}–vanillomandelic acid complexation. The straight line was obtained by least-squares analysis, calculated from the data given in Table II.

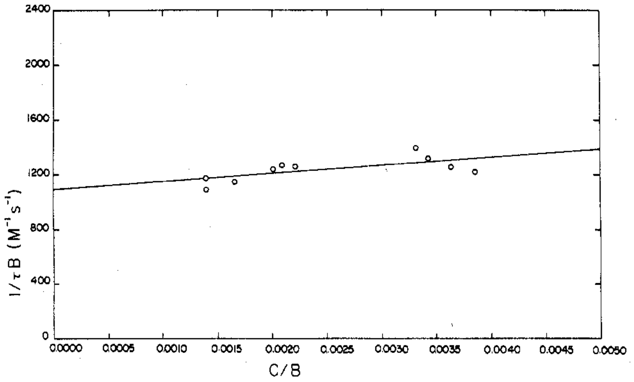


Figure 2. Plot of $1/\tau B$ vs. C/B for VO^{2+}–mandelic acid complexation. The straight line was obtained by least-squares analysis, calculated from the data given in Table II.

The relaxation expression can be written as follows:

$$\frac{1}{\tau B} = k_1 + k'_1\left(\frac{C}{B}\right) \tag{5}$$

where

$$B = [VO^{2+}]\alpha_2 + [HL^-]\alpha_3 + \frac{[H^+] + [VOL]\alpha_1}{K_c} \tag{6}$$

$$C = [VOOH^+]\alpha_2 + [HL^-]\alpha_4 + \frac{K_{OH}}{K_c} \tag{7}$$

The α_1, α_2, α_3, and α_4 terms arise from the contributions of

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(15) Kustin, K.; Swinehart, J. *Prog. Inorg. Chem.* **1970**, *13*, 107.

(16) (a) Eigen, M. *Z. Phys. Chem.* (*Wiesbaden*) **1954**, *1*, 176. (b) Fuoss, R. M. *J. Am. Chem. Soc.* **1958**, *80*, 5059.

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(18) Mentasti, E.; Pelizzetti, E.; Secco, F.; Venturini, M. *Inorg. Chem.* **1979**, *7*, 2007.

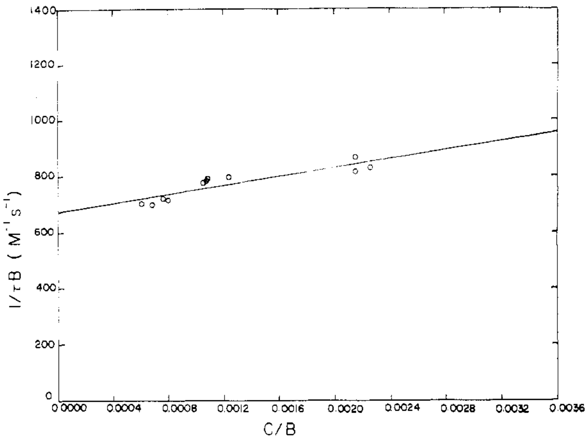

Figure 3. Plot of $1/\tau B$ vs. C/B for VO^{2+}–thiolactic acid complexation. The straight line was obtained by least-squares analysis, calculated from the data given in Table II.

the rapid protolytic equilibria to the overall rate equation and are defined by eq 8–11. The value of K_{OH} used in the calculations was 1×10^{-6} M.[10] Plots of $1/\tau B$ vs. C/B for the three systems studied are shown in Figures 1, 2, and 3. The results are tabulated in Table III.

$$\alpha_1 = \left(1 + \frac{[H^+]}{K_{a1} + [H^+]} - \frac{K_{OH}}{K_{OH} + [H^+]}\right) \Big/ \left(1 + \frac{C_{In}K_{In}}{(K_{In} + [H^+])^2} + \frac{[HL^-]}{[H^+] + K_{a1}} + \frac{[VOOH^+]}{[H^+] + K_{OH}} + \frac{K_W}{[H^+]^2}\right) \quad (8)$$

$$\alpha_2 = \frac{[HL^-]}{[H^+] + K_{a1}} + \frac{K_{a1}}{[H^+] + K_{a1}} \quad (9)$$

$$\alpha_3 = 1 - \frac{[VOOH^+]}{[H^+] + K_{OH}} - \frac{K_{OH}}{K_{OH} + [H^+]} \quad (10)$$

$$\alpha_4 = \frac{[VOOH^+]}{K_{OH} + [H^+]} + \frac{K_{OH}}{K_{OH} + [H^+]} \quad (11)$$

Discussion

In the final kinetics analysis the formation of $VOHL^+$ was not postulated in the overall reaction scheme since potentiometric data indicated the direct loss of two protons upon complex formation. A comparison of literature values[19] also shows that the stability constant of a vanadyl–α-hydroxycarboxylic acid complex is 20 times greater than that for a vanadyl–carboxylic acid complex. Enhanced stability would be expected with the participation of the α-hydroxyl group in chelate formation. Further support for this contention comes from a number of studies which have shown that the deprotonation of alcoholic groups occurs easily upon ligand complexation by oxovanadium(IV).[9,20,21] Deprotonation of the –SH moiety is expected to occur even more readily due to the higher acidity of the thiol group.

For all three ligand systems, initial postulation of an H_2L–VO^{2+} reaction in the mechanism resulted in a negative (close to zero) rate constant for this pathway, indicating that formation of VOL from H_2L and VO^{2+} does not occur under the conditions of this study. The concentration of the L^{2-} form of vanillomandelic and mandelic acids is negligible since the pK_a of the α-hydroxyl proton in both these acids is greater than 14. Thus, the L^{2-}–VO^{2+} reaction pathway was excluded from the overall reaction scheme for these two ligands. For the thiolactic acid system, however, the presence of free L^{2-} was taken into consideration in the preliminary analysis. A rate constant of ca. 10^8 M^{-1} s^{-1} was obtained for the reaction $L^{2-} + VO^{2+} \rightleftarrows VOL$, which considerably exceeds the value of about 6×10^3 M^{-1} s^{-1} predicted by the dissociative mechanism. This very large rate constant value might be ascribed to ligand coordination at the axial position of the vanadyl ion ($k_{H_2O}^{axial} \geq 5 \times 10^7$ s^{-1} [10]). However, numerous studies[9,10,22-24] have shown that for stable coordination to occur, bidentate ligands must chelate the vanadyl ion at the equatorial positions of the inner-coordination sphere. A mechanism where initial axial coordination by the ligand precedes a water-exchange process in which the axial ligand becomes equatorial can also be excluded since a rate constant value lower than 10^8 M^{-1} s^{-1} would be expected for this process. Thus, attack by L^{2-} was eliminated from the final scheme on the grounds that the calculated rate constant would have to be unreasonably high for this pathway to contribute to the rate of complex formation.

Table IV. Reanalyzed Rate Constants of Vanadyl Complexation from Earlier Published Relaxation Data

ligand	$10^{-4}k_1$,[a] M^{-1} s^{-1}	$10^{-3}k_1$,[b] M^{-1} s^{-1}	ref
HOOCC(OH)HC(OH)HCOOH	3 ± 1	1.40	3
$HOOCCH_2COOH$	~2	2.18	3
HOOCCOOH	~4	~1	3
SCN^-	1.15 ± 0.1	~1	5
SO_4^{2-}	1.50	~1	4

[a] Scheme without $VOOH^+$ interaction. [b] Scheme with $VOOH^+$ interaction.

Values of k_1 obtained from analysis of the relaxation data by Scheme II were used in the determination of K_{ip}'s for the three ligand systems. These calculated ion-pair formation constants, which fall into the range of 1.35–2.26 M^{-1}, were in much better agreement with the expected K_{ip} value for a (2+, 1−) system than those determined by using Scheme I.

Because of these results, we decided to reanalyze the data of earlier studies that had reported anomalously high forward rate constants for vanadyl complex formation. Hoffman and Ulbricht[3] determined rate constants of $\sim 2 \times 10^4$, $\sim 4 \times 10^4$, and 3×10^4 M^{-1} s^{-1} for VO^{2+} complexation with malonic (L^{2-}), oxalic (L^{2-}), and tartaric (HL^-) acids, respectively. Their value of k_1 for the formation of the vanadyl–tartaric acid complex was 2 orders of magnitude greater than the value ($k_1 = 1.7 \times 10^2$ M^{-1} s^{-1}) determined in these laboratories.[9] Wendt and co-workers studied the complexation reactions of VO^{2+} with SCN^- and SO_4^{2-}.[4,5] Their reported forward rate constants were 1.15×10^4 M^{-1} s^{-1} for the VO^{2+}–SCN^- system and 1.5×10^4 M^{-1} s^{-1} for VO^{2+}–SO_4^{2-} complex formation. With these high values for k_1, ion-pair formation constants were obtained in the range 23 M^{-1} < K_{ip} < 80 M^{-1}.

Since all of these investigations were carried out in a pH range of 2–4, the participation of the $VOOH^+$ species in the overall reaction mechanism is likely to occur.[5] Relaxation data reported in these earlier studies was reanalyzed by a scheme which included formation of the VOL complex from $VOOH^+$ and an accurate K_{OH} value.[10] For the tartaric acid system, which has the same reactive group as that of vanillomandelic and mandelic acids, a k_1 of 1.4×10^3 M^{-1} s^{-1} was obtained. For the VO^{2+}–malonic acid complexation reaction, a k_1 of 2.18

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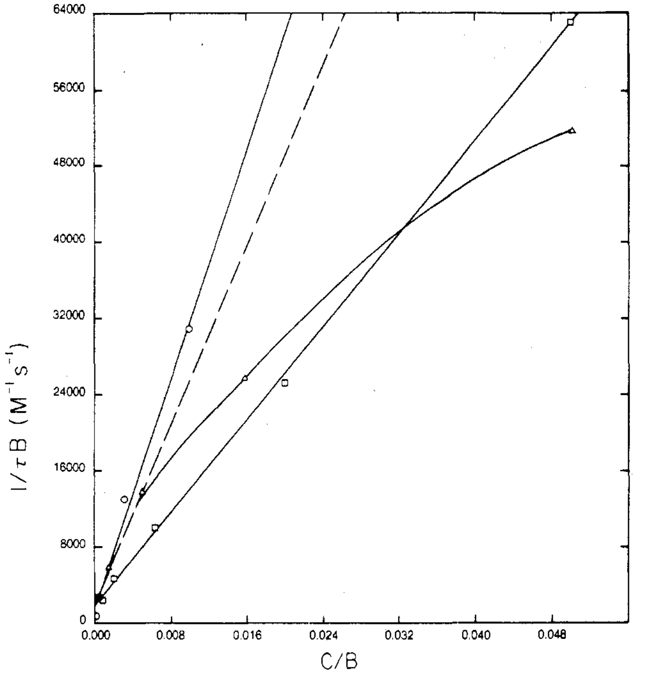

Figure 4. Plots of $1/\tau B$ vs. C/B for VO^{2+} complexation with (○) tartaric, (□) malonic, and (△) oxalic acids. For the tartaric and malonic acid systems, the straight solid lines were obtained by least-squares data analysis. For the oxalic acid system, a smooth curve has been drawn through all the data points; the dashed straight line arises from the extrapolation of the linear portion of the curve related to the formation of the monocomplex. The B and C expressions for these three dibasic acid ligand systems are slightly different from those given in eq 6–11 in that the second acid-dissociation constant is included in the α_1 and α_2 terms.

× 10^3 M^{-1} s^{-1} was determined. For the other ligand systems, the experimental conditions were such that higher order species (i.e., ML_2) were present and curved plots (e.g., oxalate, Figure 4) were obtained. Extrapolation of the linear portion of the graphs to a zero value of C/B resulted in intercept values of ca. 10^3 M^{-1} s^{-1}. Thus, analysis via a scheme including $VOOH^+$ interaction gave results (Table IV) more consistent with a "normal" dissociative pathway for vanadyl complex formation.

In light of these results, it is of interest to consider the vanadyl–glycine reaction $VO^{2+} + HGly^0 \rightleftarrows VOHGly^{2+}$, where $HGly^0$ denotes glycine. Even though the $VOOH^+$ species was not included in the analytical scheme (the experiments were done in the pH range 2–3), a "normal" rate constant of 1.3 × 10^3 M^{-1} s^{-1} was obtained. However, if one considers the relative unreactivity of a zwitterion[25-27] such as $HGly^0$, such a k_1 value is quite unexpected. The relatively high reactivity of the zwitterion species in the glycine study might be due to the presence of the labilized $VOOH^+$ species.

Table V. Substitution Rate Constants for the M^{n+} and $MOH^{(n-1)+}$ Forms of Al^{3+}, Fe^{3+}, and Rh^{3+}

metal ion	ligand	M^{n+} k_1, M^{-1} s^{-1}	$MOH^{(n-1)+}$ k'_1, M^{-1} s^{-1}	k'_1/k_1	ref
Al^{3+}	H_2O	1.3×10^{-1}	1.2×10^3	9.2×10^3	29
	SO_4^{2-}	1.2×10^3	8.5×10^5	7.1×10^2	30
	$Fe(CN)_6^{3-}$	6.6×10^{-1} [a]	7.8×10^2	1.2×10^3	31
Fe^{3+}	CH_3COOH	2.7×10	2.8×10^3	1.0×10^2	32
	HSali[b]	2.5×10	6.5×10^2	2.6×10	33
	$HC_2O_4^-$	1.4×10^3	4.8×10^4	3.4×10	34
	H_2SS^- [c]	1.5	5.5×10^3	3.7×10^3	35
	H_2Sal[d]	3.0	5.5×10^3	1.8×10^3	36
	acac (enol)[e]	5.2	4.4×10^3	4.8×10^2	37
	acac (keto)	2.9×10^{-1}	5.4	1.9×10	37
Rh^{3+}	H_2O	2.0×10^{-5}	3.0×10^{-3}	1.5×10^2	38

[a] First-order rate constant (s^{-1}). [b] HSali = salicylaldehyde. [c] H_2SS^- = sulfosalicylic acid. [d] H_2Sal = salicylic acid. [e] acac = acetylacetone.

By comparing values of k'_1/k_1 determined in the present study with those obtained for a number of other metal ions (Table V), one may observe a trend with regards to the labilization effect of a hydroxyl molecule on the substitution rates of these metal ions. The presence of a negatively charged hydroxyl group decreases the overall positive charge on the metal ion, labilizing the remaining water molecules. For metal ions such as Al^{3+}, Fe^{3+}, Rh^{3+}, and VO^{2+} that can undergo ligand substitution via a dissociative mechanism, the replacement of an inner-sphere water molecule by an OH^- group increases the rate of substitution by up to 3 orders of magnitude. Such an effect can be expected since the rate-determining step for dissociative substitution is the release of an inner-coordination water molecule.

Examination of the results obtained by using Scheme II (Table III) shows that the k_1 values decrease while the k'_1 values increase with decreasing ligand basicity. These trends are unexpected since dissociative substitution is independent of ligand characteristics. A number of mechanisms such as sterically controlled substitution,[2] internal H bonding of the ligand,[18] or deprotonation-dependent substitution[2] fail to explain the observed trends because the complex formation rate constants are not lower than those predicted by the Eigen mechanism. The lower k_1 value obtained for the VO^{2+}–thiolactic acid system might be related to an error in the experimentally determined stability constant due to the presence of contaminating CH_3CH_2COSH. The ratio k'_1/k_1, for the thiolactic acid system is 2 times greater than those obtained for the vanillomandelic and mandelic acid systems due to the lower k_1 value obtained for VO^{2+}–thiolactic acid complexation. The dissociation rate constants (k_{-1}'s), which are indicative of ligand characteristics[28] and complex stability, show the expected decrease in value with decreasing ligand basicity.

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Appendix

To determine k_f and k_r values, we used the following relaxation expression (derived from Scheme II):

$$\frac{1}{\tau D} = k_f + k_r\frac{F}{D} \tag{12}$$

where

$$k_f = k_1 + k'_1\frac{K_{OH}}{[H^+]} \tag{13}$$

$$k_r = k_{-1} + k'_{-1}\frac{1}{[H^+]} \tag{14}$$

$$D = [VO^{2+}]\alpha_2 + [HL^-] \tag{15}$$

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and

$$F = [\mathrm{VOL}]\alpha_1 + [\mathrm{H}^+]\alpha_3 \tag{16}$$

The α_1, α_2, and α_3 terms were previously defined by eq 8, 9, and 10, respectively. Plots of $1/\tau D$ vs. F/D yielded straight lines with intercepts equal to k_f and slopes equal to k_r with the equalities $K_c = k_1/k_{-1}$ and $K_c/K_{OH} = k'_1/k'_{-1}$, the equilibrium constant $K_c = [\mathrm{VOL}][\mathrm{H}^+]/[\mathrm{VO}^{2+}][\mathrm{HL}^-]$ can be calculated from the ratio k_f/k_r.

Registry No. VO^{2+}, 20644-97-7; vanillomandelic acid, 55-10-7; mandelic acid, 90-64-2; thiolactic acid, 79-42-5.

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Reduction of Hydrogen Peroxide by Ruthenium(II) Ammine Complexes: The Surprisingly Identical Mechanism for $Ru(NH_3)_6^{2+}$, $Ru(NH_3)_5OH_2^{2+}$, and $Ru(NH_3)_5(1\text{-}CH_3imH)^{2+}$

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In phosphate buffer (pH 6.86) the reductions of H_2O_2 by $Ru(NH_3)_6^{2+}$, $Ru(NH_3)_5OH_2^{2+}$, or $Ru(NH_3)_5(1\text{-}CH_3imH)^{2+}$ (1-CH_3imH = 1-methylimidazole) all exhibit a first-order dependence in $[Ru(NH_3)_5L^{2+}]$ and a saturation dependence in $[H_2O_2]$. The activation parameters for the three systems using $Ru(NH_3)_5L^{2+}$ reductants are nearly identical: L = NH_3, $\Delta H^{\ddagger} = 5.87 \pm 1.27$ kcal/mol, $\Delta S^{\ddagger} = -41.9 \pm 4.3$ eu; L = H_2O, $\Delta H^{\ddagger} = 5.32 \pm 0.36$ kcal/mol, $\Delta S^{\ddagger} = -36.8 \pm 1.2$ eu; L = 1-CH_3imH, $\Delta H^{\ddagger} = 5.46 \pm 0.48$ kcal/mol, $\Delta S^{\ddagger} = -50.6 \pm 1.6$ eu. A common two-electron redox mechanism is proposed in which a distorted structure $Ru(NH_3)_5L^{2+*}$, which has a substantial interaction with at least one solvent molecule, adds H_2O_2 as a seventh ligand to promote electron transfer. Comparisons are made to the two-electron pathway for the $Ru(NH_3)_6^{2+}/O_2$ system studied previously by Taube et al. In the range of $[H_3O^+]$ between 0.010 and 0.500 M the rate becomes zero order in $[Ru(NH_3)_5L^{2+}]$ (only L = NH_3 was studied in detail) and the rate proceeds by $[H_3O^+]$-independent and $[H_3O^+]$-dependent paths. Rates in 0.050 M acetate buffer (pH 4.6) are more rapid than predicted by H_3O^+ catalysis alone. The catalysis by H_3O^+ and complexing ligands is attributed to monomeric or labilized Fe(III) complexes. The iron is present at impurity levels from the reagents and electrolytes. The polymeric iron species, present in the phosphate buffer domain, are not catalytic. However, monomerization by H_3O^+ or complexation of the impurities by acetate ion or edta^{4-} converts the iron species into catalytically active forms. The active iron catalysts allow a facile inner-sphere pathway for the reduction of H_2O_2 since the electron transfer between $Ru(NH_3)_5L^{2+}$ and the Fe(III) complexes is rapid. For the noncatalyzed pathway, first order in $Ru(NH_3)_5L^{2+}$, the symmetry advantage of O_2 as an oxidant is compensated by the larger free energy change with H_2O_2 as an oxidant such that at low concentrations of O_2 and H_2O_2, $k_{O_2} \simeq 10^2 k_{H_2O_2}$.

Introduction

The reduction of H_2O_2 by metal centers having labile coordination sites is generally about 10^4 times faster than when H_2O_2 is restricted to an outer-sphere role.[1] The inner-sphere pathway remains the preferred pathway for reduction even when the overall driving force is very large, as for example with $Cr(CN)_6^{4-}$.[2] The reduction of H_2O_2 by simple aquo transition-metal reductants ($Cr(H_2O)_6^{2+}$, $Fe(H_2O)_6^{2+}$, $Ti(H_2O)_6^{3+}$) proceeds predominantly by one-electron paths with hydroxyl radical (HO·) as the initial product.[3-5]

We have begun to examine the mode of reactivity of H_2O_2 with complexes of the iron triad family. The oxidation of $(CN)_5Fe(Him)^{3-}$ (Him = imidazole) by H_2O_2 is much more rapid than for $Fe(CN)_6^{4-}$. Dissociation of the imidazole ligand from $(CN)_5Fe(Him)^{3-}$ followed by substitution of H_2O_2 on the $Fe(CN)_5^{3-}$ center limits the electron-transfer step, generating HO·.[6] It is also known that photodissociation of CN^- from $Fe(CN)_6^{4-}$ accelerates the $H_2O_2/Fe(CN)_6^{4-}$ reaction.[7] The parallels between the spectral properties and chemical reactivities of the $(CN)_5FeL^{3-}$ and $(NH_3)_5RuL^{2+}$ complexes (L = aromatic heterocyclic ligand) have been well documented.[8-10] The question arose as to whether the Ru(II) systems behave the same (via HO·) or whether a two-electron path is used for Ru(II). Pladziewicz, Meyer, Broomhead, and Taube have reported on the oxidation of $Ru(NH_3)_6^{2+}$ by O_2.[11,21] The evidence concerning the $Ru(NH_3)_6^{2+}/O_2$ system

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