

g., 0.264 mmol) was placed in the bottom of a quartz hot tube. The tube was packed with ceramic saddles and sublimer maintained at -78° was attached. A high vacuum was applied and the hot tube was heated to 650° . The solid was then sublimed up the hot tube by heating with a silicone oil bath between 250 and 290° . Thirty milliliters of silica gel was added to the sublimate which was dissolved in methylene chloride. The solvent was removed on a rotary evaporator, and the solids were mounted on a column of silica gel (600 ml dry volume) in hexane. The column was then eluted with hexane gradually enriched with methylene chloride giving eight fractions identified as orange 4,10,1,7-(C_5H_5)₂Co₂C₂B₈H₁₀ (XI) (105 mg, 0.029 mmol, 11%), orange 2,8,1,12-(C_5H_5)₂Co₂C₂B₈H₁₀ (XII) (90 mg, 0.0238 mmol, 9%), 4,12,1,7-(C_5H_5)₂Co₂C₂B₈H₁₀ (XIII) (10 mg, 0.0026 mmol, 1.0%), red 2,10,1,7-(C_5H_5)₂Co₂C₂B₈H₁₀ (XIV) (28 mg, 0.093 mmol, 3%), purplish 2,9,1,12-(C_5H_5)₂Co₂C₂B₈H₁₀ (XV) (10 mg, 0.0026 mmol, 1%), orange 2,5,1,7-(C_5H_5)₂Co₂C₂B₈H₁₀ (XVI) (9 mg, 0.0024 mmol, 0.9%), orange 2,4,1,7-(C_5H_5)₂Co₂C₂B₈H₁₀ (X) (15 mg, 396 mmol, 1.5%), and red 3,6,1,2-(C_5H_5)₂Co₂C₂B₈H₁₀ (IX) (70 mg, 0.0185 mmol, 7%).

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Interaction of Catechol and Catechol Derivatives with Dioxovanadium(V). I. Kinetics of Complex Formation in Acidic Media¹

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Abstract: The kinetics of complexation of dioxovanadium(V) by catechol and a series of catechol derivatives have been studied at $25.0 \pm 0.5^\circ$ and ionic strength 1.0 *M* (ClO_4^-) in acidic media (0.2–1.0 *M* $HClO_4$). Upon mixing acidic solutions of vanadium(V) and catechol (or catechol derivatives) a highly colored complex is formed which subsequently disappears due to oxidation of the ligand. Rate constants for complex formation (k_f) and dissociation (k_r) have been determined by stopped flow. The rate constants show no detectable $[H^+]$ dependence; it is therefore concluded that $HOVO^{2+}$ is not important, and the reactive species are VO_2^+ and fully protonated ligand. Both k_f and k_r are sensitive to the nature of the complexing ligand. For catechol, pyrogallol, 1,2,4-benzenetriol, L-dopa, and epinephrine, the respective k_f values are 1.84×10^4 , 4.36×10^4 , 9.91×10^4 , 1.12×10^4 , and $1.70 \times 10^4 M^{-1} sec^{-1}$ and for k_r 41.9, 8.39, 10.8, 55.2, and $66.6 sec^{-1}$. The values of k_f represent lower limits on the substitution rate constants. For example, with catechol, the vanadium(V) water exchange rate constant, k_0 , is $k_0 \geq 6 \times 10^4 sec^{-1}$. This value is greater than k_0 for V(IV) and is explained by electrostatic effects on the bonding to the remaining water molecules; namely, the additional oxide ligand compensates for the higher charge on the central metal atom. The order in k_f and K , the complex stability constant, is the same, and may also be explained by an electrostatic effect. Substitution rate constants of V(V) in media of pH 0–9 lie within the narrow range 1 to $10 \times 10^4 M^{-1} sec^{-1}$ due probably to rate controlling loss of coordinated aquo ligands.

Complexes of metal-containing oxo ions and organic ligands have long been employed in quantitative chemical analysis. However, interest in kinetics studies of complexation of d^0 ions such as those of Mo(VI), W(VI), Cr(VI), and V(V) is a late development. The lack of experimental

data was due to the complex equilibria of these metal-containing ions, in which changes in coordination number, polymerization, and extensive hydrolysis occur as conditions are varied. Furthermore, complex formation frequently occurs so rapidly that fast reaction techniques are required. A

further complication of studies with dioxovanadium(V) is the oxidation of ligand by the metal during or shortly after complex formation—a problem also encountered in this study. Fortunately, the two successive events of complexation and oxidation–reduction could be separated; the kinetics study of ligand oxidation by V(V) appears in the following paper.²

Recent reports have dealt with the kinetics and mechanism of complexation of V(V),³ Mo(VI),^{4–6} and W(VI)^{6,7} in slightly alkaline media, where the metal ions assume various anionic forms. It has been suggested that the rate constants for formation of V(V) complexes in such media are virtually independent of the nature of the complexing ligand. Ligand independence is assumed to reflect a rate determining loss of coordinated hydroxo or aquo ligands from the metal center. On the other hand, the rate constants for complexation of Mo(VI) and W(VI) by catechol and catechol derivatives,^{4,7} as well as by 8-hydroxyquinolines,^{5,6} vary, although not markedly, with choice of ligand.

This study explores vanadium(V) complex formation in acid solution, where the free metal ion is present as the aquated cation VO_2^+ . In addition to providing a comparison with the complexing of anionic vanadium(V), changing the complexing ligand species reveals details of the ligand substitution mechanism on VO_2^+ .

Experimental Section

Materials. Stock solutions of vanadium(V) perchlorate (Fisher), perchloric acid (Baker and Adamson), and lithium perchlorate (Fisher) were prepared and standardized as described previously.⁸ Perchloric acid in the stock vanadium(V) perchlorate solutions was 0.555 *M*. Stock solutions of ligand were prepared just prior to use from materials obtained from Fisher Scientific Co. (catechol), Baker Chemical Co. (pyrogallol), Aldrich (1,2,4-benzenetriol), Nutritional Biochemical Corporation (*L*-dopa), and Calbiochem (*L*-epinephrine). Distilled water used in all experiments was obtained in polyethylene containers from Belmont Springs Co., Belmont, Mass.

Kinetics Studies. All kinetics studies were carried out at 485 nm using the stopped-flow spectrophotometer and data storage device which have already been described.^{8–10} Ionic strength was kept at unity by addition of LiClO_4 . In all experiments $[\text{V(V)}]$ was sufficiently large to ensure that all reactions were pseudo-first-order and to preclude the formation of 1:2 (metal:ligand) or higher complexes. All kinetics studies were conducted in the presence of air.

Spectral Studies. When acidic solutions of V(V) and either catechol or its derivatives are mixed, a readily distinguishable red color appears rapidly and then disappears. The color arises from the formation of a V^{V} -ligand complex which subsequently disappears due to the oxidation of ligand by V(V).² A 4.35×10^{-3} *M* solution of V(V) in 1.0 *M* HClO_4 was mixed with a 1.02×10^{-3} *M* solution of catechol also 1.0 *M* in HClO_4 in the stopped-flow spectrophotometer. Absorbance as a function of time was obtained at 25-nm intervals from 400 to 625 nm. The absorbance at all wavelengths was greater than that of either V(V) or catechol alone. From the value of the absorbance extrapolated to the time of mixing and corrected for the absorbance due to excess V(V), the spectrum of the intermediate was determined; it is shown in Figure 1. There is a single maximum at 485 nm. The rapid disappearance of complex precludes the static determination of the equilibrium quotients for these V^{V} -catechol complexes. Rather, these constants have been evaluated kinetically (see below). The value of the molar absorptivity of the catechol- V^{V} complex, calculated using optical path-length $l = 1.1$ cm and apparent stability constant $K = 440 \pm 40$ M^{-1} , is found to be $3.1 \pm 0.2 \times 10^3$ $\text{M}^{-1} \text{cm}^{-1}$ at 485 nm.

Some solutions show the red color for a short, though appreciable time, as the oxidation–reduction reaction does not follow “immediately” after mixing. To such a solution we added an excess of strongly chelating EDTA, whereupon the color disappeared. If the intermediate were a partially oxidized ligand–vanadium complex, then EDTA would not be expected to perturb the system and no color change would ensue. This experiment supports the assign-

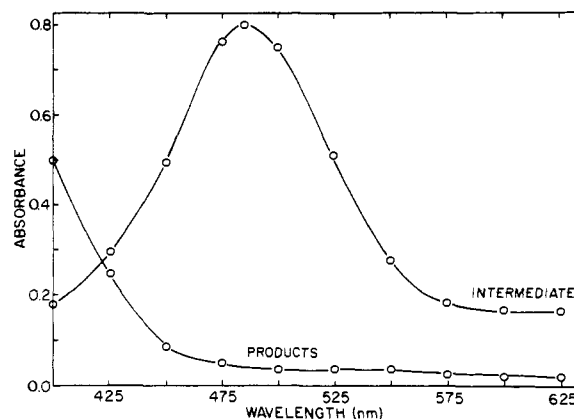


Figure 1. Optical spectrum of the V^{V} -catechol complex. A 4.35×10^{-3} *M* solution of V(V) was mixed with a 1.02×10^{-3} *M* solution of catechol in the stopped-flow spectrophotometer. Perchloric acid concentration was 1.0 *M*. Absorbance at the time of flow stop was obtained by extrapolation as described. Absorbance of the reaction product mixture was determined 60 sec later after mixing.

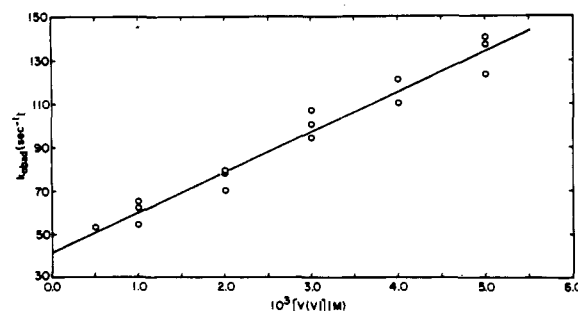


Figure 2. Plot of k_{obsd} vs. total [vanadium(V)]. The line through the points is calculated by linear least squares.

ment of the intermediate spectrum to a reversibly formed unoxidized ligand- V^{V} complex.

Results and Treatment of Data

The pseudo-first-order rate constants for formation of the V(V) complexes studied at 25° and ionic strength 1.0 *M* (ClO_4^-) are presented in Table I. Each kinetics experiment was first order in [ligand]. To a close approximation the rate constant for approach to equilibrium for a system of this type can be expressed as $k_{\text{obsd}} = k_f([\text{M}] + [\text{L}]) + k_r$; where k_f , k_r , $[\text{M}]$, and $[\text{L}]$ represent the bimolecular rate constant for complex formation, the unimolecular rate constant for complex dissociation, and the equilibrium concentrations of the metal ion and ligand, respectively. Under the pseudo-first-order conditions of the present study, $[\text{M}] + [\text{L}]$ can be approximated as the initial concentration of V(V). Values of k_f and k_r were obtained by linear least-squares analysis of k_{obsd} vs. $[\text{V(V)}]$. No significant hydrogen ion dependence of either k_f or k_r was observed in any of the systems investigated. For example, in the V^{V} -catechol system, at hydrogen ion concentrations of 0.1, 0.2, and 0.5 *M*, respective values of $(1.91 \pm 0.04, 1.94 \pm 0.17, \text{ and } 1.78 \pm 0.10) \times 10^4$ $\text{M}^{-1} \text{sec}^{-1}$ for k_f and $(42.7 \pm 1.1, 44.2 \pm 5.3 \text{ and } 37.0 \pm 3.5) \text{sec}^{-1}$ for k_r were found. A plot of k_{obsd} vs. $[\text{V(V)}]$ for the formation of the V^{V} -catechol complex is shown in Figure 2. Linear least-squares analysis of k_{obsd} vs. $[\text{V(V)}]$, including data at all acidities, gives values of $1.84 \pm 0.1 \times 10^4$ $\text{M}^{-1} \text{sec}^{-1}$ and $41.9 \pm 3.3 \text{sec}^{-1}$ for k_f and k_r , respectively. Least-squares values of k_f , k_r , and K for all systems are presented in Table II.

Table I. Kinetics Data for the Complex Formation of V(V) with Catechol and Catechol Derivatives in Acidic Media^a

Ligand	[H ⁺], M	10 ³ [Ligand], M	10 ³ [V(V)], M	<i>k</i> _{obsd} , ^b sec ⁻¹	<i>k</i> _{calcd} , ^c sec ⁻¹
Catechol	0.10	5.0	0.5	52.9 ± 1.9	51.1
			1.0	61.8 ± 2.6	60.3
			2.0	79.1 ± 3.0	78.7
			3.0	100 ± 6	97
			4.0	121 ± 5	116
	0.20	5.0	5.0	137 ± 6	134
			1.0	65 ± 2.2	60
			2.0	78 ± 2.7	79
			3.0	107 ± 7	97.2
			5.0	140 ± 5	134
	0.50	5.0	1.0	54.2 ± 4.4	60.3
			2.0	70 ± 3.2	79
			3.0	94.0 ± 4.1	97
			4.0	110 ± 6	116
			5.0	123 ± 5	134
Pyrogallol	0.20	1.0	0.161	16.1 ± 2.6	15.4
			0.323	20.4 ± 2.8	22.5
			0.645	38.7 ± 2.9	36.5
		2.0	1.29	63.3 ± 1.4	64.6
			1.94	80.9 ± 6.1	92.9
	2.58		121 ± 5	121	
	0.60	1.0	3.23	149 ± 7	149
			4.84	212 ± 15	219
			0.161	15.0 ± 2.5	15.4
		2.0	0.323	21.6 ± 2.6	22.5
			0.645	34.9 ± 1.3	36.5
	1.29		66.3 ± 2.6	64.6	
	1.0	1.0	1.93	83.0 ± 2.3	92.5
			2.58	111 ± 10	121
			0.161	16.4 ± 1.5	15.4
2.0		0.323	22.9 ± 2.1	22.5	
		0.645	38.2 ± 1.1	36.5	
1,2,4-Benzenetriol	0.2	1.0	1.29	71.1 ± 1.0	64.6
			1.94	94.9 ± 6.3	92.9
			2.58	126 ± 5	120
		1.98	3.23	172 ± 10	149
			0.096	20.3 ± 2.6	19.6
	0.6	1.0	0.161	25.0 ± 1.1	25.1
			0.354	48.7 ± 2.5	41.6
			0.645	75.1 ± 3.9	66.5
		1.29	1.29	112 ± 8	121
			1.935	194 ± 11	177
	1.0	1.0	0.161	30.0 ± 1.8	25.1
			0.322	49.4 ± 1.6	38.9
			0.645	84.3 ± 6.9	66.5
		1.29	1.29	161 ± 10	121
			1.935	224 ± 9	177
L-Dopa	0.1	5.0	0.161	27.3 ± 1.9	25.1
			0.322	40.4 ± 2.6	38.9
			0.645	63.1 ± 5.6	66.5
			1.29	122 ± 8	121
			1.94	122 ± 8	121
	1.0	5.0	0.5	54.4 ± 3.0	60.1
			1.0	61.1 ± 4.1	66.4
			2.0	75.3 ± 2.6	77.6
			3.0	85.9 ± 4.0	88.7
			4.0	96.7 ± 3.0	99.9
	0.2	5.4	5.0	101 ± 7	111
			0.5	66.2 ± 3.0	60.8
			1.0	70.0 ± 1.1	66.4
			2.0	81.1 ± 2.3	77.6
			3.0	92.3 ± 4.1	88.7
Epinephrine	0.2	5.4	4.0	109 ± 4	100
			5.0	116 ± 8	111
			1.29	91.3 ± 1.5	88.6
			1.94	106 ± 7	100
			2.58	105 ± 7	110
	0.6	5.4	3.23	114 ± 2	122
			4.83	131 ± 3	149
			1.29	94.5 ± 4.0	88.6
			1.94	102 ± 3	100
			2.58	107 ± 7	110
	1.0	5.4	3.22	116 ± 2	121
			4.83	131 ± 3	149
			1.29	98.9 ± 5.9	88.6
			1.94	113 ± 11	100
			2.58	108 ± 7	110

Table I (Continued)

Ligand	[H ⁺], M	10 ⁶ [Ligand], M	10 ⁶ [V(V)], M	<i>k</i> _{obsd} ^b , sec ⁻¹	<i>k</i> _{calcd} ^c , sec ⁻¹
			3.23	111 ± 5	127.4
			6.45	200 ± 8	176
			9.67	239 ± 13	231
			12.9	285 ± 16	286.2

^a 25.0°, ionic strength = 1.0 M (ClO₄⁻). ^b Average of at least five individual runs. Error is standard deviation. ^c Calculated by linear least-squares analysis of *k*_{obsd} vs. [V(V)].

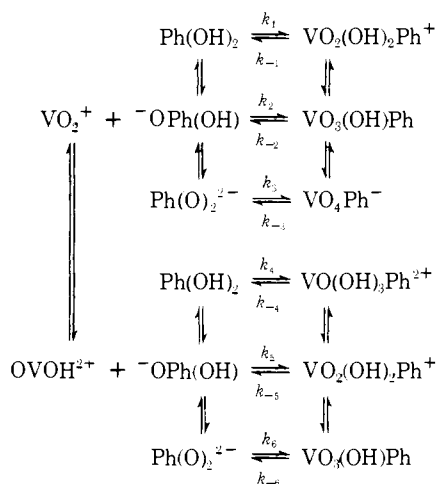
Table II. Stability and Rate Constants for V(V)-Catechol and Catechol Derivatives^a

Ligand	10 ⁻⁴ <i>k</i> _f ^b , M ⁻¹ sec ⁻¹	<i>k</i> _r ^b , sec ⁻¹	10 ⁻² <i>K</i> ^{app} ^{b,c} , M ⁻¹
Catechol	1.84 ± 0.10	41.9 ± 3.3	4.4 ± 0.4
Pyrogallol 1,2,4-	4.36 ± 0.13	8.39 ± 2.50	52.0 ± 16
Benzenetriol	9.91 ± 0.56	10.8 ± 5.4	91.8 ± 46
L-Dopa	1.12 ± 0.11	55.2 ± 3.3	2.03 ± 0.23
Epinephrine	1.70 ± 0.10	66.6 ± 4.4	2.55 ± 0.23

^a At 25.0°, ionic strength = 1.0 M (ClO₄⁻). ^b Errors are standard deviations. ^c *K*^{app}, the stability constant, was determined kinetically, as *K*^{app} = *k*_f/*k*_r.

The complete reaction scheme (Scheme I) for complex

Scheme I



formation between vanadium(V) and catechol (Ph(OH)₂) is shown below. Similar schemes for the catechol derivatives may also be written, in which more steps may be necessary where the number of dissociable protons exceeds two.

With the following stoichiometries

$$[M] = [\text{VO}_2^+] + [\text{OVOH}^{2+}]$$

$$[X] = [\text{Ph(OH)}_2] + [\text{OPh(OH)}^-] + [\text{Ph(O)}_2^{2-}]$$

$$[C] = [\text{VO}(\text{OH})_3\text{Ph}^{2+}] + [\text{VO}_2(\text{OH})_2\text{Ph}^+] + [\text{VO}_3(\text{OH})\text{Ph}] + [\text{VO}_4\text{Ph}^-]$$

the rate expression for complex formation according to Scheme I is

$$d[C]/dt = k_f[M][X] - k_r[C] \quad (1)$$

Substitution for [M], [X], and [C], with use of the rapidly established protolytic equilibria $K_M = [\text{H}^+][\text{VO}_2^+]/[\text{OVOH}^{2+}]$, $K_{L1} = [\text{H}^+][\text{Ph(OH)O}^-]/[\text{Ph(OH)}_2]$, $K_{L2} = [\text{H}^+][\text{Ph(O)}_2^{2-}]/[\text{Ph(OH)O}^-]$, $K_{C1} = [\text{H}^+][\text{VO}_3(\text{OH})\text{Ph}]/[\text{VO}_2(\text{OH})_2\text{Ph}^+]$, $K_{C2} = [\text{H}^+][\text{VO}_4\text{Ph}^-]/[\text{VO}_3(\text{OH})\text{Ph}]$, and $K_{C3} = [\text{H}^+][\text{VO}(\text{OH})_3\text{Ph}^{2+}]/[\text{VO}_4\text{Ph}^-]$ leads to a rate equation of identical form as eq 1 from which it can be shown that

$K_{C2} = [\text{H}^+][\text{VO}_4\text{Ph}^-]/[\text{VO}_3(\text{OH})\text{Ph}]$, and $K_{C3} = [\text{H}^+][\text{VO}(\text{OH})_3\text{Ph}^{2+}]/[\text{VO}_4\text{Ph}^-]$ leads to a rate equation of identical form as eq 1 from which it can be shown that

$$k_f = \frac{1}{\left(1 + \frac{[\text{H}^+]}{K_M}\right) \left(1 + \frac{K_{L1}}{[\text{H}^+]} + \frac{K_{L1}K_{L2}}{[\text{H}^+]^2}\right)} \times \left\{ k_1 + \frac{k_2K_{L1}}{[\text{H}^+]} + \frac{k_3K_{L1}K_{L2}}{[\text{H}^+]^2} + \frac{k_4[\text{H}^+]}{K_M} + \frac{k_5K_{L1}}{K_M} + \frac{k_6K_{L1}K_{L2}}{K_M[\text{H}^+]^2} \right\} \quad (2)$$

and

$$k_r = \frac{1}{\left(1 + \frac{K_{C1}}{[\text{H}^+]} + \frac{K_{C1}K_{C2}}{[\text{H}^+]^2} + \frac{K_{C3}}{[\text{H}^+]}\right)} \times \left\{ k_{-1} + \frac{k_{-2}K_{C1}}{[\text{H}^+]} + \frac{k_{-3}K_{C1}K_{C2}}{[\text{H}^+]^2} + \frac{k_{-4}[\text{H}^+]}{K_{C3}} + \frac{k_{-5}K_{C1}}{[\text{H}^+]}\right\} \quad (3)$$

Let the apparent stability quotient, *K*^{app} be defined as follows

$$K^{\text{app}} = \frac{[\text{VO}(\text{OH})_3\text{Ph}^{2+}] + [\text{VO}_2(\text{OH})\text{Ph}^+] + [\text{VO}_3(\text{OH})\text{Ph}] + [\text{VO}_4\text{Ph}^-]}{([\text{OVOH}^{2+}] + [\text{VO}_2^+])([\text{Ph(OH)}_2] + [\text{Ph(OH)O}^-] + [\text{Ph(O)}_2^{2-}])} = \frac{k_f}{k_r} \quad (4)$$

The apparent equilibrium quotient can be re-formulated in terms of the true (concentration) equilibrium constant for the principal species present under the conditions of this study (0.1 < [H⁺] < 1.0 M) as

$$K^{\text{app}} = f([\text{H}^+])K \quad (5)$$

where

$$f([\text{H}^+]) = \frac{1 + \frac{K_{C1}}{[\text{H}^+]} + \frac{K_{C2}K_{C1}}{[\text{H}^+]^2} + \frac{[\text{H}^+]}{K_{C3}}}{\left(1 + \frac{[\text{H}^+]}{K_M}\right) \left(1 + \frac{K_{L1}}{[\text{H}^+]} + \frac{K_{L1}K_{L2}}{[\text{H}^+]^2}\right)}$$

and

$$K = \frac{[\text{VO}_2(\text{OH})_2\text{Ph}^+]}{[\text{VO}_2^+][\text{Ph(OH)}_2]}$$

Some pathways in Scheme I could have been eliminated, thereby simplifying *f*([H⁺]), likewise *k*_f and *k*_r. For example, in order for the term *k*₃[Ph(O)₂²⁻] to contribute 1% to the rate, *k*₃ would have to exceed the diffusion controlled

limit by three orders of magnitude. It is easily seen that proceeding in this fashion serves only to eliminate the terms containing k_3 and k_6 from k_f and k_{-3} and k_{-6} from k_r . Still remaining is a rather complicated function of $[H^+]$.

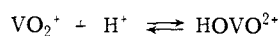
Experiments at different $[H^+]$ were carried out in an attempt to determine which were the most important kinetic pathways, *i.e.*, which species contribute significantly to K^{app} . However, variation of $[H^+]$ produced no detectable change in k_f and k_r , hence no change in k_{obsd} . Therefore, only an equivocal conclusion may be drawn. If no variation in k_{obsd} means that $f([H^+]) = 1$, then, $K_{C_1}, K_{C_2}, K_{L_1}, K_{L_2} \ll [H^+] \ll K_{C_3}, K_M$ and $K^{app} \approx K$. On the other hand, it is possible that a variation with $[H^+]$ exists but is too small to detect due to compensating changes in the numerator and denominator of K^{app} or k_f and k_r . In this case, the relative amounts of VO_2^+ and $HOVO^{2+}$, likewise $VO(OH)_3Ph^{2+}$, $VO_2(OH)_2Ph^+$, and $VO_3(OH)Ph$, cannot be inferred.

Discussion

The postulated reaction mechanism for oxidations by V(V) in acidic media with ligands like glycolic,¹¹ mandelic,¹² and tartaric¹³ acids or pinacol,¹⁴ has been the formation of a transient species between vanadium and the ligand prior to the electron transfer process. No physical evidence for such complexes was obtained. On the other hand, in the V(V) oxidations of hydrogen peroxide,¹⁵ cyclohexanol,¹⁶ and 2-mercaptosuccinic acid,¹⁷ there is direct evidence for the formation of a red intermediate complex. In the present work, there is qualitative agreement with the direct observation of the intermediate. Only one of the previously mentioned studies appears to have been quantitative.¹⁷ Unfortunately, this work was in the pH range 2.2–4.4 where there is some ambiguity concerning the form of the V(V) species.

Studies of the stereochemistry of mononuclear vanadium(V) complexes with oxalate and EDTA chelates containing the dioxovanadium(V) cation, VO_2^+ , have been reported.^{18–20} Structure determinations by X-ray diffraction analysis indicate that the configuration assumed by the VO_2^+ ion is bent with two equivalent V–O bonds (cis) and an OVO angle that ranges from 104 to 107°. The bonding in the complexes is octahedral. Preparative studies of complexes formed by 8-hydroxyquinoline²¹ with vanadium(V), by contrast, apparently show ligation with the protonated form, $OVOH^{2+}$,^{21–23} of the cation. Proton nmr has been used to examine the structures of these complexes in solution.²⁴ These studies, in which nonexchanging ligand proton resonances are measured, were interpreted on the basis of a central (cis) $VO(OH)^{2+}$ structural unit, even though direct evidence for separate oxo and hydroxo ligands was not forthcoming from the nmr data.

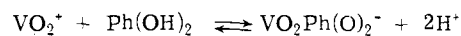
It has been postulated that in acid media the equilibrium^{14,25}



exists although no physical evidence has been provided to support this assignment. Perhaps in solutions of high sulfuric acid concentrations (>2 M) the $HOVO^{2+}$ species exists in significant concentrations. From the acidity range where our work was conducted and the result that K^{app} is $[H^+]$ independent, we conclude that VO_2^+ and $Ph(OH)_2$ are the principal reacting species in solution.

Complexes of oxo ions and metal-containing oxyanions in which hydroxy groups are bound to the central metal ion show no evidence that the proton remains attached, *e.g.*, in tartrato complexes.²⁶ A simple mixing experiment, in which the release of protons on complexation, could be determined, was not possible because of the relatively high acidi-

ty and ensuing redox reaction. We assume, therefore, that the best representation of the complex formation is^{27,28}



In terms of Scheme I, the mechanism of this process may be the step controlled by k_1 and k_{-1} , followed by rapid proton dissociation. However, loss of one or both protons may also be rate controlling. Comparison with oxovanadium(IV) substitution will shed some light on this problem.

The rate of elimination of equatorial coordinated water molecules from the inner coordination sphere of VO^{2+} ion was found to be $k_0 = 500 \text{ sec}^{-1}$ at 25°. ^{29,30} The rate of exchange of coordinated water in the axial position was estimated to be at least a factor of 10^6 greater. A comparison of the water-exchange rates from the first coordination spheres of the hydrated VO^{2+} ion and other hydrated doubly charged 3d metal ions led to the suggestion that the relatively slow exchange found for VO^{2+} is most likely due to large electrostatic contributions to the bonding of the water molecules.²⁹ In dioxovanadium(V) the net charge is less than that in oxovanadium(IV). One would then expect the V–O bond to be weaker; if the activation energy barrier for the exchange process is thereby less for V(V) than for V(IV), the V–OH₂ bond would be expected to be more labile.

In the reaction of V(IV) with tartaric acid at low pH the rate of formation of 1:1 complex was found to be less than the expected value for normal substitution.³¹ This shift in the rate determining step was explained in terms of proton transfer from an alcoholic OH group in tartaric acid ($pK_A > 14$). In catechol the proton is transferred from *acidic* (phenolic) groups ($pK_{A_1} = 9.25$, $pK_{A_2} = 12.37$).³² Therefore, either the rate determining step is water loss, and $k_0 = k_f/K_{ip} \approx (1.84 \times 10^4)/0.3 = 6 \times 10^4 \text{ sec}^{-1}$ where K_{ip} is the ion pairing constant, or the rate determining step is proton transfer in which case $k_0 \gg k_f/K_{ip}$. Thus k_f/K_{ip} is a lower limit for the substitution rate constant for V(V) complexations.³³

It is obvious from Table II that both forward and reverse rate constants are sensitive to substitution of groups on the benzene ring of catechol. For the rate constants of formation the observed order is 1,2,4-benzenetriol > pyrogallol > catechol > epinephrine > dopa. The dissociation rate constant order is epinephrine > dopa > catechol > 1,2,4-benzenetriol, pyrogallol. Although studies of the kinetics of oxo ion complex formation and dissociation are not numerous, several comparisons can be made at this time.

In mildly alkaline media, rate constants for formation of 1:1 (M:L) complexes of tungstate with catechol and some of its derivatives are also observed to depend on catechol ring substitution.⁷ If we consider only the ligands common to both the tungstate and this V(V) study, then the observed order of k_f values is (in units of $M^{-1} \text{ sec}^{-1}$) pyrogallol (692) > dopa (241) > catechol (110) for W(VI) and pyrogallol > catechol > dopa for V(V). Thus, while k_f for pyrogallol is largest in both cases, catechol and dopa exhibit the smallest k_f values for W(VI), and V(V), respectively. It is also informative to consider *relative* substitution rate constants.

The values of $k_f(\text{dopa})/k_f(\text{catechol})$ are 0.6 and 2.2 in the V(V) and W(VI) systems, respectively. This observed inversion in relative ordering of k_f values for dopa and catechol may simply be due to electrostatic effects. Under the V(V) experimental conditions dopa is present predominantly in the cationic form;³⁴ it is predominantly neutral and anionic in the W(VI) study, while catechol is a neutral molecule in both cases. Thus cationic dopa attacks positively charged VO_2^+ , but a mixture of neutral and anionic dopa attacks WO_4^{2-} (or $WO_3(OH)^-$). The same reasoning can

be applied to the ordering of k_f values for complex dissociation. For V(V) the observed order in k_f is dopa > catechol > pyrogallol and for W(VI) (in units of sec^{-1}), pyrogallol (0.6) > catechol (0.4) > dopa (0.3). Respective values of $k_f(\text{dopa})/k_f(\text{catechol})$ for V(V) and W(VI) are 1.3 and 0.8. Thus, relative to loss of neutral catechol, dissociation of less negatively charged dopa from VO_2^+ is enhanced over dissociation from anionic W(VI). Clearly, electrostatic considerations are not sufficient to account for all observed trends. For example, $k_f(\text{pyrogallol})/k_f(\text{catechol})$ has a value of 2.4 in the V(V) system. A simple statistical argument predicts a value of 2 (twice as many equivalent binding sites). However, for the W(VI) system $k_f(\text{pyrogallol})/k_f(\text{catechol})$ is found to be 6.3. Furthermore, if statistical effects are substantial, the value of k_f for V(V) complexation by 1,2,4-benzenetriol should be lower than that observed for pyrogallol. The rate constant for formation of the 1,2,4-benzenetriol-V^V complex is, however, the largest found in the present study. A thorough understanding of these effects awaits the availability of other data, such as the value of k_f for complexation of W(VI) by 1,2,4-benzenetriol.

Values of the equilibrium quotients for complexes of V(V) and catechol and its derivatives are presented in Table II. The order is identical with the rank of k_f values. The order of k_f and K^{app} values is also identical in the W(VI) system. In that system, however, the values of K^{app} are largely dependent upon k_f , since the k_f values are almost identical. In the V(V) system, values of k_f tend to increase with decreasing k_f values, leading to a much larger range of equilibrium quotients.

It has been shown previously that the rate constants for V(V) dimerization as well as for formation of V(V) complexes of EDTA and 1,2-dihydroxyanthraquinone, are essentially ligand independent in alkaline media.³ The characteristic rate constant for substitution on $\text{VO}_2(\text{OH})_2^-$ (with these anionic ligands) appears to be about $2 \times 10^4 \text{ M}^{-1} \text{ sec}^{-1}$. It is interesting to note that the values of k_f observed in the present study lie in the same region, ranging from roughly 1×10^4 to $10 \times 10^4 \text{ M}^{-1} \text{ sec}^{-1}$. Thus all observed rate constants for V(V) complex formation, obtained over a pH range of 0-9, fall within these fairly narrow limits.³⁵ This observation is consistent with the suggestion³

that loss of coordinated hydroxy and/or aquo ligands may contribute substantially to the rate determining process in such complexations.

References and Notes

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