Interaction of Catechol and Catechol Derivatives with Dioxovanadium(V). II. Kinetics of Ligand Oxidation[1]

Kenneth Kustin,* Claudio Nicolini, and David L. Toppen

Contribution from the Departments of Chemistry, Brandeis University, Waltham, Massachusetts 02154, and California State University, Northridge, California 91324.
Received April 1, 1974

Abstract: The kinetics of oxidation of catechol and a series of catechol derivatives by vanadium(V) have been studied by stopped flow at 25° and ionic strength 1.0 M (ClO_4^-) in acidic media (0.2–1.0 M $HClO_4$). The rate law is $-d[\text{ligand}]/dt = kK_2[V(V)]^2[\text{ligand}]/(1 + K_2[V(V)])$ where "ligand" is catechol or one of its derivatives, k is given by $k = k_1 + k_2[H^+]$, and $K_2 = [\text{complex}]/[V(V)][\text{ligand}]$. The mechanism most consistent with the data and chemistry of this system is the reversible formation of a complex between vanadium(V) and the reductant, followed by rate determining reaction of this complex and V(V). The redox rate constants were found to be $[H^+]$ dependent indicating that two parallel paths are important for the rate limiting step. The respective rate constants are the following (reductant, k_1 in units of M^{-1} sec^{-1}, k_2 in units of M^{-2} sec^{-1}): catechol, 23.8 ± 2.4, 71.7 ± 3.3; pyrogallol, 1200 ± 90, 1140 ± 140; 1,2,4-benzenetriol, 6080 ± 180, 775 ± 280; L-dopa cation, 11.6 ± 1.6, 31.2 ± 2.3; epinephrine cation, 10.2 ± 1.0, 26.2 ± 1.6; gallic acid, 58.6 ± 2.2, 53.3 ± 2.9. These results are discussed in terms of the Marcus cross-reaction equation for outer-sphere electron transfer reactions.

This paper is a continuation of our study of the kinetics of reaction between catechol and catechol derivatives with vanadium(V) in acidic media. The kinetics of complex formation have been previously reported.[2] We now consider the oxidation of catechol and its derivatives.

The oxidation of a variety of organic ligands by V(V) in acidic media has been the object of several studies. For example, Littler and Waters[3-5] have studied the stoichiometry and kinetics of the oxidation of pinacol, cyclopentanone, and cyclohexanone by V(V). In all cases indirect evidence for a free radical was observed and the reduction of V(V) to V(IV) by electron transfer was postulated. In the oxidation of ascorbic acid by V(V) a free radical was also detected,[6] and a mechanism was postulated consisting of the rapid formation of a complex followed by its rate limiting decomposition. The electron transfer rate constant was found to be pH independent indicating that only a single intermediate complex is important.

Two studies of reductants bearing a close structural resemblance to catechol have been reported, for which free radical mechanisms have been invoked although no direct evidence of radical intermediate formation was provided. The oxidation of *p*-hydroquinone by vanadium(V) is first order in metal and in reductant and is also $[H^+]$ dependent.[7] A two-term rate law, independent of $[H^+]$, was found for the V(V) oxidation of tiron (4,5-dihydroxybenzene-1,3-disulfonic acid);[8] both terms were linear in [V(V)], one term was linear and the other quadratic in [tiron]. Spectrophotometric evidence for a V^V–tiron complex was also found.

Kinetics studies of the reduction of V(V) by hydrazine and hydroxylamine in strongly acid aqueous solutions have been reported.[9,10] The proposed rate law for hydrazine is consistent with a mechanism that involves a (reversible) formation of a complex, followed by the reaction between this complex and "free" V(V). The reaction rate was found to be a linear function of $1/[H^+]$ and was interpreted in terms of two parallel reactions. For the hydroxylamine system, complex formation prior to the redox reaction was observed. The rate law shows two terms and a mechanism involving two reaction paths was proposed. It was suggested that the second-order term probably corresponds to an intramolecular electron transfer within the complex, and the third-order term might represent a reaction between the complex and V(V). The reaction rate was found to be $[H^+]$ independent.

On mixing solutions of vanadium(V) and catechol (or its derivatives) in aqueous acid, an intermediate appears, the formation of which produces a kinetics curve with half-lives ranging from 5 to 15 msec depending on conditions of concentration;[2] subsequently, the intermediate disappears. In this paper we are reporting the rate and mechanism of disappearance of the intermediate, which we have shown to be a vanadium(V)–catechol complex,[2] by a redox reaction with vanadium(V) in which the catechol is oxidized.

Experimental Section

Materials. Stock solutions of vanadium(V) perchlorate, (Fisher) perchloric acid (Allied), and lithium perchlorate were prepared and standardized as described previously.[6] Perchloric acid in the stock vanadium(V) perchlorate solutions was 0.55 M.

Stock solutions of ligand were prepared just prior to use from materials obtained from Fisher Co. (catechol = 1,2-dihydroxybenzene), Baker Chemical Co. (pyrogallol = 1,2,3-trihydroxybenzene), Aldrich (1,2,4-benzenetriol), Nutritional Biochemical Corporation (L-dopa = L-3,4-dihydroxyphenylalanine), Calbiochem (L-epinephrine = L-[3,4-dihydroxyphenyl]-2-methylaminoethanol), and Chem Services, Inc. (gallic acid = 3,4,5-trihydroxybenzoic acid). Distilled water was obtained in polyethylene containers from Belmont Springs Co., Belmont, Mass., or was twice distilled from an all-quartz apparatus.

Kinetics Studies. Most kinetics studies were carried out at 485 nm using the stopped-flow spectrophotometer and data storage device which have been described previously.[6,11,12] Gallic acid oxidation studies were conducted with a Cary 14 spectrophotometer modified to include a magnetic stirrer within the thermostated cell compartment. Standard syringe techniques were utilized to deliver aliquots of V(V) solutions to a constantly stirred solution of gallic acid contained in the spectrophotometer cell. Ionic strength was brought to unity by addition of $LiClO_4$. In all experiments [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.

Product Identification. To establish the stoichiometry in solutions containing excess catechol, 10 ml of a 0.1643 M solution of V(V) was added under anaerobic conditions to 50 ml of ice cold $HClO_4$ (0.1 M) containing 0.638 mmol of catechol. The highly colored solution was charged onto a Dowex 50W-X8(H^+) ion-exchange resin, eluted with three column volumes of ice cold water followed by 1.5 M $HClO_4$. The blue band of V(IV) was collected and analyzed spectrophotometrically at 750 nm:[13] amount of V(IV) produced, calcd (assuming 2 mmol V(IV) per initial mmol catechol) 1.28 mmol; found, 1.31 ± 0.02 mmol (average of three determinations). The slightly high value probably reflects some

Table I. Kinetics Data for V(V) Oxidation of Catechol and Catechol Derivatives in Acidic Media[a]

10^5[Ligand]	$[H^+]$, (M)	10^3[V(V)], (M)	k_{obsd},[b] sec^{-1}	k,[c] M^{-1} sec^{-1}	k_{calcd},[d] M^{-1} sec^{-1}
Catechol	1.00	5.80	0.389	93.4	
2.76		11.6	0.893	92.1	
		17.4	1.42	92.0	
		23.2	2.05	97.2	
		29.0	2.74	101.8	
				Av = 95.3 ± 4.2	95.5
	0.60	10.8	0.625	70.3	
		16.2	0.981	69.3	
		21.5	1.23	63.4	
				Av = 67.6 ± 3.8	66.8
	0.20	5.80	0.151	36.2	
		11.6	0.317	32.7	
		17.4	0.616	40.0	
		23.2	0.895	42.4	
				Av = 37.8 ± 4.3	38.1
Pyrogallol	1.00	1.29	2.39	2130	
1.98		1.94	4.10	2330	
		2.58	5.81	2420	
				Av = 2290 ± 150	2340
	0.60	1.94	3.75	2130	
		2.58	4.95	2060	
		3.23	5.34	1750	
				Av = 1980 ± 200	1880
	0.20	1.29	1.62	1440	
		1.94	2.26	1280	
		2.58	3.44	1430	
		3.23	4.26	1400	
				Av = 1390 ± 70	1420
1,2,4-Benzenetriol	1.00	1.29	8.64	7260	
1.98		1.94	13.2	7190	
		2.58	16.8	6790	
		3.23	19.4	6210	
				Av = 6860 ± 480	6850
	0.60	0.161	0.58	6040	
		0.322	1.65	6860	
		1.29	7.91	6650	
				Av = 6520 ± 430	6540
	0.20	0.354	1.73	6390	
		0.645	3.26	5910	
		1.29	7.71	6480	
		1.94	11.6	6330	
		2.58	14.6	6300	
		3.23	18.8	6020	
				Av = 6240 ± 220	6230
L-Dopa	1.00	3.23	0.060	47.0	
5.4		6.45	0.169	46.0	
		9.68	0.271	42.2	
		12.9	0.411	44.0	
		16.1	0.504	40.8	
				Av = 44.0 ± 2.6	42.8
	0.60	6.45	0.096	26.3	
		9.68	0.190	29.6	
		12.9	0.265	28.4	
		16.1	0.318	25.8	
				Av = 27.5 ± 1.8	30.4
	0.20	6.45	0.072	19.7	
		9.68	0.123	19.2	
		12.9	0.185	19.8	
		16.1	0.228	18.5	
				Av = 19.3 ± 0.6	17.9
Epinephrine	1.00	12.9	0.365	37.0	
5.4		16.1	0.486	37.5	
				Av = 37.2 ± 0.4	36.3
	0.60	6.45	0.098	24.8	
		12.9	0.249	25.2	
		16.1	0.317	24.4	
				Av = 24.8 ± 0.4	25.9
	0.20	6.45	0.071	17.6	
		12.9	0.159	16.0	
		16.1	0.186	14.3	
				Av = 16.0 ± 1.6	15.4
Gallic acid	1.00	0.508	0.057	112	
2.21		0.978	0.109	111	
		1.41	0.154	109	
		1.65	0.178	108	
		1.82	0.198	109	

Table I (*Continued*)

10^5[Ligand]	[H^+], (M)	10^3[V(V)], (M)	k_{obsd},[b] sec^{-1}	k,[c] M^{-1} sec^{-1}	k_{calcd},[d] M^{-1} sec^{-1}
		2.01	0.241	120	
		2.20	0.251	114	
				Av = 112 ± 4	112.0
	0.60	0.508	0.043	85.0	
		0.978	0.092	94.5	
		1.41	0.126	89.4	
		1.82	0.175	96.0	
		2.20	0.195	88.6	
				Av = 91.0 ± 5.0	90.0
	0.20	0.978	0.068	69.1	
		1.41	0.094	66.4	
		1.82	0.128	70.3	
		2.20	0.156	71.0	
				Av = 69.0 ± 2.0	69.0

[a] At 25°, ionic strength = 1.0 M (ClO_4^-). [b] Average of at least five individual runs. [c] Calculated from eq 4. [d] Calculated by linear least-squares analysis of k *vs.* [H^+].

slow product oxidation subsequent to the primary redox step. Attempts to identify products of ligand oxidation were made, 0.0231 mmol of catechol were treated with 0.0462 and 0.0924 mmol of V(V), respectively. By scanning the 300–500-nm absorption region of the spectra, a band with maximum at 380 nm corresponding to *o*-benzoquinone[14a] was detected. Repetitive scans demonstrated that the band was disappearing, presumably due to the instability of the *o*-quinone in aqueous media.[14b] This result suggests that *o*-benzoquinone is the initial product of the V(V) oxidation of catechol.

Polymerization. A series of reactions between V(V) and catechol was carried out in deaerated vials at 25° in the presence of 5% acrylonitrile. The initial concentrations of V(V) and $HClO_4$ were 1.0×10^{-3} and 1.0 M, respectively. Catechol concentrations were 0.009, 0.018, and 0.032 M. Under roughly these same conditions acrylonitrile polymerization was observed in the V^V–ascorbic acid system.[6] In the present study, however, no polymerization was detected.

Results and Discussion

The stoichiometric and product identification studies indicate that the stoichiometries for all systems investigated may be represented as

$$2H^+ + 2VO_2^+ + H_2L = 2VO^{2+} + L + 2H_2O \quad (1)$$

where H_2L and L represent catechol (or one of its derivatives) and its two-electron oxidation product, *o*-benzoquinone (or its corresponding derivative), respectively.

The pseudo-first-order rate constants k_{obsd} for the electron transfer reactions at 25° and ionic strength 1.0 M (ClO_4^-) are presented in Table I. Each kinetics experiment exhibited first-order behavior with respect to [H_2L]. Plots of k_{obsd} *vs.* total [V(V)] do not show saturation of the pseudo-first-order rate constant with increasing V(V) concentration but are almost linear with a small negative intercept. These results are consistent with the scheme

$$V(V) + H_2L \underset{k_r}{\overset{k_f}{\rightleftharpoons}} C \quad \text{(rapid)} \quad (2)$$

$$V(V) + C \xrightarrow{k} 2V(IV) + L \quad \text{(rate determining)} \quad (3)$$

for which the observed rate constant can be expressed as

$$k_{obsd} = \frac{kK_2[V(V)]^2}{1 + K_2[V(V)]} \quad (4)$$

where C represents an intermediate V^V–reductant complex of unspecified charge and degree of hydrolysis,[2] k is a second-order rate constant for electron transfer, K_2 is the equilibrium constant for reaction 2 (the apparent complex formation constant), H_2L is the reductant, and L is the oxidized product. The values of K_2 were obtained from previous kinetics studies as k_f/k_r;[2] values of k for each reductant were therefore calculated directly from eq 4 and are also presented in Table I.

Figures 1, 2, and 3, as well as Table I show that for all reductants the redox rate constant is [H^+] dependent, indicating that two paths are important. In the acidic region where these experiments were conducted (0.20–1.00 M), vanadium(V) occurs as a cation of formula VO_2^+. A possible explanation for the [H^+] dependence could be that the species $HOVO^{2+}$ is the oxidant in the acid catalyzed reaction according to the equilibrium[3]

$$VO_2^+ + H^+ \rightleftharpoons HOVO^{2+} \quad (5)$$

However, we believe that the [H^+] dependence is not likely to arise from the above equilibrium. Essentially, no evidence has been given for its existence,[15] except, perhaps, at high concentrations of sulfuric acid.[3] Furthermore, mechanisms in which the [H^+] dependence is related to a scheme in which protonated complexes originate from attack of $HOVO^{2+}$ on the ligand are inconsistent with the [H^+] independence found for the complexation process.[2]

In the oxidation of ascorbic acid by vanadium(V), for which no [H^+] dependence is observed,[6] the rate determining step was postulated to be the intramolecular decomposition of the intermediate. The mechanism incorporates a free radical, demonstrated to be produced in the reaction. In the present study, no free radicals able to initiate polymerization of acrylonitrile were detected. To account for the observed rate law, the presence of a [H^+] dependence, and the absence of radical intermediates, it is proposed that the rate limiting process (reaction 3) is best expressed as the composite of two pathways

$$C + VO_2^+ \xrightarrow{k_1} \text{products} \quad (6)$$

$$C + VO_2^+ + H^+ \xrightarrow{k_2} \text{products} + H^+ \quad (7)$$

representing H^+ independent and H^+ catalyzed routes for electron transfer, respectively. Thus, eq 4 becomes

$$k_{obsd} = \frac{(k_1 + k_2[H^+])K_2[V(V)]^2}{1 + K_2[V(V)]} \quad (8)$$

for which

$$k = k_1 + k_2[H^+] \quad (9)$$

The rate constants for the catalyzed (k_2) and noncatalyzed (k_1) paths were calculated by least-squares analysis of k *vs.* [H^+] for each system and are presented in Table II.

The reaction between iron(III) and catechol is, in many respects, similar to the V^V–catechol reaction. A complex is formed,[16] which then disappears due to oxidation.[17] However, the redox rate law is unusually complicated: the reac-

Table II. Kinetics and Thermodynamics Data for the Oxidation of Catechol and Catechol Derivatives by Vanadium(V) in Acidic Media[a]

Ligand	k_1,[b] M^{-1} sec^{-1}	k_2,[b,c] M^{-2} sec^{-1}	K_1,[d] M^{-2}	$10^{-2}K_2$,[e] M^{-1}	K_3,[f] M^{-1}	Q_0[g]	Q_h[h]
Catechol	23.8 ± 2.4	71.7 ± 3.3	1.08×10^7	4.39	2.46×10^4	1	1
Pyrogallol	1200 ± 90	1140 ± 140	5.04×10^9	52.0	9.69×10^5	8.0	2.5
1,2,4-Benzenetriol	6080 ± 180	775 ± 280	5.31×10^{13}	91.8	5.78×10^9	0.53	0.02
L-Dopa	11.6 ± 1.6	31.2 ± 2.3	5.77×10^6	2.03	2.84×10^4	0.45	0.41
Epinephrine	10.2 ± 1.0	26.2 ± 1.6	2.86×10^6	2.55	1.12×10^4	0.64	0.54
Gallic acid	58.6 ± 2.9	53.3 ± 2.9	6.24×10^6	20[i]	3.12×10^3	6.9	2.1

[a] At 25°, ionic strength = 1.0 M (ClO_4^-). [b] Calculated by least-squares analysis of k *vs.* [H^+]. Error is standard deviation. [c] k_2 corresponds to the [H^+]-catalyzed path. [d] Calculated from standard potentials of ref 16. [e] From ref 2. [f] K_3 calculated as $K_1K_2^{-1}$, see text. [g] Q_0 calculated (relative to catechol) as $Q_0 (k_{1\,(\text{ligand})}/k_{1\,(\text{catechol})})(K_{3\,(\text{catechol})}/K_{3\,(\text{ligand})})^{1/2}$. [h] Q_h calculated (relative to catechol) as $Q_h = (k_{2\,(\text{ligand})}/k_{2\,(\text{catechol})})$-$(K_{3(\text{catechol})}/K_{3(\text{ligand})})^{1/2}$. [i] This value was not determined in ref 2 and is an estimate.

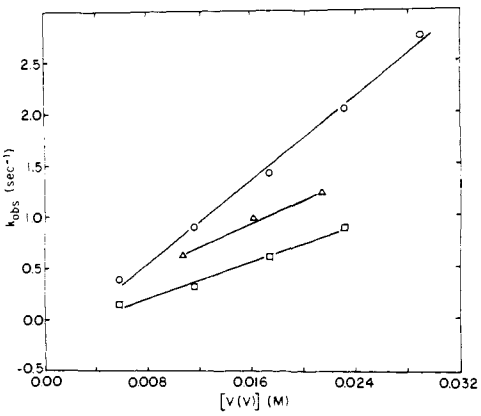

Figure 1. Plot of k_{obsd} *vs.* total [V(V)] for the oxidation of catechol by V(V) in acidic media (25°, ionic strength = 1.0 M (ClO_4^-)): O, [H^+] = 1.00 M; Δ, [H^+] = 0.60 M; □, [H^+] = 0.20 M. When K_2[V(V)] ≫ 1, eq 4 becomes $k_{obsd} \simeq k$[V(V)]. A least-squares calculated line of slope k has been drawn through the data.

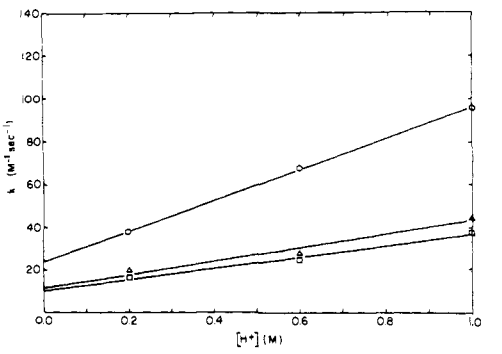

Figure 2. Plot of k *vs.* [H^+] for epinephrine (□), L-dopa (Δ), and catechol (O) (25°, ionic strength = 1.0 M (ClO_4^-)).

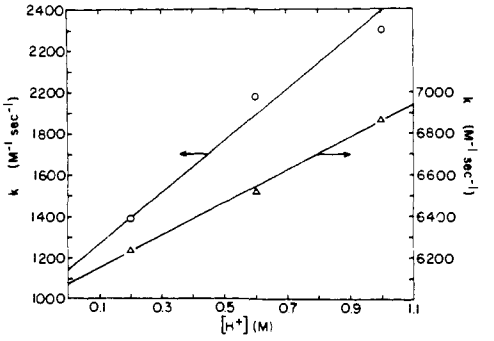

Figure 3. Plot of k *vs.* [H^+] for pyrogallol (O, k values correspond to left-hand abscissa) and 1,2,4-benzenetriol (Δ, k values correspond to right-hand abscissa) (25°, ionic strength 1.0 M (ClO_4^-)).

tion goes to equilibration, not completion, and the back reaction interferes; and an inverse [H^+] dependence is observed. Furthermore, no test for a radical intermediate was made, and comparisons with results for the oxidations of catechol derivatives were not provided. Thus, although the possible existence of inner- and outer-sphere mechanisms was mentioned, no analysis was attempted. The comparative results for catechol and its derivatives enables us to make such an analysis.

Marcus[18] has shown that a theory of electron transfer reactions can be successfully applied to the Fe(III) oxidation of a series of hydroquinones. More recently, Sullivan and coworkers[19] have utilized the Marcus cross-reaction relationship to interpret the rate data obtained from studies of the oxidation of *p*-hydroquinone and *p*-toluhydroquinone by Np(VI), Co(III), Mn(III), and Fe(III). Since the cross-reaction relationship provides an easily calculated approach to electron transfer reactions, the present studies are presented in the context of this treatment.

The known potentials[20] for the couples V(V)-V(IV) and L-H_2L permit the calculation of the corresponding values of K_1, the equilibrium constants for the reactions represented by eq 1, for all systems studied. The values of K_1 so obtained appear in Table II. The reactions virtually proceed to completion. The empirical form of the rate law suggests that reaction 3 (or a composite of processes the sum of which is stoichiometrically equal to eq 3) is rate limiting. The equilibrium constant for the rate limiting process, K_3, is readily estimated from the known equilibrium constants of (1) and (2); therefore, for (3), $K_3 = K_1K_2^{-1}$, Table II.

The Marcus cross-reaction equation may be employed to predict the variation in redox rate parameters for a series of reductants with a single oxidant.[21] Thus, the homonuclear (isotopic) self-exchange reactions are

$$V(V) + \overset{*}{V}(IV) \xrightarrow{k_{11}} V(IV) + \overset{*}{V}(V) \qquad (10)$$

and

$$H_2R + \overset{*}{R} \xrightarrow{k_{22}} R + H_2\overset{*}{R} \qquad (11)$$

for which the heteronuclear cross-reaction is

$$V(V) + H_2R \xrightarrow{k_{12}} V(IV) + R + 2H^+ \qquad (12)$$

with rate constant k_{12} expressed as

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2} \qquad (13)$$

Here, H_2R represents the reducing species, which, in the present case is the V^V-ligand complex, K_{12} is the equilibrium constant ($=K_3$) for the rate determining redox step, and the f term is given by

$$\log f \frac{(\log K_{12})^2}{4 \log (k_{11}k_{22}/Z^2)} \qquad (14)$$

where Z is the reactant collision frequency.

If this equation is utilized for a comparison of the redox rate constants for the present series of reductants with the common oxidant V(V), a rate ratio results which depends solely upon the self-exchange rate constants of the reductants, the respective redox equilibrium constants, and the corresponding f terms.[22]

$$\frac{k_{12}}{k_{12}'} = \frac{(k_{22}K_{12}f_{12})^{1/2}}{(k_2'_2'K_{12}'f_{12}')^{1/2}} \quad (15)$$

Since the values of the equilibrium constants, K_{12}, have been estimated above as K_3, this rate ratio can be expressed as

$$\frac{k_{12}}{k_{12}'}\left(\frac{K_{12}'}{K_{12}}\right)^{1/2} = \left(\frac{k_{22}f_{12}}{k_2'_2'f_{12}'}\right)^{1/2} = Q \quad (16)$$

where, in the present system, Q is calculated relative to values for catechol. Values of Q_0 (for the $[H^+]$ independent path) and Q_h (for the $[H^+]$ catalyzed path) are presented in Table II for all systems studied.

It is interesting to note that, in consideration of the k_1 pathway, observed values for Q_0 appear to fall into two categories. In spite of the wide range of rate constants (k_1 = 10.2 M^{-1} sec^{-1} for epinephrine cation and 6.08 × 10^3 M^{-1} sec^{-1} for 1,2,4-benzenetriol), those reductants which do not possess hydroxy substituents adjacent to the *o*-hydroxy binding site (*i.e.*, epinephrine cation, L-dopa cation, neutral catechol, and neutral 1,2,4-trihydroxybenzene) reveal Q_0 values which lie within the fairly narrow limits of 0.45–1.0. For the 1,2,3-trihydroxy series (pyrogallol and gallic acid), however, Q_0 values are 8.0 and 6.9, respectively. The values of Q_h (k_2 path) exhibit a similar, albeit less distinct, trend. For epinephrine cation, L-dopa cation, and catechol respective values of Q_h of 0.54, 0.41, and 1.0 are found,[22] whereas gallic acid and pyrogallol give values of 2.1 and 2.5, respectively. Despite the occurrence of dissimilar groupings, correlations among the redox rate constants through the application of the Marcus theory suggest that an outer-sphere mechanism is followed in these electron transfer reactions.

Whether these trends reflect distinct differences in the mechanisms of V(V) oxidation of the two types of reductants or if the ratio differences result from differences in the properties of the reductants themselves (*e.g.*, self-exchange rates) is not yet obvious. Determinations of the kinetics parameters for oxidation of catechol and derivatives by other oxidants will allow comparisons between the rate constants for a common reductant with a series of oxidants and are expected to shed light on this question. Such studies are being conducted in these laboratories.

References and Notes

(1) The authors gratefully acknowledge support from the National Science Foundation (Grant GB-33617 and Science Development Grant GU-3852) and the Institute of General Medical Sciences, Public Health Service (Grant GM-08893-11). This work is taken, in part, from the Ph.D. dissertation of C. Nicolini-Barison, Brandeis University, 1973.
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