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Kinetics and Complex Formation of Tungstate with Catechol and Catechol Derivatives

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Stopped-flow has been used to determine rate and stability constants for complex formation of tungstate with catechol and catechol derivatives. Pseudo-first-order and close-to-equilibrium kinetics were applied at 25°, $\mu = 0.1\ M$ (KNO_3), and $7.3 < pH < 9.0$. The overall formation (k_{1f}, $M^{-1}\ sec^{-1}$) and dissociation (k_{-1r}, sec^{-1}) rate constants, respectively for the 1:1 complexes are as follows: catechol, $(1.10 \pm 0.10) \times 10^2$, $(3.8 \pm 0.5) \times 10^{-1}$; 3,4-dihydroxybenzoic acid, $(2.40 \pm 0.09) \times 10^2$, $(2.9 \pm 1.0) \times 10^{-1}$; L-dopa, $(2.41 \pm 0.08) \times 10^2$, $(3.0 \pm 1.0) \times 10^{-1}$; gallic acid, $(6.05 \pm 0.32) \times 10^2$, $(7.3 \pm 2.0) \times 10^{-1}$; pyrogallol, $(6.92 \pm 0.39) \times 10^2$, $(6.2 \pm 2.0) \times 10^{-1}$. For catechol the apparent rate constants for formation of the bis complex are $k_{2f} = 4.0 \pm 0.1\ M^{-1}\ sec^{-1}$ and $k_{-2r} \cong 4 \times 10^{-4}\ sec^{-1}$. The apparent overall stability constants may be calculated from the relation $K_n^{app} = k_{nf}/k_{-nr}$, where $n = 1, 2$. Only one species of complex is formed; only the fully or partially protonated phenolic moieties correspond to reactive forms of the ligand. Comparison with other systems shows an approximately 100-fold variation in formation rate constant with different ligands. For catechol and its derivatives benzene ring substitution affects the formation rate constant. Pyrogallol and gallic acid, both of which have three hydroxy groups on the benzene ring, are approximately 6 times more reactive than catechol. Statistically, adding one hydroxy group at a nieghboring position to the two hydroxy groups of catechol cannot account for an enhancement factor greater than 2, indicating that the nature of the substituent plays a role in the complexation mechanism. The fact that $K_{2f} \gg K_{1f}$ for tungstocatechol complexes is due primarily to the fact that $k_{-1f} \gg k_{-2f}$. This difference in dissociation rate constant may be due to differences in the inner coordination shell, for in the mono complex hydroxo groups may be present, whereas they are almost certainly absent from the bis complex.

Although the oxy anions of V(V), Mo(VI), and W(VI) readily form complexes as do di- and trivalent cations, the mechanism of complex formation appears to be considerably different. The few studies thus far reported—for example, molybdate and tungstate with 8-hydroxyquinoline[1] or vanadate with EDTA and alizarin[2]—do not provide enough information to allow a classification of these reactions. The selection of ligands which coordinate oxy anions and ligands for whose complexes the equilibrium constants have been evaluated is presently taken from a more restricted list than those of, say, divalent metal cations. For the relatively small number of systems studied, however, a specific geometry and protonated binding sites appear to be desirable ligand properties.

Catechol and its derivatives seem to fulfill these requirements quite well, and the colored complexes formed in aqueous solution with tungstate have been used in quantitative analysis.[3-5] As in the case of molybdocatechol complex formation, spectrophotometric measurements usually yield only stability constants for formation of the 1:2 tungstate–ligand complex.[6-8] This situation is a result, mainly, of the weakness of the 1:1 relative to the 1:2 complex, a phenomenon which is widespread for oxy anions, also being observed for vanadate and stannate.[9] In a previous kinetics study on complex formation between molybdate and catechol,[10] the unusual order in the step stability constants K_1 and K_2, namely, $K_1 < K_2$, was explained in terms of large differences in the complex dissociation rate constants k_{-1} for the mono and k_{-2} for the bis complex, with $k_{-1} > k_{-2}$. The present study on complex formation of tungstate with catechol and some of its derivatives (3,4-dihydroxybenzoic acid, L-dopa (=3,4-dihydroxyphenylalanine), pyrogallol, and gallic acid) was undertaken to investigate further the mechanism of oxy anion complexation.

Experimental Section

Reagent grade catechol (Fisher), L-dopa (Nutritional Biochemicals Corp.), sodium tungstate (Baker), 3,4-dihydroxybenzoic acid (Baker), pyrogallol (Baker), and gallic acid (Baker) as well as other chemicals were used without further purification. Solutions of sodium tungstate were prepared by weight. To prevent oxidation by air, fresh solutions of catechol or catechol derivatives were prepared for each day's experiments by dissolving the necessary amounts of ligand in 0.01 M sodium bisulfite solution.

In kinetics studies under pseudo-first-order conditions, the concentration of total ligand was $1.00 \times 10^{-4}\ M$ and the metal concentrations were in at least 30-fold excess. To prevent polymerization of tungstate, all experiments were done at pH's above 7.3. The hydrogen ion concentration was kept constant by adding ammonia buffer solutions; pH values were measured to ±0.01 pH unit with a Radiometer pH meter. All solutions were thermostated at 25 ± 1° before mixing. Ionic strength, μ, was adjusted to 0.1 M with KNO_3. The details of the stopped-flow equipment are described elsewhere.[10]

The experimental method is essentially the same as before.[10] Relaxation times are obtained by least-squares analysis of the primary data on a DEC PDP-10 computer and represent averages of at least four experiments; relative error is within ±10%.

Due to the relative insolubility of the catechol derivatives, only catechol was used in excess to study higher order complex formation. In this case, where coupling of both reaction steps occurs, the approach-to-equilibrium relaxation theory was applied in evaluating the rate data.[11] The coupled reaction had a very long relaxation time, which was determined through a photographic method by graphing the last portion of the oscilloscopic trace. Relative error in these relaxation times is about ±15%.

Results and Treatment of Data

No attempt has been made to obtain the stepwise stability constants of tungstate-catechol (or catechol derivatives) com-

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[1] H. Diebler and R. E. Timms, *J. Chem. Soc. A*, 273 (1971).

[2] K. Kustin and D. Toppen, *J. Amer. Chem. Soc.*, 95, 3564 (1973).

[3] A. K. Madjumdar and C. P. Savariar, *Naturwissenschaften*, 45, 84 (1958).

[4] J. Horak and A. Okac, *Collect. Czech. Chem. Commun.*, 29, 188 (1964).

[5] S. Tsueno, K. Kimiko, O. Sakuko, and H. Kyoichi, *Bunseki Kagaku*, 15, 120 (1966).

[6] J. Halmekoski, *Ann. Acad. Sci. Fenn., Ser. A2*, 96 (1959).

[7] J. Halmekoski, *Suom. Kemistilehti B*, 36, 46 (1963).

[8] E. Pisko, *Chem. Zvesti*, 12, 95 (1958).

[9] L. G. Sillen and A. E. Martell, *Chem. Soc., Spec. Publ.*, No. 25 (1971); No. 17 (1964).

[10] K. Kustin and S.-T. Liu, *J. Amer. Chem. Soc.*, 95, 2487 (1973).

[11] G. G. Hammes and J. I. Steinfeld, *J. Amer. Chem. Soc.*, 84, 4639 (1962).

plexes by spectrophotometric methods. However, qualitatively, the uv-visible spectra of tungstate-catechol solutions indicate that both 1:1 and 1:2 oxy anion to ligand complexes exist. That is, at wavelengths higher than 400 nm, the solutions containing 1×10^{-1} *M* tungstate and 1×10^{-4} *M* catechol show only a negligible absorbance. In contrast, a solution containing 1×10^{-4} *M* tungstate with 1×10^{-1} *M* catechol has a significant absorbance in this region of the spectrum. Furthermore, at the wavelengths where neither oxy anion nor ligand absorbs, the ratios of the absorbancies of two different solutions are not constant at a variety of wavelengths. These facts show that more than one species of complex is present in solution. Equilibrium quotients for complex formation can be obtained from the kinetics data, as will be shown below.

Under pseudo-first-order conditions, with tungstate in excess and at constant pH, the reciprocal of the relaxation time, τ, or the apparent pseudo-first-order rate constant, k_{app}, can be expressed as

$$k_{\text{app}} = \tau^{-1} = \overrightarrow{k}[\text{WO}_4{}^{2-}]_0 + \overleftarrow{k} \tag{1}$$

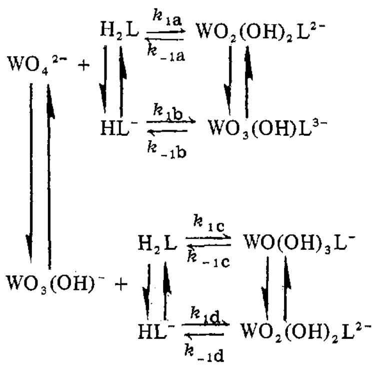
where $\overrightarrow{k}$ and $\overleftarrow{k}$ are the apparent overall association and dissociation rate constants, and $[\text{WO}_4{}^{2-}]_0$ is the total concentration of tungstate added. Linear plots of τ^{-1} *vs.* $[\text{WO}_4{}^{2-}]_0$ are given in Figure 1. A linear least-squares analysis of these data has been carried out on a PDP-10 computer to determine the best values of the rate parameters in eq 1. The values thus obtained and the observed relaxation times are summarized in Tables I and II.

Close-to-equilibrium relaxation theory was used for the reactions with catechol in excess, since coupled reactions occur. The close-to-equilibrium relaxation times for this system involve two sets of apparent overall rate constants: $k_{1\text{f}}$ and $k_{-1\text{r}}$ for the 1:1 and $k_{2\text{f}}$ and $k_{-2\text{r}}$ for the 1:2 complex. The rate constants giving the best agreement between observed and calculated reciprocal relaxation times are reported in Table III. As in the molybdate-catechol system,[10] all the observed relaxation spectra for the tungstate-catechol reactions correspond to the "negative" root of the secular determinant. Differences between τ_{obsd} and τ_- are within ±15%.

Reaction Mechanism

The complete reaction scheme (Scheme I) for the pH range of this study contains many pathways due to the various protonated forms of the reactants and products. Protolytic reactions of catechol, its derivatives, and tungstate are very rapid; all vertical steps in Scheme I are therefore assumed to be equilibrated at all times during the complexation reactions. The pertinent ligand species and relevant equilibrium data are shown in Table III. For tungstate, $K_{\text{M}} = [\text{H}^+][\text{WO}_4{}^{2-}]/[\text{WO}_3(\text{OH})^-] = 3 \times 10^{-4}$ *M*,[12] whereas the protolytic constants for the complexes

Scheme I



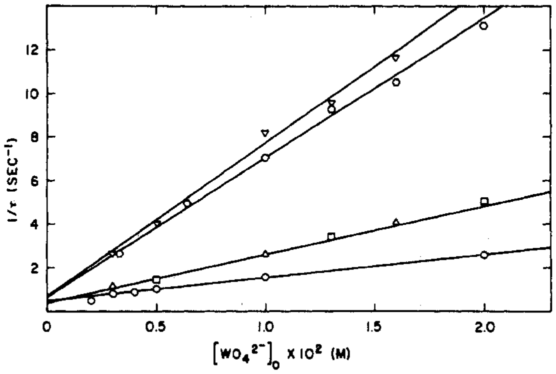


Figure 1. Plot of $1/\tau$ against $[\text{WO}_4{}^{2-}]_0$ at pH 7.90, $\mu = 0.1$ *M*, and $[\text{ligand}]_0 = 1.00 \times 10^{-4}$ *M*: ○, catechol; □, 3,4-dihydroxybenzoic acid; △, L-dopa; ⬡, gallic acid; ▽, pyrogallol. At some tungstate concentrations, both 3,4-dihydroxybenzoic acid and L-dopa have almost the same $1/\tau$ value. In these cases, only one of the two data points is shown; *cf.* Table II.

Table I. Formation of the 1:1 Tungstate-Catechol Complex[a]

$10^2[\text{WO}_4{}^{2-}]_0$, *M*	pH	$1/\tau$, sec^{-1}	$10^2[\text{WO}_4{}^{2-}]_0$, *M*	pH	$1/\tau$, sec^{-1}
0.200	7.90	0.473	1.31	8.30	1.89
0.296	7.90	0.741	1.61	8.30	2.16
0.399	7.90	0.826	2.00	8.30	3.07
0.495	7.90	0.991	0.304	8.90	0.746
0.997	7.90	1.51	0.510	8.90	0.884
2.01	7.90	2.53	0.994	8.90	1.30
0.307	8.30	0.741	1.31	8.90	1.75
0.507	8.30	0.917	1.59	8.90	2.03
1.00	8.30	1.68			

$\overrightarrow{k} = k_{1\text{f}}$, M^{-1} sec^{-1}	$\overleftarrow{k} = k_{-1\text{r}}$, sec^{-1}	pH
109 (±5)	0.38 (±0.05)	7.9
120 (±11)	0.37 (±0.05)	8.3
102 (±6)	0.38 (±0.07)	8.9
Av (1.10 ± 0.10) × 10^2	Av (3.8 ± 0.5) × 10^{-1}	

[a] At 25 ± 1°, $[\text{catechol}]_0 = 1.00 \times 10^{-4}$ *M*, and $\mu = 0.1$ *M*.

$$K^{\text{C}}_{\text{ab}} = [\text{H}^+][\text{WO}_3(\text{OH})\text{L}^{3-}]/[\text{WO}_2(\text{OH})_2\text{L}^{2-}]$$

and

$$K^{\text{C}}_{\text{cd}} = [\text{H}^+][\text{WO}_2(\text{OH})_2\text{L}^{2-}]/[\text{WO}(\text{OH})_3\text{L}^-]$$

are not known.

The experimentally observed rate equation for the formation of the 1:1 complex is

$$\text{d}[\text{C}]/\text{d}t = k_{1\text{f}}[\text{M}][\text{L}] - k_{-1\text{r}}[\text{C}] \tag{2}$$

where $[\text{M}] = [\text{WO}_4{}^{2-}] + [\text{WO}_3(\text{OH})^-]$, $[\text{L}] = [\text{H}_2\text{L}] + [\text{HL}]$, and $[\text{C}] = [\text{WO}_3(\text{OH})\text{L}] + [\text{WO}(\text{OH})_3\text{L}] + [\text{WO}_2(\text{OH})_2\text{L}]$ (charges have been neglected). With $[\text{M}] \gg [\text{L}]$, the reciprocal relaxation time for (2) is

$$\tau^{-1} = k_{1\text{f}}[\text{M}]_0 + k_{-1\text{r}} \tag{3}$$

which is identical with that for (1) with $k_{1\text{f}} = \overrightarrow{k}$ and $k_{-1\text{r}} = \overleftarrow{k}$. Under these conditions the following relationships hold between the overall rate constants and the individual reaction rate constants of Scheme I.

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[12] G. Schwarzenbach, G. Geier, and J. Littler, *Helv. Chim. Acta*, 45, 2601 (1962).

$$k_{1f}\left(1+\frac{[H^+]}{K_M}\right)\left(1+\frac{K_H}{[H^+]}\right)=k_{1a}+k_{1d}\frac{K_H}{K_M}+k_{1b}\frac{K_H}{[H^+]}+k_{1c}\frac{[H^+]}{K_M} \quad (4)$$

$$k_{-1r}\left(1+\frac{[H^+]}{K^C{}_{cd}}+\frac{K^C{}_{ab}}{[H^+]}\right)=k_{-1a}+k_{-1d}+\frac{k_{-1b}K^C{}_{ab}}{[H^+]}+\frac{k_{-1c}[H^+]}{K^C{}_{cd}} \quad (5)$$

For the tungstate-catechol complex, studies have been made at pH 7.9, 8.3, and 8.9. At these pH's the left-hand side of (4) can be simplified to $k_{1f}(1 + K_H/[H^+])$. Inspection of Table I shows that this term is constant, within experimental error. Therefore

$$k_{1f}(1 + K_H/[H^+]) \cong 120\ (M^{-1}\ \text{sec}^{-1}) \cong k_{1a} + k_{1d}K_H/K_M$$

and the pathways corresponding to k_{1b} and k_{1c} can be neglected under the conditions of this study. Consequently, $WO_2(OH)_2L^{2-}$ is the only significant 1:1 complex formed. Likewise, if we consider pH 7.9 for the catechol derivatives, $K_H/[H^+]$, $[H^+]/K_M \ll 1$ and we are left with pathways a and d.

Table II. Formation of the 1:1 Complexes of Tungstate with Catechol Derivatives[a]

Ligand	$10^2 \times [WO_4{}^{2-}]_0$, M	$1/\tau$, sec^{-1}
3,4-Dihydroxybenzoic acid	0.303	1.02
	0.501	1.32
	1.00	2.89
	1.30	3.45
	1.60	4.15
	2.01	5.00
L-Dopa	0.305	1.11
	0.498	1.38
	1.00	2.57
	1.30	3.57
	1.59	4.08
	2.01	5.10
Pyrogallol	0.300	2.57
	0.505	3.95
	1.00	8.20
	1.31	9.52
	1.60	11.5
Gallic acid	0.316	2.71
	0.628	5.25
	0.996	7.04
	1.30	9.26
	1.60	10.4

$\overrightarrow{k} = k_{1f}$, $M^{-1}\ \text{sec}^{-1}$	$\overleftarrow{k} = k_{-1r}$, sec^{-1}	Ligand
$(2.40 \pm 0.09) \times 10^2$	0.29 ± 0.10	3,4-Dihydroxybenzoic acid
$(2.41 \pm 0.08) \times 10^2$	0.30 ± 0.10	L-Dopa
$(6.92 \pm 0.39) \times 10^2$	0.62 ± 0.20	Pyrogallol
$(6.05 \pm 0.32) \times 10^2$	0.73 ± 0.20	Gallic acid

[a] At 25 ± 1°, [ligand] = 1.00×10^{-4} M, $\mu = 0.1$ M, and pH 7.90.

Table III. Consecutive Complex Formation between Tungstate and Catechol[a]

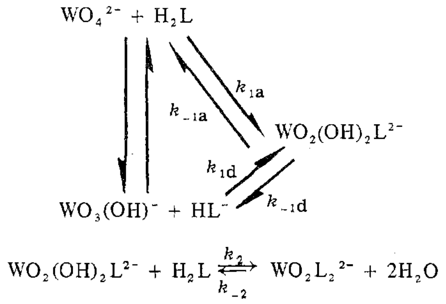
pH	$10^2[\text{catechol}]_0$, M	τ_{obsd}, sec	τ_-, sec
7.30	5.00	5.40	5.65
7.30	2.82	9.50	10.5
7.30	2.06	13.5	14.9
7.35	4.50	5.40	6.32
7.30	3.50	7.00	8.29
7.50	3.50	8.45	8.33
7.60	6.01	5.32	4.68

[a] At $[WO_4{}^{2-}]_0 = 3.00 \times 10^{-5}$ M, 25 ± 1°, and $\mu = 0.1$ M. $k_{1f} = (1.20 \pm 0.10) \times 10^2\ M^{-1}\ \text{sec}^{-1}$, $k_{2f} = 4.0 \pm 0.1\ M^{-1}\ \text{sec}^{-1}$, $k_{-1r} \cong 0.4\ \text{sec}^{-1}$, and $k_{-2r} \cong 4 \times 10^{-4}\ \text{sec}^{-1}$

Two limiting cases can now be distinguished: either $k_{1a} \gg k_{1d}K_H/K_M$ and $k_{1f} \cong k_{1a}$ or $k_{1d}K_H/K_M \gg k_{1a}$ and $k_{1f}K_M/K_H \cong k_{1d}$. The same arguments apply to the reverse steps where $k_{-1r} \cong k_{-1a} + k_{-1d}$. Regardless of which pathways predominate, the apparent stability constants can be found from the rate data; *e.g.*, $K_1{}^{app} = [C]/[M][L] = k_{1f}/k_{-1r}$. A summary of the limiting rate constants and apparent stability constants is given in Table V.

As in the molybdate-catechol system,[10] the agreement between τ_{obsd} and τ_- in solutions with catechol in excess (pH changed from 7.3 to 7.6) suggests that Scheme II is most probable for the consecutive complexation reactions. In this scheme, $k_{2f} \cong k_2$ and $k_{-2r} \cong k_{-2}$, within experimental error; these rate constants appear in Table III.

Scheme II



$$WO_2(OH)_2L^{2-} + H_2L \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} WO_2L_2{}^{2-} + 2H_2O$$

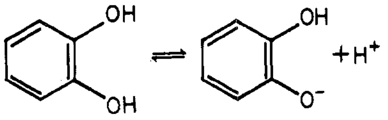
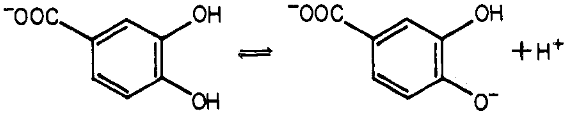
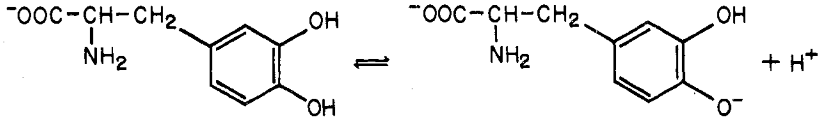
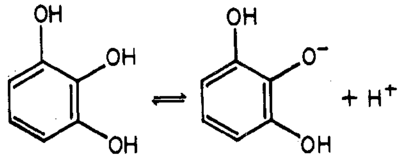
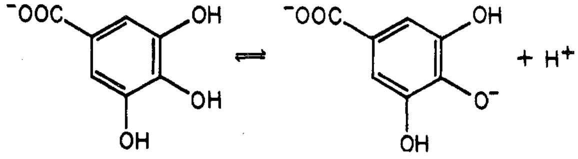
Discussion

With the exception of the tungstate-gallic acid complex, the stability constant determinations already cited show quantitative evidence for 1:2 complexes only. This result is due to the relatively higher stability constant of the 1:2 complex, resulting in proportionately larger concentrations of this species in solution, which can easily mask the presence of a 1:1 complex. However, the optical spectra and kinetics clearly indicate that both mono and bis complexes of tungstate are formed in solution. For gallic acid, kinetics measurements yield a value of $8.3 \times 10^2\ M^{-1}$ for the first stepwise stability constant; the spectrophotometrically determined value is $2.3 \times 10^3\ M^{-1}$.[6] In view of the experimental difficulties, this type of agreement suggests that the kinetics method is reliable and is the method of choice where application of other techniques is more tenuous.

In discussing the tungstate rate constants, the results previously obtained with 8-hydroxyquinoline (oxine) and its derivatives[1] will be combined with the catechol results. Tungstate, like molybdate, forms two types of mono complex with oxine (HOx), namely, $WO_3(OH)Ox^{2-}$ and $WO_2(OH)_2Ox^-$. Neutral and anionic oxine are the reactive species. Again, as with molybdate, catechol and its derivatives form only one type of mono complex with tungstate. For catechol, the formula of this complex would be $WO_2(OH)_2L^{2-}$. Only the partially and fully protonated ligand species are reactive. Specific differences between tungstate and molybdate appear when the rate data for the various ligands are compared *inter alia*.

The rate constants for the first step in the formation of the molybdate-catechol complex are quite close to those of the molybdate-oxine complex, *e.g.*, $2.9 \times 10^2\ M^{-1}\ \text{sec}^{-1}$ for H_2L compared with $4.1 \times 10^2\ M^{-1}\ \text{sec}^{-1}$ for HOx; however, larger differences are observed for the tungstate complexes.

Table IV. Protolytic Ligand Equilibria

Ligand	$K_H = [H][HL]/[H_2L]$	Reaction: $H_2L \rightleftarrows HL + H$
Catechol	4.27×10^{-10} [a]	
3,4-Dihydroxybenzoic acid	1.45×10^{-9} [b]	
L-Dopa	1.29×10^{-10} [c]	
Pyrogallol	8.91×10^{-10} [d]	
Gallic acid	3×10^{-9} [e]	

[a] R. F. Jameson and W. F. S. Neillie, *J. Inorg. Nucl. Chem.*, **27**, 2623 (1965). [b] P. J. Antikainen and M. Viro, *Suom. Kemistilehti B*, 41, 206 (1968). [c] M. L. Barr, K. Kustin, and S.-T. Liu, *Inorg. Chem.*, **12**, 1486 (1973). The equilibrium constant for deprotonation of the L-dopa amine group, $K(-NH_3^+)$, is 1.74×10^{-9}; hence, for this ligand H_2L represents a sum of neutral and anionic species, both of which should be reactive. [d] M. Bartusek and J. Zelinku, *Collect. Czech. Chem. Commun.*, 32, 992 (1967). [e] The literature values are not in agreement; this value of K_H is an average: P. J. Antikainen, M. Viro, and L. R. Sahlstrom, *Suom. Kemistilehti B*, **42**, 178 (1969); G. Ackermann, D. Hesse, and P. Vollard, *Z. Anorg. Allg. Chem.*, **377**, 92 (1970).

Table V. Stability and Rate Constants of Tungstate–Catechol and –Catechol Derivative Complexes

Ligand	$10^{-2} \times K_1^{app}$, M^{-1}	$10^{-3} \times K_2^{app}$, M^{-1}	$10^{-6} \times \beta_2$,[a] M^{-2}	$10^{-2} \times k_{1a}$, M^{-1} sec^{-1}	$10^{-8} \times k_{1d}$, M^{-1} sec^{-1}	$k_{-1r} = k_{-1a} + k_{-1d}$, sec^{-1}
Catechol	3.2	10.6	3.4	1.20	0.84	0.38
3,4-Dihydroxybenzoic acid	8.3	6.0	5.0	2.40	0.50	0.29
L-Dopa	8.0			2.41	5.60	0.30
Pyrogallol	11.2	8.6	9.6	6.92	2.0	0.62
Gallic acid	8.3			6.05	0.7	0.73

[a] Values of β_2 are from ref 6; K_2 was calculated from $K_2 = \beta_2/K_1$.

The k_{1f} of HOx ($2.4 \times 10^3\ M^{-1}$ sec^{-1}) is about 20 times higher than k_{1f} of catechol; k_{1f} of oxinesulfonate ($1.3 \times 10^4\ M^{-1}$ sec^{-1}) is about 100 times that of catechol. Differences between the two oxy anions shall again be considered when the formation of bis complexes is considered. Let us first consider the results with the catechols and tungstate.

From Figure 1 and Tables I, II, or V, it is clear that the forward rate constants of the first step of complexation are changed by substitution on the benzene ring of catechol. The order is pyrogallol > gallic acid > L-dopa, 3,4-dihydroxybenzoic acid > catechol. By substituting an acid or amino acid group on the ring, k_{1f} is increased from 120 to 240 M^{-1} sec^{-1}. Interestingly, both pyrogallol and gallic acid, which have three hydroxy groups instead of two at neighboring positions on the benzene ring, have almost the same forward rate constants, and these are about 6 times larger than that of catechol. From a statistical viewpoint addition of one hydroxy group at a neighboring position to either of the two hydroxy groups of catechol should only increase the rate constants by a factor of 2. Thus, the nature of the substituted group plays an important role in the mechanism of the reaction. This observation suggests that attachment of the ligand to the central metal ion is rate determining, making and breaking of H bonds being relatively rapid here. However, even though the forward rate constant is different from ligand to ligand, the dissociation rate constants, k_{-1r}, show a more modest variation and may, in fact, be almost the same, within experimental error. The differences among the values of the first stepwise stability constants, K_1^{app}, are then chiefly due to differences in forward rate constants.

As in the molybdate-catechol system,[10] the second stepwise stability constant, K_2^{app}, for tungstate and catechol is greater than K_1^{app} (Table V). This anomalous behavior cannot be explained in terms of differences in forward rate constants; in fact, for tungstate the opposite trend prevails:

$k_{1f} = 120\,M^{-1}$ sec^{-1} and $k_2 = 4.0\,M^{-1}$ sec^{-1}. Therefore, for both oxy anions, $K_2^{\mathrm{app}} > K_1^{\mathrm{app}}$ because of differences in the dissociation rate constants; specifically, $k_{-1r} = 0.38$ sec^{-1} *vs.* $k_{-2} = 4 \times 10^{-4}$ sec^{-1} for tungstate. This effect is even larger than that observed for molybdate, where $k_2 \cong 1.8k_{1f}$ and $k_{-1r} \cong 22k_{-2r}$. In both cases, however, the larger dissociation rate constant of the mono relative to the bis complex is due to the presence of the two hydroxo groups in the former and not in the latter compound. The almost certainly present hydroxo groups in the inner coordination shell of the mono complex may donate electrons to the orbitals of the central tungsten(VI) ion by pπ-dπ bonding from ligand donor to metal acceptor.[13] Catechol would not be expected to form π bonds to the metal ion as well as the OH$^-$ group. Therefore, the single catechol molecule in the mono complex is more effectively labilized by the two hydroxyl ions than are either of the bound catechols in the bis complex by one another.

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Registry No. WO_4^{2-}, 14311-52-5; catechol, 321-01-7; 3,4-dihydroxybenzoic acid, 27138-57-4; L-dopa, 59-92-7; pyrogallol, 87-66-1; gallic acid, 149-91-7.

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An Electron Spin Resonance Study of Hexakis(pyridine *N*-oxide)manganese(II) Perchlorate Complexes

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The esr spectra of powdered samples of hexakis(pyridine *N*-oxide)manganese(II) perchlorate complexes doped into the corresponding zinc and cadmium compounds are reported. The pyridine *N*-oxides employed were pyridine, 3-methylpyridine, 4-methylpyridine, 4-nitropyridine, and 4-cyanopyridine *N*-oxides. The analysis of the esr spectra of polycrystalline manganese(II) complexes is discussed. Most of the cadmium complexes exhibit axial symmetry while the ring-substituted zinc complexes generally show rhombic symmetry. The hyperfine coupling constants indicate manganese(II)-pyridine *N*-oxide bonding to be more covalent than manganese(II)-water bonding.

Introduction

Complexes of pyridine *N*-oxide and its derivatives with various metals have been subject of numerous investigations.[1-8] The electronic spectra of cobalt(II) and nickel(II) complexes with 4-substituted pyridine *N*-oxides have been examined both in the solid state and in solution. Values of *Dq* and β, the nephelauxetic parameter, vary from paper to paper since these ligands are labile even in such poor donor solvents as acetonitrile and partial substitution for the pyridine *N*-oxide ligands occurs. Solid-state reflectance and mull (transmission) spectra, however, indicate that pyridine *N*-oxides lie below water in the spectrochemical series for nickel(II) complexes[1] but higher in the series for cobalt(II).[2] Nephelauxetic parameters[1-3] indicate that the metal-ligand covalency in these complexes is dependent on the nature of the substituent group. Generally, the complexes are less covalent than the corresponding aquo compounds. Infrared studies[2,4,5] show substantial reduction of the N-O stretching frequency of the ligand upon complexation. The amount of reduction in the N-O stretch exhibits a marked dependence on both the metal atom and the substituent group on the *N*-oxide ligand. Nmr contact shift work[6] on the Co(II) and Ni(II) complexes of 4-methylpyridine *N*-oxide showed the observed proton shifts to be dominated by a π delocalization mechanism but the importance of the σ delocalization could not be determined due to its slight effect on the proton shift. Appreciable unpaired spin density was observed to exist even on the methyl protons. No crystal structure data are available for the hexakis complexes of pyridine *N*-oxide although the crystal structure of tetrakis(pyridine *N*-oxide)copper(II) perchlorate has been reported.[9] The ligand was shown to be coordinated to the metal *via* the oxygen atom with the pyridine ring bent out of the plane formed by the copper and oxygen atoms. Byers, *et al.*,[4] have noted in the case of the hexakis(pyridine *N*-oxide) complexes that, although the electronic spectra are often interpreted in terms of O_h symmetry, their spectra are among those of few six-coordinate complexes with monodentate ligands which show marked deviation from octahedral symmetry. They[4] pointed out that even the most symmetrical orientations of the ligands will give rise to D_{3d} symmetry while the actual symmetry is probably closer to S_6.

Since very little electron spin resonance (esr) work has been done on complexes of this type and since the magnitude of the zero-field splitting of hexakis complexes of substituted

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