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Determination of the Overall Dissociation Constants of the Group 1A Acetates and Perchlorates in Glacial Acetic Acid^{1,2}

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The overall dissociation constants of LiOAc, NaOAc, KOAc, RbOAc, and CsOAc have been determined in glacial acetic acid at 25.0 ± 0.1 °C and give pK_b values of 6.87 ± 0.09 , 6.58 ± 0.03 , 6.18 ± 0.19 , 6.14 ± 0.19 , and 6.04 ± 0.08 , respectively. The corresponding perchlorate salts at 25.0 ± 0.1 °C have pK_b values of 5.11 ± 0.18 , 5.37 ± 0.08 , 5.69 ± 0.10 , 6.17 ± 0.08 , and 5.83 ± 0.21 , respectively. The pK_b values for both series of salts have been determined at 25.0, 35.0, 45.0, 55.0, and 68.8 ± 0.1 °C, and the standard enthalpies and entropies of each system have been calculated.

Introduction

Three of the more general methods which have been utilized in the study of dissociation equilibria of alkali metal salts in nonaqueous media are potentiometry,^{3,4} conductance,⁵ and spectrophotometry.⁶ Bruckenstein and Kolthoff³ determined the dissociation constants of lithium, sodium, and potassium acetates and sodium perchlorate potentiometrically in glacial acetic acid at 25.0 ± 0.1 °C. Kolling and co-workers^{4,7,8} extended this study at 25 °C to include the remaining group 1A acetates and lithium perchlorate. These authors used a glass-calomel electrode pair in a concentration cell to measure emf values and calculate pK values by comparison with Kolthoff's value of NaOAc as a reference base. In the present study, the potentiometric method was used to determine the overall dissociation constants of the alkali metal acetates and perchlorates in glacial acetic acid at 25.0, 35.0, 45.0, 55.0, and 68.8 ± 0.1 °C. The observed trends in dissociation constants for each series are examined in terms of more recent theory. The treatment of potentiometric data also required the spectrophotometric determination of the overall dissociation constants of hydrochloric acid and pyridine in glacial acetic acid over this same temperature range. Standard enthalpies and entropies are reported for each of the above equilibria. These additional thermodynamic data have not been previously reported and will be useful in the treatment of kinetic and equilibrium studies employing these salts in glacial acetic acid.

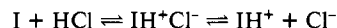
Experimental Section

Temperature. The temperature was maintained within ± 0.1 °C of the desired temperature with a thermostatically controlled bath. In potentiometric measurements the half-cells were placed directly in the bath. In spectrophotometric measurements the bath liquid was circulated through an aluminum block in the cell holder which was fabricated to snugly fit the absorption cells.

Materials. Glacial acetic acid (Mallinckrodt reagent grade) was purified and dried by the chromium(VI) oxide-boron triacetate method.⁹ Perchloric acid (Baker Analyzed, 60-62%) and *p,p'*-bis(dimethylamino)azobenzene (Merck reagent) were prepared and/or purified in the same manner as reported by Kolthoff and Bruckenstein.^{3,9} Lithium acetate dihydrate was prepared, by the usual method, from the reaction of lithium carbonate and glacial acetic acid. Lithium

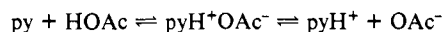
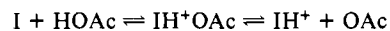
acetate, sodium acetate (Baker Analyzed reagent), potassium acetate (Matheson reagent), and sodium perchlorate (G. Frederick Smith reagent) were prepared and/or purified by conventional methods.³ The following chemicals were used without further purification: hydrogen chloride gas (Matheson Anhydrous), *p*-naphtholbenzein (Merck reagent), pyridine (Baker Analyzed reagent), chloranil and tetrachloroquinone (Eastman Kodak Practical), lithium perchlorate (G. Frederick Smith reagent), potassium perchlorate (Merck reagent), and rubidium acetate, rubidium perchlorate, cesium acetate, and cesium perchlorate (Alfa reagent grades). Rubidium acetate and cesium acetate were oven-dried at 160 °C to constant weight prior to use. Materials were protected from atmospheric moisture by preparing solutions in a dry glovebag containing dried reagents and glassware stored in desiccators.

Spectrophotometric Determination of Equilibrium Constants. The overall dissociation constant of HCl in glacial acetic acid was determined by adding a given amount of *p*-naphtholbenzein indicator, I, to a solution of hydrogen chloride gas in glacial acetic acid of known concentration to establish the equilibrium



The concentration of the IH^+ species was determined from spectra. Plots of the indicator, I, concentration vs. the IH^+ concentration for a series of experiments in which the [HCl] was constant and [I] was varied gave intermediate values of the IH^+ species for a given [HCl]. This procedure was repeated for four different HCl concentrations. These data were treated according to the Kolthoff and Bruckenstein⁹ equations to calculate equilibrium constants for the two above equilibria and the overall dissociation constant of HCl at each temperature.

The overall dissociation constant for pyridine in glacial acetic acid was determined by holding the *p,p'*-bis(dimethylamino)azobenzene indicator concentration constant and varying the pyridine concentration over a 32-fold range. The following equilibria occur:



The concentration of the IH^+ species was determined spectrophotometrically. The two equilibrium constants in the first expression were related to the equilibrium constant of the second expression by the equations of Bruckenstein and Kolthoff¹⁰ and evaluated by their method.

All absorbancies were measured with a Cary Model 14 recording spectrophotometer using matched 5-cm quartz cells.

Potentiometric Determination of Equilibrium Constants. Emf measurements were made with use of a Leeds and Northrup Model No. 7552 potentiometer in conjunction with a Minneapolis-Honeywell Model 104W1G galvanometer whose sensitivity was $0.001 \mu A/mm$. The platinum chloranil-tetrahydroquinone indicator half-cell and the modified calomel reference electrode half-cell used here were identical with those used by Bruckenstein and Kolthoff.³ The standard electromotive force of the cell, E°_{HCl} , the autoprotolysis constant of acetic acid, pK_s , and the pK values of the alkali metal acetate and perchlorate salts were measured and calculated according to the cells and equations used by Bruckenstein and Kolthoff.³

(1) When the term "glacial acetic acid" is used in this paper it refers to the commercial product that has been subjected to rigorous drying procedure in ref 9.

(2) OAc = acetate.

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Table I. Autoprotolysis Constants of Glacial Acid (pK_s)

temp, °C	10 ² C _{py} , M	E _{py} , V	pK _s
25.0 ± 0.1	2.444	0.2820	14.69 ± 0.16
35.0 ± 0.1	2.417	0.2695	14.82 ± 0.13
45.0 ± 0.1	2.391	0.2610	14.88 ± 0.12
55.0 ± 0.1	2.365	0.2505	14.99 ± 0.10
68.8 ± 0.1	2.328	0.2370	15.12 ± 0.16

Table II. Overall Dissociation Constants of Hydrochloric Acid and Pyridine

temp, °C	pK _{HCl}	pK _{py}
25.0 ± 0.1	8.34 ± 0.16	6.11 ± 0.08
35.0 ± 0.1	8.78 ± 0.12	6.20 ± 0.08
45.0 ± 0.1	9.21 ± 0.14	6.34 ± 0.05
55.0 ± 0.1	9.66 ± 0.13	6.43 ± 0.06
68.8 ± 0.1	10.20 ± 0.13	6.55 ± 0.08

Results and Discussion

Bruckenstein and Kolthoff³ studied dissociation equilibria in glacial acetic acid at 25 °C at ionic strengths of less than 10⁻⁵. They observed that at this temperature the dielectric constant of acetic acid is 6.13 and the strongest electrolytes have overall dissociation constants of ca. 10⁻⁵. These facts permitted the use of concentrations rather than activities in the treatment of their data. The ionic strength of the electrolytes in the present study are of the order of 10⁻⁶. The activity coefficients calculated from the Debye-Hückel limiting law are 0.95 and 0.96 at 20 and 70 °C, respectively. Therefore, the use of concentrations in all calculations seems justified over the temperature range reported here. The concentrations of all solutions were corrected for the thermal expansion of acetic acid according to data from ref 11.

Bruckenstein and Kolthoff³ derived three equations for calculating overall equilibrium constants in glacial acetic acid from electromotive force (*E*) data. *E*^o_{HCl} can be calculated with use of eq 1 for a given HCl concentration (C_{HCl}) from

$$E_{\text{HCl}} = E^{\circ}_{\text{HCl}} + \frac{RT}{2F} \ln K_{\text{HCl}} + \frac{RT}{2F} \ln C_{\text{HCl}} \quad (1)$$

the experimental value of *E*^o_{HCl} and the spectrophotometric value of *K*_{HCl}. Equation 2 was used to calculate the auto-

$$E_{\text{B}} = E^{\circ}_{\text{HCl}} + \frac{RT}{F} \ln K_{\text{s}} - \frac{RT}{2F} \ln K_{\text{B}} - \frac{RT}{2F} \ln C_{\text{B}} \quad (2)$$

protolysis of acetic acid, *K*_s, over the temperature range when pyridine was employed as the base with using *E*^o_{HCl} from eq 1, the spectrophotometrically determined value of p*K*_{py}, and the measured *E*_{py} for a given pyridine concentration.¹² These data are given in Tables I and II. The overall dissociation constants, *K*_B, (where B is a group 1A acetate) were also calculated from eq 2 by substituting the autoprotolysis constants, *E*^o_{HCl} from eq 1, and the potentiometrically determined *E*_B for a known concentration of acetate salt (C_B).

Equation 3 was used to calculate the overall dissociation

$$E_{\text{B,BHClO}_4} = E^{\circ}_{\text{HCl}} + \frac{RT}{F} \ln K_{\text{s}} - \frac{RT}{F} \ln K_{\text{B}} C_{\text{B}} + \frac{RT}{2F} \ln (K_{\text{B}} C_{\text{B}} + K_{\text{BHClO}_4} C_{\text{BHClO}_4}) \quad (3)$$

constants, *K*_{BHClO₄}, for the group 1A perchlorates. These

Table III. Comparison of Overall Dissociation Constants at 25.0 °C and Other Thermodynamic Data in Glacial Acetic Acid

compd	pK		10 ⁻¹ Δ <i>H</i> ^o , kJ mol ⁻¹	10 ⁻² Δ <i>S</i> ^o , J mol ⁻¹ K ⁻¹
	present study	lit.		
HCl	8.34 ± 0.16	8.55 ^a	-8.4 ± 2.2	-4.4 ± 0.8
py	6.11 ± 0.08	6.10 ^b	-2.0 ± 0.8	-1.8 ± 0.3
LiOAc	6.87 ± 0.06	0.79 ^c	-2.9 ± 0.4	-2.3 ± 0.1
		6.78 ± 0.03 ^d		
		6.80 ^e		
NaOAc	6.58 ± 0.04	6.58 ± 0.03 ^c	-2.6 ± 0.8	-2.2 ± 0.3
KOAc	6.18 ± 0.06	6.15 ± 0.7 ^c	-1.9 ± 0.5	-1.8 ± 0.2
		6.11 ± 0.02 ^d		
		6.13 ± 0.04 ^e		
RbOAc	6.14 ± 0.13	6.04 ± 0.02 ^d	-1.8 ± 0.6	-1.8 ± 0.2
		5.93 ± 0.10 ^e		
CsOAc	6.04 ± 0.06	5.84 ± 0.10 ^e	-1.8 ± 0.4	-1.8 ± 0.1
LiClO ₄	5.11 ± 0.12	5.31 ^f	-5.2 ± 0.9	-2.7 ± 0.3
NaClO ₄	5.37 ± 0.05	5.48 ± 0.07 ^c	-4.1 ± 0.6	-2.4 ± 0.2
KClO ₄	5.69 ± 0.07		-2.7 ± 0.9	-2.0 ± 0.3
RbClO ₄	6.17 ± 0.14		-2.4 ± 1.3	-2.0 ± 0.5
CsClO ₄	5.78 ± 0.13		-1.3 ± 0.8	-1.4 ± 0.4

^a Reference 9. ^b Reference 10. ^c Reference 3. ^d Reference 7. ^e Reference 4. ^f Reference 8.

calculations involved using the measured electromotive force, *E*_{B,BHClO₄}, of glacial acetic acid solutions containing known concentrations of a given alkali metal acetate, C_B, and the corresponding perchlorate salt, C_{BHClO₄}, along with *E*^o_{HCl} from eq 1 and *K*_B from eq 2.

It has been pointed out that the dissociation of an acid or base in glacial acetic acid occurs in a two-step process. The first equilibrium produces an ion pair which then dissociates in a second equilibrium step to produce separate ions.³ Potentiometric methods yield "overall dissociation constants" which are a function of both steps. Table III shows that the overall p*K* values in the present study are in good agreement with those which have been previously determined potentiometrically at 25 °C.

In reading and interpreting the p*K* data in Tables III and IV, it is useful to remember that the dissociation constant, *K*_b, is inversely proportional to the association constant, *K*_a, as well as p*K*_b. Therefore, p*K*_b and *K*_a will show the same trends. All the dissociation constants in Tables III and IV decrease (*K*_a increases) as the temperature rises. Nancollas¹³ has pointed out that *K*_a will rise over a temperature range if the temperature at which the association passes through a minimum lies above the freezing point of the solvent.

The standard enthalpies, Δ*H*^o, and standard entropies, Δ*S*^o, were obtained from plots of the p*K* in Tables III and IV vs. 1/*T*. The least-squares line through the data points gives a slope of -Δ*H*^o/*R* and an intercept of Δ*S*^o/*R*. The enthalpy change is the property most directly related to the changes in the numbers and strengths of bonds as the system passes from reactants to products. Table III shows that the change in enthalpy is fairly constant for the acetates but increases toward more positive values for the perchlorates.

When an ion pair dissociates the stoichiometric effect predicts an increase in entropy because an additional solute species appears. If the dissociation of ion pairs causes the loss of freedom of solvent molecules which become oriented around the separate ions then solvation effects lead to an entropy decrease.¹⁴ The negative values of Δ*S* obtained in the present study imply that solvation effects outweigh stoichiometric effects. Table III also shows that there is a decrease in the

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burn, E. W., Ed.; McGraw-Hill: New York, 1928; Vol. III, p 27.
(12) A mathematical error was discovered in ref 3 in the calculation of *E*_{HCl}. When the reported emf value is substituted into eq 1, a value of 0.9380 is obtained rather than the reported value of 0.9095. This correction increases the p*K*_s values in Table I of this reference by about one p*K* unit but is insignificant in the subsequent calculations of p*K*_s and p*K*_s values from eq 2.

(13) Nancollas, G. H. "Interactions in Electrolyte Solutions"; Elsevier: New York, 1966; Chapter 5, p 131.

(14) Davis, C. W. "Ion Association"; Butterworths: Washington, D.C., 1962; Chapter 12, p 132.

Table IV. Overall Dissociation Constants of Group 1A Acetates and Perchlorates at 35.0, 45.0, 55.0, and 68.8 °C

temp, °C	compd	concn, M	E, V	pK _b
35.0 ± 0.1	LiOAc	0.109 60	0.2750	7.03 ± 0.04
	NaOAc	0.096 35	0.2685	6.76 ± 0.02
	KOAc	0.146 60	0.2495	6.29 ± 0.06
	RbOAc	0.048 04	0.2610	6.26 ± 0.11
	CsOAc	0.092 96	0.2500	6.17 ± 0.14
45.0 ± 0.0	LiOAc	0.108 40	0.2675	7.26 ± 0.04
	NaOAc	0.095 31	0.2580	6.89 ± 0.08
	KOAc	0.145 00	0.2395	6.41 ± 0.06
	RbOAc	0.047 52	0.2510	6.39 ± 0.03
	CsOAc	0.091 96	0.2405	6.28 ± 0.04
55.0 ± 0.1	LiOAc	0.107 20	0.2595	7.37 ± 0.04
	NaOAc	0.094 25	0.2505	7.04 ± 0.02
	KOAc	0.143 40	0.2280	6.49 ± 0.05
	RbOAc	0.047 00	0.2410	6.44 ± 0.04
	CsOAc	0.090 93	0.2280	6.34 ± 0.08
68.8 ± 0.1	LiOAc	0.105 50	0.2460	7.49 ± 0.02
	NaOAc	0.092 77	0.2370	7.17 ± 0.06
	KOAc	0.141 10	0.2130	6.60 ± 0.03
	RbOAc	0.046 26	0.2260	6.55 ± 0.04
	CsOAc	0.089 50	0.2125	6.44 ± 0.07
35.0 ± 0.1	LiOAc/LiClO ₄	0.097 42/0.053 400	0.3195	5.32 ± 0.11
	NaOAc/NaClO ₄	0.147 90/0.243 300	0.3055	5.60 ± 0.04
	KOAc/KClO ₄	0.140 10/0.013 540	0.2530	5.81 ± 0.12
	RbOAc/RbClO ₄	0.046 17/0.004 342	0.2635	6.28 ± 0.08
	CsOAc/CsClO ₄	0.092 76/0.002 963	0.2515	5.87 ± 0.13
45.0 ± 0.1	LiOAc/LiClO ₄	0.096 37/0.052 830	0.3095	5.76 ± 0.12
	NaOAc/NaClO ₄	0.146 30/0.240 700	0.2965	5.80 ± 0.04
	KOAc/KClO ₄	0.138 60/0.013 400	0.2430	5.95 ± 0.08
	RbOAc/RbClO ₄	0.045 68/0.004 295	0.2545	6.43 ± 0.06
	CsOAc/CsClO ₄	0.091 76/0.002 932	0.2415	5.94 ± 0.17
55.0 ± 0.1	LiOAc/LiClO ₄	0.095 30/0.052 240	0.2975	6.00 ± 0.12
	NaOAc/NaClO ₄	0.144 60/0.238 000	0.2860	6.06 ± 0.05
	KOAc/KClO ₄	0.137 10/0.013 250	0.2320	6.11 ± 0.10
	RbOAc/RbClO ₄	0.045 17/0.004 248	0.2430	6.57 ± 0.04
	CsOAc/CsClO ₄	0.090 74/0.002 899	0.2300	5.95 ± 0.18
68.8 ± 0.1	LiOAc/LiClO ₄	0.093 80/0.051 420	0.2830	6.20 ± 0.07
	NaOAc/NaClO ₄	0.142 40/0.234 300	0.2710	6.26 ± 0.05
	KOAc/NaClO ₄	0.134 90/0.013 040	0.2150	6.29 ± 0.08
	RbOAc/RbClO ₄	0.044 46/0.004 181	0.2285	6.68 ± 0.10
	CsOAc/CsClO ₄	0.089 31/0.002 853	0.2145	6.11 ± 0.14

entropy change as the size of the alkali metal ion increases for both acetates and perchlorates. This trend would be expected because the magnitude of the change depends on the extent to which the separate ions are solvated.¹⁴ The experimental error of these measurements does not permit further comparison between entropy changes for the two systems.

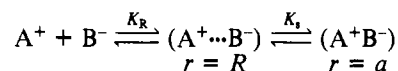
For many years investigators attempted to rationalize ion pair association constants, K_A , in terms of the following equation, which is based on the solvent continuum model:¹⁵

$$K_A = 4\pi Na^3 e^b / 3000$$

where a = the center to center ion distance and $b = e^2 / aDkT$. The exponential part of this equation predicts decreasing association with increasing ion size and dielectric constant, D . When the equation is applied to a broad spectrum of electrolytes in a variety of solvents, it is found that K_A does not always vary in a predictable manner with (1) changing ion size in the same solvent or (2) the same electrolyte in iso-dielectric solvents or solvents with different dielectric constants.

Fuoss¹⁶ has noted that the continuum model gives a good account of long-range ionic interactions, but it excludes short-range interactions arising from solvent-solute interactions. This suggested that ion pairs should be divided into two categories.¹⁷ Ions become paired by diffusing (decreasing their separation distance, r) until their cospheres overlap, i.e., $r \leq R$, where R is the diameter of the cosphere. The result is a

solvent separated ion pair. The anion in the solvent separated ion pair will diffuse back to the exterior solution or diffuse by ion solvent interchanges to contact with the cation, i.e., $r = a$, resulting in a contact ion pair. These phenomena can be illustrated by



Fuoss¹⁶ then represents the experimental K_A as the product of two terms

$$K_A = K_R(1 + K_s)$$

K_R measures the range of ion solvent interactions, and its magnitude can be described by the equation for K_A in the continuum model if " a " is replaced by " R ". $K_s = \exp(-E_s/kT)$ (where E_s is the difference in energy between the two states defined by $r = a$ and $r = R$) and depends on short-range anion-cation interaction. While the potentiometric data obtained in the present study do not permit a quantitative analysis of K_A in terms of its component constants, the above equilibria can be used to qualitatively account for the observed trends in pK data or K_A .

Tables III and IV show that pK_s for the alkali metal acetates decrease smoothly at all temperatures as the crystallographic radius of the metal ion increases. Kolling and Gracey⁴ have attributed this trend to a decrease in the Coulombic interaction with the ion pair as the cation radius increases. The new Fuoss model suggests that the observed order is consistent with contact ion pairs being the predominant ionic species in the glacial acetic acid solutions of alkali metal acetates.

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Association for the alkali metal perchlorates has been studied previously in water,¹⁸ anhydrous methanol, acetonitrile, and sulfolane,¹⁹ and in all cases K_A increases as the radius of the cation increases. Tables III and IV show that this order is generally preserved for the alkali metal perchlorates in acetic acid at all temperatures studied. The order suggests that solvent separated ion pairs are the predominant species in solution. The reverse order for CsClO_4 and RbClO_4 has been previously observed by Evans and Matesich²⁰ for the association constants of alkali metal and tetraalkylammonium chlorides in ethanol. These authors suggested that, by the time the radius reaches Cs^+ , solvation is no longer important and K_A decreases with further increase in size. A similar situation may be operative in the present study. The decrease in solvation as the size of the group 1A cations increase has been discussed quantitatively by Abraham and Liszi.²¹ These authors used a one-layer continuum model to calculate the free energies of solvation for a number of univalent cations in a variety of nonaqueous solvents over the dielectric constant range of 30-7. The calculated values were in agreement with

present experimental accuracy and showed that the ionic solvation free energy of Rb^+ is ~ 10 -12% greater than that of Cs^+ in these solvents.

Although the dissociation data reported here can be rationalized by the new model derived by Fuoss,¹⁷ it should be pointed out that it is necessary to make an important assumption. Fuoss¹⁶ cautions that his model neglects the effects of higher association and should be applied to solvents of dielectric constant > 10 . Bruckenstein and Kolthoff¹⁰ observed small spectral shifts when small amounts of water were added to acetic acid solutions of indicator bases or colorless bases such as pyridine or diethylaniline. These shifts were found to be due to the presence of hydronium acetate which had a tendency to form ion quadruplets and triplets with these bases. The potentiometric measurements in the present study did not exhibit this sensitivity to moisture when water content of the indicator electrode was deliberately increased in two trial runs to 0.25% and 0.50%, respectively. Nevertheless, all measurements reported here were made in rigorously dried glacial acetic acid.

Registry No. LiOAc, 546-89-4; NaOAc, 127-09-3; KOAc, 127-08-2; RbOAc, 563-67-7; CsOAc, 3396-11-0; LiClO_4 , 7791-03-9; NaClO_4 , 7601-89-0; KClO_4 , 7778-74-7; RbClO_4 , 13510-42-4; CsClO_4 , 13454-84-7; HOAc, 64-19-7; HCl, 7647-01-0; py, 110-86-1.

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Redox Chemistry of Metal-Catechol Complexes in Aprotic Media. 1. Electrochemistry of Substituted Catechols and Their Oxidation Products

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Cyclic voltammetric measurements of 3,5-di-*tert*-butylcatechol, catechol, hydroquinone, tetrachlorocatechol, and tetrafluorocatechol have been utilized to determine their redox chemistry and thermodynamics in acetonitrile, dimethylformamide, dimethylacetamide, and dimethyl sulfoxide. The effects of solution acidity upon the electrochemistry of these catechols, their corresponding quinones, and their redox products have been determined. On the basis of these results, electron-transfer mechanisms are proposed. The degree of interaction between a series of metal cations and the 3,5-di-*tert*-butyl-*o*-semiquinone anion has been determined.

During the past decade the importance of catechol complexes in biology has become evident. Enterobactin, the powerful sequestering agent for iron transport in *Salmonella typhimurium* and *Escherichia coli*,¹ is a tricatechol siderophore which binds iron(III) through the oxygens of the catechol moiety.² The importance of catecholato complexes to iron transport has been discussed in detail.¹⁻⁸ Likewise, the effectiveness of catechol as a "hard base" ligand for manganese,⁹⁻¹³ molybdenum,¹⁴⁻²⁰ and vanadium²¹⁻²³ ions has been

demonstrated for both aqueous and aprotic media. In addition, there have been numerous reports of *o*-semiquinone complexes of transition-metal ions in aprotic solvents.²⁴⁻²⁹

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