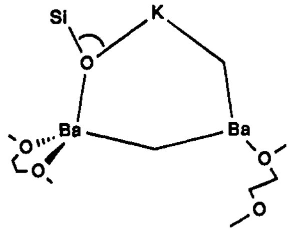
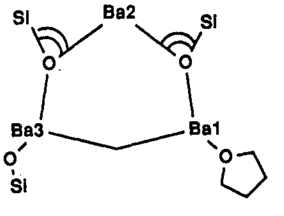
equivalent.[12] Since all of these dynamic processes occur in hydrocarbon solvent, we prefer an intramolecular $OSiPh_3$ migration mechanism to any dissociation of Ph_3SiO^-. These spectra also establish that the solid-state structure is maintained in benzene or CH_2Cl_2 solution.

Discussion

The structure reported here for $KBa_2(OSiPh_3)_5(DME)_2$ shares some features with that of $Ba_3(OSiPh_3)_6(THF)$ (see B and C).



B



C

Both have the $M_3(\mu_3\text{-}X)_2(\mu_2\text{-}X)_3$ core. Ba(2) in C plays the role of K in B in being only four-coordinate. Since C contains one more $OSiPh_3$ ligand than does B, this ligand occupies one terminal position (at Ba(3)). The corresponding metal in B is coordinated by η^2-DME. The remaining barium in each molecule coordinates only one ether oxygen. The only difference between B and C is that two μ_2-$OSiPh_3$ groups bend toward the four-coordinate metal in C, while only one of them does in B.

The observed reaction of $KOSiPh_3$ with $Ba_3(OSiPh_3)_6(THF)$ is surprising (or at least unpredictable), since it would seem destined to *add* the siloxide nucleophile to the intact Ba_3 triangle. Products such as the potassium salt of $Ba_3(OSiPh_3)_7(THF)_n^-$ might have been anticipated. Instead, there is a major reorganization of the Ba_3 triangle, one barium and two siloxides are lost, and the resulting siloxide-rich $Ba_2(OSiPh_3)_5^-$ species sequesters K^+. The apparent guiding theme is that the chemistry is dominated by the formation of (uncharged) *molecular* species, to the exclusion of (charge-separated) salts.

Acknowledgment. This work was supported by the Department of Energy. We thank Scott Horn for skilled technical assistance.

Registry No. $KBa_2(OSiPh_3)_3(DME)_2$·hexane (coordination compound entry), 137540-23-9; $KOSiPh_3$, 25221-22-1; Ph_3SiOH, 791-31-1; $KBa_2(OSiPh_3)_5(DME)_2$·hexane (salt entry), 137540-25-1.

Supplementary Material Available: Tables giving full crystallographic details and anisotropic thermal parameters (4 pages); a listing of calculated and observed structure factors (25 pages). Ordering information is given on any current masthead page.

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[12] At −80 °C, the ^{29}Si NMR spectrum further resolves into a total of seven lines. This we assign to freezing out of two conformers, as a result of the crowded nature of the molecule.

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Oxidation of Dihydroxy Aromatic Substrates by Hexachloroiridate(IV). Mechanistic Information from Volumes of Activation

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The reaction between the hexachloroiridate(IV) ion and several benzenediols has been studied kinetically in aqueous perchloric acid solution at pressures up to 100 MPa. The volumes of activation are almost independent of the aromatic substituent at a given temperature and acidity and are all within the range −20 to −30 $cm^3 mol^{-1}$. Encounter complex (ion–molecule) formation is followed by rate-determining electron transfer according to an outer-sphere electron-transfer mechanism. The latter step involves significant charge creation with consequent increasing solvent electrostriction and accounts principally for the significantly negative ΔV^* data. The results are compared with those for related systems recently reported in the literature.

Introduction

The subject of oxidation of dihydroxy aromatic compounds by metal complexes during which a quinone is produced has received considerable attention in recent years.[2-5] The redox chemistry of diol–quinone systems has its own intrinsic interest, but the identification of ubiquinone (a 1,4-quinone with a lengthy hydrocarbon chain in the 3-position), in conjunction with a metal center, as an electron acceptor in photosynthetic bacterial action has led to widespread additional interest[6] in these types of reactions. We are generally interested in the detailed redox mechanism for the oxidation of a benzenediol to a quinone by simple metal ions or complexes as oxidants. We have recently studied the oxidation of catechol, the 4-*tert*-butyl derivative of catechol, and methyl-1,4-hydroquinone by $Fe(CN)_4(bpy)^-$ in more detail.[7] The reactions were all characterized by strongly negative volumes of activation, a finding which was ascribed to the dominance of electrostriction of the solvent due to increasing charge development in forming the transition state for the overall redox reaction in (I). Another interesting aspect of these systems is the fact that

$$2Fe(CN)_4(bpy)^- + QH_2 \rightarrow 2Fe(CN)_4(bpy)^{2-} + 2H^+ + Q \quad (I)$$

the rate-determining electron-transfer step is a nonsymmetrical outer-sphere reaction in which one of the reaction partners is a neutral species. The pressure dependence of the kinetics of several other comparable redox reactions has been studied in detail recently.[8-12] We have therefore extended our earlier work[7] to a series of dihydroxy aromatic substrates and investigated the pressure dependence of their oxidation by hexachloroiridate(IV), $IrCl_6^{2-}$. The ambient-pressure kinetics of the oxidation of benzenediols and other substrates by the $IrCl_6^{2-}$ ion have been investigated in some detail both in water[4] and in mixed aqueous solvents.[12] By application of Marcus' theory the kinetics in aqueous

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Table I. Kinetic Data for Oxidation of Benzenediols at Various Pressures by $IrCl_6^{2-}$ [a,b]

benzenediol	temp, °C	pH	k_{obs},[c] s^{-1} (at various pressures) 5 MPa	25 MPa	50 MPa	75 MPa	100 MPa
catechol	25.0	0	19.7 ± 0.6	25.9 ± 0.8	36.6 ± 1.2	47.4 ± 1.5	
4-*tert*-butylcatechol	25.0	0	29.9 ± 1.7	43.1 ± 0.6	53.2 ± 1.8	66.1 ± 3.2[d]	
3,4-dihydroxybenzoic acid[e]	24.8	0	0.440 ± 0.010	0.513 ± 0.010	0.712 ± 0.012	1.01 ± 0.01	1.34 ± 0.01
2,3-dihydroxybenzoic acid	23.2	0	0.849 ± 0.009	1.04 ± 0.02	1.35 ± 0.01	1.76 ± 0.02	2.31 ± 0.03
adrenaline	24.8	0	11.6 ± 0.4	17.0 ± 0.2	24.9 ± 0.1	29.6 ± 1.5	36.3 ± 0.9
catechol	25.0	2	17.1 ± 0.2	22.2 ± 0.2	28.0 ± 0.6	35.2 ± 0.7	44.5 ± 1.8
4-tert-butylcatechol	10.3	0	16.6 ± 0.3	22.1 ± 0.8	28.4 ± 0.5	36.5 ± 1.6	46.1 ± 1.2
4-*tert*-butylcatechol	10.2	0	26.2 ± 0.9	33.8 ± 1.4	44.5 ± 2.0	53.3 ± 3.0	69.4 ± 4.1
4-*tert*-butylcatechol	10.3	2	23.4 ± 0.8	29.1 ± 0.9	36.7 ± 1.5	44.1 ± 2.3	56.2 ± 3.7
4-*tert*-butylcatechol[f]	10.0	2	14.6 ± 0.1	18.2 ± 0.3	23.9 ± 0.2	30.2 ± 0.4	37.9 ± 0.7
adrenaline	10.0	0	6.17 ± 0.08	8.16 ± 0.06	10.9 ± 0.3	14.2 ± 0.2	17.6 ± 0.1
L-dopa	9.9	0	9.04 ± 0.15	10.7 ± 0.3	15.5 ± 0.6	19.6 ± 0.7	24.1 ± 1.3
4-*tert*-butylcatechol	2.0	2	25.7 ± 0.5	31.4 ± 0.4	39.5 ± 0.5	48.9 ± 1.0	58.9 ± 1.7

[a] Ionic strength: 1.0 M ($HClO_4$ at pH 0, $HClO_4 + NaClO_4$ at pH 2). [b] Concentrations: $[K_2IrCl_6] = 8.0 \times 10^{-5}$ to 2.0×10^{-4} M; [benzenediol] $= 8.0 \times 10^{-4}$ to 4.0×10^{-3} M. [c] Reported values of k_{obs} are average values, and the error is the average deviation of individual values of k_{obs} from average k_{obs}. [d] $P = 72.5$ MPa. [e] P values of 5.9, 25.7, 50.5, 75.5, and 100 MPa. [f] Ionic strength: 0.10 M.

medium were shown[4,5] to be consistent with a rate-determining step in which a radical-cation catechol species is produced, i.e. in which proton dissociation has not yet occurred, as shown in (II).

$$QH_2 + IrCl_6^{2-} \xrightarrow{k} QH_2^{\bullet+} + IrCl_6^{3-} \qquad (II)$$

A systematic study of the pressure dependence of such reactions will not only provide further insight into the detailed electron-transfer mechanism[13] but also contribute to our understanding of the pressure dependence of electron-transfer reactions in general.[14]

Experimental Section

Materials. K_2IrCl_6 was purchased from Johnson Matthey GmbH and exhibits the characteristic absorbance maximum at 487 nm. All benzenediols employed were high-grade commercial products obtained from Aldrich, Sigma, or Merck; they were catechol (1,2-dihydroxybenzene), 4-*tert*-butylcatechol (1,2-dihydroxy-4-*tert*-butylbenzene), 3,4-dihydroxybenzoic acid, 2,3-dihydroxybenzoic acid, adrenaline (1-(3,4-dihydroxyphenyl)-2-(methylamino)ethanol), L-dopa (β-(3,4-dihydroxyphenyl)-L-alanine), and methylhydroquinone (2-methyl-1,4-dihydroxybenzene). The 4-*tert*-butylcatechol was recrystallized from benzene as described in the literature,[15] whereas the other diols were used without further purification. Reagent grade $HClO_4$ (70%) was used to adjust the acidity of the medium, and reagent grade $NaClO_4$ to adjust the ionic strength. All solutions were made up using Milli-Q water.

Methods. $HClO_4$ was standardized with NaOH. All benzenediol solutions were made up immediately prior to use. Solutions of K_2IrCl_6 were made up daily or twice daily as needed. All solutions were stored in the dark at 4 °C when not in use. pH values were measured with a Radiometer PHM 64 instrument. UV–vis spectra were recorded on a Shimadzu UV250 spectrophotometer of which the sample compartment was thermostated at 25.0 °C. Some ambient-pressure kinetic measurements were checked on a modified Aminco stopped-flow instrument, since for most systems such measurements had already been conducted.[3] Kinetic measurements at elevated pressure (up to 100 MPa) were performed on a homemade, high-pressure stopped-flow instrument[16] thermostated to within ±0.1 °C. Data acquisition and processing were performed on an online computer system.[17] The oxidation reactions were studied using a large excess of the benzenediol to ensure pseudo-first-order conditions and were followed at 487 nm as a decrease in absorbance with time due to the reduction of $IrCl_6^{2-}$ to $IrCl_6^{3-}$. The corresponding first-order plots were linear for at least 3 half-lives of the reactions. The reported rate constants are the average values of at least five kinetic experiments and showed an increase in standard deviation when small absorbance changes had to be used and especially when the reaction half-life approached the dead time (ca. 15 ms) of the high-pressure stopped-flow unit.[16] In fact, the oxidation of methylhydroquinone occurred so rapidly that no kinetic data can be reported. Activation volumes were calculated using standard least-squares programs.

Results and Discussion

Kinetics. In our earlier study of the oxidation of benzenediols by $Fe(CN)_4(bpy)^-$,[7] it was confirmed that the reactions exhibit a steep pH-dependent rate at pH > 3 as reported before.[18] All pressure dependence studies were therefore performed in the pH-independent region. In this respect the $IrCl_6^{2-}$ species is a more convenient oxidant for use with a wider range of dihydroxy compounds, as it yields a much less sensitive pH dependence than the $Fe(CN)_4(bpy)^-$ species. However, the focus is on measurements in the pH-independent region at present, since more meaningful kinetic parameters can be obtained. The kinetics of reaction II have been shown to be first order in both benzenediol and $IrCl_6^{2-}$ concentrations. The observed pseudo-first-order rate constant, k_{obs}, for the oxidation of catechol by $IrCl_6^{2-}$ at ambient pressure was measured in 1.0 M $HClO_4$ (pH 0) over a catechol concentration range from 6.0×10^{-4} to 2.0×10^{-3} M for a 5.0×10^{-5} M $IrCl_6^{2-}$ solution. k_{obs} ranged from 3.07 to 9.10 s^{-1} at 25.0 °C, yielding a second-order rate constant of 4.9×10^2 M^{-1} s^{-1}, which is close to that reported in the literature,[4] viz. 5.3×10^2 M^{-1} s^{-1}. The kinetics of oxidation of the 4-*t*-Bu-substituted catechol by $IrCl_6^{2-}$ have been studied previously[12] but not at pH 0 and 25.0 °C. Under these conditions, k_{obs} increased from 33 s^{-1} at 9.0×10^{-4} M to 113 s^{-1} at 3.0×10^{-3} M 4-*tert*-butylcatechol, which yields a second-order rate constant of 3.7×10^4 M^{-1} s^{-1}. In earlier work[12] a value for the second-order rate constant of 2.6×10^4 M^{-1} s^{-1} was reported at pH 2 and 25.0 °C. The rate-determining step has been identified[3] as that which produces the semiquinone, reaction II, followed by a rapid further reaction to produce the quinone. It follows that $k_{obs} = 2k$[benzenediol], where k is the second-order rate constant for reaction II. Although the temperature dependence of the kinetics of most of the reactions described here had been studied before,[4] that of the oxidation of 4-*tert*-butylcatechol had not. It was found that k_{obs} increased from 23.3 to 53.1 s^{-1} over the temperature range 9.3–35.5 °C for a 1.0×10^{-3} M catechol solution, which corresponds to $\Delta H^{\ddagger} = 19.6 \pm 1.2$ kJ mol^{-1} and $\Delta S^{\ddagger} = -149 \pm 4$ J K^{-1} mol^{-1}. These values are in good agreement with the available literature information[4] and demonstrate that the low activation enthalpy and very negative activation entropy are in line with an outer-sphere electron-transfer mechanism.

Values of k_{obs} as a function of pressure for the series of investigated benzenediols are summarized in Table I. In some cases the pressure range was limited by the substantial increase in k_{obs} with increasing pressure and the dead time of the stopped-flow instrument. In other cases temperatures as low as 2 °C were required in order to be able to measure the pressure dependence

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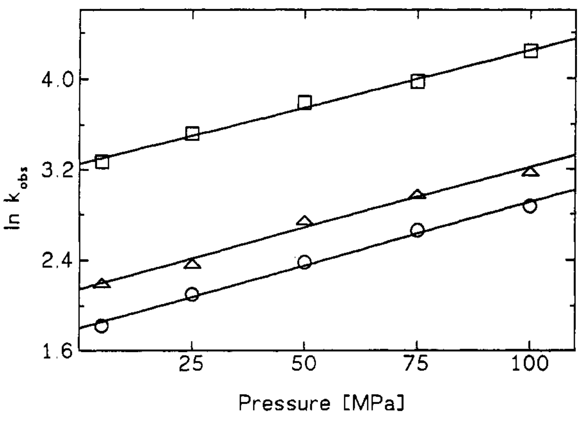

Figure 1. Dependence of rate constant upon pressure shown by a plot of ln k_{obs} versus P (in MPa): (○) $IrCl_6^{2-}$ + L-dopa, pH 0, T = 9.9 °C; (△) $IrCl_6^{2-}$ + adrenaline, pH 0, T = 10.0 °C; □ $IrCl_6^{2-}$ + 4-*tert*-butylcatechol, pH 0, T = 10.2 °C.

Table II. Volumes of Activation for Oxidation of Benzenediols by $IrCl_6^{2-}$[a]

benzenediol	temp, °C	$\Delta V^{\ddagger}$, $cm^3\ mol^{-1}$		$\Delta S^{\ddagger}$, $J\ mol^{-1}\ K^{-1}$[b]
		pH 0	pH 2	
catechol	25.0	−30.9 ± 1.3	−24.5 ± 0.9	−109
4-*tert*-butylcatechol	25.0	−28.0 ± 3.6		−149[c]
3,4-dihydroxybenzoic acid	24.8	−30.3 ± 1.3		−134
2,3-dihydroxybenzoic acid	23.2	−26.0 ± 0.2		−109
adrenaline	24.8	−29.2 ± 3.6		−138
4-*tert*-butylcatechol	10.3	−24.9 ± 1.1	−21.2 ± 0.7	
4-*tert*-butylcatechol	10.2	−23.5 ± 1.2		
4-*tert*-butylcatechol	10.0		−23.6 ± 0.7[d]	
adrenaline	10.0	−25.9 ± 1.3		
L-dopa	9.9	−25.1 ± 1.6		
4-*tert*-butylcatechol	2.0		−20.0 ± 0.6	

[a] Ionic strength: 1.0 M ($HClO_4$ at pH 0, $HClO_4$ + $NaClO_4$ at pH 2). [b] Reference 3. [c] This work. [d] Ionic strength: 0.10 M.

of k_{obs}. A few sample plots of ln k_{obs} versus pressure are given in Figure 1, from which it can be seen that the plots are linear (slope = $-\Delta V^{\ddagger}/RT$) over the investigated pressure range. The $\Delta V^{\ddagger}$ values thus obtained are listed in Table II; they vary with pH and ionic strength in the range −20 to −30 $cm^3\ mol^{-1}$. All investigated reactions exhibited a substantial acceleration with increasing pressure, and the observed effect is more significant (i.e., $\Delta V^{\ddagger}$ is more negative) than reported before[7] for the oxidation with $Fe(CN)_4(bpy)^-$. The markedly negative $\Delta V^{\ddagger}$ values are in agreement with the strongly negative $\Delta S^{\ddagger}$ values (included where available in Table II) and indicate a highly structured transition state for the electron-transfer process.

In terms of an outer-sphere electron-transfer mechanism, the observed second-order rate constant k is the product of the precursor formation constant K_{OS} and the electron-transfer rate constant k_{ET}; i.e., $k = K_{OS}k_{ET}$.[14] It is reasonable to assume that K_{OS} will be relatively small, since one redox partner is neutral and a high ionic strength was selected for the experimental measurements.[10] In addition, these factors will also cause the associated pressure dependence of K_{OS} to be negligible, such that the observed $\Delta V^{\ddagger}$ values will mainly represent the activation volume for the electron-transfer step itself.

The results in Table I and those reported before[4,7] show that the oxidation rate constants are very sensitive to the aromatic substituents. For instance, the 4-*tert*-butyl- and 4-methyl-1,2-catechols are oxidized by the $IrCl_6^{2-}$ ion 6 and 15 times faster than the unsubstituted diol, respectively. By contrast, the rate is increased 3-fold by the 4-methyl substituent when the oxidizing agent is a cobalt(III) aquo ion, and the 4-*tert*-butyl substituent exerts about a 50% rate increase, over the unsubstituted diol when $Fe(CN)_4(bpy)^-$ causes oxidation. As the activation barrier for the redox process in a given diol → quinone reaction becomes smaller, the destabilizing effect of the hydrocarbon substituents increases. Since the encounter complex formation is an ion–dipole interaction, it is more likely that the bulk of the substituent effect resides in the electron-transfer step itself, although the relative contribution from the two steps may vary depending upon the nature of the oxidant.

The $\Delta V^{\ddagger}$ data presented in Table II demonstrate that there is a consistent trend to lower absolute values of $\Delta V^{\ddagger}$ with decreasing acidity (i.e. increasing pH) and decreasing temperature. The average value of −29 ± 2 $cm^3\ mol^{-1}$ for the reactions at ca. 25 °C and pH 0 is slightly more negative than the average value of −25 ± 1 $cm^3\ mol^{-1}$ for these reactions at ca. 10 °C. Similarly, $\Delta V^{\ddagger}$ decreases a few $cm^3\ mol^{-1}$ in absolute magnitude upon increasing the pH. These trends are ascribed to secondary medium effects on the encounter complex formation equilibrium and/or the electron-transfer step within the concept of an outer-sphere electron-transfer reaction.[8] It is highly unlikely that a protonated $IrCl_6^{2-}$ species will participate in the redox process in acidic medium,[4] since an opposite trend in the $\Delta V^{\ddagger}$ data would be expected. The confluence of effects of different temperature dependences of the composite parameters of k, i.e. K_{OS} and k_{ET}, could explain the increase of ca. 4 $cm^3\ mol^{-1}$ in $\Delta V^{\ddagger}$ between the higher and lower temperatures.

Interpretation of Activation Volumes. It is difficult to judge the degree of intimacy of a benzenediol with the octahedral $IrCl_6^{2-}$ species and the extent to which such an interaction could account for the strongly negative $\Delta V^{\ddagger}$ values. A model for the latter indicates that penetration by the hydroxy groups of the diol into the spaces between the chloro ligands may occur, which would result in a volume decrease. A consequence of the contact of ion and neutral molecule (in the precursor species) or the interpenetration of reactants after encounter is that the solvent adhering to the charged iridium species and to the hydroxy groups of the diol will be displaced; in the former case this will result in an increase in volume. Therefore, the two effects are somewhat compensatory, but to what degree is not possible to estimate. It is however assumed that a considerable fraction of the 29 $cm^3\ mol^{-1}$ volume reduction observed at 25 °C is caused by additional charge development in the transition state and an increase in electrostriction. The fact that the volume reduction here is significantly larger than the −18 $cm^3\ mol^{-1}$ value of $\Delta V^{\ddagger}$ for the oxidation by $Fe(CN)_4(bpy)^-$ [7] is in accord with the explanation of the dominance of electrostriction changes in the electron-transfer step. In the latter case +1 and −2 charges are developed from 0 and −1 species, while, for the reactions with $IrCl_6^{2-}$, +1 and −3 charges are developed from 0 and −2 species. Such solvational changes can also largely account for the negative $\Delta S^{\ddagger}$ values included in Table II. In this respect it is interesting to note that the activation parameters for the oxidation of the 2,3-dihydroxy diol have relatively low absolute values compared to the other data at 25 °C, which could indicate a possible neighboring-group interaction between the –COOH and –OH groups. This could yield a slightly compressed initial state that is not sustained in the transition state, coupled to a relative decrease in the magnitudes of $\Delta V^{\ddagger}$ and $\Delta S^{\ddagger}$.

A comparison with some available literature information, summarized in Table III, permits further discussion of the factors, both intrinsic and solvent related, which contribute to the absolute magnitude of $\Delta V^{\ddagger}$. For this purpose we have selected only those electron-transfer processes which are regarded as outer-sphere and only those processes in which either one of the reactants is neutral or both reactants are of the same sign of charge. This

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Table III. Summary of $\Delta V^{\ddagger}$ Values for the Outer-Sphere Electron-Transfer Reactions[a]

reacn no.	redox partners[b]		solvent	$\Delta V^{\ddagger}$, $cm^3 mol^{-1}$	ref
1	$Co(nox)_3(BF)_2^+$	$Fe(Cp)_2$	CH_3CN	−6 ± 1	8
2	$Co(dmg)_3(BF)_2^+$	$Fe(Cp)_2$	CH_3CN	−9 ± 1	
3	$Co(dpg)_3(BC_6H_5)_2^+$	$Fe(Cp)_2$	CH_3CN	−10 ± 1	
4	$Co(dmg)_3(BF)_2^+$	$Fe(CH_3Cp)_2$	CH_3CN	−11 ± 1	
5	$Co(dmg)_3(BC_4H_9)_2^+$	$Fe(CH_3Cp)_2$	CH_3CN	−11 ± 1	
6	$Co(dmg)_3(BC_6H_5)_2^+$	$Fe(CH_3Cp)_2$	CH_3CN	−4 ± 1	
7	$Co(nox)_3(BC_6H_5)_2^+$	$Fe(CH_3Cp)_2$	CH_3CN	−9 ± 1	
8	$Co(dpg)_3(BC_6H_5)_2^+$	$Fe(CH_3Cp)_2$	CH_3CN	−14 ± 1	
9	$Co(dmg)_3(BF)_2$	$Fe(Cp)_2^+$	CH_3CN	−13 ± 1	
10	$Co(nox)_3(BC_4H_9)_2$	$Cr(CNdipp)_6^{2+}$	CH_3CN	+2.2 ± 2	9
11	$Co(nox)_3(BC_6H_5)_2$	$Cr(CNdipp)_6^{2+}$	CH_3CN	+5.6 ± 2	
12	$Co(dpg)_3(BC_6H_5)_2$	$Cr(CNdipp)_6^{2+}$	CH_3CN	+10.8 ± 1	
13	$Fe(CN)_4(bpy)^-$	catechol	H_2O	−18.3 ± 0.8	7
14		4-*tert*-butylcatechol	H_2O	−18.0 ± 1.3	
15		2-methyl-1,4-hydroquinone	H_2O	−16.7 ± 1.1	
16	$IrCl_6^{2-}$	catechol	H_2O	−30.9 ± 1.3	*c*
17		4-*tert*-butylcatechol	H_2O	−28.0 ± 3.6	
18		3,4-dihydroxybenzoic acid	H_2O	−30.3 ± 1.3	
19		adrenaline	H_2O	−29.2 ± 3.6	
20	$Fe(CN)_6^{3-}$	ascorbic acid (H_2A)	H_2O	−16.6 ± 0.5	19
21	$Fe(CN)_6^{3-}$	ascorbate anion (HA^-)	H_2O	−16.3 ± 0.4	
22	MnO_4^-	MnO_4^{2-}	H_2O	−23	20
23	$Co(en)_3^{2+}$	$Co(en)_3^{3+}$	H_2O	−20	21
24	$Ru(hfac)_3^-$	$Ru(hfac)_3$	CH_3CN	−5.5 ± 0.1	22
25	$Mn(CNR)_6^+$	$Mn(CNR)_6^{2+}$, R = CH_3	CH_3CN	−2.1 ± 0.9	23
26		$Mn(CNR)_6^{2+}$, R = CH_2CH_3	CH_3CN	−5.5 ± 0.5	
27		$Mn(CNR)_6^{2+}$, R = $C(CH_3)_3$	CH_3CN	−13.3 ± 0.9	
28		$Mn(CNR)_6^{2+}$, R = C_6H_{11}	CH_3CN	−20.2 ± 1.6	
29		$Mn(CNR)_6^{2+}$, R = $(CH_2)_3CH_3$	CH_3CN	−19.7 ± 2.4	
30	$Fe(phen)_3^{2+}$	$Fe(phen)_3^{3+}$	H_2O	−2.2 ± 0.1	24
			CH_3CN	−5.9 ± 0.5	
31	$Fe(Cp)_2$	$Fe(Cp)_2^+$	CH_3CN	−7 ± 1	25
32	$Fe(H_2O)_6^{2+}$	$Fe(H_2O)_6^{3+}$	H_2O	−11.4 ± 0.4	26
33	$Cu(dmp)_2^+$	$Cu(dmp)_2^{2+}$	CH_3CN	−3.4 ± 0.7	27

[a] Reactions 1–21: $\Delta V^{\ddagger}$ values are for 25.0 °C. Reactions 22–33: temperatures were in the range 5–45 °C, except for reaction 23, where T = 65 °C. [b] Abbreviations: nox = doubly deprotonated cyclohexanedione dioxime, dmg = doubly deprotonated dimethylglyoxime, dpg = doubly deprotonated diphenylglyoxime, Cp = cyclopentadienide, CN-dipp = 2,6-diisopropylphenyl isocyanide, bpy = 2,2′-bipyridine, en = ethylenediamine, hfac = hexafluoroacetylacetone, phen = 1,10-phenanthroline, dmp = dimethylphenanthroline. [c] This study. Values at pH 0.

restriction was made in order that large volume contributions arising from ion-pair-formation equilibria, preceding electron transfer, could as a first approximation be neglected. The variation of $\Delta V^{\ddagger}$ with the nature of the solvent has been studied for a limited number of reactions, although no obvious correlation with the bulk property of the solvent was found.[8] Consequently, only reactions carried out in water and acetonitrile, solvents frequently employed for pressure-dependent kinetic studies, within the scope of the class of reactions described, will be analyzed.

Reactions which do not involve a net change in charge (nos. 1–9; see Table III) will show no pressure dependence of the rate constant if certain assumptions are sustained. These assumptions are that the charged species have equal or very similar charge densities, the encounter ion–molecule complex has the same volume as the sum of the reactants' volumes, and the dissociation of the successor complex is not contained within the rate-determining step. When contact is made between the charged reactant and the reactant molecule, some solvent of both species is dislodged; in the case of the former, restricted solvent, CH_3CN, in reactions 1–9, is returned to its bulk state. The difference in volume accompanying this process is not known, but it is expected to cause an increase in volume. The fact that $\Delta V^{\ddagger}$ is distinctly negative has led to the suggestion[8] that the encounter complex is intimate with the occurrence of coordination spheres overlapping and interpenetration of ligands, giving rise to an overall volume decrease which predominates over a positive effect due to solvation changes.

The idea of lowered charged density in the encounter complex has been advanced to account for solvent sphere expansion.[8] However, it could be said that the charge remains with its reactant and therefore still restricts solvent around it as it did as a reactant, except for the solvent dislodged from the contact surface region. If the charge has begun to be distributed over the whole complex at this stage, then the electron-transfer step is being described. Nevertheless, a general rationalization is that the volume increase expected from solvation changes upon encounter is overwhelmed by volume reduction from the intrinsic source.

Positive $\Delta V^{\ddagger}$ values for reactions 10–12 are thought[9] to arise from charge dilution since the 0- and +2-charged reactants proceed to two +1 products, with the decrease in electrostriction masking the overlap/interpenetration effect. This is consistent with the explanation offered for reactions 1–9.

Reactions 13–23 occur in aqueous solution, so solvation changes per charge unit change will differ from those for reactions in acetonitrile. However, the number of solvent molecules of water or acetonitrile which solvate given charged species or are lost upon charge reduction cannot be quantified. In light of this and the fact that added electrolyte, nature and concentration, can cause pronounced changes in $\Delta V^{\ddagger}$ values, the comparison is, therefore, limited to qualitative considerations at present.

The systems listed as reactions 13–19 all have large negative $\Delta V^{\ddagger}$ values. There is a general correlation between the magnitude and charge development. In each case a radical cation is a product of the electron-transfer step; a −1 becomes a −2 species and a −2 becomes a −3 species in reactions 13–15 and 16–19, respectively. However, it is suggested that compression within the encounter complex relative to reactants can account for part of the observed $\Delta V^{\ddagger}$ values. Both contributions are essentially constant for a given acidity and temperature.

Reactions 20 and 21 have $\Delta V^{\ddagger}$ values which most probably represent contributions arising from changes in electrostriction.[19] The remaining reactions considered were not all carried out at 25 °C, and there are ionic strength variations, so comparison and contrast with earlier reactions must include cognizance of small variations in $\Delta V^{\ddagger}$ due to these factors. A common feature of reactions 22–33 is that they are symmetrical; i.e., there is no overall change in intrinsic volume and all register a negative $\Delta V^{\ddagger}$. Charge concentration within the transition state can account for some volume reduction. Selecting some examples suggests that the charge concentration effect (on solvent) is greater for negative than for positive charge concentration in aqueous solution; for example, contrast reaction 22 ($\Delta V^* = -22$ cm^3 mol^{-1})[20] to reactions 30 and 32 ($\Delta V^* = -2.2$ and -11.4 cm^3 mol^{-1}, respectively).[24,26] But the situation is not straightforward, as reaction 23, $Co(en)_3^{2+}$ + $Co(en)_3^{2+}$ in water,[21] has $\Delta V^* = -20$ cm^3 mol^{-1}. Hence, from this it can be concluded that the overlap/interpenetration effect contributes to considerable varying extents to the volume decrease and is complex specific. ΔV^* values become more negative as one proceeds from reaction 25 to reaction 29. These increases coincide with an increase in ligand bulkiness and flexibility in the series of reactions.[8] Therefore, the overlap and/or penetration effect contributes more to volume reduction as the volume of reactants increases.

In conclusion, this analysis supports the idea emerging from recent studies that intrinsic volume contractions arising from interpenetration of ligands coordinated to the metal centers of reaction partners or of ligands coordinated to a metal center and an organic substrate can account for the more negative ΔV^* values than expected on the basis of solvation changes due to increase in electrostriction only. This represents another type of an "intrinsic" volume change in addition to the traditional one for various mechanistic features. This means that, notwithstanding the bulkiness of some of the bound ligands in two-metal-center reactions and in metal center–organic substrate redox reactions, there seems to be a specific distance of approach that is required for electron transfer and also facilitates it. The results now available for several series of outer-sphere electron-transfer reactions produce a consistent picture for qualitative arguments and interpretation. An objective in our current research is to choose suitable reactions which allow an evaluation of the factors that seem to be critical in these electron-transfer reactions; ultimately, a quantitative explanation should be possible, and this should be compatible with existing theoretical descriptions of these processes.

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Registry No. $IrCl_6^{2-}$, 16918-91-5; catechol, 120-80-9; 4-*tert*-butylcatechol, 98-29-3; 3,4-dihydroxybenzoic acid, 99-50-3; 2,3-dihydroxybenzoic acid, 303-38-8; adrenaline, 51-43-4; L-dopa, 59-92-7.

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Kinetic Study on Bis(*N*-alkylsalicylaldiminato)nickel(II) Complexes: Chiral Discrimination in Associatively Controlled Ligand Substitution

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Normal and stopped-flow spectrophotometry was used to study the kinetics of the reaction $NiA_2 + H_2B \rightarrow NiB + 2HA$ in acetone with NiA_2 = Ni(PhEt-sal)$_2$ (bis[*N*-(1-phenylethyl)salicylaldiminato]nickel(II)) and Ni(CyEt-sal)$_2$ (bis[*N*-(1-cyclohexylethyl)-salicylaldiminato]nickel(II)) and with H_2B = H$_2$salen (1,2-diamino-*N*,*N'*-disalicylideneethane), H$_2$salpn (1,3-diamino-*N*,*N'*-disalicylidenepropane), H$_2$sal-Me-en (1,2-diamino-*N*,*N'*-disalicylidenepropane, H$_2$sal-Me$_2$-en (1,2-diamino-*N*,*N'*-disalicylidene-2-methylpropane, H$_2$sal-Me,Me-en (2,3-diamino-*N*,*N'*-disalicylidenebutane and H$_2$sal-Cy-en (1,2-diamino-*N*,*N'*-disalicylidenecyclohexane). The reaction follows a second-order rate law, rate = $k_2[NiA_2][H_2B]$, and is associatively controlled (A mechanism). For the system Ni(PhEt-sal)$_2$/H$_2$B, the rate constant k_2 (298 K) ranges from 70.2 (H$_2$salen) to 0.33 M^{-1}s^{-1} (H$_2$sal-Me$_2$-en). The reactivity of the complex Ni(PhEt-sal)$_2$ is by a factor of approximately 5 greater than that of Ni(CyEt-sal)$_2$. Preparation of the complexes Ni(PhEt-sal)$_2$ and Ni(CyEt-sal)$_2$, respectively, with the *R* and *S* enantiomers of the chiral amines 1-phenylethylamine and 1-cyclohexylethylamine, respectively, leads to the enantiomers "Ni(*RR*)" and "Ni(*SS*)" of the two complexes, which were characterized by their specific rotation in acetone. The *R* and *S* enantiomers of the ligand H$_2$sal-Me-en were obtained from the racemic ligand by HPLC techniques, and the *R*,*R* and *S*,*S* enantiomers of the ligand H$_2$sal-Cy-en were prepared from the enantiomers of the chiral amine 1,2-diaminocyclohexane by Schiff base reaction with salicylaldehyde. Ligand substitution in the systems Ni(PhEt-sal)$_2$/H$_2$sal-Me-en, Ni(PhEt-sal)$_2$/H$_2$sal-Cy-en, Ni(CyEt-sal)$_2$/H$_2$sal-Me-en, and Ni(CyEt-sal)$_2$/H$_2$sal-Cy-en with the various pairs of enantiomers results in the finding that there is chiral discrimination in the sense that rate constant k_2 for the various combinations Ni(*RR*)/(*R*)-ligand and Ni(*SS*)/(*S*)-ligand is by a factor of 1.4–2.1 greater than for the combinations Ni(*RR*)/(*S*)-ligand and Ni(*SS*)/(*R*)-ligand. Activation parameters ΔH^*, and ΔS^* are presented. Equilibrium constants for adduct formation in acetone according to $NiA_2 + 2\,\text{base} \rightleftharpoons NiA_2{\cdot}\text{base} + \text{base} \rightleftharpoons NiA_2{\cdot}2\,\text{base}$ for base = pyridine, 2-picoline and (*S*)-(−)-nicotine are presented. The results are discussed in terms of kinetic vs thermodynamic control of the observed chirality effects.

Introduction

Chiral recognition is a phenomenon of utmost importance for the functioning of biological systems and also for chemical synthesis. Stereoselectivity, as resulting from chiral recognition in reactions involving chiral and/or prochiral compounds, may arise from kinetic or thermodynamic sources. When kinetically controlled, stereoselecivity is due to the energetically differentiated formation of diastereoisomeric intermediates and/or transition states, leading to a difference in reaction rates. Thermodynamically controlled stereoselectivity results from the nonstatistical distribution of diastereoisomeric products in an equilibrium situation.

In the field of coordination chemistry, there has been a steady increase in studies involving optically active metal complexes over the past decades.[1] These studies were undertaken mainly to obtain detailed information on the stereochemical aspects of reaction mechanisms and to provide useful information for practical applications, such as separation of enantiomers and development of systems for homogeneous catalysis in enantioselective synthesis.

Electron transfer and ligand substitution represent the two most important types of reactions of metal complexes. Since transition metals are an essential part of the (chiral) active site of many redox-active proteins,[2] numerous investigations deal with stereo-

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[†] This contribution presents part of the results of the Dr.-Ing. Dissertation submitted to the Technische Hochschule Darmstadt in 1991.

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