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Oxygen-17 Nuclear Magnetic Resonance Studies on the Acetic Acid Exchange of Manganese(II), Iron(II), Cobalt(II), Nickel(II), and Copper(II) Perchlorates in Acetic Acid[1]

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Received July 25, 1985

The exchange between bulk acetic acid molecules and the acetic acid molecules bound to transition-metal cations (Mn(II), Fe(II), Co(II), Ni(II), and Cu(II)) in neat acetic acid and in mixtures involving dichloromethane-d_2 as a diluent has been studied by the oxygen-17 line-broadening method. The exchange rate constants at 25 °C and activation parameters were obtained as follows: $k = (1.6 \pm 0.1) \times 10^7\ \mathrm{s}^{-1}$, $\Delta H^\ddagger = 29 \pm 2\ \mathrm{kJ\ mol^{-1}}$, and $\Delta S^\ddagger = -10 \pm 7\ \mathrm{J\ mol^{-1}\ K^{-1}}$ for $Mn(ClO_4)_2$; $k = (5 \pm 1) \times 10^6\ \mathrm{s}^{-1}$, $\Delta H^\ddagger = 33 \pm 5\ \mathrm{kJ\ mol^{-1}}$, and $\Delta S^\ddagger = -8 \pm 20\ \mathrm{J\ mol^{-1}\ K^{-1}}$ for $Fe(ClO_4)_2$; $k = (1.3 \pm 0.2) \times 10^6\ \mathrm{s}^{-1}$, $\Delta H^\ddagger = 37 \pm 3\ \mathrm{kJ\ mol^{-1}}$, and $\Delta S^\ddagger = -6 \pm 12\ \mathrm{J\ mol^{-1}\ K^{-1}}$ for $Co(ClO_4)_2$; $k = (2 \pm 1) \times 10^5\ \mathrm{s}^{-1}$, $\Delta H^\ddagger = 40 \pm 5\ \mathrm{kJ\ mol^{-1}}$, and $\Delta S^\ddagger = -10 \pm 20\ \mathrm{J\ mol^{-1}\ K^{-1}}$ for $Ni(ClO_4)_2$. The rate constant for $Cu(ClO_4)_2$ is about $1 \times 10^7\ \mathrm{s}^{-1}$ at −25 °C. The solvent-exchange rates in acetic acid increase in the order Ni(II) < Co(II) < Fe(II) < Mn(II) < Cu(II), which is identical with that in the other solvents.

Introduction

Acetic acid (HOAc) is an interesting solvent, which has an amphiprotic character and low dielectric constant. We have investigated rates for solvent exchange of $Cu_2(OAc)_4$[2] and $Mn(ClO_4)_2$[3] in acetic acid by ^{1}H NMR and of $NiCl_2$,[4] $Ni(NO_3)_2$,[4] and $Ni(OAc)_2$[4] in acetic acid by ^{1}H and ^{17}O NMR. Our studies have been extended to kinetic studies on solvent-exchange processes of transition-metal perchlorates (Mn(II), Fe(II), Co(II), Ni(II), and Cu(II)) in neat acetic acid and in mixtures with inert solvent by means of ^{17}O NMR. As oxygen atoms in acetic acid molecules coordinate to the paramagnetic metal ions and the chemical shift of oxygen-17 is larger relative to the proton shift, the contribution of chemical exchange to the relaxation time estimated from ^{17}O NMR line-broadening data will be observed at a relatively higher temperature in comparison with that from ^{1}H NMR data. Moreover, since the preparation of oxygen-17 enriched acetic acid is easy, oxygen-17 is very suitable as a probe nucleus for an acetic acid exchange study on paramagnetic metal ions. We have compared rate parameters of solvent exchange in different solvents.

Experimental Section

Reagents. The purification of acetic acid and the preparation of hexasolventometal(II) perchlorates ($[M(HOAc)_6](ClO_4)_2$, M = Mn(II), Fe(II), Co(II), Ni(II), and Cu(II)) were described previously.[5] The crystal structure of these metal(II) perchlorates has been reported to show coordination by six acetic acid molecules.[6] Dichloromethane-d_2 (CD_2Cl_2) was distilled under vacuum over 3A molecular sieves before use. Oxygen-17 enriched acetic acid was prepared by mixing the purified acetic anhydride with the equivalent amount of oxygen-17 enriched water purchased from CEA France. The percentage of oxygen-17 is 9.89 atom % of all oxygen atoms. Extreme care was exercised against the oxidation of the iron(II) ion.

Sample Preparation. All operations for preparation of NMR sample solutions were carried out in a drybox and on a standard vacuum line. For the preparation of a series of NMR sample solutions with the same solvent composition and to make sure of safety in introduction of perchloric acid, the glass vessel illustrated in Figure 1 was used. Since a small amount of perchloric acid must be added in order to prevent solvolysis of metal(II) ions, the following processes for preparation were carried out. An aliquot of oxygen-17-enriched acetic acid and an acetic acid solution of perchloric acid were taken into section A by pipetting and then the solution was degassed by the freeze–pump–thaw method. A solution with desired composition (ca. 15 cm^3) was prepared by adding CD_2Cl_2 into section A by distillation. This reference solution containing no metal ion was used for a series of NMR sample solutions. A known amount (ca. 0.5 to 1 cm^3) of acetic acid solution of metal(II) perchlorate was taken into section B, and then the acetic acid was removed by distillation to leave the crystals of the metal(II) perchlorate in section B. After stopcock D was closed and then stopcocks C and E were opened, an aliquot (ca. 0.6 cm^3) of the reference solution already prepared in section A was transferred into section B by slanting the glass vessel. Then stopcocks C and E are closed. After the tube was disconnected at G, the transferred amount was determined by weighing. The 5-mm-o.d. NMR tube was sealed at F. The compositions of all the sample solutions studied are tabulated in Table I. We prepared the solvent with three different weight percentages (100, 20.0, and 4.94 wt % acetic acid).

NMR Measurements. Variable-temperature Fourier transform ^{17}O NMR spectra were obtained with JEOL JNM-FX60 and JNM-GX400 instruments operating at 8.16 and 54.21 MHz, respectively. The 5-mm-o.d. NMR sample tube was fixed by a Teflon spacer inside a 10-mm-o.d. NMR tube that contained D_2O or CD_3OD as a lock solvent. Pulse widths of 20 and 60 μs and pulse intervals of 0.2 and 0.15 s were used at 8.16 and 54.21 MHz, respectively. Usually the free induction decay spectrum was accumulated over 2000–12 000 pulses. Sample temperature was measured by using a thermister (SPD-02-10A, SPD-01-10A, or D11J-1031, Takara Thermister Co.) immersed in a 5-mm-o.d. NMR tube with a solution similar to the sample solution instead of an NMR sample tube. Since the sample solution was heated by ^{1}H decoupling and surrounded by a lock solvent, temperature equilibrium was achieved after 30 min. The uncertainty of the temperature was estimated to be ±0.5 °C. The freezing temperature of solvent and the solubility of metal(II) salts restricted the observed temperature range.

Treatment of NMR Line-Broadening Data. The exchange of solvent between bulk (S) and metal ion coordinated sites (S*) can be determined from the transverse relaxation rate measurements of the bulk solvent nuclei.

$$[MS^*_n]^{2+} + S \rightleftharpoons [MS^*_{n-1}S]^{2+} + S^* \qquad (1)$$

For such systems containing paramagnetic metal ions, the modified Bloch equations have been solved by Swift and Connick.[7] Since then, the theory has been expanded for wide applications.[8-21] Here we shall show

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Table I. Compositions of Sample Solutions[a]

soln	species	[M]/*m*	[HOAc]/*m*	$[CD_2Cl_2]/m$	$10^2[HClO_4]/m$	$10^4 P_M$	wt % of HOAc	atom % of ^{17}O
A0	reference solution	0	16.59	0	2.00	0	100	4.93
A1m	$Mn(ClO_4)_2$	1.06×10^{-3}	16.59	0	2.00	1.91	100	4.93
A2o	$Co(ClO_4)_2$	3.56×10^{-3}	16.59	0	2.00	6.44	100	4.93
A3n	$Ni(ClO_4)_2$	2.56×10^{-3}	16.59	0	2.00	4.64	100	4.93
A4u	$Cu(ClO_4)_2$	1.45×10^{-3}	16.59	0	2.00	2.62	100	4.93
B0	reference solution	0	3.31	9.20	2.12	0	20.0	5.98
B1m	$Mn(ClO_4)_2$	1.88×10^{-4}	3.31	9.20	2.12	1.70	20.0	5.98
B2m	$Mn(ClO_4)_2$	6.02×10^{-4}	3.31	9.20	2.12	5.46	20.0	5.98
B3o	$Co(ClO_4)_2$	1.94×10^{-3}	3.31	9.20	2.12	1.76	20.0	5.98
B4o	$Co(ClO_4)_2$	3.59×10^{-3}	3.31	9.20	2.12	3.25	20.0	5.98
B5n	$Ni(ClO_4)_2$	8.94×10^{-4}	3.31	9.20	2.12	8.11	20.0	5.98
B6u	$Cu(ClO_4)_2$	2.71×10^{-4}	3.31	9.20	2.12	2.46	20.0	5.98
B7u	$Cu(ClO_4)_2$	8.73×10^{-4}	3.31	9.20	2.12	7.91	20.0	5.98
B8f	$Fe(ClO_4)_2$	2.30×10^{-4}	3.31	9.20	2.12	2.05	20.0	5.98
B9f	$Fe(ClO_4)_2$	2.60×10^{-4}	3.31	9.20	2.12	2.40	20.0	5.98
B10f	$Fe(ClO_4)_2$	3.09×10^{-4}	3.31	9.20	2.12	2.79	20.0	5.98
C0	reference solution	0	0.817	10.94	2.16	0	4.94	7.93
C1m	$Mn(ClO_4)_2$	4.93×10^{-5}	0.817	10.94	2.16	1.81	4.94	7.93
C2u	$Cu(ClO_4)_2$	6.00×10^{-5}	0.817	10.94	2.16	2.20	4.94	7.93

[a] $m \equiv mol\ kg^{-1}$.

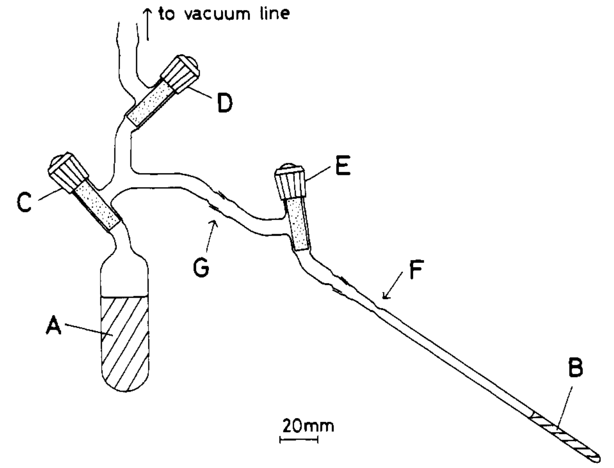

Figure 1. Glass vessel for preparation of sample solution: A, section for storing reference solution (ca. 15 cm^3); B, 5-mm-o.d. NMR sample tube including each salt; C–E, ROTAFLO stopcocks.

only some basic equations for treatment of our data.

The solvent NMR line broadening $(T_{2P}P_M)^{-1}$ due to the paramagnetic metal ion is expressed as $(T_{2P}P_M)^{-1} = \pi(\Delta\nu_{obsd} - \Delta\nu_{solv})P_M^{-1}$, where $\Delta\nu_{obsd}$ and $\Delta\nu_{solv}$ (Hz) are the half-height widths of the solvent NMR spectra in the presence and in the absence, respectively, of the paramagnetic ion and P_M is the ratio of the populations on the observed nucleus in the site bound to the paramagnetic metal ion and in the bulk site. One of two oxygen atoms in an acetic acid molecule in the inner sphere is directly bonded to the metal ion, and the other does not coordinate. The contribution of the latter to the line width should be negligible. On the other hand, the two oxygen atoms of an acetic acid molecule in bulk are equivalent. Therefore, when P_M' is defined as the ratio of the number of solvent molecules in the inner sphere of the metal ion to that of bulk solvent molecules, P_M is half of P_M'. $(T_{2P}P_M)^{-1}$ is given by eq 2. where

$$\frac{1}{T_{2P}P_M} = \frac{1}{\tau_M}\,\frac{T_{2M}^{-2} + (\tau_M T_{2M})^{-1} + (\Delta\omega_M)^2}{(\tau_M^{-1} + T_{2M}^{-1})^2 + (\Delta\omega_M)^2} + \frac{1}{T_{2O}} \tag{2}$$

τ_M and T_{2M} are the mean lifetime and the transverse relaxation time of the observed nucleus of solvent in the inner sphere of the paramagnetic ion, $\Delta\omega_M$ is the difference in the resonance frequency between the observed nucleus of solvent in the inner sphere and that of free solvent, and T_{2O}^{-1} is the relaxation term due to the interaction in the outer sphere. The temperature dependence of the relaxation terms is given as follows:[4,9]

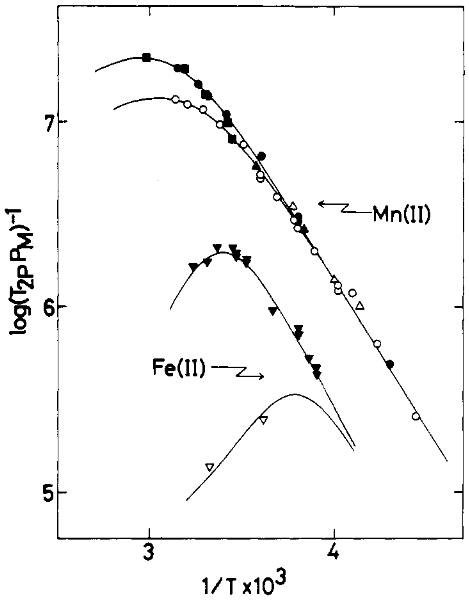

Figure 2. Temperature dependence of log $(T_{2P}P_M)^{-1}$ for the oxygen-17 of bulk acetic acid in the presence of $Mn(ClO_4)_2$ or $Fe(ClO_4)_2$: (■) $Mn(ClO_4)_2$ solution A1m at 54.21 MHz; (○) $Mn(ClO_4)_2$ solution B1m and B2m at 8.16 MHz; (●) $Mn(ClO_4)_2$ solution B1m and B2m at 54.21 MHz; (△) $Mn(ClO_4)_2$ solution C1m at 8.16 MHz; (▲) $Mn(ClO_4)_2$ solution C1m at 54.21 MHz; (▽) $Fe(ClO_4)_2$ solution B10f at 8.16 MHz; (▼) $Fe(ClO_4)_2$ solution B8f and B9f at 54.21 MHz. The curves in Figures 2–4 were calculated with the NMR and kinetic parameters obtained.

$\tau_M^{-1} = (k_BT/h)\exp(-\Delta H^*/RT + \Delta S^*/R)$; $\Delta\omega_M = -C_\omega/T$; $T_{2M}^{-1} = (C_M/T)\exp(E_M/RT)$; $T_{2O}^{-1} = (C_O/T)\exp(E_O/RT)$. The NMR and kinetic parameters were calculated with use of a nonlinear least-squares program (SALS).[22]

Results and Discussion

All line-broadening data are tabulated in the supplementary material (Table s-I). The temperature dependence of NMR line widths of oxygen-17 in reference solutions that involve no paramagnetic metal ion is given in Figure s-1 (supplementary material). Logarithmic values of line widths show a linear relation with the

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Table II. Activation Parameters for Exchange Reactions of Acetic Acid Coordinating to Metal(II) Perchlorates

	k(25 °C)/ s^{-1}	k(−25 °C)/ s^{-1}	ΔH^*/kJ mol^{-1}	ΔS^*/J mol^{-1} K^{-1}
$Mn(ClO_4)_2$	(1.6 ± 0.1) × 10^7	(1.3 ± 0.2) × 10^6	29 ± 2	−10 ± 7
$Fe(ClO_4)_2$	(5 ± 1) × 10^6	(2.6 × 0.1) × 10^5	33 ± 5	−8 ± 20
$Co(ClO_4)_2$	(1.3 × 0.2) × 10^6	(5.4 ± 0.1) × 10^4	37 ± 3	−6 ± 12
$Ni(ClO_4)_2$	(2 ± 1) × 10^5		40 ± 5	−10 ± 20
$Cu(ClO_4)_2$		≃1 × 10^7		

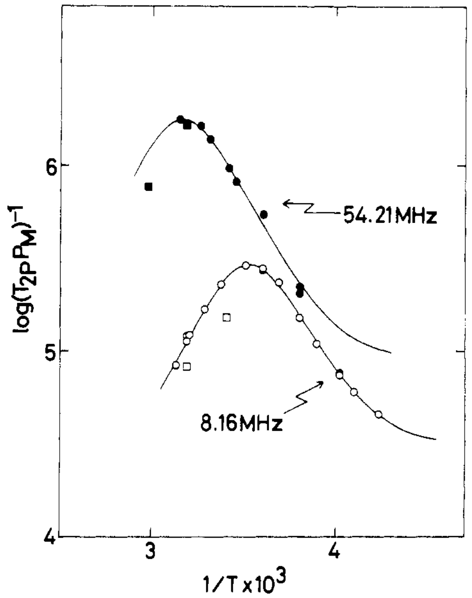

Figure 3. Temperature dependence of log $(T_{2P}P_M)^{-1}$ for the oxygen-17 of bulk acetic acid in the presence of $Co(ClO_4)_2$: (□) solution A2o at 8.16 MHz; (■) solution A2o at 54.21 MHz; (○) solution B3o and B4o at 8.16 MHz; (●) solution B3o and B4o at 54.21 MHz.

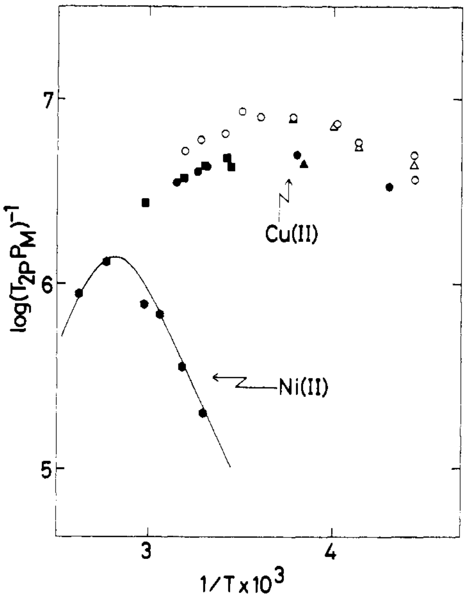

Figure 4. Temperature dependence of log $(T_{2P}P_M)^{-1}$ for the oxygen-17 of bulk acetic acid in the presence of $Ni(ClO_4)_2$ or $Cu(ClO_4)_2$: (●) $Ni(ClO_4)_2$ solution A3n at 54.21 MHz; (■) $Cu(ClO_4)_2$ solution A4u at 54.21 MHz; (○) $Cu(ClO_4)_2$ solution B6u and B7u at 8.16 MHz; (●) $Cu(ClO_4)_2$ solution B6u and B7u at 54.21 MHz; (△) $Cu(ClO_4)_2$ solution C2u at 8.16 MHz; (▲) $Cu(ClO_4)_2$ solution C2u at 54.21 MHz.

reciprocal of temperature and are independent of the observed frequencies.

Manganese(II) Perchlorate. The temperature dependence of line widths log $(T_{2P}P_M)^{-1}$ for manganese(II) perchlorate is presented in Figure 2. The observed line widths, log T_{2P}^{-1}, for 1.88 × 10^{-4} and 6.02 × 10^{-4} m manganese(II) perchlorate solutions (solutions B1m and B2m) were found to be proportional to the concentration, and thus the log $(T_{2P}P_M)^{-1}$ value is independent of the manganese(II) concentration. The chemical exchange region where the τ_M^{-1} term predominantly contributes to the line width (the straight part declined to the right in Figure 2) is the same for the samples of 100, 20.0, and 4.94 wt % acetic acid. Thus the solvent-exchange rates are independent of the concentration of acetic acid. It is reasonable that the chemical-exchange region is identical for two observed frequencies (8.16 and 54.21 MHz). NMR and kinetic parameters calculated under conditions where $T_{2M}^{-2} >> (\Delta\omega_M)^2$ and T_{2O}^{-1} can be neglected are tabulated in Table s-II (supplementary material), and the activation parameters for chemical exchange are summarized in Table II. Since the chemical-exchange region in the present case of ^{17}O NMR extends over about 2 orders of magnitude in relaxation rate as apparent from Figure 2, the activation parameters for chemical exchange obtained from ^{17}O NMR should be much more precise than those estimated from analysis of ^1H NMR data.[3] Thus the line-broadening data of ^1H NMR were recalculated by fixing ΔH^* = 29 kJ mol^{-1}, obtained from the data of ^{17}O NMR. The results of the recalculation (shown in Table s-III) indicate that the data of ^1H NMR are consistent with the results of the ^{17}O NMR data.[23]

Iron(II) Perchlorate. The temperature dependence of line widths log $(T_{2P}P_M)^{-1}$ for iron(II) perchlorate is represented in Figure 2. The data of the 20.0 wt % HOAc sample solutions at 54.21 MHz were analyzed with negligible contribution of T_{2O}^{-1} and T_{2M}^{-1} assumed. This assumption seems to be reasonable, judging from the values of line width at 8.16 MHz. The curve for 8.16 MHz in Figure 2 was depicted by using values of parameters obtained from data at 54.21 MHz.

Cobalt(II) Perchlorate. Figure 3 shows the temperature dependence of line widths for cobalt(II) perchlorate. The chemical exchange regions for the 100 and 20.0 wt % HOAc sample solutions seem to be identical. The value of log $(T_{2P}P_M)^{-1}$ at 54.21 MHz is much larger than at 8.16 MHz over the temperature range of $1/T < 3.5 \times 10^{-3}$ K^{-1}. This indicates that the chemical shift term $(\Delta\omega_M)$ makes a large contribution to the line width. Values of C_ω were obtained to be 1.10 × 10^9 K rad s^{-1} at 54.21 MHz and 1.57 × 10^8 K rad s^{-1} at 8.16 MHz (Table s-II). The experimental values of C_ω can be used to calculate the scalar coupling constant $(A/\hbar)$ of 6.8 × 10^7 rad s^{-1}.

Nickel(II) Perchlorate. The temperature dependence of log $(T_{2P}P_M)^{-1}$ for the 100 wt % HOAc solution of nickel(II) perchlorate at 54.21 MHz is shown in Figure 4. The activation parameters estimated are given in Table II. These values are similar to those for acetic acid exchange on nickel(II) nitrate in mixtures of acetic acid with CD_2Cl_2 (k(25 °C) = (3 ± 1) × 10^5 s^{-1}, ΔH^* = 37 ± 5 kJ mol^{-1}, and ΔS^* = −18 ± 20 J mol^{-1} K^{-1}).[4] This is quite reasonable because both perchlorate and nitrate ions do not exist in the inner sphere of nickel(II) ion although these salts exist as nondissociated species in acetic acid.

Copper(II) Perchlorate. The temperature dependence of log $(T_{2P}P_M)^{-1}$ for copper(II) perchlorate shown in Figure 4 is not enough to calculate the activation parameters. Only the exchange rate at −25 °C was roughly estimated to be about 10^7 s^{-1}. This estimation was only possible by means of ^{17}O NMR, and we could not obtain informations about the chemical exchange by the ^1H NMR method (temperature dependence of log $(T_{2P}P_M)^{-1}$ for the HOAc methyl protons and hydroxyl proton given in Figure s-2 (supplementary material)).

Comparison of the Rate Parameters. All activation parameters are summarized in Table II. For divalent first-row transition-metal ions, Merbach and his associates[24-27] found a trend in volumes

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[23] The chemical exchange region in the case of ^1H NMR was very narrow (only 0.2 as logarithmic unit) and in addition measurements of the T_{2O} region were limited due to freezing of solvent. Consequently, in ref 3 E_Q was underestimated and ΔH^* was overestimated.

[24] (a) Ducommun, Y.; Newman, K. E.; Merbach, A. E. *Inorg. Chem.* **1980**, *19*, 3696. (b) Merbach, A. E. *Pure Appl. Chem.* **1982**, *54*, 1479.

Table III. First-Order Rate Constants (s^{-1}, 25 °C) for Solvent Exchange on Mn(II), Fe(II), Co(II), and Ni(II) Ions in Seven Solvents[a]

	$Mn(ClO_4)_2$	$Fe(ClO_4)_2$	$Co(ClO_4)_2$	$Ni(ClO_4)_2$
CH_3OH	$3.7 \times 10^{5\,b}$	$5.0 \times 10^{4\,b}$	$1.8 \times 10^{4\,j}$	$1.0 \times 10^{3\,j}$
CH_3CN	$1.4 \times 10^{7\,c}$	$6.6 \times 10^{5\,c}$	$2.6 \times 10^{5\,k}$	$3.1 \times 10^{3\,o}$
Me_2SO	$6.3 \times 10^{6\,d}$	$1.0 \times 10^{6\,i}$	$3.1 \times 10^{5\,l}$	$3.2 \times 10^{3\,l}$
DMF	$2.4 \times 10^{6\,e}$	$1.7 \times 10^{6\,i}$	$3.9 \times 10^{5\,m}$	$3.8 \times 10^{3\,m}$
H_2O	$2.1 \times 10^{7\,f}$	$4.4 \times 10^{6\,f}$	$3.2 \times 10^{6\,f}$	$3.2 \times 10^{4\,p}$
NH_3	$3.6 \times 10^{7\,g}$		$7.2 \times 10^{6\,n}$	$7.0 \times 10^{4\,q}$
HOAc	$1.6 \times 10^{7\,h}$	$4 \times 10^{6\,h}$	$1.3 \times 10^{6\,h}$	$2 \times 10^{5\,h}$

[a] In making a choice among the available solvent-exchange data, we prefer higher values of the enthalpy of activation obtained from measurements over a wider range of temperature: Newman, K. E.; Meyer, F. K.; Merbach, A. E. *J. Am. Chem. Soc.* **1979**, *101*, 1470. [b] Reference 29. [c] Reference 30. [d] Reference 31. [e] Reference 32. [f] Reference 24a. [g] Reference 33. [h] This work. [i] Reference 34. [j] Reference 35. [k] Reference 36. [l] Reference 37. [m] Reference 38. [n] Reference 39. [o] Reference 40. [p] Reference 41. [q] Reference 42.

of activation for solvent-exchange reaction along the series: the dissociative character of the activation process increases with increasing atomic number. The activation enthalpy increases also with increasing atomic number. It has recently been stated[28c,d] that, as the mechanism becomes less dissociative, the exothermic bond formation occurs concurrently with the endothermic bond breaking: the energy needed for the bond-breaking process should be more or less compensated by the energy evolved in the exothermic bond formation. In consequence, the less dissociative the reaction mechanism, the lower the activation enthalpy. This was found not only for the acetic acid exchange but also for the exchange reaction of the other solvents, such as CH_3OH, CH_3CN, Me_2SO (dimethyl sulfoxide), DMF (*N*,*N*-dimethylformamide), H_2O, and NH_3. As seen from Table III, the rate of solvent exchange is the reverse of the order found for the activation enthalpy of the solvent exchange for solvents including acetic acid: Ni(II) < Co(II) < Fe(II) < Mn(II) < Cu(II).

The activation enthalpy of solvent exchange, $\Delta H^{\ddagger}$, has been correlated with the enthalpy of dissociation of solvent molecules from solvento metal ions (ΔH_d) and the evaporation enthalpy of the solvent (ΔH_v)[28]

$$\Delta H^{\ddagger} = a\Delta H_d + b\Delta H_v \qquad (3)$$

where a and b are coefficients characteristic of the metal ion. When the Born equation is used for calculation of ΔH_d for acetic acid, we obtain a large negative ΔH_d. This is because of the positive temperature coefficient of the dielectric constant of acetic acid. This is the opposite situation to that for usual solvents for which the dielectric constant decreases with increasing temperature. A high exothermicity for the solvent dissociation from a metal ion appears quite anomalous and unacceptable. Thus we think it inappropriate to calculate ΔH_d in acetic acid by the Born equation.

On the other hand, with the known value of ΔH_v of acetic acid (23.0 kJ mol^{-1}) and the previously determined coefficients a and b in eq 3,[28a,c] we can estimate an average value of ΔH_d to be 24.8 kJ mol^{-1}. This value does not seem unreasonable taking into account both the low dielectric constant and the low basicity of acetic acid. In fact the ΔH_d value increases slightly with increasing atomic number (i.e. with decreasing atomic radii) for solvents such as CH_3CN, ammonia, DMF, Me_2SO, CH_3OH, and water:[28a] for example, ΔH_d for CH_3CN increases with 22.4 kJ mol^{-1} for manganese to 24.2 kJ mol^{-1} for nickel. Such a small difference of ΔH_d produces less than 2 kJ mol^{-1} of difference in the calculated $\Delta H^{\ddagger}$, which is within the experimental uncertainty of most NMR studies. Then if we accept, as an empirical parameter, the estimated ΔH_d value of 24.8 kJ mol^{-1} for all the studied metal ions in acetic acid, we can calculate the activation enthalpy according to eq 3 (calcd $\Delta H^{\ddagger}$/kJ mol^{-1}): 24.7 for manganese; 33.5 for iron; 39.6 for cobalt; 45.2 for nickel. Thus with the empirical ΔH_d value of 24.8 kJ mol^{-1}, eq 3 reproduces the activation enthalpy of acetic acid exchange at these metal ions to within 5 kJ mol^{-1}.

Jordan et al. have proposed a correlation of the activation enthalpy for solvent exchange and crystal field and solvent effects[43]

$$\Delta H^{\ddagger}(\text{M-S}) = f_M Dq_{\text{Ni-S}} + b_s \qquad (4)$$

where f_M is a constant for the metal ion and b_s is dependent only on the solvent. By use of the available Dq (9.87 kJ mol^{-1}) of nickel(II) ion in acetic acid[44] and f_M values obtained by Jordan et al. in fitting $\Delta H^{\ddagger}$ to Dq for several metal–solvent pairs, we have b_s(acetic acid) = 4.60 kJ mol^{-1}. Then we can compute the activation enthalpy (kJ mol^{-1}) for acetic acid exchange according to eq 4: 22.4 for manganese; 32.4 for iron; 37.3 for cobalt; 46.6 for nickel. Therefore eq 4 predicts the activation enthalpy of acetic acid exchange at these metal ions to within 7 kJ mol^{-1}.

T_{2M}^{-1} consists of both the dipole–dipole interaction term and the hyperfine interaction term.[32,45-47] In the present systems, T_{2M}^{-1} is decided by the hyperfine interaction (Table s-IV, supplementary material). The T_{2M}^{-1} term for Mn(II) and Cu(II) depends on the observed frequency.[9,48] For Mn(II), as apparent from Figure 2, the higher the operating frequency, the larger the value of T_{2M}^{-1}. This makes τ_{e1} dependent on an operating frequency since $1 \ll \omega_s^2\tau_{e2}^2$. The correlation times τ_{e1} and τ_{e2} are related as follows: $\tau_{e1}^{-1} = T_{1e}^{-1} + \tau_M^{-1}$ and $\tau_{e2}^{-1} = T_{2e}^{-1} + \tau_M^{-1}$, where T_{1e} and T_{2e} are the longitudinal and transverse relaxation times of the electron, respectively, and ω_s is the resonance angular frequency of the electron. On the contrary, for Cu(II) the T_{2M}^{-1} value is smaller for the higher operating frequency. This means that $\omega_s^2\tau_{e2}^2 \simeq 1$, i.e., $\tau_{e2}^{-1} \simeq \omega_s$ at either 8.16 or 54.21 MHz.

Acknowledgment. The present work was supported by a Grant-in-Aid for Scientific Research (No. 59430010) from the Japanese Ministry of Education, Science, and Culture.

Registry No. $[Mn(HOAc)_6](ClO_4)_2$, 20298-15-1; $[Fe(HOAc)_6](ClO_4)_2$, 100993-93-9; $[Co(HOAc)_6](ClO_4)_2$, 19644-55-4; $[Ni(HOAc)_6](ClO_4)_2$, 18897-39-7; $[Cu(HOAc)_6](ClO_4)_2$, 100993-95-1; HOAc, 64-19-7.

Supplementary Material Available: Oxygen-17 line-broadening data (Table s-I), values of $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, C_M, E_M, C_O, E_O, and C_ω for $Mn(ClO_4)_2$, $Fe(ClO_4)_2$, $Co(ClO_4)_2$, $Ni(ClO_4)_2$, and $Cu(ClO_4)_2$ in acetic acid and in

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mixtures involving CD_2Cl_2 (Table s-II), values of ΔH^*, ΔS^*, C_M, E_M, C_O, E_O, and C_ω recalculated for proton line-broadening data of $Mn(ClO_4)_2$ (Table s-III), values of S, τ_{e2}, τ_{c2}, C_{DD}, A, and C_{HF} (Table s-IV), temperature dependence of the line widths for oxygen-17 of HOAc in the absence of metal ions (Figure s-1), and temperature dependence of proton line broadening for $Cu(ClO_4)_2$ in a mixture of acetic acid with CD_2Cl_2 (Figure s-2) (9 pages). Ordering information is given on any current masthead page.

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EPR Studies of the Electronic Structure and Dynamic Jahn–Teller Effect in Cobalt(II) Mixed-Sandwich Compounds

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Received July 12, 1985

EPR studies are reported on the 19-electron sandwich complex $Co(cp)(Bz)^+$ ($(\eta^5\text{-}C_5H_5)Co(\eta^6\text{-}C_6H_6)^+$) and some of its ring-methylated derivatives in several diamagnetic host lattices and frozen solutions. The results are consistent with a d^7 configuration for cobalt with the unpaired electron in the e_{1g} orbital having largely metal (d_{xz},d_{yz}) character. The dependence of the EPR parameters on the host lattice is mainly attributed to the rhombic splitting caused by the unsymmetrical host lattice potential acting on the dynamically Jahn–Teller-coupled $^2\pi$ ground state. The bonding parameters have been compared with those of analogous compounds with the covalency decreasing as $Ni(cp)_2^+ > Co(Pmcp)(hmBz)^+ > Co(cp)(Bz)^+ > Co(cp)_2^+ > Fe(cp)(Bz)$. The variation of line width with temperature has been used to derive information on the energy of the first excited Kramers doublet.

Introduction

Electron paramagnetic resonance of sandwich compounds with degenerate or nearly degenerate electronic ground states yields information on the bonding parameters on the one hand and the dynamic Jahn–Teller effect on the other.[2] The systems studied are mostly d^5 and d^7 sandwich compounds of the first-row transition-metal series. The main phenomenon observed in all the above cases is a dependence of the EPR parameters—g and A tensors—on the host lattice, attributable mainly to the changes in the relative composition of the ground electronic state wave function caused by the changes in the low-symmetry components of the solvent fields and, to a lesser degree, by variations in the amplitudes of the dynamic Jahn–Teller distortions.[3]

We present in this paper the results of the investigation of a series of cobalt(II) mixed-sandwich compounds, $Co(C_5R_5)(C_6R'_6)^+$ with R and R′ being CH_3 or H. Also included are the results for the bis(hexamethylbenzene)cobalt(II) dication, $Co(C_6Me_6)_2^{2+}$ (see Figure 1).[1d] A detailed report on the preparative, electrochemical, and NMR investigation on some of the complexes studied here has been presented earlier,[4] and preliminary results of the EPR studies on some of the complexes are also mentioned. In this earlier work only alkylated derivatives could be synthesized and studied by EPR, and these invariably suffer from large orthorhombic distortions (crystal field splitting $\delta >$ spin–orbit coupling ζ). It has now been possible to investigate the unsubstituted species $Co(cp)(Bz)^+$,[1d] which is expected to be the least distorted in a variety of hosts, and to derive useful information about the dynamic Jahn–Teller parameters. We have also studied $Co(Pmcp)(Bz)^+$ and $Co(cp)(hmBz)^+$ wherein the effect of methylation can be analyzed, and further we have provided the data on $Co(Pmcp)(hmBz)^+$ wherein both the rings are fully methylated. For the sake of comparison, we have included the results on $Co(hmBz)_2^{2+}$.

The motivation of this study is to investigate (1) the mixed sandwich effect, (2) the effect of methylation, (3) a comparison of the effect, especially of covalency parameters, with that for other d^7 sandwiches including cobaltocene and its methylated derivatives, Fe(I) sandwich compounds, and Ni(III) sandwich compounds, (4) the degree of orthorhombic distortion in various host lattices, and (5) the relaxation behavior, through line width studies.

Whereas large δ values (obtainable through methylation) are required for narrow EPR line widths, accessibility of spectra up to high temperatures, and for the close approach to the static limit, low values of δ (unmethylated compound) are required for significant dynamic effects so that the whole range of $V = 0\text{–}1$ (i.e. dynamic to static Jahn–Teller cases) can be investigated.

Experimental Section

Synthesis. Preparation and handling of all the complexes and solvents were carried out under a purified N_2 atmosphere with Schlenk-type apparatus.

The diamagnetic air-stable dications were reduced in solution with cobaltocene to the paramagnetic monocations, which were stable only under rigorous exclusion of air below −30 °C. A side product is the diamagnetic cobaltocenium cation. From this resulting salt mixture the cobaltocene salt was separated by fractional crystallization from methylene chloride/toluene, where it is much less soluble than the monocation mixed-sandwich salts. These monocations were directly measured in solution, or a large excess of the matrix salt was added until a saturated solution was obtained and a diamagnetically diluted microcrystalline precipitate was obtained on adding pentane. This was then filtered, dried under vacuum, and transferred to EPR tubes and sealed under a He atmosphere.

EPR Measurements. EPR spectra were recorded on a Varian E-line spectrometer operating at X-band frequency. The magnetic field was calibrated by using a Varian NMR gaussmeter, and the microwave frequency was measured by using a EIP frequency counter. Temperature control was achieved by using an Oxford Instruments ESR-9 liquid-helium cryostat of the continuous flow type, and temperature measurements were made by using a thermocouple situated just below the sample tube. Quartz EPR sample tubes were charged in a nitrogen-filled glovebox and sealed under 500 mbar of He gas in order to improve heat exchange. The EPR spectra were simulated by using a powder simulation program.[5]

Theoretical Background

As in metallocenes, the d-orbital splitting in bis(arene) and mixed-sandwich compounds can be described by a pseudoaxial symmetry[6] even though the exact molecular point groups are D_{6h} and C_s, respectively.[7] Thus, analogous to that of $Co(cp)_2$, the ground state is expected to be $^2E_{1g}$ (in the D_{6h} notation) or $^2\pi$ (in the $C_{\infty v}$ notation), with the unpaired electron in the e_{1g} orbital having the metal (d_{xz},d_{yz}) character.

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(7) Our semiempirical molecular orbital calculations indicate that the low-symmetry splittings in the doubly degenerate orbitals of $Co(cp)(Bz)^+$ and its methylated derivatives are negligible.