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Solvent-Exchange Kinetics in Acetic Acid Solution of Tetrakis(μ-acetato)-dicopper(II) Studied by Nuclear Magnetic Resonance Line Broadening[1]

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Measurements have been made of the temperature dependence of the solvent proton line broadening and shift for solutions of tetrakis(μ-acetato)-dicopper(II) in acetic acid (HOAc), HOAc–chloroform, and HOAc–dichloromethane solutions. No exchange effects were observed in pure HOAc at room temperature, while at low temperature in mixtures with $CDCl_3$ and CD_2Cl_2 proton exchange was measurable. The rate constant of the methyl proton exchange is $(9.4 \pm 0.5) \times 10^3$ s^{-1} at 25 °C ($\Delta H^{\ddagger} = 53 \pm 5$ kJ mol^{-1} and $\Delta S^{\ddagger} = 8 \pm 8$ J mol^{-1} K^{-1}). These activation parameters are independent of the composition of the solvents studied. The slow rate of exchange of methyl protons suggests that the HOAc on the axial site of dimeric copper(II) acetate forms a hydrogen bond to one of the carboxyl oxygens of the dimer acetate bridges. The methyl proton must exchange with the whole acetic acid molecule. The hydroxyl proton exchange occurs at a faster rate (k_{OH}(25 °C) = $(7.5 \pm 1) \times 10^6$ s^{-1}, $\Delta H^{\ddagger} = 38 \pm 8$ kJ mol^{-1}, and $\Delta S^{\ddagger} = 13 \pm 10$ J mol^{-1} K^{-1}) compared to the methyl protons.

Introduction

Nuclear magnetic resonance techniques have been widely employed to determine solvent-exchange rates for transition-metal ions in a number of solvents.[2,3] Some attempts have been made to correlate the activation enthalpies for solvent exchange on first-row dipositive transition-metal ion.[4-6] There is no study of solvent exchange on metal ions in acetic acid, which is an interesting nondissociating solvent of low dielectric constant and amphiprotic character.

Recently the reactions of dimeric copper(II) acetate have been used for biological processes which distinguish between ribo- and deoxyribonucleosides.[7,8] Thus information on the reactivity of the dimeric copper entity should be valuable from the biological point of view.

The reaction of tetrakis(μ-acetato)-dicopper(II) (henceforth we call it dimeric copper(II) acetate) with lithium chloride and hydrogen chloride in acetic acid has been studied.[9] This study prompted us to investigate the acetic acid exchange at dimeric copper(II) acetate. The present work describes a proton NMR study of dimeric copper(II) acetate in acetic acid and in mixtures with inert solvents.

Experimental Section

Reagents. It is very important that all reagents be as dry as possible. Therefore, extreme care was taken in the purification and preparation of all reagents and compounds. The preparation of acetic acid and tetrakis(μ-acetato)-dicopper(II) ($Cu_2(OAc)_4$) was described previously.[9] Chloroform-*d*, dichloromethane-d_2, and tetramethylsilane ($SiMe_4$) were stored under vacuum over 3A molecular sieves, and all operations for preparation were carried out on a standard vacuum line. Solvent sample solutions not involving $Cu_2(OAc)_4$ were prepared by transfer of CD_2Cl_2 or $CDCl_3$ and $SiMe_4$ into acetic acid by distillation. Sample solutions containing $Cu_2(OAc)_4$ were prepared by transfer of the solvent mixture obtained above into a NMR tube containing the crystals of $Cu_2(OAc)_4$. The solution molalities (mol kg^{-1} ≡ *m*) were determined by weighing. A total of 20 different samples were prepared. The compositions of the sample solutions are tabulated in Table I.

Measurements. The NMR spectra were obtained on a JNM-C-60H high-resolution spectrometer (JEOL Ltd.) equipped with a JNM-VT-3C variable-temperature controller (JEOL Ltd.). The temperature was determined by measurement of the peak separation in 1,2-propanediol and methanol, by a thermister (SPD-02-10A, Takara Thermister Co.) or by a potentiometer (P-1B, Yokokawa Electric Co.) with a copper-constantan thermocouple. The uncertainty in the temperature is estimated to be ±0.5 °C. $SiMe_4$ (ca. 0.5 wt %) was used as an internal standard for the chemical shift measurements. Care was taken to keep the radio frequency level low enough to avoid saturation. Inert solvents ($CDCl_3$ and CD_2Cl_2) were added to lower the freezing temperature of the solvent and to measure the chemical exchange of acetic acid. The concentration of $Cu_2(OAc)_4$ and the experimental range of temperature were both limited by the low solubility of $Cu_2(OAc)_4$. The sample solutions contained at most 1.5×10^{-3} mol kg^{-1} of water. Some NMR spectra were measured in the presence of water which was added deliberately. There was no effect of water at least up to 10^{-2} mol kg^{-1}.

Basic Equation for Treatment of Data. The presentation and analysis of the NMR results given below are based on theories and experimental procedures that have been extensively discussed in the literature.[2,10-12] For brevity we shall not describe these theories in detail, and we shall show only some basic equations for treatment of our data.

We interpret our data of line broadening and chemical shift using the formulas derived by Swift and Connick.[10] The solvent proton NMR line broadening caused by the paramagnetic species can be expressed as eq 1 where $\Delta\nu_{obsd}$ and $\Delta\nu_{solv}$ are the full widths at

$$\frac{1}{T_{2P}P_M} = \frac{\pi(\Delta\nu_{obsd} - \Delta\nu_{solv})}{P_M} \tag{1}$$

half-height of the solvent NMR spectra in the presence and absence, respectively, of the paramagnetic species, and P_M is the ratio of the concentration of solvent bound to the paramagnetic ion to the concentration of free solvent. The value of $(T_{2P}P_M)^{-1}$ depends on the solvent-exchange lifetime (τ_M), relaxation time of the coordinated solvent nucleus (T_{2M}), and the difference between the chemical shift of the coordinated proton and that of the solvent proton in the bulk diamagnetic environment ($\Delta\omega_M$)

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

where T_{2O} is the solvent nuclear relaxation time of molecules outside the first coordination sphere of the metal ion.[11] The observed chemical shift of the solvent proton resonance, defined as the resonance frequency observed for the bulk solvent in a solution containing the paramagnetic species minus the resonance frequency of the solvent, is given by eq 3.[10] The usual assumptions, i.e., slow passage, low radio frequency power level, and dilute solutions ($P_M \ll 1$), are made

$$\frac{\Delta\omega_{obsd}}{P_M} = \frac{-\Delta\omega_M}{(1 + \tau_M/T_{2M})^2 + (\tau_M\Delta\omega_M)^2} \tag{3}$$

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Table I. Solution Compositions

soln	$[Cu_2(OAc)_4]/m$	$[HOAc]/m$	$[CDCl_3]/m$	$[CD_2Cl_2]/m$	P_M	wt % of HOAc
A0	0	16.65			0	100
A1	2.50×10^{-2}	16.65			3.01×10^{-3}	100
A2	3.65×10^{-2}	16.65			4.40×10^{-3}	100
A3	6.75×10^{-2}	16.65			8.18×10^{-3}	100
A4	8.61×10^{-2}	16.65			1.05×10^{-2}	100
B0	0	7.93	4.35		0	47.6
B1	2.66×10^{-2}	7.93	4.35		6.75×10^{-3}	47.6
B2	4.31×10^{-2}	7.93	4.35		1.10×10^{-2}	47.6
B3	8.17×10^{-2}	7.93	4.35		2.11×10^{-2}	47.6
C0	0	3.99	6.31		0	24.1
C1	8.37×10^{-3}	3.99	6.31		4.19×10^{-3}	24.1
C2	1.92×10^{-2}	3.99	6.31		9.65×10^{-3}	24.1
C3	3.65×10^{-2}	3.99	6.31		1.85×10^{-2}	24.1
D0	0	1.62		10.4	0	9.8
D1	6.85×10^{-3}	1.62		10.4	8.48×10^{-3}	9.8
D2	1.30×10^{-2}	1.62		10.4	1.62×10^{-2}	9.8
D3	2.38×10^{-2}	1.62		10.4	3.01×10^{-2}	9.8
E0	0	0.72		11.0	0	4.3
E1	3.45×10^{-3}	0.72		11.0	9.64×10^{-3}	4.3
E2	5.45×10^{-3}	0.72		11.0	1.53×10^{-2}	4.3

in the derivation of eq 2 and 3. The temperature dependence of the individual terms is given by[13] eq 4–7.

$$\tau_M^{-1} = \frac{kT}{h} \exp\left(\frac{-\Delta H^\ddagger}{RT} + \frac{\Delta S^\ddagger}{R}\right) \tag{4}$$

$$T_{2M}^{-1} = \frac{C_M}{T} \exp(E_M/RT) \tag{5}$$

$$T_{2O}^{-1} = \frac{C_O}{T} \exp(E_O/RT) \tag{6}$$

$$\Delta\omega_M = -\frac{C_\omega}{T} \qquad (7)^{14}$$

Results

All data for line width T_{2P}^{-1} and chemical shift $\Delta\omega_{obsd}$ are given in supplementary material.

Acetic Acid Methyl Proton Exchange. The temperature dependencies of line width $(T_{2P}P_M)^{-1}$ for the HOAc methyl protons in acetic acid–inert solvent solutions of $Cu_2(OAc)_4$ are shown in Figures 1 and 2. P_M is given by eq 8 where

$$P_M = \frac{n[Cu_2(OAc)_4]}{[HOAc] - n[Cu_2(OAc)_4]} \tag{8}$$

$[Cu_2(OAc)_4]$ is the concentration of dimeric copper(II) acetate and n is the number of solvent molecules in the first coordination sphere of the complex. As evident from the composition of copper carboxylates in various solvents[15a] and the crystal structure of acetic acid adduct of dimeric copper acetate,[15b] n should be 2 instead of the previously assumed coordination number of 1.[16] Both line width and line shift are proportional to the concentration of $Cu_2(OAc)_4$. A least-squares best-fit treatment[17] of the line-broadening data gives the following parameters: values of $\Delta H^\ddagger$/kJ mol^{-1} and $\Delta S^\ddagger$/J mol^{-1} K^{-1} for sample solutions C, D, and E are 53 ± 4 and 13 ± 8, 51 ± 4 and 3 ± 8, and 53 ± 4 and 10 ± 8, respectively. The values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ were not very sensitive to variations in E_M, E_O, C_M, and C_O.[5] The difference of the activation parameters for chemical exchange in different solvents does not appear

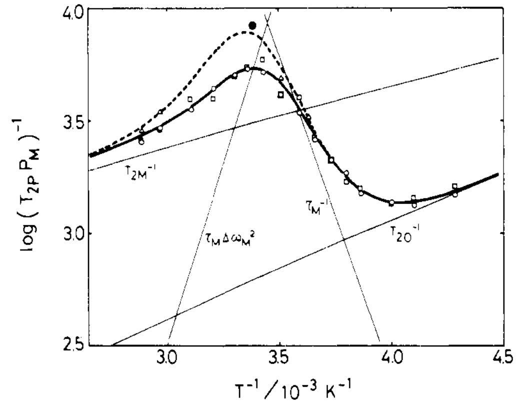

Figure 1. Temperature dependence of log $(T_{2P}P_M)^{-1}$ for the HOAc methyl protons in acetic acid–chloroform solutions (solution C) of $Cu_2(OAc)_4$. The solid curves are calculated with the parameters obtained: $\Delta H^\ddagger$ = 53 kJ mol^{-1}, $\Delta S^\ddagger$ = 13 J mol^{-1} K^{-1}, $C_M = 2.9 \times 10^5$ s^{-1} K, $E_M = 2.8 \times 10^3$ J mol^{-1}, $C_O = 1.6 \times 10^4$ s^{-1} K, $E_O = 6.0 \times 10^3$ J mol^{-1}, and $C_\omega = 2.5 \times 10^6$ rad s^{-1} K. ● represents data at 100 MHz. The dotted curve is calculated by using the value of C_ω at 100 MHz.

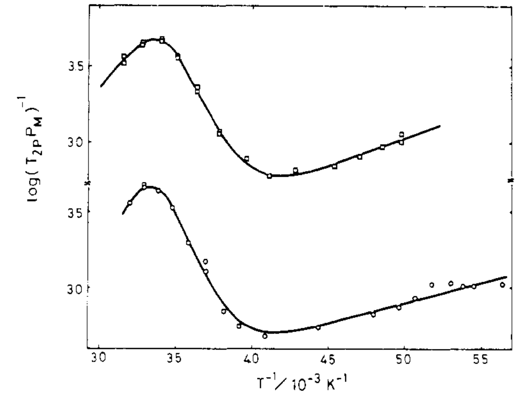

Figure 2. Temperature dependence of log $(T_{2P}P_M)^{-1}$ for the HOAc methyl protons in acetic acid–inert solvent solutions of $Cu_2(OAc)_4$: □, solution D; ○, solution E. The curves are calculated with the parameters obtained.

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(14) (a) Bloembergen[14b] gave the equation $\Delta\omega_M = -(A/\hbar)[\omega_O\mu_{eff}(S(S+1))^{1/2}/3\gamma_N kT]$, where the symbols have their usual meaning.[14c] The magnetic moment and the spin situation of copper(II) acetate have been thoroughly studied.[14d,e] In our experimental conditions, eq 7 is obtained by assuming that μ_{eff} is independent of temperature. μ_{eff} does not change with solvent.[14f] (b) Bloembergen, N. *J. Chem. Phys.* **1957**, *27*, 572. (c) Rusnak, L.; Jordan, R. B. *Inorg. Chem.* **1972**, *11*, 196. (d) Kato, M.; Jonassen, H. B.; Fanning, J. C. *Chem. Rev.* **1964**, *64*, 99. (e) Catterick, J.; Thornton, P. *Adv. Inorg. Chem. Radiochem.* **1977**, *20*, 291. (f) Kondo, M.; Kubo, M. *Bull. Chem. Soc. Jpn.* **1958**, *62*, 468.

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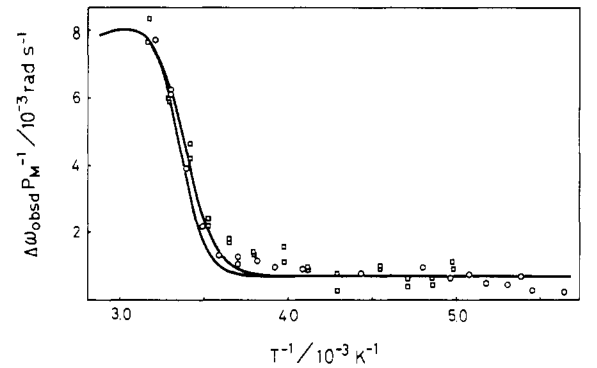

Figure 3. Temperature dependence of $\Delta\omega_{obsd}/P_M$ for the HOAc methyl protons in acetic acid–inert solvent solutions of $Cu_2(OAc)_4$. The curves are calculated with the parameters obtained from the data of line broadening: □, solution D; ○, solution E.

to exceed the experimental error. From various fits for the three sample solutions, it seems reasonable to conclude that the activation parameters for the methyl proton exchange are $k_{CH_3}(25\ °C) = (9.4 \pm 0.5) \times 10^3\ s^{-1}$, $\Delta H^{\ddagger} = 53 \pm 5$ kJ mol^{-1} and $\Delta S^{\ddagger} = 8 \pm 8$ J mol^{-1} K^{-1}. The NMR spectra of sample solution C at 22 °C were measured by a 100-MHz spectrometer. The value of $(T_{2P}P_M)^{-1}$ is in agreement with that calculated by using a value of C_ω equal to 100/60 times the C_ω at 60 MHz (dotted curve in Figure 1).

It may be noted that the contribution of T_{2O}^{-1} to the line width is smaller at lower concentrations of HOAc. T_{2O}^{-1} is given by eq 9[11,13] where ρ is the solvent density, S is the spin

$$T_{2O}^{-1} = \frac{(4.14 \times 10^{13})S(S+1)\rho}{d_0^3}\,\frac{[S]}{n}f_D(\tau_D) \qquad (9)$$

of the paramagnetic ion, d_0 is the average distance of closest approach of the nucleus in the second coordination sphere and the metal ion center, $f_D(\tau_D)$ is a function of the correlation time for the nuclear–electron interaction, and [S] is the concentration of the exchanging solvent. Actually $f_D(\tau_D)$ will vary with solvent composition if the viscosity changes. If the effect is neglected, the difference in values of T_{2O}^{-1} for different solvents is accounted for by [S]. At 4.5×10^{-3} K^{-1} (Figures 1 and 2), T_{2O}^{-1} is an approximately linear function of [HOAc] as expected from eq 9. The calculation of $f_D(\tau_D)$ with the assumption that $\rho = 1$ g cm^{-3}, $d_0 = 5$ Å, and $n = 2$, rather qualitative though it is, gives the correlation time of about 4×10^{-9} s.

The temperature dependences of line shift $\Delta\omega_{osbd}P_M^{-1}$ for the HOAc methyl protons are shown in Figure 3. At low temperature ($1000/T > 3.5$ K^{-1}), the exchange between coordination sphere and bulk acetic acid is too slow to shift the bulk peak, and only a very small shift is observed. In the intermediate part of Figure 3, the observed shift depends on the rate of exchange ($\Delta\omega_M$ and $1/\tau_M$ are of the same order of magnitude) and thus strongly on the temperature. At high temperature ($1000/T < 3$ K^{-1}), the methyl proton exchange is rapid, and a weighted average shift of solvated and bulk HOAc is obtained. The whole behavior is given by eq 3. The curves in Figure 3 are calculated from this equation with use of the same parameters as in the interpretation of the relaxation rates. In this calculation, the zero of the frequency-shift scale was adjusted to the average of the low-temperature observations. As seen from Figure 3, this adjustment is small (2 Hz) and hardly more than the accuracy of the measurements. Such a shift can be expected as it is of the order of magnitude of the shifts observed in solutions of diamagnetic compounds.[11,18]

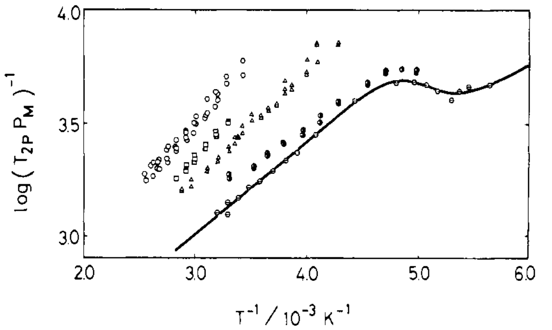

Figure 4. Temperature dependence of log $(T_{2P}P_M)^{-1}$ for the HOAc hydroxyl proton in acetic acid–inert solvent solutions of $Cu_2(OAc)_4$: ○, solution A; □, solution B; △ solution C; ▲, data at 100 MHz; ◑, solution D; ⊖, solution E. The curve for solution E is a theoretical curve calculated with the parameter obtained.

Table II. Kinetic Data for Solvent Exchange on Copper(II) Complexes

systems	k/s^{-1} (temp/°C)	$\Delta H^{\ddagger}$/ kJ mol^{-1}	$\Delta S^{\ddagger}$/ J mol^{-1} K^{-1}	ref
Cu^{2+}-methanol	10^8 (25)	42	55	*a*
	7.4×10^7 (25)	25	−11	19
Cu^{2+}-H_2O	5×10^9 (25)			19, *b*
$CuCR^{2+}$-H_2O[c]	2×10^4 (0)			14
$CuCR^{2+}$-DMF	5×10^4 (−60)			14
$Cu_2(OAc)_4$-HOAc (ethanol)	3.0×10^4 (25)	44.8	9.2	8
$Cu_2(OAc)_4$-HOAc ($CDCl_3$ or CD_2Cl_2)	$(9.4 \pm 0.5) \times 10^3$ (25)	53 ± 5	8 ± 8	this work

[a] Breivogel, F. W., Jr. *J. Chem. Phys.* **1969,** *51,* 445. [b] Lewis, W. B.; Alei, M., Jr.; Morgan, L. O. *Ibid.* **1966,** *44,* 2409. [c] See text.

Acetic Acid Hydroxyl Proton Exchange. The temperature dependence of $(T_{2P}P_M)^{-1}$ for the hydroxyl proton of acetic acid is shown in Figure 4. Here, we assume $n = 2$ (vide infra). The line width was proportional to the concentration of $Cu_2(OAc)_4$. No exchange effects were observed for sample solutions A, B, C, and D due to freezing of solvents at lower temperatures. It is apparent that the hydroxyl and methyl protons are exchanging at different rates. This is contrary to the result obtained in the ethanol–acetic acid mixture.[16] Chemical shifts are very small, and the values of line broadenings for measurements at 60 and 100 MHz at 22 °C are the same as those shown in Figure 4. Thus in the case $T_{2M}^{-2} \gg \Delta\omega_M^2$, eq 2 reduces to eq 10. The least-squares analysis[17]

$$(T_{2P}P_M)^{-1} = \frac{1}{T_{2M} + \tau_M} + \frac{1}{T_{2O}} \qquad (10)$$

of data for sample solution E is given as follows: $\Delta H^{\ddagger} = 38 \pm 8$ kJ mol^{-1}, $\Delta S^{\ddagger} = 13 \pm 10$ J mol^{-1} K^{-1}, $C_M = 2.4 \times 10^3$ s^{-1} K, $E_M = 9.7 \times 10^3$ J mol^{-1}, $C_O = 6.6 \times 10^4$ s^{-1} K, $E_O = 3.7 \times 10^3$ J mol^{-1}. The rate constant k_{OH} for the hydroxyl proton exchange is $(7.5 \pm 1) \times 10^6$ s^{-1} at 25 °C and $(4 \pm 1) \times 10^3$ s^{-1} at −70 °C.

Discussion

It should be noted that dilution of the exchanging solvent (HOAc) by inert solvent $CDCl_3$ and CD_2Cl_2 does not affect the exchange rate of methyl protons, that is, the exchange rate is independent of the concentration of HOAc, and that the exchange rate obtained here agrees with that obtained in acetic acid–ethanol mixtures (see Table II). The dielectric constants (25 °C) of $CHCl_3$ and CH_2Cl_2 are 4.7 and 9.1, respectively, which are similar to that of HOAc, while ethanol with potential of coordination has the dielectric constant of 24.3 at

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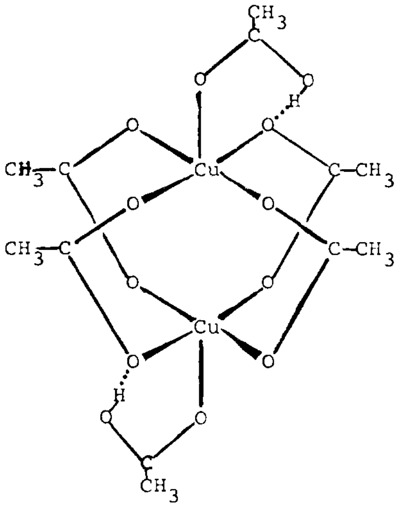
(18) Luz, Z. *J. Chem. Phys.* **1964,** *41,* 1756.

25 °C. We observed no effect of the variation of dielectric constant.

Poupko and Luz[19] have pointed out that since there is fast intramolecular inversion of the distorted axis of solvato copper(II), only weighted averaged parameters over the axial and equatorial solvent molecules are obtained for the exchange of solvation shell molecules of aqueous $Cu(ClO_4)_2$ solutions. Rusnak and Jordan[13] have estimated a lower limit of the rate constants for solvent exchange on the (2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaene)copper(II) complex ($CuCR^{2+}$) in water and *N*,*N*-dimethylformamide (DMF) from ^1H NMR line-broadening effects. Such solvent-exchange rates reported are very fast compared to that of $Cu_2(OAc)_4$ (see Table II).

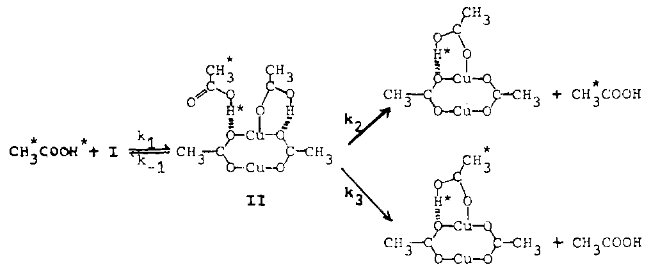
According to Grasdalen, in ethanol slution the axial ethanol molecule on the dimeric copper acetate is readily replaced by acetic acid.[16] This is contrary to the prediction based on the difference in the basicity between acetic acid and ethanol: the latter is much more basic than the former. Moreover, in the NMR spectra of solvents for solutions of dimeric copper acetate involving ethanol and acetic acid, the ethanol signals are the same as those of pure ethanol while the HOAc signals are very broad and shifted. These facts point to a strong interaction of HOAc with the copper species present. The geometry should thus favor the coordination of acetic acid by an extra hydrogen bonding with the bridging acetate as in I.[15b,16]



I

According to the study of intermolecular hydrogen bonding in acetic acid by means of ultrasonic absorption measurements,[20,21] the free energy for one hydrogen bond is ca. 13 kJ mol^{-1}. The hydrogen bonding as seen in I appears to account for the unexpectedly slow exchange rate of acetic acid in dimeric copper acetate. Therefore, we conclude that the rate-determining step for the methyl proton exchange, i.e., the acetic acid exchange, is the cleavage of the copper–oxygen bond at the axial site in the preequilibrium of the dissociation of the hydrogen bond between the hydroxyl group of acetic acid on the axial site and one of the carboxyl oxygens of the dimer acetate bridges.

Scheme I



The fact that the hydroxyl and methyl protons are exchanging at different rates indicates that the hydroxyl proton does not exchange with the whole acetic acid molecule. The hydroxyl proton can exchange by proton dissociation from coordinated acetic acid as in I or possibly by protonation (eq 11) with the oxygen of bridged acetates (where O< represents

$$CH_3CO_2H_2^+ + O< \rightleftharpoons CH_3CO_2H + {}^+HO< \qquad (11)$$

one of the oxygens of bridged acetates in dimeric copper(II) acetate). If proton exchange occurs by reaction 11, then $(T_{2P}P_M)^{-1}$ should show a first-order dependence on hydrogen ion concentration. In this system the experiment could not be performed in the presence of the strong acid such as $HClO_4$ because of decomposition of dimeric copper(II) acetate by the addition of $HClO_4$. The solvent is weakly dissociated:

$$2HOAc \overset{K_i}{\rightleftharpoons} AcOH_2^+ + AcO^-$$

where $K_i = [AcOH_2^+][AcO^-] = 10^{-14.45}$ at 25 °C.[22] With this assumption and the rate constant determined from the NMR line broadening, a value of the rate constant for reaction is calculated to be $\sim 10^{13.5}\ m^{-1}\ s^{-1}$, which is too large to be reasonable from the standpoint of diffusion-controlled rate.

The fast hydroxyl proton exchange by direct proton dissociation from coordinated acetic acid is unreasonable because of existence of hydrogen bonding as described above. A mechanism which does seem to be consistent with the observations is described by Scheme I where II is an assumed structure of a dimeric copper(II) acetate molecule (only two bridges shown) with one axial HOAc solvent and one hydrogen-bonding HOAc. In this case, the rate of incorporation and dissociation of bulk solvent at the bridged oxygen is assumed to be very fast. Since an axial HOAc molecule may rotate readily around the Cu–O axis, the hydroxyl proton of the axial HOAc collides with protons of hydrogen-bonding HOAc. The hydroxyl proton exchange will be controlled by the k_2 path in Scheme I. The k_3 path in Scheme I corresponds to the methyl proton exchange described above.

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Registry No. $Cu_2(OAc)_4$, 23686-23-9.

Supplementary Material Available: A table of proton line broadening and proton chemical shifts for $Cu_2(OAc)_4$ in acetic acid and in mixtures with inert solvents (3 pages). Ordering information is given on any current masthead page.

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