

intensity involving these contributions will be for the $\Delta M_J = 0$ transition to the $E_{1/2}$ level of ${}^2\Pi_g$. The x -polarized intensity previously described to one orbital component of ${}^2\Delta_g$ satisfies the selection rule $\Delta M_J = \pm 2$, but is quite weak.

In summary, the largest vibronic intensity found for the ${}^2\Sigma_g^+ \rightarrow {}^2\Delta_g$ transition involves spin-orbit borrowing from the relatively strong z -polarized vibronic ${}^2\Sigma_g^+ \rightarrow {}^2\Pi_g$ transition induced by coupling to the degenerate bending mode. The computed value is smaller than the experimental value by a factor of 50, which may reflect either inaccuracies in the wave functions or an overlapping of absorption transitions to ${}^2\Pi_g$ and ${}^2\Delta_g$. Extension of the spectral studies to energies less than 0.5 eV to look for the ${}^2\Pi_g$ state is highly desirable.

Finally, it is not surprising that the vibronic moments are more sensitive than the CT moments to the difference between the Cl(3P) and Cu(3d) Coulomb integrals,

for this difference largely determines the energy denominators to the CT states from which the intensity is "borrowed" in the Herzberg-Teller description.²³ It should be noted, however, that our procedure⁴ works directly with adiabatic wave functions, thus avoiding the necessity of expanding the wave function for the distorted molecule on the basis of both odd- and even-parity states of the $D_{\infty h}$ molecule.²⁴

Acknowledgment.—The author wishes to thank Mr. Gary Simons for assistance with the computations.

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(24) NOTE ADDED IN PROOF.—The bending frequencies (ν_2) have recently been observed for $MnCl_2$, $FeCl_2$, $CoCl_2$, and $NiCl_2$ in matrix isolation ir experiments (K. R. Thompson and K. D. Carlson, *J. Chem. Phys.*, in press). The values range from 83 to 95 cm^{-1} , comparable to our calculated value of 93 cm^{-1} for $CuCl_2$, but definitely greater than the 49 to 51 cm^{-1} values assumed for all five dichlorides in a fit of thermodynamic properties (L. Brewer, G. R. Somayajulu, and E. Brackett, *Chem. Rev.*, **63**, 111 (1963)).

CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF MONTANA STATE UNIVERSITY, BOZEMAN, MONTANA 59715

The Chemical Form of Copper(II) Acetate in Acetic Acid Solutions

By ANDREW T. A. CHENG AND REED A. HOWALD¹

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Potentiometric measurements with glass and copper electrodes in dry and wet acetic acid solutions, together with the corresponding spectrophotometric data, show that copper(II) acetate is predominantly dimeric in dry acetic acid solutions. The dissociation constant of the dimer increases as water is added, reaching $(6 \pm 3) \times 10^{-4}$ at 3 M H_2O . The dimer has an absorption maximum at 670 $m\mu$ with a molar absorptivity of 97.5 ± 2.5 , while the monomer absorbs around 740 $m\mu$ with $\epsilon_{740} - \epsilon_{500} = 39 \pm 3$. The equation $\log K = -5.0 + 4 \log C_{H_2O}$ fits the data within experimental error over the range from 3 to 10 M H_2O .

Following the determination of the crystal structure of $Cu_2(CH_3COO)_4 \cdot 2H_2O$ ² showing the presence of dimeric species with a Cu-Cu distance of 2.64 Å, there has been widespread interest in the chemical form of copper (II) acetate in solution.³⁻⁵ It is clear from data on magnetic moment,⁴ freezing points,⁴ and distribution between phases⁵ that the copper acetate dimers persist in solutions in dioxane and chloroform. However these studies have left the chemical form of copper acetate in solvents whose coordinating ability is greater than that of dioxane but less than that of water open to question.

The most definitive previous data on acetic acid solutions give the value of $K = 10^{-4}$ for the monomer-dimer equilibrium obtained from kinetic data.⁷ This value is

however inconsistent with the fact that Beer's law is followed for solutions in this region of concentrations.⁸ This work was undertaken to clarify this situation. When the spectrophotometric data alone were found not to be sufficiently decisive, the study was extended to include potentiometric measurements.

The glass electrode gives quite reliable readings in "basic" acetic acid solutions.⁹ The voltage of a copper electrode measured against the glass electrode should be given by the equation¹⁰

$$E = E^\circ - (0.05916/n) \log (C_{CuAc_2} \gamma_{CuAc_2} / a_{HAc}^2)$$

Even with considerable uncertainty in the activity coefficients it should be easy to distinguish between the values of 4 and 2 for n , appropriate for the dimer and monomer, respectively. If the dimeric form predominates, the equation assumes the form

$$E = E^\circ - (0.05916/4) \log (C_{Cu_2Ac_4} \gamma_{Cu_2Ac_4} / a_{HAc}^4)$$

(1) Inquiries should be directed to this author at Montana State University.

(2) J. N. van Niekerk and F. R. L. Schoening, *Acta Crystallogr.*, **6**, 227 (1953).

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(7) J. K. Kochi and R. V. Subramanian, *Inorg. Chem.*, **4**, 1527 (1965).

(8) R. P. Eswein, E. S. Howald, R. A. Howald, and D. P. Keeton, *J. Inorg. Nucl. Chem.*, **29**, 437 (1967).

(9) A. T. Cheug, R. A. Howald, and D. L. Miller, *J. Phys. Chem.*, **67**, 1601 (1963).

(10) Throughout this paper the symbol Ac is used to represent acetate, CH_3COO , and not acetyl.

Experimental Section

Our experiments have been done with a Beckman spectrophotometer, Model DK-2. The absorbances due to both copper acetate and water were automatically recorded in each run. The sealed spectrophotometer cells used have been described earlier.⁸

The potential measurements were made with a John Fluke Mfg. Co. dc differential voltmeter, Model 881-A. This voltmeter was much superior to the pH meters used earlier⁹ in that even with the glass electrode one can easily obtain readings to tenths of 1 mV. When three electrodes were used, measurements were made comparing both of the other electrodes to the copper electrode. However, all of the measurements reported in this paper are for a particular Beckman general-purpose glass electrode *vs.* copper electrodes constructed from 20-gauge copper wire. All electrodes used were placed in the titration cell constructed with a 100-ml flask fitted with five long necks as used in the previous work⁹ except that a stream of nitrogen was introduced at the bottom of the flask both displacing air and stirring the solution. Stirring was discontinued for each reading. The titration cell was immersed in a water bath adjusted to 25°.

In the course of trying a mercury-mercurous acetate electrode as a third electrode, we rediscovered that a thin layer of Hg on the Cu wire improves the reproducibility of a Cu electrode.¹¹ Such amalgamated copper electrodes were used in the potentiometric titrations reported here.

The potential measurements were performed in series, adding successive portions of water or copper acetate solutions to the solution in the titration cell. Portions of sample were pipetted into the spectrophotometric cells at the beginning and end of each series to determine or check the copper acetate and water concentrations.

Two kinds of saturated solutions were prepared: one by adding a known amount of CuAc₂ solution in water to glacial acetic acid and the other by adding excess solid CuAc₂·H₂O (Baker and Adamson, reagent) into a series of 50-ml volumetric flasks containing glacial acetic acid mixed with various measured amounts of water. In all cases these solutions stood at least 24 hr with intermittent shaking for equilibration, and for the titrated samples this was done in a water bath at 25°. The supernatant liquids of the saturated solutions were pipetted into the spectrophotometric cells and into the titration cell for potentiometric titrations with HClO₄ in acetic acid. The perchloric acid had been standardized against sodium carbonate. These titrations introduced considerable acid errors and drifts in the glass electrode; however, they were all performed after the main series of potentiometric readings.

Copper acetate is not a strong enough base for a direct titration with perchloric acid in glacial acetic acid. The addition of acetonitrile has been suggested,¹² but this alone was not enough. In order to get sharper end points in the titrations, an excess measured amount of LiCl was added partially to convert CuAc₂ into LiAc, which is a stronger base. When 5.00 ml of a dry, saturated solution was treated with 5 ml of 0.10 M LiCl and 1 ml of acetonitrile before titration, the voltage changed by over 30 mV/0.10 ml of 0.1420 M HClO₄ near the end point. The potential break at the end point with the saturated solution 6.74 M in H₂O was only about half this large, but the equivalence point was still clear.

Results

The potential of the copper electrode *vs.* the glass electrode varies with the concentrations of both copper and water. In general, the potential increases when water is added, and the increase is largest at low copper acetate concentrations. Fortunately the potential does not change more than a few millivolts over the range 0–1 M H₂O even for dilute solutions, and one can

group all of the readings for relatively dry solutions to show the copper acetate dependence. Thus Figure 1 shows the results over the range from 0.0 to 0.30 M H₂O.

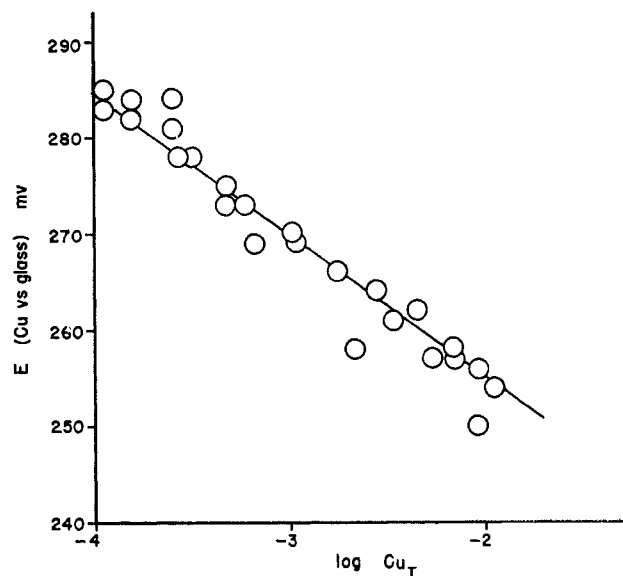


Figure 1.—Potential of glass *vs.* Cu electrodes in dry acetic acid solutions as a function of the copper acetate concentration. The solid line is drawn with a slope of 14.8 corresponding to $n = 4$.

These data show a scatter of the order of the ± 5 mV expected from our earlier work with the glass electrode.⁹ They are well fitted by a straight line with a slope of 16 ± 2 mV, and the line shown with the theoretical slope for copper acetate dimer ($n = 4$, slope of 14.8 mV) is an entirely adequate representation of the data.

Thus copper acetate exists as dimeric molecules in nearly dry acetic acid solutions. Wet solutions, 4–8 M H₂O, show more variation of the potential with the concentration of copper acetate, as expected for solutions containing both monomer and dimer.

The Effect of Water on the Dimer.—For solutions where the dimer is the predominant species the equation

$$E = 221.1 - 14.8 \log (C_d \gamma_d / a_{\text{HAc}}^4)$$

can be approximated by

$$14.8 \log (\gamma_d / a_{\text{HAc}}^4) = 225.6 - E - 14.8 \log C_t$$

where the subscripts "d" and "t" stand for dimer and total copper, respectively. Figure 2 shows a plot of $(225.6 - E - 14.8 \log C_t)$ *vs.* the molarity of H₂O from measured potentials at fairly high copper concentrations; $C_t = 0.006$ – 0.012 M.

The line through the points in Figure 2 gives a value of 0.326 for $\gamma_d / a_{\text{HAc}}^4$ at 6 M H₂O. Since the activity of acetic acid at this water concentration is about 0.788,¹³ the activity coefficient of the dimer (referred to dimer in pure acetic acid) is 0.125. Thus the addition of water stabilizes the dimer to some extent. In fact, at 6 M H₂O the dimer is probably predominantly Cu₂Ac₄.

(11) R. F. Nielsen and D. J. Brown, *J. Amer. Chem. Soc.*, **49**, 2423 (1927).
 (12) A. K. Holliday and A. G. Massey, "Inorganic Chemistry in Non-Aqueous Solvents," Pergamon Press Ltd., Oxford, 1965.

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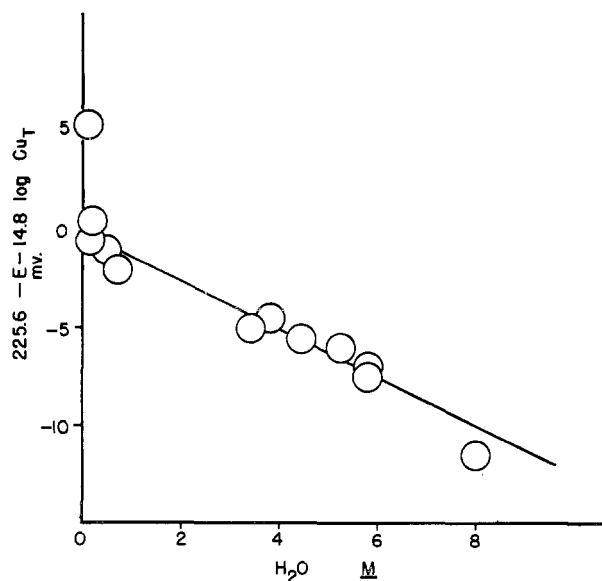


Figure 2.—Corrected potential vs. water concentration in acetic acid.

$2\text{H}_2\text{O}$. However the dimer is not stabilized by coordination to water nearly as much as the monomer where the coordination can occur in two of the four main square-planar positions. There is no compelling evidence either from the potentiometric data of Figure 2 or from the spectra to treat the hydration of the dimer as anything more than a medium effect; *i.e.*, one can formulate it as Cu_2Ac_4 regardless of the species coordinated at the two free axial positions.

There is some additional evidence on the effect of water on the dimer molecules from the solubility of $\text{Cu}_2\text{Ac}_4 \cdot 2\text{H}_2\text{O}$ crystals. There is a minimum in the solubility around 3–4 M H_2O so pronounced that supersaturated solutions are easily prepared by adding either H_2O or acetic acid to moderately concentrated solutions of copper acetate in the other solvent. Solid $\text{Cu}_2\text{Ac}_4 \cdot 2\text{HAc}$ is in equilibrium with dry, saturated solutions,¹⁴ but $\text{Cu}_2\text{Ac}_4 \cdot 2\text{H}_2\text{O}$ crystals form over the whole range from wet acetic acid to pure water.

Table I summarizes the experimental data on a series of saturated solutions. As explained below the absorbance at 670 $m\mu$ is due predominantly to the dimer present. The formulation of the equilibrium as $\text{Cu}_2\text{Ac}_4 \cdot 2\text{H}_2\text{O}(c) = \text{Cu}_2\text{Ac}_4 \cdot n\text{H}_2\text{O} + (2 - n)\text{H}_2\text{O}$ suggests that the dimer concentration should decrease first and then stay relatively constant as H_2O is added. The absorbance data in Table I abundantly confirm this expectation. Above 4 M H_2O the total copper acetate concentration is increasing as is shown by the titrimetric results, and this is clearly due to the increasing amounts of monomer present.

The calculations on the monomer–dimer equilibrium below are based on the assumption that the spectrum of the dimer is not affected by its degree of hydration. The spectra of the dimer in benzene and CHCl_3 with various axial ligands^{5,15} indicate that this is not an unreasonable assumption.

(14) A. W. Davidson and E. Griswold, *J. Amer. Chem. Soc.*, **53**, 1341 (1931); **57**, 423 (1935); W. H. McAllister, *ibid.*, **52**, 507 (1930).

(15) D. P. Graddon and R. A. Schulz, *Aust. J. Chem.*, **18**, 1731 (1965).

TABLE I
SOLUBILITY OF COPPER ACETATE^a

[H ₂ O], M	<i>a</i> ₆₇₀ - <i>a</i> ₈₀₀	<i>C</i> _t from		<i>a</i> ₆₇₀ - <i>a</i> ₈₀₀	<i>C</i> _t from
		titration, M	[H ₂ O], M		
0.1	7.0	0.037	3.8	1.53, 1.47	
1.0	2.76		3.9	1.55, 1.42	
1.2	2.74		4.0	1.46, 1.42	
1.7	2.09, 1.94		5.3	1.59	0.015
1.8	2.16, 1.96	0.016	6.7	1.70	
3.2	1.49, 1.42		9.2	1.92	0.025
3.6	1.39	0.011			

^a Data are given for acetic acid solutions containing various amounts of water and saturated with copper acetate at room temperature or 25°. The symbol a_λ represents absorbance at the wavelength λ . The absorption peak of the copper acetate dimer is at 670 $m\mu$. C_t is defined in the text as the concentration of copper acetate calculated as the monomer.

The Spectrum of the Monomer.—The copper acetate dimer in dry acetic acid has a maximum at 670 $m\mu$ with a molar absorptivity of about 97.5 ± 2.5 . This corresponds to a value of 195 ± 5 per mole of copper.^{8,16} The monomer has a peak in the same neighborhood, about 740 $m\mu$, but with a much lower molar absorptivity. This accounts for the phenomenal effects of water and lithium acetate on the molar absorptivity of copper acetate reported earlier.⁸ It also permits the simple calculation of the dissociation constants for the dimer as described below.

Unfortunately, it also makes it quite difficult to observe the spectrum of the monomer. For the absorbances of monomer and dimer to be approximately equal it is necessary to have a 10-fold excess of monomer, and this is not attainable even at 8 M H_2O except in solutions so dilute that the absorbance is not accurately measurable.

For this reason the most accurate data on the spectrum of the monomer come from aqueous solutions. The first and second ionization constants of copper acetate have been widely studied^{17–19} in aqueous solution. The equilibrium constant for the reaction $\text{CuAc}^+ = \text{Cu}^{2+} + \text{Ac}^-$, K_1 , is 0.0057 increasing to 0.019 at an ionic strength of 0.20. K_2 , the equilibrium constant for $\text{CuAc}_2 = \text{CuAc}^+ + \text{Ac}^-$, is not known so accurately, but the limiting value is close to 0.04. In calculating the fraction of the copper in each of the three forms, we have used these values (0.0057 and 0.040) together with activity coefficients from the Debye–Hückel limiting law. Since the ionic strength depends on the calculated concentrations, a successive approximation type of calculation was required. In this way we constructed a table of equilibrium concentrations of Cu^{2+} , CuAc^+ , and CuAc_2 with which it was a simple matter to

(16) This value has been revised down slightly in the light of additional data from that reported in our earlier publication.⁸

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(18) L. G. Sillén and A. E. Martell, "Stability Constants of Metal Ion Complexes," Special Publication No. 17, The Chemical Society, London, 1964.

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interpolate to fit each experimental total copper concentration.

For each experimental aqueous copper acetate solution we measured the absorbance at 750 $m\mu$ minus that at 500 $m\mu$, automatically correcting in this way for errors in setting 100% transmission. We then subtracted the absorbance due to Cu^{2+} using the concentration from the table and a value of $\epsilon_{750} - \epsilon_{500}$ for Cu^{2+} of 11.3 obtained with the same spectrophotometer on copper nitrate solutions. Dividing the remaining absorbance by the total concentration of CuAc^+ and CuAc_2 gives a mean molar absorptivity, $\bar{\epsilon}$, which is shown in Figure 3 plotted against the fraction as CuAc_2 . There is considerable scatter for dilute solutions where the absorbance is small and the correction for Cu^{2+} is substantial, but the intercepts are close to 24 and 40.

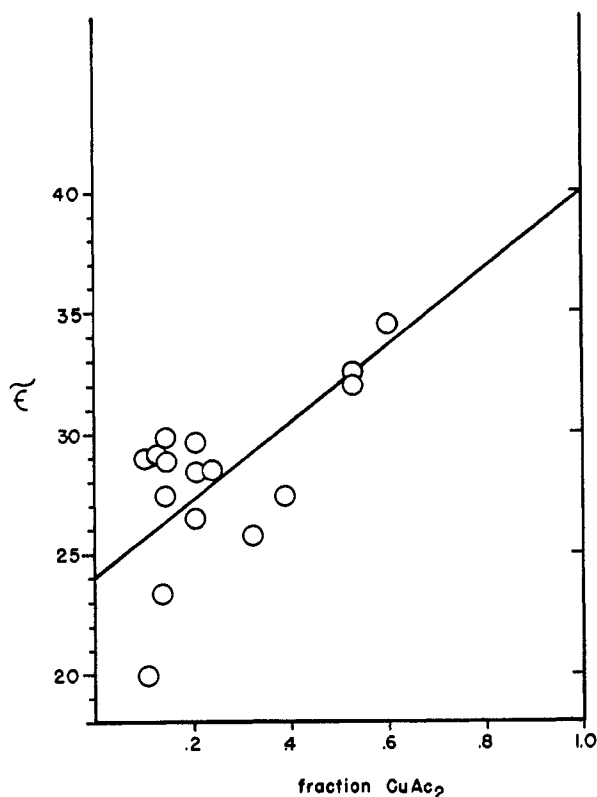


Figure 3.— $\bar{\epsilon}$ for mixtures of CuAc^+ and CuAc_2 in aqueous solutions.

To test the sensitivity of the calculation to the value assumed for K_2 the calculations were repeated with $K_2 = 0.03$. This gave intercepts of 23 and 38. In either case $\epsilon_{750} - \epsilon_{500}$ for CuAc_2 is adequately represented as 39 ± 3 . Both CuAc^+ and CuAc_2 have maxima near 750 $m\mu$ and somewhat smaller absorbance at 670 $m\mu$. From the peak shapes for aqueous copper acetate solutions one obtains the value 31 ± 3 for $\epsilon_{670} - \epsilon_{500}$ for the species CuAc_2 . Table II summarizes the spectral data for the full range of copper species from Cu^{2+} to Cu_2Ac_4 .

The Monomer-Dimer Equilibrium.—The Cu vs. glass potentiometric data provide a reasonable estimate of the equilibrium constant for dimerization,

TABLE II
SUMMARY OF SPECTRA

Species	$\lambda_{\text{max}}, m\mu$	$\epsilon_{\lambda} - \epsilon_{500}$
Cu^{2+}	800	11.3
CuAc^+	750	24 ± 3
CuAc_2	740	39 ± 3
Cu_2Ac_4	670	95

$K_d = C_m^2/C_d$. If $\gamma_d/a_{\text{HAc}^0}$ is taken from Figure 2, the equation

$$E = 221.1 - 14.8 \log (C_d \gamma_d / a_{\text{HAc}^0})$$

can be solved to give C_d . The monomer concentration, C_m , can then be obtained by difference, and a value can be calculated for K_d . Two particular dilute copper acetate solutions of about 4.4 M water content gave K values of 4.6×10^{-4} and 2.3×10^{-3} . Thus K_d at 4.4 M H_2O is of the order of magnitude of 10^{-3} , but unfortunately an uncertainty of ± 5 mV in E corresponds to an uncertainty of a factor of about 5 in K_d .

With the DK2 spectrophotometer the apparent molar absorptivities of copper acetate solutions are reproducible within about $\pm 5\%$ over a wide range of conditions. Assuming that the only important copper species present are the monomer and dimer, the molar absorptivity gives directly the fraction present as the monomer, $x = (190 - \bar{\epsilon}) / (190 - 31)$. Then the equilibrium constant, K_d , is given by $2x^2 C_t / (1 - x)$.

Values of K_d calculated in this way from the molar absorptivity are plotted against the water concentration in Figure 4. The values are most accurate for solutions with a substantial fraction of the copper in both forms, $\bar{\epsilon}$ between 70 and 150. These values are shown with circles in Figure 4. The rest of the data (triangles in Figure 4) show even wider scatter including a lot of small and negative values for drier solutions which cannot be shown on the logarithmic scale of Figure 4. The data are reasonably well fitted by the line $\log K_d = -4 + 0.29 C_{\text{H}_2\text{O}}$ above 3 M H_2O . There is a suggestion of curvature, and there is an equally good fit by the line $\log K_d = -5.0 + 4.0 \log C_{\text{H}_2\text{O}}$. This function is shown as the dotted line in Figure 4. A fourth power dependence of K_d on $C_{\text{H}_2\text{O}}$ is consistent with the formulation of the equilibrium as $\text{Cu}_2\text{Ac}_4 + 4\text{H}_2\text{O} = 2\text{CuAc}_2 \cdot 2\text{H}_2\text{O}$, which agrees with the idea that the axial ligands are relatively unimportant.

Our earlier work shows a spectral shift corresponding to increased dissociation on heating copper acetate solutions to about 55° . The best value from these data is $K = 1.3 \times 10^{-3}$ at 3.3 M H_2O and 54° . This lies within the scatter of the points for 25° , so the temperature dependence of the equilibrium is not large. We can easily conclude that ΔH for dissociation of the dimer is positive, but less than 5 kcal/mol.

Dissociation of the Dimer in Dry Solutions.—The points in Figure 4 show too much curvature for a reliable extrapolation to 0.0 M H_2O . Since Beer's law is followed in dry copper acetate solutions, it is clear that K for dissociation of the dimer must be quite small. Table III summarizes Keeton's data on dry dilute solutions, giving an average of 189 with a standard deviation

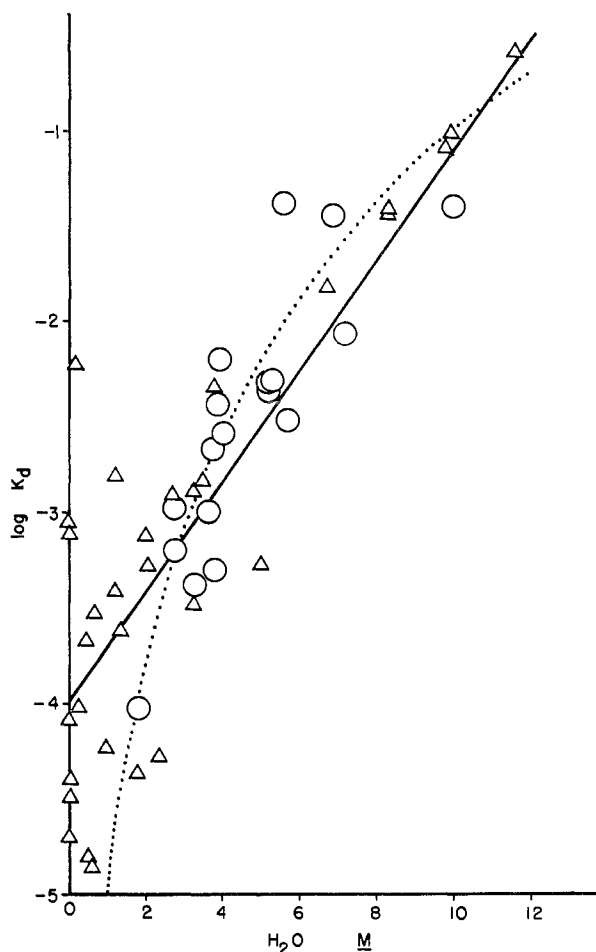


Figure 4.—Dissociation constant of the dimer as a function of the water concentration in acetic acid.

TABLE III

ABSORBANCE OF DRY DILUTE COPPER ACETATE SOLUTIONS^a

C_t, M	$a_{670} - a_{500}$	$\bar{\epsilon} = (a_{670} - a_{500})/C_t$
0.00040	0.073	183
0.00040	0.077	192
0.00067	0.128	192

^a This is a test of Beer's law at low concentrations of copper acetate in dry acetic acid solutions. Data for more concentrated solutions give the value $\bar{\epsilon} = 190 \pm 5$ when the concentration of the monomer is negligible.

tion of 5 for $\epsilon_{670} - \epsilon_{500}$. The lowest possible value consistent with these data is about 179, which corresponds to a maximum value for K of 4×10^{-6} at room temperature. It is likely that K is of the order of 10^{-8} or even smaller in dry acetic acid.

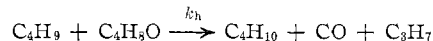
Comparison with the Data of Kochi and Subramanian.—The data reported above are inconsistent with the values reported by Kochi and Subramanian⁷ in at least three major points. In the first place their values for the dissociation constant are considerably larger than ours at least in fairly dry solutions. Also they report a much larger temperature dependence ($\Delta H = 12$ kcal/mol) and a much smaller effect of added water (little change out to 1.6 M H_2O). We can only conclude that they have measured something other than the monomer-dimer equilibrium for copper acetate.

Kochi and Subramanian have based their analysis on

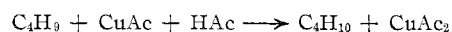
the assumption that butene is formed only by the reaction



which is in competition with hydrogen abstraction from butyraldehyde or some similar solute



The Cu(I) species is an important chain-carrying intermediate, and the inclusion of a step such as



provides an alternative explanation for their observed dependence of the $C_4H_8:C_4H_{10}$ ratio on the copper acetate concentration. There is no necessity for the assumption that the dimer Cu_2Ac_4 does not react with alkyl free radicals. In fact, since k_h/k_e varies by less than a factor of 4 over the range from 0 to 64 mol % H_2O ,⁷ the dimer must be almost as good a catalyst as the monomer.

Salt Effects on Dimerization.—Both coordinating ability and polarity of the solution are important in shifting the copper acetate equilibrium toward the monomer. This is particularly apparent in the effect of lithium perchlorate on the spectra as shown in Table IV. Lithium perchlorate has practically no effect on

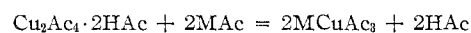
TABLE IV
DISSOCIATION OF THE COPPER ACETATE DIMER
IN THE PRESENCE OF LITHIUM PERCHLORATE

C_t, M	$\bar{\epsilon}$	K_d^a	$[LiClO_4], M$	$[H_2O], M$
0.0040	179	4.2×10^{-5}	0.198	0.09
0.00394	143	9.8×10^{-4}	0.195	1.04
0.00388	109	4.1×10^{-4}	0.192	2.00
0.00394	137	1.3×10^{-3}	0.606	0.82
0.00387	85	9.9×10^{-3}	0.596	1.92
0.00375	48	5.6×10^{-2}	0.577	3.74

^a Dissociation constant for the dimer at room temperature calculated from the measured absorbance.

the spectrum of dry copper acetate solutions. However, if there is some water present to serve as a ligand in the monomer, the effect of lithium perchlorate can be very profound. At 3.74 M H_2O and 0.58 M $LiClO_4$ the absorption maximum is at about 700 $m\mu$ with $\epsilon_{700} - \epsilon_{500}$ of only 48. Apparently in this solution one has over 90% monomer, and the observed spectrum is entirely compatible with that for aqueous monomer as calculated above with some contribution from the 670- $m\mu$ peak.

The acetate ion, as in lithium acetate, can apparently serve both as a ligand and as a polarity increaser. The solubility equilibria of Davidson and Griswold¹⁴ should apparently be reformulated as



but, without additional spectrophotometric data on the solutions, one cannot tell how much copper acetate has dissolved as the dimer.

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Elaine S. Howald and David P. Keeton for permission to include some of their spectrophotometric data in this paper.

CONTRIBUTION FROM THE CENTRAL RESEARCH DEPARTMENT,
MONSANTO COMPANY, ST. LOUIS, MISSOURI 63166

Redistribution Equilibria on Dimethylsilicon

By KURT MOEDRITZER AND JOHN R. VAN WAZER

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Equilibrium constants are reported for the exchange on the dimethylsilicon moiety of the substituent pairs halogen or pseudo-halogen *vs.* phenoxy, aceto, methylthio, or dimethylamino groups and of methylthio *vs.* aceto groups. These constants are included in a general tabulation of the random *vs.* nonrandom character of pairs of exchangeable substituents on the dimethylsilicon moiety.

Equilibria involving exchange of pairs of monofunctional substituents on the dimethylsilicon moiety have been studied quite extensively.¹ Owing to the ready availability of derivatives of dimethylsilane and the simple equilibrium involved, exchange reactions on the dimethylsilicon moiety have served as a test case for determining the deviations from randomness in the scrambling of a given pair of substituents. Such studies are noteworthy since as a general rule^{1,2} the random or nonrandom behavior of a given pair of substituents is independent to a first order of the central moiety. This allows extrapolation of the results obtained on dimethylsilicon to other central moieties. Therefore the study of the exchange equilibria of as many pairs of substituents as possible on any one kind of central moiety is desirable. The present paper reports additional equilibrium constants for dimethylsilicon systems involving the exchange of halogens or pseudohalogens with phenoxy, aceto, methylthio, or dimethylamino groups and of methylthio with aceto groups.

Experimental Part

Materials.—Dimethyldichlorosilane was purchased from Peninsular ChemResearch Inc., Gainesville, Fla., and redistilled before use. Dimethyldibromosilane,³ dimethyldiphenoxysilane,⁴ diacetodimethylsilane,⁵ dimethyldi(methylthio)silane,⁶ dimethylbis(dimethylamino)silane,⁷ dicyanodimethylsilane,⁸ and diisocyanatodimethylsilane⁹ were prepared according to methods of the literature.

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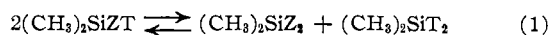
Procedures and Data Treatment.—The experimental procedures for obtaining the equilibrium data and the calculations of the equilibrium constants were the same as described previously.⁸ Proton nuclear magnetic resonance (nmr) chemical shifts of the compounds as seen at equilibrium are presented in Table I, for which the parameter *R* is closest to unity. The shifts are reported to the third decimal place only to show the kind of resolution found for each system. Changes in the over-all composition as denoted by *R* led to shift changes in the range of 0.05 ppm. The conditions for reaching equilibrium are listed in Table II showing the equilibrium constants.

In addition to the systems described in this paper several other pairs of dimethylsilane derivatives were investigated, the evaluation of which however had to be abandoned owing to extensive side reactions occurring at the temperatures required for equilibration. These are the systems: (CH₃)₂Si(OCH₃)₂ *vs.* (CH₃)₂Si(OOCCH₃)₂ (apparent equilibrium reached after 25 days at 120°); (CH₃)₂Si(NCO)₂ *vs.* (CH₃)₂Si[N(CH₃)₂]₂ (apparent equilibrium reached after 90 hr at 120°); (CH₃)₂Si[N(CH₃)₂]₂ *vs.* (CH₃)₂Si(OOCCH₃)₂ (apparent equilibrium reached after 17 days at 120°; solid reaction products were formed in some of the samples); (CH₃)₂Si(CN)₂ *vs.* (CH₃)₂Si(OCH₃)₂ (apparent equilibrium reached after 21 days at 120°; solid reaction products were formed in some of the samples).

For the systems (CH₃)₂Si(SCH₃)₂ *vs.* (CH₃)₂Si(NCO)₂ and (CH₃)₂Si(CN)₂ *vs.* (CH₃)₂Si[N(CH₃)₂]₂ fairly good equilibrium data could be obtained. However, in the first system, the material balance was off by more than 15% owing to unknown reasons and some of the samples of the second system had decomposed before equilibrium was reached. Therefore these data are not presented in this paper although they were used for an estimate of the respective equilibrium constants.

Results and Discussion

Redistribution equilibria in systems (CH₃)₂SiZ₂ *vs.* (CH₃)₂SiT₂, where Z and T are monofunctional exchangeable substituents and (CH₃)₂Si is a moiety which under the conditions of the equilibration remains intact, are described by the reaction



Accordingly a single equilibrium constant corresponding to eq 1 is sufficient to determine the concentrations of the three species present at equilibrium in such systems

$$K = [(\text{CH}_3)_2\text{SiZ}_2][(\text{CH}_3)_2\text{SiT}_2]/[(\text{CH}_3)_2\text{SiZT}]^2 \quad (2)$$