

Supplementary Material Available: Tables SI-SIX, containing a full tabular presentation of crystallographic and experimental data, additional atomic parameters, and complete lists of interatomic distances and bond

angles (15 pages); Tables SX and SXI, containing F_o-F_c values for $[V(\text{hedtra})(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}$ and $\text{K}[\text{VO}(\text{hedtra})]\cdot \text{H}_2\text{O}$ (27 pages). Ordering information is given on any current masthead page.

Notes

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Monomer-Dimer Equilibrium of Copper(II) Decanoate in Benzene Containing Decanoic Acid

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Received April 25, 1989

Polymerization and adduct formation are quite common to metal carboxylates² and play a very important role in understanding their stability and reactivity in solutions. Copper(II) carboxylates are particularly interesting because they are present almost exclusively as a dimer and give adduct compounds not only in the solid state but also in organic solvents.³ Thus Kochi and Subramanian have determined the dimerization constant as $\log K'_{\text{dim}} = 3.24$ at 57 °C from kinetic data for copper(II) acetate in glacial acetic acid.⁴ Extrapolation of their data to 25 °C results in $\log K'_{\text{dim}} = 4.1$, which seems too low, judging from spectral changes of the complex in the UV region.⁵ Another evidence for the dissociation of copper(II) acetate in this solvent has been given by the two groups⁶⁻⁹ as a function of water or alcohol concentration. Dissociation of copper(II) decanoate in solvating solvents has recently been studied by means of the solvent extraction method¹⁰⁻¹² and potentiometry.¹³ The results from these studies show that solvent molecules with strong coordination power replace the solvating carboxylic acids to give rise to breakdown of the dinuclear structure. On the other hand, a previous extraction study has clearly revealed partial dissociation of the copper(II) decanoate dimer in benzene, which is a typical nonsolvating solvent, with $\log K'_{\text{dim}}$ of about 6.¹⁴ At that time, however, only a semiquantitative conclusion could be drawn concerning the chemical formula of the monomeric species and the corresponding equilibrium constant, since the equilibrium lies so far to the dimer that it is inevitable to work at extremely low levels of copper(II) concentrations. Modern development of equipment has enabled us to determine a very low concentration of copper(II) with accuracy, and in this paper, we report some results on the dissociation of the dimeric copper(II) decanoate in benzene containing decanoic acid from a solvent extraction study.

Experimental Section

Reagents. *n*-Decanoic acid (chemically pure) was double distilled, and the middle fraction distilling at 269–271 °C was collected. Its purity turned out to be 99.5 ± 0.5% from alkalimetry. Copper(II) perchlorate was prepared by dissolving copper metal (99.99%) in hot aqueous perchloric acid. The copper(II) perchlorate hydrate crystallized from water was dissolved in a 0.1 mol dm⁻³ sodium perchlorate aqueous solution. The dilute copper(II) solution was freshly prepared and its concentration was determined colorimetrically by the use of 1-(2-pyridylazo)-2-naphthol as a chromogenic reagent. Sodium perchlorate (analytical grade) was recrystallized from water after precipitation of heavy metal impurities as hydroxides. All other chemicals were of analytical grade and used without further purification.

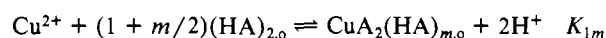
Measurements. All measurements were performed in a room thermostated at 25 ± 0.5 °C. Partition of copper(II) was carried out at 1 × 10⁻⁴ mol dm⁻³ initial concentration of copper(II) in the aqueous phase and 0.25–2 mol dm⁻³ decanoic acid in the organic phase. The ionic strength in the aqueous phase was kept constant at 0.1 mol dm⁻³ in (Na,H)ClO₄. A portion (15 cm³) of the aqueous phase was equilibrated with an organic phase of equal volume in a 50 cm³ stoppered centrifuge tube by vigorous shaking for 1 h in a water bath at 25.0 ± 0.2 °C. Hydrogen ion concentration was measured with an Orion M-901 microprocessor ionalyzer. The pH reading of the equipment was converted to hydrogen ion concentration by using a calibration curve prepared in advance. The copper(II) content in an aliquot of organic phase was back-extracted quantitatively with 10 cm³ of 0.1 mol dm⁻³ hydrochloric acid by shaking for 10 min, followed by the determination of the copper(II) concentration by anodic stripping voltammetry.¹⁵ A Yanaco P-1100 polarographic analyzer was employed for preelectrolysis and for monitoring current-voltage curves. A glassy-carbon electrode, GC-30 (5 mm o.d. × 50 mm), was used as a working electrode for stripping analysis. The relative error was about 3% at the 5 × 10⁻⁸ mol dm⁻³ level of copper(II) concentration after blank correction.

Results and Discussion

The dominant copper(II) decanoate species is dimeric in most nonpolar solvents according to the literature so far published,^{2,3} though the previous study has unambiguously shown the dissociation into monomers to a certain extent.¹⁴ When monomeric and dimeric copper(II) decanoates are denoted as $\text{CuA}_2(\text{HA})_m$ and $\text{Cu}_2\text{A}_4(\text{HA})_n$, respectively, the total copper(II) concentration in the organic solution, $C_{\text{M},o}$, is written as

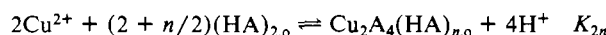
$$C_{\text{M},o} = \sum_m [\text{CuA}_2(\text{HA})_m]_o + 2 \sum_n [\text{Cu}_2\text{A}_4(\text{HA})_n]_o \quad (1)$$

where the subscript o refers to the organic phase. Extraction of the respective species may be formulated as follows:



$$K_{1m} = [\text{CuA}_2(\text{HA})_{m,o}][\text{H}^+]^2 / [\text{Cu}^{2+}][(\text{HA})_{2,o}]^{(1+m/2)} \quad (2)$$

and



$$K_{2n} = [\text{Cu}_2\text{A}_4(\text{HA})_{n,o}][\text{H}^+]^4 / [\text{Cu}^{2+}]^2[(\text{HA})_{2,o}]^{(2+n/2)} \quad (3)$$

Substitution of eq 2 and 3 into eq 1 gives

$$C_{\text{M},o}[\text{H}^+]^2 / [\text{Cu}^{2+}] = \sum_m K_{1m}[(\text{HA})_{2,o}]^{(1+m/2)} + 2 \sum_n K_{2n}[(\text{HA})_{2,o}]^{(2+n/2)}[\text{Cu}^{2+}] / [\text{H}^+]^2 \quad (4)$$

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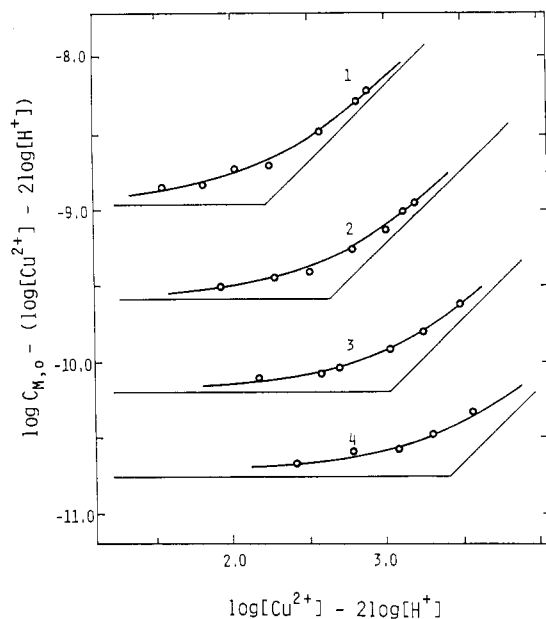


Figure 1. Variation in the polymerization degree of copper(II) decanoate in benzene at four different concentrations of decanoic acid C_{HA} : (1) 2.00, (2) 1.00, (3) 0.500, and (4) 0.250 mol dm⁻³. The solid curves are the best-fit ones calculated with the equilibrium constants $\log K_1 = -8.91$ and $\log K_2 = -11.45$.

On the assumption that the acid concentration in the organic phase is kept constant at a certain value, eq 4 can be rewritten as

$$\log C_{m,o} - (\log [Cu^{2+}] - 2 \log [H^+]) = \log (P + Q[Cu^{2+}]/[H^+]^2) \quad (5)$$

where $P = \sum_m K_{1m} [(HA)_2]_o^{(1+m/2)}$ and $Q = 2 \sum_n K_{2n} [(HA)_2]_o^{(2+n/2)}$. The values of m , n , K_1 and K_2 may be evaluated by the graphic method,^{16,17} where $[(HA)_2]_o$ is kept constant in each run. In the range where the monomer predominates, the plot of the values of the left-hand side of eq 5 as a function of $\log [Cu^{2+}] - 2 \log [H^+]$ should approach a horizontal line, $Y = \log P$. As the dimer prevails, however, it should approach a line with a slope of unity, $Y = \log Q + \log [Cu^{2+}] - 2 \log [H^+]$. Thus P and Q can be found from the Y value of the horizontal asymptote and from the intersection of the asymptote with a slope of unity and the Y axis at $\log [Cu^{2+}] - 2 \log [H^+] = 0$, respectively. The experimental results are shown in Figure 1, which clearly indicates that both the monomeric and dimeric copper(II) decanoates are responsible for the equilibrium in the organic phase. In Figure 2 the values of $\log P$ and $\log Q$ are plotted against $\log [(HA)_2]_o$ calculated from the total concentration of decanoic acid in the organic phase by use of its dimerization constant.¹⁸ Linear variation of $\log P$ with $\log [(HA)_2]_o$ illustrates the presence of a sole species of monomeric copper(II) decanoate ($m = 2$). A plot of $\log Q$ versus $\log [(HA)_2]_o$ results in a slope of 3; i.e., $n = 2$. Thus the dimer has the form $Cu_2A_4(HA)_2$, which has repeatedly been shown to exist from solvent extraction studies.² The equilibrium constants K_{12} and K_{22} were determined from the intercepts of the lines in Figure 2, and the least-squares method gave $\log K_{12} = -8.91 \pm 0.05$ and $\log K_{22} = -11.45 \pm 0.05$. The latter appears to be in fairly good agreement with those from the previous studies,^{19,20} while the former is the first value that has been reported with accuracy so far as we know.

The stability of dimeric copper(II) carboxylates is so high that no appreciable amount of a monomer has so far been detected

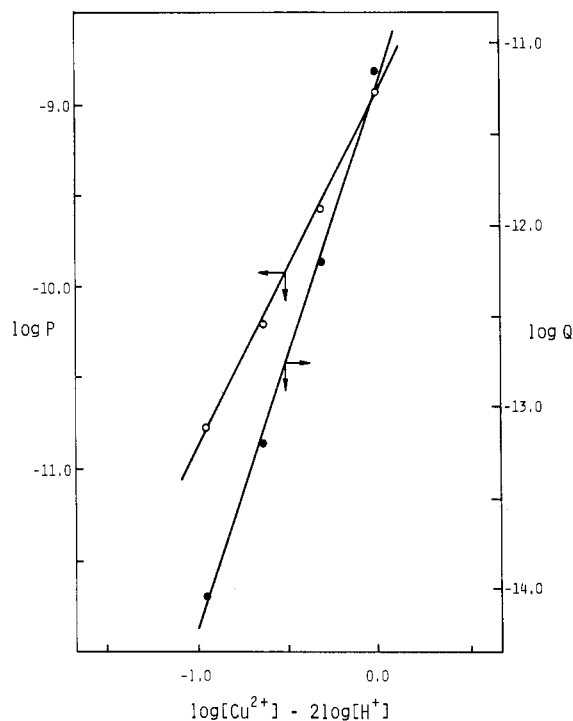
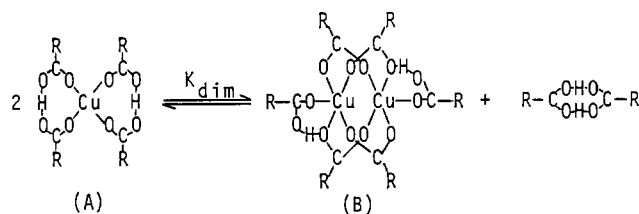


Figure 2. Determination of the number of carboxylic acid moieties involved in the copper(II) decanoate species in benzene.

Scheme I



in most nonpolar organic solvents, except for some bulky carboxylate/benzene systems.² In the present study, however, we have succeeded in finding the monomeric species, $CuA_2(HA)_2$, and in determining the corresponding equilibrium constant. Thus, the relevant monomer-dimer equilibrium in the benzene phase is formulated as



with $\log K_{dim} = \log K_{22} - 2 \log K_{12} = 6.37 \pm 0.15$. This high value reflects the equilibrium lying far to the right.

According to the NMR studies by Grasdalen⁷ and Funahashi et al.^{5,21} on dinuclear copper(II) acetate in acetic acid as solvent, the hydroxyl proton of HA is involved in strong intramolecular hydrogen bonding with an oxygen atom of a bridging carboxylate group. This point has been confirmed from a crystallographic study on acetic acid solvated dimeric copper(II) acetate.²² On the other hand, it is likely that dimeric carboxylate can act as a bidentate ligand AHA^- in the monomeric complex.¹⁹ Therefore, eq 6 may be envisaged as Scheme I, where carboxylic acids are denoted as RCOOH.

As seen from eq 6, carboxylic acid in benzene serves as a solvating molecule. It is clear from the equilibrium that addition of carboxylic acid to the system favors dissociation of the dimeric copper(II) carboxylate. In a solution of copper(II) acetate in acetic acid, this solvent itself can solvate to the complex. Grasdalen and Svare⁶ have studied the dimerization of copper(II) acetate in this solvent containing ethanol or water. They defined the apparent

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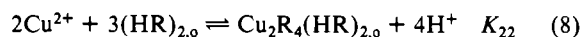
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dimerization constant for the following equilibrium as

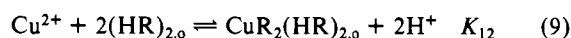


where $K'_{\text{dim}} = [\text{Cu}_2\text{A}'_{4,0}]/[\text{CuA}'_{2,0}]^2$. Solvation of acetic acid itself is not expressed explicitly in this formulation and this is why the species are primed. They have estimated $\log K'_{\text{dim}} \geq 5.3$ for pure acetic acid by extrapolating to $[\text{H}_2\text{O}]_0 = 0 \text{ mol dm}^{-3}$. Recently, Sawada and his coworkers have determined this apparent constant as $\log K'_{\text{dim}} = 6.2$ from spectral changes in UV-vis regions.²³

Kojima et al. have studied the extraction of copper(II) with a series of *n*-carboxylic acids HR into benzene, and found that the extraction constant K_{22} is constant irrespective of the alkyl chain length of an extractant¹⁹



They have interpreted this constancy on the basis of the regular solution theory.²⁵ This rule of equality may also be applied to the extraction of a mononuclear complex:



Since stoichiometric consideration leads to the following relationship:

$$K_{\text{dim}} = K_{22}/(K_{12})^2 \quad (10)$$

these dimerization constants must be identical irrespective of the kind of carboxylic acid HR as extractant dissolved in benzene. Thus

$$K_{\text{dim}}(\text{acetic acid}) \simeq K_{\text{dim}}(\text{decanoic acid}) \quad (11)$$

According to Hildebrand and Scott²⁴, the absolute activity, a_i , of species i is interrelated with its mole fraction x_i as follows:

$$\ln a_i = \ln x_i + V_i\phi_s^2(\delta_i - \delta_s)^2/RT \quad (12)$$

where δ_i and δ_s are solubility parameters of a solute i and a solvent s , respectively. V_i is the molar volume of i , and ϕ_s is the volume fraction of the solvent, which may be approximated to unity. As the dimerization constant based on the activity scale is identical in whatever solvent, change in K_{dim} based on the concentration scale may be calculated from the following expression, when the solvent is changed from benzene (B) to acetic acid (E):^{20,25-27}

$$RT(\ln K_{\text{dim}}^{\text{E}} - \ln K_{\text{dim}}^{\text{B}})/(\delta_{\text{B}} - \delta_{\text{E}}) = V_2(D - 2\delta_2) + V_d(D - 2\delta_d) - 2V_1(D - 2\delta_1) \quad (13)$$

where the subscripts 1, 2, and d denote the species $\text{CuA}_2(\text{HA})_2$, $\text{Cu}_2\text{A}_4(\text{HA})_2$ and $(\text{HA})_2$, respectively. D is a sum of solubility parameters of these two solvents.

The molar volumes and solubility parameters for metal complexes may be evaluated in a common way as:^{20,25,26}

$$V_1 = 2 \times 0.9V_d \quad V_2 = 3 \times 0.9V_d$$

$$\delta_1 = \delta_2 = (1/0.9)^{1/2}\delta_d$$

The following data are available:

$$\delta_d \simeq \delta_{\text{E}} = 13.01 \text{ (cal/cm}^3)^{1/2} \quad \delta_{\text{B}} = 9.15 \text{ (cal/cm}^3)^{1/2}$$

$$V_d = 57.24 \times 2 \text{ cm}^3/\text{mol} \quad V_{\text{B}} = 88.85 \text{ cm}^3/\text{mol}$$

Substitution of these numerical values into eq 13 results in

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$$\log K_{\text{dim}}^{\text{E}} - \log K_{\text{dim}}^{\text{B}} = -0.28 \quad (14)$$

The regular solution theory is constructed on the mole fraction scale, though experimental extraction studies are carried out ordinarily on the molar scale. Fortunately, the dimerization constant on the latter scale can be equated to that on the former one in this case, because the number of species involved is identical for both sides in eq 6, i.e. K_{dim} is a dimensionless constant. Furthermore K'_{dim} equals to K_{dim} on the mole fraction scale, on the assumption that acetic acid is composed primarily of dimeric species $(\text{HA})_2$,^{28,29} whose mole fraction is equal to unity. Thus

$$\log K'_{\text{dim}}(\text{in acetic acid}) = 6.37 - 0.28 = 6.09 \quad (15)$$

This value agrees well with the experimental one²³ and accounts for the great stability of dinuclear copper(II) acetate in anhydrous acetic acid.²

Registry No. HA, 334-48-5; HOAc, 64-19-7; Cu, 7440-50-8; C_6H_6 , 71-43-2; copper(II) acetate, 142-71-2; copper(II) decanoate, 28567-33-1.

Supplementary Material Available: A table of experimental data for distribution of copper(II) between benzene and aqueous solutions at 25 °C (1 page). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

Isolation and Characterization of
Ti(O)(OAr-2,6Pr¹)₂(NC₅H₄-4NC₄H₈)₂ (OAr-2,6Pr¹ =
2,6-Diisopropylphenoxide; NC₅H₄-4NC₄H₈ =
4-Pyrrolidinopyridine): A Mononuclear Aryloxo Compound
Containing a Terminal Titanium(IV)-Oxo Group

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Received February 16, 1989

The last few years have seen a burgeoning of research interest into the structure and reactivity of early-transition-metal compounds containing terminal oxo ligands.¹⁻⁵ However, despite this activity, there is still a dearth of examples of group 4 metal compounds containing this functional group.¹ During our studies of the group 4 metal organometallic chemistry supported by sterically demanding aryloxo ligation, we have been able to obtain an η^2 -imine derivative of titanium, which serves as a useful precursor to low-valent aryloxo derivatives of this metal.⁶ We wish to report here on the reactivity of this compound toward water, a reaction that under suitable circumstances allows the isolation of a mononuclear oxo derivative of titanium(IV).³

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