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Kinetic Determination of the Monomer–Dimer Equilibrium for Cupric Acetate in Acetic Acid Solutions

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The dissociation constant for the dimer of cupric acetate has been determined in glacial acetic acid. The method employs a kinetic study of the oxidation of alkyl radicals by monomeric cupric species in the presence of hydrogen donors. In glacial acetic acid, cupric acetate is highly dimerized, and the dissociation constant is $5.8 \pm 0.3 \times 10^{-4}$ M at 57°. For the dissociation of the dimer at 57°, $\Delta F = 4.9 \pm 0.4$ kcal./mole, $\Delta H = 12 \pm 1$ kcal./mole, and $\Delta S = 22 \pm 4$ cal./deg. mole. Water and pyridine promote dissociation of the dimer. The dissociation constant is determined at several concentrations of water and pyridine in acetic acid. Acetates, as alkali metal salts, in glacial acetic acid also effect efficient dissociation of the dimer, presumably to acetatocuprate ions.

Cupric acetate is representative of several metal acetates which exist in the crystalline phase as a dimeric entity. The crystal structure of cupric acetate monohydrate determined by X-ray crystallography shows the presence of an extremely short (2.64 Å.) Cu–Cu distance in which the Cu atoms are bridged by four acetato groups.[1] The two axial positions are occupied by water. Similar bridging acetato groups have been shown to exist in other dimeric and polymeric complexes of chromium(II),[2] molybdenum(II),[3,4] rhodium(II),[5,6] rhenium(II),[7] beryllium(II),[8] palladium, and ruthenium compounds.[9]

In addition to cupric acetate, a number of other cupric carboxylates have also been formulated as dimeric species by their abnormally low magnetic moments.[10–13] The latter has been attributed to a spin-exchange mechanism which results from the close proximity of copper atoms in the dimer. Recently, a number of copper(II) complexes with short Cu–Cu bond distances have been found which exhibit normal magnetic moments.[14] Dimer formation or closeness of copper atoms in a complex, thus, is not alone a necessary criterion for subnormal magnetic moments. The nature of the Cu–Cu interaction in dimeric cupric acetate has been treated theoretically by several workers.[15] A δ-model and a σ-bond model have both been proposed, but the resolution of this dichotomy is still pending a detailed treatment.[16]

The dimeric structure of cupric acetate persists in many nonaqueous solvents.[17] Protic solvents such as water and methanol promote dissociation. Pyridine also destroys the dimeric structure because of its strong coordinating power with copper(II).[18] Ethers, aromatic hydrocarbons, and carbon tetrachloride qualitatively effect slight dissociation in varying degrees. The methods which have been employed to determine

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(1) J. N. Van Niekerk and F. R. L. Schoening, *Acta Cryst.*, **6**, 227 (1953).

(2) J. N. Van Niekerk, F. R. L. Schoening, and J. F. de Wet, *ibid.*, **6**, 501 (1953).

(3) T. A. Stephenson, E. Bannister, and G. Wilkinson, *J. Chem. Soc.*, 2538 (1964).

(4) D. Lawton and R. Mason, *J. Am. Chem. Soc.*, **87**, 921 (1965).

(5) M. A. Porai-Koshits and A. S. Antshyskina, *Dokl. Akad. Nauk SSSR*, **146**, 902 (1962).

(6) S. A. Johnson, H. R. Hunt, and H. M. Neumann, *Inorg. Chem.*, **2**, 960 (1963).

(7) F. Taha and G. Wilkinson, *J. Chem. Soc.*, 5406 (1963).

(8) W. H. Bragg and G. T. Morgan, *Proc. Roy. Soc.* (London), **A104**, 437 (1923).

(9) T. A. Stephenson, *et al.*, *J. Chem. Soc.*, 3632 (1965). See also K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p. 197 ff.

(10) (a) B. N. Figgis and R. L. Martin, *J. Chem. Soc.*, 3837 (1956); (b) B. Bleaney and K. D. Bowers, *Proc. Roy. Soc.* (London), **A214**, 451 (1952); (c) H. Abe and J. Shimada, *Phys. Rev.*, **90**, 316 (1953); *J. Phys. Japan*, **12**, 1255 (1957). (d) The Cu–Cu bond is rather weak and the dimer is diamagnetic only at low temperature (20°K.). The variations of the magnetic susceptibility and electron spin resonance with temperature indicate that the triplet state is only 300 cm.$^{-1}$ (0.9 kcal./mole) above the singlet ground state and readily accessible thermally. Anilino ligands reduce the singlet–triplet separation [E. Kokot and R. L. Martin, *Inorg. Chem.*, **3**, 1306 (1964)].

(11) For an informative review see M. Kato, H. B. Jonassen, and J. C. Fanning, *Chem. Rev.*, **64**, 99 (1964); A. Earnshaw and K. S. Patel, *J. Inorg. Nucl. Chem.*, **27**, 1805 (1965).

(12) R. L. Martin and H. Waterman, *J. Chem. Soc.*, 1359, 2545, 2960 (1957).

(13) R. Tsuchida and S. Yamada, *Nature*, **176**, 1171 (1955).

(14) M. Inouye, M. Kishita, and M. Kubo, *Inorg. Chem.*, **3**, 239 (1964); **4**, 626 (1965).

(15) I. G. Ross, *Trans. Faraday Soc.*, **55**, 1057, 1064 (1959); **60**, 840 (1964); L. S. Forster and C. J. Ballhausen, *Acta Chem. Scand.*, **16**, 1385 (1962); see also A. E. Hansen and C. J. Ballhausen, *Trans. Faraday Soc.*, **61**, 631 (1965).

(16) E. A. Boudreaux, *Inorg. Chem.*, **3**, 506 (1964).

(17) R. Tsuchida, S. Yamada, and H. Nakamura, *Nature*, **178**, 1192 (1956); R. L. Martin and A. Whitley, *J. Chem. Soc.*, 1394 (1958).

(18) M. Kondo and M. Kubo, *J. Phys. Chem.*, **62**, 468 (1958).

the nature of the copper(II) species include magnetic susceptibility measurements, absorption spectra, and, in a few cases, actual isolation of dimeric copper(II) complexes. At best, these measurements have been highly qualitative. For example, the weak absorption band at 375 mμ has been attributed to the dimer,[19] but no quantitative determination of its importance has been evaluated.

The degree of dissociation of cupric carboxylates (CuX_2) has also been qualitatively related to the acid dissociation constant of the conjugate acid (HX).[11] Thus, cupric salts of the strong trihaloacetic acids show normal magnetic moments and no absorption at 375 mμ.

In order to relate bulk magnetic susceptibility measurements to magnetic moments of cupric complexes, it is desirable to know the population of each species in solution. Our interest in this problem stems from the use of cupric salts in kinetic studies. Alkyl free radicals such as butyl radicals are readily oxidized in solution by cupric carboxylates.[20] The determination of the rate of this reaction requires information about the nature and concentration of kinetically distinguishable cupric complexes.

In the following section, a brief background will be laid for the kinetic determination of these species.

Oxidation of Alkyl Radicals by Copper(II).—The decomposition of peroxides is catalyzed by cuprous species in the presence of cupric salts. Compared to the latter, the former is present in only low steady-state concentrations.[21] A radical-chain mechanism involving the capacity of copper species to undergo oxidation and reduction with free radical intermediates has been proposed[21] and has received extensive support.[22,23] The mechanism is described for valeryl peroxide by eq. 1–3.[24]

$$(C_4H_9CO_2)_2 + Cu^I \longrightarrow C_4H_9CO_2\cdot + C_4H_9CO_2Cu^{II} \qquad (1)$$

$$C_4H_9CO_2\cdot \longrightarrow C_4H_9\cdot + CO_2 \qquad (2)$$

$$C_4H_9\cdot + Cu^{II}O_2CC_4H_9 \xrightarrow{k_e} C_4H_8 + C_4H_9CO_2H + Cu^I \qquad (3)$$

Step 3 of the chain mechanism involves the oxidation of the intermediary butyl radicals by copper(II) salt to butene-1 and the concomitant regeneration of copper(I) salt. In the presence of substrates (RH) possessing labile hydrogens, the butyl radicals also form butane in a competing hydrogen-transfer reaction (eq. 4). The latter reaction serves as a convenient

$$RH + C_4H_9\cdot \xrightarrow{k_h} C_4H_{10} + R\cdot \qquad (4)$$

internal monitor for measuring the rate of oxidation of butyl radicals by copper(II) salts (eq. 3).

In 64 mole % *aqueous acetic acid* the rate of reactions 3 and 4 increased linearly with cupric acetate and hydrogen donor, respectively.[25] A first-order dependence on hydrogen donor and cupric ion is indicated. In *glacial acetic acid*, the hydrogen-transfer reaction (eq. 4) is still first-order in hydrogen donor, whereas the oxidation reaction (eq. 3) is half-order with respect to *total* copper acetate. Such a discrepancy is readily reconcilable if one considers the dimer to be the predominant form of cupric acetate in glacial acetic acid. In aqueous solutions cupric acetate is extensively dissociated. It is apparent from these studies that of the extant cupric complexes in solution, only the monomeric cupric species are capable of oxidizing alkyl radicals.

The oxidation of butyl radicals by cupric salts (eq. 3) as well as the hydrogen-transfer reactions (eq. 4) with hydrogen donors can, thus, both be considered second-order reactions.[26] The relative rate of oxidation and reduction is given by eq. 5.

$$\frac{k_e}{k_h} = \frac{[C_4H_8]}{[C_4H_{10}]}\,\frac{[RH]}{[Cu(II)]} \qquad (5)$$

If the dimer of cupric acetate[27] is dissociated according to eq. 6, the concentration of the monomeric cupric

$$Cu_2(OAc)_4 \overset{K}{\rightleftharpoons} 2[Cu(OAc)_2] \qquad (6)$$

species in equilibrium with dimer is expressed by eq. 7. The total cupric acetate, $[Cu(OAc)_2]_t$, is given

$$[Cu(OAc)_2] = K^{1/2}[Cu_2(OAc)_4]^{1/2} \qquad (7)$$

by the conservation equation (8). The simultaneous

$$[Cu(OAc)_2]_t = 2[Cu_2(OAc)_4] + [Cu(OAc)_2] \qquad (8)$$

$$= 2K^{-1}[Cu(OAc)_2]^2 + [Cu(OAc)_2] \qquad (9)$$

solution of eq. 5 and 9 yields eq. 10 after rearrangement.

$$\frac{[Cu(OAc)_2]_t}{[RH]}\,\frac{[C_4H_{10}]}{[C_4H_8]} = 2K^{-1}\left(\frac{k_h}{k_e}\right)^2\frac{[C_4H_8]}{[C_4H_{10}]}[RH] + \frac{k_h}{k_e} \qquad (10)$$

The left-hand side of eq. 10 is readily evaluated by determining the relative yields of butane and butene-1 obtained from the decomposition of valeryl peroxide in the presence of known amounts of total cupric acetate and hydrogen donor. Hence a plot of $\{[Cu(OAc)_2]_t/[RH]\}\{[C_4H_{10}]/[C_4H_8]\}$ against $[C_4H_8][RH]/[C_4H_{10}]$ should be linear with intercept k_h/k_e and slope $2K^{-1}(k_h/k_e)^2$.

Results and Discussion

Figure 1 illustrates the linearity obtained from eq. 10 by plotting $\{[Cu(OAc)_2]_t/[RH]\}\{[C_4H_8]/[C_4H_{10}]\}$ against $[C_4H_8][RH]/[C_4H_{10}]$. In a particular determination, the concentration of the hydrogen donor was usually maintained constant and the cupric acetate varied over an approximately tenfold range. At 1 *M* *n*-butyraldehyde, the solvent consists of 94 mole % (92 vol. %) glacial acetic acid and at 0.32 *M* it is 98

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[19] S. Yamada, H. Nakamura, and R. Tsuchida, *Bull. Chem. Soc. Japan*, **30**, 953 (1957); **31**, 303 (1958); C. W. Riemann, G. F. Kokoszka, and G. Gordon, *Inorg. Chem.*, **4**, 1083 (1965); D. P. Graddon, *J. Inorg. Nucl. Chem.*, **14**, 161 (1960).

[20] H. E. DeLaMare, J. K. Kochi, and F. F. Rust, *J. Am. Chem. Soc.*, **85**, 1437 (1963).

[21] J. K. Kochi, *ibid.*, **85**, 1958 (1963).

[22] J. K. Kochi, *Tetrahedron*, **18**, 483 (1962).

[23] For review see J. K. Kochi and H. E. Mains, *J. Org. Chem.*, **30**, 1862 (1965).

[24] Unless where necessary for the discussion, coordination around copper is not included.

[25] R. V. Subramanian and J. K. Kochi, to be published.

[26] Competitive kinetics does not allow the determination of the kinetic order in butyl radicals for the oxidation and reduction reactions, other than to indicate that it is the same for both. However, it is not critical for the determination of *K*. The contrary notwithstanding, we assume in the following discussion that both reactions are first order in butyl radical.

[27] The dimer of cupric acetate is actually $Cu_2(OAc)_4(HOAc)_2$ [D. P. Graddon, *J. Inorg. Nucl. Chem.*, **17**, 222 (1961)] and the monomer is probably $Cu(OAc)_2$ or $Cu(OAc)_2(HOAc)_2$.

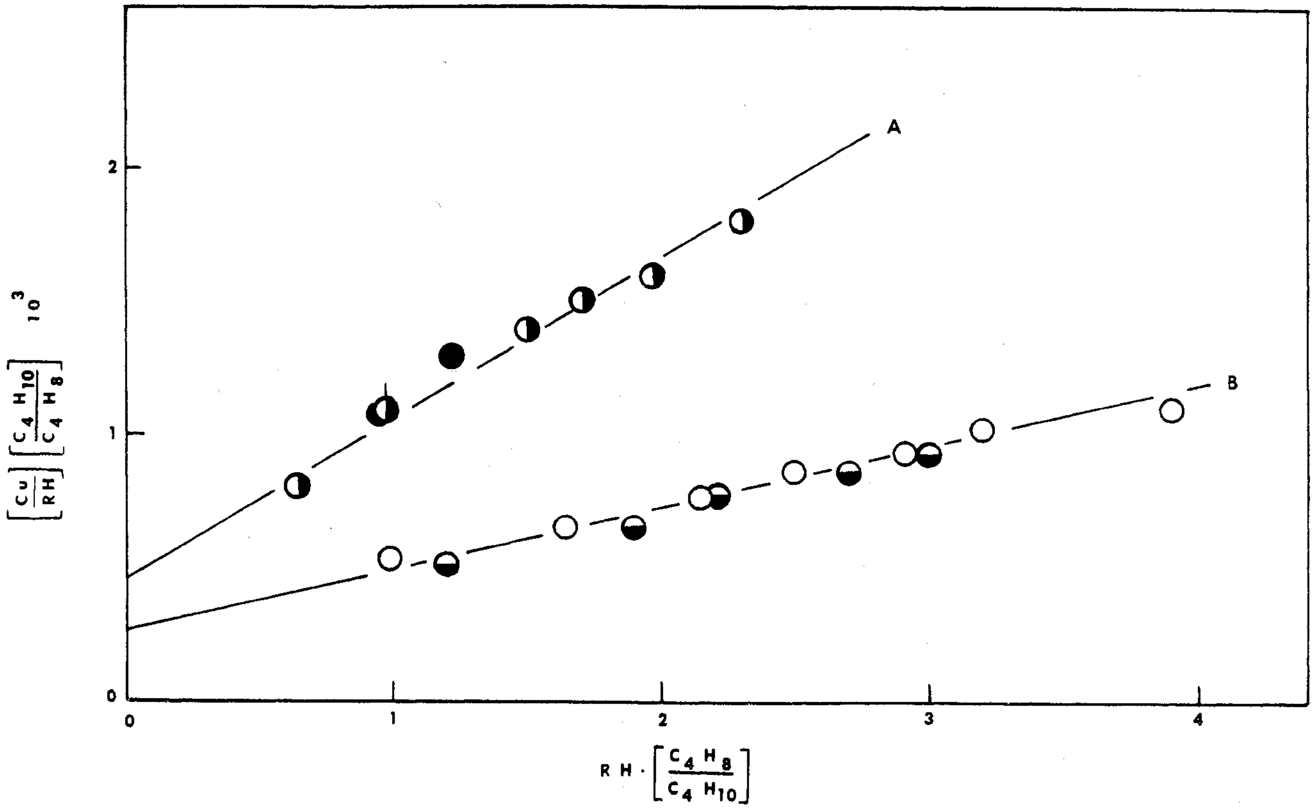

Figure 1.—Determination of K and k_h/k_e at various hydrogen-donor and cupric acetate concentrations. A, n-butyraldehyde: ◑, 0.966 M; ȯ, 0.644 M; ●, 0.322 M. B, dibenzyl ether: ○, 0.751 M; ◒, 0.451 M.

TABLE I

DISSOCIATION CONSTANT FOR COPPER(II) ACETATE DIMER IN GLACIAL ACETIC ACID[a]

Cupric acetate,[b] M	Hydrogen donor (M)	k_h/k_e	$-\log K$
5.20×10^{-4}–4.16×10^{-3}	n-Butyraldehyde (0.966)	4.4×10^{-4}	3.21
5.20×10^{-4}–4.16×10^{-3}	Isobutyraldehyde (0.941)	9.9×10^{-4}	3.18
5.39×10^{-4}–3.23×10^{-3}	Dibenzyl ether (0.751)	2.6×10^{-4}	3.22
5.32×10^{-4}–2.65×10^{-3}	Dibenzyl ether (0.451)	2.3×10^{-4}	3.30
5.20×10^{-4}–4.16×10^{-3}	Dichloroacetic acid (1.04)	3.4×10^{-4}	3.27

[a] In solutions containing 0.07 M valeryl peroxide at 57°. [b] Lower and upper limit of the variation in the cupric acetate concentration.

mole % (97 vol. %). Such ranges of solvents have largely the properties of *glacial acetic acid* with respect to the monomer–dimer equilibrium of cupric acetate. Thus, variation of the hydrogen donor in the concentration range 0.3–1 M does not materially alter the equilibrium constant. The data fit on the same linear correlation independent of the concentration of cupric acetate and RH within the aforementioned solvent composition. With such neutral hydrogen donors as aldehyde and ethers, it is not surprising that limited amounts have an immeasurable effect on the cupric species. Moreover, in this range the derived value of the dissociation constant is independent of the hydrogen donors listed in Table I. The best value for the dissociation constant of the cupric acetate dimer in glacial acetic acid is $5.8 \pm 0.3 \times 10^{-4}$ M at 57°. At 2×10^{-3} M cupric acetate[28] this equilibrium constant corresponds to 30% dissociation of the dimer. The accompanying *ionization* of the cupric acetate species in glacial acetic acid is several orders of magnitude smaller than the dissociation of the dimer.[29] The contribution from cationic cupric species to the over-all dissociation constant is, therefore, unimportant. The value of the dissociation constant is higher in acetonitrile, being 9.1×10^{-3} M (75% dissociated at 2×10^{-3} M) at the same temperature.

The temperature was varied incrementally between 41 and 82°, and the dissociation constants were 2.2×10^{-4} M at 41°, 4.7×10^{-4} M at 51°, 1.3×10^{-3} M at 71°, and 2.4×10^{-3} M at 82°. The logarithm of the dissociation constant plotted against temperature is linear. The free energy of dissociation at 57° in glacial acetic acid is 4.9 ± 0.4 kcal./mole, assuming unit activity at the low concentrations of salt employed. The enthalpy change is 12 ± 1 kcal./mole and the entropy of dissociation is 22 ± 4 cal./deg. mole.

Energetically, the values compare favorably with

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[28] Unless stated otherwise, the concentration of cupric acetate is based on the monomer.

[29] O. W. Kolling and J. L. Lambert, *Inorg. Chem.*, **3**, 202 (1964), compared the ionic dissociation of cupric acetate with a number of other monomeric metal acetates in glacial acetic acid. Its behavior was not unusual. The dissociation process which they are measuring for cupric acetate is ambiguous, since monomeric and dimeric species must both be considered in the light of our results. See also A. T. Casey and K. Starke, *Anal. Chem.*, **31**, 1060 (1959).

TABLE II

DISSOCIATION CONSTANT FOR COPPER(II) ACETATE DIMER IN AQUEOUS ACETIC ACID SOLUTIONS[a]

Water, mole %	Hydrogen donor (M)	Cupric acetate, M[b]	k_h/k_e	$-\log K$	Dissociation, %[c]
0	*n*-Butyraldehyde (0.966)	5.20×10^{-4}–4.16×10^{-3}	4.4×10^{-4}	3.21	24–53
8.6	*n*-Butyraldehyde (1.61)	2.12×10^{-4}–2.08×10^{-3}	1.3×10^{-4}	3.21	29–70
29	*n*-Butyraldehyde (1.61)	1.59×10^{-4}–1.56×10^{-3}	1.1×10^{-4}	2.27	61–94
64	*n*-Butyraldehyde (2.58)	2.60×10^{-4}–2.60×10^{-3}	1.7×10^{-4}	1.46	85–100
			1.8×10^{-4}	1.30[d]	
64	*n*-Butyraldehyde (1.61)	2.60×10^{-4}–1.95×10^{-3}	1.7×10^{-4}	1.72	88–100
			1.8×10^{-4}	1.92[d]	
64	*n*-Valeraldehyde (1.63)	2.60×10^{-4}–2.60×10^{-3}	1.5×10^{-4}	1.89	85–100
64	Dichloroacetic acid (1.04)	5.20×10^{-4}–3.12×10^{-3}	3.1×10^{-4}	0.70	83–100

[a] In solutions containing 0.07 M valeryl peroxide at 57°. [b] Lower and upper limits of variation in cupric acetate concentration. [c] Lower and upper limits of dissociation of cupric acetate dimer corresponding to cupric acetate concentration given in column 3 (upper and lower, respectively). [d] Obtained from C_3H_8–C_3H_{10} formed from propyl radicals produced by the secondary source.

TABLE III

EFFECT OF PYRIDINE ON THE DISSOCIATION CONSTANTS OF CUPRIC ACETATE DIMER IN GLACIAL ACETIC ACID[a]

Pyridine, M	Hydrogen donor (M)	Cupric acetate, M	k_h/k_e	$-\log K$
0	Dibenzyl ether (0.451)	0.532–2.65×10^{-3}	2.3×10^{-4}	3.30
0.184	Dibenzyl ether (0.451)	0.534–2.60×10^{-3}	8.2×10^{-5}	1.89
0.368	Dibenzyl ether (0.451)	0.532–2.12×10^{-3}	1.0×10^{-4}	2.49
0.736	Dibenzyl ether (0.451)	0.106–1.06×10^{-3}	1.9×10^{-4}	2.05
1.06	Dibenzyl ether (0.451)	0.534–2.67×10^{-3}	2.9×10^{-4}	1.72
...[b]	Dibenzyl ether (0.451)	0.512–2.56×10^{-3}	5.2×10^{-4}	2.38
...[c]	Butyraldehyde (1.61)	0.260–1.30×10^{-3}	2.9×10^{-4}	2.03

[a] In solutions containing 0.07 M valeryl peroxide at 57°. [b] In glacial acetic acid with 1:1.1 mole ratio Cu(II) to α,α'-bipyridine. [c] In 64 mole % aqueous acetic acid with 1:1.1 mole ratio Cu(II) to α,α'-bipyridine.

those obtained by Cotton and Fackler[30] for the related dissociation of the trimer of bis(2,6-dimethyl-3,5-heptanedionato)nickel(II) in toluene. In the latter case at 25°, $\Delta F = 5.7 \pm 0.3$ kcal./mole, $\Delta H = 15.0 \pm 1$ kcal./mole, and $\Delta S = 31 \pm 5$ cal./deg. mole have been reported.

In *aqueous acetic acid* solutions, the apparent dissociation constant of cupric acetate dimer increases with the water content of the medium as given in Table II. However, the relationship between the concentration of water and the dissociation constant (or the logarithm of the dissociation constant) is not linear. Small amounts of water have very little effect on the dissociation of cupric acetate dimer. Glacial acetic acid used in these studies contained less than 0.1% water by Karl Fischer titration. When the water content of acetic acid was reduced to 0.01% (5×10^{-3} M) by reaction with a small excess of acetic anhydride followed by distillation, the value of K was not materially altered. Moreover, deliberate addition of water up to 8–6 mole % also did not affect this value. No doubt acetic acid, which as solvate occupies the axial coordination sites in anhydrous cupric acetate dimer, is partially replaced by water.[1,27] However, at low concentrations of water this does not materially alter the dissociation constant of cupric acetate dimer.

A concentration of 30 vol. % water is sufficient to maintain cupric acetate (10^{-3} M) almost completely as monomeric entities. The effect of water on the dissociation is at least twofold: aquation and partial hydrolysis of the dimeric cupric acetate. The large difference in the dielectric constant of water (78.5) compared to acetic acid (6.2) also favors dissociation.[11] The equilibrium constant obtained in aqueous acetic acid solutions undoubtedly represents a composite value including several monomeric neutral and cationic cupric species, such as $Cu(OAc)_2(H_2O)_n$, $Cu(OAc)(H_2O)_m^+$, and $Cu(H_2O)_p^{+2}$. This approximation is not the only limiting factor for determinations in aqueous solutions. The dissociation constant obtained from eq. 10 is highly sensitive to the value of k_h/k_e and the slope, since it is obtained from the latter by dividing it by the square of k_h/k_e. Under conditions in which K exceeds 10^{-2} M, the slope is shallow and the determination of K is subject to greater error from k_h/k_e. High reproducibility of the dissociation constant is difficult to obtain under these conditions. The dissociation constant of the dimer in 64 mole % aqueous acetic acid is 2×10^{-2} M (98% dissociation at 2.6×10^{-4} M).

When aldehydes are used as hydrogen donors, it is possible to employ the alkane/alkene ratio for the alkyl moiety derived from the decarbonylation of the aldehyde, as well as that obtained from the peroxide. For example, the decomposition of valeryl peroxide in the presence of butyraldehyde generates butyl radicals from the former and propyl radicals from the intermediate propionyl radicals

$$CH_3CH_2CH_2CHO + CH_3CH_2CH_2CH_2\cdot \longrightarrow CH_3CH_2CH_2CO\cdot + CH_3CH_2CH_2CH_3 \quad (11)$$

$$CH_3CH_2CH_2CO\cdot \longrightarrow CH_3CH_2CH_2\cdot + CO \quad (12)$$

$$CH_3CH_2CH_2\cdot \xrightarrow{C_4H_8O} C_3H_8 + CH_3CH_2CH_2CO\cdot\text{, etc.} \quad (13)$$

$$CH_3CH_2CH_2\cdot \xrightarrow{Cu(II)} C_3H_6 + Cu(I)\text{, etc.} \quad (14)$$

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(30) F. A. Cotton and J. P. Fackler, Jr., *J. Am. Chem. Soc.*, **83**, 2818 (1961).

It is shown in Table II that the equilibrium constant based on the alkane/alkene ratio derived from the aldehydic donor is essentially the same as that obtained from peroxide. Furthermore, the behavior of alkyl radicals is independent of their origin, and propyl radicals derived from the secondary source (butyraldehyde donor) are the same as those derived from the primary source (butyryl peroxide). It is assured, therefore, that values obtained for the dissociation constant of cupric acetate dimer are independent of the peroxidic and hydrogen-donor components.

A consistency is further obtained in the relative rates of reduction and oxidation, k_h/k_e, with changing solvent and hydrogen donors. Within experimental error, this ratio is the same for *n*-propyl and *n*-butyl radicals as given in Table II. It is also largely independent of the water content of aqueous acetic acid solutions. This contrasts with the large variation in the dissociation constant with the same variations in solvent. Hydrogen-transfer rates k_h of free radicals are generally invariant with solvent changes.[31] The constancy of k_h/k_e implies that the oxidation rate constant k_e for cupric acetate is also remarkably insensitive to changes in water concentrations.

Pyridine.—The effect of pyridine in acetic acid is shown in Table III. The dissociation constant is affected to a much larger degree by pyridine than it is by water at the same concentration. At concentrations of pyridine as low as 0.2 *M*, cupric acetate (10^{-3} *M*) is 88% dissociated. This is not surprising in view of the large value of the association constant between cupric ion and pyridine in aqueous solutions.[32] The value for the dissociation constant obtained by this method is a composite value (as it is in water) since pyridine is undoubtedly involved in multiple coordination with cupric acetate. The dissociation constant as well as k_h/k_e appears to reach a slight minimum as the pyridine concentration is increased from approximately 0.1 to 1 *M*. The experimental significance of such a small change is difficult to ascertain. However, if the reasonable assumption is made that k_h is affected by pyridine in a minor way, the variation of k_h/k_e with pyridine indicates that k_e approaches a maximum at a pyridine concentration of approximately 0.1 to 0.2 *M*. This pyridine concentration may represent the optimum for

$$Cu_2(OAc)_4(HOAc)_2 + 2py \rightleftarrows Cu_2(OAc)_4py_2 + 2HOAc \qquad (15)$$

$$Cu_2(OAc)_4py_2 + n(py) \rightleftarrows 2Cu(OAc)_2py_{1+m} \quad n = 2m = 0, 1, 2, 3 \qquad (16)$$

the monopyridine complex as a monomer, $Cu(OAc)_2 \cdot py$ ($m = 0$), as well as a dimer $Cu_2(OAc)_4py_2$. The latter complexes as the benzoates have recently been isolated.[33]

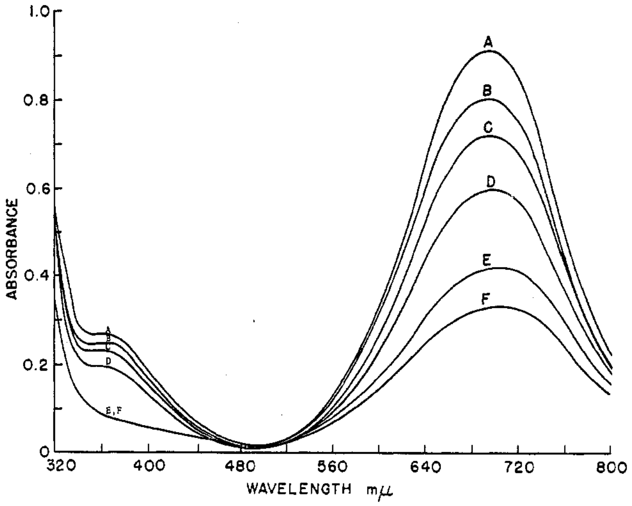

Figure 2.—Dissociation of cupric acetate dimer (4.48 × 10^{-3} *M*) by lithium acetate in glacial acetic acid: A, 0.01 *M*; B, 0.20 *M*; C, 0.30 *M*; D, 0.50 *M*; E, 1.0 *M*; F, 2.0 *M*.

TABLE IV

EFFECT OF SALTS ON THE DISSOCIATION CONSTANT OF CUPRIC ACETATE DIMER IN GLACIAL ACETIC ACID[a]

Salt (*M*)	Cupric acetate,[b] *M*	k_h/k_e	$-\log K$
None	0.532–2.65 × 10^{-3}	2.3 × 10^{-4}	3.30
$LiClO_4$ (0.085)	0.532–2.66 × 10^{-3}	1.4 × 10^{-4}	3.34
$LiClO_4$ (0.21)	0.532–2.66 × 10^{-3}	7 × 10^{-5}	3.7
NaOAc (0.085)	0.520–3.12 × 10^{-3}	4 × 10^{-5}	3.1[c]
NaOAc (0.23)	0.532–2.66 × 10^{-3}	1.3 × 10^{-4}	2.70
LiOAc (0.21)	0.520–2.60 × 10^{-3}	1.4 × 10^{-4}	2.50
LiOAc (1.04)	0.520–3.12 × 10^{-3}	2.3 × 10^{-4}	<0.5[d]

[a] In glacial acetic acid containing 0.451 *M* dibenzyl ether and 0.07 *M* valeryl peroxide at 57°. [b] Range of Cu(II) concentrations examined. [c] Approximate value, correction for blank very large. [d] Dimer completely dissociated, none detectable.

α,α′-Bipyridine in stoichiometric amounts also increases the dissociation of cupric acetate dimer. In glacial acetic acid containing a 1.1 equiv. of α,α′-bipyridine, cupric acetate (4 × 10^{-3} *M*) is not completely monomeric, since the dissociation constant given in Table III represents 50% dissociation.

Acetate.—Addition of acetate salts to a solution of cupric acetate in glacial acetic acid changes its color from green to blue. Its effect is similar but distinct from pyridine.[34] Changes in the absorption spectra by acetate ion shown in Figure 2 diagnose a simultaneous disappearance of the dimer. Measurements of the dissociation constant by the kinetic method clearly demonstrate that acetate ion effects complete dissociation of the dimer at concentrations as low as 1 *M* (Table IV). At 0.2 *M*, a solution of cupric acetate (4 × 10^{-3} *M*) is 46% dissociated. Acetate ion causes proportionately less dissociation as its concentration is decreased to zero. Unlike pyridine, lithium acetate

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(31) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1960; F. R. Mayo, Abstracts, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965, p. 14P.

(32) L. G. Sillén and A. E. Martell, "Stability Constants of Metal-Ion Complexes," Chemical Society Special Publication, No. 17, London, 1964, p. 440.

(33) R. D. Gillard, D. M. Harris, and G. Wilkinson, *J. Chem. Soc.*, 2838 (1964); *cf.* also G. A. Barclay and C. H. L. Kennard, *ibid.*, 5244 (1961); F. Hanic, D. Stemplova, and K. Hanicova, *Chem. zvesti*, **15**, 102 (1961); *Acta Cryst.*, **17**, 633 (1964).

(34) The effect of pyridine on cupric acetate in glacial acetic acid is only *partially* due to acetate from metathesis, HOAc + py ⇄ pyH^+ + OAc^-: K. Heymann and H. Klaus, "Chemistry in Lower Fatty Acids and Derivatives," H. Spandau and C. Addison, Ed., Interscience Publishers, New York N. Y., 1963, p. 19ff.

causes no maximum in K at low concentrations.[35] Lithium perchlorate as a neutral salt does not increase the dissociation of the dimer.

$$Cu_2(OAc)_4(HOAc)_2 + n\text{OAc}^- \rightleftharpoons 2Cu(OAc)_{2+m}{}^{-m} + 2HOAc \quad n = 2m = 2, 4 \qquad (17)$$

Anionic together with cationic complexes of cupric acetate are readily formed in aqueous solutions.[36] Triacetatocuprate ($m = 1$) is the preferred anionic species, and tetraacetatocuprate ($m = 2$) is only available at high acetate concentrations. The relevant complexation constants in solutions of ionic strength 1 M are[36]: $\beta_1 = 47\ M^{-1}$, $\beta_2 = 450\ M^{-2}$, $\beta_3 = 1150\ M^{-3}$, $\beta_4 = 750\ M^{-4}$.

The values of the dissociation constants obtained by the kinetic method are consistent with qualitative observations of the visible absorption and electron spin resonance spectra. In glacial acetic acid, cupric acetate appears as a green solution, due to the broad absorption at 690 mμ (apparent extinction coefficient = 200 l./mole-cm., calculated on the basis of monomeric cupric species). A weak band also appears at 370 mμ (ϵ_{app} 60). The intensity of both bands decreases with increasing water content of the medium at constant cupric concentrations. For example, ϵ_{app} decreases progressively from 200 to 120 as the water concentration is increased from 0 to 20%. The band at 370 mμ disappears altogether at greater than 25% water. The latter solutions are spectrally indistinguishable from aqueous solutions of cupric ion. Perchloric acid has a much larger effect than water, and addition of only small amounts to glacial acetic acid solution causes instantaneous decoloration of the green color to a very pale solution reminiscent of aquo Cu(II) ions.

Cupric acetate in glacial acetic acid shows a very weak and broad electron spin resonance absorption at 3200 gauss.[37] The same solutions containing small amounts of perchloric or trichloroacetic acid show a pronounced absorption characteristic of monomeric cupric species. Furthermore, in progressively aqueous solutions, the signal also increases as the absorption band at 690 mμ decreases and reaches a maximum at approximately 15–25% water. At the high water concentrations cupric acetate is highly dissociated, and if the results in 25% aqueous acetic acid are *simply* extrapolated to glacial acetic acid solutions, a value for the dissociation constant of a cupric acetate in glacial acetic acid is calculated as approximately 10^{-4} M at 25°. The latter value is consistent with that obtained by the kinetic method.

Experimental

Materials.—Anhydrous cupric acetate ($Cu(OAc)_2$) was from McGean Chemical Co. A stock solution of cupric acetate was prepared in glacial acetic acid. Dichloroacetic acid was Fisher purified reagent. N-Valeraldehyde, n-butyraldehyde, and isobutyraldehyde (Matheson Coleman and Bell, reagent grade) were redistilled and preserved under argon at 0°. Dibenzyl ether (Eastman Organic, reagent grade) was distilled *in vacuo* [b.p. 120–130° (5 mm.)] and preserved under argon at 0°. Acetonitrile (Fisher certified reagent) was distilled from phosphorus pentoxide and sodium carbonate. Glacial acetic acid was Du Pont or Baker and Adamson reagent grade. Its water content determined by Karl Fischer titration was less than 0.1%. Argon was from the Linde Company.

N-Valeryl peroxide was prepared from n-valeryl chloride and hydrogen peroxide as described earlier.[38]

Decompositions.—The required amounts of stock solutions of the peroxide, cupric acetate, and hydrogen donor were pipetted into a 100-ml. reaction flask. Enough solvent was added from a buret so that the volumes of the reactants together with the solvent added up to 35 ml. The reaction flasks were stoppered with self-sealing rubber serum caps and bound with rubber bands to maintain a gas-tight seal under pressure. The reaction mixtures were then stirred for 40 min. while being deaerated with a slow stream of argon introduced with hypodermic needles. The flasks were cooled in an ice bath without freezing the contents during deaeration, in order to minimize entrainment of the contents. After flushing, the reaction flasks were placed in a thermostated bath (±0.1°) for approximately 2 hr. Reaction was terminated by removing the flask from the bath and cooling it in an ice bath. Less than 3 mmoles of peroxide was employed, and in most cases it was not decomposed completely. Hence, the concentration of the substrate remained practically unchanged during the reaction. Since the concentration of cupric acetate is not altered, the ratio $[RH]/[Cu(OAc)_2]$ was essentially constant during the decomposition.

Analysis.—The reaction flasks were equilibrated at room temperature and samples of gas withdrawn and analyzed by gas chromatography on a 15-ft. column of 30% Dowtherm on firebrick at 20° (propane, 5 min.; propylene, 6 min.; butane, 12 min.; and butene-1, 15 min.) Known volumes of the pure gases (Matheson Co. or Phillips pure grade) were mixed in various ratios of volumes. They were equilibrated over the solvent used in the reactions and then analyzed to obtain a calibration factor relating the gas chromatography area ratios of the gases to their molar ratios. The calibration factor was invariant over the range of molar ratios examined. Reaction mixtures containing glacial acetic acid were diluted with water to 34 wt. % aqueous solutions and equilibrated before removal of gases for analysis. The calibration factor previously obtained for 34% aqueous acetic acid solutions could be used in converting area ratios to volume ratios.

The observed area ratios of the gases were first corrected for formation of butane from the solvent (acetic acid) itself acting as a poor hydrogen donor

$$\left(\frac{C_4H_{10}}{C_4H_8}\right)_{obsd} = \frac{k_s[HOAc]}{k_e[Cu(OAc)_2]} + \frac{k_h[RH]}{k_e[Cu(OAc)_2]} \qquad (18)$$

$$= \left(\frac{C_4H_{10}}{C_4H_8}\right)_S + \left(\frac{C_4H_{10}}{C_4H_8}\right)_{RH} \qquad (19)$$

where S refers to solvent. The value of $(C_4H_{10}/C_4H_8)_S$ for the solvent blank was determined from the ratio of butane to butene formed in the absence of substrate and at various concentrations of cupric acetate. The desired value of $(C_4H_{10}/C_4H_8)_{RH}$ was then obtained by subtracting $(C_4H_{10}/C_4H_8)_S$ from $(C_4H_{10}/C_4H_8)_{obsd}$. This ratio, $(C_4H_{10}/C_4H_8)_{RH}$, was further converted to the molar ratio with the calibration factor determined earlier. The molar ratio was then used in subsequent calculations to evaluate the equilibrium constant and k_h/k_e as illustrated in Table V for a typical case.

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[35] Strictly speaking, it is not the acetate ion, but metal acetate which is involved in the dissociation, since alkali metal acetates and even perchlorates are only slightly ionized in glacial acetic acid: L. H. Sutcliffe and J. Proll, *Trans. Faraday Soc.*, **57**, 1078 (1961); S. Bruckenstein and I. M. Kolthoff, *J. Am. Chem. Soc.*, **78**, 2974 (1956).

[36] I. Lundqvist, *Acta Chem. Scand.*, **18**, 858, 1125 (1964).

[37] B. Bleaney and K. D. Bowers, *Proc. Roy. Soc.* (London), **A214**, 451 (1952); A. H. Maki and B. R. McGarvey, *J. Chem. Phys.*, **29**, 31, 35 (1958); D. Kivelson and R. Nieman, *ibid.*, **35**, 149, 156, 162 (1961); H. R. Gersmann and J. D. Swalen, *ibid.*, **36**, 3221 (1962); H. C. Allen, G. F. Kokoszka, and R. G. Inskeep, *J. Am. Chem. Soc.*, **86**, 1023 (1964).

[38] J. K. Kochi and R. V. Subramanian, *ibid.*, **87**, 5108 (1965).

TABLE V

TYPICAL DATA FOR THE EVALUATION OF THE EQUILIBRIUM CONSTANT K^a

$\left(\frac{C_4H_{10}}{C_4H_8}\right)_{obsd}$	$\left(\frac{C_4H_{10}}{C_4H_8}\right)_S$	$\left(\frac{C_4H_{10}}{C_4H_8}\right)_{RH(area)}$	$\left(\frac{C_4H_{10}}{C_4H_8}\right)_{RH}{}^b$	$\left(\frac{C_4H_8}{C_4H_{10}}\right)_{RH}[RH]$	$\left(\frac{C_4H_{10}}{C_4H_8}\right)_{RH}\frac{[Cu(OAc)_2]}{[RH]}$
0.83	0.14	0.69	0.58	1.7	1.6×10^{-3}
0.95	0.16	0.79	0.66	1.5	1.4×10^{-3}
1.5	0.28	1.2	1.0	0.97	1.1×10^{-3}
2.3	0.50	1.8	1.5	0.64	0.81×10^{-3}

[a] RH = *n*-butyraldehyde (0.966 *M*); solvent: glacial acetic acid. [b] $(C_4H_{10}/C_4H_8)_{area} = 1.2 \times (C_4H_{10}/C_4H_8)_{molar}$.

According to eq. 18 and 19, the ratio of butane to butene in the blank divided by that in the presence of hydrogen donor should be related to the solvent and hydrogen-donor concentrations as in eq. 17. At constant substrate and varying cupric acetate concentration, the right-hand side of eq. 20 should be

$$\left[\frac{C_4H_{10}}{C_4H_8}\right]\left[\frac{C_4H_8}{C_4H_{10}}\right]_{RH} = \frac{k_5[HOAc]}{k_6[RH]} \quad (20)$$

constant, if the treatment is valid. This check is established in Table VI for a typical example.

TABLE VI

ALKANE/ALKENE FROM THE BLANK AS CORRECTION^a

Cupric acetate, *M*	$\left(\frac{C_4H_{10}}{C_4H_8}\right)_S$	$\left(\frac{C_4H_{10}}{C_4H_8}\right)_{RH}$	$\left(\frac{C_4H_{10}}{C_4H_8}\right)_S \Big/ \left(\frac{C_4H_{10}}{C_4H_8}\right)_{RH}$
2.60×10^{-3}	0.012	0.24	0.050
6.50×10^{-4}	0.044	0.89	0.050
3.90×10^{-4}	0.066	1.4	0.047
2.60×10^{-4}	0.10	2.0	0.050

[a] RH = *n*-butyraldehyde (2.58 *M*) in 64 mole % aqueous acetic acid.

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The Reaction of Vanadium(IV) and Chromium(II) Ions in Acid Solution. Kinetics and Mechanism of Decomposition of a Dinuclear Cr(III)–V(III) Intermediate[1]

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A study has been made of the kinetics of the reaction of vanadium(IV) and chromium(II) in acidic perchlorate solutions. Rate measurements at low $[H^+]$ establish that the major fraction of the reaction occurs quite rapidly; a small portion of the reaction proceeds by way of a dinuclear intermediate, $VO(OH)_nCr^{4-n}$. The direct reaction and the intermediate formation occur rapidly ($k > 8 \times 10^3$ M^{-1} sec.$^{-1}$ at 5.0°). The intermediate decomposes to $V^{3+} + Cr^{3+}$ at a measurable rate obeying pseudo-first-order kinetics. The rate exhibits a complex dependence upon hydrogen ion concentration (0.01–1 F $HClO_4$ at 1.00 M ionic strength). A mechanism is proposed involving an acid ionization equilibrium which can be verified independently from spectral studies on the intermediate. The equilibrium quotient and decomposition rates were measured at 5–25° and the corresponding thermodynamic activation parameters were evaluated. The rate of this decomposition reaction is compared with that in several related systems, and a general correlation found of decomposition rate and substitution lability of the metal ion involved.

Introduction

During a previous study[2] of the kinetics of reaction of vanadium(III) and chromium(II) ions, kinetic evidence was found for the existence of steady-state concentrations of an unstable reaction intermediate, $V(OH)_nCr^{4-n}$,[3] formally a V(III)–Cr(II) or V(II)–Cr(III) species. This paper describes a study of the formation and decomposition of a previously unknown V(III)–Cr(III) dimeric species.

A Cr(III)–Cr(III) binuclear ion, $CrOCr^{4+}$, the major Cr(III)-containing product of reaction of Cr(IV) (presumably) and Cr(II),[4] is a solution species with reasonably well-understood structure and reaction properties.[5,6] A dimer of vanadium(III), VOV^{4+}, is an intermediate present at low concentration during reaction of V(IV) and V(II).[7] A dimer of Fe(III) is

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[1] This work was performed in the Ames Laboratory under the auspices of the U. S. Atomic Energy Commission. Presented before the Division of Inorganic Chemistry at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1965.

[2] J. H. Espenson, *Inorg. Chem.*, **4**, 1025 (1965).

[3] The extent of proton association and the degree of hydration and the matter of oxo or hydroxo bridging remains unresolved by these experiments.

[4] M. Ardon and R. A. Plane, *J. Am. Chem. Soc.*, **81**, 3197 (1959).

[5] (a) R. E. Connick and Sr. M. G. Thompson, 148th National Meeting of the American Chemical Society, Inorganic Division, Papers 23, 24, Sept. 1964; (b) Sr. M. G. Thompson, Thesis, University of California, Berkeley, 1964, UCRL 11410; (c) R. W. Kolaczkowski and R. A. Plane, *Inorg. Chem.*, **3**, 322 (1964).

[6] In many instances it is convenient to write the "simplest" formula for these dimeric ions, even in the case of the chromium(III) dimer, for which the formula is $[Cr(OH_2)_4OH]_2^{4+}$ (ref. 5). In addition, there are at least two other dimeric chromium(III) species which can reach equilibrium with this ion; the species $CrOHCr^{5+}$ and/or $CrOHCrOH^{4+}$ are the ones which decompose directly to monomeric Cr(III) (ref. 5b).

[7] T. W. Newton and F. B. Baker, *Inorg. Chem.*, **3**, 569 (1964).