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Trivalent Copper. I. A Pulse Radiolytic Study of the Chemical Properties of the Aquo Complex[1]

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The mechanism of decomposition of the aquo trivalent copper ions in neutral and acid solutions was investigated. The effect of NO_2^-, Br^-, CH_3OH, and H_2O_2 on the disappearance of Cu(III)(aq) was studied. It is concluded that in neutral solutions the trivalent copper exists in the form of $CuOH^{2+}$(aq) or $Cu(OH)_2^+$(aq) and decomposes *via* $2CuOH^{2+} \rightarrow 2Cu^{2+} + H_2O_2$. In acid solutions the mechanism involves the formation of hydroxyl radicals probably *via* $Cu^{3+}(aq) \rightleftarrows Cu^{2+} + OH$. The reaction $Cu^+ + CuOH^{2+}$(aq) is diffusion controlled.

Trivalent copper ions were shown to be formed in radiolyzed solutions[2] by the reaction

$$Cu^{2+} + OH \longrightarrow Cu(III) \qquad (1)$$

The specific rate of this reaction has been measured as $k_1 = 3.5 \times 10^8\ M^{-1}\ sec^{-1}$.[2] From the effect of pH on the absorption spectrum of Cu(III) it has been suggested that the equilibrium

$$Cu^{3+} + H_2O \rightleftarrows CuOH^{2+} + H^+ \qquad (2)$$

exists and that $K_2 = [CuOH^{2+}][H^+]/[Cu^{3+}] = (0.9 \pm 0.1) \times 10^{-3}\ M$.[2] The mechanism of disappearance of Cu(III) ions has not been studied in detail though it has been suggested that the mechanism approached a first-order process.[2] From the isotopic composition of the oxygen formed in the reaction

$$4Cu(III) + 2H_2O \longrightarrow 4Cu^{2+} + 4H^+ + O_2 \qquad (3)$$

it was concluded that hydroxyl radicals are formed as an intermediate in reaction 3.[3]

It was decided to study in detail the mechanism of the oxidation of water by Cu(III). Furthermore, the effect of different reductants on the mechanism of the disappearance of Cu(III) has been studied.

Experimental Section

The procedure of preparation of the samples was identical with that described earlier in detail.[4] The pulse radiolytic experiments were carried out by using a 0.4-μsec, 15-MeV, 20–160-mA electron pulse from the linear accelerator at Argonne National Laboratory or by using a 0.1–1.3-μsec, 5-MeV, 200-mA pulse from the linear accelerator at the Hebrew University in Jerusalem. At both linear accelerators the dose per pulse was $(1–10) \times 10^{19}$ eV $l.^{-1}$. The formation and disappearance of Cu(III) was followed at 300 nm unless otherwise stated. The experimental setups at Argonne[4] and Jerusalem[5] and the methods used for evaluating the results have been described elsewhere in detail.

Results and Discussion

The radiolysis of water may be described by

$$H_2O \xrightarrow{\gamma} e_{aq}^-,\ H,\ OH,\ H_2,\ H_2O_2,\ H_3O^+$$

the yields of the products being $G_{e_{aq}^-} = 2.6$, $G_{OH} = 2.65$, $G_H = 0.6$, $G_{H_2} = 0.45$, and $G_{H_2O_2} = 0.75$. The radicals e_{aq}^-, H, and OH formed are known to react with Cu^{2+}(aq) ions, the specific rate constants being 3.3×10^{10},[6a] 5×10^8,[6b] and $3.1 \times 10^8\ M^{-1}\ sec^{-1}$, respectively. In order to increase the yield of trivalent copper ions, $G(Cu(III)) = G(OH)$, and decrease the yield of monovalent copper ions, $G(Cu(I)) = G(e_{aq}^-) + G(H)$, N_2O-saturated solutions can be used. Under these conditions the reaction

$$e_{aq}^- + N_2O \longrightarrow OH + N_2$$

takes place ($k_{e_{aq}^- + N_2O} = 5.6 \times 10^9\ M^{-1}\ sec^{-1}$,[7] $[N_2O] = 2 \times 10^{-2}\ M$). Therefore, in neutral ($k_{e_{aq}^- + H_3O^+} = 2 \times 10^{10}\ M^{-1}\ sec^{-1}$),[7] dilute copper solutions saturated with N_2O, $G(Cu(III)) \approx 5.3$ and $G(Cu(I)) \approx 0.6$. The molar extinction coefficient of Cu(III) at 300 nm in neutral solutions is $\epsilon\ 5.7 \times 10^3\ M^{-1} cm^{-1}$,[2] and that of Cu^+ is very small.[2]

Neutral solutions containing $(1–10) \times 10^{-4}\ M$ $CuSO_4$ or $Cu(ClO_4)_2$ saturated with N_2O have been irradiated. The spectrum of the transient formed has been recorded and found to have a peak at 290 nm. The specific rate of reaction 1 was determined as $k_1 = (3.1 \pm 0.3) \times 10^8\ M^{-1}\ sec^{-1}$. These results are in good agreement with the results of Baxendale, *et al.*[2] The specific rate of reaction 1 is independent of pH in the range of pH 3–6 within the experimental accuracy. It has been impossible to follow this reaction below pH 3 as the rate of disappearance of Cu(III) increases with the decrease in pH (see below) and there is no separation between the formation and disappearance reactions below pH 4. The corrections introduced in the calculations become too large below pH 3.

The mechanism of disappearance of the Cu(III) formed in N_2O-saturated solutions containing $5 \times 10^{-4}\ M$ Cu^{2+} at pH 6.0 was found to consist of two parts: a minor fast process, the proportion of which

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[1] Based in part on work performed under the auspices of the U. S. Atomic Energy Commission.

[2] J. H. Baxendale, E. M. Fielden, and J. P. Keene, "Pulse Radiolysis," M. Ebert, J. P. Keene, A. J. Swallow, and J. H. Baxendale, Academic Press, New York, N. Y., 1965, p 217.

[3] M. Anbar and I. Pecht, *Trans. Faraday Soc.*, **64**, 744 (1968); M. Anbar and I. Pecht, *Isr. J. Chem. Proc.*, **3**, 29 (1965).

[4] D. Meyerstein and W. A. Mulac, *J. Phys. Chem.*, **72**, 784 (1968).

[5] Internal report of the accelerator laboratory, Hebrew University, Jerusalem, Israel.

[6] (a) M. Anbar and E. J. Hart, *J. Phys. Chem.*, **69**, 973 (1965); (b) D. Meyerstein, Ph.D. Thesis, Hebrew University, Jerusalem, Israel, 1965.

[7] M. Anbar and P. Neta, *Int. J. Appl. Radiat. Isotop.*, **18**, 493 (1967).

increased with increasing Cu^{2+} concentration, followed by a second-order process with $2k/\epsilon_{300} = 8 \times 10^{8}$ or $2k = (4.6 \pm 0.6) \times 10^{7}\ M^{-1}\ sec^{-1}$ (independent of the anion SO_4^{2-} or ClO_4^{-}). This rate is much slower than the rate quoted in the literature for the decay of Cu(III) formed in argon-saturated neutral solutions.[2] The disappearance of Cu(III) formed in argon-saturated solutions has been reinvestigated, and it was found that though the decay plots could be fitted approximately by assuming a first-order process, the specific rates obtained were dependent on the dose of the pulse. However, though the results do not fit a second-order disappearance mechanism, the initial slopes of these curves were independent of dose rate, yielding $k/\epsilon_{300} = (7.5 \pm 1.5) \times 10^{5}$. These results can be explained by assuming that the reaction

$$\mathrm{Cu(III)} + \mathrm{Cu(III)} \xrightarrow{k_4} 2\mathrm{Cu}^{2+} + \mathrm{H_2O_2} \qquad (4)$$

has a specific rate of reaction of $k_4 = (2.3 \pm 0.3) \times 10^{7}\ M^{-1}\ sec^{-1}$, whereas the reaction

$$\mathrm{Cu(III)} + \mathrm{Cu}^{+} \xrightarrow{k_5} 2\mathrm{Cu}^{2+} \qquad (5)$$

is faster. In N_2O-saturated solutions $G(\mathrm{Cu(III)}) \approx 5.0$ and

$$G(\mathrm{Cu}^{+}) = G_{\mathrm{H}} + \frac{(k_{e_{aq}^{-}+\mathrm{Cu}^{2+}})[\mathrm{Cu}^{2+}]}{(k_{e_{aq}^{-}+\mathrm{N_2O}})[\mathrm{N_2O}]} G_{e_{aq}^{-}}$$

or $G(\mathrm{Cu}^{+}) \approx 1.0$ for a $5 \times 10^{-4}\ M\ Cu^{2+}$ solution. The small yield of Cu^{+} causes the observed small initial fast decay of Cu(III) which increases with Cu^{2+} concentration. In argon-saturated solutions $G(\mathrm{Cu(III)}) \approx 2.6$ and $G(\mathrm{Cu}^{+}) \approx 3.2$. The disproportionation reaction

$$2\mathrm{Cu}^{+}(\mathrm{aq}) \longrightarrow \mathrm{Cu}^{0} + \mathrm{Cu}^{2+}(\mathrm{aq}) \qquad (6)$$

is very slow[8] relative to reaction 5. Therefore the disappearance of Cu(III) under these conditions is described by

$$-\frac{d[\mathrm{Cu(III)}]}{dt} = k_5[\mathrm{Cu(III)}][\mathrm{Cu}^{+}]$$

As the yield of Cu^{+} is larger than that of Cu(III), the reaction will not be described by a second-order process. However as under these conditions $G(\mathrm{Cu}^{+}) \simeq 1.2G(\mathrm{Cu(III)})$, the initial rate of disappearance of Cu(III) should be

$$-\left(\frac{d[\mathrm{Cu(III)}]}{dt}\right)_{i} = 1.2k_5[\mathrm{Cu(III)}]^{2}$$

From the experimental initial rate of $k/\epsilon_{300} = (7.5 \pm 1.5) \times 10^{5}$ the specific rate of reaction 5 can be calculated, $k_5 = (3.6 \pm 1.2) \times 10^{9}\ M^{-1}\ sec^{-1}$.

The rate of disappearance of Cu(III) in N_2O-saturated solutions increases with decreasing pH in the range of pH 3–6. This disappearance reaction is better described by a first-order process below pH 3.8 (though dependent on the pulse intensity). Furthermore the rate of disappearance of Cu(III) below pH 4 decreases when the Cu^{2+} ion concentration increases. Some typical results are summarized in Table I. The effect of pH on the rate of disappearance suggested that Cu^{3+}(aq) formed in acid solutions according to equilibrium 2 disappears faster than $CuOH^{2+}$(aq). It was decided, therefore, to check whether the effect of pH on the initial absorption of Cu(III) is dependent on Cu^{2+} concentration. The results are summarized in Table II. For $5 \times 10^{-4}\ M\ Cu^{2+}$ solutions saturated with N_2O, the effect of pH down to pH 3 was found to resemble that observed by Baxendale, *et al.*,[2] though for the more acidic solutions the accuracy is low due to the large corrections in extrapolating to time zero. At the more concentrated Cu^{2+} solutions the latter difficulty disappears as the formation of Cu(III) is over in less than 1 μsec. The results clearly indicate that equilibrium 2, which was suggested in order to explain the pH effect,[2] is not sufficient to explain all the results.

TABLE I

THE EFFECT OF pH AND Cu^{2+} CONCENTRATION ON THE RATE OF DISAPPEARANCE OF Cu(III)[a]

$[Cu^{2+}]$, M	pH	First-order rate of reacn, sec^{-1}	Second-order rate of reacn, $M^{-1}\ sec^{-1}$
4×10^{-4}	6.00	...	2.3×10^{7}
4×10^{-4}	4.36	$\sim 2.5 \times 10^{2}$	2.5×10^{8}
4×10^{-4}	4.09	3.9×10^{2}	$\sim 3 \times 10^{8}$
4×10^{-4}	3.69	4.4×10^{2}	...
4×10^{-4}	3.21	1.7×10^{3}	...
4×10^{-4}	2.98	2.8×10^{3}	...
1×10^{-4}	3.28	2.6×10^{3}	...
2×10^{-4}	3.28	2.0×10^{3}	...
1×10^{-3}	3.21	7.0×10^{2}	...

[a] All solutions were N_2O saturated. The Cu^{2+} was introduced as $Cu(ClO_4)_2$ and the acid was $HClO_4$. The pulse intensity was 350 rads/pulse. The accuracy of the first-order rate constants is ±25% and was obtained by taking an average slope.

TABLE II

THE EFFECT OF pH ON THE INITIAL ABSORPTION BY Cu(III)[a]

pH	$5 \times 10^{-4}\ M$ Cu^{2+} [b]	$2 \times 10^{-2}\ M$ Cu^{2+} [c]	$1 \times 10^{-1}\ M$ Cu^{2+} [c]
7.0	1	...	...
5.0	...	1	...
4.5	...	1	...
4.1	...	0.92	1
3.4	...	0.77	1
3.3	0.75	...	...
3.0	0.57	0.68	0.84
2.5	...	...	0.74
2.2	...	0.57	...
2.0	0.21	0.50	0.65
1.5	...	...	0.48
1.1	...	...	0.27

[a] Relative values. All solutions were Ar saturated. [b] From ref 2; measured at 300 nm. [c] This work measured at 330 nm (due to absorption of the solutions at 300 nm); accuracy of the absolute values ±15%. From these values the relative values were calculated.

A plausible explanation of the effect of Cu^{2+} concentration on the specific rate of disappearance of Cu(III) is that hydroxyl radicals are formed as intermediates in this reaction and that their equilibrium concentration decreases with increasing Cu^{2+} concentration due to reaction 1. In order to check this hy-

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(8) K. Shaw and J. H. Espenson, *Inorg. Chem.*, **7**, 1619 (1969).

pothesis, the effect of H_2O_2, NO_2^-, Br^-, and CH_3OH on the rate of disappearance of Cu(III) has been studied. The results are summarized in Table III. The specific rates of reaction of these compounds with OH radicals are included for comparison.

TABLE III

APPARENT SPECIFIC RATES OF REACTION OF REDUCTANTS WITH Cu(III)[a]

Reductant	pH	$[Cu^{2+}]$, M	$k_{Cu(III)+R}$,[b] M^{-1} sec^{-1}	k_{OH+R},[c] M^{-1} sec^{-1}
NO_2^-	5.2	1×10^{-3}	$(4.5 \pm 1) \times 10^7$	8×10^9 [d]
	5.2	2×10^{-4}	$(1.6 \pm 0.3) \times 10^7$	
Br^-	5.4	1×10^{-3}	$<1 \times 10^6$	6×10^8
CH_3OH	5.4	1×10^{-3}	$<1 \times 10^6$	5×10^8
H_2O_2	5.2	$(2\text{–}10) \times 10^{-4}$	$(6 \pm 3) \times 10^5$	$(2\text{–}4.5) \times 10^7$
NO_2^-	3.65	1×10^{-3}	$(5.9 \pm 1.0) \times 10^8$	8×10^9
	3.65	2×10^{-4}	$(9.0 \pm 1.5) \times 10^8$	
Br^-	3.86	1×10^{-3}	$\sim 1 \times 10^8$	
	3.65	1×10^{-3}	$(1.9 \pm 0.3) \times 10^8$	2.5×10^9
	3.65	2×10^{-4}	$(5.0 \pm 1.0) \times 10^8$	
	3.50	1×10^{-3}	$(3.4 \pm 0.5) \times 10^8$	
CH_3OH	3.65	1×10^{-3}	$(2.8 \pm 0.5) \times 10^7$	5×10^8
	3.50	1×10^{-3}	$(4.9 \pm 1.0) \times 10^7$	
H_2O_2	3.65	1×10^{-3}	$(6.5 \pm 1.5) \times 10^6$	$(2\text{–}4.5) \times 10^7$
	3.65	2×10^{-4}	$(1.1 \pm 0.25) \times 10^7$	

[a] All solutions were saturated with N_2O. [b] The specific rates are the apparent reaction rates of Cu(III) with the reductants; as to the actual reactions taking place, see the text. [c] Values from the literature.[7] [d] Recent results: G. V. Buxton, *Trans. Faraday Soc.*, **65**, 2150 (1969); A. Treinin, private communication.

The results clearly indicate that in neutral solutions the hydroxyl radical is not an intermediate in the decomposition reaction of Cu(III). Thus H_2O_2 reacts with Cu(III) at least at the same specific rate as Br^- though Br^- reacts much faster than H_2O_2 with OH radicals. The effect of concentration of Cu^{2+} on the specific rate of reaction with NO_2^- can be explained by assuming that the reaction does not proceed *via*

$$\mathrm{Cu(III)} + NO_2^- \longrightarrow Cu^{2+} + NO_2 \qquad (7)$$

but *via*

$$Cu^{2+} + NO_2^- \rightleftarrows CuNO_2^+ \qquad (8)$$

$$\mathrm{Cu(III)} + CuNO_2^+ \longrightarrow Cu^{2+} + CuNO_2^{2+} \qquad (9)$$

$$CuNO_2^{2+} \longrightarrow Cu^{2+} + NO_2 \qquad (10)$$

The equilibrium constant for reaction 8 is known, $K_8 \simeq 20$, and, therefore, about 2% of the NO_2^- in a 10^{-3} M Cu^{2+} solution will be in the complexed form. The specific rate of reaction 9 has to be, therefore, of the order of $k_9 \simeq 3 \times 10^9$ M^{-1} sec^{-1}. A similar mechanism has been suggested for the oxidation of glycine by Cu(III).[9]

In acid solutions, *e.g.*, pH 3.65, the apparent relative rates of reaction of Cu(III) with NO_2^-, Br^-, CH_3OH, and H_2O_2 (Table III) are 1:0.32:0.047:0.011, respectively, in good agreement with the relative rates of reaction of OH radicals with the same reductants which are 1:0.31:0.062:0.0056. (The reactions with Cu(III) are however over an order of magnitude slower than those of OH radicals.) These results can be explained by assuming the mechanism

$$\mathrm{Cu(III)} \underset{k_1}{\overset{k_{-1}}{\rightleftarrows}} Cu^{2+} + \mathrm{OH} \qquad (1)$$

$$\mathrm{OH} + \mathrm{R} \xrightarrow{k_{11}} \mathrm{P} \qquad (11)$$

where R is the reductant and P a product. The rate of disappearance of Cu(III) is

$$-\frac{d[\mathrm{Cu(III)}]}{dt} = k_{-1}[\mathrm{Cu(III)}] - k_1[Cu^{2+}][\mathrm{OH}]$$

and

$$\frac{d[\mathrm{OH}]}{dt} = k_{-1}[\mathrm{Cu(III)}] - k_1[Cu^{2+}][\mathrm{OH}] - k_{11}[\mathrm{R}][\mathrm{OH}]$$

Using the steady-state assumption for the OH radicals one obtains

$$-\frac{d[\mathrm{Cu(III)}]}{dt} = \frac{k_{-1}k_{11}}{k_1[Cu^{2+}] + k_{11}[\mathrm{R}]}[\mathrm{R}][\mathrm{Cu(III)}]$$

The observed specific rate constant, k_{obsd}, for the disappearance of Cu(III) in the presence of a reductant will be therefore

$$k_{obsd} = \frac{k_{-1}k_{11}}{k_1[Cu^{2+}] + k_{11}[\mathrm{R}]}$$

Since under the experimental conditions used $(k_{11}[\mathrm{R}]/k_1[Cu^{2+}]) < 0.5$, k_{obsd} seemed nearly independent of [R]. As all the parameters but k_{-1} in the last formula are known, k_{-1} can be calculated. The calculation yields $k_{-1} = (2.8 \pm 1.0) \times 10^4$ sec^{-1} and $k_{-1} = (4.2 \pm 1.4) \times 10^4$ sec^{-1} or $K_1 = 9.0 \times 10^{-5}$ M and $K_1 = 1.3 \times 10^{-4}$ M for pH 3.65 and 3.50, respectively. The calculated value for K_1 suggests that the redox potential of the Cu(III)–Cu^{2+} couple at pH 3.65 is only about 0.2 V lower than that of the OH–H_2O couple at the same pH.

The effect of pH on the specific rate of decomposition of Cu(III) in the presence and absence of the reductants suggests that reaction 1 is more complicated. A plausible mechanism is

$$\mathrm{OH} + Cu^{2+}(aq) \longrightarrow CuOH^{2+}(aq) \qquad (1a)$$

or

$$\mathrm{OH} + Cu^{2+}(aq) \longrightarrow Cu^{3+}(aq) + OH^- \qquad (1b)$$

followed by

$$Cu^{3+}(aq) \rightleftarrows CuOH^{2+}(aq) + H_3O^+ \qquad (2)$$

or perhaps by the formation of $Cu(OH)_2^+(aq)$. If the reaction

$$Cu^{3+}(aq) \longrightarrow Cu^{2+}(aq) + \mathrm{OH} + H_3O^+ \qquad (-1a)$$

is much faster than the reaction

$$CuOH^{2+}(aq) \longrightarrow Cu^{2+}(aq) + \mathrm{OH} \qquad (-1b)$$

a decrease in pH increases the concentration of OH radicals. Reaction −1a might be faster than reaction −1b due to the stabilization of the trivalent copper by the hydroxide ligand and a corresponding lowering of the redox potential of the couple $CuOH^{2+}$–$CuOH^+(aq)$ relative to the couple Cu^{3+}–Cu^{2+}.

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[9] D. Meyerstein and W. A. Mulac, *Isr. J. Chem. Proc.*, **6**, 53 (1968); D. Meyerstein, to be submitted for publication.

The mechanism suggested above also explains in part the effect of pH on the specific rate of disappearance of Cu(III) in the absence of added OH scavengers. The most probable mechanism in acid solutions is

$$\mathrm{OH} + \mathrm{Cu(III)} \longrightarrow \mathrm{Cu^{2+}} + \mathrm{H_2O_2} \qquad (12)$$

$$\mathrm{OH} + \mathrm{OH} \longrightarrow \mathrm{H_2O_2} \qquad (13)$$

These reactions are much faster than reaction 4. These reactions suggest that the decay of Cu(III) in the absence of OH scavengers should be a second-order process. However, the decay plots suggest a first-order decay process (though the calculated rates depend on the dose delivered). These facts might be explained in part by the fact that the yield of Cu^+ increases and the yield of Cu(III) decreases with decreasing pH due to the competition between the reactions $e_{aq}^- + H_3O^+ \rightarrow H$ and $e_{aq}^- + N_2O \rightarrow N_2 + OH$. Thus at pH 3 and 5×10^{-4} *M* Cu^{2+} the calculated yields are $G(Cu^+) = 1.5$ and $G(Cu(III)) = 4.5$. The increased rate of the disappearance of Cu(III) and the fact that it approaches a first-order mechanism cannot be due only to the increase in $G(Cu^+)$ because $G(Cu(III)) > G(Cu^+)$. It seems that the solutions contained a very small concentration, about 1×10^{-6} *M*, of an impurity which is a good OH radical scavenger. This impurity was probably introduced with the N_2O and might be NO or NO_2. Alternatively the possibility exists that OH radicals do react with N_2O with a specific rate of about 10^5 M^{-1} sec^{-1}. That the OH scavanger was introduced with the N_2O was checked by diluting the N_2O with Ar. The results indicated a somewhat slower decay of Cu(III) as expected. However, their quantitative analysis is difficult due to the accompanied increase in the yield of Cu^+. The suggested effect of pH and Cu^{2+} concentration on the concentration of $CuOH^{2+}$, Cu^{3+}, and OH explains also their effect on the initial absorption after the pulse. The value of K_2 was not calculated because at least two equilibria are involved and the limit of accuracy of the results was ±15%. The shift of the maximum of the absorption band to the uv with decreasing pH seems to be mainly due to the larger contribution of OH radicals to the absorption, having a maximum at 230 nm,[10] though also a difference in absorbance between $Cu^{3+}(aq)$, $CuOH^{2+}(aq)$, and $Cu(OH)_2^+(aq)$ is expected.[2] (The maximum of absorption of CuO_2^- is in the range of 400 nm.[11])

The mechanism suggested for the decomposition of Cu(III) in aqueous solutions explains in part the role of Cu^{2+} as a catalyst in several redox reactions where Cu(III) has been suggested to be an intermediate.[12] Cu(III) can be formed by different oxidants in the presence of ligands which lower the redox potential of the couple Cu(III)–Cu^{2+}. The trivalent copper ions seem to oxidize slowly, if at all, reductants which are not ligands in the inner sphere of the copper ions. However the Cu(III) ions form OH radicals in a low concentration for a relatively long time due to equilibrium 1. It is suggested that these OH radicals are the oxidizing agents in part of the catalytic reactions involving trivalent copper.

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[10] P. Pasberg, H. Christensen, J. Rabani, G. Nilsson, J. Fenger, and S. O. Nielsen, *J. Phys. Chem.*, **73**, 1029 (1969).

[11] I. Pecht, Ph.D. Thesis, The Weizmann Institute of Science, Rehovoth, Israel, 1967.

[12] For a general discussion see M. Anbar, *Advan. Chem. Ser.*, **No. 49**, 126 (1965).

Notes

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Solid–Solid Phase Transitions Determined by Differential Scanning Calorimetry. III. Organosilicon Compounds

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When Gilman first reported the synthesis of tetrakis(trimethylsilyl)silane, he commented on its unusually high melting point (261–263°) in comparison with that of the linear dodecamethylpentasilane, which is a liquid at room temperature.[1] We have found that tetrakis(trimethylsilyl)silane undergoes a solid-state transition at −32 to −35° to a plastic crystalline mesophase, a temperature that does not differ greatly from the reported melting point of dodecamethylpentasilane, −34°.[2] The analogy of this system with the *n*-pentane–neopentane system is obvious. Although *n*-pentane melts at −129.7°, neopentane must be heated to −16.5° for fusion but has a solid-state transition at −133°.[3] On thermal analysis, tetrakis(trimethylsilyl)silane sublimes at 282–285°, which is close to the value for the boiling point of dodecamethylpentasilane that can be obtained by extrapolating its reported boiling point, 135–136° (13 mm). The mesocrystalline phase of tetrakis(trimethylsilyl)silane is stable to such a high temperature that it has virtually no liquid range.

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[2] M. Kumada and M. Ishidawa, *J. Organometal. Chem.*, **1**, 153 (1963).

[3] I. Nitta, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, **112**, 234 (1959).