

constant at  $\sim 30\%$  under the experimental conditions tried. Such an initial relatively rapid exchange is characteristic of many solid-fluid heterogeneous exchange reactions,<sup>10</sup> representing rapid exchange between the reactant on the surface of the solid and the reactant in the fluid. Subsequent exchange may be much slower, occurring by slow self-diffusion and/or recrystallization. Although the accuracy of the heterogeneous run measurements was poor, these experiments indicate that the rapid exchange found for the homogeneous systems is probably an exchange actually occurring predominantly in the solution phase and not on the precipitate surface introduced in the chemical separation.

Within the experimental error, complete exchange of radiotungsten between  $W(CN)_8^{-4}$  and  $W(CN)_8^{-3}$  in aqueous solution was found for all concentrations and  $pH$  values noted in Table I. Although within the experimental error, the apparent trend toward incomplete exchange with rising  $pH$  for the homogeneous exchange at 0.0001  $f$  complex ion concentration may possibly indicate that the experiments at  $pH$  11.3 are approaching measurable rates. Inasmuch as our mixing apparatus was not designed for shorter reaction times and the separation method was already giving some troubles at this low concentration, we were unable to check this possibility experimentally.

Because kinetic measurements could not be made, the possibility of rapid exchange arising during the separations could not be excluded. If the observed exchange be not separation-induced, and if we assume that the rate law is first order in each of the

(10) O. E. Myers and R. J. Prestwood, Chap. 1, "Radioactivity Applied to Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1951 (A. C. Wahl and N. A. Bonner, editors).

tungsten reactants and that the homogeneous exchange at 0.0001  $f$  reactant concentrations may have been incomplete by as much as 20%, then the specific rate at  $1-2^\circ$  is greater than  $4 \times 10^4$  liter mole $^{-1}$  sec. $^{-1}$ . This lower limit on the specific rate is roughly an order of magnitude larger than that estimated by Wolfgang<sup>8</sup> for the  $Mo(CN)_8^{-4} - Mo(CN)_8^{-3}$  radiomolybdenum exchange at  $2^\circ$  (estimated 5-second exchange time) and than the specific rates measured by Sheppard and Wahl<sup>5</sup> and by Wahl and Deck<sup>6</sup> for the  $MnO_4^- - MnO_4^-$  radiomanganese exchange at  $1^\circ$  and the  $Fe(CN)_6^{-4} - Fe(CN)_6^{-3}$  radioiron exchange at  $4^\circ$ , respectively.

The very slow exchange of radiocarbon between  $CN^-$  and either  $W(CN)_8^{-4}$  or  $W(CN)_8^{-3}$  reported by us in the preceding paper<sup>8</sup> and the large coördination number of the tungsten in these complexes suggest that the apparent rapid charge-transfer reaction does not occur through a bridged activated complex of the kind demonstrated by Taube<sup>11,12</sup> as valid for many charge-transfer exchange reactions. Theoretical considerations made by Libby<sup>13</sup> and by Marcus, Zwolinski and Eyring<sup>14</sup> suggest that electron transfer between anions may be very rapid. However, Sheppard and Wahl<sup>5</sup> have remarked that electron transfer between  $MnO_4^-$  and  $MnO_4^-$  in aqueous solution is relatively improbable, since the exchange rate was observed to be smaller than the collision frequency in spite of presumably small Franck-Condon restrictions.

(11) H. Taube, H. Myers and R. L. Rich, *This Journal*, **75**, 4118 (1953).

(12) H. Taube and H. Myers, *Ibid.*, **76**, 2103 (1954).

(13) W. F. Libby, *J. Phys. Chem.*, **56**, 883 (1952).

(14) R. J. Marcus, B. J. Zwolinski and H. Eyring, *Ibid.*, **58**, 432 (1954).

LOS ANGELES, CAL.

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORIES, HARVARD UNIVERSITY]

## The Reduction of Cupric Chloride by Carbonyl Compounds

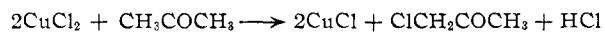
BY JAY K. KOCHI

RECEIVED MARCH 2, 1955

Cupric chloride is easily reduced to cuprous chloride by organic carbonyl compounds which are oxidized to the chloro compounds. With acetone the reaction is:  $2CuCl_2 + CH_3COCH_3 \rightarrow 2CuCl + ClCH_2COCH_3 + HCl$ . The kinetics of this reaction have been studied.

The first indications that solutions of cupric chloride in acetone are abnormal were reported by Jones and Veazey<sup>1</sup> and Kohlschütter,<sup>2</sup> who were unable to get reproducible results in electrical conductivity experiments with this system. Kohlschütter noted the formation of cuprous chloride, acid and chlorinated products.

We find that the reaction between cupric chloride and acetone proceeds readily at room temperature according to the following stoichiometry



The rate of the reaction is increased by increasing acetone concentration (in aqueous solutions) and by chloride ion, decreased by neutral salt and is inhibited

by the products, hydrogen chloride (or acid) and cuprous chloride. The dependence on copper concentration is half-order in gross copper. The variation in half-order rate constant at constant copper concentrations shows a first-order dependence on chloride ion.

### Experimental

**Materials.** Acetone.—Mallinckrodt analytical reagent grade acetone was refluxed with chromic anhydride overnight, decanted and distilled from more chromic anhydride and then from sodium hydroxide pellets. The foreruns were discarded; b.p.  $56.6^\circ$ .

**Cupric Chloride.**—Mallinckrodt analytical reagent grade material was recrystallized from dilute hydrochloric acid and desiccated by heating on a steam-bath *in vacuo*. The brown crystals analyzed correctly for  $CuCl_2$ .

**Lithium Chloride.**—J. T. Baker analyzed reagent grade crystals were dissolved in water, filtered, and the solution standardized with silver nitrate potentiometrically.

(1) H. C. Jones and W. Veazey, *Z. physik. Chem.*, **61**, 641 (1908).

(2) V. Kohlschütter, *Ber.*, **37**, 1153 (1904).

**Buffer.**—Fisher certified reagent grade monochloroacetic acid was crystallized from water, assayed with standard sodium hydroxide, and neutralized half way.

**Lithium and Sodium Perchlorates.**—Standard solutions were made by neutralizing lithium carbonate and sodium hydroxide with a standard perchloric acid solution.

**The Stoichiometry of the Reaction.**—A solution of 150 ml. of acetone, 50 ml. of water, 6 g. of LiCl and 12 g. of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  was refluxed under purified nitrogen for 24 hours on a water-bath. The resulting clear yellow solution was then analyzed as follows.

A 10-ml. aliquot was quenched in 50 ml. of a deaerated 0.07 N ferric ammonium sulfate-3 M sulfuric acid solution. It was then rapidly titrated with a standard 0.08 N ceric ammonium sulfate-0.5 M sulfuric acid solution to the ferrous-phenanthroline end-point.<sup>8</sup> It was found that the endpoint drifted slightly but the error was negligible when the titration was carried out rapidly. A 10-ml. aliquot of copper solution was treated with excess potassium iodide and filtered quickly. The liberated iodine was titrated with standard sodium thiosulfate for the cupric content and the resulting colorless copper-free solution titrated with standard sodium hydroxide to the brom cresol purple end-point. Chloroacetone determinations were made by vacuum distilling a 100-ml. aliquot of the copper-acetone solution into a Dry Ice trap. An additional 30 ml. of water was added to the dry residue and the vacuum distillation carried out to dryness again. In this way chloroacetone and hydrogen chloride were quantitatively separated from the copper salts. The brown-black amorphous residue on treatment with water immediately turned colorless and precipitated colorless cuprous chloride. In most cases the pure cuprous chloride (by ceric titration) which separated in this manner was isolated in 70-80% yield. The clear colorless vacuum distillate was then thawed and diluted to volume in a 250-ml. volumetric flask. Twenty-five ml. aliquots were titrated with standard silver nitrate solutions. Other aliquots were treated with excess potassium hydroxide pellets, warmed on a steam-bath for two hours, acidified with dilute nitric acid and titrated for total chloride potentiometrically with a silver-silver chloride electrode. Some representative results are shown in Table I.

TABLE I

ANALYSIS OF THE REACTION MIXTURE<sup>a</sup>

Length heat- ing, Run hr.	CuI, meq. <sup>b</sup>	Cu <sup>II</sup> , meq. <sup>b</sup>	H <sup>+</sup> , meq.	Free chlo- ride, meq.	Total Cl, meq.	CICH <sub>2</sub> - COCH <sub>3</sub> , meq.
11	3.32	0.21	1.82	1.71	3.22	1.51
12 <sup>c</sup>	1.95	1.65	0.93	0.92	1.98	1.02
13	3.14	0.51	1.50	1.48	2.97	1.49

<sup>a</sup> Analysis given for a 10-ml. aliquot. <sup>b</sup> Theoretical total copper is 3.64 meq. <sup>c</sup> Solution contains 50 volume per cent. acetone.

**Isolation of Products.**—A solution of 150 ml. of acetone, 50 ml. of water, 12 g. of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  and 6 g. of LiCl was refluxed for 24 hours and then rapidly distilled. Material boiling between 56-100° was collected and resubjected to careful distillation through a five-foot helix-packed vacuum jacketed column to remove the acetone. The lachrymatory residue (about 15 ml.) separated into two layers on cooling. The material was centrifuged and the oily lower layer was distilled through an eighteen-inch vacuum jacketed spiral column. The material was thus separated into two constant boiling fractions: I (b.p. 89°)<sup>4</sup> which separated into two layers on cooling and consisted of chloroacetone and water in the ratio of approximately 5:1, and II (b.p. 118°) which is pure chloroacetone. The 2,4-dinitrophenylhydrazone<sup>5</sup> of chloroacetone made in this manner did not depress the melting point (125-126°) of an authentic sample.<sup>6</sup> The approximate chloroacetone yield is 60%.

(3) L. Hatch and R. Estes, *Anal. Chem.*, **18**, 136 (1946); N. Furman, "Newer Methods of Volumetric Chemical Analysis," D. Van Nostrand Co., New York, N. Y., 1938, p. 27 ff.

(4) L. H. Horsley, "Azeotropic Data," American Chemical Society, Washington, D. C., 1952, p. 6.

(5) E. H. Huntress, "Organic Chlorine Compounds," John Wiley and Sons, New York, N. Y., 1948, p. 687.

(6) R. Van Atta, H. Zook and P. Elving, *THIS JOURNAL*, **76**, 1185 (1954).

Five grams of cupric chloride dihydrate was dissolved in a minimum amount of water (4 ml.). Reagent grade acetone (1 liter) was then added and the green solution deaerated by bubbling purified nitrogen through it for 15 minutes. The solution was then warmed at 40-50° in an atmosphere of nitrogen for 24 hours. After several hours clusters of fine colorless needles of cuprous chloride began to form on the side of the flask.

*Anal.* Calcd. for  $\text{CuCl}$ : Cu, 64.18; Cl, 35.82. Found<sup>7</sup>: Cu, 64.02; Cl, 35.67.

The reaction with sodium acetate in aqueous acetone solutions is not homogeneous, since cupric hydroxide precipitates. However, the cupric chloride reduction can be carried out rapidly if a concentrated aqueous solution of sodium acetate is added dropwise to a refluxing solution of cupric chloride and lithium chloride in aqueous acetone. The reaction is complete in three to four hours as compared to the 20 hours required for the unneutralized case.

Solutions of cuprous chloride and lithium chloride in anhydrous acetone are colorless. They absorb oxygen from the atmosphere very readily and precipitate a green solid. For example, 3.5 g. of cuprous chloride and 2.98 g. of lithium chloride dissolved in 45 ml. of anhydrous acetone absorbed 221 ml. of oxygen at atmospheric pressure. Half the total oxygen consumption took place in about 24 minutes at 25° with a magnetically stirred solution. The stoichiometry is<sup>8</sup>



**The Reaction of Carbonyl Compounds with Cupric Chloride.**—Various carbonyl compounds were tested for reaction with cupric chloride by dissolving it in the pure compound with the aid of lithium chloride. The solutions were deoxygenated, sealed, and heated in a steam-bath for 48 hours. The resulting cuprous chloride was titrated by the ceric method. The organic components were not identified. Both diethyl ketone and acetophenone form deep red solutions with cupric chloride and lithium chloride. They were decolorized to a light brown solution after four hours of heating. Glacial acetic acid and ethyl acetate dissolved cupric chloride with difficulty and formed brown-yellow solutions which did not change noticeably on heating. All four compounds formed appreciable amounts of cuprous chloride. Ethanol gave a green yellow solution which on heating turned brown yellow and reverted to its original color on cooling. Purified ethanol and acetonitrile gave very little evidence of reducing cupric chloride. Toluene which did not dissolve cupric chloride, did not react with a concentrated aqueous solution of cupric chloride.

Ferric chloride hexahydrate was dissolved in reagent acetone and lithium chloride added. The sealed ampule was heated in a steam-bath for 14 hours. The green solution showed no signs of change and did not consume ceric solution.<sup>9</sup>

**The Kinetics of the Reaction.**—The kinetics of the reduction of cupric chloride in acetone-water solutions was followed by titrating the liberated cuprous chloride with standard ceric solution. The rate was measured at 25.5° in 75 volume per cent. acetone-water and at 55.7° in 50 volume per cent. acetone-water solutions. The apparatus used was a three-neck 200-ml. round bottomed flask. Through the center neck was passed a calibrated fast flowing 10-ml. automatic pipet controlled by a three-way stopcock. The stem of the pipet extended to the bottom of the flask and the tip inserted into an overflow trap. One end neck was used for a nitrogen bubbler and the other neck was attached to a ballast flask maintained at 1 p.s.i. In this way reproducible aliquots of copper solution could be rapidly extracted out of contact with air.

Runs were made by mixing the appropriate volumes of standard cupric chloride, lithium chloride and buffer solutions and adjusting the ionic strength with standard sodium perchlorate solution.<sup>10</sup> The acid to salt ratio of the buffer was initially at one, and the concentration of each was

(7) Microanalyses were done by Mr. S. Nagy at the Massachusetts Institute of Technology.

(8) Cf. A. Korvezee, *Rec. trav. chim.*, **50**, 1085 (1931); G. Filson and J. Walton, *J. Phys. Chem.*, **36**, 740 (1932).

(9) P. Kovacic and N. Brace, *THIS JOURNAL*, **76**, 5491 (1954).

(10) In solutions of this nature "constant ionic strength" is illusory since we do not know the population of the various ionic species. Constant ionic strength was calculated assuming no complex formation.

always at least three times the concentration of the cupric salt. In most cases it was in tenfold excess. Comparable determinations with cupric nitrate and lithium chloride solutions gave the same results. Infinite time titers were checked by allowing the fast runs to proceed to ten half-lives. These values agree within 2% of the infinite titers obtained by heating sealed tube samples in a steam-bath for 24 hours.

It is interesting to note that acetone is salted out by lithium chloride from aqueous solutions and salted in by sodium perchlorate. This enables one to study some reactions in high chloride concentrations. Higher chloride concentrations could also be used in runs at lower temperatures since acetone has a negative solubility coefficient in this system.

The aqueous solution was made up in a 100-ml. volumetric flask from components made up in standard solutions. The aqueous solution was poured into the reaction vessel placed in the thermostated bath, and oxygen-free nitrogen was bubbled through the solution for ten minutes. One hundred milliliters of acetone contained in a volumetric flask was warmed to 35–40° and at the desired time poured into the reaction vessel. The solution was deoxygenated for an additional 30 seconds.

In order to test the reliability of this method careful pains were taken to degas the system composed of the separated acetone and aqueous components in a modified Warburg cell by repeated freezings and evacuations at 0.01  $\mu$ . Purified nitrogen was then introduced into the flask, the solutions brought to temperature, the components mixed, and samples extracted with a hypodermic syringe. There was no determinable difference in the rates of the reaction obtained in this manner from the more convenient method outlined above.

A few additional rates were measured on a Beckman Model DU spectrophotometer with a thermostatic arrangement using sealed Pyrex cells with quartz spacers (optical path length of 2 mm.). The rates obtained by following the rate of change of the 400  $m\mu$  peak were similar to those obtained by the titrimetric methods.

The complexion of the rate of the reaction is shown in Fig. 1. All the solutions contained the same cupric (141 meq.) and chloride (564 meq.) concentrations. With the exception of curve E, which was obtained in an unbuffered 75 volume per cent. acetone–water solution, all runs were done in 50 volume per cent. aqueous acetone. Curve C measures the rate of appearance of cuprous chloride. This rate is adversely affected by added salt (curve B, 106 meq. sodium perchlorate) and added acid (curve A, 70 meq. perchloric acid). The curves show that the acid produced is inhibiting the reaction since the buffered solutions D (106 meq. chloroacetate–106 meq. chloroacetic acid) and F (106 meq. acetate–25 g. acetic acid) at the same gross copper and chloride concentrations as B proceeded at a much faster rate. The more basic acetate buffer as well as 2,6-lutidine buffer were unsatisfactory since small amounts of cupric hydroxide precipitated from the reaction. Curve D was thus obtained from a reaction containing small amounts of uniformly suspended cupric hydroxide. Neither doubling the buffer concentration (chloroacetate) nor addition of gross amounts of *p*-benzoquinone (21 meq.) affected the rate substantially.

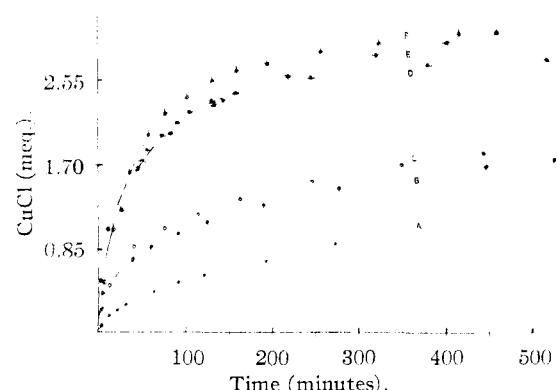


Fig. 1.—Rate of cuprous chloride formation (see text).

Addition of solid cuprous chloride to the system initially affected the rate as shown in Fig. 2. Curve G represents the rate of cuprous formation from a 50 volume per cent. aqueous acetone solution containing cupric (14.1 meq.) chloride (343 meq.), buffer (140 meq.) and sodium perchlorate (50.3 meq.). Addition of 4.04 meq. of solid cuprous chloride affects the initial rate as shown in curve H. In curve J, 7.08 meq. of cuprous chloride was added after nine minutes. Curve K represents the rate with 12.1 meq. of cuprous chloride; it is superimposable on curve J. The effect of cuprous chloride is shown more dramatically in solutions containing smaller chloride concentrations. Curve L was obtained from a solution containing 17.5 meq. of cupric, 175 meq. of chloride and 182 meq. of sodium perchlorate at the same buffer concentration and the same medium as those curves above. Curve M was done in a solution containing the same amounts of components as L but with 5.05 meq. of added cuprous chloride. The initial added cuprous chloride titer was subtracted from curve M so it would have the same origin. The diminution in the rate cannot be accounted for on the basis of the decrease in free chloride ion concentration due to complexation with cuprous ion. Assuming a trichloro complex,  $CuCl_3^{+}$ ,<sup>11</sup> the decrease in rate due to the tying up of the chloride ions at this low cuprous concentration does not materially affect the rate as was determined from chloride ion variation of rates.

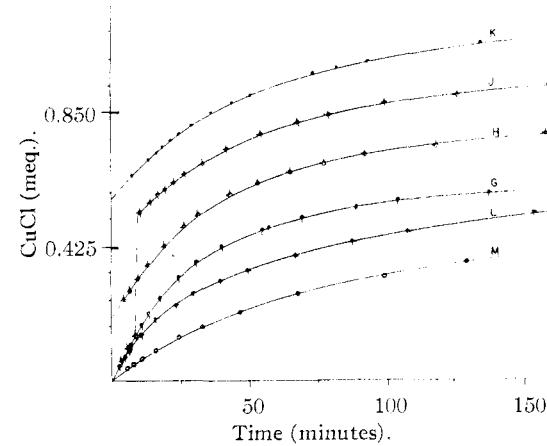


Fig. 2.—Effect of added cuprous chloride (see text).

**The Visible Spectrum.**—The absorption spectrum of cupric chloride in 75 volume per cent. acetone–water solutions at 25° is shown in Fig. 3. Measurements were made on a Beckman Model DU spectrophotometer using 2 mm. cells. The maximum at 400  $m\mu$  is increased markedly by chloride and cupric ions and slightly by added neutral salt. The variation in the spectrum with chloride ion concentration is shown in Fig. 3. Similar but larger effects are shown by cupric ions and smaller effects are shown by lithium perchlorate. The maximum is unaffected by acid (perchloric). This behavior of the species absorbing at 400  $m\mu$  is consistent with the tetrachlorocupric anion which has been studied previously in concentrated aqueous solutions.<sup>12</sup>

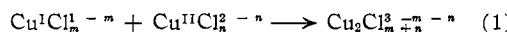
### Results and Discussion

A complete analysis of the rate data is complex. Within a given kinetic run the apparent variation in the gross copper concentration followed clean second-order kinetics to greater than 80% of the reaction. In situations where the Cl/Cu ratio was high (approximately 18) the rate substantially followed second-order kinetics to virtually 100% of the reaction. The variation in the rate with gross

(11) A. Noyes and M. Chow, *THIS JOURNAL*, **40**, 746 (1918); K. Chang and Y. Cha, *J. Chinese Chem. Soc.*, **2**, 293 (1934); G. Bodlander and O. Storbeck, *Z. anorg. Chem.*, **31**, 1, 458 (1902); St. Naray-Szabo and Z. Szabo, *Z. physik. Chem.*, **A166**, 230 (1933).

(12) T. Moeller, *J. Phys. Chem.*, **48**, 111 (1944); E. Doehlemann and H. Fromherz, *Z. physik. Chem.*, **A171**, 353 (1954); G. Spaci and J. Murgulescu, *ibid.*, **A170**, 71 (1954).

copper did not follow the expected order; for example a fourfold increase in cupric led to a seventeen-fold decrease in the second-order rate constant. This fact indicated that the products of the reaction were affecting the rate. When cuprous chloride was added to the reaction initially the initial rate was decreased as shown in Fig. 2. A "saturation effect" was realized when approximately one-half the amount of cuprous chloride equivalent to cupric chloride was added. These results indicate that the cupric ion is being partially tied up as a cupro-cuprichloride complex



McConnell and Davidson<sup>13</sup> have given convincing spectroscopic evidence for the existence of these complexes. When cuprous chloride is added to solutions containing smaller Cl/Cu ratios the inhibiting effect is larger, indicating that there is a competition between cupric chloride and chloride for the cuprous chloride. A detailed analysis of the inhibiting effect of cuprous chloride may help to elucidate the nature of these binuclear complexes.

The complication due to the cuprous-cupric chloride complexes forced us to analyze only the initial portion of the rate data. The initial rates of cuprous chloride formation is one-half order in gross copper as shown in Table II. Table III lists a few half-order rate constants at various chloride concentrations. At very high chloride to cupric ratios (*cf.* runs 15 and 16) the rate constant decreases

TABLE II

HALF-ORDER RATE CONSTANTS<sup>a</sup>

Run	Gross Cu, meq.	$10^3 k, \text{min.}^{-1}$	Run	Gross Cu, meq.	$10^3 k, \text{min.}^{-1}$
1 <sup>b</sup>	70.1	5.48	16 <sup>c</sup>	17.6	8.81
2 <sup>b</sup>	28.0	5.61	26 <sup>c</sup>	14.1	9.10
4 <sup>b</sup>	14.0	5.29	27 <sup>c</sup>	8.8	8.88

<sup>a</sup> 50 volume per cent. acetone-water with 140 meq. half-neutralized chloroacetic acid and sodium perchlorate at 55.7°. <sup>b</sup> 280 meq. chloride. <sup>c</sup> 350 meq. chloride.

TABLE III  
HALF-ORDER RATE CONSTANTS AT VARIOUS CHLORIDE CONCENTRATIONS<sup>b</sup>

Run	Added chloride, meq.	Cupric chloride, meq.	$10^3 k, \text{min.}^{-1}$
16	308	17.5	9.10
15	280	17.5	9.26
19	280 <sup>a</sup>	17.5	9.04
17	252	17.5	7.83
21	252 <sup>a</sup>	17.5	8.38
22	224	17.5	7.00
24	224 <sup>a</sup>	17.5	8.18
23	196	17.5	6.02
25	140	17.5	4.82
12	224 <sup>a</sup>	28.0	7.64
5	140	28.0	5.05
13	84.0	28.0	3.86
6	56.0	28.0	2.82
7	0.0	28.0	1.17

<sup>a</sup> No neutral salt added. <sup>b</sup> In solutions containing 100 ml. of acetone and 100 ml. of water and 140 meq. of buffer at 55.7°.

(13) H. McConnell and N. Davidson, THIS JOURNAL, 72, 3168 (1950).

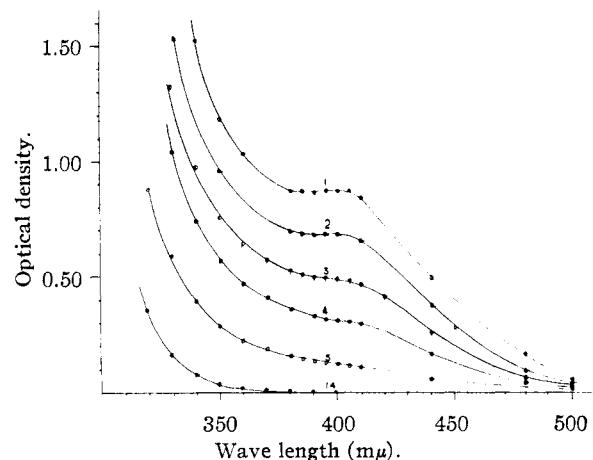
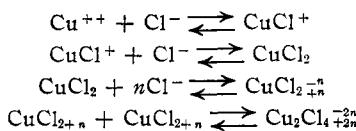


Fig. 3.—Variation in spectrum with chloride ion in 75 volume per cent. acetone-water solutions, 0.009 M in cupric nitrate: 1 (0.09 M); 2 (0.18 M); 3 (0.27 M); 4 (0.36 M); 5 (0.45 M); 14 (0.54 M, no acetone).

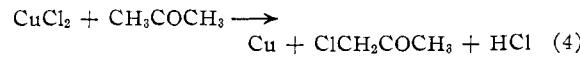
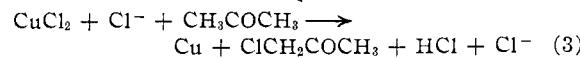
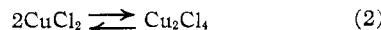
with increasing chloride ion. Run 16 represents the solution with the highest chloride content obtainable. At higher chloride concentrations the acetone was salted out of the water, and at lower cupric concentrations the amount of cuprous was too small to measure accurately.

A rigorous kinetic treatment of the cupric chloride reduction must necessarily take into account all the complex equilibria involving cupric and chloride ions



in addition to the cuprous-cupric equilibria given by equation 1.

We can account for our results by considering a somewhat simplified scheme in terms of the following principal equations



If steps 3 and 4 are slow, the initial rate is given by

$$\frac{d(\text{CuCl})}{dt} = [k_4 + k_3(\text{Cl}^-)] (\text{CuCl}_2)(\text{CH}_3\text{COCH}_3)$$

Since  $\text{Cu}_g = \text{CuCl}_2 + 2\text{CuCl}_4$ , where  $\text{Cu}_g$  is the gross cupric concentration

$$\frac{d(\text{CuCl})}{dt} = [k_4 + k_3(\text{Cl}^-)] \left[ \frac{-1 + (1 + 8K_2\text{Cu}_g)^{1/2}}{4K_2} \right] (\text{CH}_3\text{COCH}_3) \quad (7)$$

$K_2$ ,  $k_3$  and  $k_4$  are the equilibrium constant and rate constants of equations 2, 3 and 4, respectively.

Expression 7 is consistent with our observed half-order kinetics in gross cupric ion and limited first-

(14) G. Brauer, "Handbuch der präparativen anorganischen Chemie," F. Enke, Stuttgart, 1954, p. 72.

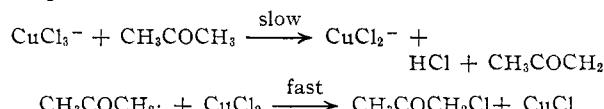
order dependence on chloride ion. A more detailed dependence on chloride can be made at lower and higher Cl/Cu ratios than we employed. There is, however, a disadvantage to working with high ratios in that acetone is readily salted out of water by chloride, and in order to operate in solutions of high chloride to cupric ratios and still maintain measurable cupric concentrations a sensitive method of detecting cupric concentration must be found. The ambiguity of the spectral method of determining cupric complexes<sup>15</sup> makes the use of this possibility of following low copper concentration changes dubious at the present time.

Other mechanisms not involving acetone (in large excess), or involving a combination of other cupric chloride complexes may also be formulated which are consistent with the results. At present we are not able to distinguish among these processes. Indications from the behavior of the spectrum of cu-

(15) R. Kruh, *This Journal*, **76**, 4865 (1954).

pric chloride in acetone with changing acid and salt concentrations disfavor either  $\text{CuCl}_3^-$  or  $\text{CuCl}_4^-$  as active intermediates. It seems reasonable that in media of such low dielectric constant as acetone and acetone-water solutions such neutral species as  $\text{CuCl}_2$  and its dimer would predominate.

The results from the benzoquinone experiment indicate that a free radical process for the reduction of cupric chloride by acetone is unlikely. For example, we can write



This possibility, however, cannot be entirely eliminated on the basis of the evidence on hand.

**Acknowledgment.**—I would like to thank Dr. J. Kumamoto for many illuminating discussions.

CAMBRIDGE, MASS.

[CONTRIBUTION NO. 1993 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

## The Molecular Structure of Formyl Fluoride

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The structure of  $\text{HCOF}$  has been investigated by electron diffraction in the gas phase. The parameters were refined by a least squares technique based upon the observations and calculated intensity curves. The parameter values and limits of error (taken as  $2\sigma$ ) are  $\text{C}-\text{F} = 1.351 \pm 0.013 \text{ \AA}$ ,  $\text{C}=\text{O} = 1.192 \pm 0.011 \text{ \AA}$ ,  $\text{O}\dots\text{F} = 2.225 \pm 0.019 \text{ \AA}$ ,  $\text{C}-\text{F}/\text{C}=\text{O} = 1.134 \pm 0.005$  and  $\angle \text{O}-\text{C}-\text{F} = 121.9 \pm 0.9^\circ$ .

Carbon-halogen bond lengths show interesting variations. For example, the distances in methylene fluoride, fluoriform, carbon tetrafluoride, carbonyl fluoride and acetyl fluoride ( $1.358^1$ ,  $1.332^2$ ,  $1.323^3$ ,  $1.324^4$  and  $1.37 \text{ \AA}^5$ , respectively) are all shorter than the distance in methyl fluoride ( $1.391 \text{ \AA}^3$ ), but, while the chloro- and bromomethanes show similar but less marked distance variations (the data for the iodomethanes are incomplete), the carbon-chlorine, -bromine, and -iodine distances in the acetyl halides ( $1.82$ ,  $2.00$  and  $2.21 \text{ \AA}^5$ ) are all considerably longer than is found in the corresponding methyl halides ( $1.781$ ,  $1.939$ , and  $2.139 \text{ \AA}^6$ ). We therefore felt it would be worth while to study the structure of formyl fluoride.

### Experimental

Formyl fluoride was prepared from formic acid, sodium fluoride and benzoyl chloride,<sup>7</sup> collected in a Dry Ice trap, vacuum distilled at  $-40$  and  $-35^\circ$  and passed over sodium fluoride to remove hydrogen chloride. The resulting product boiled at  $-24^\circ$ .

The methods used for obtaining photographs and for calculating radial distribution and theoretical intensity curves

have been outlined in recent reports from this Laboratory.<sup>8</sup> Visual interpretations of the photographs were made independently by two authors. Comparisons were made with photographs of formic acid,<sup>9</sup> which are very similar to those of formyl fluoride, in order to help with the interpretations. Our two visual curves are in excellent agreement on all points except the relative depths of minima 5, 7 and 8, where re-examination of the photographs showed curve K.H. is to be preferred (Fig. 1).

### Results

The radial distribution curve (Fig. 1) has strong peaks centered at  $1.27$  and  $2.22 \text{ \AA}$ , corresponding to  $\angle \text{O}-\text{C}-\text{F} \sim 122^\circ$ . Theoretical intensity curves were therefore calculated with  $Z_{\text{H}}^{\text{eff}} = 1.25$  for  $\text{C}-\text{H} = 1.09 \text{ \AA}$ ,  $1.072 \leq \text{C}-\text{F}/\text{C}=\text{O} \leq 1.197$ ,  $117^\circ \leq \angle \text{O}-\text{C}-\text{F} \leq 127^\circ$ , and  $a_{\text{C}-\text{H}} = 0.0016$  ( $a_{ij} = \frac{1}{2}(\overline{\delta r^2}_{ij} - \overline{\delta r^2}_{\text{C}=\text{O}})$ ); for most of the curves the  $\text{O} \dots \text{H}$  and  $\text{F} \dots \text{H}$  terms were omitted and  $a_{\text{C}-\text{F}}$  and  $a_{\text{O} \dots \text{F}}$  were set equal to zero.

Qualitative comparisons of these curves and our observations led to  $\text{C}-\text{F}/\text{C}=\text{O} = 1.136 \pm 0.009$  and  $\angle \text{O}-\text{C}-\text{F} = 121.7 \pm 1.7^\circ$  for the shape of the molecule. We decided, however, to verify and refine the results by least squares.<sup>10</sup> The param-

(8) See K. Hedberg and A. J. Stosick, *This Journal*, **74**, 954 (1952).

(9) J. M. O'Gorman and V. Schomaker, *ibid.*, **69**, 2638 (1947).

(10) W. Hamilton and V. Schomaker have discussed the use of least squares with visual electron diffraction data and have treated bicyclo-(2,2,1)heptadiene and bicyclo(2,2,2)octane as examples, and O. Bastiansen, L. Hedberg and K. Hedberg have applied least squares to sector-microphotometer data for 1,3,5,7-cyclooctatetraene, refining simultaneously five distance parameters and six vibration parameters. In anticipation of the publication of these more typical applications of the method (its advantages are especially important for many-parameter problems) we here only sketch its use for formyl fluoride.

(1) D. R. Lide, *This Journal*, **74**, 3548 (1952).

(2) S. N. Ghosh, R. Trambarulo and W. Gordy, *J. Chem. Phys.*, **20**, 605 (1952).

(3) L. O. Brockway, *Acta Cryst.*, **7**, 682 (1954).

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(5) P. W. Allen and L. E. Sutton, *Trans. Faraday Soc.*, **47**, 236 (1951).

(6) S. L. Miller, L. C. Aamodt, G. Dousmanis, C. H. Townes and J. Kraitchman, *J. Chem. Phys.*, **20**, 1112 (1952).

(7) A. N. Nesmejanow and E. J. Kuhn, *Ber.*, **67**, 370 (1934).