was removed by filtration and the filtrate was analyzed by nmr spectrometry. The spectra were run at minimum sweep width (50 cps); low radio frequency field use minimized saturation.

Hydrolysis of the Chloro Sulfides.—Each of the product mixtures was combined with 50 ml of water and stirred overnight. The layers were separated, the aqueous phase was extracted once with carbon tetrachloride, and the combined organic phase was washed once with water and dried over calcium chloride. Examination of the aldehydic region of the nmr spectra of the hydrolysates and augmentation indicated that predominant chlorination had occurred as indicated in Scheme I. The yields of aldehyde appeared to be essentially quantitative. The aldehydic proton of *m*-fluorobenzaldehyde appeared as two peaks, as noted by Klinck and Stothers.[15]

Acknowledgment.—Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

[15] R. E. Klinck and J. B. Stothers, *Can. J. Chem.*, **40**, 1071 (1962).

The Chlorination of Aldehydes by Cupric Chloride

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Butyraldehyde and isobutyraldehyde undergo α chlorination in almost quantitative yield on refluxing with $CuCl_2$ in aqueous isopropyl alcohol or aqueous acetone (which is not attacked). A kinetic study of the isobutyraldehyde reaction in aqueous acetone shows a process first order in both aldehyde and copper, catalyzed by both acid and chloride ion and retarded by CuCl. Comparison with literature data indicates that the chlorination is more rapid than acid-catalyzed enolization and possible reaction paths are discussed.

The chlorination of acetone by cupric chloride was first observed by Kohlschütter,[2] and the kinetics of the reaction were studied by Kochi,[3] who also showed[4] its significance in the Meerwein reaction between diazonium salts and olefins. More recently Kosower[5] has reported that the reaction, conducted in dimethylformamide solvent, is a good general procedure for ketone halogenation, and both he[5,6] and Castro[7] have examined the reactions of cupric chloride with a number of other substrates and have reviewed the older literature in detail.

In the course of an investigation aimed at generating radicals *via* redox processes we have found that aldehydes are also cleanly halogenated by cupric chloride in partially aqueous systems *via* the reaction shown in eq 1.

$$R_2CHCHO + 2CuCl_2 \rightarrow R_2CClCHO + HCl + 2CuCl \quad (1)$$

Since reaction of aldehydes with inorganic oxidizing agents leads in general to either formation of acids or extensive degradation, this little known reaction is both striking and of potential synthetic value. As far as we are aware, its only mention in the literature is a brief observation by Castro[7] and a description of a high temperature continuous process in the patent literature for the chlorination of isobutyraldehyde.[8]

General Characteristics of the Reaction.—The products of reaction between aldehydes and cupric chloride depend markedly on reaction conditions. In nonaqueous solvents the copper is reduced, but either HCl produced or copper salts acting as Lewis acids lead to extensive acid-catalyzed reactions. Thus refluxing *n*-butyraldehyde with a small amount of $CuCl_2$ either alone or in acetonitrile yields chiefly 2-ethyl-2-hexenal, while in isopropyl alcohol the major products are acetals. In contrast, refluxing equimolar quantities of $CuCl_2$ and butyraldehyde (1.02 *M* in 3:1 isopropyl alcohol–water) for 1 hr gives 90% α-chlorobutyraldehyde by gas–liquid partition chromatography (glpc) on the basis of eq 1 with the balance of the aldehyde remaining unchanged. The reaction also proceeds in aqueous *t*-butyl alcohol and aqueous acetone, with, in the last case, negligible chlorination of solvent.

Isobutyraldehyde is chlorinated even more rapidly and in refluxing 4:1 isopropyl alcohol–water gives 95% α-chloroisobutyraldehyde in 5 min. In aqueous acetone the yield is 96%, again without chlorination of solvent. When cupric acetate was used in place of $CuCl_2$, no reaction was detected.

The reaction of acetaldehyde is much more sluggish and the products were not investigated, while no reduction of copper was observed on heating $CuCl_2$ in aqueous isopropyl alcohol with either benzaldehyde or pivalaldehyde. Reactions of other metal halides were not investigated in detail, but ferric chloride, which is not reduced by refluxing aqueous acetone, was observed to react slowly with added isobutyraldehyde, giving α-chloroisobutyraldehyde in 77% yield based on iron reduced. The effects of some other variables on the $CuCl_2$ reaction are discussed below, but, in summary, the reaction appears a remarkably clean and simple route for the chlorination of aldehydes possessing reactive α-hydrogen, perhaps taking advantage of the catalysis by acid and chloride ion mentioned below.

Kinetics.—Since the reaction in aqueous solvents closely follows the stoichiometry of eq 1, kinetics were followed by consumption of cupric ion, determined by iodometric titration, using, in general, excess aldehyde to maintain essentially constant aldehyde concentrations. No attempt was made to ensure constant ionic strength, since only gross effects were investigated.

Although cuprous chloride is insoluble in aqueous acetone or isopropyl alcohol, a significant quantity remains in solution at the end of the reaction, apparently solubilized by chloride ion from the HCl pro-

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[1] Postdoctoral Fellow on leave from Montecatini Edison S.p.A., Bollate (Milano), Italy. Support of this work by Montecatini Edison S.p.A. is gratefully acknowledged.

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

[3] J. K. Kochi, *J. Am. Chem. Soc.*, **77**, 5274 (1955).

[4] J. K. Kochi, *ibid.*, **77**, 5090 (1955).

[5] E. M. Kosower, W. J. Cole, G. S. Wu, D. E. Cardy, and G. Meisters, *J. Org. Chem.*, **28**, 630 (1963).

[6] E. M. Kosower and G. S. Wu, *ibid.*, 633 (1963).

[7] C. E. Castro, E. J. Gaughan, and D. C. Owsley, *ibid.*, **30**, 587 (1965).

[8] Farbewerke Hoechst A. G., French Patent 1,369,565 (Aug 14, 1964); *Chem. Abstr.*, **62**, 10340 (1965).

duced. In early stages of the reaction it is also solubilized by complex formation with cupric chloride[9] (0.11 *M* $CuCl_2$ in 4:1 acetone–water dissolves 1 equiv of CuCl with marked fading of the green color of the solution) and precipitation does not begin from reaction mixtures until more than half of the cupric chloride has been reduced. A sharp drop in reaction rate is also observed at about this point, suggesting that the $CuCl_2 \cdot CuCl$ complex, whatever its structure, is a less reactive chlorinating agent than $CuCl_2$ itself and, consistent with this, addition of cuprous chloride significantly retards the initial reaction. Because of this complication, subsequent discussion is based on initial rates.[10]

Results of pertinent experiments with isobutyraldehyde in aqueous acetone at 30° are summarized in Table I. A few runs in isopropyl alcohol or with butyraldehyde as the substrate gave qualitatively similar results.

TABLE I
KINETICS OF REACTION OF ISOBUTYRALDEHYDE WITH $CuCl_2$[a]

$[RCHO]_0$	$[CuCl_2]$	[Other]	Rate x, 10^6 moles/l. sec
0.50	0.10		1.28
1.00	0.10		2.08
1.50	0.10		2.84
2.00	0.10		3.90
1.00	0.20		4.08
1.00	0.25		5.40
1.00	0.10	$HClO_4$, 0.053	10.9
1.00	0.10	$HClO_4$, 0.108	16.1
1.00	0.10	$HClO_4$, 0.212	29.8
1.00	0.10	$HClO_4$, 0.415	61.0
1.00	0.10	LiCl, 0.05	2.40
1.00	0.10	LiCl, 0.10	3.40
1.00	0.10	LiCl, 0.20	5.32
1.00	0.10	LiCl, 0.30	5.26
1.00	0.10	HCl, 0.0515	16.3
1.00	0.10	HCl, 0.104	37.0

[a] In acetone–water 4:1 by volume at 30°.

The data of Table I show that the reaction is close to first order in both cupric ion and aldehyde, is strongly acid catalyzed, and is also accelerated by added chloride ion. With added hydrochloric acid, the two latter effects are roughly additive. Without added chloride ion, results correspond to the expression given in eq 2 with $k_0 = 2.1 \times 10^{-5}$, $k_a = 1.4 \times$

$$-\frac{d[Cu(II)]}{dt} = k_0[Cu(II)][RCHO] + k_a[H^+][Cu(II)][RCHO] \qquad (2)$$

10^{-3}. At 59° the acid-catalyzed process was not measured but $k_0 = 59 \times 10^{-5}$, giving an over-all activation energy E_0 = 23 kcal/mole. Calculated the same way for comparison, k_0 for *n*-butyraldehyde is only approximately 3.3×10^{-5} at 61°.

The catalytic effect of the chloride ion appears to level out at a LiCl:$CuCl_2$ ratio of 2, suggesting that $CuCl_4^{2-}$ may be a species participating in a rate-determining step. It is of synthetic interest that lithium chloride also prevents both the precipitation of CuCl and the pronounced drop in rate in later stages of the reaction. Kosower[5] has also pointed out its beneficial effect in ketone halogenations.

Discussion

Our kinetic results agree with Castro's observation[7] that the reaction of butyraldehyde in dimethylformamide is first order in copper and aldehyde and accelerated by chloride ion. They differ, however, from Kochi's more detailed study of the $CuCl_2$–acetone process.[3] Kochi reports chloride ion catalysis and inhibition by CuCl as we find, but he observes half-order dependence on copper and states that the reaction is *inhibited* by acid, although the latter conclusion is based on a single experiment and is not accounted for in his kinetic analysis.

Before attempting to formulate a mechanism for the reaction consistent with our data, it is well to review what is known about related systems. In 1961, Waters suggested that many oxidations of carbonyl compounds by metal ions undergoing one electron change in oxidation state proceed (in acid solution) through preliminary enolization.[11] In the case of isobutyraldehyde and V(V)[12] and of acetophenone and Mn(III) (but not Co(III))[13] enolization is apparently the rate-controlling step and sets an upper limit to the reaction rate. Possible mechanisms for the $CuCl_2$–ketone reaction have been discussed at some length by Kosower and Wu;[6] their alternatives involve copper–enolate complexes and they prefer a simultaneous one-electron reduction of two copper(II) species. On the other hand, Castro suggests a Cu(II)-catalyzed enolization, followed by a rapid 2-electron reduction to Cu(O).

It seems that simple enolization can be ruled out in our case since our rates of reaction, at 30° in the absence of added acid (pH 3), calculated as first-order reactions of isobutyraldehyde (2.1×10^{-6} sec^{-1}) are almost as fast as Jones and Water's rates at 25° in 1 *M* $HClO_4$ (9×10^{-6})[12] and eq 2 predicts a rate in the reaction of 1 *M* $HClO_4$ with 0.1 *M* Cu of approximately 140×10^{-6}. Even allowing for small differences in temperature and solvent the discrepancy seems irreconcilable, particularly since our rates are first order in copper, so the enolization step cannot be rate determining. Since the substitution pattern and insensitivity of the reaction rate or products to benzoquinone or methyl methacrylate make a radical chain very unlikely, we are left with some sort of bimolecular rate-determining step, aided by chloride ion and also subject to acid catalysis. Copper-catalyzed enolization, as in Castro's scheme, may be consistent with this, as might also simple electron transfer to unenolized aldehyde with concerted proton loss. Since addition of a proton to the aldehyde should both interfere with its complexing with copper for enolization and decrease its ability to donate an electron, addition of the proton to the Cu(II) complex seems required. The crucial role of chloride ion in turn may be either to give a more reactive Cu(II) complex or to stabilize Cu(I) in an electron-transfer step. This latter process would imply two successive one-electron transfers

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(9) H. McConnell and N. Davidson, *J. Am. Chem. Soc.*, **72**, 3168 (1950).

(10) Plotts of $[Cu^{II}]$ *vs.* time were in general linear to 30–50% reaction. Apparently consumption of Cu^{II} and retardation by Cu^{I} approximately compensate for catalysis (vide infra) by the HCl generated as the reaction progresses.

(11) W. A. Waters, *Progr. Org. Chem.*, **5**, 1 (1961).

(12) J. F. Jones and W. A. Waters, *J. Chem. Soc.*, 352 (1963).

(13) R. Van Helden and E. C. Kooyman, *Rec. Trav. Chim.*, **86**, 57 (1961).

and an intermediate "enolate" radical as shown in eq 3 and 4. Such an intermediate was discounted by both

$$R_2CHCHO + Cu(II) \rightarrow R_2CCHO + H^+ + Cu(I) \quad (3)$$

$$R_2CCHO + Cu(II)Cl_x \rightarrow R_2CClCHO + Cu(I)Cl_{x-1} \quad (4)$$

Kochi[3] and Kosower[6] because Kochi reported no effect of benzoquinone on the acetone reaction. However, the very high rate of ligand transfer reactions between $CuCl_2$ and carbon radicals which has now been demonstrated[14] makes this criticism dubious, and dimers of such species have actually been found in some Cu(II) oxidations of carbonyl compounds (although under rather different conditions—base catalysis in the presence of amines and triphenylphosphine).[15]

In summary, while our data serve to rule out ordinary acid-catalyzed enolization as a step in the $CuCl_2$–aldehyde reaction and imply a direct, acid-catalyzed bimolecular process, there are still a number of alternatives for a detailed formulation of this interesting and rapid reaction.

Experimental Section

Reagents were commercial materials, purified by conventional means and purity checked by physical constants. Reference samples of α-chlorobutyraldehyde (bp 108-110°) and α-chloroisobutyraldehyde (bp 87–88°) were prepared by SO_2Cl_2 chlorination of the aldehydes as described by Stevens.[16]

$CuCl_2$–Butyraldehyde Reactions.—One hundred and ten cubic centimeters of a reaction mixture that was 1.02 *M* in freshly distilled *n*-butyraldehyde and 1.02 *M* in $CuCl_2$ isopropyl alcohol–water 3:1 by volume was refluxed (81°) for 1 hr under nitrogen. After 15 min CuCl began to precipitate and, at the end of the reaction 4.5 g had separated from the green solution. Titration of aliquots showed 0.0945 mole of copper to be reduced and 0.0475 mole of HCl produced. The yield of α-chloroaldehyde by glpc was 98% on the basis of copper consumed, and it was identified by collection and comparison with authentic material. Only a few minor by-products were detected and most of the excess aldehyde remained unreacted. Experiments in acetone–water and *t*-butyl alcohol–water gave similar results, while one in 4:1 methanol–water apparently yielded chiefly the dimethyl acetal of α-chlorobutyraldehyde. Refluxing 50 cc of aldehyde with 4 g of $CuCl_2$ in the absence of solvent gave complete reduction of the copper, but 2-ethyl-2-hexenal as the chief product, identified by comparison with authentic material.

$CuCl_2$–Isobutyraldehyde.—Eighty-five cubic centimeters of a solution that was 1.3 *M* in isobutyraldehyde and $CuCl_2$ in 2:1 acetone–water was refluxed under nitrogen (60–65°) for 1.5 hr. At the end of this time the solution was almost colorless, and copper reduction was 94.5% and 5.5 g of CuCl had precipitated. Analysis showed a 96% yield of α-chloroisobutyraldehyde, identified by isolation and comparison with authentic material. Again only minor by-products and no α-chloroacetone were detected. Under similar conditions in 4:1 isopropyl alcohol–water at 76° reaction was almost complete in 5 min, yield 95%. A number of other experiments were carried out similarly.

Kinetic experiments were conducted in a thermostat with stirring under nitrogen and followed by removal of aliquots, addition of KI, and titration with thiosulfate. Rate plots were close to linear to 30–50% reaction and initial rates are summarized in Table I. Added methyl methacrylate or benzoquinone had little effect on rate, although the latter increased total yield of chlorination products by reoxidation of cuprous ion.

Registry No.—Cupric chloride, 7447-39-4; butyraldehyde, 123-72-8; isobutyraldehyde, 78-84-2.

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[14] *Cf. e.g.*, J. K. Kochi and R. V. Subramanian, *J. Am. Chem. Soc.*, **87**, 4855 (1965).

[15] W. Brackman and H. C. Volger, *Rec. Trav. Chim.*, **85**, 446 (1966).

[16] C. L. Stevens and B. T. Gillis, *J. Am. Chem. Soc.*, **79**, 3449 (1957).

The Silver Tetrafluoroborate Induced Rearrangement of N-Chloroketimines[1a,b]

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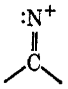
Silver tetrafluoroborate reacts with N-chloroketimines in aqueous dioxane to produce amides of rearranged structure. The group *trans* to the nitrogen–chlorine bond migrates to the nitrogen atom as the silver ion assists the removal of the chlorine. The resulting nitrilium ion has been trapped in aprotic solvents. No evidence was found for the intermediacy of a methylenimine cation.

The methylenimine cation 1 is a particularly intriguing species for it is theoretically capable of existing in either a singlet or triplet state. Lansbury,[2] observing an insertion of cationic nitrogen into the carbon–hydrogen bond, has recently presented strong evidence for the intermediacy of methyleniminium ions in the Schmidt and Beckmann rearrangements of substituted indanones and their derivatives. It is widely believed that methyleniminium ions are normally not intermediates in the Beckmann or Schmidt rearrangements[3] but it has been postulated that the particular geometry of the indanone system does not permit facile participation of the aryl group in the loss of the positively charged group from nitrogen.[2,4]



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The interesting theoretical and synthetic possibilities posed by the methyleniminium ion have resulted in an exploration in these laboratories of synthetic routes which might provide a greater structural variety of such cations. An essential feature of any such synthesis must be the removal of the leaving group from the nitrogen without anchimeric assistance and concomitant rearrangement of either of the groups attached to the adjacent carbon atom. Such a situation might arise if the intramolecular assistance to ionization were replaced by a suitable external driving force. The reaction of N-chloroketimines with silver ion appeared to be a good candidate to test this hypothesis.

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[1] (a) A portion of this work was supported by Petroleum Research Fund Grant 654 G-1. (b) Presented at the 154th National Meeting of the American Chemical Society, Chicago, Ill., 1967. (c) NSF undergraduate research participant, 1965.

[2] P. T. Lansbury, J. G. Colson, and N. R. Mancuso, *J. Am. Chem. Soc.*, **86**, 5225 (1964); P. T. Lansbury and N. R. Mancuso, *ibid.*, **88**, 1205 (1966).

[3] P. A. S. Smith in "Molecular Rearrangements," Vol. 1, P. deMayo, Ed., John Wiley and Sons, Inc., New York, N. Y., 1963, p 483.

[4] R. Huisgen, J. Witte, and I. Ugi, *Chem. Ber.*, **90**, 1844 (1957).