The solvent isotope effect data presented in Table III are completely in keeping with expectation for hydrolysis reactions involving proton transfer in the rate-determining step. The total isotope effect on the observed rate constant is a combination of two effects, and can be expressed on the basis of eq 6 as follows.

$$k^{\mathrm{H}}/k^{\mathrm{D}} = (k_0{}^{\mathrm{H}} + k_1{}^{\mathrm{H}}[\mathrm{H}^+])/(k_0{}^{\mathrm{D}} + k_1{}^{\mathrm{D}}[\mathrm{D}^+]) \quad (8)$$

At very low acid concentration, (8) reduces to the expression $k^{\mathrm{H}}/k^{\mathrm{D}} = k_0{}^{\mathrm{H}}/k_0{}^{\mathrm{D}}$. This ratio is seen to have a value of about 1.3 (Table III, data at pH 4.63), exactly of the order of magnitude to be expected for water-catalyzed hydrolyses.[20] In the more strongly acidic solutions, a contribution is made to the total isotope effect by the relative values of $k_1{}^{\mathrm{H}}$ and $k_1{}^{\mathrm{D}}$. For a direct proton transfer mechanism, the ratio $k_1{}^{\mathrm{H}}/k_1{}^{\mathrm{D}}$ can in theory be as high as 7, though smaller values are often observed.[21] We assign a value $k_1{}^{\mathrm{H}}/k_1{}^{\mathrm{D}} = 3.3$ and, using eq 8 and the requisite experimental parameters, calculate the figures for $k^{\mathrm{H}}/k^{\mathrm{D}}$ shown in the alternate columns of Table III. There is seen to be a good measure of agreement between observed and calculated values. Certainly, the fact that the solvent isotope effect results in $k^{\mathrm{H}}/k^{\mathrm{D}}$ values greater than unity rules out the possibility of a proton preequilibration mechanism for the ring opening of the carbonato cobaltic complexes. This is in sharp contrast with the proposal for the phosphato analog,[19] for which a $k^{\mathrm{H}}/k^{\mathrm{D}}$ ratio of less than unity is to be expected,[22] and could be as small as 0.3.[23]

Acknowledgment. Financial support of this work by the U. S. Atomic Energy Commission through Contract No. AT(30-1)-1578 with the State University of New York at Buffalo is gratefully acknowledged.

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[20] E. R. Thornton, "Solvolysis Mechanisms," The Ronald Press Co., New York, N. Y., 1964, p 213.

[21] R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, Chapter XI.

[22] E. L. Purlee, *J. Amer. Chem. Soc.*, **81**, 263 (1959).

[23] NOTE ADDED IN PROOF. A value for k_0 of 5×10^{-5} sec^{-1} is recently reported for the (en)$_2$ complex in 1.0 *M* NaClO$_4$ at 25°: D. J. Francis and R. B. Jordan, *ibid.*, **91**, 6626 (1969). The agreement with our rather approximate value of 10^{-4} sec^{-1} for this constant under very different ionic strength conditions is as good as can be expected.

The Reaction of Amines with Haloalkanes. II. The Dissolution of Copper in *n*-Butylamine–Carbon Tetrachloride Solutions

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Abstract: Despite earlier reports that copper metal initiates reaction between amines and haloalkanes at room temperature, it has been found that the metal is inactive in the absence of oxygen. A kinetic study has been made of the dissolution of copper in CCl$_4$–*n*-butylamine solutions saturated with O$_2$ at a total pressure of 1 atm. Similarities to the dissolution of copper in aqueous solutions of ammonia or amines under O$_2$ at high pressure have been found, but in the system studied here the rate-determining step is the formation of copper(I) chloride on the surface of the metal. A mechanism involving a charge-transfer complex formed between amine and CCl$_4$ is proposed to account for the results obtained.

Rapid reaction of amines with haloalkanes can be initiated by ultraviolet light, by daylight at certain concentrations, or by Cu (I) or Fe (II) salts.[1] It has also been reported[2–5] that copper metal initiates reaction at room temperature. The experiments on which those reports were based were preliminary in nature and did not reveal the cause of the great effect reported for the copper metal. The problem was complicated at that time by the lack of recognition of the existence of the several other initiatory processes and by the lack of information on the course of the reactions following initiation. With better understanding of those matters now on hand,[1] it has been possible to study the action of the copper metal with greater certainty.

We have found that copper metal is rendered inactive by exclusion of oxygen and we have made a study of the dissolution of the copper in the presence of oxygen in solutions of *n*-butylamine and carbon tetrachloride. The results are in accord with a mechanism in which the oxygen forms activated sites on the metal surface, followed by adsorption of amine at those sites, and, finally, by reaction of metal, amine, and carbon tetrachloride at those activated sites. The reaction probably involves charge-transfer complex formation and generates trichloromethyl radicals.

Experimental Section

Materials. The *n*-butylamine and carbon tetrachloride were prepared as before.[1] Reagent-grade methanol (Baker) was dried

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[1] For a recent study of the photochemical and metal-ion initiations and for references to other studies of the reaction, see W. J. Lautenberger, E. N. Jones, and J. G. Miller, *J. Amer. Chem. Soc.*, **90**, 1110 (1968).

[2] G. J. Beichl, Ph.D. Dissertation, University of Pennsylvania, 1953; G. J. Beichl, J. E. Colwell, and J. G. Miller, *Chem. Ind.* (London), 203 (1960).

[3] N. H. Cromwell, P. W. Foster, and M. M. Wheeler, *ibid.*, 228 (1959).

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[5] G. Heublein, *J. Prakt. Chem.*, **31**, 76 (1966).

over Linde Type 4A molecular sieves. *n*-Butylamine hydrochloride (Eastman) was crystallized three times from methanol–ether solution (mp 198°, lit.[6] 195°); after drying *in vacuo* it was stored in a desiccator. Zinc dibenzyldithiocarbamate (Eastman) was used without further purification.

Airco oxygen was passed over Ascarite and Drierite before admission to the reaction systems. Airco hydrogen was passed through an Engelhard Deoxo Purifier and then over Ascarite and Drierite.

High purity (99.997%) copper rods were supplied by the American Smelting and Refining Co. The rods were cut into right cylinders of basal areas 0.1, 1, and 4 cm^2 and were inserted in heavy-walled Teflon tubing plugged with glass rod at one end so that only a single basal surface was exposed flush with the end of the tubing. This exposed surface was then refaced and polished with a graded series of water-wet silicon carbide papers and finally with crocus cloth. After polishing, it was rinsed with distilled water, followed by reagent grade acetone, and was finally dried before use. Duplicate experiments run without refinishing the copper surface resulted in negligible change in dissolution rate, showing that the surface area of the copper remained substantially constant during the dissolution.

Apparatus. The reaction vessels used were for the great part constructed from three-necked 250-ml round-bottom flasks. The necks were used variously[7] to connect to the vacuum and pressure-measuring lines or to the gas-inlet systems, to hold sampling or injecting ports, and to admit a motor driven stirrer. Cylindrical cavities were blown in these flasks to hold the Teflon sheathed copper cylinders so that their exposed flat metal surfaces lay flush with the walls of the flask. In all of the experiments the vessels were immersed in a constant-temperature bath maintained at 30.00 ± 0.03°.

Procedures. For studies of the rate of dissolution of copper, a motor-driven stirrer was used to stir the liquid phase and the shaft speed was measured. The copper was first inserted into the oven-dried reaction vessel and then a measured amount (200 ml) of the carbon tetrachloride was introduced. The stirring was started and pure oxygen was bubbled in close to the stirrer blades at a constant pressure of 1 atm. A small amount of methanol (5 ml) was then added to prevent precipitation of any of the products of reaction. The amine was added last of all and it was injected into the stirred system at zero time.

Analyses of the reaction system were made by withdrawing aliquots through a sampling port and quenching with standard aqueous hydrochloric acid. The analyses of the organic and aqueous layers were then carried out as described earlier.[1] For the determination of the amount of copper dissolved, separate aliquots were taken and the carbamate method[8] was employed. The change in weight of the copper cylinders was in good agreement with those analyses. The dissolved copper was in the cupric state in the solutions; separate analyses revealed only negligible amounts of cuprous ion.

In a special experiment designed to investigate the effect of excluding oxygen, 10 ml of the amine and a disk of copper were placed in separate ampoules on the vacuum line. The amine was degassed by six freeze–pump–thaw cycles and the copper was reduced with pure hydrogen at 500° overnight. The ampoules were sealed and placed in the reaction vessel; 110 ml of CCl_4 was added and refluxed under vacuum and stirring for 20 min and then put through three degassing cycles. After the system came to temperature, the ampoules were broken. No sign of reaction was detected for 8 hr although after that time the copper started to dissolve very slowly. In other experiments, where less complete exclusion of oxygen was used, the delay and slowness of reaction were found proportional to the extent of exclusion of oxygen.

Results

General Remarks. Pure *n*-butylamine and pure CCl_4 do not react separately with copper either in the presence or absence of oxygen at room temperature.[2] Although their mixtures possess oxidizing power,[1,2,4,5] that power is insufficient to oxidize copper metal, as revealed by our tests with exclusion of oxygen. A small concentration of oxygen is needed, and when the oxygen concentration is high the mixtures dissolve the copper rapidly. Owing to the uncontrollably variable and lengthy induction periods met at low oxygen concentrations, we have studied the dissolution with solutions saturated with pure oxygen at a total pressure of 1 atm.

Oxygen has normal solubility in CCl_4[9,10] and it was not necessary to use higher pressures of oxygen to avoid diffusion control as was done in the studies of the dissolution of copper in aqueous solutions of ammonia or amines.[11] At the pressure used here it was found that the rate leveled off to a constant value for any solution when the stirrer speed exceeded 700 rpm, and the determinations of rate were run at 930 rpm throughout.

In order to avoid initiation of reaction due to visible light,[1] the amine concentration was kept below 0.5 *M*. Methanol, used to prevent precipitation of reaction products, does not react with the copper and does not cause reaction of the solutions. In the absence of the methanol, amine hydrochloride and other insoluble products precipitate shortly after the start of reaction, thereby complicating the dissolution process and introducing error into the analyses.

The chief difficulty in this study is caused by chain reactions in the solution initiated by the surface dissolution reaction. Amine, CCl_4, and oxygen participate[1] in these chain reactions and cuprous ions can act in both the initiating and propagating steps.[1,2,12] This has made it necessary to restrict our attention to the process taking place at the surface and to measure that dissolution process before the ensuing reactions in the solution affect the composition of the solutions appreciably.

The Red Layer on the Copper Surface. Within a few seconds after the amine is added to start reaction, the copper surface becomes coated with a dark red layer and, in an unstirred system, streamers are put forth rapidly from this layer. These streamers dissolve and diffuse in the solution, taking on the characteristic cupric–amine blue color a short distance from the layer. When the system is stirred, one sees only the red layer on the metal and the blue color of rapidly increasing intensity in the liquid. The red layer persists until all of the amine is consumed.

The layer was examined by X-ray diffraction. The copper cylinder with the layer attached was removed from the reaction system. After washing with water, it was dried *in vacuo*. During the drying it changed to a straw color. The X-ray pattern was that of cuprous chloride.

Chemical tests of freshly formed specimens of the layer also showed it is a cuprous compound. It dissolved readily in methanol or ethanol and the solution formed reduced Ag^+ to Ag and formed the cuprous color with dimethylglyoxime.

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(7) For details, see the Ph.D. Dissertations of E. N. Jones and W. J. Lautenberger, University of Pennsylvania, 1967.

(8) E. B. Sandell, "Colorimetric Determination of Traces of Metals," Interscience Publishers, New York, N. Y., 1950, p 204.

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(10) J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes," 3rd ed, Reinhold Publishing Corp., New York, N. Y., 1950, p 243.

(11) (a) J. Halpern, *J. Electrochem. Soc.*, **100**, 421 (1953); (b) J. I. Fisher and J. Halpern, *ibid.*, **103**, 282 (1956); (c) J. Halpern, H. Milants, and D. R. Wiles, *ibid.*, **106**, 647 (1959); (d) S. C. Sircar and D. R. Wiles, *ibid.*, **107**, 164 (1960).

(12) M. Asscher and D. Vofsi, *J. Chem. Soc.*, 2261 (1961); 1887 (1963); *J. Chem. Soc., B*, 947 (1968); M. Asscher, *Chem. Ind.* (London), 1430 (1965).

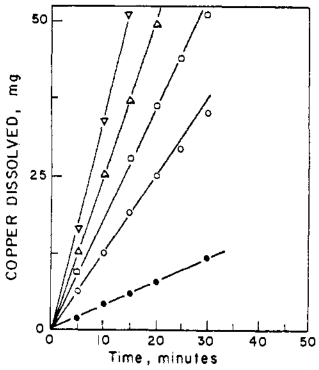

Figure 1. Rate of reaction of 1.0-cm² copper surface at different amine concentrations: ▽, 0.471; △, 0.178; □, 0.130; ○, 0.083; ●, 0.035 *M*.

Effect of Surface Area and Initial Amine Concentration. The effect of initial amine concentration on the rate of dissolution of copper of 1.0-cm² surface area is shown in Figure 1. The good linearity over a long period permitted accurate estimation of the rates of dissolution at zero time. Separate experiments using different volumes of solution and different surface areas of copper showed that the initial rates were independent of the volume of solution and were closely proportional to the surface area of the copper. For example, with 0.176 *M* amine the initial rates for surfaces of 0.1, 1.0, and 4.0 cm² were 0.257, 2.485, and 10.425 mg min^{-1}, respectively, giving an average value of 2.55 ± 0.04 mg cm^{-2} min^{-1} for the absolute initial rate value at that amine concentration. This rate was the same when volumes as small as one-half the usual volume of solution were used.

Figure 2 is a plot of the initial rates against initial amine concentrations. The curve drawn was found to obey the equation

$$\text{initial rate} = -\frac{1}{S}\frac{\mathrm{dCu}}{\mathrm{d}t} = \frac{k[\mathrm{A}]^2}{1 + k'[\mathrm{A}] + k''[\mathrm{A}]^2} \quad (1)$$

where S is the surface area of the copper and [A] is initial amine concentration. The conformity of the data to that equation is shown in Table I.

Table I. Verification of the Rate Equation[a]

[A], mol/l.	$-(1/S)(\mathrm{dCu}/\mathrm{d}t)$, calcd, mg/(min cm²)	$-(1/S)(\mathrm{dCu}/\mathrm{d}t)$, obsd, mg/(min cm²)
0.055	0.95	0.95
0.13	2.1	1.9
0.18	2.5	2.5
0.23	2.8	2.8
0.32	3.1	3.1
0.47	3.4	3.4

[a] k = 797.6 mg l.²/(min mol² cm²), k' = 17.45 l./mol; k'' = 190.35 l.²/mol².

There is no sign of an autocatalytic effect of the cupric ions such as found by Lu and Graydon[13] for the dissolution of copper in aqueous solutions of ammonia saturated with air at 1 atm pressure.

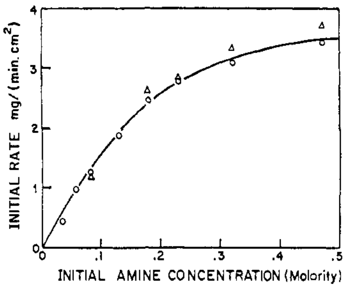

Figure 2. Effect of initial amine concentration on intial rate of dissolution. Copper surface area: ○, 1.0²; △, 0.1 cm².

The principal products of the reactions following the attack on copper, in addition to cupric ions, were identified and found the same as those that resulted from the reaction of amine with CCl_4 in the presence of a high concentration of oxygen in the absence of copper,[1] namely, *n*-butylamine hydrochloride, N,N′-di-*n*-butylurea, ammonium chloride, and butylidenebutylamine, with only minor amounts of chloroform and hexachloroethane.

Discussion

Halpern and those who followed him in the study of the dissolution of copper in aqueous solutions of ammonia and amines[11] showed that the dissolving process involved two steps following the formation by oxygen of oxidized sites on the copper surface. The first of those two steps appeared to be a rapid equilibrium adsorption of ammonia (or amine) on an oxidized site, and the second, the rate-determining step, was an attack on the same site by either the ammonia (amine) molecule or an ammonium (aminium) ion.

$$\mathrm{Cu_o + A \rightleftharpoons Cu_oA} \quad (2)$$

$$\mathrm{Cu_oA + A \longrightarrow CuA_2^{2+}} \quad (3)$$

$$\mathrm{Cu_oA + AH^+ \longrightarrow CuA_2^{2+} + H^+} \quad (4)$$

The symbol Cu_o denotes a copper atom at an oxidized site, the nature of which was not determined, while A and AH^+ denote the ammonia or amine and the conjugate acid, respectively. The adsorption equilibrium (reaction 2) was observed directly,[14] using carbon-14 labeled methylamine. By using ethylenediamine as amine, it was shown[11d] that the sites for reactions 2, 3, and 4 are the same.

The dissolution of copper in CCl_4 solutions of *n*-butylamine in the presence of oxygen is similar to that in the aqueous solutions in many respects, but the rate-determining step is the formation of cuprous chloride on the copper surface in the CCl_4 solutions. Amine–oxygen and CCl_4–oxygen systems separately do not dissolve copper. A charge-transfer complex between *n*-butylamine and CCl_4 is known to exist[1] and accounts for the ability of the mixture to dissolve the copper in the presence of oxygen. We propose the following mechanism, which is consistent with the rate equation

$$\mathrm{Cu + O_2 \rightleftharpoons Cu_o} \quad (5)$$

$$\mathrm{Cu_o + A \rightleftharpoons Cu_oA} \quad (6)$$

$$\mathrm{Cu_oA + A \rightleftharpoons Cu_oA_2} \quad (7)$$

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[13] B. C.-Y. Lu and W. F. Graydon, *J. Amer. Chem. Soc.*, 77, 6136 (1955).

[14] See unpublished work of F. I. Nagi and D. R. Wiles quoted in M. Kulkarni and D. R. Wiles, *Can. J. Chem.*, 43, 1978 (1965).

$$\mathrm{Cu_oA_2 + CCl_4 \rightleftarrows Cu_oA_2\cdot CCl_4} \qquad (8)$$

$$\mathrm{Cu_oA_2\cdot CCl_4 \longrightarrow Cu(A_2)Cl + \cdot CCl_3} \qquad (9)$$

where $\mathrm{Cu_o}$, $\mathrm{Cu_oA}$, and $\mathrm{Cu_oA_2}$ have the meaning introduced earlier, and $\mathrm{Cu_oA_2\cdot CCl_4}$ denotes a charge-transfer complex formed between adsorbed amine and $\mathrm{CCl_4}$ at an oxidized site.

Reaction 9 is taken to be the rate-determining step, $\mathrm{Cu(A)_2Cl}$ being written as the composition of the red layer. This layer dissolves rapidly and its cuprous ions are oxidized rapidly to cupric ions in solution by the oxygen and by the charge-transfer complex.[1] The other reaction products are accounted for by reactions[1] involving the trichloromethyl radicals formed in reaction 9.

This mechanism yields the rate expression

$$-\frac{\mathrm{dCu}}{\mathrm{d}t} = \frac{\mathrm{d[Cu^{2+}]}}{\mathrm{d}t} = \frac{k_9K_6K_7K_8fS[\mathrm{A}]^2[\mathrm{CCl_4}]}{1 + K_6[\mathrm{A}] + K_6K_7[\mathrm{A}]^2} \qquad (10)$$

where S is the surface area of the copper, f is the fraction of the area covered by oxidized sites, k_9 is the velocity constant of the rate-determining step, and K_6, K_7, and K_8 are the equilibrium constants of reactions 6, 7, and 8, respectively. If f is taken as constant when the oxygen pressure is constant, and since the $\mathrm{CCl_4}$ is present in large excess, this rate expression becomes the same as that observed (eq 1).

The same result is obtained for the conditions of our experiments if the mechanism is altered to replace reactions 7 and 8 by a single process in which a preformed charge-transfer complex attaches to an oxidized site

$$\mathrm{Cu_oA + A\cdot CCl_4 \rightleftarrows Cu_oA_2\cdot CCl_4} \qquad (11)$$

but we prefer the use of reactions 7 and 8 because of the earlier extensive work,[11] which proved the rapid adsorption of two molecules of amine to each oxidized site, and also because of the low concentration of the charge-transfer complexes in the solution.[1]

Preliminary experiments showed that the protonated amine is nearly as effective as amine in dissolving copper in our systems. This may be accounted for, as in the case of the aqueous systems,[11] by transfer of the proton to oxygen attached to the activated site. In the two runs in which the amine hydrochloride was added to the system instead of amine, induction periods of 2 and 7 min occurred and the red layer did not appear until the induction periods ended and the copper started to dissolve.

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Rates of Ozone–Paraffin Reactions in Carbon Tetrachloride Solution[1]

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Abstract: The second-order rate constants of ozonation in carbon tetrachloride solution at 25° have been determined for nine paraffins: isobutane, *n*-pentane, isopentane, neopentane, 3-methylpentane, 2,3-dimethylbutane, *n*-octane, cyclopentane, and cyclohexane. Different types of CH bonds in the paraffin molecules show large differences in reactivity, with primary < secondary < tertiary. Rate constants have been also determined for the following three alcohols: *t*-butyl alcohol, *n*-butyl alcohol, and cyclopentanol, and are found to increase rapidly in that order.

Reactions of ozone with unsaturated hydrocarbons have been investigated very extensively.[3] Much less work has been done on the corresponding reactions with saturated hydrocarbons and, in particular, relatively few determinations of the absolute values of second-order rate constants for ozone–paraffin reactions have been made. Schubert and Pease[4] have determined the second-order rate constants in the gas phase for methane, propane, *n*-butane, and isobutane and found that they depend on the strength of the CH bonds in the paraffins. This was shown by a 14-fold increase in the rate constant at 25° and a decrease in activation energy from 14.9 to 10.3 kcal/mol in going from methane, which has only primary H atoms, to isobutane, which has a tertiary H atom. On the other hand, in subsequent extensions of this work, Schubert and coworkers[5,6] have found no difference in the activation energies of methane, ethane, and propane and, surprisingly, a somewhat *greater* reactivity of the primary H atoms in ethane than of the less strongly bound secondary H atoms in propane. Hamilton, Ribner, and

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[1] Issued as NRC No. 11330.

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