439. *Chlorine Activation by Redox-transfer. Part I. The Reaction between Aliphatic Amines and Carbon Tetrachloride.*

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A free-radical chain mechanism is suggested for the reaction between aliphatic amines and carbon tetrachloride catalysed by copper chloride. According to this mechanism, the amine is chlorinated by carbon tetrachloride to an α-chloro-amine. Chloroform is the second product. Unchanged amine eliminates hydrogen chloride from the α-chloro-amine, producing amine hydrochloride. Copper ions appear to function as chlorine-atom carriers, providing a pathway for chain transfer. The effect of this " redox-transfer " appears as an enhanced apparent reactivity of carbon tetrachloride.

REACTION between carbon tetrachloride and aliphatic amines is already known;[1-3] strong catalysis by copper and cupric salts was noted by Foster and his co-workers.[3a] This observation is now confirmed for a series of primary, secondary, and tertiary amines, and a more detailed study made of the ethanolamines; catalysis by ferric and ferrous chloride was also noted. The possibility that this reaction may proceed *via* a free-radical chain mechanism is supported by the following: (*a*) On addition of traces of cupric and cuprous chloride to a solution of triethanolamine and carbon tetrachloride in methanol, at room temperature, there is a well-defined induction period (also in a thoroughly degassed system), during which the initially blue solution becomes green. The onset of reaction can be seen by the appearance of a precipitate of amine hydrochloride and a rise in the temperature. (*b*) The reaction induces the addition of carbon tetrachloride to aliphatic olefins, which is known to be a free-radical chain process.[4] (*c*) The reaction can be inhibited by small amounts of styrene.

These observations and the formation of chloroform and amine hydrochloride as main products can be accounted for by assuming a mechanism consisting of the following elementary steps:

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\begin{array}{lrcll}
\text{Initiation} & \mathrm{Cu^{2+} + R{\cdot}CH_2{\cdot}NR'R''} & \longrightarrow & \mathrm{Cu^{+} + R{\cdot}\dot{C}H{\cdot}NR'R'' + H^{+}} & \ldots\ldots\ (1) \\
 & \mathrm{Cu^{+} + CCl_4} & \longrightarrow & \mathrm{Cu^{+}(Cl) + {\cdot}CCl_3} & \ldots\ldots\ (2) \\
\text{Propagation} & \mathrm{{\cdot}CCl_3 + R{\cdot}CH_2{\cdot}NR'R''} & \longrightarrow & \mathrm{CHCl_3 + R{\cdot}\dot{C}H{\cdot}NR'R''} & \ldots\ldots\ (3) \\
 & \mathrm{R{\cdot}\dot{C}H{\cdot}NR'R'' + Cu^{+}(Cl)} & \longrightarrow & \mathrm{R{\cdot}CHCl{\cdot}NR'R'' + Cu^{+}} & \ldots\ldots\ (4) \\
\text{Termination} & \mathrm{2R{\cdot}} & \longrightarrow & \text{products} & \ldots\ldots\ (5)
\end{array}
$$

The α-chloro-amine formed in stage (4) is extremely reactive towards nucleophiles[5] and will immediately react with excess of amine, ultimately eliminating hydrogen chloride to form the amine hydrochloride and coloured resins.[6,7] This scheme indicates that copper ions are necessary in the initiation as well as in the propagation steps. Their rôle in propagating the chain is inferred from the absence of any reaction when benzoyl peroxide is added instead of copper. The generation of benzoyloxy-radicals in presence of tertiary amines at room temperature has been demonstrated before.[6,8]

The inhibition of reaction by styrene is indicative that the trichloromethyl radical is

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[1] Collins, *Chem. and Ind.*, 1957, 704; Sharada and Vasudeva Murthy, *Current Sci.*, 1960, **29**, 179.

[2] Beichl, Collwell, and Miller, *Chem. and Ind.*, 1960, 203.

[3] (*a*) Cromwell, Foster, and Wheeler, *Chem. and Ind.*, 1959, 228; (*b*) Foster, *Chem. and Ind.*, 1960, 1354.

[4] Kharasch, Jensen, and Urry, *J. Amer. Chem. Soc.*, 1947, **69**, 1100.

[5] Böhme, Lehners, and Keitzer, *Chem. Ber.*, 1958, **91**, 340; Böhme, Ellenberg, Herboth, and Lehners, *ibid.*, 1959, **92**, 1608.

[6] Horner and Schwenk, *Annalen*, 1950, **566**, 69; Horner, Brüggemann, and Knapp, *ibid.*, 1959, **626**, 1.

[7] Henbest and Slade, *J.*, 1960, 1558.

[8] Walling and Indictor, *J. Amer. Chem. Soc.*, 1958, **80**, 5814.

one of the chain carriers, since styrene is an efficient scavenger[9] for this radical. The resulting benzyl-type radical is apparently not chain-sustaining in the present case.

The individual steps of the above scheme are supported:

Step 2. It was shown by Doughty[10] that cuprous ion in aqueous ammonia is instantaneously oxidised by carbon tetrachloride at room temperature; a trichloromethyl radical and a chloride ion are initially presumably formed. In the presence of an amine, the same reaction probably occurs. The driving force is no doubt the high stability of cupric ion in co-ordination with amine or ammonia. Without amine, much higher temperatures are required for reaction (2) (unpublished results).

Step 3. The formation of chloroform as a major product is in accord with the ready abstraction by free radicals of α-hydrogen atoms from amines.[10a]

Step 4. Free radicals readily abstract halogen from cupric or ferric halides.[11,12,13] Entwistle[13a] pointed out that the donor-acceptor relation between radical and substrate can be of far greater importance for interactions between a radical and a metal halide than for ordinary homolytic displacements. The amine radical is probably one of the strongest donors known, owing to the great stability of the corresponding cation, as reflected by the salt-like nature of α-chloro-amines.[5] Therefore, very strong donor properties will be conferred both on amine as substrate in reaction (3), and on the amine radical. This will greatly facilitate reactions (3) and (4).[14]

The induction period in the reaction, catalysed by cupric chloride, between triethanolamine and carbon tetrachloride in methanol, can be eliminated by a small amount of ethanolamine hydrochloride. The colour of the solution is then green from the start.

Cuprous chloride, which according to reaction (2) should immediately generate trichloromethyl radicals and thus initiate the reaction, nevertheless shows an induction period in the absence of added hydrochloride. It appears, therefore, that a certain minimum concentration of chloride ions is needed for the reaction.

The following mobile equilibrium is established in the reaction medium:

$$\underset{\text{(I)}}{\text{Cu}^{2+}\text{(amine)(solvent)}} + \text{Cl}^- \rightleftharpoons \underset{\text{(II)}}{\text{Cu}^{+}\text{(amine)(solvent)(Cl)}} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

Complex (I) is blue and complex (II) green.[15] Apparently, a cupric complex ion like (II), with at least one chlorine bound to copper, is needed for step (4),[11] and perhaps also for step (1). In the presence of a large excess of amine and methanol, equilibrium (5) is displaced too far to the left, and chloride ions have to be furnished, or slowly produced during the induction period, in order to obtain a fast reaction. [In the reaction scheme we have written Cu$^+$(Cl) instead of (II) for the sake of brevity.] Consistent with this view is the fact that in isopropyl alcohol or t-butyl alcohol, both of which solvate cupric ion much less than does methanol, the solution is green from the start and there is a much shorter induction period. Ethylenediaminetetra-acetic acid, on the other hand, has a pronounced retarding effect, for it is a strong sequestering agent for cupric ion.

We have no direct evidence for step (1), but it was reported[16] that cupric chloride is reduced by acetone in a reaction which is catalysed by chloride ions.

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[9] Robb and Vofsi, *Trans. Faraday Soc.*, 1959, **55**, 566.

[10] Doughty, *J. Amer. Chem. Soc.*, 1919, **41**, 1131.

[10a] Bamford and White, *Trans. Faraday Soc.*, 1956, **52**, 716; Schenck and Zunft, *Angew. Chem.*, 1957, **69**, 595; Urry and Juveland, *J. Amer. Chem. Soc.*, 1958, **80**, 3322; Henbest and Patton, *J.*, 1960, 3557.

[11] Kumamoto, de la Mare, and Rust, *J. Amer. Chem. Soc.*, 1960, **82**, 1935.

[12] Bamford, Jenkins, and Johnston, *Proc. Roy. Soc.*, 1957, *A*, **238**, 214.

[13] (*a*) Entwistle, *Trans. Faraday Soc.*, 1960, **56**, 284; (*b*) Bamford, Jenkins, and Johnston, *Trans. Faraday Soc.*, 1959, **55**, 421.

[14] Walling, *J. Amer. Chem. Soc.*, 1948, **70**, 2561; " Free Radicals in Solution," Wiley, New York, 1957, p. 158; Russell, *J. Amer. Chem. Soc.*, 1956, **78**, 1047.

[15] Udovenko and Artemenko, *Zhur. neorg. Khim.*, 1959, **4**, 353.

[16] Kochi, *J. Amer. Chem. Soc.*, 1955, **77**, 5274; Dickerman, Weiss, and Ingberman, *J. Org. Chem.*, 1956, **21**, 380.

Step (4) is in itself a chain-breaking reaction,[11,12,13,17] but in conjunction with step (2) it provides a pathway for chain transfer. This mode of transfer, which we will call " redox-transfer," is brought about by copper or iron ions as chlorine-atom carriers, and manifests itself in a much greater apparent reactivity of carbon tetrachloride. Redox-transfer will in principle be possible only for compounds in which halogen is bound to a strongly electronegative group, for otherwise the vital step (2) will be reversed, as in step (4).

The net result of steps (4) and (2) is a normal homolytic displacement:

$$\mathrm{R{\cdot}\dot{C}H{\cdot}NR'R'' + CCl_4 \longrightarrow R{\cdot}CHCl{\cdot}NR'R'' + {\cdot}CCl_3} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (7)$$

Foster's results [3b] do not allow a conclusion as to whether step (7) can take place at room temperature, or whether traces of metal ions, which are not easily excluded, are responsible for the reaction which he observed between triethylamine and carbon tetrachloride.

Isopropyl alcohol, when used as a solvent for reaction between amine and carbon tetrachloride, is concurrently chlorinated by an entirely analogous redox-transfer mechanism, giving 2-chloropropan-2-ol, which immediately decomposes into acetone and hydrochloric acid.[18] This results in the formation of additional amine hydrochloride. t-Butyl alcohol, on the other hand, is an inert solvent, for it cannot be dehydrogenated by a trichloromethyl radical (see Experimental).

EXPERIMENTAL

Materials.—" AnalaR " carbon tetrachloride and triethanolamine (Eastman White Label) were used as supplied. Methanol was Fisher spectrograde product, and 1-octene a Phillips pure-grade material.

Reaction of Triethanolamine with Carbon Tetrachloride.—(a) *Detection of chloroform.* To a solution of triethanolamine (10 g., 0·067 mole) in isopropyl alcohol (20 g.) and carbon tetrachloride (10 g.) were added 10 drops of a 1·5% solution of cupric chloride dihydrate in isopropyl alcohol (≡2·5 mg. of $CuCl_2$). The reaction vessel was stoppered and kept at 25°. A precipitate began to appear after 6 min., and after 1 hr., water (200 c.c.) was added. The lower layer was separated and distilled (steam-bath). The distillate (8·4 g.) was analysed by gas-liquid chromatography at 38° (on silicone oil as the stationary phase, in a 1-m. column), and consisted of 33% chloroform, 61% carbon tetrachloride, and 6% acetone. Acetone is a product of the concurrent chlorination of isopropyl alcohol by carbon tetrachloride [see (b)].

(b) *Concurrent chlorination of triethanolamine and isopropyl alcohol.* The experiment was carried out as in (*a*). After 1 hr., the precipitate which had formed was sucked off, washed with isopropyl alcohol and acetone, and dried for 12 hr. at 70° (Found: Cl, 19·4. Calc. for triethanolamine hydrochloride: Cl, 19·1%), m. p. and mixed m. p. 178—180° (lit., m. p. 177°). The yield of hydrochloride before recrystallisation was 7·05 g. (=0·038 mole), 13% in excess of the theoretical yield. This excess reflects the extent to which isopropyl alcohol has been chlorinated by carbon tetrachloride in the presence of amine.

When the same reaction was carried out in t-butyl alcohol, and catalysed by a 1·5% solution of cupric chloride in t-butyl alcohol, 98·5% of the theoretical yield of the salt (Found: Cl, 19·4%) was obtained.

(c) *Variables affecting the induction period.* To a mixture (10 g.) of equal weights of triethanolamine, carbon tetrachloride, and methanol was added cupric chloride dihydrate (4 mg.). After 15 min. the blue solution became green, and the hydrochloride began to precipitate. After 20 min. the solution began to boil. When ferrous chloride tetrahydrate (14 mg.) was used instead of cupric chloride, precipitation began without an induction period, but the reaction was slower and less exothermic. When to the same amount of mixture, ethanolamine hydrochloride (30 mg.) was added, and thereafter 3 drops of a 2·5% solution of cupric chloride dihydrate in methanol (≡1 mg. of chloride), the solution immediately became faintly green and warmed, as triethanolamine hydrochloride began to precipitate, again without an induction period. When ethanolamine hydrochloride was omitted and 8 drops of the same methanolic cupric chloride solution were added, there was an induction period of 55 min. When instead

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[17] Kochi, *J. Amer. Chem. Soc.*, 1956, **78**, 4815.

[18] Razuvaev, Moryganov, and Volkova, *Zhur. obshchei Khim.*, 1955, **25**, 495.

of methyl alcohol, isopropyl alcohol or t-butyl alcohol was taken as the solvent, the precipitation of the salt started almost immediately on addition of cupric chloride.

Reaction between 1-*Octene and Carbon Tetrachloride in the Presence of Ethanolamine.*—Cupric chloride dihydrate (50 mg.) in t-butyl alcohol (10 g.) was added to a mixture of ethanolamine (3 g.), oct-1-ene (28 g., 0·25 mole), carbon tetrachloride (77 g., 0·5 mole), and t-butyl alcohol (20 g.), and the blue solution was refluxed for 10 hr. After cooling, the mixture was poured into 0·5 l. of water, the lower layer separated, and the aqueous layer extracted twice with carbon tetrachloride and discarded. The extracts were added to the separated lower layer, washed twice with water, and dried ($CaCl_2$). The solvent was removed by distillation and the residue distilled; unchanged oct-1-ene (5 g.) was collected (b. p. 35—40°/25 mm.), followed by a fraction (42 g.) of b. p. 80—105°/0·3 mm. (bath up to 160°); a brown oily residue (9·2 g.) remained, presumably mostly an adduct of 2 moles of oct-1-ene to 1 mole of carbon tetrachloride. The fraction, b. p. 80—105°/0·3 mm., was redistilled: it had b. p. 78—80°/0·3 mm. (Found: Cl, 51·5, 51·7. Calc. for 1,1,1,3-tetrachlorononane: Cl, 53·3%). A vapour-phase chromatogram showed that the product (77%) was almost homogeneous.

Reaction of Ethylene and Carbon Tetrachloride [19] *in the Presence of Triethanolamine.*—A 100-c.c. stainless-steel autoclave, fitted with a magnetic stirrer, was charged with triethanolamine (4 g.), methyl alcohol (20 g.), carbon tetrachloride (60 g.), and cupric bromide (66 mg.). Without previous purging, the vessel was left for 1½ hr. under an ethylene pressure of 61 atm., while the contents were stirred. The ethylene source was disconnected and stirring continued during 65 hr. at room temperature. After release of the excess of ethylene and opening of the autoclave, the solution was filtered from the precipitate of triethanolamine hydrochloride (2·9 g.) and freed from methanol and excess of carbon tetrachloride by distillation at atmospheric pressure (bath temperature up to 140°). Distillation was continued up to 180° (bath) at 25 mm. and up to 140° (bath) at 0·3 mm. The combined distillate (58·1 g.) was analysed by gas–liquid chromatography at 200° on silicone oil as the stationary phase, in a 0·76-m. column; it consisted of 3% of 1,1,1,3-tetrachloropropane, 44% of 1,1,1,5-tetrachloropentane, 36% of 1,1,1,7-tetrachloroheptane, 14% of 1,1,1,9-tetrachlorononane and 3% of 1,1,1,11-tetrachloroundecane. Conversion of carbon tetrachloride was 65%.

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[19] Joyce, Hanford, and Harmon, *J. Amer. Chem. Soc.*, 1948, **70**, 2529; Bolt and Joyce, *Chem. Eng. News*, 1947, **25**, 1866; Nesmeyanov, Freidlina, *et al.*, *Quart. Rev.*, 1956, **10**, 333.