[CONTRIBUTION OF THE CHEMISTRY RESEARCH DEPARTMENT, U. S. NAVAL ORDNANCE LABORATORY]

Metal Halide Catalyzed Hydrolysis of Trichloromethyl Compounds

MARION E. HILL[1a]

Received January 8, 1960

Ferric chloride, gallium chloride, and antimony pentachloride catalyze the hydrolysis of carbon tetrachloride to phosgene in high yield under mild conditions. The catalysts are dehydrated by the hydrolysis reaction, affording a convenient means of preparing anhydrous ferric and gallium chlorides. The hydrolysis of other halomethanes, trichloromethylaryl compounds, and trichloroethane is also easily accomplished with ferric chloride catalysis. A complex of the metal halide with the chlorocarbon which readily reacts with water is proposed as a highly reactive intermediate in the hydrolysis reaction.

Carbon tetrachloride and other chlorinated hydrocarbons have produced phosgene under oxidative conditions by passing the vapor mixed with air over heated metals, metal oxides and chlorides at elevated tmperatures[1b-3] and by irradiation with light of wave length 2537 Å in the presence of oxygen.[4] Phosgene from wet carbon tetrachloride in the presence of metals such as copper and iron has been observed qualitatively, but little information of the nature of the reaction was reported.[5] Recently we detected a small amount of phosgene in the reaction vessel after conducting a Friedel-Crafts type reaction involving ferric chloride as catalyst in carbon tetrachloride solvent. In subsequent experiments to determine the source of the phosgene we found that ordinary commercial pure sublimed ferric chloride and carbon tetrachloride would evolve phosgene. The apparent hydrolysis of the solvent by small amounts of water in the anhydrous ferric chloride was confirmed by the preparation of phosgene by adding water to a mixture of carbon tetrachloride and catalyst at reflux temperature. These observations prompted us to study the heretofore unreported easily catalyzed hydrolysis of carbon tetrachloride and other trichloromethyl compounds by iron, gallium, and antimony chlorides under very mild conditions.

RESULTS

The hydrolysis of carbon tetrachloride in the presence of ferric chloride was a convenient method for the preparation of phosgene, one mole of phosgene being produced for each mole of water added. In the general study comparing catalysts and their hydrates in the hydrolysis reaction, phosgene was not isolated but was swept out of the system by nitrogen into an ether solution of aniline which reacted with phosgene and hydrogen chloride. The diphenylurea which precipitated was isolated and the phosgene yields calculated. Aniline hydrochloride also precipitated in the correct ratio for the overall reaction

$$CCl_4 + H_2O \xrightarrow{FeCl_3} COCl_2 + 2HCl$$

$$COCl_2 + 2HCl + 6\,C_6H_5NH_2 \longrightarrow C_6H_5NHCONHC_6H_5 + 4C_6H_5NH_2\cdot HCl.$$

When phosgene was desired, the effluent gases were swept into cold traps and the phosgene recovered from the condensate by redistillation.

Although water may be added directly to the heterogeneous catalyst-carbon tetrachloride mixture, water in the form of the tetrahydrate of ferric chloride and lesser hydrates readily reacted. The phosgene began evolving slowly at 60°, increasing in evolution rate up to reflux temperature. The hexahydrate of ferric chloride did not undergo reaction. Antimony pentachloride and gallium chloride were also efficient in promoting carbon tetrachloride hydrolysis. With antimony pentachloride it was difficult to prevent the formation of its oxychlorides by reaction with water. Gallium chloride was easily made inactive by the addition of water in excess of the dihydrate equivalent. Neither the hydrate of aluminum chloride nor a mixture of anhydrous aluminum chloride with a small amount of hydrated catalyst would react with carbon tetrachloride.

In the course of the hydrolysis reaction the catalysts were dehydrated. For example, ferric chloride tetrahydrate, which initially was an orange oil, was observed to become crystalline, eventually having the particulate blue green anhydrous ferric chloride form. Iron oxide formation, which usually occurs when ferric chloride hydrates are heated, was not observed. Therefore, this procedure provided a simple way of preparing anhydrous ferric chloride without employing the inconvenient high temperature sublimation procedure. Gallium chloride was also dried by the hydrolytic action without formation of oxide and has been obtained in good purity.[6] Although aluminum chloride hydrate

---

[1a] Present address: Stamford Research Institute, Menlo Park, California.

[1b] E. Bielsalski, *Z. angew. Chem.*, **37**, 314 (1924).

[2] B. Sjoberg, *Svensk. Kem. Tidskr.*, **64**, 63 (1952).

[3] W. B. Crummett, and V. A. Stenger, *Ind. Eng. Chem.*, **48**, 434 (1956).

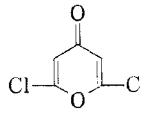
[4] E. H. Lyons, and R. G. Dickinson, *J. Am. Chem. Soc.*, **57**, 443 (1935).

[5] A. W. Doughty, *J. Am. Chem. Soc.*, **39**, 2685 (1917).

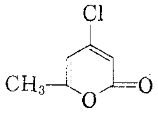
[6] W. F. Sager, George Washington University, private communication; using the procedure as described by us for ferric chloride, crude gallium chloride was dried and redistilled to give pure gallium chloride crystals.

would not react with carbon tetrachloride, its anhydrous state could be restored by refluxing its mixture with anhydrous ferric chloride until phosgene evolution stopped, yielding a reactive mixed metal halide catalyst.

Other halomethanes such as dichlorodibromomethane and bromotrichloromethane reacted with water and ferric chloride, producing low yields of phosgene and molecular bromine by-product. Chloroform was almost completely unaffected even after prolonged reaction periods, and was subsequently used as a convenient solvent for other trichloromethyl compounds which were being hydrolyzed. 1,1,1-Trichloroethane reacted very vigorously at room temperature with hydrated ferric chloride, giving acetic acid as the hydrolysis product. However, as the catalyst become anhydrous, dehydrohalogenation became predominant and vinylidene chloride was formed. In addition a small amount of a solid side reaction product was isolated. Elemental analysis indicated that it had an empirical formula $C_6H_5O_2Cl$. Infrared analysis showed a strong carbonyl, double bond, and some ring absorption. This spectrum plus qualitative organic analytical tests and melting point indicated that the compound was the same as the $C_6H_5O_2Cl$ compound isolated by Wichterle and Vogel[7] as a side product from the acetylation of vinylidene chloride by acetyl chloride in the presence of aluminum chloride. This seemed reasonable as both vinylidene chloride from dehydrohalogenation and acetyl chloride as an intermediate in the hydrolysis of the methylchloroform were present. Additionally, in a separate experiment, ferric chloride did catalyze the condensation of vinylidene chloride and acetyl chloride to the C_6 compound. Wichterle and Vogel[7] proposed that the compound was either 2-methyl-6-chloro-4H-pyran-4-one, I, or 6-methyl-4-chloro-2H-pyran-2-one, II.



I



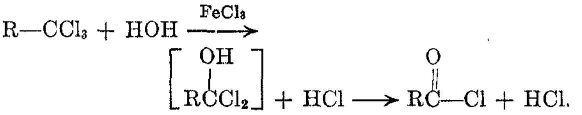
II

From physical data obtained on the compound we prefer to consider the product to be the α-pyrone, II. The ultraviolet absorption curve in methanol gave a single peak at 300 mμ, log ε = 3.38, which is not consistent with the absorptions found for γ-pyrones of log ε 4.08–4.23 at 250–260 mμ, and corresponds to the observations of Berson[8] that the α-compounds absorb at pronouncedly longer wave lengths and lower intensities than the γ-compounds. Furthermore, it is difficult to correlate the structure of I with the fact that catalytic hydrogenation of the product in methanol[7] gave methyl caproate. Prior published work has consistently reported that only the double bonds of γ-pyrones have been reduced by catalytic hydrogenation without ring cleavage.[9]

Although previous catalytic hydrolysis reactions of aryl trichloromethyl compounds have been reported,[10] we reinvestigated the hydrolysis of these compounds because of the unusually high temperature of 150° employed to hydrolyze them by prior investigators. We found that benzotrichloride in chloroform solution reacted very vigorously with hydrated ferric chloride, cooling to 0° being necessary to moderate the reaction. Similarly, *m*- and *p*-hexachloroxylene reacted extremely vigorously at room temperature, producing nearly quantitative yields of isophthalic and terephthalic acids respectively.

DISCUSSION

In considering a mechanism for this reaction, the simplicity of the procedure indicates that an unexpected activation of the chlorinated hydrocarbons by the weak Lewis acids is a principal factor influencing the reaction. Such consideration should be consistent with the observed activity of iron, gallium, and antimony chlorides in anhydrous and hydrated states in contrast to the lack of activity by aluminum chloride. The reaction must proceed by a nucleophilic attack by water on a reactive trichloromethyl complex with the metal halide-, the overall reaction being



$$R{-}CCl_3 + HOH \xrightarrow{FeCl_3} \left[\begin{array}{c} OH \\ | \\ RCCl_2 \end{array}\right] + HCl \longrightarrow R\overset{\overset{O}{\|}}{C}{-}Cl + HCl.$$

Such a mechanism is not inconsistent with the lack of reaction with chloroform because in its hydrolysis the intermediate, $HOCHCl_2$, would have to split out hydrogen to form phosgene, or alternatively to split out hydrogen chloride to form the very unstable formyl chloride. No evidence of either course of reaction was found.

There remains then the question of the form of the complex and why it apparently exists in the presence of water. Consideration of its possible structure is aided by two recent explanations which were used to account for the results of kinetic measurements on Friedel-Crafts reactions. The effectiveness of ferric chloride, gallium chloride, and antimony pentachloride in promoting the hydrolysis of carbon tetrachloride is similar to the observations of Jensen and Brown,[11] who found that in benzoyl chloride solvent these chlorides catalyzed the benzoylation of toluene more effectively than did aluminum chloride. They ex-

---

(7) O. Wichterle and J. Vogel, *Collection Czechoslovak Chem. Commun.*, **19**, 1197 (1954).

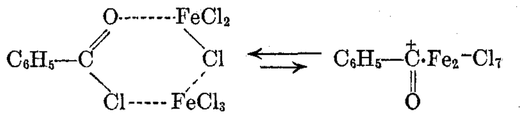
(8) (a) J. A. Berson, *J. Am. Chem. Soc.*, **75**, 3521 (1953). (b) E. R. Riegl and M. C. Reinhard, *J. Am. Chem. Soc.*, **48**, 1334 (1926).

(9) L. F. Cavalieri, *Chem. Rev.*, **41**, 525 (1947).

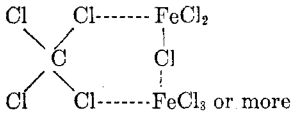
(10) W. Griehl, *Faserforsch. u. Textiltech.*, **4**, 464 (1953).

(11) F. R. Jensen and H. C. Brown, *J. Am. Chem. Soc.*, **80**, 3039 (1958).

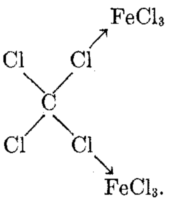
plained the observed third order kinetics by proposing the existence of a kinetically significant amount of a 1:2 compound of acyl halide with the metal halide dimer, $C_6H_5COCl:M_2X_{2n}$. Ahmad[12] has suggested that the same results could be accounted for by a cyclic intermediate or transition state in which the iron atom or gallium atom of the



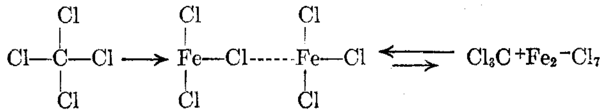
second molecule of MX_n has more than eight valency electrons. More specifically in the hydrolysis reaction it seems reasonable that the halogen bridge of the metal halide dimer is opened and replaced by coordination with the chlorocarbon, forming by analogy



or more extremely,



In essence the complex may have at least the form of I in equilibrium with a very small amount of the



$$\mathrm{Cl{-}\overset{Cl}{\underset{Cl}{C}}{-}Cl \longrightarrow \overset{Cl}{\underset{Cl}{Fe}}{-}Cl{\cdots}\overset{Cl}{\underset{Cl}{Fe}}{-}Cl \rightleftarrows Cl_3C^{+}Fe_2^{-}Cl_7}$$

I II

very reactive carbonium ion–metal halide pair, II. That weak Lewis acids must very easily form such complexes is strongly indicated by the ability of the ferric chloride hydrate to react with the trichloromethyl compounds. Such complexes can similarly be formed by the gallium and antimony chlorides, the latter chloride having been observed by Meyer[13] to exist in a stable complex as a dimer with acetophenone. It is not presumed that a complex does not form with aluminum chloride, as many Friedel Crafts condensations involving aluminum chloride and carbon tetrachloride can be explained by proposing reactive intermediate carbonium ion complexes with the catalyst. However, in this system the affinity of aluminum chloride for water as the hydrate must be greater than its affinity for chlorine in a similar manner proposed for aluminum chloride in acylation[11] and cannot enter into reaction with carbon tetrachloride. The ability of the added anhydrous ferric chloride to dry the hydrated aluminum chloride can be explained by considering that the ferric chloride–carbon tetrachloride complex simply reacts with the water of the aluminum chloride hydrate lattice.

EXPERIMENTAL

Hydrolysis of carbon tetrachloride. (A) Water, 4.0 g., 0.22 mole, was added dropwise to a mixture of 60 ml. of carbon tetrachloride and 8.1 g. (0.05 mole) of commercial anhydrous ferric chloride over a period of 4 hr. at reflux temperature. The gases evolved were swept by nitrogen into a spiral Dry Ice condenser equipped with a round bottom flask as receiver and then into an aqueous methanol trap. After the water addition, the catalyst-carbon tetrachloride mixture was heated an additional 2 hr. and then cooled. The Dry Ice condenser spirals contained a small amount of ice from entrained water. The product collected in the Dry Ice trap receivers was then redistilled, passing the vapor through mossy zinc to remove small amounts of hydrogen chloride. The phosgene obtained, 90% yield based on added water, b.p. 8.0, was partially distilled into 100 ml. of an ether solution containing 12 g. of aniline. The precipitate formed was collected, washed with water, and recrystallized from alcohol. The derivative, *sym*-diphenylurea, m.p. 240°, was identical with known diphenylurea as determined by mixed melting point and infrared traces.

(B) A mixture of 2.34 g. of ferric chloride tetrahydrate, m.p. 73°, (0.023 mole water) was heated with 35 ml. of carbon tetrachloride at reflux temperature for 3 hr., the efflux gases being swept into a solution of 0.1 mole of aniline in 250 ml. of ether. The precipitate was collected and dried, 12.55 g., and then slurried with water to recover the diphenylurea. This plus a small amount obtained by concentration of the ether weighed 4.00 g., 0.019 mole, 82%. The weight of aniline hydrochloride, 9.95 g., 0.077 mole, gave a ratio of the hydrochloride to diphenylurea of 4.05 *vs.* 4.00 required by theory.

In 10 hr. the same system gave 94% of phosgene as determined by diphenylurea, and about 24 hr. were required before phosgene detection was virtually nil.

Table I summarizes the results obtained by using the general procedure of (A). Where applicable, phosgene yields were determined by formation of diphenylurea derivative; otherwise the reaction products were isolated.

TABLE I

CATALYZED HYDROLYSIS OF Cl_3C— COMPOUNDS

$RCCl_3$ Compound	Solvent	Moles Catalyst	% Yield, Product[a]
CCl_4	—	0.1 -$SbCl_5$	90, $COCl_2$
CCl_4	—	0.01-$GaCl_3$	89, $COCl_2$
CCl_4	—	0.01 $AlCl_3$	nil
CCl_4	—	0.01 $ZnCl_2$	nil
Cl_2CBr_2	—	0.013 $FeCl_3$	30, $COCl_2$
p-$(CCl_3)_2C_6H_4$	$CHCl_3$	$FeCl_3$	98,[b] *p*-$(COOH)_2C_6H_4$
m-$(CCl_3)_2C_6H_4$	$CHCl_3$	$FeCl_3$	98,[b] *m*-$(COOH)_2C_6H_4$
$C_6H_5CCl_3$	$CHCl_3$	$FeCl_3$	88,[c] C_6H_5COOH
CH_3CCl_3	—	$FeCl_3$	70,[b] CH_3COOH

[a] Based on water added. [b] Stoichiometric amount of water added; reaction temperature, 25°. [c] Reaction temperature, 0°.

Catalyst drying. (A) A mixture of 16.25 g. (0.1 mole) of commercial anhydrous ferric chloride and 75 ml. of carbon tetrachloride was held at reflux temperature for 24 hr. while sweeping the efflux gases from the system with nitrogen. The catalyst after this period was finely divided dark blue green to reflected light. A reddish deposit was identified as ferric chloride and not iron oxide. Similarly, gallium chloride (0.01 mole) was dried in carbon tetrachloride with nitrogen sweep until phosgene evolution was virtually nil.

(B) A mixture of 2.14 g. (0.01 mole) of aluminum chloride hexahydrate, 0.82 g. of anhydrous ferric chloride, and 40 ml. of carbon tetrachloride was heated with stirring at reflux

---

[12] M. S. Ahmad, G. Baddeley, and R. M. Topping, *Chem. Ind.*, **1958**, 1327.

[13] K. H. Meyer, *Ber.*, 41, 2568 (1908).

temperature for 24 hr. The solvent was decanted from the dried mixed catalyst, which readily catalyzed the acylation of toluene (in excess) with benzoyl chloride, 4.20 g., 0.03 mole, giving *p*-methylbenzophenone in 60% yield.

Hydrolysis of 1,1,1-trichloroethane. A mixture of 21 g. of ferric chloride (0.13 mole) containing 3 g. (0.028 mole) of water and 72 g. (0.54 mole) of 1,1,1-trichloroethane was warmed gently until hydrogen chloride began to evolve. As reaction progressed, 3.0 g. of water was added over a period of 4 hr. while maintaining a temperature of 30° by water bath. When gas evolution had ceased, the reaction mixture consisted of an organic layer and a heavier layer containing the catalyst as a black oil. The organic layer was combined with several milliliters of product distilled under reduced pressure from the catalyst oil, and then fractionated, giving 6.3 g. of acetic acid (70% yield based on water added), 5.5 g. of vinylidene chloride, and 22 g. of methylchloroform. The inorganic residue was triturated with water which turned a deep violet color, leaving out of solution a tarry oil which eventually partially crystallized. The mixture was extracted with ether, decolorized and dried. Evaporation of the ether left a crystalline deposit which when recrystallized from hexane yielded 4.9 g. of white needlelike crystals, m.p. 85–6.

Anal. Calcd. for $C_6H_5ClO_2$: C, 49.84; H, 3.49; Cl, 24.53. Found: C, 50.10; H, 3.63; Cl, 24.36.

Infrared analysis in carbon tetrachloride gave an extremely intense absorption at 1744 cm.$^{-1}$ In methanol solution, maximum absorption occurred at 300 mμ, log ϵ = 3.38. Qualitative organic analytical tests for carbonyl and active chlorine were negative; bromine would not add; hydrolysis by acid solution was negative.

SILVER SPRING, MD.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF RESOURCES UTILIZATION, TOKYO INSTITUTE OF TECHNOLOGY]

O-Alkyl- and Aryl-*N*,*N*-ethyleneurethanes. I. Preparation and Reaction with Amines[1]

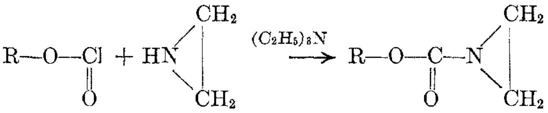
YOSHIO IWAKURA AND AIKO NABEYA

Received December 1, 1959

Several *O*-alkyl- or aryl-*N*,*N*-ethyleneurethanes were prepared, and the reactions of these urethanes with some aromatic amines were investigated. *O*-Alkyl-*N*,*N*-ethyleneurethanes gave only O-alkyl-*N*-(β-substituted ethyl)urethanes as the reaction products with amines. In the case of *O*-phenyl-*N*,*N*-ethyleneurethane, however, 1-substituted imidazolidinones-2 were obtained in addition to *O*-phenyl-*N*-(β-substituted ethyl)urethanes. This unexpected result was also observed in the reaction of other *O*-aryl-*N*,*N*-ethyleneurethanes with amines.

In our previous paper,[2] we reported the reaction of *N*-thiocarbamyl- and carbamyl derivatives of ethylenimine with several nucleophilic reagents. The results obtained there are summarized as follows: (1) *N*-phenyl- or cyclohexyl-*N'*,*N'*-ethylenethiourea is isomerized to thiazoline derivatives by heating in a high boiling solvent such as decalin or more smoothly in acids such as hydrochloric[3] or acetic. (2) The derivatives react with thiophenol giving *N*-phenyl- or cyclohexyl-*N'*-(β-phenylthioethyl)thiourea in good yields, and (3) in all cases, they show a strong tendency to polymerize by ring opening. In the case of *N*-phenyl-*N'*,*N'*-ethyleneurea, however, (1) the tendency to polymerize is not marked, and (2) isomerization to the oxazoline derivative is only observed in the reaction with picric acid, but (3) it reacts with thiophenol, hydrochloric acid, benzoic acid, and *p*-nitrobenzoic acid to give *N*-phenyl-*N'*-(β-substituted ethyl)-urea. Summarizing these results, it may be said that the substituent groups on the nitrogen of ethylenimine exert a strong influence upon the ring opening reaction of ethylenimine compounds.

We have extended the study to *N* - alkoxycarbonyl- or aryloxycarbonylethylenimine. The preparation of *O*-ethyl-*N*,*N*-ethyleneurethane (Ia) was described by Bestian.[4] In the same manner, we prepared several *O*-alkyl- and aryl-*N*,*N*-ethyleneurethanes from chloroformic acid esters and ethylenimine.



I

R = alkyl or aryl

O-Alkyl-*N*,*N*-ethyleneurethanes of lower molecular weight, in general, can be isolated by distillation and stored in a sealed tube for years without any appreciable change. But, the *O*-phenyl derivative (Id) seemed to be very unstable, especially on heating, and our attempts to isolate it by distillation under high vacuum were unsuccessful. Moreover, Id could not be crystallized by strong cooling in a Dry Ice–acetone bath. Accordingly, the purification of Id was only performed by extracting impurities with petroleum ether. *O*-*p*-substituted phenyl derivatives (Ie–Ih) were re-

---

(1) Presented at the annual meetings of the Chemical Society of Japan, April 1957 and April 1958, and at the symposium of Organic Synthetic Chemistry of Japan, November 1958.

(2) Y. Iwakura and A. Nabeya, in part in the paper, J. *Chem. Soc. Japan, Pure Chem. Sect,* **77**, 773 (1956), and in part presented at the symposium of Organic Synthetic Chemistry of Japan, November 1958.

(3) Reported by S. Gabriel and R. Stelzner, *Ber.*, **28**, 2929 (1895).

(4) H. Bestian, *Ann.*, **566**, 210 (1950).