[CONTRIBUTION FROM THE PENNSALT CHEMICALS CORPORATION AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CAMBRIDGE]

Aliphatic Halogen Compounds. I. Conversion of Carbonyl Halides into Tetrahalomethanes[1]

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Carbonyl halides COXY (X and Y = Cl or F) are converted into tetrahalomethanes such as CCl_4, CF_2Cl_2, CF_3Cl, $CFCl_3$ or CF_4 (a) by reaction with a phosphorus halide, *e.g.*, $COXY + PCl_5 \rightarrow CCl_2XY + POCl_3$, (b) by pyrolysis, *e.g.*, $COF_2 + COCl_2 \rightarrow CF_2Cl_2 + CO_2$; $2COFCl \rightarrow CF_2Cl_2 + CO_2$.

A carbonyl halide COXY can be regarded as a potential source of a CXY group provided that reactions can be found other than those where the acyl halide properties predominate. Two main routes have been found to convert COXY into a tetrahalomethane, thus utilizing the CXY group to the full, particularly for the preparation of important chemicals such as carbon tetrachloride and dichlorodifluoromethane.

Reaction of Carbonyl Halides with Phosphorus Halides.—The first method shows that a carbonyl halide has ketonic properties, since the following reactions have been effected

$$COCl_2 + PCl_5 \longrightarrow CCl_4 + POCl_3$$

$$COF_2 \xrightarrow[\text{or } PF_3Cl_2]{PCl_5} CF_2Cl_2$$

Reaction of phosgene with phosphorus pentachloride in an autoclave at 300–400° gives carbon tetrachloride in 60–70% conversion. Reaction of phosphorus pentachloride with carbonyl fluoride at 100–400° gives a lower conversion (10–15%) to dichlorodifluoromethane, since halogen exchange occurs to form carbonyl chlorofluoride, phosgene and phosphorus chlorofluorides, *e.g.*, $COF_2 + PCl_5 \rightleftarrows PF_xCl_{5-x} + COCl_2$. At higher temperatures subsequent reaction of phosphorus pentachloride with the phosgene so produced yields carbon tetrachloride as a major product. Fluorination of dichlorodifluoromethane by carbonyl or phosphorus fluorides also occurs to give chlorotrifluoromethane. Phosphorus trifluorodichloride was used with carbonyl fluoride in an attempt to reduce the halogen exchange reaction, but even here dichlorodifluoromethane and carbon tetrachloride were produced in approximately equal yields. The yields of tetrahalomethanes based on the amount of carbonyl halide actually consumed during reaction with a phosphorus halide are substantially higher than the conversions.

Extensions of this type of reaction can be visualized, *e.g.*

$$COFCl \xrightarrow{PCl_5} CFCl_3$$

$$COBr_2 \xrightarrow{PCl_5} CCl_2Br_2\ (+\ CCl_3Br + CCl_4)$$

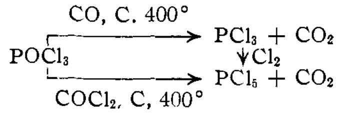
$$COF_2 \xrightarrow{PF_3Br_2} CF_2Br_2$$

The original reaction of phosgene was with an *excess* of phosphorus pentachloride. As a simple extension of this experiment the reaction of carbon monoxide and chlorine under pressure in presence of an excess of carbon (impregnated with iron and nickel halide) and with *less* than one molar ratio of phosphorus trichloride was found to give carbon tetrachloride in 48% conversion based on carbon monoxide. Based on the phosphorus trichloride taken, however, the conversion of carbon monoxide (or phosgene) to carbon tetrachloride is 96%. This yield is so high, it is in fact higher than that from reaction of phosgene with an excess of phosphorus pentachloride, that it is evident that the phosphorus pentachloride is being regenerated *in situ*. This can be interpreted as

$$CO + Cl_2 \longrightarrow COCl_2$$

$$PCl_3 + Cl_2 \longrightarrow PCl_5$$

$$COCl_2 + PCl_5 \longrightarrow CCl_4 + POCl_3$$



$$POCl_3 \xrightarrow{CO,\ C,\ 400^\circ} PCl_3 + CO_2 \qquad POCl_3 \xrightarrow[COCl_2,\ C,\ 400^\circ]{} PCl_5 + CO_2 \qquad PCl_3 \xrightarrow{Cl_2} PCl_5$$

It is known that phosphorus oxychloride can be converted into phosphorus trichloride by reaction with carbon monoxide.[4]

The over-all reaction is thus

$$2CO + 2Cl_2\ (\text{or } 2COCl_2) \xrightarrow{PCl_3} CCl_4 + CO_2$$

with the phosphorus trichloride acting more as a catalyst, but a series of equilibria between carbon monoxide and chlorine, phosphorus trichloride and chlorine, phosphorus trichloride and phosgene, etc., is clearly involved also. The yield of carbon tetrachloride from carbon monoxide calculated on the basis of this equation is 48%.

The possibility that thermal decomposition of phosgene might give carbon tetrachloride and carbon dioxide has been investigated earlier, but the yields obtained were extremely low (<1%) and the reaction was not reproducible.[5] Fink and Bonilla concluded that "the reaction $2COCl_2 \rightarrow CO_2 + CCl_4$ was attempted in both directions and the reverse reaction quantitatively studied, and indications were obtained of the existence of an undetermined factor which prevents the reaching of the theoretical equilibrium." The reaction $COCl_2 \rightarrow CO + Cl_2$ predominated.

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[1] For a preliminary communication see *Nature*, **179**, 1361 (1957). Presented at the A.C.S. Meeting, New York, N. Y., 1957.

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[4] German Patent 492,061 (Feb. 15, 1930).

[5] F. J. Machalske, U. S. Patent 880,100 (Dec. 26, 1905); A. Stock, W. Wustrow, H. Lux and H. Ramser, *Z. anorg. Chem.*, **195**, 129, 140, 149 (1931); A. Stock and W. Wustrow, *ibid.*, **147**, 245 (1925); C. G. Fink and C. F. Bonilla, *J. Phys. Chem.*, **37**, 1152 (1933).

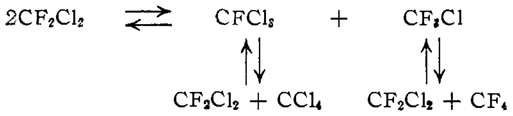
The reaction of phosgene with phosphorus tri- or pentachloride apparently does not involve just the pyrolysis of phosgene to give carbon tetrachloride and carbon dioxide, since when an excess of phosphorus pentachloride is used, the yield of carbon dioxide is extremely small and far less, on a molar basis, than the amount of carbon tetrachloride obtained.

When phosphorus trichloride is used more in the sense of a catalyst, *i.e.*, when it is present in less than an equimolar ratio with the carbon monoxide or phosgene, carbon dioxide is a product in an amount approximately equal to that of the carbon tetrachloride produced; it clearly arises from the phosphorus oxychloride–carbon monoxide reaction.

Pyrolysis and Copyrolysis of Carbonyl Halides.—The second route for the preparation of tetrahalomethanes from carbonyl halides involves their pyrolysis or copyrolysis

$$COF_2 + COCl_2 \rightleftharpoons CF_2Cl_2 + CO_2$$
$$2COFCl \rightleftharpoons CF_2Cl_2 + CO_2$$

Copyrolysis of carbonyl fluoride and phosgene at 300–700° by a flow technique using a platinum or carbon tube packed with activated carbon gave a conversion to dichlorodifluoromethane of approximately 10% and to chlorotrifluoromethane of about 5%. Control experiments showed that dichlorodifluoromethane is partly disproportionated in contact with active carbon under these conditions, particularly if the carbon contains ferric halide deliberately added or produced by attack on the steel connecting parts of the apparatus[6]



$$\begin{tikzcd}
2CF_2Cl_2 \arrow[r, shift left] & CFCl_3 \arrow[l, shift left] \arrow[d, shift left] & + & CF_3Cl \arrow[d, shift left] \\
 & CF_2Cl_2 + CCl_4 \arrow[u, shift left] & & CF_2Cl_2 + CF_4 \arrow[u, shift left]
\end{tikzcd}$$

but some of the chlorotrifluoromethane probably arises by reaction of carbonyl chlorofluoride with carbonyl fluoride

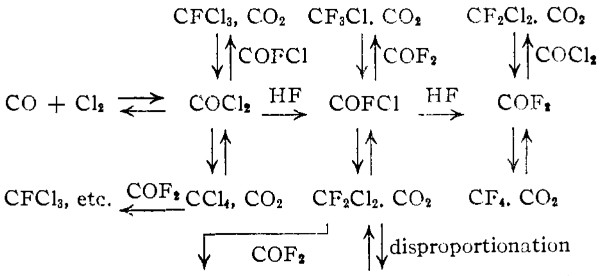
$$COF_2 + COCl_2 \rightleftharpoons 2COFCl$$
$$COFCl + COF_2 \rightleftharpoons CF_3Cl + CO_2$$

and by fluorination of dichlorodifluoromethane by carbonyl fluoride.

Carbonyl chlorofluoride also yields dichlorodifluoromethane by pyrolysis at 300–700° and may in fact be the intermediate for formation of this tetrahalomethane when carbonyl fluoride and phosgene are copyrolyzed. A series of equilibria is possible.

Better conversions to tetrahalomethanes (*e.g.*, CF_2Cl_2, 56%; CF_3Cl, 12%; $CFCl_3$, 12%) are obtained when carbonyl chlorofluoride, or carbonyl fluoride and phosgene, are heated in an autoclave at 300–550°. The pressure is higher than in the flow method, but the main improvement probably is caused by the better and prolonged reactant contact. Iron salts impregnated on the active carbon catalyze the reaction; they also catalyze the disproportionation of dichlorodifluoromethane. Addition of chlorine to the reaction mixture helps to cut down the dissociation of phosgene at these temperatures and, by attack on the vessel, produces metal chlorides (and thence fluorides) which probably act as catalysts.

The carbonyl fluoride or chlorofluoride can be prepared *in situ* so that heating phosgene with hydrogen fluoride under these conditions gives good conversions to tetrahalomethanes (*e.g.*, CF_2Cl_2, 47%; CF_3Cl, 13%; $CFCl_3$, 7%; CCl_4, 7%). Basically therefore the reaction becomes that of carbon monoxide, chlorine and anhydrous hydrogen fluoride



$$\begin{tikzcd}
 & CFCl_3, CO_2 \arrow[d, shift left] & CF_3Cl, CO_2 \arrow[d, shift left] & CF_2Cl_2, CO_2 \arrow[d, shift left] \\
CO + Cl_2 \arrow[r, shift left] & COCl_2 \arrow[l, shift left] \arrow[u, shift left, "COFCl"'] \arrow[r, "HF"] \arrow[d, shift left] & COFCl \arrow[u, shift left, "COF_2"'] \arrow[r, "HF"] \arrow[d, shift left] & COF_2 \arrow[u, shift left, "COCl_2"'] \arrow[d, shift left] \\
CFCl_3, \text{etc.} & CCl_4, CO_2 \arrow[l, "COF_2"'] \arrow[u, shift left] & CF_2Cl_2, CO_2 \arrow[u, shift left] \arrow[dll, "COF_2"] \arrow[d, shift left, "\text{disproportionation}"] & CF_4, CO_2 \arrow[u, shift left] \\
CF_3Cl, \text{etc.} & & CF_3Cl + CFCl_3 + CCl_4 + CF_4 \arrow[u, shift left] &
\end{tikzcd}$$

Under the conditions used the possibility of a catalyzed disproportionation of phosgene to give carbon tetrachloride and carbon dioxide cannot be eliminated; this would explain the formation of this tetrahalomethane in 5–25% yields in some experiments.

Carbonyl fluoride is known[7] to disproportionate as $2COF_2 \rightleftarrows CF_4 + CO_2$ at high temperatures; the equilibrium constants of the forward and backward reactions are almost equal at 1000°. The formation of a tetrahalomethane by pyrolysis of carbonyl chlorofluoride or copyrolysis of carbonyl fluoride and phosgene thus occurs at a much lower temperature than formation of carbon tetrafluoride from carbonyl fluoride alone. The alternative reaction $COXY \rightleftarrows CO + XY$ does not occur when $X = Y = F$ or $X = F$, $Y = Cl$, although it is the major reaction when $X = Y = Cl$.

Experimental

Preparation of Carbonyl Fluoride.[8]—In a typical experiment, phosgene (500 g.) was heated at 285° for 17 hr. in a 2.7 l. autoclave containing antimony trifluoride (1390 g.) and chlorine (85 g., to form pentavalent antimony salts). The valve on the rocking autoclave required heating continuously to prevent blockages. The gaseous products were fractionated to give carbonyl fluoride (95% pure as determined by infrared spectroscopic analysis and contaminated only by small amounts of carbon dioxide) in 80–85% yield.

Preparation of Carbonyl Chlorofluoride[8] and Phosphorus Trifluorodichloride.[9]—The first compound was prepared by the interaction of an excess of phosgene and antimony trifluoride (3.5:1 mole ratio) containing 1–5% of antimony pentachloride in a rocking autoclave at 145–150° for 1–2 hr. The carbonyl chlorofluoride (b.p. −44°) was distilled through a 7-ft. column, and infrared spectroscopic analysis revealed a purity of approx. 95% with carbon dioxide as the main impurity.

Phosphorus trifluoride was prepared by the reaction of phosphorus trichloride with an excess of antimony trifluoride in a Pyrex flask. The phosphorus trifluoride (b.p. −101°) distilled out as soon as formed into a second flask through which a slow stream of chlorine was passing. The phosphorus trifluorodichloride thus produced was redistilled (b.p. 8°) before use.

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[6] Chlorofluoromethanes are known to disproportionate on contact with metal halides, *e.g.*, U. S. 1,994,035, 2,426,637, 2,426,638.

[7] O. Ruff and G. Miltschitsky, *Z. anorg. Chem.*, **221**, 154 (1934).

[8] *Cf.* H. J. Emeléus and F. J. Wood, *J. Chem. Soc.*, 2185 (1948).

[9] *Cf.* H. S. Booth and A. R. Bozarth, THIS JOURNAL, **61**, 2927 (1939); C. Poulenc, *Compt. rend.*, **113**, 75 (1891).

Infrared Spectra.—A Perkin–Elmer Model 21 Double Beam Spectrophotometer with rock salt optics was used for the analysis of the tetrahalomethanes. Reference spectra were obtained by using known mixtures of the tetrahalomethanes covering a wide range of composition. Full details will be published elsewhere. Analyses are accurate to ±5%. Fractional distillation was used in experiments on a larger scale to check the spectroscopic analyses. Reference spectra were recorded for phosgene, carbonyl fluoride, carbonyl chlorofluoride, carbon dioxide and silicon tetrafluoride.

Reaction of Carbonyl Fluoride with Phosphorus Pentachloride.—A series of experiments was carried out to study the effect of temperature, concentration, etc. Pressures usually were not recorded, since a pressure gage on the autoclave was soon blocked by phosphorus halides. In a typical experiment, phosphorus pentachloride (0.48 mole) was added to a carefully dried 300-ml. stainless steel or Monel autoclave which was then closed, evacuated to 10^{-1} mm. and cooled in liquid oxygen. Carbonyl fluoride (0.38 mole) was distilled in under a vacuum, and the autoclave was then heated and shaken at 265° for 16 hr. The volatile products were transferred to traps cooled in liquid oxygen, and the autoclave finally was heated at 10^{-1} mm. to transfer less volatile products to the cooled traps. A sample of the crude product was examined by infrared spectroscopy and found to contain CF_2Cl_2, CF_3Cl, $CFCl_3$, $COCl_2$, COF_2, COFCl and CO_2. The total crude product was then washed with 15% aqueous potassium hydroxide and the residual gas, analyzed spectroscopically, contained only CF_2Cl_2 (10% conversion) and CF_3Cl (approx. 5% conversion). These conversions are based on the carbonyl fluoride taken and are thus appreciably lower than yields based on the carbonyl fluoride actually used up (approx. 20%) during the reaction. Dichlorodifluoromethane and chlorotrifluoromethane were produced by similar reactions carried out at temperatures as low as 100° but in lower conversion and yield.

When phosphorus pentachloride (1.0 mole) and carbonyl fluoride (0.38 mole) were heated at 350° for 12 hr., carbon tetrachloride was detected spectroscopically in the crude product as well as the compounds listed above. After washing with aqueous alkali, the conversion to CCl_4 was 30% and to CF_2Cl_2 was 5%. Approximately 30% of the carbonyl fluoride was recovered.

Reaction of Carbonyl Fluoride and Phosphorus Trifluorodichloride.—In a typical experiment using the apparatus and techniques given above, carbonyl fluoride (0.14 mole) and phosphorus trifluorodichloride (0.27 mole) were heated at 300° for 12 hr. The gaseous products contained $COCl_2$, COFCl, unchanged COF_2, CO_2 and CF_2Cl_2. Only dichlorodifluoromethane (5% conversion based on carbonyl fluoride taken) remained when the gases were washed with aqueous alkali. The liquid products from this reaction were carbon tetrachloride (approx. 5% conversion) and phosphorus oxychloride.

Reaction of Phosgene with Phosphorus Pentachloride.—In a typical experiment phosgene (50 g., 0.5 mole) and phosphorus pentachloride (125 g., 0.6 mole) were sealed *in vacuo* in a 300-ml. stainless steel autoclave which was then heated at 365–375° for 18.5 hr. Spectroscopic and vapor phase chromatographic examination of the gaseous product showed that it was mainly phosgene together with a very small amount (0.0005 mole) of carbon dioxide. The autoclave was heated and pumped out *via* traps cooled in liquid oxygen; carbon tetrachloride was adsorbed heavily by the active carbon. The liquid product, b.p. >15°, was washed with water, dried and distilled to give carbon tetrachloride (64% conversion based on phosgene taken), b.p. 76°; its identity was confirmed by means of its infrared spectrum.

In other similar experiments the liquid reaction products were distilled without being washed with water: only CCl_4, $POCl_3$ and small amounts of PCl_3 were present.

Experiments carried out at temperatures between 50 and 100° at atmospheric pressure failed to yield carbon tetrachloride, and pressure reactions below 300° gave appreciably lower yields of carbon tetrachloride than those above 300°.

Carbon Tetrachloride from Carbon Monoxide and Chlorine in Presence of Carbon and Phosphorus Trichloride.—To a 100-ml. stainless steel autoclave two-thirds full of active carbon pellets (Sutcliffe–Speakman 207C) mixed with animal charcoal powder (10 g.) was added anhydrous ferric chloride (3.1 g.), chlorine (2 g.), nickel carbonyl (1.5 g.) and iron carbonyl (2.0 g.). The autoclave was heated to 400° for 12 hr., then cooled to room temperature and pumped out for 5 hr. Carbon monoxide (0.20 mole), chlorine (0.25 mole) and phosphorus trichloride (0.05 mole) were added to the autoclave which was then heated to 400° for 9 hr. Only carbon dioxide (0.031 mole, 31%), carbon monoxide and phosgene were detected as volatile products when the autoclave was opened at room temperature. The less volatile products were removed *in vacuo* while the autoclave was heated to 350° during 2 hr. After being washed with dilute aqueous sodium hydroxide, the liquid products were distilled from phosphoric anhydride to give only carbon tetrachloride (0.044 mole, 44%), b.p. 75–76°. In a second experiment using the same catalyst and mole ratios of reactants as above, reaction at 430° for 16 hr. gave carbon tetrachloride (0.048 mole, 48%) and carbon dioxide (0.037 mole, 37%). Conversions in the above experiments are calculated on the basis of the reaction

$$2CO + 2Cl_2 \longrightarrow CCl_4 + CO_2$$

Pyrolysis of Carbonyl Fluoride and Phosgene Using a Flow Technique.—A platinum-lined 0.75 in. internal diameter nickel tube heated by means of a tube furnace over a 30-in. length was used for these experiments. Approximately two-thirds of its volume was filled with $^6/_{18}$ in. mesh active carbon pellets (Cliffchar No. 6, Cliff–Dow Co., or CXA carbon, Carbide and Carbon, Inc.). The carbonyl fluoride and phosgene were in small steel cylinders connected to the pyrolysis tube by means of a steel T-junction and a glass mixing vessel. The rates of flow of the gases were controlled directly from the cylinders and followed by means of flow meters made of a fluoropolymer and containing a fluoro-oil and by the rate of change in weight of the cylinders. The pyrolysis products were condensed in traps cooled by liquid oxygen. Attack of phosgene on the steel connecting parts of the apparatus produced ferric chloride which sublimed into the pyrolysis tube and impregnated the carbon packing. The flow of nitrogen used as diluent in some experiments was controlled by means of a calibrated flow meter. Thermocouples were placed along the side of the pyrolysis tube.

A carbon tube (0.75 in. internal diameter, wall thickness 0.37 in.), heated over a 30-in. length, was used in later experiments. It was placed in a 36-in. nickel pipe (1.88 in. internal diameter, wall thickness 0.3 in.) to act as support, and the annular space between the tubes was filled with fine carbon powder and closed at the ends by asbestos–graphite packing. Threaded steel caps on each end of the nickel tube enabled gases to be passed through the carbon tube, which was packed with activated carbon granules (32 g., Cliffchar).

A number of experiments were carried out using the platinum-lined tube at temperatures between 250 and 450°. In a typical experiment, carbonyl fluoride (0.1 mole) and phosgene (0.1 mole) were passed during 2 hr. at a temperature of 420–430° with a nitrogen dilution of 10 l./hr. The gaseous products, washed with 25% aqueous sodium hydroxide, were analyzed spectroscopically and found to contain only CF_2Cl_2 (7% conversion) and CF_3Cl (3% conversion). Infrared spectroscopic examination of a sample of the crude gaseous product showed it to contain COFCl, traces of CF_4, CO_2, unchanged reactants (approx. 50%), CF_2Cl_2 and CF_3Cl. At 340–350° a similar reaction gave a 6% conversion to dichlorodifluoromethane with approx. 60% of the reactants unchanged.

The carbon tube enabled higher temperatures to be investigated. No diluent gas was used. In a representative experiment, carbonyl fluoride (0.26 mole) and phosgene (0.31 mole) were passed through the tube at 425° during 3 hr. Spectroscopic examination of the crude product showed the same components as given above; after washing twice with aqueous sodium hydroxide, a 3% conversion to dichlorodifluoromethane and a 3% conversion to chlorotrifluoromethane were obtained.

Passage of carbonyl fluoride (0.29 mole) and phosgene (0.31 mole) at 640–660° during 3 hr. gave a crude product which was washed with aqueous alkali to remove unchanged reactants (*ca.* 50%) and carbon dioxide, then analyzed spectroscopically; the conversion to dichlorodifluoromethane was 10% and to chlorotrifluoromethane was 5%.

Reaction of Carbonyl Fluoride and Phosgene in an Autoclave.—Two 300-ml. autoclaves were used for most of these experiments: one of stainless steel, the other of Monel with a stainless steel head. The autoclave was approximately two-thirds filled with active carbon (Cliffchar No. 6 or CXA) granules (60–100 g.) and pretreated with anhydrous hydrogen fluoride (5–10 g.) at 225–350° for 8 hr. to convert silicate into silicon tetrafluoride and remove moisture and any impurities in the ash content of the carbon which might react with carbonyl fluoride. The volatile products from the pretreatment were removed *in vacuo*.

A reaction temperature of 400–450° with a pressure of >100 atm. was found suitable for the preparation of dichlorodifluoromethane. In a typical experiment, carbonyl fluoride (0.13 mole) and phosgene (0.36 mole) were condensed into the pretreated autoclave which was then heated in a salt-bath at 425° for 17 hr. The weight of crude product, obtained by venting the autoclave while still at 250°, then pumping out the hot autoclave, amounted to 90% of that of the reactants. Spectroscopic examination of a sample of the crude product revealed the presence of all the chlorofluoromethanes, CF_4, CCl_4, COFCl, CO_2 and unchanged reactants (10–15%). The crude product was washed with 15% aqueous sodium hydroxide to leave CF_2Cl_2 (56% conversion), CF_3Cl (12% conversion), $CFCl_3$ (23% conversion) and smaller amounts of CF_4 (some of which gets lost during the washing process) and CCl_4. Conversions are based on carbonyl fluoride taken.

A similar experiment with a reaction time of 8 hr. gave the following conversions based on carbonyl fluoride taken: CF_2Cl_2, 43%; CF_3Cl, 21%; $CFCl_3$, 4%; CF_4, 8%; and a 27% conversion to CCl_4 based on phosgene.

In a further experiment, a 0.1-l. stainless steel autoclave containing 63 g. of an activated carbon catalyst which had been used in an earlier experiment and was impregnated with 26–27% of ferric chloride was charged with carbonyl fluoride (0.13 mole), phosgene (0.33 mole) and chlorine (3 g.). Reaction at 425° for 6 hr. gave CF_2Cl_2 (34% conversion), CF_3Cl (21%), $CFCl_3$ (25%), CF_4 (5%) and CCl_4 (11%).

Pyrolysis of Carbonyl Chlorofluoride.—Carbonyl chlorofluoride (30.5 g.), heated to 420° for 8.5 hr. in a 0.1 l. stainless steel autoclave, gave gaseous products (27.5 g.) which were washed with 15% aqueous potassium hydroxide in the usual way. Infrared spectroscopic analysis revealed dichlorodifluoromethane (3% conversion) and chlorotrifluoromethane (1% conversion).

In a second experiment carbonyl chlorofluoride (30 g.) was heated to 425° for 19 hr. in presence of a silicate-free activated carbon catalyst (60 g.), impregnated with 27% ferric chloride. The conversions, calculated on the basis that two moles of carbonyl chlorofluoride yield one mole of chlorofluoromethanes, were: CF_2Cl_2, 13%; CF_3Cl, 38%; CF_4, 13%.

Reaction of Phosgene with Hydrogen Fluoride.—Phosgene (60 g.), anhydrous hydrogen fluoride (12.5 g.) and chlorine (7.5 g.) were heated at 425° for 17 hr. in a 0.3 l. Monel autoclave containing pretreated activated carbon catalyst (102 g.), impregnated with 27% ferric chloride. The conversions (based on $COCl_2$ taken) were: CF_2Cl_2, 14%; CF_3Cl, 54%; and CF_4, 4%.

The above experiment, repeated at 350° for 6 hr., gave: CF_2Cl_2, 47%; CF_3Cl, 13%; $CFCl_3$, 7%; and CCl_4, 7%.

In a third experiment phosgene (0.5 mole), hydrogen fluoride (0.45 mole) and chlorine (0.1 mole) were heated as above at 340° for 6.25 hr. The conversions were: CF_2Cl_2, 34%; CF_3Cl, 20%; $CFCl_3$, 10%; CF_4, 4%.

Disproportionation of Dichlorodifluoromethane.—The activated carbon catalyst (100 g., CXA carbon) was prepared *in situ* in a 0.3 l. nickel autoclave by treatment with anhydrous hydrogen fluoride (30 g.) at 350° for 1.5 hr. The autoclave was then pumped out while maintained at 350° for 1.5 hr. The catalyst was used for a reaction between phosgene and anhydrous hydrogen fluoride as described earlier, after which it was heated at 350° *in vacuo* for 1.5 hr. before further use. Dichlorodifluoromethane (152 g.) was next condensed into the autoclave which was heated to 350° for 6 hr. The autoclave was cooled and the gaseous products collected in a cooled trap. Heating the catalyst at 300° *in vacuo* for an hour yielded further product by desorption from the carbon. Distillation and analysis gave CF_2Cl_2 (79.0 g.), CF_3Cl (17.3 g.), $CFCl_3$ (18.0 g.), CCl_4 (14.8 g.) and a small amount of CF_4. Using these figures, 1 mole of CF_2Cl_2 would give 0.52 mole CF_2Cl_2, 0.13 mole CF_3Cl, 0.10 mole $CFCl_3$ and 0.076 mole CCl_4.

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Carbonium Ions. VI. σ^+-Parameters[1]

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A comparison is made between independently determined σ^+-values. A combination of literature data and more extensive work on arylmethanol–arylmethyl cation equilibria permitted the evaluation of σ^+-parameters for a total of nineteen substituents. All nineteen were *p*-substituents and the σ- and σ^+-values in each case were markedly different.

Although Pearson[2] and ourselves[3] had published a few σ^+-values, it was Brown and Okamoto[4,5] who evaluated a total of ten such parameters and critically tested their applicability. These authors found nineteen reaction series in which the log k/k_0 *vs.* σ plots were more linear with σ^+-values than with the usual values of σ. These authors also reviewed the development of this field.

The most critical test of the generality of σ^+-values is whether values independently calculated from different reaction series are invariant. We have found only four reaction series in which σ^+-values can be independently determined. A comparison of these values is presented in Table I and the agreement is encouraging although it is by no means within experimental precision. Of these four series, only the solvolysis of α,α-dimethylbenzyl chlorides[4] has a sufficient number of points, ten, to firmly establish the value of ρ[6] for the series. Rho for the other three series were based on two to four points (listed in Table I) which would be sufficient due to the wide range of σ-values encompassed if complete reliance could be placed on these few points.

Since the value of ρ for the arylmethanol arylmethyl cation equilibria was based on only four points, we have decided to recompute ρ for this

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[1] Grateful acknowledgment is made to the National Science Foundation for support of this work.

[2] D. E. Pearson, J. F. Baxter and J. C. Martin, *J. Org. Chem.*, **17**, 1511 (1952).

[3] N. Deno and A. Schriesheim, THIS JOURNAL, **77**, 3051 (1955).

[4] H. C. Brown and Y. Okamoto, *ibid.*, **79**, 1913 (1957).

[5] Y. Okamoto and H. C. Brown, *J. Org. Chem.*, **22**, 485 (1957).

[6] For the definitions of σ and ρ, see refs. 2–5, and L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, Chapter VII.