of radioactive recoil particles, as from the radiodecomposition of Pb*, can be avoided.

Summary

The method of Leighton and Mortensen employing natural radio-lead in Paneth mirrors has been modified and used for the detection of low concentrations of free radicals.

In this way the existence of free radicals in the pyrolysis of acetaldehyde at 500° has been detected.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DUKE UNIVERSITY]

The Action of Elementary Fluorine upon Organic Compounds. VII. The Vapor Phase Fluorination of Ethyl Chloride

BY JOHN D. CALFEE, NOBUKAZU FUKUHARA, DEWALT S. YOUNG AND LUCIUS A. BIGELOW

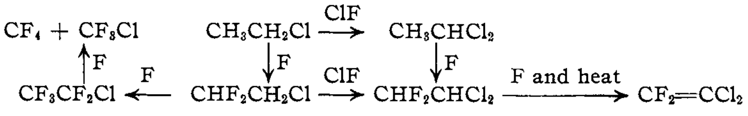
In the third paper of this series,[1] we discussed the vapor phase fluorination of hexachloroethane over copper gauze, which resulted in the substitution of chlorine by fluorine, and yielded *sym*-difluorotetrachloroethane. Since then we have developed an improved technique for the fluorination of organic gases,[2] and this paper deals with the interesting results obtained by applying it to ethyl chloride. Fluorination and chlorination took place simultaneously during the reaction.

Results and Discussion

The ethyl chloride was fluorinated smoothly in a metal apparatus, over copper gauze, under conditions described fully before.[2] The products were condensed by liquid air, transferred to a Booth–Podbielniak low temperature fractionating unit, separated, rectified and analyzed. There were formed carbon tetrafluoride, trifluorochloromethane, CF_3Cl, b. p. −80° (−80°)[3]; pentafluorochloroethane, CF_3CF_2Cl, b. p. −38° (−38°)[4] m. p. −106°; 1,1,2,2-difluorodichloroethylene, $CF_2{=}CCl_2$, b. p. 0° (15°?),[4] m. p. −116°; 1,1,2-difluorochloroethane, CHF_2CH_2Cl, b. p. 35° (35°)[5]; and other products. The observed molecular weights agreed well with the calculated values. The last of these compounds was washed with dilute alkali, dried and distilled in the ordinary way, and the ethylene derivative was passed through a 5% sodium hydroxide solution before analysis. The difluoro- and pentafluoroethyl chloride, as well as the difluorodichloroethylene, have not been obtained before by direct fluorination.

Henne and Renoll[5] gave the boiling point of $CF_2{=}CCl_2$ as 15°, whereas we have found it to be 0°. However, they did not report any molecular weight or analysis, while the values given in Table II leave no doubt as to the composition of the sample which we have examined. The only possible isomer of this compound, $CFCl{=}CFCl$, boils at 20.9° according to Booth and collaborators.[6]

In addition to the compounds which were isolated, several others were produced in lesser quantities. A small fraction boiling near 60° was observed repeatedly, and when a larger portion containing this material was distilled at reduced pressure, two small samples were obtained, one of which had a molecular weight of 135, and the other of 98. Now the compound CHF_2CHCl_2 (mol. wt. 135) boils at 60°,[7] and ethylidene chloride CH_3CHCl_2 (mol. wt. 99), distils at 57°. It therefore seemed likely that the two last-named compounds were formed during the reaction. Granting this, a partial mechanism for the fluorination of ethyl chloride may be represented tentatively as



$$\begin{tikzcd}
CF_4 + CF_3Cl & CH_3CH_2Cl \arrow[r, "ClF"] \arrow[d, "F"] & CH_3CHCl_2 \arrow[d, "F"] & \\
CF_3CF_2Cl \arrow[u, "F"] & CHF_2CH_2Cl \arrow[l, "F"'] \arrow[r, "ClF"] & CHF_2CHCl_2 \arrow[r, "F\ and\ heat"] & CF_2{=}CCl_2
\end{tikzcd}$$

This mechanism involves the substitution of chlorine by fluorine, $RCl + 2F \longrightarrow RF + ClF$, and chlorination by chlorine fluoride, $RH + ClF \longrightarrow RCl + HF$. The reaction $RCl + HF \longrightarrow RF + HCl$ may occur, but this seems doubtful.

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(1) Miller, Calfee and Bigelow, THIS JOURNAL, **59**, 198 (1937).

(2) Calfee and Bigelow, *ibid.*, **59**, 2072 (1937); Calfee, Fukuhara and Bigelow, *ibid.*, **61**, 3552 (1939).

(3) Ruff and Keim, *Z. anorg. allgem. Chem.*, **201**, 245 (1931).

(4) Locke, Brode and Henne, THIS JOURNAL, **56**, 1726 (1934).

(5) Henne and Renoll, *ibid.*, **58**, 889 (1936).

(6) Booth. Burchfield, Bixby and McKelvey, THIS JOURNAL, **55**, 2231 (1933).

(7) M. Swartz, *Bull. soc. chim.*, **35**, 1557 (1924).

Several fluorinations were run, using different gas volume ratios of fluorine to ethyl chloride, and in one case the fluorine was diluted with nitrogen. The copper gauze was protected at all times from air and moisture, which decreased its efficiency greatly. This effect was not observed when ethane was fluorinated.[2] Table I shows the proportions in which the more important products were formed expressed in liquid volume per cent. of the total condensate, as has been done previously. The figures have been rounded off to the nearest 5% and are significant.

Table I

The Fluorination of Ethyl Chloride

	Gas volume ratios of $F/C_2H_5Cl/N$			
Liquid volume % of:	2/2/0	3/2/0	4/2/0	4/2/4
CF_4	10	10	10	trace
CF_3Cl	5	10	15	trace
CF_3CF_2Cl	trace	5	10	5
$CF_2{=}CCl_2$	0	5	5	trace
CH_3CH_2Cl	70	40	10	20
Residue b. p. > 12°	5	15	20	40
Transition fractions	15	20	30	40

The total volumes of liquid condensate in the four runs were 50, 32, 21 and 26 ml., respectively, calculated on a ten-hour operating basis. The results were in general consistent, since the more highly fluorinated products increased in quantity as the ratio of F/C_2H_5Cl increased, and decreased sharply when the fluorine was diluted. The material boiling above 12° was collected together and subsequently redistilled.

Method of Analysis

We believe that the development of a precise, convenient procedure for the quantitative analysis of stable low boiling organic fluoro-chloro gases for both halogens is a matter of importance, and have devoted considerable time to this problem, which is not as simple as might at first appear. The procedure finally adopted was based on the one described by Hubbard and Henne,[8] but differs from it in several important respects, the most significant of which is that our gas samples were weighed. In the older method, gas volumes were measured, which admittedly involved the question of how closely the sample behaved as a perfect gas.

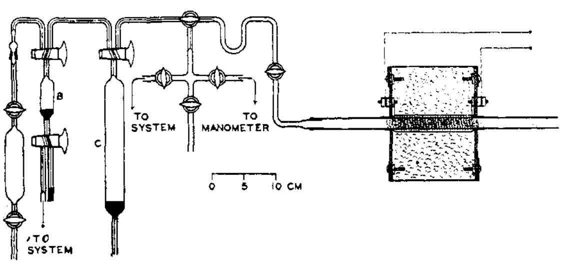

Fig. 1.—Analytical apparatus.

The combustions were run on a semi-micro scale, but the samples were conveniently weighed on an ordinary analytical balance, which necessitated the taking of gas aliquots. The complete apparatus is illustrated to approximate scale in Fig. 1. It was mounted on the same frame as the Booth–Podbielniak unit, and connected directly to that system. The furnace consisted of a 46-cm. length of clear silica tubing with a 13 mm. bore, which was wrapped with asbestos paper, wound directly with no. 24 Chromel wire over about 13 cm. of its length and surrounded by an insulating unit made of aluminum sheet and filled with powdered asbestos. This combustion tube was packed with ground silica, about 20 mesh, held in place at the ends by larger pieces of the same material. It was sealed to the system and also to the absorption apparatus by means of de Khotinsky cement. The maximum temperature in the furnace was maintained at approximately 900° by a calibrated rheostat. The volumes of container A (about 60 ml.) together with the connecting line, and B (about 12 ml.) were determined accurately by calibration with mercury.

The operating procedure was as follows: The container A was exhausted and the sample allowed to expand into it, through B, up to atmospheric pressure, after which it was detached and the gain in weight noted (0.2–0.3 g.). Then B was exhausted and the sample allowed to expand into it, giving a known quantity of material, about one-fifth of the original amount. This gas was next conducted into C, where it was mixed with 100 ml. of oxygen, and then pushed slowly through the furnace during a period of 50 min., and into the absorption vessel. This consisted of a U-tube with a half dozen bulbs, similar to that described before,[8] and contained 10 ml. of 1.0 *N* sodium hydroxide solution and 1 ml. of superoxol. The sample was followed successively by 200 ml. of oxygen, 100 ml. of nitrogen, 200 ml. of hydrogen and finally by nitrogen directly from the tank for one and one-half hours, all at the rate of approximately 200 ml. per hour. The excess of oxygen was necessary to prevent back diffusion of the sample into the nitrogen, with subsequent failure to burn, and the hydrogen was used to reduce silicon oxychloride.[8] Also it was necessary to remove any accumulation of silica deposited in the entrance arm of the absorption apparatus during a combustion, since it tended to retain halogen. Finally, the alkaline solution was washed out, 1 ml. of superoxol added and the mixture heated to boiling. Then it was made up to 200 ml., and aliquot portions of 25 and 50 ml. taken for the determination of fluoride and chloride ions, respectively.

The fluoride ion was titrated with approximately 0.01 *N* thorium nitrate solution, according to the well-known Hoskins and Ferris[9] procedure. Approximately 180 ml. was collected in the distillation, which was made up to 200 ml., and the average value obtained by titrating four or five 25-ml. aliquot portions of this was taken as the correct one. It was found desirable to use a small light box with a blue bulb for constant illumination at the end-point, but care should be taken on account of the heat effect. The chloride ion was titrated with standard silver

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[8] Hubbard and Henne, This Journal, **56**, 1078 (1934).

[9] Hoskins and Ferris, *Ind. Eng. Chem., Anal. Ed.*, **8**, 6 (1936).

nitrate solution using a dichlorofluorescein adsorption indicator according to Kolthoff and collaborators.[10] This method is applicable in the presence of silica, and has proved very efficient. We have not found the Volhard procedure to be satisfactory in this work.

Finally the several products obtained by the fluorination of the ethyl chloride were analyzed and results are summarized in Table II.

TABLE II

ANALYTICAL VALUES

	Calcd.		Found			
Compd.	F	Cl	F		Cl	
CF_2Cl_2[a]	31.4	58.7	31.4	...	58.7	...
CF_3Cl	54.5	34.0	54.6	54.3	34.0	34.0
CF_3CF_2Cl	61.5	23.0	61.4	61.5	23.1	23.1
$CF_2{=}CCl_2$	28.6	53.4	28.6	28.6	53.3	53.6
CHF_2CH_2Cl[b]	37.8	35.3	37.8	38.0	35.2	...

[a] Analysis of purified Freon, to test the procedure.
[b] Decomposed in a Parr bomb.

These results leave no doubt as to the composition of the compounds which were isolated in this work.

Summary

Ethyl chloride was fluorinated in the vapor phase over copper gauze under varying conditions, and the relative amounts of the more important products determined.

The compounds CF_4, CF_3Cl, CF_3CF_2Cl, $CF_2{=}CCl_2$ and CHF_2CH_2Cl were isolated from the reaction mixture. The last three of these have not been obtained before by the action of elementary fluorine on an organic compound.

A precise analytical procedure for determining fluorine and chlorine in stable organic gases has been described.

DURHAM, NORTH CAROLINA RECEIVED AUGUST 4, 1939

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(10) Kolthoff, Lauer and Sunde, THIS JOURNAL, **51**, 3273 (1929).

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

The Electrostatic Influence of Substituents on Reactions Rates. I

BY F. H. WESTHEIMER AND MARTIN W. SHOOKHOFF

Ingold has postulated that the effect of a polar substituent on the rate of saponification of an aliphatic ester, like the effect of such a substituent on the ionization constant of an acid, is largely electrostatic. In 1930[1] he employed Bjerrum's quantitative electrostatic formulation[2] to compute, from the ratios of the rates of saponification of the first and second ester groups, the separation of the carbalkoxy groups in a series of esters of dibasic acids. Ingold's evidence went far toward establishing his hypothesis in those cases in which the molecule is long and the substituent can be regarded as a negative charge.

Kirkwood and Westheimer[3] have recently refined Bjerrum's approximate computations of the electrostatic free energy involved in a chemical reaction; the success of the new equations, while general, has been most conspicuous in the considerations of the ionization constants of short dibasic and of dipole substituted acids,[4] cases for which the older formulation is inadequate. The shortcomings of Ingold's modified equation[5] have been presented previously.

The present paper deals with the rate of alkaline hydrolysis of esters and amides in cases in which the substituent is a negative charge, a positive charge and a dipole, all placed close to the seat of the reaction. When the substituent is close to the ester or amide bond that is broken, the rates of hydrolysis of the substituted and unsubstituted compounds differ by a factor of a hundred or more. Since the measurements were made by conductivity, very slow and very fast reactions were excluded: the former because of action of alkali on the glass of the cell, the latter because of the time required to attain thermal equilibrium. These considerations necessitated a careful selection of the pairs of compounds employed.

To illustrate the effect of a negative charge as substituent, the rate of alkaline hydrolysis of the sodium salt of oxamic acid was compared with the rate for oxamide; to illustrate the effect of a positive charge, the rate of saponification of the chloride of the tertiary butyl ester of betaine was compared with the rate for the tertiary butyl ester of dimethylglycine; and to illustrate the

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(1) Ingold, *J. Chem. Soc.*, 1375 (1930), 2170 (1931); Ingold and Mohrhenn, *ibid.*, 1482 (1935).

(2) Bjerrum, *Z. physik. Chem.*, **106**, 219 (1923).

(3) Kirkwood and Westheimer, *J. Chem. Phys.*, **6**, 506 (1938); Westheimer and Kirkwood, *ibid.*, **6**, 513 (1938).

(4) Westheimer and Shookhoff, THIS JOURNAL, **61**, 555 (1939); Westheimer, *ibid.*, **61**, 1977 (1939); *cf.* Eucken, *Z. angew. Chem.*, **45**, 203 (1932).

(5) Ingold, *J. Chem. Soc.*, 2179 (1931).