[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DUKE UNIVERSITY]

The Action of Elementary Fluorine upon Certain Aromatic Organic Compounds under Various Conditions. I

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Fluorine is the most reactive, as well as the most electronegative, of all the elements, and it is surprising, therefore, to find that the direct fluorination of organic compounds has received scant attention from earlier investigators.[1] This is due in part to the enormous reactivity of the fluorine, which combines explosively with most organic compounds when the two are brought in contact; and in part also to the fact that the reactions of free fluorine, at least upon aromatic compounds, do not seem to follow well-recognized lines which might be predicted by analogy and studied readily. The work to be described in this paper represents the initial stage of a careful study of the controlled reactions of elementary fluorine upon a variety of aromatic organic compounds, under a number of differing types of experimental conditions.

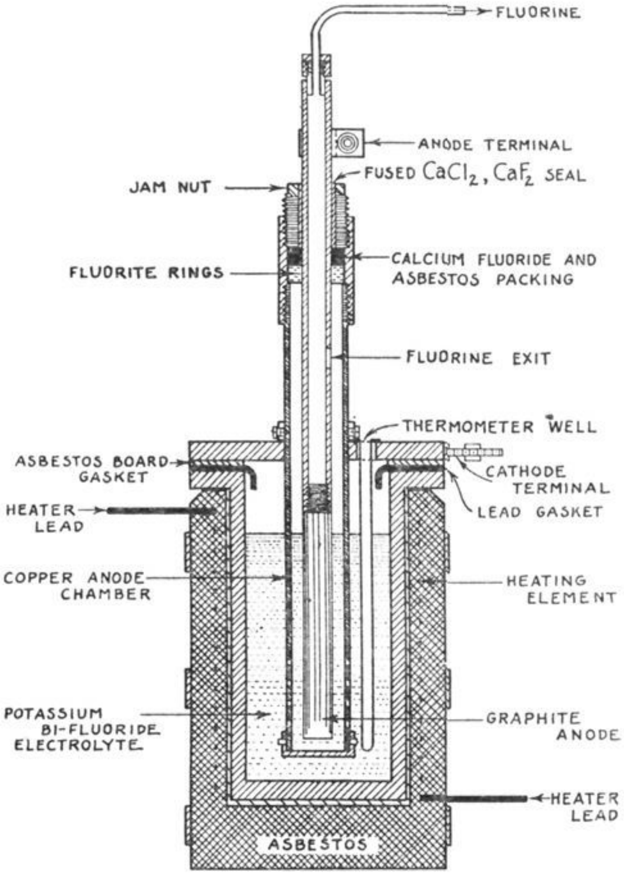

Fig. 1.—Fluorine generator.

The Apparatus

The fluorine was generated by the electrolysis of molten potassium bifluoride, at 250–300°, in an electrolytic cell made of heavy copper, and illustrated in detail in Fig. 1. This generator was designed several years ago by Paul M. Gross and J. S. Buck in this Laboratory, and was similar in principle to several which have been described previously in the literature. It differed significantly from these, however, in that the copper pipe which held the graphite anode also served as the exit for the fluorine, and was supported by means of a fluorite ring, which was both insulating, and entirely inert, even under severe operating conditions. The gas, after being set free at the anode, was passed through a copper tube approximately 63 × 3.5 cm. filled with anhydrous

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(1) The most important literature references are as follows: Moissan, *Compt. rend.*, **102**, 1543 (1886); **103**, 202, 256, 600 (1886); Humiston, *J. Phys. Chem.*, **23**, 572 (1919); Fichter and Humpert, *Helv. Chim. Acta*, **9**, 692 (1926); Bancroft and Jones, *Trans. Electrochem. Soc.*, **53**, 183 (1929); Bancroft and Whearty, *Proc. Nat. Acad. Sci.*, **17**, 183 (1931); Whearty, *J. Phys. Chem.*, **35**, 3121 (1931); Ruff and Keim, *Z. anorg. Chem.*, **201**, 245 (1931).

sodium fluoride, in order to remove quantitatively[2] any hydrogen fluoride which it might contain. From a charge of 2 kg. the generator delivered a steady flow of nearly pure fluorine for about 35 hours, using an electrolyzing current of 5 amp. at a potential of 8–10 volts.

In our first experiments, the fluorine was passed directly into carbon tetrachloride solutions of the materials to be tested, contained in a three-necked Pyrex flask, closed with rubber stoppers, equipped with a mechanical stirrer of the ordinary type, and immersed in an efficient ice bath. The glass proved surprisingly resistant and the stoppers did not burn, but the arrangement was not so satisfactory in cases where explosions might occur.

Then it was found that a brass reaction vessel was quite as suitable as one of glass, being even more resistant, essentially unbreakable, and without effect upon the course of the reactions involved. It was made from a piece of 10-cm. heavy duty brass pipe, 18 cm. long, with a bottom soldered in; and had an inset lid, which carried a metal bearing for a copper stirrer, and copper inlet and outlet tubes for the fluorine. The lid was held in place by means of springs, so that even in the event of an explosion no damage could be done to the apparatus or the operator.

In the preliminary work it was noticed that the reactions were always accompanied by occasional bright flashes of light, which appeared in the vapor phase, either within the inlet tube or above the solution. It was thought, therefore, that if the vapor phase were essentially eliminated, not only the flashing but also all detonations might be prevented. Accordingly, an apparatus was designed to accomplish this. It was made of heavy copper, and is illustrated in detail in Fig. 2. The diagram is self-explanatory, but certain features of the design may perhaps be mentioned especially. The lid, provided with a ground joint, was held in place by springs, and had only two openings. One of these was for the stirrer, and the other for the inlet and outlet tubes for the fluorine, one of which was inside the other. The stirrer was activated by a jet of air playing on a paddle wheel, and the bearing in which it turned was so arranged as to be sealed from the action of the fluorine when the apparatus was full of liquid.

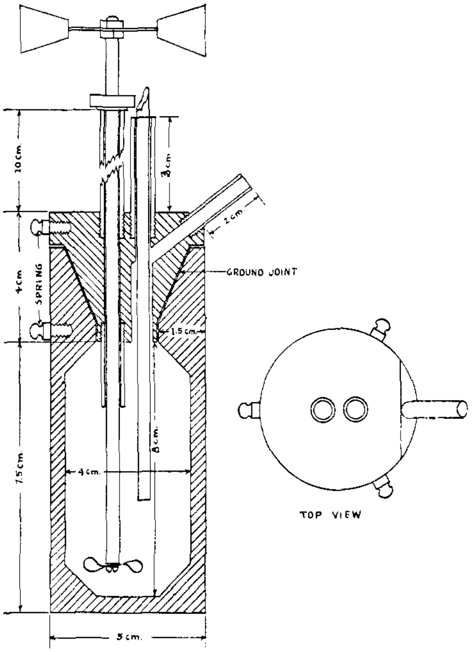

Fig. 2.—Copper reaction vessel.

Discussion of Procedure and Results

In carrying out a study of the direct action of elementary fluorine upon aromatic organic compounds, the first problem which had to be met was that of controlling the reaction. From a survey of the literature, it appeared that this would be extremely difficult, but it soon was found that

[2] Dennis, Veeder and Rochow, THIS JOURNAL, **53**, 3263 (1931).

numerous organic compounds, either dissolved or suspended in purified carbon tetrachloride, could be exposed to the action of the gas for many hours in succession without the slightest danger, provided that the mixtures were kept at 0°, and adequately stirred. Not only this, but the halogen could be passed directly into certain aromatic organic liquids at temperatures as high as 25° without danger under similar conditions, provided also that no significant vapor phase was present. It seems, therefore, that these reactions are much easier to handle than has been supposed heretofore. However, it is important to bear in mind that the simple conditions just described *must* be fulfilled. Otherwise disastrous explosions may occur without warning, involving a significant degree of danger to the operator.

Fluorine has been shown unquestionably to liberate chlorine from carbon tetrachloride at 0°, contrary to the statement of Ruff and Keim,[1] and in a sufficiently active state to chlorinate dissolved *toluene* to form hexachlorobenzene over a period of a few hours. The displacement is rather slow, however; and if a compound is present in the solution which will react with the fluorine at a more rapid rate, it will be fluorinated only. Otherwise it will be both fluorinated and chlorinated. These observations show that the statement by Ruff and Keim already alluded to can no longer be accepted without qualification.

When the gas was passed into a solution of naphthalene in carbon tetrachloride, 3% by weight, at 0°, a dark colored precipitate was formed, which, after being filtered off and dried, became light gray. It was amorphous in character, could not be crystallized from any ordinary solvent and could be purified only in part by precipitating its solution in ether by the addition of ligroin. The material, which seemed to be a polymerized addition product, was not very stable, melted after purification at 176–177° (decomp.) and was found upon analysis to contain considerable fluorine and but little chlorine. The progressive fluorination of such a solution, for six-hour periods, yielded first a gray material, containing 37.7% F, and decomposing at 98–104°; then a yellowish one with 45.9% F, decomposing at 158–170°; and finally a white powder, quite stable in air, with no less than 52.4% F, decomposing at 148–155°. The figures are average checked values. This procedure removed the naphthalene quantitatively from the carbon tetrachloride solution. The white product thus otained was found to possess some sufficiently remarkable properties. When dissolved in ether and treated with sodium carbonate solution, it was decomposed readily, but it could be boiled for several hours with fuming nitric acid, in which it was quite soluble, and yet be recovered not greatly changed. When subjected to this latter treatment, the fluorine content of the material progressively increased, until finally there was obtained a white powder which contained no less than 57.4% F.

Oxidation of the fluorinated naphthalene by means of alkaline permanganate solutions at 20, 50 and 100° failed to yield either phthalic acid or any of its derivatives, but the sample was mostly destroyed in each case. Acid permanganate solutions gave no better results, while chromic anhydride in acetic anhydride solution at 70° did not oxidize the material at all. Furthermore, catalytic reduction with hydrogen under pressure in the presence of a platinum catalyst did not change the material, whereas fluorobenzene could be reduced readily to cyclohexane by this treatment.

The question soon arose as to whether the formation of this type of fluorinated product was a property of naphthalene alone, or of the naphthalene ring system. It was found that α-methylnaphthalene yielded a fluorinated product containing 30.7% F; β-methyl-, 27.2%; α-methoxy-, 33.3%; β-methoxy-, 30.4%; α-hydroxy-, 30.4%; β-hydroxy-, 29.8%; α-nitro-, 34.4%; α-bromo-, 35.9%; tetrahydro-, 26.4%. These materials were similar in properties to that obtained from the parent hydrocarbon, and all decomposed from approximately 90–110°. Also, decahydronaphthalene yielded no derivative of this type. This fact is significant, as it indicates clearly that the reaction is a property of the aromatic organic nucleus, as distinguished from the cycloparaffins. It is interesting to note that neither the nitro group nor the bromine atom was displaced completely by the fluorine, and the α-nitro derivative gave the highest yield. Also, the α-derivatives gave in every case a higher yield than the corresponding β-compounds, under comparable conditions.

Turning now to another phase of the work, it has been found that certain derivatives of dibenzyl gave fluorinated compounds of a type similar to those just described. When fluorine was passed into suspensions of benzoin, desoxybenzoin, dibenzoylmethane, or benzil in carbon tetrachloride at 0° in the absence of a vapor phase, reaction occurred, and the materials in suspension were replaced gradually by fluorinated products. These were gray to white amorphous solids, decomposing from 115–150°, and which could not be crystallized, but could be purified in part only, by the ether–ligroin treatment. They contained, in the order named, 25.6, 31.2, 30.7, 30.5% F; and 1.3, 6.4, 8.6, 2.2% Cl. The more readily enolizable hydrogen atom there was in the original material, the higher the chlorine content of the fluorinated product, showing that chlorination was taking place mostly along well-recognized lines; but the fluorine content followed no such order, indicating, at any rate, that the fluorination was taking place by a different mechanism. This idea was supported by the fact that the product obtained from benzil, which contains no hydrogen at all in the chain, contained much fluorine, and but little chlorine.

The product obtained from desoxybenzoin, like the naphthalene derivatives, was sensitive, when dissolved in ether, to sodium carbonate solution, and resistant to fuming nitric acid. When it was boiled with the latter reagent, however, about three-fourths of the sample was recovered, but it had lost about one-third of its fluorine content in the process. The presence of vanadium pentoxide as a catalyst did not have any effect. No benzoic acid, or any of its derivatives, could be detected among the oxidation products, which is a strong indication that both of the aromatic rings present were involved in the reaction.

The fluorinated material discussed thus far was totally different in character from the numerous fluorine substitution products which have been prepared by indirect methods and described in the literature. The products seemed to be polymerized, but numerous attempts to determine their molecular weights were unreliable, since their solutions were usually colloidal. The question as to whether these materials still retained their original carbon skeletons, or whether they consisted of highly polymerized aliphatic fragments, cannot be answered definitely at the present time; but indications are that a general breakdown of the molecular structure did not take place during the fluorinations.

The situation was quite different from what has been outlined above, when a monocyclic aromatic hydrocarbon, such as toluene, was fluorinated in carbon tetrachloride solution, 15% by volume, at 0°. The reaction was carried out in the presence of a trace of iodine. In this case no precipitation, other than that of a little free carbon, occurred, and the reaction apparently took place at a very much slower rate than before. A dark colored, fuming solution was obtained, which obviously contained unstable products, as it underwent color changes when neutralized. After the removal of the solvent, and most of the excess of toluene, a highly unstable liquid product remained, which was difficult to deal with. However, if the mixture was boiled with alkali just previous to the removal of the excess of hydrocarbon, then a stable dark red oil was formed, which could be distilled without difficulty under reduced pressure. The material was first fractionated in the ordinary way and separated into a light yellow oil, a white crystalline solid, and a considerable tarry residue. The solid, much to our surprise, turned out to be hexachlorobenzene, showing that nascent chlorine, in the presence of fluorine, was sufficiently active to chlorinate the ring completely even at 0°, and to remove the methyl group as well.

The oil was redistilled at 4 mm. in the usual manner, and then continuously fractionated at 4 mm., using a Hickman Auto-Vac Still, provided with attachments for introducing and withdrawing samples from the system without disturbing the vacuum. This procedure was continued until it was evident that no complete separation could be obtained by distillation with the apparatus at our disposal. The lowest boiling fraction was a colorless oil, boiling at 54–57° at 4 mm. and was shown by analysis and oxidation to consist largely of *p*-chlorotoluene. The other four were mixtures and boiled from 74–100, 100–121, 118–129 and 128–138°, respectively, at 4 mm. In the same order, their average molecular weights were 153, 212, 227 and 244. They contained 10.8, 14.0, 12.0, 7.8% F and 38.5, 43.4, 47.4, 52.7% Cl. Thus the molecular weight and the chlorine content rose progressively with the boiling point, while the fluorine content at first rose and then fell off again.

An analysis of the analytical figures shows, first, that no significant degree of polymerization could have taken place in this case, if it is assumed that the products were in any sense derivatives of toluene. Also, since the halogen content and the molecular weight of each fraction were known, the ratio of fluorine to chlorine in each could be calculated. The values were 1:2; 1:2; 1:1.7 and 1:3.6, in the order of increasing boiling points.

Oxidative degradation of these materials with potassium permanganate in alkaline solution, or chromic anhydride in acetic anhydride solution, destroyed the fluorine-containing constituents of the samples; while catalytic reduction did not remove any appreciable quantity of fluorine from the compounds. Alcoholic potassium hydroxide solution removed about 36% of the chlorine present in the mixed distillates, but none of the fluorine, which fact lends support to the idea that the latter halogen was not present in an additive condition. Furthermore, no oxalic acid was found in the filtrates obtained in the last procedure, from which it seems unlikely that a complete hydrolysis of the highly halogenated molecules had occurred.

It is obvious from the reactions just described that the chlorine set free from the solvent by the fluorine was a complicating and undesirable factor. Also, it had been found that the flashing and very likely the explosions which had occurred took place entirely in the vapor phase. Consequently, the copper apparatus already described was designed, and fluorine was passed directly into liquid toluene in the absence of any considerable vapor phase, at temperatures even as high as 25°. Under these conditions there was no sign of explosion or of flashing, and the fluorine could be passed through the hydrocarbon for hours without the slightest difficulty. Vigorous reaction took place, however, accompanied by the evolution of smoke, and the deposition of free carbon, but the recovered toluene contained no fluorine. In several experiments various halogenation catalysts, including iodine, iron powder, antimony fluoride, ferric fluoride and aluminum chloride were used, but entirely without effect, in one case even after twenty-four consecutive hours of fluorination at 0°. Nitrobenzene, dimethylaniline and acetophenone were tried also, but, although the reactions could be controlled easily, they approximated incomplete combustion, and the recovered compounds contained no halogen. In spite of these negative results, however, it is believed that this controlled fluorination has far-reaching possibilities, and it represents, to the best of the writers' knowledge, the first time that it has been possible to pass fluorine through relatively large quantities of organic liquids over considerable periods of time in complete safety.

The analytical method for the estimation of fluorine used in this work was a modification of that recommended by Vaughn and Nieuwland.[3] The halogen was weighed as calcium fluoride, which was previously washed with acetone and heated to constant weight at 160–170°. A correction of 17 mg. per liter was made to allow for the solubility of calcium fluoride in water. The method gave results within 0.5% of the calculated values as shown by the analysis of pure *p*-fluorobenzoic acid.

The results described in the preceding paragraphs show that the action of elementary fluorine on various aromatic organic compounds can be controlled without difficulty, and leads to a variety of interesting and significant products. They are presented at this time as the beginning of an attack upon the general, and very difficult, problem of the mechanism of the action of elementary fluorine upon the aromatic organic nucleus. The work is to be continued actively in this Laboratory.

We are pleased to acknowledge here the friendly interest of Dr. Paul M. Gross, who originally suggested this line of investigation, and who has contributed many valuable suggestions as the work has progressed.

Summary

Several procedures have been described for reaction of elementary fluorine with various aromatic organic compounds, and two types of metal apparatus designed for this purpose.

The action of fluorine on toluene, naphthalene, and twelve naphthalene derivatives, in carbon tetrachloride solution, has been investigated; and products containing over 50% of fluorine isolated.

A study has been made of the action of fluorine on a number of derivatives of dibenzyl in carbon tetrachloride suspension.

Free fluorine has been passed directly through certain organic liquids, at temperatures as high as 25° in the absence of any significant vapor phase. No violent reaction occurred under these conditions although free carbon was deposited.

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[3] Vaughn and Nieuwland, *Ind. Eng. Chem., Anal. Ed.*, **3**, 274 (1931).