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The following papers were read:

Chemistry. — "*Benzene fluoride and some of its derivations.*" By
Prof. A. F. HOLLEMAN and Dr. J. W. BEEKMAN.

(Communicated in the meeting of September 26, 1903).

Benzene fluoride has, up to the present, been a not at all readily accessible substance. The best known method of preparation is that of WALLACH and HEUSLER (A. 245, 255) which consists in first preparing benzenediazopiperidide and decomposing this with

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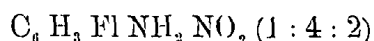
hydrogen fluoride. These chemists are even of opinion that benzene fluoride may thus be readily prepared by the kilo. As regards the course of the reaction our experiences are quite in harmony with those of WALLACH and HEUSLER, but we differ in the appreciation of the convenience of the method. Apart from the fact that in our numerous experiments we have never succeeded in obtaining the yield of 50% (on an average we only got 30% from the aniline employed) which they claim to obtain, the recovery of the piperidine proved to be very tedious. Notwithstanding its price is considerably lower than it used to be, as it is now prepared by electrolytic reduction of pyridine, it is still such that this recovery could not be avoided. The base must be again isolated in a state of perfect purity, because the yield of diazopiperidide becomes very small if the smallest impurity should be present. The method is also very tedious as not more than 10 grams of diazopiperidide at a time should be treated with hydrofluoric acid, otherwise the reaction becoming too violent. After having prepared about 150 grams of benzene fluoride in this way we, therefore, decided to abandon this method and to endeavour to obtain benzene fluoride by the direct diazotation of aniline.

For this purpose VALENTINER and SCHWARTZ have taken out a patent (Centralblatt 1898 I, 1224) consisting in heating a solution of benzenediazonium chloride with hydrogen fluoride. We may surmise that the product will be a benzene fluoride contaminated with benzene chloride; on following their directions this proved to be the case to such an extent that after repeated fractionation of the product 100 grams of aniline yielded only two grams of fairly pure benzene fluoride. This showed that in the diazotation of aniline, intended for the preparation of benzene fluoride hydrochloric acid should be avoided.

I do not wish to enter into particulars as to the various ways in which we have tried to prepare benzene fluoride directly from aniline. Dr. BEERMAN has stated something about this in his dissertation. It will be sufficient to mention here that the yield of the desired product increased with the amount of hydrofluoric acid employed. This is the method which we finally adopted: 93 grams of aniline are dissolved in sulphuric acid and diazotated in the usual manner, care being taken that the volume of liquid does not exceed 1.25 litre. The ice-cold solution is then poured slowly with vigorous stirring into a copper vessel containing 500 cc. of 55% hydrofluoric acid heated nearly to the boiling point and kept at that temperature. The benzene fluoride distills over and is condensed in a leaden worm-condenser surrounded by ice and salt. The distillate consists of a colorless liquid, which is freed from traces of phenol

by washing with a little alkali. After drying over calcium chloride it at once distilled over at a constant temperature of 85°. From 93 grams of aniline 37 grams of benzene fluoride are thus obtained in a perfectly pure condition, that is to say 40% of that required by theory. The deficiency in the yield is caused by the formation of phenol. Probably this may be reduced to a minimum if instead of hydrofluoric acid a mixture of sulphuric acid and calcium fluoride is used in such a manner that the concentration of the hydrogen fluoride remains about constant. As this plan involves vigorous stirring and as our mechanical appliances were inadequate to stir the resulting paste of gypsum, we have not been able to practically confirm this obvious conclusion.

In quite an analogous manner the para- and metanitrobenzene fluoride may be prepared from the corresponding nitranilines and the three toluene fluorides from the toluidenes. Anthranilic acid, however, only yielded small quantities of *o*-fluorobenzoic acid and was nearly all converted into salicylic acid. It was very interesting to notice that, when treated by this process, orthonitraniline did not yield a trace of ortho-nitrobenzene fluoride but only resinous masses. WALLACH has also been unable to prepare this substance by his own method as he did not succeed in purifying the piperidide required. We have made two further attempts to prepare this substance. Firstly by isolating it from the nitration product of benzene fluoride, but as this contains but little of it we did not succeed either by freezing or by fractional distillation. Secondly from parafluoronitrobenzene; the *p*-aniline fluoride obtained by its reduction yields when nitrated in sulphuric acid solution



so that by eliminating the amido-group, *o*-nitrobenzene fluoride must be formed. But only resinous masses were again produced here.

The determination of carbon, hydrogen and nitrogen in the fluorine compounds could be done in the usual manner. For that of the fluorine we used a platinum tube 35 cm. in length and 1.8 cm. in diameter in which the substance was introduced mixed with CaO. After heating the mass contains the fluorine as calcium fluoride, which is then freed from the excess of lime by treatment with dilute acetic acid, collected on a filter and weighed. As we never found lime to be perfectly soluble in dilute acetic acid, it was purified by dissolving it in dilute acetic acid, precipitating with ammonium carbonate and igniting the carbonate so obtained.

The physical constants of some of the compounds prepared by us, were accurately determined and the following values were found:

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	m. p.	b. p.	sp. gr. at 84°.48
<i>m</i> -nitrobenzene fluoride	1°.7	205°	1.2532
<i>p</i> - " " "	26°.5	205°	1,2583
<i>p</i> -aniline fluoride	—	187°	—
nitraniline fluoride(1.2:4)	98°	—	—
benzene fluoride	—41°.2	85°	1.0236 (at 20°/4)

It is a well known fact that the halogen in the halogen benzenes is very inert but that on further substitution in the benzene nucleus its displacement may be much facilitated. In how far this is the case with benzene fluoride and its derivatives has received but insufficient notice up to the present. WALLACH and HEUSLER (A. 243, 242) state that sodium acting at a gentle heat on an ethereal solution of benzene fluoride abstracts all the fluorine with formation of diphenyl. We repeated this experiment, but noticed but little formation of diphenyl although considerable quantities of resin were formed. Moreover, the sodium was but little attacked. Another process for studying the decomposition of halogen benzenes is that of LÖWENHERZ consisting in dissolving the compound in a large excess of alcohol and then adding sodium. If we call ($N\alpha$) the number of gram-atoms of sodium which is present at a given moment in a kilo of solvent, a the original halogen compound and x the portion then converted we have according to him the relation

$$\frac{dx}{d(N\alpha)} = K(a - x)$$

in which K is a constant which he gives the name of "useful effect" (Nutzeffect).

We repeated one of LÖWENHERZ's experimental series with benzene chloride and found the useful effect to be 0.261 whereas he had found 0.254 and 0.268.

On applying the process to benzene fluoride it was found that sodium when acting on its alcoholic solution does not abstract a trace of fluorine, so that the useful effect = 0. This result is surprising, because according to the investigations of LÖWENHERZ the useful effect is about equally great for the other halogen benzenes. It shows that the fluorine in the nucleus is more firmly combined than the other halogens; some data of WALLACH and HEUSLER agree with this view, for instance, that by the action of sodium on an ethereal solution of *p*-benzene fluorobromide for 8 days a large amount of sodium bromide had separated but not a trace of NaFl.

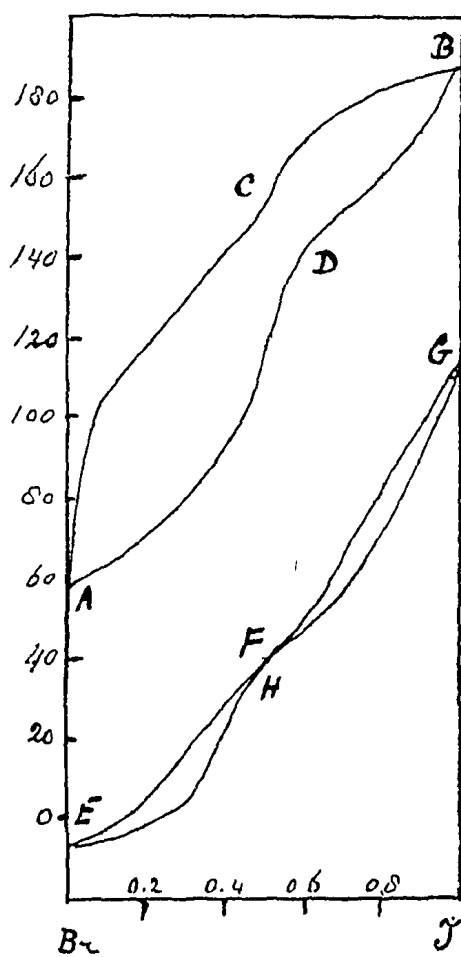
On the other hand we notice the great facility with which the fluorine of the benzene nitrofluorides reacts with sodium methylate;

the *m*- and *p*-compounds, when heated for a short time with this reagent in a methyl alcoholic solution, are quantitatively converted into the corresponding nitro-anisols. In the case of benzene dinitro-fluoride (Fl. $\text{NO}_2 : \text{NO}_2 = 1 : 2 : 4$) the progressive action of the sodium methylate was studied by the method employed by LUIJERS for the corresponding Cl-compound and it appeared that the reaction was quite completed within a few minutes. Owing to this great celerity, accurate quantitative measurements were very difficult; but it was found that the reaction constant in round numbers is 600 times larger than with the chlorine compound.

Groningen, Sept. 1903. Chem. Lab. University.

Chemistry. — “*The system Bromine + Iodine.*” By Prof. H. W. BAKHUIS ROOZEBOOM.

(Communicated in the meeting of September 26, 1903.)



The elements chlorine and iodine yield two chemical compounds which have been accurately investigated by STORTENBEKER. Up to the present the relations of the other halogens remained in obscurity. The system Bromine and Iodine investigated by Mr. MEERUM TERWOGT gave, provisionally, the results represented in our temperature-concentration figure.

First of all the two boiling lines ADB and ACB, which were both determined at 1 Atm. pressure. The first line represents the boiling points of the series of liquid mixtures from 100% Br. to 100% I; the second line represents the vapours yielded by these mixtures. The corresponding points are situated on horizontal joining lines.

The figure shows that these curves are continuous, but