the same way as the ethyl derivatives. In addition the "orotic acid methyl ester" synthesized by Bachstez[7] from oxalacetic acid methyl ester must be 5-(carbmethoxymethylidene)-hydantoin.

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Summary

1. It has been demonstrated that the condensation of ethyloxalacetate with urea in acid solution yields the ester of a substituted hydantoin rather than the ester of orotic acid (4-carboxyuracil), as previously reported.
2. This ester or the corresponding acid 5-(carboxymethylidene)-hydantoin can be converted to orotic acid by treatment with aqueous alkali.
3. Ultraviolet absorption spectra in aqueous solutions are given for 5-(carbethoxymethylidene)-hydantoin, 5-(carboxymethylidine)-hydantoin, 5-(acetic acid)-hydantoin and orotic acid.
4. The ethyl ester of 5-(acetic acid)-hydantoin has been described.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF WASHINGTON]

The Preparation of Fluorine Perchlorate from Fluorine and Perchloric Acid

BY GILSON H. ROHRBACK AND GEORGE H. CADY

It has been known since 1934 that fluorine reacts with nitric acid to form a gaseous compound whose formula is NO_3F.[1] This fact suggests the possibility that other acids may react in a similar manner, forming products in which the hydrogen of the acid has been replaced by fluorine. As a part of a study now under way to test the validity of this suggestion, the gaseous products of the direct fluorination of perchloric acid have been examined. One of the substances found was similar to fluorine nitrate, NO_3F, in many ways, including the tendency to explode easily and with violence.

Products formed in solution by the action of fluorine upon perchloric acid have been reported by Fichter and Brunner.[2]

Experimental

Preparation.—The reaction chamber used through most of this research is shown in Fig. 1. It consisted of a glass column packed with glass chips through which 60% perchloric acid flowed slowly. The acid supply was maintained by slow addition from the dropping funnel at a rate of about one drop per second. The fluorine supply tube entered near the top of the column and ran down through glass packing to a point just above the liquid seal. Undiluted fluorine gas then traveled upward against the counter flow of perchloric acid at an approximate flow rate of 2.5 liters per hour. The column was enclosed with a water jacket for temperature control. Any gaseous reaction product was carried out from the top of the chamber and collected in a trap cooled with liquid oxygen.

In addition to varying quantities of SiF_4, O_2 and OF_2, a white crystalline solid collected on the sides of the cold trap and on warming melted to a clear liquid. When appreciable quantities of this liquid were collected, a yellow substance, apparently chlorine, was also present. The liquid was purified by fractional distillation and the boiling point of the colorless liquid remaining after the removal of the yellow substances was −15.9° at 755 mm. pressure. As a precautionary measure no sample of liquid larger than about 4 ml. was collected in any experiment.

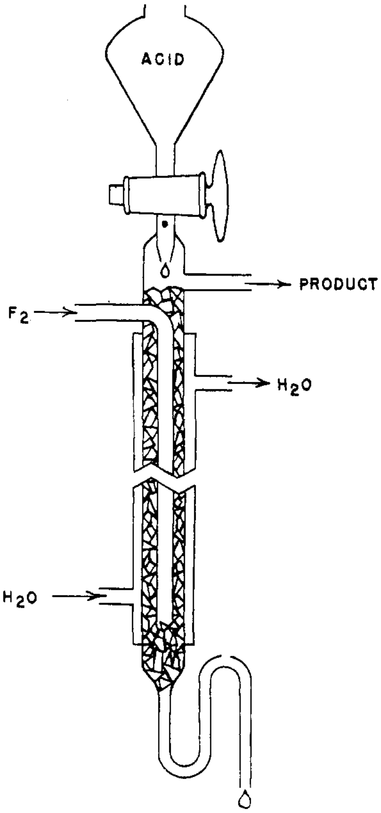

Fig. 1.

The described method for the preparation of this liquid was very inefficient. About one hundred cc. of 60% per-

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[1] G. H. Cady, THIS JOURNAL, **56**, 2635 (1934).

[2] Fr. Fichter and E. Brunner, *Helv. Chim. Acta*, **12**, 305–313 (1929).

chloric acid was used for each cc. of the liquid produced. Increasing the reaction temperature up to about 60° increased the rate of production somewhat, but the process was still highly inefficient. With a view toward increasing both the efficiency and production rate, as well as elimination of SiF_4 as a by-product, a carbon apparatus was constructed similar in design to the glass reaction chamber with the exception that the fluorine entered directly at the bottom. The column was packed with graphite chips and was water-jacketed to permit control of the temperature. The results in using this carbon reaction column were surprising. Instead of the desired product, only a mixture of OF_2 and O_2 was obtained. Density measurements on the mixture of these gases indicated that the weight fraction of OF_2 constituted about 58% of the mixture.

It was found later that the colorless explosive substance could be produced by passing undiluted fluorine directly over 72% perchloric acid in a platinum boat. The yield of the desired product formed by this direct method at 21° was found to be about 90% of the theoretical amount obtainable from the quantity of perchloric acid consumed.

Density of Gas Vapor.—Using a modification of the gas density apparatus of Cady and Rarick,[3] a density value of 4.85×10^{-3} g./ml. at 25° was obtained. Assuming ideality, this would correspond to a molecular weight of 120 (theoretical for ClO_4F is 118.46).

Freezing Point.—The determination of the freezing point proved extremely difficult, because the pure substance exploded while freezing. It was planned to run warming curves for determination of the freezing temperature, but on each of two attempts the purified liquid exploded when liquid oxygen was placed around the trap. On a third trial a cooling curve was obtained in which the temperature stopped falling and remained constant at −167.3° for the last eight minutes before the explosion. It is felt that this figure represents the freezing point, for it is close to a preliminary value of −170° obtained using a sample contaminated with some chlorine.

Odor.—The gas has a sharp acid-like odor and irritates the throat and lungs producing prolonged coughing.

Stability.—While working with the gas, it was discovered that it may be readily exploded. Either a small flame or spark will cause an explosion which will shatter an open-end test-tube containing the gas. Grease, small specks of dirt, or contact with rubber tubing likewise will cause a sharp explosion and one sample of the gas exploded when placed in contact with 2 *M* potassium iodide solution. The instances of explosions at the freezing point have been described.

Analysis.—The gas was caused to react with potassium iodide by allowing a measured sample to diffuse through air into a flask containing 50 ml. of 1% potassium iodide solution. The liberated iodine was titrated with standard sodium thiosulfate solution. Considering the gas to be ideal, the number of moles of iodine liberated per mole of gas was found in two cases to be 0.976 and 0.997 (theoretical for ClO_4F is 1.00).

The analysis was carried out by the reaction of a known volume of approximately 60 cc. of the gas with an excess of 4 *M* sodium hydroxide solution. Qualitative tests indicated the presence of fluoride and perchlorate ions. Fluorine was determined by the method of Hawley[4] wherein the fluoride ion was precipitated as lead chlorofluoride. This precipitate was dissolved in hot 25% nitric acid, an excess of standard silver nitrate was added and the sample was then back titrated with potassium thiocyanate. Chlorine was determined by precipitation of the perchloric acid with nitron.[5] With the four analyses carried out, the percentages of fluorine determined were 16.1 and 16.0%, and those of chlorine 29.2 and 29.4% (theoretical values for ClO_4F are 16.0 and 29.9%).

In the reaction of the gas with a solution of sodium hydroxide, it was found that one volume of the gas liberated one half volume of oxygen.

Discussion

The molecular weight, percentage composition, and chemical behavior of the colorless explosive compound lead to the conclusion that its formula is ClO_4F.

Equations for its reactions with solutions of potassium iodide and sodium hydroxide are, respectively

$$ClO_4F + 2I^- \longrightarrow I_2 + ClO_4^- + F^-$$

$$2ClO_4F + 4OH^- \longrightarrow O_2 + 2ClO_4^- + 2F^- + 2H_2O$$

Fluorine perchlorate was chosen as the name for the compound because many chemists have made it a practice to call NO_3F fluorine nitrate. Another name ending in fluoride might have been a better choice, but it would have had the disadvantage of not calling to mind the correct formula as readily as does the name fluorine perchlorate.

The reaction of fluorine with perchloric acid is rather slow at room temperature. At first the acid appears to be made more concentrated by reactions such as

$$2H_2O + 2F_2 \longrightarrow O_2 + 4HF$$

and

$$H_2O + 2F_2 \longrightarrow OF_2 + 2HF$$

As the concentration increases, the proportion of ClO_4F in the product becomes greater. The nature of the material used to make the reaction vessel is an important factor in determining the relative proportions of the gaseous products.

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Summary and Conclusions

The reaction of fluorine with concentrated perchloric acid produces fluorine perchlorate (ClO_4F), oxygen difluoride, and other gaseous substances. The relative proportion of the gases produced is dependent on the material used in the reaction vessel.

Fluorine perchlorate is highly reactive and it may easily be caused to explode. It freezes at −167.3° and boils, under 755 mm. pressure, at −15.9°.

SEATTLE 5, WASH. RECEIVED FEBRUARY 27, 1947

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(3) H. P. Cady and M. J. Rarick, THIS JOURNAL, **63**, 1357–1360 (1941).

(4) F. G. Hawley, *Ind. Eng. Chem.*, **18**, 573–574 (1926).

(5) O. Loebich, *Z. anal. Chem.*, **68**, 34–36 (1926).