

like, are all influenced by chemical forces. Indeed, before substances can unite chemically, their particles must be brought first into proper subdivision and proximity, by solution, fusion, ionization, or even by mere pressure as has been demonstrated by W. Spring, who caused fine dry powders to combine by high pressure.

If the degree of subdivision is not profound enough to permit of the combination of isolated atoms or ions with each other, chemical combination in the strict sense may not occur, but there may be produced "adsorption compounds" resulting from the union of atomic or ionic mobs in indefinite or non-stoichiometric proportions, under the influence of more or less modified chemical forces.

On the other hand, if the degree of subdivision proceeds far enough, real chemical reactions may occur and be rendered irreversible by the diffusion or adsorption of one or more of the products into a surrounding colloidal sol or gel. When we consider the great variety of bio-colloids and their susceptibility to changes of structure and diffusive or adsorptive capacity, we can easily understand the almost infinite number of reactions that may go on within their recesses, as they swing the balance of the law of mass action over particles reduced to a reactive degree of subdivision. And we must not be surprised to see technical processes develop upon the basis of these principles.

NEW YORK, N. Y.

---

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF CORNELL UNIVERSITY.]

## THE NITRATION PRODUCTS OF TETRACHLOROFLUORAN AND SOME OF THEIR DERIVATIVES.

By W. R. ORNDORFF AND J. J. KENNEDY.

Received November 20, 1916.

**Tetrachlorofluoran.**—This compound, first made by Orndorff and Black,<sup>1</sup> is analogous in every respect to fluoran and is formed as a by-product in the preparation of phenoltetrachlorophthalein. The tetrachlorophthalic acid residue enters the two phenol molecules in the *o*-positions to the hydroxyl groups, and at the same time, the hydroxyl groups lose a molecule of water. Tetrachlorofluoran is formed in the condensation of phenol and tetrachlorophthalic acid with sulfuric acid to the extent of about ten per cent. of the calculated amount.<sup>2</sup>

The tetrachlorofluoran was purified by boiling it several times with a 5% aqueous solution of sodium hydroxide, filtering and washing thoroughly with hot water until the wash water passed through colorless. This process was repeated until on boiling with the sodium hydroxide solution, only a faint purple color resulted; that is, until practically all

<sup>1</sup> *Am. Chem. J.*, 41, 366 (1909).

<sup>2</sup> *THIS JOURNAL*, 38, 2487 (1916).

of the phenoltetrachlorophthalein was removed. It was then dissolved in a 5% solution of alcoholic sodium hydroxide. After filtering, the solution was poured into a large amount of water. The tetrachlorofluoran slowly precipitated out, leaving the remaining phenoltetrachlorophthalein in the solution. The tetrachlorofluoran thus obtained was entirely free from phenoltetrachlorophthalein. It was then dissolved in benzene, and after boiling several times with small amounts of bone black, a colorless solution resulted. After a few crystallizations from benzene, it was obtained in colorless, well-defined crystals, melting sharply with decomposition at 290–291°. Fractions crystallized from acetone and also from methyl alcohol showed no variation in the melting point.<sup>1</sup> The crystals contain no water or solvent of crystallization, and gave the following results on analysis:<sup>2</sup>

Subst., I, 0.3004; II, 0.2141; cc. 0.1 *N* AgNO<sub>3</sub>, I, 27.54; II, 19.60.

Calc. for C<sub>20</sub>H<sub>8</sub>Cl<sub>4</sub>O<sub>3</sub>: Cl, 32.39. Found: I, 32.50; II, 32.46.

Tetrachlorofluoran is readily soluble in acetone, benzene, and glacial acetic acid, rather difficultly soluble in methyl and ethyl alcohols. It is only very slightly soluble in hot concentrated nitric acid. Fluoran dissolves in cold concentrated sulfuric acid, with a yellow color, showing marked greenish fluorescence, while tetrachlorofluoran dissolves readily in the same reagent in the cold with an orange color showing weak greenish fluorescence. It is precipitated unchanged from this solution by water. When tetrachlorofluoran is treated with fuming sulfuric acid, it dissolves with a dark red color, probably owing to the formation of the ceroxonium salt.<sup>3</sup> Aqueous alkalies do not act upon tetrachlorofluoran, even on boiling. It dissolves in alcoholic caustic soda, probably forming a salt of the carbinol carboxylic acid, but on the addition of water the tetrachlorofluoran precipitates slowly from the solution.

**Mononitrotetrachlorofluoran.**—The method of R. Meyer and L. Friedland<sup>4</sup> for the preparation of mononitrofluoran was followed. Ten grams of tetrachlorofluoran were suspended in 200 cc. of glacial acetic acid and boiled for a half hour, less than one-half of the tetrachlorofluoran dissolving. After cooling, 50 cc. of fuming nitric acid (sp. gr. 1.5) were added, and the solution heated to boiling. The tetrachlorofluoran dissolved completely, and at the end of 45 minutes a bright yellow crystalline precipitate began to separate out of the boiling solution. At the end of an hour, the solution was allowed to cool, and after standing several hours,

<sup>1</sup> The statement of Orndorff and Black, *Am. Chem. J.*, **41**, 372 (1909), that tetrachlorofluoran does not melt even when heated to 300° is certainly incorrect.

<sup>2</sup> All the chlorine determinations were made by the lime method, *Am. Chem. J.*, **41**, 393 (1909). International atomic weights for 1916 are used in this article.

<sup>3</sup> *Ann.*, **348**, 215 (1906).

<sup>4</sup> *Ber.*, **32**, 2108 (1899).

the product was filtered off, washed first with glacial acetic acid, and then repeatedly with boiling water.

By crystallizing from glacial acetic acid, it was obtained as bright yellow, well-defined crystals, melting sharply at 317–318°. A fraction, crystallized from nitrobenzene with the addition of ethyl alcohol, showed no change in the melting point. The following results obtained were on analysis of the air-dried crystals:

Subst., I, 0.2177; II, 0.2475; cc. 0.1 *N* AgNO<sub>3</sub>, I, 18.05; II, 20.47.

Calc. for C<sub>20</sub>H<sub>7</sub>Cl<sub>4</sub>O<sub>5</sub>N: Cl, 29.37. Found: I, 29.40; II, 29.34.

Subst.,<sup>1</sup> 0.6321; cc. 0.1 *N* HCl, 12.59.

Calc. for C<sub>20</sub>H<sub>7</sub>Cl<sub>4</sub>O<sub>5</sub>N: N, 2.90. Found: 2.79.

Mononitrotetrachlorofluoran is characterized by its insolubility in most of the ordinary organic solvents. It is practically insoluble in methyl and ethyl alcohols, benzene, ether, acetone, and carbon tetrachloride. It is sparingly soluble in glacial acetic acid; more readily soluble in nitrobenzene. It is insoluble in 10% aqueous sodium hydroxide solution, even on boiling. Cold alcoholic potassium hydroxide has no effect, but on boiling a small amount dissolves, imparting a yellow color to the solution. On diluting with water mononitrotetrachlorofluoran slowly precipitates. It is readily soluble in cold, concentrated sulfuric acid, with an orange color, but without fluorescence. On the addition of water it is precipitated unchanged. No indications were found of the formation of an isomeric mononitro compound.

**2,7-Dinitrotetrachlorofluoran.** — R. Meyer and L. Friedland<sup>2</sup> obtained dinitrofluoran by nitrating fluoran in ten times its weight of fuming nitric acid (sp. gr. 1.5), the solution being heated on a boiling water bath until an energetic reaction began. When tetrachlorofluoran was nitrated under these conditions, a pure trinitrotetrachlorofluoran was obtained. A thorough investigation of the action of fuming nitric acid (sp. gr. 1.5) on tetrachlorofluoran showed that a considerable amount of the trinitro derivative was always formed even when the temperature was held at 0°. A pure dinitro compound was finally made as follows: Eighteen grams of tetrachlorofluoran were added to 300 cc. of glacial acetic acid and 300 cc. of nitric acid (sp. gr. 1.5) and the mixture heated on a water bath for half an hour, until all the tetrachlorofluoran dissolved. After standing 24 hours, the clear solution was poured into a large amount of water, and the pale yellow flocculent precipitate resulting was coagulated by passing steam into the liquid. The product became granular and, after filtering, was washed thoroughly with water and dried. The yield was practically quantitative.

<sup>1</sup> All determinations of nitrogen were made by first reducing the nitro compounds by means of zinc dust and concentrated sulfuric acid and then proceeding as in the Kjeldahl-Gunning method.

<sup>2</sup> *Ber.*, 32, 2108 (1899).

The nitration product was then fractionally crystallized from acetone. The first three fractions, amounting to about 12 g., melted above 300°, while all the subsequent fractions had a rather indefinite and much lower melting point. The product melting above 300° was further purified by careful fractional crystallization from both acetone and glacial acetic acid. All fractions finally melted at 317–318°. A fraction from benzene also melted sharply at 317–318°. Mononitrotetrachlorofluoran melts at the same temperature, but this product differs markedly from the mononitro compound in its greater solubility in acetone and glacial acetic acid, and also in being less soluble in concentrated sulfuric acid. Analyses showed that it was pure dinitrotetrachlorofluoran.

Subst., I, 0.2438; II, 0.2382; cc. 0.1 *N* AgNO<sub>3</sub>, I, 18.50; II, 18.02.

Calc. for C<sub>20</sub>H<sub>6</sub>Cl<sub>4</sub>O<sub>7</sub>N<sub>2</sub>: Cl, 26.87. Found: I, 26.91; II, 26.83.

Subst., 0.2637; cc. 0.1 *N* HCl, 10.27.

Calc. for C<sub>20</sub>H<sub>6</sub>Cl<sub>4</sub>O<sub>7</sub>N<sub>2</sub>: N, 5.31. Found, 5.46.

This dinitrotetrachlorofluoran melting at 317–318° and corresponding to the 2,7-dinitrofluoran of Meyer and Friedland,<sup>1</sup> was found to be quite soluble in acetone and glacial acetic acid; sparingly soluble in benzene, and comparatively insoluble in ethyl and methyl alcohols. It dissolves in cold, concentrated sulfuric acid (but not nearly as readily as the mononitro product) with a bright yellow color but no fluorescence. On moderate warming, the color is more pronounced, changing to a deep orange; on cooling, however, the solution again becomes yellow. Aqueous caustic alkalis have no effect on dinitrotetrachlorofluoran even on boiling. It dissolves in *hot* alcoholic potassium hydroxide solution with a yellow color; on diluting with water, dinitrotetrachlorofluoran slowly separates from the solution.

The product melting below 300° gave results on analysis for a pure dinitrotetrachlorofluoran, showing the presence of an isomer. It is a mixture of the 2,7-dinitrotetrachlorofluoran, just described, and an isomeric dinitrotetrachlorofluoran, which will now be described.

*iso*-Dinitrotetrachlorofluoran. — The product melting below 300°, from which most of the 2,7-dinitrotetrachlorofluoran was separated by the greater insolubility of the latter in acetone, was fractionally crystallized from acetone and also from glacial acetic acid. However, neither solvent seemed to effect any separation, the product still having a very indefinite melting point, softening at about 180°, and not melting completely until 280°. The eutectic mixture was then boiled with ethyl alcohol, in which it is difficultly soluble. After several extractions, the residue melted somewhat higher than the material that had dissolved in the ethyl alcohol, showing that a partial separation had been effected. Finally methyl alcohol was tried, and this proved to be a better solvent

<sup>1</sup> *Ber.*, 31, 1739 (1898); 32, 2108 (1899).

for separating the two isomers. After extracting the product repeatedly with methyl alcohol, the residue was recrystallized from acetone and melted sharply at  $317-318^{\circ}$ , showing that it was the 2,7-dinitro derivative above described. After repeatedly crystallizing the product more readily soluble in methyl alcohol, about two grams were obtained with a sharp melting point of  $249-250^{\circ}$ , which gave the following results on analysis:

Subst., I, 0.2412; II, 0.2349; cc. 0.1 *N* AgNO<sub>3</sub>, I, 18.25; II, 17.82.

Calc. for C<sub>20</sub>H<sub>6</sub>Cl<sub>4</sub>O<sub>7</sub>N<sub>2</sub>: Cl, 26.87. Found: I, 26.82; II, 26.90.

Subst., 0.4011; cc. 0.1 *N* HCl, 15.49.

Calc. for C<sub>20</sub>H<sub>6</sub>Cl<sub>4</sub>O<sub>7</sub>N<sub>2</sub>: N, 5.31. Found: 5.41.

*iso*-Dinitrotetrachlorofluoran is very similar to the 2,7-dinitrotetrachlorofluoran in its behavior towards concentrated sulfuric acid, and aqueous and alcoholic solutions of caustic alkalis. It differs from the latter in its greater solubility in acetone, glacial acetic acid and in methyl and ethyl alcohols. The two isomers form eutectic mixtures which are very difficult to separate by fractional crystallization.

**Trinitrotetrachlorofluoran.**—As mentioned above, the method of Meyer and Friedland for the preparation of dinitrofluoran gave a trinitro compound in the case of tetrachlorofluoran. Fourteen grams of tetrachlorofluoran were added slowly to 100 g. of nitric acid (sp. gr. 1.5). After shaking for a time, complete solution took place with the evolution of heat. The mixture was heated on a boiling water bath for about 15 minutes, and the orange-colored solution allowed to stand overnight. The clear solution was then poured into a large amount of water, and the pale yellow precipitate resulting recrystallized from acetone. It was finally obtained in yellow, well-defined crystals, which melted sharply at  $275-276^{\circ}$ . Fractions from glacial acetic acid and also from benzene showed no variation in the melting point. The following results were obtained on analysis:

Subst., I, 0.2004; II, 0.2006; cc. 0.1 *N* AgNO<sub>3</sub>, I, 14.04; II, 14.00.

Calc. for C<sub>22</sub>H<sub>5</sub>Cl<sub>4</sub>O<sub>9</sub>N<sub>3</sub>: Cl, 24.76. Found: I, 24.85; II, 24.75.

Subst., I, 0.3070; II, 0.2967; cc. 0.1 *N* HCl, I, 16.29; II, 15.85.

Calc. for C<sub>20</sub>H<sub>5</sub>Cl<sub>4</sub>O<sub>9</sub>N<sub>3</sub>: N, 7.34. Found: I, 7.43; II, 7.48.

Trinitrotetrachlorofluoran is readily soluble in acetone and glacial acetic acid, sparingly soluble in benzene, and practically insoluble in ethyl and methyl alcohols. It is slightly soluble in hot ten per cent. caustic alkali, imparting a yellow color to the solution. It dissolves in *cold* alcoholic potassium hydroxide solution with a reddish *orange* color. On diluting the alcoholic solution with water, *no* precipitate appears. Trinitrotetrachlorofluoran is not soluble in cold concentrated sulfuric acid. On heating moderately, it partially dissolves, imparting an orange color but no fluorescence to the solution. On cooling, the color changes to a bright yellow. When a mixture of 2,7-dinitrotetrachlorofluoran and *iso*-dinitrotetrachlorofluoran was nitrated on a boiling water bath with nitric

acid (sp. gr. 1.5), the *same* trinitrotetrachlorofluoran described above was obtained.

An investigation of the action of fuming nitric acid (sp. gr. 1.5) on tetrachlorofluoran revealed the fact that the trinitrotetrachlorofluoran is always the main product formed. When the nitration is carried on at  $0^{\circ}$ , a mixture consisting mainly of the trinitrotetrachlorofluoran, together with a small amount of the dinitro derivative, is obtained. This mixture can be separated by fractional crystallization only with the greatest difficulty, and even then only partially. When the nitration is brought about at the boiling point of nitric acid, pure trinitrotetrachlorofluoran is obtained, no evidence of higher nitration products being found, even when the amount of nitric acid is increased.

In the preparation of trinitrotetrachlorofluoran no isomeric trinitro compound was formed.

**Tetranitrotetrachlorofluoran.** — The preparation of this compound free from other nitration products of tetrachlorofluoran was carried out in the following manner: Five grams of trinitrotetrachlorofluoran were dissolved in a mixture of 150 g. of nitric acid (sp. gr. 1.5) and 50 g. of sulfuric acid (sp. gr. 1.84). The orange-colored solution resulting was heated on a boiling water bath for an hour. After standing 24 hours, the clear solution was poured into a large amount of water, the yellow precipitate filtered off, washed well with water and dried. It was found to be quite insoluble in all the ordinary solvents. In acetone it dissolved to the extent of about half a per cent., and by using large amounts of this solvent, the product was obtained, after a few crystallizations, as a pale yellow, finely crystalline powder, which did not melt when heated to  $325^{\circ}$ . The following results were obtained on analysis:

Subst., I, 0.3114; II, 0.2242; cc. 0.1 *N* AgNO<sub>3</sub>, I, 21.00; II, 14.43.

Calc. for C<sub>20</sub>H<sub>4</sub>Cl<sub>4</sub>O<sub>11</sub>N<sub>4</sub>: Cl, 22.95. Found: I, 22.88; II, 22.82.

Subst., 0.2378; cc. 0.1 *N* HCl, 15.35.

Calc. for C<sub>20</sub>H<sub>4</sub>Cl<sub>4</sub>O<sub>11</sub>N<sub>4</sub>: N, 9.07. Found: 9.04.

It dissolves readily in hot nitrobenzene, but is only sparingly soluble in acetone and in glacial acetic acid, and practically insoluble in ethyl and methyl alcohols. It is slightly soluble in hot 10% caustic alkali with a yellow color. It dissolves in *cold* alcoholic potassium hydroxide solution with a reddish *orange* color, and *no* precipitate forms on the addition of water. It is insoluble in cold concentrated sulfuric acid; moderate heating has no effect. The mononitro- and tetranitrotetrachlorofluorans resemble each other in their marked insolubility in most of the organic solvents. The trinitro derivative is the most soluble of all the nitration products, while the dinitro derivatives stand intermediate in solubility. Mononitrotetrachlorofluoran dissolves readily in concen-

trated sulfuric acid, but the solubility decreases with the successive introduction of nitro groups into the tetrachlorofluoran molecule.

Tetranitrotetrachlorofluoran was also obtained by nitrating tetrachlorofluoran according to the same conditions under which Meyer and Friedland obtained *pentanitrofluoran* from fluoran. Seven grams of tetrachlorofluoran were dissolved in 15 cc. of concentrated sulfuric acid, and the solution gradually added to a mixture of 14 cc. of concentrated sulfuric acid and 15 cc. of nitric acid (sp. gr. 1.5). A precipitate immediately appeared. The mixture was heated on a water bath for about half an hour, but no appreciable amount of the precipitate dissolved. It was then heated on a metal bath to 130° for one hour, when quite a violent reaction ensued. After cooling, the mixture was poured into a large amount of water, the precipitate filtered off and fractionally crystallized from acetone. The bulk of the product was found on analysis to be pure tetranitrotetrachlorofluoran. A small amount of trinitrotetrachlorofluoran was also obtained. A pentanitrotetrachlorofluoran could not be obtained.

**Pentanitrofluoran.**—As Meyer and Friedland in their article on the nitration products of fluoran make no mention of a tetranitrofluoran, their work on the preparation of pentanitrofluoran was repeated. Sixteen grams of fluoran were dissolved in 40 cc. of concentrated sulfuric acid, and the solution gradually added to a mixture of 40 cc. of concentrated sulfuric acid and 40 cc. of nitric acid (sp. gr. 1.5). A clear solution was obtained, but gradually heat developed and an exceedingly lively reaction ensued, copious amounts of oxides of nitrogen being given off and an abundant precipitate appearing. The mixture was then heated on the boiling water bath for half an hour, the solution poured into water and the precipitate purified in the usual manner. The product obtained did not melt when heated to 325°, and agreed in all respects with the pentanitrofluoran described by Meyer and Friedland. An analysis of the compound crystallized from acetone gave the following results:

Subst., I, 0.2161; II, 0.2321; cc. 0.1 N HCl, I, 20.32; II, 21.78.

Calc. for  $C_{20}H_7O_{13}N_5$ : N, 13.34. Found: I, 13.17; II, 13.15.

The compound obtained by Meyer and Friedland is, therefore, undoubtedly a pentanitrofluoran. The corresponding pentanitrotetrachlorofluoran, however, could not be made, which would indicate that the fifth nitro group in pentanitrofluoran is in the phthalic acid residue.

**2,7-Diaminotetrachlorofluoran.**—Eight grams of 2,7-dinitrotetrachlorofluoran were added to 70 grams of alcohol saturated with dry hydrochloric acid gas, and containing 40 g. of crystallized stannous chloride. After heating on a boiling water bath for half an hour quite a vigorous reaction ensued, and the double tin salt of the diamino compound began to separate from the orange-colored solution. After standing several

hours, it was filtered off, washed with hydrochloric acid, dissolved in water and the solution filtered to remove a small amount of unchanged dinitrotetrachlorofluoran. Hydrogen sulfide was then passed through the warm solution and the tin completely precipitated as the sulfide. Ammonium hydroxide was carefully added to the clear filtrate, from which the excess of hydrogen sulfide had been expelled by boiling, and the free base separated as a bright yellow amorphous powder. It was filtered off, and after crystallizing a few times from alcohol, obtained in the form of orange-colored needles. The following results were obtained on analysis of the air-dried product:

Subst., I, 0.1861, II 0.1580; cc. 0.1 *N* AgNO<sub>3</sub>, I, 15.88; II, 13.47.

Calc. for C<sub>20</sub>H<sub>10</sub>Cl<sub>4</sub>O<sub>3</sub>N<sub>2</sub>: Cl, 30.31. Found: I, 30.25; II, 30.23.

Subst., 0.2122; cc. 0.1 *N* HCl, 8.88.

Calc. for C<sub>20</sub>H<sub>10</sub>Cl<sub>4</sub>O<sub>3</sub>N<sub>2</sub>: N, 5.99. Found: 5.86.

2,7-Diaminotetrachlorofluoran does not melt when heated to 325°. It shows characteristic color reactions which for the most part correspond to those of the diaminofluoran described by Meyer and Friedland.<sup>1</sup> It dissolves in cold concentrated sulfuric acid, with a bright yellow color; on heating the solution becomes an intense cherry-red, and on cooling shows a faint yellow fluorescence. If the red sulfuric acid solution be diluted with water, the color changes to a deep green, and soon the colorless sulfate begins to crystallize from the solution. According to Meyer and Friedland, diaminofluoran dissolves in hot glacial acetic acid, with a violet color, which on cooling goes over into a weak rose color. Diaminotetrachlorofluoran, however, dissolves in hot glacial acetic acid, giving a colorless solution, which does not change on cooling.

Diaminotetrachlorofluoran does not dissolve in ten per cent. sodium hydroxide solution, even on boiling. It dissolves in hot alcoholic potassium hydroxide solution with a pale yellow color and no precipitate forms on the addition of water, probably owing to the formation of a *stable* orthoquinoid salt (page 101). When heated in concentrated hydrochloric acid, the *orange*-colored crystals of the diamino-compound change to those of the *colorless* hydrochloride, which remain suspended in the solution. The hydrochloride is readily soluble in pure water; in water containing hydrochloric acid, it is difficultly soluble and can be crystallized from the latter in short-thick needles.

#### Hydroquinonetetrachlorophthalein.

By diazotizing diaminotetrachlorofluoran sulfate and decomposing the diazonium salt with water, hydroquinonetetrachlorophthalein was obtained, and the constitution of diaminotetrachlorofluoran established.

Three grams of diaminotetrachlorofluoran were dissolved in 225 cc. of concentrated sulfuric acid and a 2% solution of sodium nitrite added

<sup>1</sup> *Ber.*, 31, 1742 (1898).



dropwise from a buret until a positive test for free nitrous acid was obtained. During the addition of sodium nitrite the contents of the flask were cooled and continually shaken. After standing a short time, the solution was heated to about  $150^{\circ}$  until all the nitrogen had been evolved. It was then poured into a large excess of boiling water, when the flocculent brown precipitate first formed gradually became granular. It was filtered off, washed with water until free from sulfuric acid, and dried. It was repeatedly crystallized from methyl alcohol with the use of bone-black, and was finally obtained as well-defined crystals with a faint yellow color. The following result was obtained on analysis:

Subst., 0.2101; cc. 0.1 *N* AgNO<sub>3</sub>, 17.78.

Calc. for C<sub>20</sub>H<sub>8</sub>Cl<sub>4</sub>O<sub>5</sub>: Cl, 30.18. Found: 30.01.

(The chlorine content of diaminotetrachlorofluoran (30.31%) and that of the hydroquinonetetrachlorophthalein (30.18%) are so close that a nitrogen determination was made to show conclusively that both amino groups were replaced by hydroxyl groups. *No nitrogen was found.*)

Hydroquinonetetrachlorophthalein does not melt when heated to  $325^{\circ}$ . It dissolves in dilute alkalis with the same violet color, characteristic of hydroquinonephthalein. On long standing, or on the addition of excess alkali, the color disappears, owing to the formation of the salt of the carbinol acid. When the dilute alkaline solution is heated, the violet color is intensified, but on cooling, the color gradually fades and returns to the original shade of color. Hydroquinonetetrachlorophthalein dissolves in concentrated sulfuric acid with a red color, similar to that given by hydroquinonephthalein. It is readily soluble in methyl and ethyl alcohols, sparingly soluble in benzene and chloroform, and practically insoluble in ligroin.

Various attempts were made to condense hydroquinone and tetrachlorophthalic anhydride. Small amounts of the hydroquinonetetrachlorophthalein were unquestionably formed as proved by the characteristic violet color imparted to alkaline solutions. However, it was impossible to separate the small amount of phthalein from the large amount of tar that was always formed.

**Monoaminotetrachlorofluoran.**—Four grams of mononitrotetrachlorofluoran were added to 35 g. of absolute alcohol, saturated with hydrochloric acid gas and containing 10 g. of crystallized stannous chloride. The solution was heated on a boiling water bath for an hour, but owing to the insolubility of the mononitrotetrachlorofluoran, a considerable amount of it remained undissolved. It was separated by filtration and treated again as described above. The treatment had to be repeated a third time before all the mononitro compound was reduced. The solutions thus obtained were mixed and an equal amount of water added.

A flocculent precipitate appeared, and after standing for some time, was filtered off and dried. It proved to be the free base, as it was insoluble in water, unacted upon when boiled with ammonium polysulfide, and left no residue on ignition. After crystallizing a few times from alcohol, it was obtained as bright yellow, well-defined crystals, which melted sharply, with decomposition, at 279–280°. The following results were obtained on analysis:

Subst., 0.1990; cc. 0.1 *N* AgNO<sub>3</sub>, 17.53.

Calc. for C<sub>20</sub>H<sub>9</sub>Cl<sub>4</sub>O<sub>3</sub>N: Cl, 31.32. Found: 31.23.

Subst., 0.5467; cc. 0.1 *N* HCl, 11.61.

Calc. for C<sub>20</sub>H<sub>9</sub>Cl<sub>4</sub>O<sub>3</sub>N: N, 3.09. Found: 2.97.

Monoaminotetrachlorofluoran dissolves in concentrated sulfuric acid with an orange color; on heating, the color becomes an intense cherry-red; on diluting with water a bright green and on neutralizing this solution with sodium hydroxide, a violet color. Cold alcoholic potassium hydroxide has no effect on the amino compound, but on heating it dissolves to form a pale yellow solution, from which no precipitate separates on the addition of water, probably owing to the formation of a *stable* orthoquinoid salt (page 101).

Monoaminotetrachlorofluoran was diazotized in the same manner as the diaminotetrachlorofluoran (page 95). When the diazonium compound was decomposed by boiling with water, tetrachlorofluoran was formed instead of the expected hydroxyl derivative. This behavior is in accord with that of monoaminofluoran, described by Meyer and Friendland.<sup>1</sup>

**Triaminotetrachlorofluoran.**—Six grams of trinitrotetrachlorofluoran were added to 35 g. of alcohol saturated with dry hydrochloric acid gas, and containing 20 g. of crystallized stannous chloride. On heating to boiling, the trinitro product dissolved. After standing for some time, the clear orange-colored solution was diluted with an equal volume of water, whereupon the double tin salt of the base began to separate out. It was filtered off, washed with hydrochloric acid, dissolved in water and the tin removed as the sulfide. Ammonium hydroxide was carefully added until the solution was slightly alkaline, whereupon the free base separated as a bright yellow flocculent precipitate. It was filtered off and crystallized several times from absolute alcohol when it appeared as well-defined crystals, with a reddish brown color. From dilute alcohol it separated in very fine microscopic crystals, yellow in color. The yellow modification on crystallizing from absolute alcohol was obtained with a reddish brown color. This difference in color seems to be due entirely to the size of the crystals. The following results were obtained on analysis of the material dried at 150°:

<sup>1</sup> *Ber.*, 32, 2109 (1899).

Subst., I, 0.1820; II, 0.2705; cc. 0.1 *N* AgNO<sub>3</sub>, I, 14.96; II, 22.24.

Calc. for C<sub>20</sub>H<sub>11</sub>Cl<sub>4</sub>O<sub>3</sub>N<sub>3</sub>: Cl, 29.37. Found: I, 29.14; II, 29.16.

Subst., 0.2300; cc. 0.1 *N* HCl, 14.16.

Calc. for C<sub>20</sub>H<sub>11</sub>Cl<sub>4</sub>O<sub>3</sub>N<sub>3</sub>: N, 8.70. Found: 8.63.

Triaminotetrachlorofluoran does not melt even when heated to 325°. When dissolved in concentrated sulfuric acid, it does not give the color reactions which characterize the monoamino- and the diaminotetrachlorofluoran. It dissolves in the cold in concentrated sulfuric acid practically without color; when heated, a faint yellow color develops and on dilution with water an amorphous brown precipitate slowly appears. It is insoluble in a 10% solution of sodium hydroxide. It dissolves with a reddish orange color in hot alcoholic potassium hydroxide solution; on diluting with water, no precipitate forms.

The triaminotetrachlorofluoran was diazotized and the resulting product boiled with water, the procedure being identical with that described for the preparation of hydroquinonetetrachlorophthalein. The compound obtained was a phthalein, dissolving in alkalis with an orange-red color, and being precipitated on the addition of acids. Owing to the small amount of the substance and the difficulty of obtaining it in pure condition, it was impossible to identify the phthalein. The results show, however, that the triaminotetrachlorofluoran behaves like the diaminotetrachlorofluoran, and it is highly probable that the phthalein is hydroxyhydroquinonetetrachlorophthalein or 2,5,7-trihydroxytetrachlorofluoran.

**Tetraaminotetrachlorofluoran.**—Six grams of tetranitrotetrachlorofluoran were added to 80 g. of alcohol saturated with dry hydrochloric acid gas and containing 60 g. of crystallized stannous chloride. The solution was heated to boiling for an hour when complete reduction of the tetranitrotetrachlorofluoran ensued. There was no separation of the double tin salt from the clear solution even on long standing, so it was evaporated on the water bath to small volume to expel the alcohol. It was then diluted with water and the tin completely precipitated as the sulfide. The clear filtrate was made alkaline with ammonium hydroxide, whereupon the tetraaminotetrachlorofluoran was precipitated in yellow flocks. After crystallizing several times from dilute alcohol, the compound was obtained as dark yellow, well-defined crystals which decomposed slightly but did not melt when heated to 325°. The following results were obtained on analysis of the material previously dried at 125°.

Subst., 0.2297; cc. 0.1 *N* AgNO<sub>3</sub>, 18.27.

Calc. for C<sub>20</sub>H<sub>12</sub>Cl<sub>4</sub>O<sub>3</sub>N<sub>4</sub>: Cl, 28.48. Found: 28.20.

Subst., 0.2623; cc. 0.1 *N* HCl, 20.76.

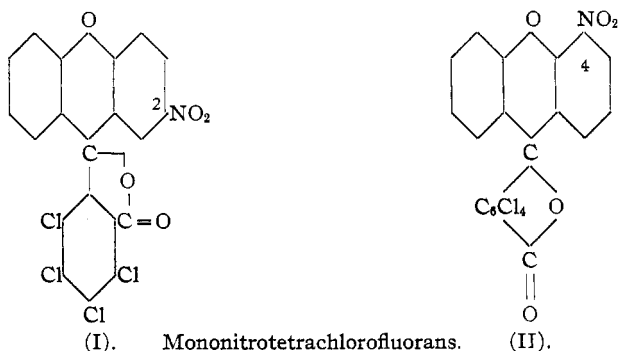
Calc. for C<sub>20</sub>H<sub>12</sub>Cl<sub>4</sub>O<sub>3</sub>N<sub>4</sub>: N, 11.25. Found: 11.09.

Tetraaminotetrachlorofluoran is insoluble in water, but dissolves readily in ethyl alcohol. It is insoluble in aqueous ten per cent. caustic alkalis, but dissolves readily in a hot alcoholic solution of potassium

hydroxide with a reddish orange color. No precipitate appears on diluting with water. Like triaminotetrachlorofluoran, it dissolves in cold concentrated sulfuric acid, practically without color; when heated, a faint yellow color develops, and on diluting with water a brown amorphous precipitate slowly forms.

### Theoretical.

In regard to the structure of mononitrotetrachlorofluoran, it is reasonable to suppose that the nitro group occupies a position *meta* to the tetrachlorophthalic acid residue and either *ortho* or *para* to the pyrone oxygen atom. Either of the following formulas, therefore, would represent the structure of this compound:



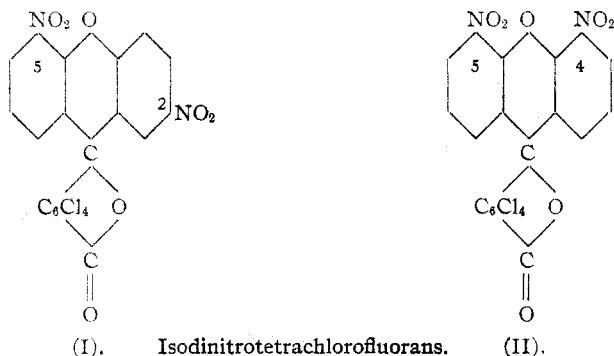
In the formation of mononitrotetrachlorofluoran, no evidence of the presence of an isomer was found, although one may have been formed in very small amount. If but one mononitrotetrachlorofluoran exists, then in the light of more conclusive proof, which will be considered in showing the structure of the dinitrotetrachlorofluorans (see below), Formula I best represents the structure of the mononitrotetrachlorofluoran. It is only this mononitro compound which could give both the 2,7- and the 2,5-dinitrotetrachlorofluoran. The fact that the mononitro compound, when reduced and this amino product diazotized and the resulting solution boiled with water, gives tetrachlorofluoran instead of the expected hydroxyl derivative, is quite remarkable, although as pointed out by Meyer and Friedland,<sup>1</sup> similar cases have been cited before.

When tetrachlorofluoran is nitrated in a medium containing equal parts, by volume, of nitric acid (sp. gr. 1.5) and glacial acetic acid, two isomeric dinitrotetrachlorofluorans are obtained, one melting at 249–250°, and the other at 317–318°. When the latter, which is formed in much greater amount, is reduced to the corresponding diamino compound, this compound diazotized and the resulting solution boiled with water, *hydroquinonetetrachlorophthalein* is obtained. This transformation shows that the two nitro groups must be in different benzene rings, and occupy

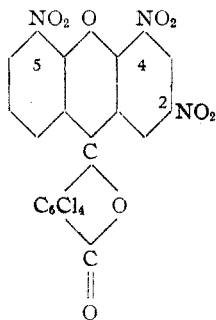
<sup>1</sup> Ber., 32, 2108 (1899).

the *p*-positions to the pyrone oxygen atom; in other words, the dinitrotetrachlorofluoran must be the 2,7-product.

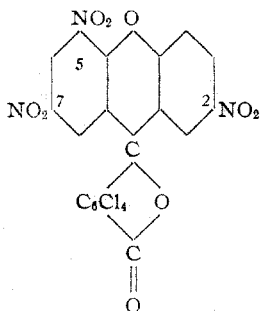
Isodinitrotetrachlorofluoran, melting at 249–250°, may be represented by either of the following formulas assuming that the nitro groups go into different benzene rings:



If the compound has the structure shown in Formula II, it should yield an isomeric trinitrotetrachlorofluoran,



on further nitration, while if it has the structure shown by Formula I, it could give the *same* trinitro product that the 2,7-dinitro compound does. In view of the fact that a *mixture* of the two isomeric dinitrotetrachloro-

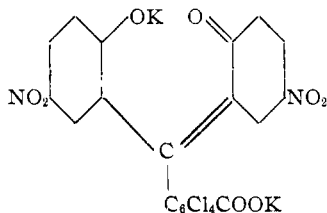


Trinitrotetrachlorofluoran.

fluorans on nitration (page 93) gives but *one* trinitrotetrachlorofluoran, Formula I best represents the structure of the isodinitrotetrachlorofluoran, and further, trinitrotetrachlorofluoran can only be represented by the preceding formula.

Tetranitrotetrachlorofluoran has been made by nitrating either tetrachlorofluoran or the trinitro derivative and has unquestionably the nitro groups in positions 2, 4, 5 and 7.

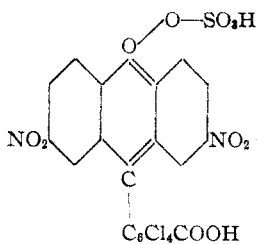
Mononitrotetrachlorofluoran and the two isomeric dinitrotetrachlorofluorans are quite similar in their behavior toward caustic alkalis. They are not affected by aqueous caustic alkalis, but dissolve in a *hot* alcoholic solution of potassium hydroxide with a *yellow* color. Moreover, the tri- and tetranitrotetrachlorofluorans dissolve to a slight extent in hot aqueous alkali solutions and are readily soluble in *cold* alcoholic potassium hydroxide with an *orange* color. In each case an ortho-quinoid salt is probably formed as is shown in the following formula for the potassium salt of the 2,7-dinitro compound which is representative of all:



Dipotassium salt of 2,7-dinitrotetrachlorofluoran.

On diluting these alkaline solutions with water, the tri- and tetranitrotetrachlorofluorans are not precipitated, showing that the salts of these compounds are quite stable. However, in the case of the salts of the mono-, di- and isodinitrotetrachlorofluorans, the corresponding nitrotetrachlorofluorans slowly precipitate on diluting the alkaline solutions with water.

Tetrachlorofluoran dissolves readily in cold concentrated sulfuric acid, but the solubility decreases with the successive introduction of nitro groups into the tetrachlorofluoran molecule. Mononitrotetrachlorofluoran is readily soluble in cold concentrated sulfuric acid with a yellow color, while the tetranitro derivative is insoluble even on moderate heating. When water is added to the colored concentrated sulfuric acid solutions of the mono-, di-, isodi-, or trinitrotetrachlorofluoran, the precipitation of the corresponding nitro derivative takes place immediately. The compounds formed in sulfuric acid solution are therefore not sulfonic acids, but probably oxonium sulfates, as is shown in the following formula for the salt of 2,7-dinitrotetrachlorofluoran, which may be considered typical of all:



2,7-Dinitrotetrachlorofluoran oxonium sulfate.

By the reduction of mononitro-, 2,7-dinitro-, trinitro-, and tetranitrotetrachlorofluorans by means of an alcoholic solution of stannous chloride, saturated with dry hydrochloric acid gas, the corresponding aminotetrachlorofluorans are obtained. These compounds, therefore, are represented by formulas similar to those given for the nitro compounds substituting amino groups for the nitro groups.

The monoamino- and diaminotetrachlorofluorans dissolve in *hot* alcoholic potassium hydroxide solution with a yellow color. The triamino- and tetraaminotetrachlorofluoran dissolve more readily with a reddish orange color. In no case does a precipitate form on the addition of water, probably owing to the formation of stable *o*-quinoid salts, similar to that shown on page 101.

The monoamino and diamino compounds dissolve in concentrated sulfuric acid with a yellow color; when heated these solutions turn cherry-red and when diluted with water, green. In the case of the diamino product, a colorless crystalline precipitate of the sulfate slowly separates out of the green solution on standing. These color changes are probably due to the formation of oxonium salts analogous to those of the nitro compounds (page 101). The triamino and tetraamino products dissolve in the cold in concentrated sulfuric acid practically without color; when heated, a faint yellow color develops and on dilution with water a brown amorphous precipitate separates from these solutions on long standing.

### Summary.

The results of this investigation on the nitration products of tetrachlorofluoran may be briefly stated as follows:

Five nitro derivatives have been prepared, namely: Mono-, di-, isodi-, tri-, and tetranitrotetrachlorofluoran.

When tetrachlorofluoran is dissolved in fuming nitric acid (sp. gr. 1.5) trinitrotetrachlorofluoran results as the main product at 0° or at the boiling point of the solution. If the nitration is performed in a medium of four parts, by volume, of acetic acid and one part of nitric acid (sp. gr. 1.5), the mononitro compound alone results, while if the nitrating solution consists of equal parts, by volume, of acetic acid and nitric acid (sp. gr. 1.5),

the two isomeric dinitrotetrachlorofluorans are formed. Tetranitrotetrachlorofluoran results when tetrachlorofluoran is nitrated in a solution of one part of nitric acid (sp. gr. 1.5) and two parts of concentrated sulfuric acid. By this method Meyer and Friedland obtained a pentanitrofluoran. However, pentanitrotetrachlorofluoran could not be made. This seems to show that one of the nitro groups in pentanitrofluoran is in the phthalic acid residue.

The solubility of tetrachlorofluoran in concentrated sulfuric acid decreases with the successive introduction of nitro groups into the molecule, while the solubility in an alcoholic solution of caustic potash increases.

Dinitrotetrachlorofluoran has been reduced and the resulting diamino compound diazotized and this solution boiled with water. *Hydroquinone-tetrachlorophthalein* results showing that the nitro groups must be in different benzene rings and occupy the *p*-positions to the pyrone oxygen atom and the *m*-positions to the tetrachlorophthalic acid residue.

Mononitrotetrachlorofluoran, when reduced and the resulting amino compound diazotized and this solution boiled with water, gives *tetrachlorofluoran* instead of the expected hydroxyl derivative.

Mono-, di-, tri-, and tetranitrotetrachlorofluorans have been reduced in an alcoholic solution of stannous chloride saturated with hydrochloric acid gas, and the corresponding aminotetrachlorofluorans have thus been prepared.

ITHACA, N. Y.

---

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WASHINGTON UNIVERSITY.]

## THE TRANSFORMATION OF NITRILES INTO AMIDES BY HYDROGEN PEROXIDE.

BY L. McMASTER AND F. B. LANGRECK.

Received November 20, 1916.

The first use made of hydrogen peroxide as a hydrolytic agent for converting nitriles into amides was by Radziszewski.<sup>1</sup> The action takes place according to the equation:



Radziszewski found that the reaction took place easily in the presence of a small amount of alkali and at a temperature of about 40°. He was of the opinion that it would proceed especially well in all cases where the amide formed is insoluble in water, and gave as examples the formation of benzamide from benzonitrile and capronamide from capronitrile. Radziszewski used a 3% solution of hydrogen peroxide.

Deinert<sup>2</sup> applied this method to different nitriles, and obtained very fair yields of the corresponding amides from benzonitrile and *p*-tolunitrile,

<sup>1</sup> *Ber.*, 18, 355 (1885)

<sup>2</sup> *J. prakt. Chem.*, [2] 52, 431 (1895).