2. The rate of change of the enolic form of the ester when prepared in this way was over 10 times slower than the (calculated) best values previously reported.

3. The velocity constants for the change have been measured in presence of known amounts of various substances.

Baltimore, Maryland

[Contribution from the Department of Chemistry, West Virginia University]

FLUOSILICATES OF SOME ORGANIC BASES[1]

By C. A. Jacobson and H. A. H. Pray

Received July 11, 1928 Published November 6, 1928

Introductory

It is well known that fluosilicic acid is a relatively strong acid which yields insoluble salts with most inorganic bases, a large number of which have been prepared. However, few attempts have been made to prepare the salts of this acid with organic bases. E. Ebler and E. Schott[2] have described a fluosilicate of hydrazine, $N_2H_4 \cdot H_2SiF_6$, and of hydroxylamine, $(NH_2OH)_2 \cdot H_2SiF_6$. On the other hand, a number of hydrofluorides of organic bases have been isolated and found to be well-defined, crystalline compounds. Weinland and Lewkowitz[3] report upon the hydrofluorides of aniline, aminophenol, aminophenetole, aminobenzoic acid, etc.

This paper describes the preparation and properties of fluosilicates of aniline, methylaniline and *o*-, *m*- and *p*-toluidine.

Experimental

For the preparation of the aniline salt, redistilled aniline, dissolved in about three times its volume of 95% ethyl alcohol, was treated with a 30% aqueous solution of fluosilicic acid in such a way that the aniline was kept in excess. The precipitated product was washed free from excess aniline with cold 95% ethyl alcohol. The precipitate was then recrystallized twice from hot 95% alcohol and dried, first in the air and finally in a desiccator over sulfuric acid.

The product thus prepared was found to be a snow-white powder composed of small plate-like crystals of irregular shape. Upon heating it sublimed, the sublimation being rapid at a temperature of about 230°. It was insoluble in absolute ethyl alcohol, methyl alcohol, acetone, carbon tetrachloride, chloroform, ethyl ether and carbon disulfide, slightly soluble in hot acetone, but extremely soluble in water. When heated a gas was evolved which when passed into water caused the precipitation of gelati-

---

[1] In memory of Ira Remsen.

[2] Ebler and Schott, *J. prakt. Chem.*, [2] **78**, 338 (1908); [2] **81**, 552 (1910).

[3] Weinland and Lewkowitz, *Z. anorg. Chem.*, **45**, 39–51 (1905).

nous silicic acid, thus indicating that the material was a fluosilicate. Inorganic fluosilicates behave in the same way. A further indication that the substance was a fluosilicate lies in the fact that in water solution it reacts quantitatively with a solution of sodium hydroxide as do the other fluosilicates.

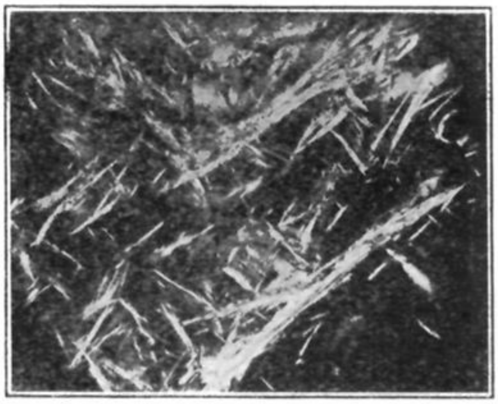

Fig. 1.—Di-aniline fluosilicate.

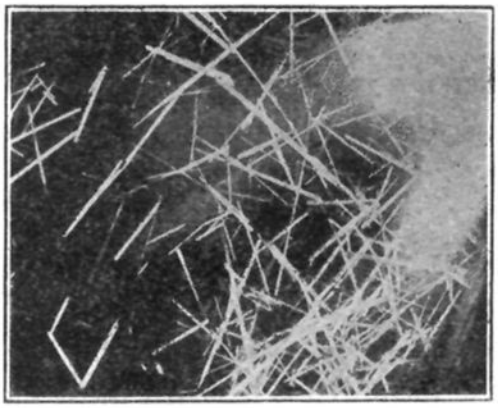

Fig. 2.—Di-methylaniline fluosilicate.

In order to arrive at the empirical formula of the compound, quantitative determinations of nitrogen by the Kjeldahl-Gunning-Arnold method, as well as quantitative determinations of the fluosilicic acid radical, by a method previously devised by one of us,[4] were employed. The latter method consists of the titration of a weighed quantity of the salt dissolved in hot water by a standard solution of sodium hydroxide. An

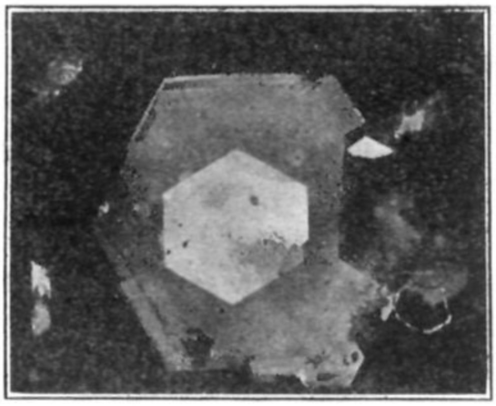

Fig. 3.—Di-*o*-toluidine fluosilicate.

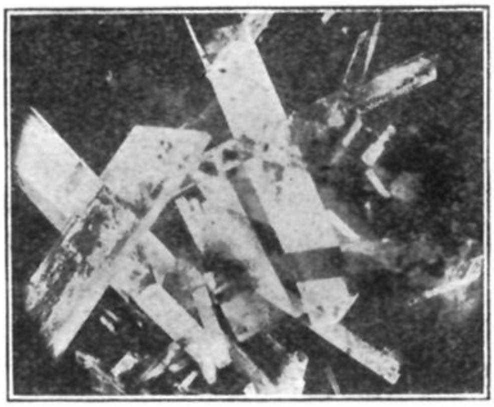

Fig. 4.—Di-*m*-toluidine fluosilicate.

electrometric titration showed the end-point to be within the range of phenol red; consequently, this indicator was used for the determinations of the acid radical part of the salts. These determinations show that the compound under investigation is a di-aniline fluosilicate whose formula is $(C_6H_5NH_2)_2 \cdot H_2SiF_6$.

Anal. Calcd.: N, 8.49; H_2SiF_6, 43.68. Found: N, 8.48, 8.60; H_2SiF_6, 43.60, 43.21.

---

[4] Jacobson, *J. Phys. Chem.*, **28**, 506 (1924).

It has already been mentioned that this di-aniline fluosilicate sublimes at a relatively low temperature, and it seemed of importance to learn if the composition of the sublimed product was the same as that of the recrystallized. The following nitrogen determinations show that the composition is not changed by sublimation.

Anal. Calcd.: N, 8.49. Found: N, 8.32, 8.33.

In a similar manner it was shown that, unlike the fluorides, no other fluosilicate compound with aniline is obtained by precipitating with excess of the acid. A product so obtained showed the same composition and properties as described above.

The method of preparing and purifying the other salts of fluosilicic acid was identical with that described for the di-aniline fluosilicate. The following table gives the analytical data obtained for the five new salts prepared, together with their crystal forms.

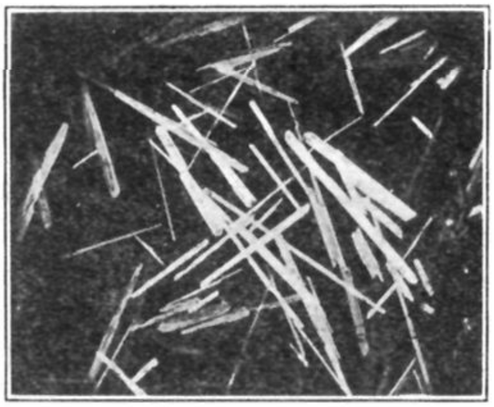

Fig. 5.—Di-*p*-toluidine fluosilicate.

Work is now in progress on other basic fluosilicates such as tolidine and urea. These two compounds are also obtained in nice crystalline form.

The di-*p*-toluidine fluosilicate (No. 5) is the most unstable. The crystals are at first pure white but in a few days they begin to turn yellow and after two or three months assume a deep brown color at the surface of the glass which has been exposed to diffused sunlight, and more and more yellow toward the center of the mass. The irregular outline of the crystals shown in Fig. 5 also indicates the unstable character of this compound.

TABLE I

ANALYTICAL DATA AND CRYSTALLINE FORM

		Nitrogen, %			H_2SiF_6, %			
No.	Fluosilicate	Calcd.	Found		Calcd.	Found		Crystal form
1	Di-aniline	8.49	8.48,	8.60	43.68	43.60	43.21	Irreg. plates
2	Di-methylaniline	7.82	7.85,	7.80	40.22	40.05,	39.97	Monoclinic needles sharp outline
3	Di-*o*-toluidine	7.82	7.68	7.69	40.22	40.14,	39.90	Orthorh. plates
4	Di-*m*-toluidine	7.82	7.73,	7.98	40.22	40.03,	40.18	Rect. plates
5	Di-*p*-toluidine	7.82	7.50,	7.59	40.22	39.90,	40.30	Needle-like, irreg. outline

Summary

Five new crystalline compounds have been made and analyzed. They are the fluosilicates of aniline, methylaniline, *o*-, *m*- and *p*-toluidine, and are the direct addition products of two molecules of the base with one of fluosilicic acid.

The physical properties of these salts have been investigated and microphotographs taken which depict a wholly different crystalline form for each one. The fact that the salts crystallized easily from hot alcohol enabled us to prepare them in very pure condition.

MORGANTOWN, WEST VIRGINIA

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

ALKYL ORTHOSILICATES[1]

BY A. W. DEARING[2] AND E. EMMET REID

RECEIVED JULY 24, 1928 PUBLISHED NOVEMBER 6, 1928

Though ethyl orthosilicate was discovered as long ago as 1846 by Ebelmen,[3] it has not been extensively studied. Khotinsky and Seregenkoff[4] found that one and only one of its ethoxy groups is exchanged for the radical of the Grignard reagent. It seemed desirable to learn more about the preparation and reactions of alkyl orthosilicates.

Results

The method of preparing ethyl orthosilicate has been improved, the yield being brought up to 70%. New esters were made from *n*-butyl, *n*-amyl, *n*-heptyl, *n*-octyl and β-chloro-ethyl alcohols, though the last two were impossible to purify as they are liquids which could not be distilled Attempts to obtain orthosilicates from secondary alcohols proved unsuccessful, the reaction taking another course. With mercaptan silicon tetrachloride reacts only partially, even when heated to 200° for twenty hours.

It has long been known that ethyl orthosilicate ethylates water and acetic acid. It has been found to yield diethyl phthalate with phthalic anhydride, according to this equation:

$$C_6H_4(CO)_2O + (C_2H_5O)_4Si \longrightarrow C_6H_4(CO_2C_2H_5)_2 + (C_2H_5O)_2SiO$$

Similarly ethyl acetate is obtained with acetanhydride. With sulfuric acid, diethyl sulfate is formed. Benzoic acid reacts with it very sluggishly but ethyl benzoate is formed. *p*-Nitrobenzoic acid could not be made to react. It could not be made to react with phenol, β-naphthol or thiophenyl. In the presence of aluminum chloride benzene is ethylated by it even up to hexa-ethylbenzene.

When ethyl, or methyl, orthosilicate reacts with water or acetic acid under the proper conditions, the silicic acid produced separates as a gel. This is of interest since it does not contain electrolytes which are so difficult

---

[1] In memory of Ira Remsen.

[2] From the Ph.D. dissertation of A. W. Dearing, 1927.

[3] Ebelmen, *Ann.*, **57**, 334 (1846).

[4] Khotinsky and Seregenkoff, *Ber.*, **41**, 2948 (1908).