NOTE ON THE ACTION OF OXYCHLORIDES OF SILICON ON SODIUM SALTS OF FATTY ACIDS.

By J. E. Zanetti.

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The action of oxychlorides of non-metals on salts of acids has long been used in the synthesis of anhydrides. As far back as 1853, Gerhardt[1] used phosphorus oxychloride on potassium acetate and obtained acetic anhydride, potassium chloride, and potassium phosphate, according to the reaction:

$$6KOOCCH_3 + POCl_3 = K_3PO_4 + 3KCl + 3(CH_3CO)_2O.$$

Hentschel[2] used carbonyl chloride to obtain acetic anhydride from sodium acetate, and the Chemische Fabrik vorm. Hoffman and Schottensach[3] took out a patent in 1884 for the commercial utilization of this process, which they extended to the manufacture of propionic and butyric anhydrides.

The use of sulphuryl chloride, SO_2Cl_2, for the manufacture of anhydrides, has been long known and commercially successful, and numerous patents have been taken out on modifications of its applications.[4] Mixtures of oxychlorides and of alkali and earthy salts of fatty acids have also been used at various times in the manufacture of anhydrides.

The action of oxychlorides of silicon has, however, never been tried, although, silicon's place in the periodic table being in the neighborhood of that of those elements whose oxychlorides have been used, it might be expected to react similarly. One does not have to search far to account for this neglect. The preparation of the oxychlorides of silicon is by no means an easy matter; the yields are poor, the separation of the individual oxychlorides from each other difficult, and the stimulus of commercial production of anhydrides absent, owing to the much higher cost of the silicon oxychlorides as compared to that of sulfur and carbon, and even phosphorus oxychlorides.

This research was undertaken to determin whether the oxychlorides of silicon reacted similarly to those of phosphorus, carbon and sulfur, but unfortunately, owing to the writer's change in plans, had to be abandoned before completion, and, as it may not be taken up again for some time at least, it has seemed advisable to publish the present results even in their incomplete form.

Silicon gives a large number of oxychlorides. The simplest, Si_2OCl_6, was prepared by Friedel and Ladenburg[5] by passing the vapors of silicon tetrachloride through a red hot porcelain tube. Troost and Haute-

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[1] *Ann.*, 87, 149.

[2] *Ber.*, 17, 1285.

[3] *J. Soc. Chem. Ind.*, 4, 497.

[4] *Ibid.*, 21, 1497; 21, 51; 26, 179. *Bull. soc. ind. Mulhouse*, 1902, 198.

[5] *Ann.*, 147, 355.

feuille,[1] by passing chlorine and oxygen over heated silicon, obtained a mixture of oxychlorides which on fractionation yielded at least five more compounds having the following boiling points and formulas:

136°–139°	Si_2OCl_6
152°–154°	$Si_4O_3Cl_{10}$
198°–202°	$Si_4O_4Cl_8$
300°	$Si_8O_8Cl_{10}$
400°–440°	$Si_2O_3Cl_2$
440°+	$Si_4O_7Cl_2$

With the exception of $Si_4O_7Cl_2$, which is a solid, they are all liquids at ordinary temperatures, easily attacked by water with the formation of silicic and hydrochloric acids.

For the purposes of this research, the oxychlorides were prepared by the method of Troost and Hautefeuille. The reaction product consisted of $SiCl_4$ and oxychlorides. The silicon tetrachloride, boiling at 59°, was distilled off and the residue of oxychlorides fractionated. The mixture of oxychlorides constituted about one-fourth of the original distillate.

Further fractionation was then carried out, but, owing to scarcity of material and lack of time, only the oxychlorides boiling at 136°–139° and 198°–202° could be obtained in tolerably pure condition. The middle fraction between 140°–190°, which consisted mostly of a mixture of $Si_4O_3Cl_{10}$ and $Si_4O_4Cl_8$, was not large enough to permit careful fractionation and was used as such, as was also the fraction boiling above 202°.

The salts used were the sodium salts of acetic, propionic and butyric acids. They were fused, powdered, and kept in tightly stoppered bottles.

The reaction was carried out by adding a slight excess of the fused salt to a weighed amount of the oxychloride in a distilling flask fitted with a return condenser. On slightly warming the flask with a flame for a few moments, the reaction started and proceeded violently in the case of the lower oxychlorides, more slowly in the case of the higher ones. In either case, heating was stopped as soon as the reaction began and the mixture allowed to stand for about two hours. The flask was then heated in an oil bath, and the anhydride distilled off under reduced pressure. The distillate was further fractionated with the addition of a little of the salt used to destroy any chloride present, and redistilled. The residue left in the flask consisted of sodium chloride and silica, colored light brown by slight charring of the organic matter.

The reaction in the case of the Si_2OCl_6 and sodium acetate is, therefore

$$Si_2OCl_6 + 6NaC_2H_3O_2 = 6NaCl + 2SiO_2 + 3(CH_3CO)_2O.$$

If insufficient sodium acetate was used, or if the oxychloride was poured

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[1] Compt. rend., **73**, 561.

on top of the salt in the flask so that it did not have an opportunity to react rapidly on the whole of the salt, acetyl chloride was formed, and appeared in the distillate with the anhydride.

The crude anhydride obtained was slightly colored, and boiled between 130°–138°. The yield was about 82% of the theoretical, calculated from the oxychloride. On further distillation with a little sodium acetate, it gave a water-white product, boiling at 138°, free from chlorine or oxychlorides of silicon, and giving the usual reactions for acetic anhydride, such as the formation of acetanilide with aniline (m. p. 112°), and of amyl acetate with amyl alcohol. On evaporation with water in a weighed platinum crucible, no weighable residue was left, showing absence of any silicon compound.

The oxychloride boiling at 198°–202° gave similar results. A mixture of the oxychlorides boiling between 140°–190° also reacted with sodium acetate, giving acetic anhydride, as did also a mixture of the oxychlorides boiling above 200°.

With sodium propionate and propionic, anhydride was likewise obtained, the yield, however, being only 60% of the theoretical. Sodium butyrate gave only a small yield of anhydride, which was darkly colored, showing considerable decomposition. The reaction in this case did not work as smoothly as in the previous ones.

From the above results it is established that the action of these oxychlorides on sodium salts of fatty acids is similar to that of the oxychlorides of carbon, sulphur and phosphorus, resulting in the formation of anhydrides, sodium chloride and silica.

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THE REACTIONS OF CERTAIN FUMAROID AND MALEINOID COMPOUNDS WITH AROMATIC AMINES.[1]

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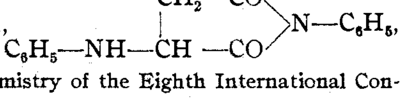
Interest in the behavior of fumaric and maleic acids with aniline is due, in a measure, to the reaction itself, the result of which is quite different from that expected, but especially to the possibility it offers of further insight into the nature of the relationship of these two isomers. From analogy we should expect each acid to form its anilide but the reaction departs from the usual course and yields one and the same product, namely, phenylaminosuccinphenylimide,



$$\begin{array}{r}CH_2-CO\\ |\qquad\qquad\\ C_6H_5-NH-CH-CO\end{array}\!\!>N-C_6H_5,$$

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[1] Read before Section IV on Organic Chemistry of the Eighth International Congress of Applied Chemistry, Washington and New York, September 4–13, 1912.