

and silver perchlorate were also made. The gas formed precipitates in solutions of these salts acidified with pure bromic and perchloric acids respectively. The perchlorate was prepared by dissolving silver oxide in pure concentrated perchloric acid. Care was taken to have the silver salt strongly acid. When acetylene gas was passed in the solution, a fine crystalline precipitate was obtained. This substance, even in the moist condition, is almost as explosive as nitrogen iodide. On one occasion simple contact of the wet substance with a glass rod resulted in an explosion that shattered the vessel. No smoke or precipitate of carbon accompanies these explosions, thus differing in this respect from the other silver acetylene compounds. These detonations are accompanied with a flash of pale blue light. The smallest quantities of the substance are dangerous. The amount that usually "creeps" up the sides of the vessel in the preparation of the compound, has been known to pulverize the containing beaker when touched with a glass rod. The product formed in very dilute solution is, however, not quite so explosive. Owing to the dangerous nature of this compound, no analysis was attempted. None of the silver compounds of acetylene give the iodoform reaction, and all except the phosphate are quickly blackened by diffuse daylight. Investigation of other metallic derivatives of acetylene is now being made in the laboratory.

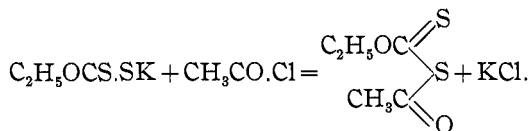
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### NOTES.

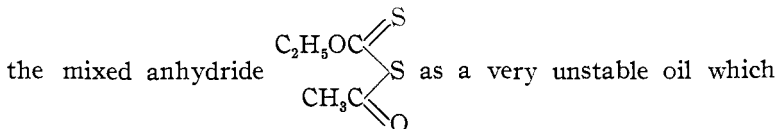
*A Preliminary Note on the Reactions between Acid Chlorides and Potassium Ethylxanthate.*—In the spring of 1902 the author undertook to study the action of various acid chlorides on potassium ethylxanthate,  $C_2H_5OCS.SK$ . Owing to press of other work this study has been subject to numerous delays and postponements; it has therefore been deemed advisable to make a preliminary announcement of the work done.

*Action of Acetyl Chloride.*—The products obtained by the action of acetyl chloride on potassium ethylxanthate vary with slight changes in conditions. Ideally, there should be obtained the mixed anhydride of ethylxanthic and acetic acids according to the reaction



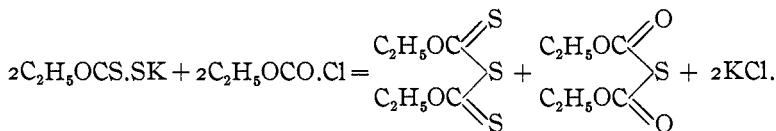
On heating, two molecules of ethylxanthoacetic anhydride should break up to give one molecule of ethylxanthic anhydride and one of thioacetic anhydride according to the well-known rule obtaining with mixed anhydrides of the fatty acids. In practice, however, the reaction takes different courses according to conditions, giving products all of which have not yet been identified with certainty.

When acetyl chloride is added to a well-cooled flask containing potassium ethylxanthate suspended in much ether, there is formed



on moderate heating decomposes, not into the simple anhydrides one would expect, but into ethyl acetate, carbon disulphide, and other products. When, however, potassium ethylxanthate is treated with acetyl chloride in the presence of but small amounts of solvent and without cooling, the reaction takes to some extent the normal course; in this way ethylxanthic anhydride was obtained in fairly large amount. The substance was identified by its melting-point ( $54^\circ$ ), by its properties as described by Welde,<sup>1</sup> and by a sulphur determination which gave 45.91 per cent. S; calculated for  $(\text{C}_2\text{H}_5\text{O})_2\text{C}_2\text{S}_3$ , 45.71 per cent.

*Action of Chlorcarbonic Ester.*—Chlorcarbonic ester and potassium ethylxanthate react with energy. Besides potassium chloride there is obtained an oil containing ethylxanthic anhydride in solution in smaller amount than one would expect from the reaction:



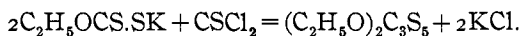
After complete removal of ethylxanthic anhydride from the

<sup>1</sup> J. pr. Chem. [2] 15, 45.

oily reaction product there is left a complex mixture which has not yet been completely resolved into its constituents.

It is not unlikely that an exhaustive study of these reactions will reveal evidence of the temporary existence of interesting dissociation products, and it is from this standpoint that the reactions will be studied when the work is resumed.

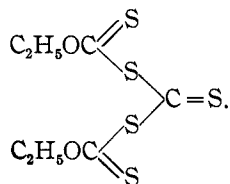
*Action of Thiophosgene, CSCI<sub>2</sub>.*—To the calculated amount of thiophosgene contained in a small flask was added an ice-cold water solution of potassium ethylxanthate in proportion to satisfy the equation:



The water solution became slightly turbid at once, but no further action appeared to take place. The flask was put away in a cool place and occasionally shaken. The lower layer of thiophosgene gradually lost its mobility, becoming finally a dark-brown waxy mass. The water was then poured off and the waxy mass extracted with boiling alcohol. This treatment left undissolved a white crystalline solid soluble in benzene, from which it was recrystallized. Analysis gave the following results: 0.1426 gram substance gave 0.5810 gram BaSO<sub>4</sub> (Carius' method). 0.3444 gram substance gave 0.3582 gram CO<sub>2</sub> and 0.1045 gram H<sub>2</sub>O.

	Calculated for (C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> C <sub>3</sub> S <sub>5</sub> . Per cent.	Found. Per cent.
C .....	29.37	28.36
H .....	3.49	3.37
S .....	55.94	55.93

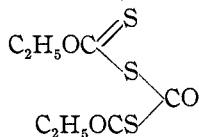
This substance is probably the diethyl ester of the hypothetical pentathiotricarbonic acid, C<sub>3</sub>S<sub>5</sub>(OH)<sub>2</sub>:



It crystallizes from hot benzene in microscopic crystals; it melts with decomposition at 160°, and is quite stable toward dilute acids and alkalies. Hot concentrated sulphuric acid decomposes it with liberation of much sulphur. The same substance is immediately precipitated along with potassium chloride

when thiophosgene diluted with acetone is added to an acetone solution of potassium ethylxanthate. The acetone filtrate yields on evaporation a thick, yellowish-brown oil of unknown composition.

*Action of Phosgene, COCl<sub>2</sub>.*—From analogy with the result obtained as described above, it was expected that the diethyl ester of the hypothetical tetrathiotricarbonic acid, C<sub>2</sub>S<sub>5</sub>O(OH)<sub>2</sub>, would be obtained when phosgene in toluene solution was allowed to act on potassium ethylxanthate; however, none of the compound



was obtained. The reaction is apparently complex. Ethylxanthic anhydride in large amount was found in the reaction product.

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*Carborundum and Siloxicon.*—I have read with considerable interest the account of experiments conducted by Messrs. S. A. Tucker and Alexander Lampen on the measurements of temperature in the formation of carborundum, which appeared in this Journal in its July number.

The methods pursued by them were ingenious, but I would say that the temperature they arrived at was somewhat lower than I had anticipated, although I had not made any definite measurements relating to them.

There seems to be, in the text of their article, some confusion regarding siloxicon. This word I coined as a name of a silicon-oxygen-carbon compound and not for amorphous silicon carbide, as stated by them. The zone of material immediately surrounding carborundum (crystalline carbide of silicon) is mainly or wholly composed of an oxygen compound with carbon as an impurity, this carbon being eventually utilized for the extraction of the residual oxygen and formation of a definite silicon carbide. While this apparent inaccuracy does not in any way detract from the interest and value of their determinations, I can scarcely let such a positive statement of the chemical composition of siloxicon pass unnoticed.

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