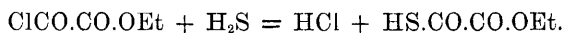


LVII.—*Thioxalic Ether.*

By H. FORSTER MORLEY, D.Sc., and W. JOHNSTON SAINT.

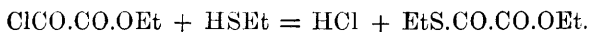
FIVE years ago one of us endeavoured, in the laboratory of Professor Kekulé, to prepare an acid ethereal salt of the unknown thioxalic acid by acting on chloroxalic ether with sulphuretted hydrogen—



The attempt was, however, unsuccessful.

Nevertheless we thought that, considering the interest which attaches to the derivatives of thiocetic and the various thiocarbonic acids, it was worth while to prepare corresponding derivatives of oxalic acid.

Chloroxalic ether acts readily on mercaptan in the following manner:—



It is best to add the mercaptan in small quantities, and to cool the flask containing the mixture in ice-cold water, the heat developed by the reaction being very considerable. When the calculated quantity of mercaptan has been added, the product is heated to boiling (an inverted condenser being attached to the flask), when torrents of hydrochloric acid are disengaged; the liquid is then distilled. The first portion, which comes over at 128° C., is unaltered chloroxalic ether; the thermometer then rises quickly to 210°, the rest coming over between 210° and 212°. This high-boiling liquid still contains mercaptan and chloroxalic ether, from which it is freed by repeated distillation. The purified substance boils at 211° (uncorr).

The combustion was effected with a mixture of coarsely powdered lead chromate and copper oxide.

I. 0.1575 gram substance gave 0.2565 gram CO<sub>2</sub> and 0.0890 gram H<sub>2</sub>O.

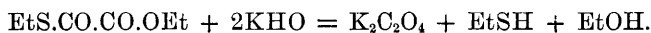
II. 0.221 gram substance gave 0.3585 gram CO<sub>2</sub> and 0.126 gram H<sub>2</sub>O.

It was not found possible to determine the sulphur by Carius's method, which gave only about 0.1 per cent.; accordingly we resorted to a modification of the method recently described by Plimpton and Graves for the estimation of chlorine (this Journal, 41, 119). We employed potash free from sulphate to absorb the products of combustion, and found that 0.226 gram of substance produced 0.3328 gram baric sulphate. The combustion lasted half an hour, and we found by a subsequent experiment that our coal-gas produced 0.0162 gram  $\text{BaSO}_4$  when burning under the same conditions for a like interval. Deducting this, we find 0.3166 gram as the amount of sulphate formed by the combustion of the above quantity of substance.

From these data the following results are calculated:—

	Found.			Calculated for $\text{C}_6\text{H}_{10}\text{SO}_3$ .
	I.	II.	III.	
C.....	44.41	44.24	—	44.44
H.....	6.28	6.33	—	6.17
S.....	—	—	19.24	19.75

Thioxalic ether is a colourless liquid, having a faint odour like that of garlic, a specific gravity of 1.1446 at  $0^\circ$ : it boils at  $217^\circ$  C. (corr.). Aqueous potash readily decomposes it, especially on warming, in accordance with the equation—



The quantity of oxalic acid produced in this way was determined by adding calcium chloride to the solution acidified with acetic acid, and igniting the precipitate.

I.	0.5344	gram	substance	gave	0.3270	gram	$\text{CaCO}_3$ .
II.	0.5195	„	„	„	0.3181	„	„

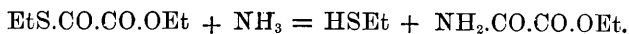
The amount of hydric oxalate produced by the decomposition of thioxalic ether is found therefore to be—

	I.	II.	Calculated.
$\text{H}_2\text{C}_2\text{O}_4$ .....	55.01	55.11	55.56

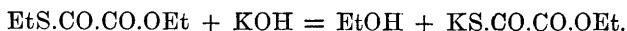
Thioxalic ether sinks in water and decomposes slowly into oxalic acid, alcohol, and mercaptan; the decomposition is more rapid if the temperature be raised. On exposure to moist air, it changes to a crystalline mass of oxalic acid.

On passing dry ammonia into thioxalic ether an odour of mercaptan is developed, whilst the liquid quickly solidifies. The solid mass when crystallised from spirit has the characteristic appearance of oxamethane, and melts at  $112^\circ$ . Oxamethane melts at  $110^\circ$ .

Ammonia therefore decomposes thioxalic ether into mercaptan and oxamethane—



While we have little hope of obtaining thioxalic acid itself, we thought it probable that thioethyloxalic acid might be formed by the action of alcoholic potash on thioxalic ether—



We added the calculated quantity of caustic potash dissolved in absolute alcohol to an alcoholic solution of thioxalic ether; the liquid was at once filled with pearly crystalline plates, but mercaptan was also produced.

The crystals were separated from the liquor, recrystallised from dilute alcohol, and ignited.

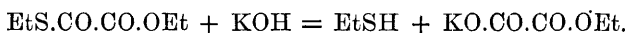
I. 0.1500 gram substance gave 0.0662 gram potassic carbonate.

II. This treated with sulphuric acid gave 0.0825 gram potassic sulphate.

From these data the percentage of potassium is found to be—

	I.	II.	Calculated for $\text{K}(\text{C}_2\text{H}_5)_2\text{C}_2\text{O}_4.$
K. . . . .	24.93	24.67	25.00

The crystals are therefore potassic ethyl oxalate, and in fact qualitative analysis shows them to be free from sulphur. The decomposition, therefore, takes place thus:—



Although thioethyloxalic acid cannot be prepared in this way, it is of course possible that by employing an alcoholic solution of potassic sulphhydrate instead of potash it may yet be obtained.

An attempt to prepare thioxalic ether by distilling oxalic ether over pentasulphide of phosphorus was not successful, the ether not being attacked. We do not, however, regard this experiment as conclusive, as we were subsequently astonished to find that neither commercial pentasulphide (from Kahlbaum) nor a specimen which we ourselves prepared by heating amorphous phosphorus and roll-sulphur together, had any action on acetic ether, although it is well known that Kekulé long since showed that these substances act with violence on one another, producing thiactic ether.

These experiments were made in the laboratory of University College, London.