XXX.—*Contributions to the History of Cyanuric Chloride and Cyanuric Acid.*

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RECENT experiments on cyanuric acid and melamine have shown beyond much doubt that these substances are normal, and not iso in their constitution. Nevertheless, it seemed interesting to extend the data upon which this view rests by the preparation and study of other cyanuric derivatives. With this object, I have investigated the action of cyanuric chloride on the salts of various organic acids.

Sodium Acetate.—If this salt be heated with cyanuric chloride in a closed tube for eight hours at 100° , a reaction takes place, and on opening the tube the characteristic odour of acetyl chloride is perceived. By treating the contents of the tube with cold ether, the

acetyl chloride is readily dissolved, whilst any unchanged cyanuric chloride, being but sparingly soluble, remains for the greater part with the residue. By repeated washing with hot ether, the whole of the cyanuric chloride can be removed and a yellow residue is left, mostly sodium cyanurate. This when dissolved in water gives, on the addition of hydrochloric acid, a crystalline precipitate, which readily responds to the cuprammonium test for cyanuric acid.

The reaction, therefore, is quite different from what was expected. It was hoped that a triacetyl cyanurate would be formed thus:—

instead of which the following took place:—

By converting the acetyl chloride into acetic acid, and finally into silver acetate, the proportion formed was ascertained to be 22·5 per cent. of the theoretical yield.

Between silver acetate, in place of sodium acetate, and cyanuric chloride, no reaction was observed, and in the same manner cyanuric acid itself could not be induced to act on acetic anhydride.

Sodium Formate.—This salt behaves in a manner similar to the acetate. On opening the tube a gas is evolved, which on examination was found to be carbon monoxide, whilst the residue contains cyanuric acid in abundance. Apparently formyl chloride is produced in the first instance, immediately, however, breaking down into carbon monoxide and hydrochloric acid. The reaction is therefore—

Sodium Benzoate.—In the benzoyl series, the same general reaction takes place, but whereas in the previous instances it was only partial, here 88 per cent. of the theoretical yield of benzoyl chloride is obtained. The reaction is expressed by the following equation:—

Action of Cyanuric Chloride on Benzamide.—In the hope of obtaining a benzoyl substituted melamine, cyanuric chloride and benzamide were heated in a closed tube for eight to ten hours at 100°. It was thought possible that instead of the desired action melamine and benzoyl chloride might be formed. But on opening the tube, there was a distinct odour of bitter almonds, and treatment with cold ether yielded abundance of an oily liquid having the character of benzonitrile, and easily converted into benzamide by treatment with concentrated sulphuric acid. The residue in the tube was almost pure cyanuric acid. The following action, therefore, had taken place:—

Notably, the cyanuric chloride, acting like phosphorus pentachloride, takes away water from the amide, leaving the nitrile, while it is itself resolved by the liberated water into cyanuric acid and hydrogen chloride.

Action of Benzoyl Chloride on Silver Cyanurate.—While I was engaged in these experiments, J. Ponomarew's "Zur Frage über die Constitution der Cyanursäure" appeared (*Ber.*, **18**, 3261), in which the author describes triacetyl cyanurate, one of the substances which I was seeking. It is obtained by the action of the acid chloride on silver cyanurate. By this elegant method, it seemed easy to prepare the other acid derivatives, and, in fact, it has already given me the corresponding tribenzoyl cyanurate.

Benzoyl chloride has no action on silver cyanurate in the cold, but by heating a mixture of the two in theoretical proportions, in closed tubes, for eight to ten hours at 100° , an action takes place, and on opening the tube much of the odour of the benzoyl chloride is found to have disappeared. The contents are extracted with boiling chloroform, which on evaporation gives a crystalline precipitate representing 25 to 30 per cent. of the theoretical yield. This recrystallised from chloroform, gives colourless needles of *tribenzoyl cyanurate*, $C_3N_3(OC_7H_5O)_3 = C_{24}H_{15}N_3O_6$, which requires—

	Theory.		Experiment.	
			I.	II.
C_{24}	288	65·31	65·32	—
H_{15}	15	3·40	3·86	—
N_3	42	9·52	—	10·23
O_6	96	21·77	—	—
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	441	100·00		

The new compound shows no distinct melting point, being decomposed on heating. It is but sparingly soluble in chloroform, and insoluble in ether. By heating with water, it is converted into cyanuric and benzoic acids, this being effected very readily if the substance is enclosed in a tube with water and heated for a short time at 100° . This behaviour with water, which Ponomarew observed to occur in an analogous manner in the case of the acetyl-derivative, characterises this class of compound as mixed anhydrides.

In conclusion, I may mention that two experiments were instituted to obtain two cyanuric nuclei joined to each other. Cyanuric chloride was brought together, in closed tubes, with melamine, and also with silver cyanurate, but no reaction took place at temperatures from 100° to 250° .

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