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Formation of Tetranitromethane from Nitroform and Nitryl Chloride

by

T. URBAŃSKI, Z. NOWAK and E. MORĄG

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It is known that nitryl chloride is a relatively strong nitrating agent [1], [2]. It was also found that this reagent can act both as nitrating and chlorinating agent [1], [3]—[6].

We examined now the possible introduction of a C-nitro group into an aliphatic nitro compound with an active hydrogen atom. Nitroform was used as a simple model. It has been found that silver and potassium salts of nitroform can react with nitryl chloride to form tetranitromethane. The silver salt suspended in chloroform gave a low yield (*c.* 20%) of this compound, probably owing of the fact that this salt is only known in hydrated form and the water is likely to reduce the yield.

Potassium salt gave a quantitative yield of tetranitromethane. Also potassium chloride free of nitrate and nitrite resulted.

By acting with nitryl chloride on nitroform a lower yield (*c.* 65%) was obtained.

All the reactions were carried out in anhydrous medium.

We suggest an ionic mechanism of the reactions, considering that nitryl chloride is the source of the nitronium ion:

(1) $$(O_2N)_3C^- M^+ + NO_2^+ \rightarrow C(NO_2)_4 + M^+$$

(2) $$(O_2N)_3C^- H^+ + NO_2^+ \rightarrow C(NO_2)_4 + H^+$$

Experimental

Nitroform was prepared from tetranitromethane by the action of alcoholic KOH yielding potassium salt of nitroform [7]. This on acidifying with conc. sulphuric acid yielded nitroform m.p. 22°.

Reaction of potassium salt of nitroform with nitryl chloride

The potassium salt of nitroform (9.4 g., 0.05 mol.) was suspended in 50 ml. ether. Nitryl chloride was introduced until the yellow colour of the salt disappeared (*c.* 1 hr.). Pure potassium chloride precipitated and was filtered off. The ether was evaporated and tetranitromethane (9.2 g., 94% yield) remained.

The product purified by distillation at 124—125° gives constants: $n_D^{20} = 1.4399$ and $d_4^{20} = 1.6293$ corresponding to the pure product.

Reaction of nitroform with nitryl chloride

Nitroform (7.5 g., 0.05 mol.) was dissolved in ether. Nitryl chloride was introduced until the originally yellow solutions became colourless (*c.* 2 hrs.). The solution was washed with water, dried over sodium sulphate and ether. After evaporation of ether tetranitromethane (6.5 g., c. 65% yield) was collected.

TECHNICAL MILITARY COLLEGE, WARSAW
(WOJSKOWA AKADEMIA TECHNICZNA, WARSZAWA)

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