more difficult to nitrate as in the presence of acetic acid. Here also it was probably the nitronium ion that was responsible for nitration.

Nitric acid salts in mixtures with other acids

In the days when anhydrous nitric acid was not easily available, nitric acid salts ($NaNO_3$, KNO_3) mixed with sulphuric acid were widely used for nitration. Such mixtures acted similarly to the mixture of nitric and sulphuric acids. Later, as synthetic nitric acid became one of the most readily available chemical products, and the production of nitric acid salts from nitric acid had started, nitrating mixtures with sodium or potassium nitrates were abandoned. This is the principal explanation for the scarcity of investigations on the structure and action of such mixtures. It is believed that in such mixtures the nitronium ions are present, according to the equation :

$$NaNO_3 + 2H_2SO_4, \rightarrow NO_2^+ + 2HSO_4 + Na^+ + H_2O \quad (50)$$

Ingold and his co-workers proved in 1950 [39] that on introducing the NO_3^- anion into nitric acid in the presence of acetic acid or nitromethane the reaction rate decreased, since the formation of the NO_2^+ ion was hindered by the NO_3^- ion:

$$2HNO_3 \leftrightarrow H_2NO_3^+ + NO_3^- \text{ (fast reaction)} \quad (51)$$

$$H_2NO_3^+ \leftrightarrow NO_2^+ + H_2O \text{ (slow reaction)} \quad (52)$$

The nitration reaction rate depends on the kind nature of the cation. Mixtures of nitric and sulphuric acids nitrate the most slowly, and lithium nitrate acts the most rapidly. With regard to activity cations may be ranged in the following way:

$$H < NH_4 < K < Na < Ag < Li$$

This order also corresponds to the ease of conversion of bisulphates into pyrosulphates, which for the order presented is the highest for lithium salts (Klemenc and Schöller [34], K. Lauer and Oda [32], Lantz [83]).

Ceorgievskii [114] found that the yield of a nitration reaction also depends on the nature of the cation. For example, when benzene was nitrated to nitrobenzene, the best results were obtained with copper nitrate and sulphuric acid.

Fredenhagen [121] developed a method sometimes referred to as “Fredenhagen nitration” [122]. The nitrating agent consists of a nitrate, e.g. potassium nitrate in anhydrous or highly concentrated hydrogen fluoride.

Metal nitrates in the presence of Friedel-Crafts catalysts

Apart from the investigations on nitration with the nitrates of some metals in the presence of sulphuric or nitric acid Topchiyev [115] has carried out extensive studies on nitration with metal nitrates in the presence of $AlCl_3$, $FeCl_3$, $SiCl_4$, and BF_3. He showed that all the nitrates had nitrating properties, and he ordered the nitrates he studied according to their increasing nitration activity in the presence of $AlCl_3$: