The Reaction Between Thio-cyanogen and Azide Ions

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Iodine, as triiodide ions, does not react with azide ions to give nitrogen and iodide ions. However, sulphidic sulphur does catalyze this reaction. Browne et al. showed that bromine and chlorine give fine analogous bromine- and chlorine-azide reactions, but controlling experiments showed that bromine and chlorine together with sodium azide alone, give slow evolutions of nitrogen. Recently Griffith and Irving have investigated the bromine-azide reaction catalyzed by thiosulphate and by tetraethionate, and the direct reaction between bromine and azide ions.

Taking into consideration that the redox potentials of chlorine, bromine, iodine and thiocyanogen are, respectively, \(-1.36\), \(-1.07\), \(-0.54\) and \(-0.77\) volts, it seems quite possible that thiocyanogen, which often behaves like a halogen, will oxidize azide ions to nitrogen.

Thiocyanogen, \((SCN)_2\), was prepared as a carbon tetrachloride solution according to Söderbäck. This solution, when brought into contact with aqueous sodium azide solution, gave a brisk evolution of gas, while, at the same time, some decomposition of thiocyanogen took place. The gas evolved in the following experiment was analyzed according to Christiansen and Wulff. 25 ml 1 M aqueous solution of sodium azide was allowed to react with 25 ml about 1 M solution of thiocyanogen in carbon tetrachloride. The gas evolved was collected over water and paraffin oil, the latter solvent to extract vapours of carbon tetrachloride in the gas. Analysis of the gas gave the results:

- \(99.6\%\ N_2\) and \(0.5\%\ O_2\)
- \(99.7\%\ N_2\) and \(0.4\%\ O_2\)

The reaction is presumably:

\[(SCN)_2 + 2 N_3^- \rightarrow 2 SCN^- + 3 N_2\]

As thiocyanogen as well as thiocyanate ions catalyze the iodine-azide reaction, it is not unlikely that the above reaction is catalyzed by thiocyanogen as well as by thiocyanate ions. Until now attempts to obtain a homogeneous reaction between thiocyanogen and azide ions in non-aqueous solution have not succeeded.


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