STUDIES IN GAS PHASE KINETICS

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Summary

Studies in Gas Phase Kinetics

The first and major part of this thesis contains an account of the work done on the oxidation of ammonia by nitrous oxide. The second section is concerned with a description of a preliminary examination of the pyrolysis of 1,1 difluoroethylene.

The oxidation of ammonia has been examined between 650⁰ and 730⁰ C and at total pressures of up to 510 mm, using both static and flow techniques. The products of reaction were established to be nitrogen, water and hydrazine. Ammonia labelled with ¹⁵N was used to determine the source of the nitrogen formed and it was shown that no exchange of nitrogen between nitrous oxide and ammonia took place. The stoichiometry of the reaction followed the approximate equation,

\[ 7\text{N}_2\text{O} + 6\text{NH}_3 \rightarrow 9\text{N}_2 + 7\text{H}_2\text{O} + 1\text{N}_2\text{H}_4 \]

The initial rates of reaction were determined at several temperatures. Measurements were made with a constant pressure of nitrous oxide and varying
pressures of ammonia, and vice versa. From the plots of initial rate against pressure, the following empirical rate expression was formulated,

\[ \text{Rate} = k' [N_2O]^{1.56} + k'' [N_2O]^{0.61} [\text{NH}_3] \]

A free radical reaction mechanism has been suggested to account for the products and the kinetics of the reaction and involves initiation by oxygen atoms which result from the thermal decomposition of nitrous oxide. The empirical rate expression was of the same form as the theoretical expression derived from the postulated mechanism.

The results have shown that ammonia molecules were participating in the activation of nitrous oxide, a fact which was indicated by the form of the empirical rate expression. The efficiency of ammonia molecules in this activating process,

\[ N_2O + \text{NH}_3 \rightarrow N_2O^* + \text{NH}_3 \]

was calculated, assuming the efficiency of nitrous oxide to be unity.

The results of the investigations of the pyrolysis of 1,1 difluoroethylene have shown the reaction
to be complex. The pyrolyses were carried out in silica reaction vessels at temperatures between 423° and 515° C. Under these temperature conditions attack on the reaction vessel occurred with the formation of silicon tetrafluoride and carbon monoxide. Pressures of up to 450 mm of 1,1 difluoroethylene were used and the reaction products were separated by means of gas phase chromatography.

The main product of reaction was examined by molecular weight determinations, infra-red and N.M.R. spectroscopy and was identified as the dimer CF₂ = CH - CF = CH₂. A second product has been tentatively assigned the structure CH₂ = CF - CF = CH₂.