Kinetics of the Gas-phase Pyrolysis of Cyclopropylamine

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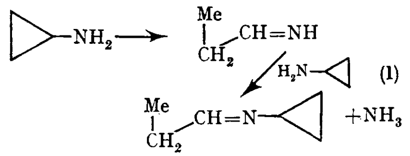
IN contrast with the great number of reports of isomerisations of alkyl cyclopropanes[1] there have been very few kinetic studies of cyclopropanes bearing any other substituents. We now report a kinetic study of the pyrolysis of cyclopropylamine to the Schiff's base *N*-propylidenecyclopropylamine and ammonia:

The study was carried out at 356—425° and 15—60 torr pressure in a static Pyrex system, with use of g.l.c. analysis to follow the course of the reaction. The above stoicheiometry applied accurately in the early stages of the reaction, although the product imine underwent a secondary isomerisation (which was slow at these temperatures) to give a heterocyclic compound; this latter reaction will be the subject of a separate study. The disappearance of cyclopropylamine was accurately *first-order* for at least three half-lives and the first-order rate constants were independent of initial pressure and fit the Arrhenius equation:

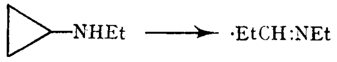
$$\log_{10}k(\text{sec.}^{-1}) = (14{\cdot}45 \pm 0{\cdot}22) - (58{,}090 \pm 650)/4{\cdot}576T$$

(the error limits being the 95% confidence limits). The reaction was completely unaffected by the presence of nitric oxide or propene; thus free-radical chains were not involved. When the surface-to-volume ratio of the reaction vessel was increased 16 times a marked ageing effect was observed, but after several runs the rate constants were the same as those obtained in the unpacked vessel; we therefore conclude that the reaction is homogeneous.

It is clear from the first-order kinetics of the overall reaction that it must involve a rate-determining first-order isomerisation of cyclopropylamine to a reactive intermediate which then reacts with a second molecule of cyclopropylamine to give the observed products; the reactive intermediate is believed to be propylideneamine (EtCH:NH):

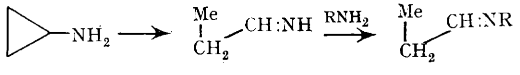


Propylideneamine has never been isolated but is presumed to exist as a reactive intermediate in the reaction of propionaldehyde with ammonia.[2] The *N*-ethyl derivative (*N*-propylidene-ethylamine, EtCH:NEt), on the other hand, is a well-known compound which is stable under the present reaction conditions. Thus, in confirmation of the reaction scheme (1), *N*-ethylcyclopropylamine isomerised cleanly to *N*-propylidene-ethylamine at a similar rate to the inferred isomerisation of cyclopropylamine to propylideneamine, and underwent no further reaction:



NN-Diethylcyclopropylamine, containing no *N*-hydrogen atoms, was recovered unchanged under the same conditions.

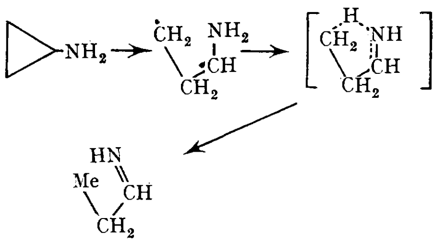
Further evidence for the proposed mechanism was obtained by pyrolysing mixtures of cyclopropylamine with alkyl amines, when the Schiff's base from the reaction of the intermediate with the added amine was observed in each case, in addition to the product obtained from cyclopropylamine alone:



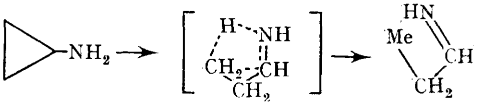
(R = C_3H_5 and Et, Pr^n, Pr^i, or allyl)

The intermediate was not allylamine since this compound was stable when heated alone or with ethylamine under the present conditions, and gave the new product shown above when heated with cyclopropylamine.

The isomerisation of cyclopropylamine to propylideneamine has all the characteristics of a unimolecular reaction, and may be readily formulated as proceeding through a biradical intermediate which undergoes a novel hydrogen-atom transfer *via* a five-centre transition state:



The activation energy of 58 kcal./mole (*cf.* 61—65 kcal./mole for the isomerisation of alkylcyclopropanes) is consistent with stabilisation of the $>\dot{\mathrm{C}}\mathrm{H{-}NH_2}$ radical centre by interaction with the nitrogen orbitals and perhaps also the lower strength of the N–H as compared with the C–H bond. Alternatively the reaction might proceed by simultaneous ring-opening and hydrogen-atom transfer:



and this possibility cannot be ruled out at present.

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[1] H. M. Frey, *Advanc. Phys. Org. Chem.*, 1966, **4**, 147.
[2] M. M. Sprung, *Chem. Rev.*, 1940, **26**, 297.