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Kinetics of the Reactions of Cyclopropane Derivatives, Part II. The Gas-Phase Pyrolysis of Cyclopropylamine

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Abstract

At temperatures of 356–425°C and pressures of 15–60 Torr, cyclopropylamine reacts to give an equimolar mixture of ammonia and N-propylidenecyclopropylamine as the initial product. The reaction is first order, homogeneous, and unaffected by the presence of radical inhibitors, and thus proceeds by an initial rate-determining unimolecular isomerization to give a reactive intermediate, which then reacts with a further molecule of cyclopropylamine to give the observed products. Reaction in the presence of added aliphatic amines gives other imines in addition, and the nature of these indicates that the intermediate is propenylamine or its tautomer propylideneamine:

$$\triangleright\!\!-\!\!-NH_2 \xrightarrow{k_1} (CH_3\cdot CH{:}CH\cdot NH_2 \rightleftharpoons CH_3\cdot CH_2CH{:}NH)$$

$$CH_3\cdot CH_2\cdot CH{:}NR + NH_3 \xleftarrow[R = c\text{-}C_3H_5,\ Et,\ Pr,\ iPr,\ allyl]{RNH_2,\ fast}$$

$$\log_{10}(k_1/s^{-1}) = (15.06 \pm 0.41) - (242.0 \pm 2.6)\ kJ\ mole^{-1}]/2.303RT$$

1. Introduction

Kinetic studies of the structural isomerizations of cyclopropane derivatives have hitherto been confined to the alkyl derivatives and a few halogenated compounds [2,3]. We now report in full our studies [4] of the pyrolysis of cyclopropylamine, as part of a program to investigate the new and interesting mechanisms made possible by the presence of other types of substituent on the cyclopropane ring.

2. Experimental

A. *Apparatus*

The apparatus and experimental procedure were similar to those described previously [1]. In the present study, pressures in the GLC sample loop were

measured by an S.E. 1150/10WG transducer (S.E. Laboratories Ltd.), the response of which was adjusted to give full-scale deflection on a 1-mV recorder for a pressure difference of 1 Torr (Torr = 101.325/760 kN m^{-2}). The gas-chromatographic analyses were performed on a Varian-Aerograph Model 200 instrument which was modified by replacing the standard column oven controller by a C.N.S. Instruments "Sirect" Mk I proportional temperature controller. Oven temperature stability was then ±0.1K at 423K. The analytical column was 5 m × 6 mm 20% Apiezon L grease on 80–100 mesh Celite, and signals from the F.I.D. were integrated by a Kent Chromalog digital integrator, which reproduced peak areas to better than 0.5%. For ammonia analyses, a katharometer detector was used, with hydrogen as carrier gas.

B. *Materials*

Cyclopropylamine (Koch-Light Laboratories Ltd.), distilled through a 1-m Buchi spinning band column, had bp 49.5°C/755 Torr (lit. [5] 49°C/750 Torr). The compound obtained in this way gave only one peak when chromatographed on 5-m columns containing Apiezon L, dinonyl phthalate, or polyethylene glycol, all on Celite at 140°C. The IR and ^{1}H NMR spectra were identical with those previously published [6,7].

Reaction [8–10] of cyclopropylamine (29 g, 0.50 mole) and propionaldehyde (29 g, 0.5 mole) followed by distillation from crushed KOH through a 1-m Podbielniak column gave N-propylidenecyclopropylamine (44 g, 0.45 mole, 90%) (bp 102°C/755 Torr) which gave only one peak on the three GLC columns listed previously. The ^{1}H NMR spectrum [11] supported the proposed structure. The IR spectrum (Perkin-Elmer Model 257) showed the following bands: 745w, 760w, 845w, 880m, 900w, 950s, 1015m, 1025m, 1035m (shoulder), 1090m, 1176m, 1300m, 1330m, 1375m (shoulder), 1389m, 1425m (shoulder), 1450s, 1460m, 1660vs, 2840vs, 2880s (shoulder), 2975vs, 3095s, and 3100m cm^{-1}.

Other imines required for GLC references were similarly prepared. Ammonia was obtained from ammonium hydroxide solution and purified by fractional condensation.

Addition of bromoethane (22 g, 0.20 mole) to cyclopropylamine (23g, 0.40 mole) at 5°C, followed by distillation of an ether extract of the products through a 1-m Podbielniak column, gave N-ethylcyclopropylamine (8.5 g, 0.10 mole, 50%) (bp 75–77°C). The ^{1}H NMR spectrum (Perkin-Elmer R10 at 60.00 MHz) supported the structure

$$\underset{(CH_2)_2}{\overset{e,e'}{}}\underset{CH}{\overset{b}{}}\cdot\underset{NH}{\overset{a}{}}\cdot\underset{CH_2}{\overset{c}{}}\cdot\underset{CH_3}{\overset{d}{}}$$

where *a*: τ 6.2, 1H, s; *b*: 7.8, 1H, tt, $|J_{be}| \approx 7.5$ Hz, $|J_{be'}| \approx 5$ Hz; *c*: 7.2, 2 H, q, $|J_{cd}| = 5$ Hz; *d*: 8.8, 3H, t, $|J_{dc}| = 5$ Hz; *e*: 9.5, 4H, complex.

Gas-liquid chromatography (5 m Apiezon L at 140°C) showed that the

product contained cyclopropylamine (ca. 4%) and other trace impurities, but the material was used without further purification.

Pyrolysis of N-propylidenecyclopropylamine at ca. 360°C gave (without pressure change) a product **A**, bp 130°C, which was also formed as a secondary product during the pyrolysis of cyclopropylamine. This component reacted further on storage and was not unambiguously identified, but was thought to be a cyclic imine, possibly of the structure $\overset{\frown}{CH{:}N\cdot(CH_2)_3\cdot CHMe}$.[1] The IR spectrum showed the following main bands: 790w, 843w, 913m, 933m, 985w, 1000w (shoulder), 1070w, 1090w, 1145w (shoulder), 1162m, 1210s (shoulder), 1222s, 1280w, 1310s (shoulder), 1320s, 1340s, 1375s, 1400w, 1430m (shoulder), 1460vs, 1620vs, 2880s, 2940s (shoulder), 2970s, and 3010s (shoulder) cm^{-1}. The ^1H NMR spectrum (Varian HA-100 at 100.00 MHz and Perkin-Elmer R10 at 60.00 MHz) showed five regions of absorption, at τ 2.5, 1H, d of comp; 6.2, 1H, t of comp; 7.7, t of comp; 7.9–9.0, comp; 9.0, d of comp (last three bands 9H total).

3. Results

Preliminary experiments showed that cyclopropylamine reacts at temperatures above 340°C to give ammonia and N-propylidenecyclopropylamine as the main products. In accordance with eq. (1),

(1) $$2 \quad \triangleright\!\!-NH_2 \rightarrow NH_3 + \quad \triangleright\!\!-N{=}CHEt$$

there was no pressure change, and GLC analysis (see Fig. 1) showed that in the initial stages of the reaction the two products were formed in amounts which were equal to each other and jointly equal to the reactant disappeared. At the higher temperatures (ca. 380°C), there was a slow secondary isomerization of the N-propylidenecyclopropylamine to the cyclic imine **A** of incompletely identified structure (see experimental section), and this proceeded at about the rate expected from experiments with this compound alone as reactant. It is clear from the figure, however, that the sole primary reaction is eq. (1) and that its rate could be measured by GLC analyses for the reactant. Such measurements were carried out at temperatures from 356° to 425°C and with initial pressures from 15 to 60 Torr. Under these conditions, the reaction was found to be first order; plots of log (pressure of reactant) against time were linear for as long as they were followed, which in some instances was up to 3 half-lives. The first-order rate constants were independent of pressure and are summarized in Table I.

The plot of $\log_{10}$ (rate constant) against $1/T$ was accurately linear and corresponds to the Arrhenius equation (2)[2]:

(2) $$\log_{10}(k_{overall}/s^{-1}) = (15.36 \pm 0.41) - (242.0 \pm 2.6)\ \text{kJ mole}^{-1}/2.303RT$$

[1] After this paper was submitted, we learned of another paper in press [16] in which **A** is reported to be 5-ethyl-1-pyrroline, formed by reaction (11), and kinetic parameters are given for its formation.

[2] The preliminary A-factor previously reported [4] contained in addition an arithmetic error.

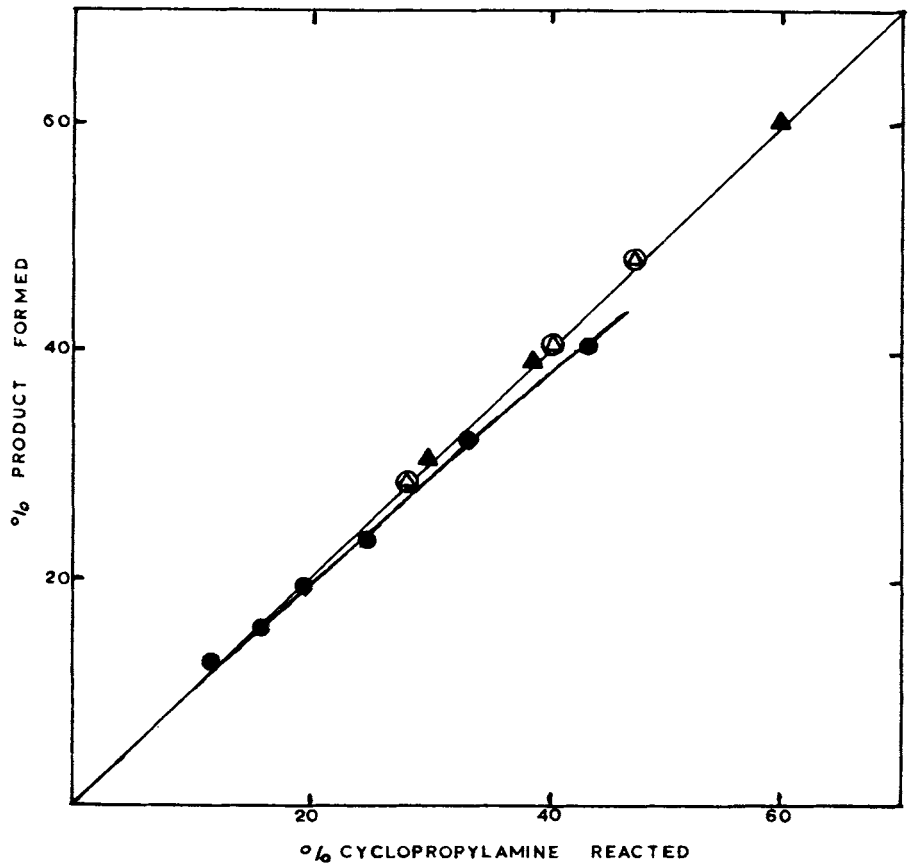


Figure 1. Demonstration of stoicheiometry of reaction: (○) and (●) imine produced; (△) and (▲) ammonia produced [both as per cent of initial reactant based on stoicheiometry of eq. (1)]; open points, at 629K; filled points, at 656K.

TABLE I. Mean first-order rate constants k for disappearance of cyclopropylamine.

Temp., K	Number of runs	Initial pressure, Torr	10^5k, s^{-1}	$10^5\sigma(k)$, s^{-1}[a]
628.8	5	20–60	1.84	0.03
646.0	7	15–60	5.67	0.22
656.0	8	15–60	12.1	0.3
662.0	15	15–60	20.2	0.4
673.2	4	20–63	36.3	0.3
698.2	3	20–60	168.3	0.7

[a] $\sigma(k)$ is the estimated population standard deviation of k.

(the error limits being the statistical 95% confidence limits, giving equal weight to each experimental point).

To determine the effect of surfaces on the reaction, a number of runs were carried out in a vessel packed with Pyrex glass tubes. The packed and unpacked vessels had surface-to-volume ratios of 16.1 and 1.09 cm^{-1}, respectively. A substantial increase in the rate of decomposition of cyclopropylamine was observed when runs were carried out in the clean packed vessel; and even after aging for 100 hr, the rate was still decreasing and approaching the value obtained in the unpacked vessel. However, after 150 hr, the first-order rate constants (Table II) were identical to those obtained in the unpacked vessel. We therefore conclude that the reaction as studied is homogeneous.

TABLE II. Comparison of mean rate constants $\bar{k}$ in the packed and unpacked reaction vessels.

Temp., K	Reaction vessel	Number of runs	Initial pressure, Torr	$10^5\bar{k}$, s^{-1}	$10^5\sigma(k)$, s^{-1}
628.8	packed	2	20–60	1.87	—
628.8	unpacked	5	20–60	1.84	0.03
673.2	packed	2	20–60	36.9	—
673.2	unpacked	4	20–60	36.3	0.3

The reaction was also studied in the presence of nitric oxide and propene, with pressures of inhibitor varying from 25% to 100% of the initial pressure of reactant. The reaction was again accurately first order, and the rate constants (Table III) were indistinguishable from those for the uninhibited reaction; any radical chain mechanism can thus be ruled out.

TABLE III. Comparison of mean rate constants $\bar{k}$ in the presence and absence of inhibitors.

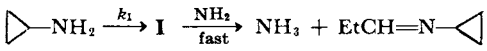
Temp., K	Number of runs	Initial pressure of reactant, Torr	Nature and amount of inhibitor	$10^5\bar{k}$, s^{-1}	$10^5\sigma(k)$, s^{-1}
628.8	4	20–40	25–50% C_3H_6	1.89	0.04
628.8	5	20–60	NONE	1.84	0.03
673.2	3	20–40	25–50% C_3H_6	36.3	0.3
673.2	4	20–60	NONE	36.3	0.3
673.2	2	20–40	25–50% NO	35.9	—

To assist the mechanistic interpretation, cyclopropylamine was also copyrolyzed in qualitative experiments with added amines (ethylamine, propylamine, isopropylamine, and allylamine). In each case the products were found to contain

a new compound in addition to those normally present, the new product being the N-propylidene derivative of the added amine (EtCH:NR from amine RNH_2). Identification was achieved by GLC comparison on the various columns listed above, with the authentic imines prepared from propionaldehyde and the appropriate amines and characterized by NMR spectroscopy [11].

4. Discussion

It has thus been concluded that the pyrolysis of cyclopropylamine to give an equimolar mixture of ammonia and N-propylidenecyclopropylamine involves only homogeneous molecular processes. Since the reaction is unambiguously first order, the overall reaction (1) must occur by an initial rate-determining first-order reaction of cyclopropylamine, and this is most readily formulated as isomerization to a reactive intermediate **I**, which then reacts with a further molecule of cyclopropylamine to give the observed products as in eq. (3):

(3) 

The rate of disappearance of cyclopropylamine by the first step is half the total rate of consumption of cyclopropylamine, and the rate constant k_1 is therefore given by the Arrhenius equation (4),

(4) $\log_{10}(k_1/s^{-1}) = (15.06 \pm 0.41) - (242.0 \pm 2.6)\ kJ\ mole^{-1}/2.303RT$

in which the error limits are again 95% confidence limits. Unimolecular falloff would not be expected to be significant for a molecule of this complexity at the pressures used [12].

The validity of the above scheme (3) was supported by observing that it is possible to replace cyclopropylamine in the second step by other amines. Thus, cyclopropylamine was copyrolyzed in separate experiments with ethylamine, propylamine, isopropylamine, and allylamine, and in each case the N-propylidene derivative of the added amine was formed in addition to N-propylidenecyclopropylamine; the new reactions are interpreted as in eq. (5):

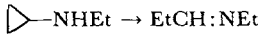
(5) $$\mathbf{I} + RNH_2 \xrightarrow[\text{allyl, } c\text{-}C_3H_5]{R = Et,\ n\text{-}Pr,\ iPr,} NH_3 + EtCH{=}NR$$

The nature of the intermediate **I** cannot be unambiguously deduced from the present results, but there is a strong presumption from the structure of the products that it is in fact propylideneamine (propionaldimine, EtCH:NH) or its tautomer propenylamine ($MeCH{:}CHNH_2$). This compound has not been isolated but is presumed to exist as a reactive intermediate in the reaction of propionaldehyde with ammonia [9]. Its subsequent reaction with amines in reaction (5) is readily

formulated as analagous to the amine displacement reaction used preparatively [8], e.g., scheme (6),

(6) $$RCH{=}NR' + R''NH_2 \rightleftarrows RCH(NHR')(NHR'') \rightleftarrows RCH{=}NR'' + R'NH_2$$

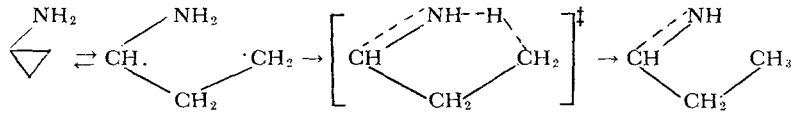
where R′ = H in the present reaction. Further evidence in favor of the above intermediates was obtained by pyrolyzing N-ethylcyclopropylamine at 356°–383°C and 20–40 torr. The sole product, identified by GLC on several columns, was N-propylidene-ethylamine, eq. (7):

(7) 

This material was unreactive under the conditions used, and presumed to be analogous to the reactive intermediate formed from cyclopropylamine. Such reactions are superficially analogous to the reported catalytic isomerization of cyclopropanol to propionaldehyde [13].

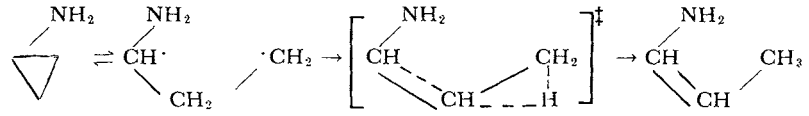
The intermediate is definitely not allylamine, since the latter is stable when heated alone or with ethylamine under the present conditions, and in the presence of cyclopropylamine gives N-propylideneallylamine, which is not formed in the pyrolysis of cyclopropylamine on its own. The other isomers of the same empirical formula (C_3H_7N) are $(CH_3)_2C{:}NH$ and its tautomer $CH_2{:}CMeNH_2$, which would both be expected to give rise to branched-chain products, none of which were found. It is also formally possible that ammonia is released in the unimolecular rate-determining step, giving cyclopropene, methylacetylene, or allene as the intermediate, but it is difficult to formulate the subsequent reaction of these compounds with amines to give the observed products.

It was originally proposed [4] that the initial isomerization gave propylideneamine via a biradical intermediate and a novel five-center hydrogen atom transfer as in eq. (8):

(8) 

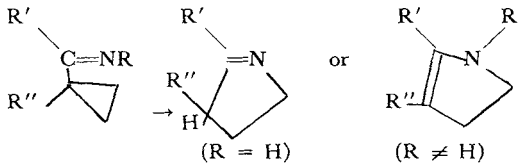
The lowering of the activation energy compared with that for alkylcyclopropane isomerization (242 cf. 260–275 kJ/mole [2]) was attributed to extra stabilization of the $>\dot{C}H{-}NH_2$ radical center by interaction with the nitrogen orbitals, and also to the relative weakness of the N–H bond being broken (ca. 350 kJ/mole, cf. ca. 420 kJ/mole for C–H fission). The above mechanism involves a relatively tight transition state, however, and regardless of whether this is reached via a biradical or directly [2], one would expect the *A*-factor to be substantially lower than that normally found for cyclopropane isomerizations. Since in fact the *A*-factor ($10^{15.1}$ s^{-1}) is in the upper range of observed values, it seems that loss of

rotational freedom does not occur and that the mechanism is more probably (9), leading to the tautomer propenylamine as the initial intermediate:

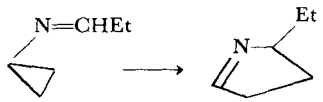
(9) 

This mechanism is completely analagous to that proposed for methylcyclopropane (for example), and a similar *A*-factor would be expected, as is observed. The lowering of activation energy is then to be attributed predominantly to stabilization of the $>\dot{C}H—NH_2$ radical center, and a total stabilization energy of ca. 30 kJ/mole is suggested. The same effect is presumably at least partially responsible for the low activation energy for hydrogen abstraction from$CH_3—N<$ compared with$>CH_3—C\leftarrow$, the lowering being ca.12 kJ/mole [14]. The tautomer initially formed [propylideneamine from (8) or propenylamine from (9)] would rapidly isomerize to the equilibrium tautomeric mixture so either could participate in the exchange reaction (6); it is quite possible, in fact, that this proceeds through the enamine as intermediate. It was incidentally observed that different amines reacted at different rates in this step, with approximate reactivities c-$C_3H_5NH_2$: $iPrNH_2$:$EtNH_2$ $\approx$ 3:1.5:1. Our failure to detect products arising from allylamine formation indicates that H migration in the biradical to the $—\dot{C}H(NH_2)$ group is at least 100 times slower than H migration to the $—\dot{C}H_2$ group; this again is consistent with considerable resonance stabilization and hence with lack of reactivity of the $—\dot{C}H(NH_2)$ radical center.

The secondary isomerization of N-propylidenecyclopropylamine to an incompletely identified cyclic imine **A** (see experimental section) has some sort of precedent [15] in the acid-catalyzed isomerization (10) (cf. also the ring expansion of vinylcyclopropanes [2,3]:

(10) 

A related reaction of the present compound might be expected to proceed according to eq. (11),

(11) 

but our NMR spectrum of the product is inconclusive, and further work is required to characterize this potentially interesting reaction.[1]

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