The Thermal Decomposition of tert.*-Butylamine.*

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The thermal decomposition of *tert.*-butylamine has been studied in a static system in the temperature range 498—541° and over the pressure range 5—18 cm. The reaction was followed by pressure measurements and by analysis of the products. The pressure increase is due to the alternative simultaneous homogeneous first-order molecular scissions :

$$CMe_3{\cdot}NH_2 \longrightarrow CMe_2{:}CH_2 + NH_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and

$$CMe_3{\cdot}NH_2 \longrightarrow C_3NH_7 + CH_4 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

together with a subsequent slow reaction of the products, for which a correction can be readily applied. The ratio of ammonia to methane was 1 : 2·5 ± 0·1 over the temperature range studied, indicating that the activation energies of reactions (1) and (2) do not differ by more than 1 kcal./mole. A least-squares Arrhenius plot gave an overall rate constant

$$k = 10^{14\cdot 79} \exp\,(-67{,}100/\boldsymbol{R}T) \text{ sec.}^{-1}.$$

A LARGE number of unimolecular decompositions are known in which one molecule splits directly into two normal molecules. These reactions may be called " molecular-split " reactions, to distinguish them from reactions in which free radicals are formed. The simplest reactions of this class are those which occur through a transition state containing a ring of four atoms and they are often called four-centre reactions. The activation energies of many of these reactions have been measured. In Table 1 are given the activation energies of some of the simplest of them (including the results of this research). However, no satisfactory interpretation of the variations in their activation energies has yet been given. In an attempt to throw light on the general theoretical problem by provision of further results the decompositions of ethanethiol and *iso*butanethiol (2-methyl-propane-2-thiol) were examined. Our experimental results with the former are exactly similar to those of Trenner and H. A. Taylor (*J. Chem. Phys.*, 1933, **1**, 77), though we regard their mechanism involving the initial formation of polysulphides as rather improbable since the sulphur–sulphur bond is not strong. Very similar results were found by us with *iso*butanethiol so that it was not suitable for the present purpose either. This was disappointing, as a consideration of the bond strengths might lead one to suppose that the behaviour of the alkanethiols would be similar to that of the alkyl chlorides and bromides. The decomposition of *tert.*-butylamine was expected to occur smoothly because of its similarity to *tert.*-butanol. It was found that *tert.*-butylamine decomposed by way of the two molecular-split mechanisms (1) and (2) (above), having rate constants given respectively by the expressions $k_1 = 1{\cdot}7 \times 10^{14} \exp(-67{,}000/\boldsymbol{R}T)$ sec.$^{-1}$ and $k_2 = 4{\cdot}4 \times 10^{14} \exp(-67{,}000/\boldsymbol{R}T)$ sec.$^{-1}$. This is of interest because examples of a molecule reacting by two distinct molecular-split mechanisms are rare, though of course, numerous reactions are known which proceed by different ionic or free-radical mechanisms.

TABLE 1. *Activation energies (in kcal./mole) of reaction of the type*
$CH_3{\cdot}CR_2X \longrightarrow CH_2{:}CR_2 + HX$.

	HX				
$CH_3{\cdot}CR_2X$	HCl	HBr	H_2O	NH_3	CH_4
Et X	60·8 [a]	53·9 [d]	—	—	—
Pr^iX	50·5 [b]	47·8 [d]	—	—	—
Bu^tX	41·4 [c]	42·2 [d]	65·5 [e]	67·1 [f]	59·3 [g]
$Bu^t{\cdot}NH_2$	—	—	—	67·1 [f]	67·1 [f]

[a] Barton and Howlett, *J.*, 1949, 148. [b] Barton and Head, *Trans. Faraday Soc.*, 1950, **46**, 114. Barton and Onyon, *ibid.*, 1949, **45**, 725. [d] Blades and Murphy, *J. Amer. Chem. Soc.*, 1952, **74**, 6220; Green, Harden, Maccoll, and Thomas, *J. Chem. Phys.*, 1953, **21**, 178. [e] Schultz and Kistiakowsky, *J. Amer. Chem. Soc.*, 1934, **56**, 395. [f] This work. [g] Peard, Stubbs, and Hinshelwood, *Proc. Roy. Soc.*, 1952, *A*, **214**, 330.

However, this work has complicated rather than clarified the general problem of the factors affecting the activation energy of molecular-split reactions.

EXPERIMENTAL AND RESULTS

Materials.—*tert.*-Butylamine (B.D.H.), distilled through a 30-plate column (reflux ratio 8 : 1), had b. p. 64·2°/757 mm. The toluene was a highly purified sample. Before use the reagents were carefully degassed by bulb-to-bulb distillation *in vacuo*.

Apparatus and Procedure.—The reaction vessel was a 2-l. Pyrex bulb supported in a thermostatically controlled furnace, as used in our previous work (*Proc. Roy. Soc.*, 1953, *A*, **217**, 563). The reaction was followed by means of a mercury manometer connected to the reaction vessel.

Results.—A typical plot of the logarithm of (initial pressure − pressure increase) against time is shown in Fig. 1. An initial fast reaction is observed, followed by a first-order reaction represented by the linear portion of the curve, which appears to accelerate after about two half-lives as is shown by the downward curvature of the plot. This curvature is believed to be caused by a secondary reaction of the products of the main reaction. The addition of toluene had no effect on the slope of the linear portion of the graph but eliminated the initial fast reaction. This was therefore supposed to be an alternative method of decomposition which proceeded by a free-radical chain mechanism; it was suppressed by the toluene when it was present or, when no toluene had been added, by the chain inhibitors (such as butene) produced in the decomposition. This hypothesis was tested by admitting more *tert.*-butylamine into the reaction vessel during a run. As predicted, the fast reaction did not recur.

The rate constant (k_3) for the secondary reaction (3) (the nature of which is discussed in a later section of this paper), was found by following the pressure increase after the main reaction had proceeded virtually to completion. It was assumed that this reaction also was a molecular split in which one of the product molecules split in two. Any other reasonable assumption would be equally good for the present purpose. Let k be the rate constant of the principal reaction; then $k \gg k_3$, and it can be shown that a correction for the second reaction may be made by subtracting a quantity $p_0(1 - e^{-k_3t})$ from the observed pressure at a time t, where p_0 is the initial pressure of the reactant. At 527°, k_3 was less than $0{\cdot}05k$ and this simple correction was shown to be justified. k_3 was determined only at 527° because the measurement was lengthy and little error could be introduced by assuming that reaction (3) has the same temperature coefficient as the main reaction. An Arrhenius plot of the results is given in Fig. 2 for runs with initial pressures of reactant between 5 and 18 cm. The straight line corresponding to the equation $k = 6{\cdot}1 \times 10^{14} \exp(-67{,}100/\boldsymbol{R}T)$ sec.$^{-1}$ was obtained by the method of least squares, based only on the values obtained in an unpacked vessel in the absence of toluene. It can be seen that the values obtained in the presence of toluene and in a packed vessel of eight times the surface area of the unpacked vessel show no deviations outside the experimental error.

FIG. 1. *Typical plot of logarithm of (initial pressure—pressure increase) against time.*

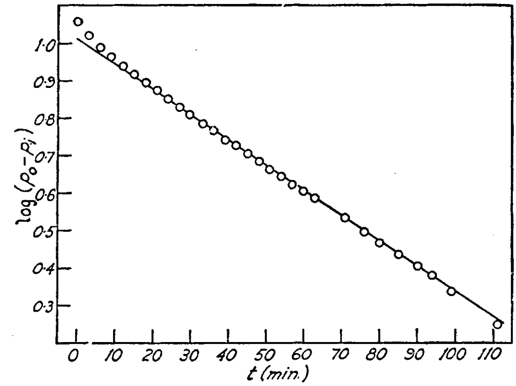
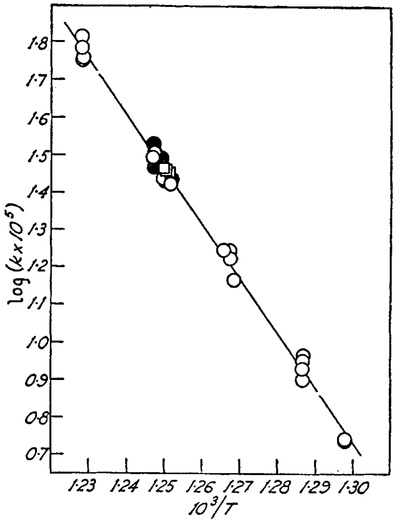


FIG. 2.



Arrhenius plot of results :
○ *Runs in unpacked vessel.*
● *Runs in packed vessel.*
☐ *Runs with toluene.*

Analysis.—At the end of a run the stopcock S_1 was opened to admit the products into the analysis system shown in Fig. 3. At first with stopcocks S_2 and S_4 closed the gases were pumped by the two-stage mercury-diffusion pump P, through the pumped-down nitrogen-cooled trap T at $-217°$, into the 2-l. bulb B, to which a manometer M was attached. All the products except the hydrogen, which was subsequently identified by absorption in the heated copper oxide tube T_2, were condensed out and the pressure of the hydrogen was measured.

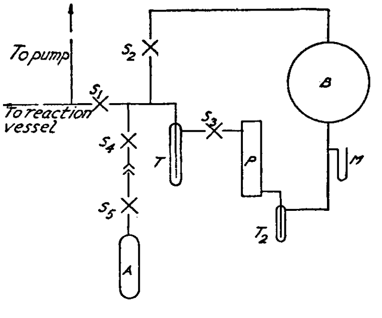


FIG. 3. *Diagram of analysis apparatus.*

T was then warmed to the temperature of liquid oxygen, and the pressure of methane measured, after which the non-condensable gases were pumped away. The pressures in the system when T was at a temperature of $-78°$ and at room temperature were then measured. These measurements gave the pressure of products whose composition will be considered later, and the total amount of gas withdrawn from the reaction vessel. The whole mixture was then distilled into the bulb A, which contained an excess of previously degassed dilute sulphuric acid; *A* was removed from the system, allowed to warm, shaken to ensure satisfactory gas absorption, reattached to the vacuum-system, and cooled with solid carbon dioxide. Then the pressure of non-basic volatile gases was measured. As the amines present in the products were not volatile at −78°, the difference in the pressures read with the products at this temperature, before and after absorption, gave the pressure of ammonia in the products. The volatile products were then shaken with concentrated sulphuric acid to absorb unsaturated compounds. It was found that an amount of gas equal to the amount of hydrogen formed in the reaction was not absorbed by the acid. By its vapour pressure this gas was identified as propane. It was established empirically for seven runs that the identity

$$\text{Pressure of gas volatile at } -78^\circ = 2 \times \text{pressure of } NH_3 + 2 \times \text{pressure of } H_2$$

held. This was used for calculating the ratios of methane to ammonia produced. It may be interpreted by supposing that an amount of *iso*butene is formed equal to the amount of ammonia as is required by reaction (1), and that the hydrogen is produced by the secondary reaction (3) by which an equivalent amount of propane and of some other gas that is absorbed by sulphuric acid are also produced. We have not been able to continue a plausible reaction scheme to account for these products and they may be produced by a rather complex mechanism. However, the gases only represent some 4% of the total products. The hypothesis receives some confirmation from the reasonable agreement between the amount of hydrogen produced and the amount calculated by assuming that it is produced by reaction (3) (cf. cols. 5 and 6 of Table 2).

The complete analytical results, given in Table 2, show that the conversion calculated from the pressure change in the reaction vessel is always some 10—15% higher than that calculated from the analytical results except for the two runs to which toluene was added. We believe that the discrepancy is caused by the formation by the initial rapid reaction of products which polymerise on leaving the reaction vessel. This view is supported by the observation of a deposit in the connecting tubes and the trap *T*, and by the fact that if a correction is made for the products formed in the free-radical reaction the two methods of calculating the conversions agree very well. Accordingly, it may be concluded that the main reactions are those suggested here.

TABLE 2.

Run	Temp.	Total press.*	H_2 *	$\frac{H_2}{Total}$, %	Calc. % corr.	CH_4 *	NH_3 *	$\frac{CH_4}{NH_3}$	Conversion, %, by :	
									pressure change	analysis
16	498°	5·033	0·111	2·2	2·6	1·107	0·436	2·54	37·8	32·8
20	498	4·738	0·117	2·5	2·6	0·971	0·406	2·39	34·9	31·5
21	498	—	0·075	—	—	1·031	0·418	2·47	—	—
26A	516	4·868	0·091	1·9	1·2	0·845	0·330	2·56	29·6	26·0
29	516	4·715	0·110	2·3	1·8	0·965	0·378	2·55	35·0	—
30	516	5·120	0·116	2·3	1·7	0·984	0·374	2·63	34·9	28·8
33	541	—	0·108	—	—	0·911	0·348	2·62	—	—
35	541	—	0·084	—	—	0·781	0·336	2·32	—	—
37	541	—	0·103	—	—	0·948	0·385	2·46	—	—
† 48	§ 527	3·938	0·104	2·6	1·3	0·700	0·266	2·64	28·0	27·1
† 48A	§ 527	3·824	0·091	2·4	1·6	0·671	0·289	2·32	28·8	27·8
† 48B	527	5·148	0·116	2·3	1·6	1·116	0·433	2·58	34·9	32·3
† 48C	527	5·061	0·127	2·5	1·5	1·047	0·366	2·86	34·1	30·5

* These pressures are in cm. in the analysis system and have no absolute significance.

† Run in packed vessel. § Run with added toluene.

The exact nature of the substance C_3NH_7 is not known. It could be $CMe_2{:}NH$, which might well exist in the gas phase, or $NH_2{\cdot}CMe{:}CH_2$. It does not seem likely that a suitable analytical method could be devised to detect these products in the quantities found here, but some light might be thrown on this problem by studying the decomposition of $(CH_3)_3C{\cdot}ND_2$ as the methane formed would be CH_4 or CH_3D, depending upon whether the carbon atom drew its hydrogen from the amino- or from a methyl group. The compound C_3NH_7 is certainly a derivative of either the keto- or the enol form of acetone, for acetone diphenylhydrazone was obtained from the solution of the amine in dilute sulphuric acid.

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