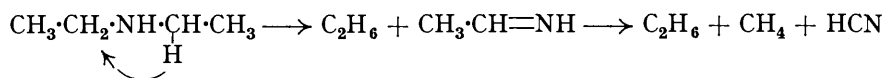


**271.** *The Homogeneous Catalysis of Gaseous Reactions. The Influence of Iodine on the Decomposition of Simple Aliphatic Amines and of Hexane.*

By S. BAIRSTOW and C. N. HINSHELWOOD.

SINCE the decomposition of compounds containing the group C-O-C is very effectively catalysed by iodine, while various other types of reaction are almost uninfluenced, it seemed of interest to investigate the behaviour of compounds containing the atoms C-NH-C, which may be regarded in some respects as the analogues of the ethers.

If it behaves like diethyl ether, diethylamine will give the following reactions :



The intermediate aldimine has never been prepared, so it must be very unstable or reactive. Consequently its removal, in the above reaction, by some condensation is just as likely as its clean decomposition.

Among the ethers, methyl ether is anomalous in that it is not catalysed. Dimethylamine was therefore examined with the object of finding out whether this "methyl ether effect" is general.

All the catalytic decompositions described in the preceding paper can be formulated as the movement of a hydrogen atom. In the secondary amines there are two types of hydrogen atom. To ascertain how far the hydrogen of the imino-group is important, experiments were also made with tertiary amines.

Ethylamine, from the present point of view the analogue of an alcohol, should not be catalysed.

Hexane provides an example of a compound which completes a series: C-O-C, C-NH-C, C-CH<sub>2</sub>-C.

*Diethylamine.*—Two pure specimens of this substance were used and gave identical results. Both were dried over solid potassium hydroxide and distilled over a range of 0.3°. The increase in decomposition rate caused by various amounts of iodine is shown in the following table.

Temperature, 452°; initial pressure of amine, 100 mm.

Catalyst, as mm. of decomp.

isopropyl iodide .....	0.044	0.113	0.227	0.328	0.593	1.17	2.5	8.0	11.5	17.0
(Rate with I <sub>2</sub> )/(rate without I <sub>2</sub> )	5.3	7.9	8.6	11.5	17.8	26.6	40.3	83	96	105

The relation between rate and catalyst concentration is of some interest, but discussion of it is deferred to a later section where the results for all the amines can be considered together. Experiments with a packed bulb showed the catalysis to be homogeneous.

The relation between the pressure increase and the time is not expressed by a simple equation of the first or of the second order, but is characteristic of a unimolecular reaction followed by other reactions. In the following table  $t_{1/4}$ ,  $t_{1/2}$ , etc., are the times, expressed relative to  $t_{1/2}$ , for the corresponding fractions of the total pressure change, at 452°.

Catalyst, mm.	$t_{1/4}$ .	$t_{1/2}$ .	$t_{3/4}$ .
0	0.41	1.00	1.63
0.227	0.39	1.00	1.83
0.328	0.395	1.00	1.90
1.17	0.41	1.00	2.12

For a unimolecular reaction the ratios would be 0.41, 1.00, and 1.585. The more the primary reaction is accelerated by the catalyst, the more nearly unimolecular the earlier stages of the whole change become, and the more evident the relative prolonging of the later stages which are less influenced by the iodine.

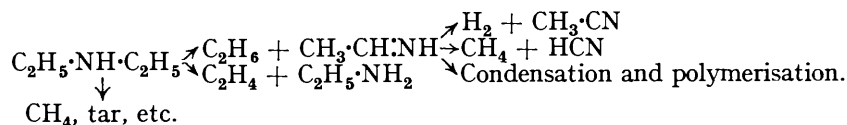
If the diethylamine reacted quantitatively according to the equation  $C_2H_5 \cdot NH \cdot C_2H_5 = C_2H_6 + CH_4 + HCN$ , the increase of pressure would be 200% of the initial value. Actually it was 163% for the uncatalysed reaction at 459° and smaller still in the presence of iodine, being 148% for 1 mm. and 114% for 8 mm. of catalyst. One of the most obvious explanations of the deficit is condensation of the aldimine, which, as shown above, is a possible intermediate product. This is consistent with the observation that, although hydrogen cyanide is present, analysis of the products shows that there is much less than the amount required by the simple equation.\* Moreover, the yield of hydrogen cyanide decreases with increasing concentration of catalyst, *i.e.*, with diminishing total pressure change. In order to estimate the hydrogen cyanide, a measured fraction of the gaseous reaction products was withdrawn into an evacuated gas pipette, dissolved in water, and treated with excess of standard silver nitrate. After filtration from the silver cyanide the excess silver was determined by the Volhard method. Knowing the volume and temperature of the reaction bulb, the pressure of gaseous hydrogen cyanide originally present could be calculated. At temperatures between 450° and 500°, from 15 to 30% of the theoretical amount could be detected for the uncatalysed reaction. In the presence of the catalyst, the amount fell to 5 or 10%. (The latter results are not influenced by any iodine withdrawn with the sample.) If the hypothetical aldimine disappeared as such, *e.g.*, by polymerisation, there would be a deficit of methane corresponding to that of hydrogen cyanide, and thus the ratio of ethane to methane in the products would always be greater than unity. Analysis shows, however, that the methane deficit is by no means as great as required. In the uncatalysed reaction the methane exceeds the ethane; *e.g.*, at 504° in the absence of iodine the ratio  $CH_4 : C_2H_6 = 1 : 0.75$ , though in the presence of 1 mm. of catalyst the ratio is 1 : 1.3. These results are most easily interpreted by assuming that some process yielding methane compensates for that lost with the hydrogen cyanide. Any general disruption of the molecule would be likely to give a large proportion of methane, thermodynamically the stablest of the hydrocarbons. The existence of complex side reactions can be seen from the presence of considerable amounts of tarry deposit in the reaction vessel. Nevertheless, the formation of hydrogen cyanide, ethane, and methane, on the one hand, and the absence of any considerable amounts of olefins on the other hand, show that the reactions anticipated do in fact occur. The following are typical analyses of the products of the catalysed reaction at 504°. The gases were first washed with potassium hydroxide and with sulphuric acid to remove hydrogen cyanide and any traces of unchanged base.

	Catalysed.		Uncatalysed.		Catalysed.		Uncatalysed.
$C_2H_4$ , %	7.3	6.8	5.2	$CH_4$ , %	37.7	38.4	50.8
$H_2$ , %	6.3	5.9	6.2	$C_2H_6$ , %	48.7	48.9	37.8

The above analyses were made in a Bone and Wheeler apparatus. The total unsaturated hydrocarbons are recorded as ethylene. The hydrogen was determined by fractional combustion with copper oxide at 275°.

\* Direct experiments showed that hydrogen cyanide was stable in presence of iodine at this temperature.

The formation of hydrogen can be simply explained as an alternative decomposition of the aldimine, and the results can now be summarised in the following way :



Although these reactions are more complex than the catalytic decomposition of the ethers, one of the principal changes catalysed by the iodine can still be interpreted as an analogous movement of a hydrogen atom. This primary process gives rise to the large amounts of ethane actually found. The aldimine formed at the same time is so reactive that it cannot be expected to undergo the further clean decomposition suffered by the intermediate aldehydes formed from the ethers.

*Dimethylamine.*—The behaviour of dimethylamine is qualitatively similar to that of diethylamine in that the rate of the catalysed reaction is not linearly proportional to the iodine concentration but tends to a limiting value.

Temperature, 487°; initial pressure of amine, 100 mm.

Catalyst, mm. ....	0.5	5.0
(Rate with I <sub>2</sub> )/(rate without I <sub>2</sub> ) .....	6.9	11.6

In connexion with the possible analogy to dimethyl ether, it is important to note that, although iodine catalyses the reaction, the increase in rate is almost a power of ten smaller than with diethylamine.

Hydrogen cyanide was again found in the reaction products, but the simple equation  $\text{CH}_3\cdot\text{NH}\cdot\text{CH}_3 = \text{CH}_4 + \text{H}_2 + \text{HCN}$  can only be applied with reservations, as with diethylamine.

*Triethylamine.*—The base was dried over potassium hydroxide and twice distilled, being collected finally over a range of 0.2°.

The decomposition is rather strongly catalysed, and, moreover, the rate is approximately proportional to the concentration of iodine.

Temperature, 409°; initial pressure of amine, 100 mm.

Catalyst, mm. ....	3.0	3.5	6.5	9.0	11.5	14.5
Catalysed/uncatalysed rate .....	37	42	81	124	145	196
Rate/catalyst concn. × 10.....	123	120	124	137	126	135

The course of the reaction is not represented by a simple equation for a change of the first or second order : it is illustrated by the following figures (relative to  $t_{1/2}$ ), characteristic of a composite reaction.

	$t_{1/4}$ .	$t_{1/2}$ .	$t_{2/3}$ .	$t_{3/4}$ .
Uncatalysed .....	0.37	1.00	1.70	2.18
11.5 Mm. of catalyst .....	0.37	1.00	2.06	3.16

The catalytic reaction is homogeneous. In the sphere-packed bulb the rate was in fact slightly slower, but this can be fully accounted for by the different proportion of condensation reactions. Actual average values were : unpacked bulb,  $t_{1/2} = 146$  secs.; packed bulb,  $t_{1/2} = 186$  secs.

The above results prove that the catalysis of the amines is not dependent on the amino-hydrogen. This being so, there is little reason to doubt that the chemical reactions occurring in the decomposition of triethylamine and diethylamine are similar. Detailed analyses were, therefore, not made.

*Trimethylamine.*—The decomposition is catalysed, but the “methyl ether” effect is again in evidence, to the extent that the maximum increase in rate is only about one-tenth of that observed with triethylamine. The rate appears to approach a limiting value as the iodine concentration increases.

Temperature, 443°; initial pressure of amine, 100 mm.

Catalyst, mm. ....	3.0	6.0	12.0	18.0	29.5
(Rate with I <sub>2</sub> )/(rate without I <sub>2</sub> ) .....	5.0	8.7	11.2	13.2	16.7

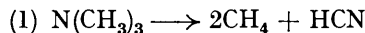
The reaction is homogeneous : half-life in packed bulb (6 mm. catalyst) 467 secs., in unpacked bulb 418 secs. Again there is a slightly smaller rate in the packed bulb. We do not regard this as due to the existence of any sort of chain reaction, since it can be quite well explained by the various condensations occurring.

The existence of consecutive reactions in the decomposition is plainly shown by the time-pressure increase curves, which have an inflexion becoming more and more pronounced with a greater iodine concentration. The analysis of these curves is rather complicated and not relevant to the present issue, but the *later* stage of the reaction appears to possess a rate *proportional* to the concentration of the catalyst.

The gaseous products of the reaction, after being washed with potassium hydroxide and with sulphuric acid to remove hydrogen cyanide and free base, contained 2% of unsaturated compounds, and 5% of incombustible residue, presumably nitrogen. The remainder was methane; combustion gave the ratios carbon dioxide : contraction : oxygen used = 1.00 : 2.01 : 2.01. Hydrogen and ethane, if present at all, were in very small amounts, as shown by fractional combustion.

The products of complete decomposition, at the temperature of the reaction bulb, contained about 10% by volume of hydrogen cyanide and 5–10% of a base.

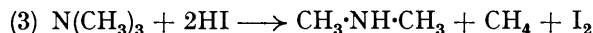
Leaving out of account side reactions giving highly condensed products. we can explain the course of the decomposition by the following equations :



This does not account either for the presence of base or for the observed ratio  $\text{CH}_4 : \text{HCN} = 7 : 1$  approx., which suggests that there may have been some reduction of the trimethylamine to methane and another, more stable, base, possibly ammonia. If any decomposition occurs by the simple movement of a hydrogen atom, already discussed, hydrogen is a possible product :



There can then follow formation of hydrogen iodide and



The dimethylamine can be decomposed or further reduced by hydrogen iodide to methylamine and ammonia. These reductions are probably responsible for that part of the reaction where, as mentioned above, the rate becomes proportional to the catalyst concentration. Their occurrence also explains why little free iodine was observed on withdrawing the reaction products. Instead, a white deposit appeared, presumably formed by the combination of hydrogen iodide and the base.

*Ethylamine.*—The, predominantly homogeneous, decomposition of ethylamine is catalysed by iodine to a relatively small extent. Thus at 528° with an initial pressure of 100 mm. the following results were obtained :

Catalyst, mm. ....	5	18	30.5	48
(Rate with I <sub>2</sub> )/(rate without I <sub>2</sub> ) .....	1.5	4.8	7.1	12.2

The iodine affects the actual course of the reaction profoundly, as shown by large changes in the "end-point." The mechanism was not investigated in detail, but appears to be partly catalytic and partly dependent on reduction by hydrogen iodide in a way similar to that discussed in connexion with methyl alcohol.

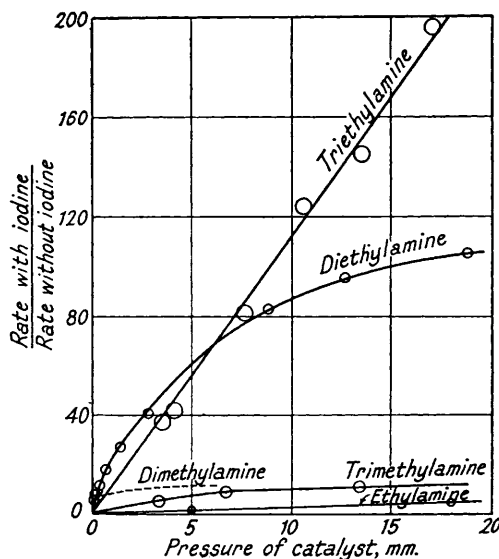
*Hexane.*—The decomposition of hexane at 545° is influenced to some extent by iodine, but it is very doubtful how much of the effect can really be called catalysis. The non-condensable reaction products consist of about 30% of unsaturated compounds, so that, if any hydrogen is produced, which can form hydrogen iodide, there is every opportunity for the latter to enter into chemical reactions.

Catalyst, mm. ....	2.5	5	10	15	37
(Rate with I <sub>2</sub> )/(rate without I <sub>2</sub> ) .....	2.8	4.0	4.6	5.4	5.4

*The Relation between Rate of Reaction and Concentration of Catalyst.*—In the fig. the results for all the amines investigated are plotted on the same scale for comparison. The relation between rate and concentration of catalyst is in general not linear. Over a corresponding range the curves for ethers and for acetaldehyde are straight lines. While it is difficult to rule out the possibility that deviations from linearity in any one example are due to specific causes of no importance to a theory of catalysis, nevertheless the curves appear to form a regular series with the straight line included as a special case. This suggests that perhaps the most general form of relation is that in which the rate reaches a limiting value as concentration increases. The theoretical interpretation of such a relation is simple, and requires no hypotheses beyond those current in the theory of reaction kinetics. The catalyst activates the molecule of the reactant in a collision, and may or may not remain temporarily associated with it in the form of a complex. The activated molecule or complex is susceptible to deactivation by a further collision with a molecule of catalyst, and will therefore be deactivated in this way unless in the meantime it has rearranged itself to give the products of the chemical change. As the catalyst concentration increases, a state is ultimately reached where further additions cause as much increase in deactivation as in activation: the rate then reaches a limiting value. If the uncatalysed reaction is negligible, we have: (i) rate of production of activated molecules or complex =  $k_1nc$ , where  $n$  and  $c$  are the concentrations of reactant and catalyst respectively; (ii) rate of deactivation =  $k_2ca$ , where  $a$  is the concentration of active molecules, or complex, established in the system; and (iii) rate of chemical transformation =  $k_3a$ . Equating rates of production and removal of activated molecules, or complex, and solving the equation, we have

$$\text{rate of reaction} = k_3a = k_1nc/(1 + k_2c/k_3).$$

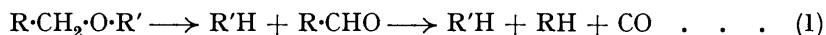
This gives a curve which, for small values of  $c$ , is linear, but ultimately reaches a limiting value. The larger the ratio  $k_2/k_3$ , the sooner the limit is approached. When  $k_2$  is very small or  $k_3$  is very large, the curve remains linear up to the highest concentrations of catalyst. This state of affairs, which corresponds to the chemical transformation of all the activated molecules produced, is realised with the ethers and aldehydes, but since the values of the various constants are highly specific, every variety of behaviour is to be expected in a series of different compounds.



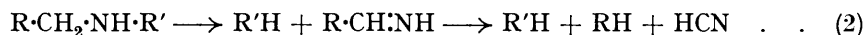
#### SUMMARY.

The influence of iodine on the homogeneous decomposition of various amines has been studied in the temperature range 400—550°, as part of a general investigation of the types of compound susceptible to the catalytic action which iodine exerts on the ethers, aldehydes, and esters.

The structural analogy between C—O—C and C—NH—C is reflected in a certain similarity of the catalysed decompositions of the amines and the ethers. The latter have already been shown to react as follows:



The products derived from the amines are explained qualitatively by the equation



With the methyl compounds, hydrogen can be formed and then give hydrogen iodide, which reduces some of the amine.

The intermediate aldehydes of equation (1) decompose cleanly, but the corresponding aldimines of (2) appear to enter into complex reactions which destroy any simple quantitative relations. The hydrogen attached to the nitrogen plays no essential part, since triethylamine and diethylamine are both catalysed, and to about the same extent.

Among the ethers, methyl ether is anomalous in that it is not catalysed: although dimethylamine and trimethylamine are not uninfluenced by iodine, the acceleration produced by 3 mm. of it is only of the order of ten-fold, in contrast with an order of a hundred-fold with diethylamine and triethylamine.

In some of the reactions the rate is directly proportional to the catalyst concentration; in others it reaches a limit as this increases. The linear relation can be regarded as a special case of the more general one, which can be derived from simple kinetic considerations.

The influence of iodine on the decomposition of ethylamine and of hexane is small: how far it can be called catalytic is doubtful.

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PHYSICAL CHEMISTRY LABORATORY, BALLIOL COLLEGE AND  
TRINITY COLLEGE, OXFORD.

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