Catalysis by Hydrogen Halides in the Gas Phase. Part XXVII.† *N*-t-Butylacetamide and Hydrogen Chloride

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The gas-phase hydrogen chloride catalysed decomposition of *N*-t-butylacetamide (NBA) into t-butylamine, isobutene, acetonitrile, and acetic acid at 380 °C is reported. Acetyl chloride is believed to be formed as the intermediate. The experimental evidence presented also suggests that acetyl chloride is in equilibrium with keten and hydrogen chloride, the former reacting with NBA to yield the observed products. The decomposition appears to be homogeneous and molecular. The kinetic form, which is basically first-order in each reactant, is altered by t-butylamine either produced in the reaction or added initially.

THE homogeneous and unimolecular thermal decomposition (uncatalysed) of *N*-t-butylacetamide (NBA)[1] into isobutene and acetamide between 390 and 460 °C has been described already. A simultaneous minor decomposition of NBA to yield t-butylamine and keten was also observed. It was shown that the product acetic acid catalysed the latter reaction. As Aspden[2] had noted that hydrogen chloride was about ten times as efficient a catalyst as acetic acid in bringing about the decomposition of acetamide into ammonia, acetic acid, and acetonitrile, it was of interest to study the effect of hydrogen chloride on the thermal decomposition of NBA. Typical experiments performed are listed in the following section. The uncatalysed decomposition of NBA at 380 °C is insignificant. The preparation and purification of materials, the apparatus, and the experimental procedures employed have been described previously.[1,3] It was difficult to estimate the t-butylamine and NBA quantitatively because these were lost as the solid ammonium salts during collection of the products. The reactions were carried out in a vessel conditioned with the products of pyrolysis of NBA.

RESULTS

NBA (134·0 mmHg) was added to hydrogen chloride (127·8 mmHg) at 378 °C, and the pressure increase was followed for 30 min. Product analysis indicated the presence of t-butylamine, acetic acid, isobutene (41·4 mmHg), and acetonitrile (40·0 mmHg). In a similar experiment when hydrogen chloride (107·0 mmHg) reacted with NBA (99·0 mmHg) overnight, the pressure increased by approximately the initial pressure of NBA [final pressure *ca.* (99 + 99 + 107) mmHg]. Product analysis showed the presence of isobutene (54·0 mmHg) and acetonitrile (53·0 mmHg) amongst other products. These experiments show that isobutene and acetonitrile are formed in equal amounts. In a third experiment propan-2-ol (74·8 mmHg) and hydrogen chloride (80 mmHg) were introduced into the reaction vessel at 378·8 °C. NBA (130·0 mmHg) was blown in after 2 min and the reaction was followed for a further 16 min. The pressure increased by 61 mmHg during this time. The product analysis showed the presence of propene (18% of the isobutene) amongst other products. When hydrogen chloride (80·0 mmHg) and propan-2-ol (103·6 mmHg) were left in the reaction vessel for 18 min at 378·7 °C, the pressure increased by only 1 mmHg. This suggests that the propene is not produced from the reaction of hydrogen chloride with propan-2-ol. The results are consistent with the hypothesis that in the reaction between NBA and hydrogen chloride, the added propan-2-ol reacts with an intermediate to yield isopropyl acetate, which then decomposes to yield propene.

Pyrolysis of acetyl chloride. When acetyl chloride (140·0 mmHg) was introduced into the reaction vessel at 378·8 °C, the pressure increased rapidly (in 1 min) by 50% of its initial value. It stayed constant for another 2 min, after which it started to decrease slowly (presumably owing to polymerisation of keten). The product analysis showed the presence of less than 2% chloromethane and carbon monoxide in the pyrolysate.

Further acetyl chloride pyrolyses were performed at

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† Part XXVI, A. Maccoll and S. S. Nagra, *J.C.S. Perkin II*, 1974, 1099.

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[2] J. Aspden, A. Maccoll, and R. A. Ross, *Trans. Faraday Soc.*, 1968, **64**, 965.

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373·8 °C in a vessel fitted with an automatic transducer pressure gauge. The pressure increase was followed on a chart recorder at a speed of 600 mm min^{-1}. The initial rate constants as a function of initial pressure are listed in Table 1, where ΔP = [(final maximum pressure — initial pressure)/initial pressure] × 100.

TABLE 1

Pyrolysis of acetyl chloride at 373·8 °C

Pressure of acetyl chloride (mmHg)	Initial rate constant $10^2k_1/s^{-1}$	% Pressure increase ΔP/mmHg
9·0	4·3	90·0
127·0	3·9	50·0
130·0 *	4·0	48·0
158·0	4·2	40·0

* With added cyclohexene.

At lower initial pressures of acetyl chloride, the decomposition is greater than at higher initial pressures. These observations, together with the fall in the observed pressure after it has been constant, are consistent with the equilibrium (1).* The involvement of this equilibrium was

$$\mathrm{MeCOCl} \rightleftharpoons \mathrm{CH_2{=}C{=}O + HCl} \qquad (1)$$

confirmed by the following experiment. Propan-2-ol does not decompose at 378·4 °C. When acetyl chloride (120·0 mmHg) was introduced into the reaction vessel at 378·4 °C the pressure increased to 154·0 mmHg in 1 min. Propan-2-ol (135·4 mmHg) was then added. The pressure of the mixture dropped by 23 mmHg in 1 min, and then started to increase rapidly. The pressure–time curve for this run is shown in Figure 1. Product analysis showed the presence of a significant amount of propene in the pyrolysate. If acetyl chloride reacts with propan-2-ol according to equation (2), no pressure drop would be expected initially.

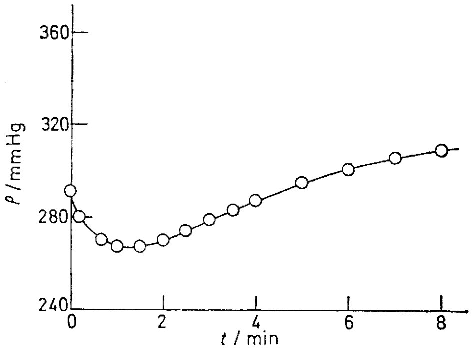

FIGURE 1 Pressure–time curve for the reaction between isopropyl alcohol and keten

$$\mathrm{MeCOCl + Pr^iOH \longrightarrow Pr^iO{\cdot}COMe + HCl} \qquad (2)$$

From this observation it is concluded that propan-2-ol reacts rapidly with keten to form isopropyl acetate according to equation (3), which accounts for the initial decrease in pressure (Figure 1) and the formation of propene.

$$\begin{tikzcd}
\mathrm{Pr^iOH + CH_2{=}C{=}O} \arrow[r] & \mathrm{Pr^iO{\cdot}COMe} \arrow[d] \\
& \mathrm{MeCH{=}CH_2 + MeCO_2H}
\end{tikzcd} \qquad (3)$$

The reaction of keten with NBA was also studied at 378·7 °C. When NBA (127·8 mmHg) was added to keten (117·2 mmHg) at 378·7 °C the pressure had increased by 43 mmHg after 10 min. Product analysis showed the presence of acetonitrile (53·0 mmHg) and isobutene (50·0 mmHg) amongst other products. Also when keten (130·0 mmHg) alone was left in the reaction vessel for 10 min at 378·6 °C, the pressure decreased by 13 mmHg. This explains why the pressure increase in the former experiment is less than that to be expected from the formation of acetonitrile and isobutene. These results are consistent with the reaction of keten and NBA to yield isobutene, acetonitrile, and acetic acid according to equation (4). This reaction is analogous to the reaction of

$$\mathrm{MeCO{\cdot}NHBu^t + CH_2{=}C{=}O \longrightarrow Me_2C{=}CH_2 + MeCN + MeCO_2H} \qquad (4)$$

keten with acetamide [2] to form acetonitrile and acetic acid, which is believed to proceed through the formation of acetylacetamide (diacetamide) according to equation (5).

$$\begin{tikzcd}
\mathrm{MeCO{\cdot}NH_2 + CH_2{=}C{=}O} \arrow[r] & \mathrm{[(MeCO)_2NH]} \arrow[d] \\
& \mathrm{MeCN + MeCO_2H}
\end{tikzcd} \qquad (5)$$

In the light of all these observations, the hydrogen chloride catalysed decomposition of NBA can be represented by equations (6).

$$\begin{tikzcd}
\mathrm{MeCO{\cdot}NHBu^t + HCl} \arrow[r, dash] & \mathrm{Bu^tNH_2 + MeCOCl} \arrow[d, shift left] \\
& \mathrm{CH_2{=}C{=}O + HCl} \arrow[u, shift left]
\end{tikzcd} \qquad (6)$$

$$\mathrm{MeCO{\cdot}NHBu^t + CH_2{=}C{=}O \longrightarrow Me_2C{=}CH_2 + MeCN + MeCO_2H}$$

The pressure–time curves for NBA alone and NBA in the presence of hydrogen chloride are shown in Figure 2 (A and B). The associated log plot is shown in Figure 2C. From the stoicheiometry the pressure increase would be

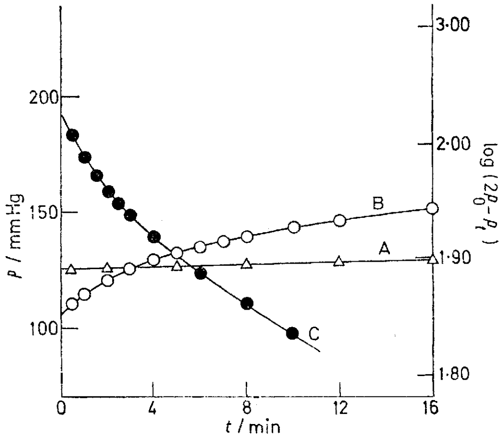

FIGURE 2 Pressure–time curve for the decomposition of NBA (A) alone and (B) in the presence of hydrogen chloride; curve C is the log plot corresponding to B

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* The equilibrium involving acetyl chloride, keten, and hydrogen chloride has been thoroughly studied by Tilley (M.Sc. Thesis, University of New England, 1972), as well as the kinetics of the forward and reverse reactions.

expected to reflect the change from 2 mol of NBA to 4 mol of products, but Figure 2 shows that the log plot departs from linearity steadily from the beginning of the reaction.

Initial first-order rate constants (k_1^0) were obtained from the initial rate of pressure increase. The results (Table 2) indicate that at a constant pressure of hydrogen chloride the reaction is first-order in NBA. Second-order rate constants ($k_2 = k_1/[\mathrm{HCl}]$) are also shown.

TABLE 2

Variation of initial first-order rate coefficients with the pressure of NBA, at a constant pressure (*ca.* 80 mmHg) of hydrogen chloride and at 378·8 °C

P_{NBA}/ mmHg	$10^4k_1^0$/ $\mathrm{s^{-1}}$	10^6k_2/ $\mathrm{s^{-1}\,mmHg^{-1}}$	P_{NBA}/ mmHg	$10^4k_1^0$/ $\mathrm{s^{-1}}$	10^6k_2/ $\mathrm{s^{-1}\,mmHg^{-1}}$
43·7	24·7	31·2	135·8	26·0	33·2
50·3	26·0	32·5	165·0	24·7	31·2
68·8	24·0	30·0	215·7	26·4	33·0
65·6	24·5	30·7	221·5	25·7	32·3
81·5	26·6	33·2	270·5	25·6	32·0
106·0	23·6	26·5	291·0	26·3	33·0

TABLE 3

Variation of initial rate coefficients with the pressure of hydrogen chloride at 378·8 °C

P_{HCl}/mmHg	P_{NBA}/mmHg	$10^4k_1/\mathrm{s^{-1}}$	$10^6k_2/\mathrm{s^{-1}\,mmHg}$
21·9	99·9	14·3	65·1
30·0	113·0	18·4	61·4
41·5	112·0	13·9	33·4
90·1	113·3	19·6	32·9
102·4	98·0	27·5	26·8
120·9	126·2	32·2	26·6
128·9	118·2	34·5	26·8
152·8	127·5	36·8	22·3
172·7	108·0	38·5	22·2
209·1	127·0	41·3	19·7

Table 3 shows the effect upon the initial first-order rate coefficients of varying the pressure of hydrogen chloride, with the pressure of NBA kept roughly constant. The results indicate that the rate coefficients are not linearly proportional to the pressure of hydrogen chloride. The rate coefficients are considerably less at higher pressures of hydrogen chloride. They further indicate that hydrogen chloride and keten are in competition for the NBA, as demanded by equations (4) and (6).

When t-butylamine was added initially in the hydrogen chloride catalysed decomposition of NBA at 378·8 °C, the nitial rate of decomposition fell markedly (Table 4). In these experiments t-butylamine and hydrogen chloride were introduced into the reaction vessel and NBA was added after about 5 min. A limiting value of k_1^0 was reached when large amounts of t-butylamine were added.

TABLE 4

Variation of initial rate coefficient of the decomposition of NBA with the addition of t-butylamine (TB) at a constant pressure of hydrogen chloride (80·0 mmHg) and at 378·8 °C

P_{TB}/mmHg	P_{NBA}/mmHg	$10^4k_1/\mathrm{s^{-1}}$
	106·0	22·0
3·1	64·1	11·3
18·5	101·4	8·7
39·0	86·2	7·0
58·9	122·5	4·5
66·4	123·9	3·8
80·8	96·9	3·6

In one experiment when NBA reacted in the presence of hydrogen chloride (81·4 mmHg) and dimethylamine (118·0 mmHg) and the reaction was followed for 20 min, analysis of products showed the presence of *NN*-dimethylacetamide. All the results in the hydrogen chloride catalysed decomposition of NBA were unaltered when the experiments were performed either in the presence of cyclohexene (inhibitor) or in a packed vessel with surface-to-volume ratio up to five times that of the unpacked vessel.

DISCUSSION

Ritter and Minieri[4] observed that the hydrolysis of NBA in alkaline solution required prolonged treatment under drastic conditions. However, with acid catalysis the reaction occurred rapidly, with quantitative loss of ammonia, and yielded the corresponding alkene instead of the expected amine [equation (7)]. It seems possible

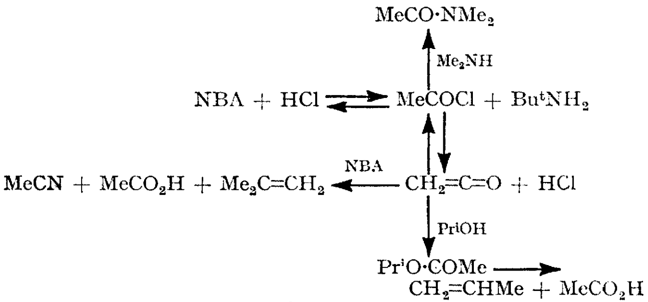
$$\mathrm{MeCO{\cdot}NHBu^t} \xrightarrow{\mathrm{H_2O,\ H^+}} \mathrm{Me_2C{=}CH_2 + MeCO_2H + NH_3} \quad (7)$$

that the amine formed underwent acid-catalysed elimination to yield ammonia and isobutene.

A reduction in rate, similar to that produced by t-butylamine initially added in the hydrogen chloride catalysed decomposition of NBA, was observed when methanol (or ethanol or water) was added in the hydrogen bromide catalysed decomposition of methyl trimethylacetate studied by Stimson *et al.*[5-7] These workers confirmed the occurrence of esterification and transesterification in this system, and concluded that this reduction was due to the reversal of the reaction [equation (8)]. As ROH builds up the rate falls. When

$$\begin{tikzcd} \mathrm{Me_3C{\cdot}CO_2R + HBr} \arrow[r, shift left] & \mathrm{Z} \arrow[l, shift left] \arrow[d] & \mathrm{+\ ROH} \\ & \mathrm{Me_2C{=}CH_2 + CO + HBr} & \end{tikzcd} \quad (8)$$

ROH was added in quantity the initial rate fell. We can account for the observations in the present system of NBA and hydrogen chloride in an analogous way, leading to the illustrated Scheme.



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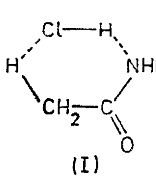
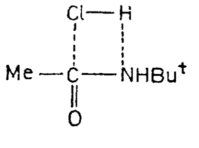
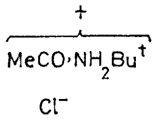
The added amines presumably intervene by reacting with the acetyl intermediate. This Scheme also explains why the log plot (Figure 2C) departs from linearity steadily from the beginning of the reaction: first, the reaction is reversed by the amine produced; and secondly, the keten formed does not react with the NBA instantaneously to yield the observed products and therefore the proposed stoicheiometry of 2 mol of reactants (NBA) yielding 4 mol of products is not accounted for.

Feasible transition states are represented by structures (I)—(III). The six-centred transition state (I) leads directly to keten, HCl, and t-butylamine, but it does not explain the formation of the acetyl chloride intermediate. However, the evidence presented does suggest that acetyl chloride is the intermediate formed. The four-centred transition state (II), in which the bond fission may be homolytic or heterolytic, is consistent with this observation. The basicity of *N*-alkylamides [8,9] makes the ion-pair transition state (III), in which the bonds are broken heterolytically, a possibility. These compounds form cations of the type $\mathrm{R^1CO{\cdot}\overset{+}{N}HR^2R^3}$ when treated with strong mineral acids in solution. Also they form stable polar chloroplatinates.[9] The NBA hydrochloride [10] and hydrobromide are formed when the corresponding dry hydrogen halide (gas) is passed through a solution of the amide in chloroform. The nature of the bonding in the salts of these *N*-alkylamides is not known with certainty, but various structures involving protonation at oxygen or at nitrogen have been suggested.[8]


(I)

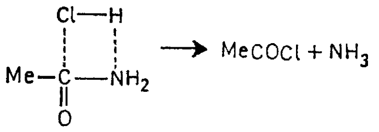

(II)


$\overbrace{\mathrm{MeCO{\cdot}NH_2Bu^t}}^{+}\ \mathrm{Cl^-}$

(III)

The analogy [11] between the gas-phase eliminations and the solvolytic reactions (S_N1 or $E1$ in polar solvents [12]) makes the existence of polar interactions [transition state (III)] between hydrogen chloride and NBA in the gas phase a strong possibility.

For the hydrogen chloride catalysed decomposition of acetamide [2] into ammonia, acetonitrile, and acetic acid, the mechanism implied by direct analogy with the present system involves the transition state (IV).


(IV)

However Aspden [2] thought it doubtful that acetyl chloride would decompose readily enough to account for the observed rate of catalysis. The present work shows that acetyl chloride is in equilibrium with keten and hydrogen chloride at 380 °C. Aspden noted that in the pyrolysis of acetamide (424—545 °C), keten reacted with acetamide instantaneously to yield acetonitrile and acetic acid. Therefore in this temperature range the equilibrium (9) will be displaced in the forward

$$\mathrm{MeCOCl} \rightleftharpoons \mathrm{CH_2{=}C{=}O} + \mathrm{HCl} \qquad (9)$$

direction owing to the rapid reaction of keten with acetamide. It seems most probable now that a four-centred transition state (IV) (of which the extreme case is $\mathrm{MeCO\overset{+}{N}H_3Cl^-}$) cannot be ruled out in the hydrogen chloride catalysed decomposition of acetamide studied by Aspden.[2]

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