842. *Nitramines and Nitramides. Part XI.** *The Acid-catalysed Decomposition of Various* ON-*Dialkylnitramines.*

By Peter Bruck and Alex. H. Lamberton.

It appears that the acid-catalysed decomposition of R·N:NO·OR′ (R and R′ being alkyl groups) proceeds by scission of the R–N and N–OR′ bonds. Electron donation by R strongly favours decomposition; with R′ constant the relative rates are R = Me $<$ Et $<$ *neo*-C_5H_{11} $<$ $Pr^i \ll Bu^t$. With R constant, changes in R′ act mildly in the opposite direction. Some of the activation energies concerned have been measured. Water molecules are not covalently involved in the transition state, since the rate of decomposition of Me·N:NO·OMe in suitable conditions is proportional to the acidity function h_0, rather than to $[H_3O^+]$.

The bond-scissions may occur essentially in one stage, or successively: if successively, the apparent influence of both R and R′ shows the first scission to be rate-determining.

We include a brief discussion of these, and earlier, observations regarding the stability of aliphatic *N*-nitro-compounds towards acids.

In an earlier paper of this series [1] we investigated the acid-catalysed hydrolysis of *ON*-dialkylnitramines (R·N:NO·OR′ + $H_2O \longrightarrow$ ROH + N_2O + R′OH) by an examination of the *O*-methyl-*N*-*iso*propyl compound. It was shown, experimentally, and to a small extent by consideration of work of long standing in the literature, that : (1) the reaction did not proceed by way of the primary nitramine (Pr^i·NH·NO_2), and probably involved scission of the alkyl–nitrogen bond to yield Pr^{i+}; (2) the rate of decomposition was proportional to $[H^+][Pr^i·N:NO·OMe]$ over a 2000-fold range of concentration of hydrochloric acid; and (3) the reaction exhibited general acid-catalysis, since acetic acid had a catalytic effect additional to that dependent upon its ionisation. In a subsequent paper [2] further evidence was given for the production of alkyl cations by the heterolysis of the alkyl–nitrogen bond in primary nitramines and *ON*-dialkylnitramines.

---

* Part X, *J.*, 1956, 921.

[1] Bruck and Lamberton, *J.*, 1955, 3997.

[2] Bruck, Denton, and Lamberton, *J.*, 1956, 921.

Scission of the molecules $\mathrm{R{\cdot}NH{\cdot}NO_2}$ or $\mathrm{R{\cdot}N{:}NO{\cdot}OR'}$ thus occurs at the R–N bond, but another rupture is required to yield nitrous oxide, which is produced from both types of compound. By analogy with the acid-catalysed hydrolysis of esters,[3] this second rupture might occur in the dialkyl compounds at either the O–R′ or the N–OR′ bonds; for various reasons the possibility of O–R′ rupture can now be eliminated. In the first place, such a split would not lead directly to nitrous oxide, as does the breaking of the N–OR′ (and R–N) bonds. Secondly, the removal of R′ alone would give rise to the primary nitramine $\mathrm{R{\cdot}NH{\cdot}NO_2}$ by such a route as $\mathrm{R{\cdot}N{:}NO{\cdot}OR'} \xrightarrow{+\mathrm{H}^+} \mathrm{R{\cdot}N{:}NO{\cdot}\overset{+}{O}HR'} \xrightarrow{-\mathrm{R'}^+} \mathrm{R{\cdot}N{:}NO{\cdot}OH} \rightleftharpoons \mathrm{R{\cdot}NH{\cdot}NO_2}$; and there is no evidence of the production of either the cation $\mathrm{R'^+}$ or the nitramine $\mathrm{R{\cdot}NH{\cdot}NO_2}$. In our earlier paper[1] we stated this argument in more detail, and showed that *O*-methyl-*N*-*iso*propylnitramine did not yield *iso*propylnitramine in the course of decomposition. We have now examined *N*-methyl-*O*-*iso*propylnitramine (in which O–R′ fission would be facilitated by electron donation from the *iso*propyl group), but again decomposition does not proceed by way of hydrolysis to the primary nitramine. Further, the acid-catalysed decompositions of primary nitramines and of *ON*-dialkylnitramines are presumably closely allied, and O–H bond fission of the *aci*-form of a primary nitramine ($\mathrm{R{\cdot}N{:}NO{\cdot}OH}$) would be meaningless from the point of view of decomposition.

Finally, we have obtained positive evidence of N–OR′ bond fission by preparing and decomposing (+)-*O*-*sec.*-butyl-*N*-methylnitramine; the reaction cycle $(+)\text{-}\mathrm{Bu^sOH} \longrightarrow (-)\text{-}\mathrm{Bu^sBr} \longrightarrow (+)\text{-}\mathrm{Me{\cdot}N{:}NO{\cdot}OBu^s} \longrightarrow (+)\text{-}\mathrm{Bu^sOH}$ was performed with at least 56% retention of optical activity. Since considerable racemisation is known to occur on conversion of *sec.*-butyl alcohol into the bromide, the overall retention of 56% of the activity left little scope for racemisation at other stages, and the final decomposition must be highly stereospecific. This conclusion strongly favours scission of the $\mathrm{N{-}OBu^s}$ bond.

The mechanism of the reaction has been further studied by the extension of our previous work[1] on *O*-methyl-*N*-*iso*propylnitramine to a variety of *ON*-dialkylnitramines, and our results are presented in Tables 1 and 2. The rates of decomposition have been measured manometrically, or by observation of optical density in the ultraviolet region. These methods, based respectively on the appearance of the final product (Gas), and the disappearance of the nitramine (U.V.), had already been shown[1] to be in agreement for *O*-methyl-*N*-*iso*propylnitramine: whenever both methods were used on one compound the results now reported confirm (though see footnote to Table 1) our previous observations. Again, in accordance with the behaviour of *O*-methyl-*N*-*iso*propylnitramine, the rates of decomposition of all the compounds investigated were proportional to $[\mathrm{H^+}][\mathrm{R{\cdot}N{:}NO{\cdot}OR'}]$. The second-order rate coefficients are reported as the catalytic constants, $k_{\mathrm{H^+}}$; though the results given later in Table 5 also show that, where there is a difference, the proportionality is to the acidity function h_0, rather than to $[\mathrm{H^+}]$. The lines obtained by plotting the first-order rate coefficients in Table 1 against the acid concentration all converge on the origin; there is thus no appreciable catalysis by water at 45°.

Inspection of Table 1 shows that the $k_{\mathrm{H^+}}$ values fall into three main groups: those for the *N*-ethyl compounds are approximately 10 times, and those for the *N*-*iso*propyl compounds nearly 100 times as great as the values obtained for the *N*-methyl compounds. The values given in Table 2 may be included in the comparison, though not directly. The compounds dealt with therein were less soluble in water, and solvents containing 20—25% of methyl alcohol had to be used. Trials with *ON*-dimethylnitramine (Table 4) showed that this change reduced the rate by about 20%; conversely, we believe that if the catalytic constants of Table 2 are increased by one-quarter, the resultant figures compare reasonably with those in Table 1.

In Table 3 variations of the catalytic constant are set out in ratio form. It is obvious

[3] Ingold, "Structure and Mechanism in Organic Chemistry" Bell and Sons, London, 1953, Chapter XIV.

TABLE 1. *Decomposition of* ON-*dialkylnitramines, initially* 0·05M *in hydrochloric acid, at* 45°.

Run no.	Compound	Acid (mole l.$^{-1}$ at 20°)	Method of measurement	First-order rate coeff., 10^3k (min.$^{-1}$)	Catalytic constant, $k_{\mathrm{H^+}}$ (l. mole^{-1} min.$^{-1}$)
1	Me·N:NO·OMe	0·520	U.V.	25·0	0·048
2	,,	0·493	Gas	23·3	0·047
3	,,	0·300	Gas	16·4	0·055
4	,,	0·0250	U.V.	1·35	0·054
5	Me·N:NO·OEt	0·500	Gas	22·1	0·044
6	,,	0·300	Gas	12·9	0·043
7	,,	0·100	Gas	4·4	0·044
8	Me·N:NO·OPr$^{\mathrm{i}}$	0·500	Gas	18·8	0·038 *
9	,,	0·300	Gas	11·4	0·038 *
10	Et·N:NO·OMe	0·101	Gas	40·5	0·40
11	,,	0·0500	Gas	20·4	0·41
12	,,	0·0250	Gas	9·9	0·40
13	Et·N:NO·OEt	0·1007	Gas	37·8	0·38
14	,,	0·0250	Gas	10·4	0·42
15	Et·N:NO·OPr$^{\mathrm{i}}$	0·1007	Gas	29·0	0·29
16	,,	0·0500	Gas	14·3	0·29
—	Pr$^{\mathrm{i}}$N:NO·OMe	(From Part IX, *J.*, 1955, 3997)		—	3·6
17	Pr$^{\mathrm{i}}$N:NO·OEt	0·0250	U.V.	79·0	3·2
18	,,	0·0050	U.V.	16·5	3·3
19	,,	0·0050	Gas	16·0	3·2

* In this case only there is some discrepancy between the " gas " and " U.V." measurements: interpolation from U.V. results at 35°, 40°, and 50° (Table 4) gives 0·044 for this rate.

TABLE 2. *Decomposition of* ON-*dialkylnitramines, initially* 0·05M *in hydrochloric acid containing methanol, at* 45°.

Run no.	Compound	Acid (mole l.$^{-1}$ at 20°)	Method of measurement	First-order rate coeff., 10^3k (min.$^{-1}$)	Catalytic constant, $k_{\mathrm{H^+}}$ (l. mole^{-1} min.$^{-1}$)
20	Pr$^{\mathrm{i}}$·N:NO·OPr$^{\mathrm{i}}$	0·0250 (*a*)	U.V.	39·1	1·57
21	,,	0·0050 (*a*)	U.V.	7·9	1·59
22	,,	0·0050 (*a*)	Gas	8·2	1·65
23	Bu$^{\mathrm{t}}$·N:NO·OMe	$6{\cdot}85 \times 10^{-5}$ (*b*)	U.V.	23·5	291 (*c*)
24	,,	$9{\cdot}0 \times 10^{-5}$ (*b*)	U.V.	30·0	294 (*c*)
25	,,	$10{\cdot}5 \times 10^{-5}$ (*b*)	U.V.	33·0	281 (*c*)
26	,,	$20{\cdot}0 \times 10^{-5}$ (*b*)	U.V.	63·5	301 (*c*)
27	,,	$50{\cdot}1 \times 10^{-5}$ (*b*)	U.V.	154·0	303 (*c*)
56	,,	$18{\cdot}6 \times 10^{-5}$ (*b*)	U.V.	64·3	328 (*c*)
57	,,	$18{\cdot}6 \times 10^{-5}$ (*b*)	U.V.	62·1	317 (*c*)
28	$\mathrm{C_5H_{11}{}^{neo}}$·N:NO·OMe	0·100 (*a*)	U.V.	51·0	0·51
29	,,	0·050 (*a*)	U.V.	26·3	0·53
30	,,	0·025 (*a*)	U.V.	13·2	0·53

(*a*) Methanol, 25% v/v. (*b*) Methanol, 20% v/v. The acid concentration was determined by means of a pH meter. (*c*) *N-tert.*-Butyl-*O*-methylnitramine shows catalysis by water at 45°: the " spontaneous " rate (10^3k, 3·7 min.$^{-1}$ at 45°, see footnote, Table 4) has been deducted before calculation of the catalytic constant.

TABLE 3. *Values of the catalytic constant* $k_{\mathrm{H^+}}$ *for the decomposition of compounds* R·N:NO·OR′ *in water at* 45°, *set out as ratios.*

For changes in R, with R′ constant				For changes in R′, with R constant			
Nature of R	Nature of R′			Nature of R′	Nature of R		
	(1) Me	(2) Et	(3) Pr$^{\mathrm{i}}$		(4) Me	(5) Et	(6) Pr$^{\mathrm{i}}$
Me	1·0	1·0	1·0	Me	1·0	1·0	1·0
Et	8	9	7·5	Et	0·8$_5$	1·0	0·9
Pr$^{\mathrm{i}}$	71	73	50 †	Pr$^{\mathrm{i}}$	0·7$_5$	0·7	0·6 †
Bu$^{\mathrm{t}}$	7000 †	—	—				
$\mathrm{C_5H_{11}{}^{neo}}$	13 †	—	—				

* Size of unit in each vertical column: 1, 0·051; 2, 0·044; 3, 0·038; 4, 0·051; 5, 0·40; 6, 3·6 l. mole^{-1} min.$^{-1}$.

† Approx. values, based on 5/4 times observed rate in the presence of methanol.

that the rates of decomposition are connected with the ability of the group R (in R·N⁚NO·OR′) to release electrons by the inductive mechanism: the rates lie in the theoretical order Me $<$ Et $<$ Pr^i $\ll$ Bu^t, and *neo*-C_5H_{11} falls in the expected position between ethyl and *iso*propyl. In this, the reaction resembles the hydrolysis of alkyl bromides in moist formic acid, investigated by Hughes and his colleagues;[4] quantitatively, ethyl appears to be more, and *tert.*-butyl less, effective in the nitramine decomposition than in the bromide hydrolysis. As in the bromide hydrolysis, the rate for *neo*pentyl is comparable with that for ethyl; but in the nitramine decomposition the *neo*pentyl group appears to be the more effective. Dostrovsky and Hughes[4] considered that their values might still contain some contribution from a bimolecular mechanism of hydrolysis; and we suggest that the rate sequence for the *ON*-dialkylnitramine decomposition follows the theoretical one, for the inductive effect in a unimolecular mechanism, fully as well as in any other reaction previously investigated.

It thus seems safe to assume that the ease of fission of the *N*-alkyl bond plays a major part in the mechanism of decomposition. Changes in R′ have a comparatively small effect, in the opposite sense to changes in R. We regret that an attempt to prepare an *O-tert.*-butyl compound was unsuccessful.

Some measurements have been made of the parameters A and E in the kinetic equation $k = A \exp(-E/\mathbf{R}T)$. Good linear plots were obtained, in the range 25—50°, of log k_{H^+} against $1/T$(°K), and the results are given in Table 4. Comparison of the second and the last line of the Table shows that a change in the activation energy has been the main factor in determining the change in rate: the observed change in A acts in the opposite sense. The more rapid decomposition of Pr^{i}N⁚NO·OMe (line d) compared with Me·N⁚NO·OMe (line a) seems to be due partly to a fall in E, and partly to a rise in A; the values of the parameter A are reasonable, but inconclusive. If we write A in the form PZ, and take[5] the collision frequency Z to be 3×10^{11} l. mole^{-1} sec.$^{-1}$, then the values of the probability factor P range from 0·3 to 20: these slightly favour a unimolecular mechanism, since in only one case is P less than unity.[6]

TABLE 4. *The parameters A and E in the kinetic equation* $k = A \exp(-E/\mathbf{R}T)$.

Run nos., solvent, and notes	Compound (initially 0·05M)	Mean values of k_{H^+} (or k_{h_0} if applicable) in l. mole^{-1} min.$^{-1}$, measured by the U.V. technique at temperatures of					$\log_{10} A$ (l. mole^{-1} sec.$^{-1}$)	E (kcal. mole^{-1})
		25°	35°	40°	45°	50°		
a	Me·N⁚NO·OMe	0·0053	0·0178	0·0305	0·051	0·093	11·6	21·3
b	Me·N⁚NO·OMe	—	0·013	0·023	0·041	0·076	12·6	23·0
c	Me·N⁚NO·OPr^i	—	0·0153	0·0255	—	0·077	11·6	21·4
d	Pr^i·N⁚NO·OMe	0·38	1·29	2·13	3·60	5·95	12·8	20·4
e	Bu^t·N⁚NO·OMe	66	150	—	323	—	11·0	15·0

Run nos. are grouped in order of increasing temperature. a: 58; 31, 32; 33, 34; 1–4; 35, 36; in HCl–H_2O. b: 37; 38; 39; 40; in HCl–H_2O–MeOH, H_2O–MeOH 80/20, v/v. c: 41, 42; 43, 44; 45, 46; in HCl–H_2O. d: 25° and 45°, *loc. cit.*[1]; remaining temp., 47, 48; 49; 50, 51; in HCl–H_2O. e: 52, 53; 54, 55; 56, 57; all in the same solvent (HCl–H_2O–MeOH, H_2O–MeOH 80/20, v/v) of [H^+] $1·86 \times 10^{-4}$ mole l.$^{-1}$ at 25°, to avoid errors in E which might be introduced by the measurement of various pH values; and after making allowance for water catalysis. Water-catalysis gave the following rates in 0·015M-sodium hydroxide solution: 10^3k 3·7, 1·0, and 0·2 min.$^{-1}$ at, respectively, 45°, 35°, and 25°.

Reference has already been made, on several occasions in this paper, to the catalytic constant k_{h_0} as an alternative to k_{H^+}. In dilute acid, when the Hammett acidity function H_0 is equal to pH, k_{h_0} is identical with k_{H^+}. In more concentrated acid, the rate of a unimolecular acid-catalysed reaction is dependent upon the acidity function, whilst the rate of a bimolecular reaction involving a molecule of water depends on the stoicheiometric

---

[4] Bateman and Hughes, *J.*, 1940, 945; Dostrovsky and Hughes, *J.*, 1946, 171.

[5] Hammett, " Physical Organic Chemistry," McGraw-Hill, New York, 1940, p. 115.

[6] Hinshelwood and Winkler, *J.*, 1936, 376.

concentration of hydrogen ion.[7] Application of this test to *ON*-dimethylnitramine (Table 5) showed that water is not covalently involved in the rate-determining stage of the decomposition: graphically the plot of $\log_{10}k$ against H_0 is linear, with unit slope, whilst that against pH is curved. A similar conclusion can be drawn for *N-iso*propylnitramine, though with less certainty, from the results reported in Table 6: in this case the best line in the plot of $\log_{10}k$ against H_0 has a slope of 0·94, whilst the values from runs 64, 65, and 66 are precisely linear, with a slope of 0·91.

TABLE 5. *Decomposition of* ON-*dimethylnitramine, initially* 0·05M *in hydrochloric acid, at* 25°.

Run no.	$[H^+]$ (mole l.$^{-1}$ at 25°)	h_0 at 25°	10^3k_1 (min.$^{-1}$)	$10^3k_{H^+}$ (l. mole^{-1} min.$^{-1}$)	$10^3k_{h_0}$ (l. mole^{-1} min.$^{-1}$)
58	1·01	1·15	6·1	5·9	5·3
59	2·25	4·17	22·5	10	5·4
60	3·01	8·22	46	15	5·6
61	4·07	19·05	104	26	5·5
62	5·01	41·70	256	51	6·0

All measurements were made by the U.V. method. The h_0 figures are derived from published values [8] of H_0.

TABLE 6. *Decomposition of* N-iso*propylnitramine, initially* 0·05M *in hydrochloric acid, at* 45°.

Run no.	$[H^+]$ (mole l.$^{-1}$ at 25°)	h_0 at 25°	10^3k_1 (min.$^{-1}$)	$10^3k_{H^+}$ (l. mole^{-1} min.$^{-1}$)	$10^3k_{h_0}$ (l. mole^{-1} min.$^{-1}$)
63	0·77	0·89	0·75	0·97	0·84
64	2·20	4·1	3·3	1·5	0·80
65	3·10	7·9	6·0	1·9	0·76
66	4·40	25·1	13·3	3·0	0·53

All measurements were made by the manometric method. The h_0 figures are derived from published values [8] of H_0.

DISCUSSION

It was recognised by early workers that the acid-catalysed decomposition of nitramines was linked with the occurrence of the " iso " structure (·N:NO·O·), either as such in the molecule (*e.g.*, *ON*-dialkylnitramines, R·N:NO·OR′), or as a possible tautomer (*e.g.*, primary nitramines, $R{\cdot}NH{\cdot}NO_2 \rightleftharpoons R{\cdot}N{:}NO{\cdot}OH$). Of the other groups of aliphatic *N*-nitro-compounds at present known, two—the secondary nitramines [$(Alkyl)_2N{\cdot}NO_2$] and the secondary nitramides [$(Alkyl)(Acyl)N{\cdot}NO_2$]—cannot give rise to " iso " structures, and are remarkably stable in acid media.[9] The remaining group—the primary nitramides ($Acyl{\cdot}NH{\cdot}NO_2$)—can give rise to " iso " structures, and are in fact irreversibly decomposed by acid, though relatively slowly. The kinetics of this reaction have not been investigated in detail, but, at least in the case of nitroguanidine,[10] the products have been successfully predicted by analogy with the acid-catalysed decomposition of primary nitramines: salts of nitroguanidine [*e.g.*, $NO_2{\cdot}NH{\cdot}C(NH_2)_2{}^+X^-$] were classified as primary nitramides, since the amidinium portion $C(NH_2)_2{}^+$ could be regarded as acylic in character.[10]

For those groups which are relatively stable in acids—in particular the nitramides, both primary and secondary—the position is complicated by denitration as an alternative mode of decomposition. In suitable solvents (60% $HClO_4$, 80—100% H_2SO_4) equilibrium is established between nitration and denitration.[11] In general, primary nitramides are more rapidly decomposed by the denitration reaction than by the irreversible decomposition

---

[7] Ingold, *op. cit.* (ref. 3), p. 772; Hawke and Stimson, *J.*, 1956, 4676, give a number of recent references.

[8] Bell, Dowding, and Noble, *J.*, 1955, 3106.

[9] Holstead and Lamberton, *J.*, 1952, 1886.

[10] *Idem, J.*, 1954, 2391.

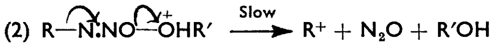
[11] Simkins and Williams, *J.*, 1952, 3086; 1953, 1386; Holstead, Lamberton, and Wyatt, *J.*, 1953, 3341; Holstead and Lamberton, *J.*, 1953, 3349; Hardy-Klein, *J.*, 1957, 70.

with which we are here concerned; but the irreversible decomposition is distinct in that it gives different products and, in particular, results in the loss of nitrogen from the system in the form of nitrous oxide.

In this, and earlier papers (refs. 1, 2, 12, 13) it has been shown that the acid-catalysed irreversible decomposition of the structure R·N:NO·OR′ (R = alkyl, R′ = alkyl or H) (*a*) involves scission of the molecule at the R–N and N–OR′ bonds, (*b*) gives rise to the ion R^+, (*c*) is favoured by electron-donation from R, and (*d*) proceeds at a rate directly proportional to the ability of the solvent and solute molecules, taken as a whole, to furnish protons to the molecule which will undergo decomposition.

These results suggest a mechanism of decomposition analogous to the mode of acid hydrolysis of esters which Ingold[3] designates as $A_{AC}1$, but with an additional shift of electrons leading to the liberation of the cation R^+ (equations 1 and 2).

$$\text{(1)}\quad \mathrm{R{\cdot}N{:}NO{\cdot}OR' + H^+ \overset{Fast}{\rightleftharpoons} R{\cdot}N{:}NO{\cdot}\overset{+}{O}HR'}$$



$$\text{(2)}\quad \mathrm{R{-}N{:}NO{-}\overset{+}{O}HR' \xrightarrow{Slow} R^+ + N_2O + R'OH}$$

The Arrhenius parameters are at least consonant with this mechanism. The dispersion of charge, in the transition state of (2), should produce a slight increase of rate on reducing the polarity of the solvent.[14] We find in fact a slight decrease : this may well be due to an alteration in equilibrium (1)—*i.e.*, to a less efficient catalysis, by a given quantity of acid, in the less polar medium.

For simplicity, we prefer to present the bond scissions as concurrent parts of a single mechanistic stage. The scissions may, however, be successive; in this case the protonated complex would break down according to equations (3) and (4), or (5) and (6).

$$\text{(3)}\quad \mathrm{R{\cdot}N{:}NO{\cdot}\overset{+}{O}HR' \xrightarrow{Slow} R{\cdot}N{:}\overset{+}{N}O + R'OH}$$

$$\text{(4)}\quad \mathrm{R{\cdot}N{:}\overset{+}{N}O \xrightarrow{Fast} R^+ + N_2O}$$

$$\text{(5)}\quad \mathrm{R{\cdot}N{:}NO{\cdot}\overset{+}{O}HR' \xrightarrow{Slow} R^+ + \overset{-}{N}{:}NO{\cdot}\overset{+}{O}HR'}$$

$$\text{(6)}\quad \mathrm{\overset{-}{N}{:}NO{\cdot}\overset{+}{O}HR' \xrightarrow{Fast} N_2O + R'OH}$$

Both R and R′ have an influence upon the rate of decomposition, and though the evidence is weaker for R′ than for R, it certainly rules out reaction (6), and probably reaction (4), as rate-determining stages: (4) and (6), if they occur at all, must be fast with respect to (3) and (5). It should be added that, in principle, reactions (3) and (5) could be treated as rapidly established equilibria, and variations in R and R′ could exert their effect by changing the position of equilibrium. If this were so, reactions (4) and (6) could be rate-determining; but we suggest that this treatment is inadmissible in the context of the actual conditions of the decomposition. In (3) there would seem to be no good reason to postulate the reaction of $\mathrm{R{\cdot}N{:}\overset{+}{N}O}$ exclusively with R′OH rather than with water molecules, which are at least a thousand times more numerous; and any reaction with water molecules would remove $\mathrm{R{\cdot}N{:}\overset{+}{N}O}$ to produce the relatively stable primary nitramine $\mathrm{R{\cdot}NH{\cdot}NO_2}$—which is not observed. Similarly, (5) could not be formulated as an equilibrium, since R^+ would be removed by reaction with water, or olefin formation: decomposing solutions would contain $\mathrm{\overset{-}{N}{:}NO{\cdot}\overset{+}{O}HR'}$ (or a tautomer thereof), and the ultraviolet absorption spectrum would be changed. Quite generally, the agreement between the spectroscopic and the manometric method of analysis suggests the first bond-scission to

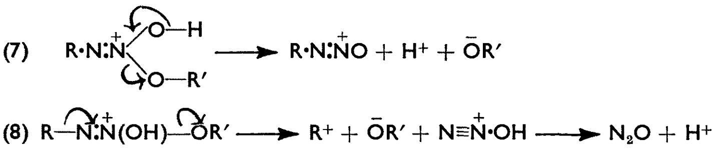
---

[12] Barrott, Denton, and Lamberton, *J.*, 1953, 1998.
[13] Denton and Lamberton, *J.*, 1955, 1655.
[14] Ingold, *op. cit.* (ref. 3), p. 347.

be rate-determining; and whilst we do not deny that (3) and (5)—if they occur at all—are in theory reversible, we consider that the extent of any reverse reaction cannot be of significance.

We would formulate the acid-catalysed decomposition of primary nitramines in similar terms (*viz.*, equations 1 and 2, R = alkyl, R′ = H). The observed rate of decomposition will here depend, not only on the stability of the structure $R{\cdot}N{:}NO{\cdot}OH$, but also on the position of the tautomeric equilibrium $R{\cdot}NH{\cdot}NO_2 \rightleftharpoons R{\cdot}N{:}NO{\cdot}OH$, which is probably very largely to the left. Variations in the position of equilibrium, with variable R, may well account for the incomplete correlation, in the primary nitramine series, of electron-donation by R with the observed rate of decomposition.[12,13]

Site of Initial Protonation.—Our choice (equation 1) was made on grounds of analogy with ester hydrolysis, and since this position of protonation leads most simply to the known products of the reaction; but alternative structures of the protonated complex are conceivable. We exclude $R{\cdot}\overset{+}{N}H_2{\cdot}NO_2$ and $R{\cdot}NH{\cdot}\overset{+}{N}O{\cdot}OH$, since these are not consistent with the stability of structures such as $R_2N{\cdot}NO_2$; and for this reason we now feel that the step $R{\cdot}NH{\cdot}NO_2 + H^+ \longrightarrow R^+ + H_2N{\cdot}NO_2$, suggested in an earlier paper,[12] is unlikely. The complex $R{\cdot}\overset{+}{N}H{:}NO{\cdot}OR'$ could initiate a decomposition analogous to equation (5), but would provide no immediate reason for the fission of the $N{-}OR'$ bond; $R{\cdot}N{:}\overset{+}{N}(OH){\cdot}OR'$ could initiate processes such as (7) or (8):



(7) $R{\cdot}N{:}\overset{+}{N}(OH)(OR') \longrightarrow R{\cdot}N{:}\overset{+}{N}O + H^+ + \overset{-}{O}R'$

(8) $R{-}N{:}\overset{+}{N}(OH){-}OR' \longrightarrow R^+ + \overset{-}{O}R' + N{\equiv}\overset{+}{N}{\cdot}OH \longrightarrow N_2O + H^+$

It is clear that the presence (or absence) of nitramine ($H_2N{\cdot}NO_2$) as an intermediate would be to some extent diagnostic. Though Davis and Blanchard[15] reported the isolation, under certain conditions, of nitramine from nitrourea, we still regard this as an open question: we have been unable, as yet, to find any sign of nitramine in decomposing solutions of primary nitramines; methylenedinitramine[16] is exceptional, and a special case. To sum up: we do not imply that these alternative protonations are impossible, but merely that they seem, on the basis of our present knowledge, to be less relevant to the process of irreversible decomposition.

EXPERIMENTAL

Reaction rates were evaluated on the basis of natural logarithms, and temperatures were controlled to within one-tenth of a degree. Acid concentrations have been corrected on the assumption that the solutions showed the same expansion as water over the range 20—50°; but, in the absence of suitable data, the h_0 values used [8] relate to 25°. The methods of measurement by the manometric [12] and spectroscopic [1] techniques have been previously described.

All compounds reported as *ON*-dialkylnitramines gave an immediate evolution of gas on treatment with 40% sulphuric acid at room temperature. *NN*-Dialkylnitramines can readily be freed from traces of their *ON*-isomerides by treatment with 40% sulphuric acid, but no method, other than repeated distillation, is yet known for the purification of the *ON*-dialkylnitramines. All the *ON*-dialkylnitramines used for kinetic observations were distilled at least twice or thrice. Even so, the residual ultraviolet absorption after decomposition indicated, in a few cases, the presence of traces of the stable *NN*-isomeride; quantitatively, the proportion of the *NN*-isomeride was never greater than 5%. Since the reaction kinetics, in a given medium, are of the first order, the results obtained manometrically are unaffected by traces of the stable

[15] Davis and Blanchard, *J. Amer. Chem. Soc.*, 1929, **51**, 1790.

[16] Lamberton, Lindley, and Speakman, *J.*, 1949, 1650.

isomeride. In the determination of rates by the spectroscopic method allowance was made, whenever necessary, for the (constant) absorption produced by traces of the *NN*-isomeride.

The silver salts employed in alkylation were precipitated from water by the action of a slight excess of silver nitrate on the *iso*propylammonium or *cyclo*hexylammonium salts of the primary nitramines: they were collected, washed successively with water, acetone, and ether, and " dried " *in vacuo*. The nitramines themselves were prepared by standard methods; [12, 13, 14] the following salts appear to be new: cyclo*hexylammonium methylnitramine*, needles, m. p. 130—131° from ethanol–chloroform (Found: C, 47·9; H, 9·7. $C_7H_{17}O_2N_3$ requires C, 48·0; H, 9·7%); *cyclo*hexylammonium *tert.*-butylnitramine, microcrystalline, m. p. 125—126°; iso*propylammonium* neo*pentylnitramine*, nacreous plates, m. p. 128°, from ethanol–ether (Found: C, 50·0; H, 10·8; N, 21·6. $C_8H_{21}O_2N_3$ requires C, 50·2; H, 11·0; N, 22·0%).

O-*Alkyl*-N-*methylnitramines*.—The *O*-methyl and *O*-*iso*propyl compounds have recently been described.[1] The *O*-ethyl compound, prepared by the same general method, had b. p. 40—42°/20 mm. (Found: C, 34·3; H, 7·6. Calc. for $C_3H_8O_2N_2$: C, 34·6; H, 7·7%): Franchimont and Umbgrove [18] reported b. p. 35°/16 mm. Refluxing a suspension of the silver salt of methylnitramine (7 g.) in ether (75 ml.) and *sec.*-butyl bromide (10 g.) for 12 hr. yielded, after removal of silver bromide and subsequent fractional distillation, (±)-O-sec.-*butyl*-N-*methylnitramine* (2 g.), b. p. 73—75°/40 mm. (Found: C, 45·2; H, 9·1. $C_5H_{12}O_2N_2$ requires C, 45·5; H, 9·1%).

O-*Alkyl*-N-*ethylnitramines*.—The following were prepared by the same general method (above, and ref. 1): *N*-ethyl-*O*-methylnitramine, b. p. 52—53°/40 mm. (Found: C, 34·8; H, 7·8. Calc. for $C_3H_8O_2N_2$: C, 34·6; H, 7·7%) (Franchimont and Umbgrove [18] gave b. p. 36—38°/20 mm.): *ON*-diethylnitramine, b. p. 45—47°/18 mm. (Found: C, 40·7; H, 8·7. Calc. for $C_4H_{10}O_2N_2$: C, 40·7; H, 8·5%) (Franchimont and Umbgrove [18] gave b. p. 46—50°/18 mm): N-*ethyl*-O-iso*propylnitramine*, b. p. 50—54°/18 mm. (Found: C, 45·8; H, 9·2. $C_5H_{12}O_2N_2$ requires C, 45·5; H, 9·1%).

O-*Alkyl*-N-iso*propylnitramines*.—The *O*-methyl and *O*-*iso*propyl compounds have recently been described.[1] O-*Ethyl*-N-iso*propylnitramine*, prepared in the same manner, had b. p. 64—65°/30 mm. (Found: C, 45·8; H, 9·2. $C_5H_{12}O_2N_2$ requires C, 45·5; H, 9·1%).

N-tert.-*Butyl*-O-*methylnitramine*.—The silver salt of *tert.*-butylnitramine (11 g.) was set aside at room temperature for 10 days with methyl iodide (10 ml.) in ether (125 ml.), and the mixture thereafter refluxed for 4 hr. Removal of silver iodide, and subsequent fractional distillation, yielded N-tert.-*butyl*-O-*methylnitramine*, b. p. 59—61°/35 mm. (Found: C, 45·8; H, 8·8. $C_5H_{12}O_2N_2$ requires C, 45·5; H, 9·1%).

Miscellaneous Compounds, and an Unsuccessful Preparation.—*O*-Methyl-*N*-*neo*pentylnitramine has recently been described.[1] The *O*- and *N*-methyl derivatives of *N*-*cyclo*hexylnitramine have been prepared, but not examined kinetically. The *cyclo*hexylammonium salt [17] of *cyclo*hexylnitramine was converted into the silver salt, and alkylated to yield N-cyclo-*hexyl-O-methylnitramine*, b. p. 100—101°/17 mm. (Found: C, 53·2; H, 8·9; N, 17·3. $C_7H_{14}O_2N_2$ requires C, 53·2; H, 8·9; N, 17·7%). *N*-Methyl*cyclo*hexylamine hydrochloride was nitrated, by the method of Kingdon and Wright,[19] to yield N-cyclo*hexyl*-N-*methylnitramine*, b. p. 88—89°/0· mm. (Found: C, 53·5; H, 9·0; N, 17·6%). An attempt to prepare *O*-*tert.*-butyl-*N*-methylnitramine was unsuccessful: on addition of *tert.*-butyl iodide (15 g.) to the silver salt of methylnitramine (8·5 g.) in ether (100 ml.) a vigorous reaction occurred; gaseous products were evolved, and the ether boiled. The mixture was cooled, and thereafter kept in the dark for 4 days. On working up in the usual manner (but with a thiosulphate wash to remove iodine) no isolable product was obtained.

Evidence against the Formation of Methylnitramine during the Decomposition of N-*Methyl*-O-iso*propylnitramine*.—A solution of *N*-methyl-*O*-*iso*propylnitramine (0·2508 g.) in 0·1M-hydrochloric acid (50 ml.) was kept at 45°, and samples (5 ml.) were withdrawn at once, and after time intervals known to correspond to 10, 20, 30, 40, 50, 60, 75, and 100% decomposition. All the samples had a titre of 9·4 ± 0·05 ml. of 0·0502M-sodium hydroxide. Methylnitramine did not undergo any decomposition in similar conditions of time (24 hr.), temperature, and acidity: a 1% yield of methylnitramine would have raised the sodium hydroxide titre by 0·042 ml.

---

[17] Curry and Mason, *J. Amer. Chem. Soc.*, 1951, **73**, 5042.

[18] Franchimont and Umbgrove, *Rec. Trav. chim.*, 1897, **16**, 359.

[19] Kingdon and Wright, *J. Amer. Chem. Soc.*, 1950, **72**, 1030.

The Reaction-cycle (+)-sec.-*Butyl Alcohol* $\longrightarrow$ (−)-sec.-*Butyl Bromide* $\longrightarrow$ (+)-O-sec.-*Butyl*-N-*methylnitramine* $\longrightarrow$ (+)-sec.-*Butyl Alcohol*.—Optically active *sec.*-butyl alcohol ($[\alpha]_D^{23}$ $+12{\cdot}3°$; 89·5% optically pure), prepared *via* the brucine hydrogen phthalate,[20] was converted into *sec.*-butyl bromide by Letsinger's [21] modification of the method of Levene and Marker.[22] The product had $[\alpha]_D^{21}$ $-17{\cdot}3°$. The reaction is known to occur with reversal of configuration and considerable racemisation: on the basis of Letsinger's [21] largest (calculated) value ($-26{\cdot}1°$) for the (−)-bromide, our product was of *not more* than 66% optical purity. This was used to alkylate the silver salt of methylnitramine, and yielded an active sample of *O-sec.*-butyl-*N*-methylnitramine, $[\alpha]_D^{21}$ $+11{\cdot}1°$, d_4^{21} 0·978 (Found: C, 45·3; H, 9·0%. For preparation and required values, see under *O*-alkyl-*N*-methylnitramines, p. 4205). By analogy with the work of Kornblum [23] on the alkylation of silver nitrite, the nitramine is probably formed with reversal of configuration, and very little racemisation: if so, pure (+)-*O-sec.*-butyl-*N*-methylnitramine would have $[\alpha]_D^{21}$ at least $+17°$. This estimate is not essential for our argument.

Active samples of *O-sec.*-butyl-*N*-methylnitramine were heated in sealed Pyrex tubes with acidified aqueous methanol until decomposition was complete, as indicated by constancy of optical rotation. Active *sec.*-butyl alcohol was unaffected by the same treatment. Duplicate experiments were carried out, with consistent results, and details are given of one set. A solution of *O-sec.*-butyl-*N*-methylnitramine [65·4 mg. made up to 1·27 ml. with methanol–water (60/40, v/v, 0·5M in hydrochloric acid); *c* 5·15%] had α_D^{21} (100 mm.) $+$ 0·64°, $[\alpha]_D^{21}$ $+12{\cdot}4°$. After 60 hr. at 60° (thermostat), the observed rotation, α_D^{21} (100 mm.), had fallen to $+0{\cdot}21°$, unchanged by a further 30 hours' heating. Quantitative liberation of the alcohol from 65·4 mg. of the *O-sec.*-butylnitramine would yield 36·7 mg. of *sec.*-butyl alcohol: hence the concentration of *sec.*-butyl alcohol in the spent solution is not more than 2·89%, and $[\alpha]_D^{21}$ not less than $+7{\cdot}3°$. A sample of the initial butyl alcohol, at comparable concentration in the same solvent, showed a negligible change (α_D^{21} $+0{\cdot}37° \longrightarrow +0{\cdot}36°$) on 70 hours' heating at 60°; the mean value gives $[\alpha]_D^{21}$ $+13{\cdot}0°$ (*c* 2·81). The alcohol produced from the nitramine cannot therefore be less than $7{\cdot}3 \times 100/(13{\cdot}0 \times 100/89{\cdot}5) = 50\%$ optically pure, and was derived from a bromide which could not have been more than 66% optically pure: the retention of activity through the whole series alcohol $\longrightarrow$ bromide $\longrightarrow$ nitramine $\longrightarrow$ alcohol is not less than $7{\cdot}3 \times 100/13{\cdot}0 = 56\%$.

We thank the Department of Scientific and Industrial Research for a Maintenance Grant (to P. B.).

STAVELEY CHEMICAL LABORATORIES,
THE UNIVERSITY, SHEFFIELD, 10.

[*Received, May 9th,* 1957.]

---

[20] Pickard and Kenyon, *J.*, 1911, 45; Ingersoll, "Organic Reactions," Vol. II, Wiley and Sons, New York, 1944, p. 403; Stevens, Morrow, and Lawson, *J. Amer. Chem. Soc.*, 1955, **77**, 2341.

[21] Letsinger, *J. Amer. Chem. Soc.*, 1948, **70**, 406.

[22] Levene and Marker, *J. Biol. Chem.*, 1931, **91**, 412.

[23] Kornblum, *J. Amer. Chem. Soc.*, 1955, **77**, 6261, 6269.