407. *Nitramines and Nitramides. Part IV.* The Acid-catalysed Decomposition of Primary Nitramines.*

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The decomposition of primary nitramines by aqueous acids probably proceeds by formation of nitramine ($NH_2{\cdot}NO_2$) and an alkyl cation. The former then yields nitrous oxide and water, whilst the latter reacts with water to give an alcohol, or loses a proton to yield an olefin, or combines with anions (*e.g.*, Cl^-) which are present in the solution. The reaction is bimolecular, the rate being $\propto [H^+][R{\cdot}NH{\cdot}NO_2]$, and is formulated as an S_E2 substitution on the " amino "-nitrogen atom: $R{\cdot}NH{\cdot}NO_2 + H^+ \longrightarrow R^+ + NH_2{\cdot}NO_2$. Electron-donation by R seems to favour decomposition, though $Bu^t{\cdot}NH{\cdot}NO_2$ is anomalous; relative rates are: $R = Pr^i > Et$ or $Bu^t > Me \gg CH_2{\cdot}CO_2H$. Precise results could not be obtained for the step-wise decomposition of the common dinitramines, but the rates fall qualitatively into a similar order.

The decomposition of primary nitramines by aqueous sulphuric acid was investigated by early workers (Van Romburgh, *Rec. Trav. chim.*, 1888, **7**, 246; Franchimont and Klobbie, *ibid.*, p. 350; Van Erp, *ibid.*, 1895, **14**, 40; Franchimont and Umbgrove, *ibid.*, 1898, **17**, 287), who found that nitrous oxide was the main, and probably the only, nitrogenous product. The reaction was formulated as $R{\cdot}NH{\cdot}NO_2 \longrightarrow ROH + N_2O$; but this appears to be an over-simplification, since Van Erp (*loc. cit.*) found that *n*-hexylnitramine yielded (besides nitrous oxide) two hexyl alcohols, a hexene, and a dihexyl ether. Van Romburgh (*loc. cit.*) found that ethylenedinitramine gave rise to an aldehyde: this was shown to be acetaldehyde by Lamberton, Lindley, Owston, and Speakman (*J.*, 1949, 1645).

We have re-investigated briefly the products of decomposition. In preliminary experiments, accurate to 5%, it was found that methyl-, ethyl-, and *iso*propyl-nitramine yielded, respectively, 1·0, 1·2, and 1·15 mols. of gas when heated with 0·5M-sulphuric acid,

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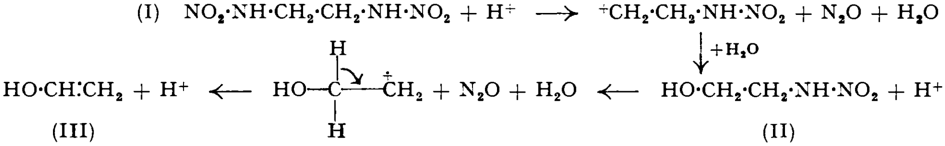
* Part III, *J.*, 1952, 1886.

whilst ethylenedinitramine yielded 1·95 mols. under the same conditions. Methylnitramine gave 1·45 mols. of gas on being heated with 1·0M-hydrochloric acid. In all cases 93—98% of the gas evolved could be removed by dissolution in ethanol: 98% of nitrous oxide was found in a more precise analysis of the gas evolved from methylnitramine and dilute sulphuric acid. Tomlinson (*J. Org. Chem.*, 1952, **17**, 648) appears to imply that a considerable quantity of nitrogen is produced from ethylenedinitramine and dilute sulphuric acid, but we are informed (personal communication) that this analysis is suspect, and under re-examination.

The excess of gas from ethyl- and *iso*propyl-nitramine was presumably (cf. Van Erp, *loc. cit.*) the corresponding olefin and, apart from a qualitative confirmation—by bubbling it through bromine water—was not specifically investigated. The unexpected excess of alcohol-soluble gas from methylnitramine and 1·0M-hydrochloric acid was shown to be methyl chloride by treatment of the alcoholic solution with pyridine and recognition of the ionisable chloride thus formed. Methyl chloride was not formed from methyl alcohol and hydrochloric acid under comparable conditions; this suggested, and subsequent experiments largely confirmed, that methyl ions were formed during the decomposition. The production of alkyl cations also affords a ready explanation of the formation of olefins, and of the conversion of ethylenedinitramine (I), *via* 2-hydroxyethylnitramine (II), into acetaldehyde (III).

The non-gaseous reaction products were also examined. Methylnitramine (0·05M) gave a 95% yield of methyl alcohol, as determined by chromic acid oxidation of the residual solution in 0·5M-sulphuric acid after complete decomposition, and the remainder of the original alkyl content may have been converted into methyl hydrogen sulphate, which is stable to the oxidising agent. Ethylenedinitramine under similar conditions gave a 46% yield of acetaldehyde, as determined by precipitation of the 2 : 4-dinitrophenylhydrazone; the results of chromic acid oxidation were consonant with the formation of *ca.* 45% of acetaldehyde and 55% of ethylene glycol. Trimethylenedinitramine (0·05M) in sulphuric acid (0·5M) gave, apparently, some propaldehyde; purification of the 2 : 4-dinitrophenylhydrazone was difficult and we submit this conclusion with reserve. No trace of 2 : 4-dinitrophenylhydrazones was obtained from any of the mononitramines.



(I) $NO_2\cdot NH\cdot CH_2\cdot CH_2\cdot NH\cdot NO_2 + H^+ \longrightarrow {}^+CH_2\cdot CH_2\cdot NH\cdot NO_2 + N_2O + H_2O$

$$\downarrow +H_2O$$

$$HO\cdot CH{:}CH_2 + H^+ \longleftarrow HO-\overset{H}{\underset{H}{C}}-\overset{+}{C}H_2 + N_2O + H_2O \longleftarrow HO\cdot CH_2\cdot CH_2\cdot NH\cdot NO_2 + H^+$$

(III) (II)

Apart from Tomlinson's work (*loc. cit.*) on ethylenedinitramine, which came to our notice after the completion of the major part of this research, no kinetic investigation of the decomposition has been published. The course of the reaction has been followed by measurement of the increase in pressure of gas confined at constant volume and temperature over a solution of the nitramine in dilute sulphuric acid; and, when the content of mineral acid was not more than four times that of the nitramine, by direct titration with alkali. In the first of these methods it is assumed that the measured rate of gas evolution, of whatever nature, is proportional to the rate of decomposition of the primary nitramine. We believe this assumption to be justified since (1) the formation of an olefin from an alkyl cation must be relatively very rapid, and (2) we have shown that nitramine ($NH_2\cdot NO_2$), which we consider to be an intermediate, decomposed (in the conditions employed) at least ten times faster than any of the primary nitramines investigated. Furthermore, the second (acidimetric) method gave, in the cases where it could be employed, results in reasonable agreement with those obtained manometrically. These conclusions apply to the mononitramines but not, without qualification (p. 2001), to the step-wise decomposition of dinitramines such as (I).

At constant acidity the mononitramines were found, by either method, to decompose in good accordance with the first-order reaction-rate law. The first-order rate coefficients thus obtained were directly proportional to the hydrogen-ion content of the solutions.

The reaction is thus bimolecular, and its speed proportional to $[H^+][R\cdot NH\cdot NO_2]$. Table 1 gives in column 5 the measured first-order coefficients, and in column 6 the corresponding second-order coefficients. Though the results obtained by acidimetry were of the same order as those obtained manometrically, they tended to be higher, especially in the case of ethylnitramine. The manometric results were more consistent than the acidimetric, but we believe the latter to be a sounder measure, in theory, of the rate of decomposition. It would be over-confident to assert that the true rates of decomposition have been ascertained with a precision greater than, say, 20%; but it can be seen that the second-order rate coefficient at 85° [10^3k, (mole/l.)$^{-1}$ min.$^{-1}$] is about 30 for methylnitramine, 40 for ethyl- or *tert.*-butyl-nitramine, 60 for *iso*propylnitramine, and only 1 for nitramino-acetic acid.

TABLE 1. *Decomposition of the nitramines,* $R\cdot NH\cdot NO_2$, *initially* 0·05M *in aqueous sulphuric acid, at* 85° ± 0·2°.

1 Run no.	2 R	3 H_2SO_4 (mole/l., at 20°)	4 Method employed	5 First-order rate coefficient, 10^3k (min.$^{-1}$)	6 Second-order rate coefficient, 10^3k [(mole/l.)$^{-1}$ min.$^{-1}$]
I, II	Me	0·500	Manometric	14·8, 15·7	31
XXVIII	,,	0·050	Acidimetric	1·5	30
III, IV	Et	0·500	Manometric	18·1, 18·3	37
V	,,	0·250	,,	9·9	41
VI	,,	0·050	,,	1·9	38
XXIX, XXX	,,	0·050	Acidimetric	2·5, 2·5	50
VII, VIII	Pr^i	0·500	Manometric	26·8, 25·6	54
IX	,,	0·250	,,	14·0	57
X	,,	0·100	,,	5·5	56
XI	,,	0·050	,,	2·7	54
XXXI to XXXVI	,,	0·050	Acidimetric	2·7 to 3·4	63
XLIV	Bu^t	0·101	Acidimetric	4·1	41
XLV, XLVI	,,	0·050	,,	2·0, 2·0	40
XII	$CH_2\cdot CO_2H$	0·500	Manometric	0·6	1

Values in column 6 are the average of the figures in column 5, divided by the appropriate value of $[H^+]$.

We suggest that the rate-determining stage of the decomposition should be formulated as $R\cdot NH\cdot NO_2 + H^+ \longrightarrow R^+ + NH_2\cdot NO_2$, that is, as an S_E2 substitution of R by H on the "amino"-nitrogen atom. It would be possible to formulate the reaction as proton addition, followed by ionisation of $[R\cdot N_2H_2O_2]^+$: on grounds of simplicity we prefer the single-stage reaction. The nitramine ($NH_2\cdot NO_2$) formed subsequently yields nitrous oxide and water, whilst the alkyl cation attacks, in the main, water to yield the alcohol ROH and restore the hydrogen-ion concentration of the solution.

Two points, at least, arise from this hypothesis. First, if a primary nitramine is decomposed by heating it with water alone, the reaction should no longer be pseudo-unimolecular, since the hydrogen-ion concentration falls as the nitramine is destroyed. In theory, since primary nitramines are weak acids, $[H^+] \propto \sqrt{[\text{Nitramine}]}$, and the order of reaction should be 1·5. To obtain measurable rates of reaction, we were obliged to work with concentrated (up to 2M) solutions of methylnitramine and, even so, only the first 20% of decomposition could be observed in a reasonable time. The order of the reaction was about 1·3 with respect to the methylnitramine, and the rate was clearly dependent upon the initial concentration. Similar results (see p. 2004) have been obtained by the use of ethylenedinitramine.

Secondly, the formation of alkyl cations should be capable of quantitative as well as qualitative demonstration. If the alkyl ions react with chloride ions instead of water, the overall decomposition becomes $R\cdot NH\cdot NO_2 + H^+ + Cl^- \longrightarrow RCl + H_2O + N_2O$. The acidity of the solution decreases by two equivalents for every equivalent of the primary nitramine destroyed, and one equivalent of chloride ion disappears. This effect has been demonstrated in certain cases. A 1·0M-solution of the nitramine in 1·02M-hydrochloric acid was kept at 85° until decomposition was complete, and the percentage yield of alkyl halide determined by (*a*) the reduction in Cl$^-$ content and (*b*) the fall in acidity over and above that due to the disappearance of the primary nitramine. As expected, the yields indicated (see Table 2) were reduced in less concentrated hydrochloric acid, and enhanced by the addition of chloride ions in the form of sodium chloride.

Since *iso*propylnitramine yielded (Table 2) so little alkyl halide even in 1·0M-hydrochloric acid, rate determinations of the usual (acidimetric) kind could be made in more dilute hydrochloric acid. These (Table 3) showed that the rate was the same as that in sulphuric acid yielding the same concentration of hydrogen ions, and was unaffected by the addition of sodium chloride.

TABLE 2. *Production of alkyl chlorides from nitramines in aqueous hydrochloric acid, at* 85° ± 0·2°.

		Yield % of R·Cl by determn. of :	
Nitramine	HCl (mole/l., at 20°)	H$^+$	Cl$^-$
1·0M-Me·NH·NO$_2$	1·02	50	48
0·5M- ,, ...	0·52	37	35
0·25M- ,, ...	0·52	39, 40	39, 37
0·25M- ,, ...	0·51 (+ 0·5M-NaCl)	67	67
1·0M-Et·NH·NO$_2$	1·02	14	14
1·0M-Pr^i·NH·NO$_2$	1·02	2	2

The decomposition of the first three members of the dinitramine series has been investigated briefly by the manometric method. Gas evolution at constant acidity no longer took place in accordance with the first-order law, and the apparent rate of reaction increased during the decomposition. This is the result to be expected from successive decompositions of comparable speed. 2-Hydroxyethylnitramine (II), the probable initial product from ethylenedinitramine, can be prepared (at least in a crude form) and was found to decompose, in 0·5M-sulphuric acid, at 85°, at the first-order rate $10^3k = 11{\cdot}5$ min.$^{-1}$. The complete curve of gas evolution from ethylenedinitramine was consonant with this value for the second stage, and $10^3k = 7{\cdot}5$ min.$^{-1}$ in 0·5M-sulphuric acid, at 85°, for the initial conversion into 2-hydroxyethylnitramine.

Tomlinson (*loc. cit.*) has measured the rate of decomposition of ethylenedinitramine by cooling samples and weighing the residual nitramine which separated. His value ($k =$ 0·175 hr.$^{-1}$ in 0·48M-sulphuric acid, at 84°, using logarithms to base 10), when converted into our units and corrected for a slight difference in acidity ($10^3k = 7{\cdot}0$ min.$^{-1}$ in 0·5M-sulphuric acid, at 84°) is close to our quite independent estimate. Using Tomlinson's method, we have recently examined the decomposition of ethylenedinitramine in water at 98°. Our values, though not in close agreement, were of the same magnitude as his. We found, as expected, that the rate of decomposition was dependent upon the initial concentration of ethylenedinitramine.

TABLE 3. *Decomposition of* iso*propylnitramine, initially* 0·05M *in aqueous hydrochloric acid, at* 85° ± 0·2°.

1	2	3	4
Run no.	HCl (mole/l., at 20°)	First-order coefficient, 10^3k (min.$^{-1}$)	Second-order coefficient, 10^3k [(mole/l.)$^{-1}$ min.$^{-1}$]
XXXIX, XL	0·204	12·1, 12·5	62
XXXVII, XXXVIII	0·102	5·9, 5·8	59
XLI	0·052	2·9	57
XLII	0·052 (+0·05M-NaCl)	2·9	57
XLIII	0·052 (+ 0·5M-NaCl)	3·3	65

Measurements were made by the acidimetric method. Values in column 4 are the average of the figures in column 3, divided by the appropriate value of [H$^+$].

The second-order rate coefficients for the initial stage of the decomposition of methylene-, ethylene-, and trimethylene-dinitramine could be estimated, very roughly, as $10^3k = 7$, 15, and 30, respectively [(mole/l.)$^{-1}$ min.$^{-1}$]. These estimates, taken with the values found for the mononitramines (Table 1), suggest that electron-donation by R favours, and electron attraction by R hinders, the acid-catalysed decomposition of R·NH·NO$_2$.

tert.-Butylnitramine is an exception to this generalisation. It may be relevant to note that an S_E2 substitution on an atom attached to a *tert.*-butyl group might have steric features in common with an S_N2 substitution of a *neo*pentyl halide.

EXPERIMENTAL

Reaction rates were evaluated on the basis of natural logarithms and are given in units of 10^3k. The hydrogen-ion concentration at 85° has been calculated on the assumption, valid to the degree of accuracy employed, that the solutions showed the same expansion as water between 20° and 85°, *i.e.*, that the concentration of acid (mole/l. at 85°) was 97% of that determined, and tabulated, for the solvents at 20°. Account has been taken, by extrapolation from Hamer's results (*J. Amer. Chem. Soc.*, 1934, **56**, 860), of the second stage of ionisation of sulphuric acid. For example, dilute sulphuric acids of 0·500, 0·250, 0·100, and 0·050 molarity at 20° have been calculated to be, respectively, 0·486, 0·244, 0·098, and 0·050M in hydrogen ions at 85°.

Materials.—The known nitramines were prepared by standard methods. Methylnitramine was finally purified by sublimation at 15 mm. on to a " cold-finger " (bath at 70°). Ethyl- and *iso*propyl-nitramine were distilled at, respectively, 98°/15 mm. and 95—96°/17 mm. The purity of the samples used was checked by titration with standard alkali.

tert.*-Butylnitramine.*—*N-tert.*-Butylnitrourethane (22·8 g.) (Curry and Mason, *J. Amer. Chem. Soc.*, 1951, **73**, 5043) and *iso*propylamine (14·2 g.) were mixed, in dry ether, and set aside overnight. The feathery needles of the *iso*propylamine salt (15 g.) were collected and acidified with potassium dihydrogen phosphate (29 g. in 210 ml. of water), and the free nitramine was extracted with ether. Evaporation and distillation yielded solid tert.*-butylnitramine* (8·2 g.) (b. p. 94—95°/16 mm.; 71°/0·6 mm.); prisms of m. p. 38° were obtained by dissolution in ether, addition of *n*-hexane, and slow evaporation at room temperature (Found : C, 39·8; H, 8·4%; equiv., 118. $C_4H_{10}O_2N_2$ requires C, 40·7; H, 8·5%; equiv., 118).

2-Hydroxyethylnitramine was obtained as an oil (Franchimont and Lublin, *Rec. Trav. chim.*, 1902, **21**, 50) of equiv. 112 (calc. for $C_2H_6O_3N_2$: 106).

Analysis of the Gas evolved on Decomposition.—The nitramine (*ca.* 1 mmole of a mono-, or 0·5 mmole of a di-nitramine) was weighed into a small tube and placed in a 200-ml. flask fitted with a 10-cm. condenser and a sealed-in tap-funnel whose stem extended nearly to the bottom of the flask. The shaft of a mercury-sealed stirrer passed through the condenser, and a side arm, above the level of the condenser jacket, was connected to a delivery tube passing into 40% aqueous potassium hydroxide. The apparatus was first flushed, through the tap-funnel, with carbon dioxide from a cylinder. The stream of carbon dioxide was then cut off, and the tap-funnel filled with the appropriate solvent (*e.g.*, 20 ml. of 0·5M-H_2SO_4). After flushing out of the small residual space in the funnel, a slower stream of gas, from powdered carbon dioxide, was introduced into the apparatus simultaneously with the opening of the tap. Residual traces of air passed up a column of the aqueous potassium hydroxide and were sucked over into, and expelled from the cup of, an attached (mercury-filled) Lunge nitrometer. Decomposition of the nitramine was then brought about by heating it on a water-bath. The gas evolved was absorbed by successive (5 ml.) portions of ethanol, the saturated ethanol being expelled from the cup of the nitrometer, and the residual gas stored meanwhile over the aqueous potassium hydroxide. Blank tests showed that a small correction (0·5 ml.) was required. The results are given in Table 4.

TABLE 4. *Mols. of gas (corrected values) from various nitramines.*

Compound	Solvent	Total gas (mols.)	Residual gas (insol. in EtOH) (mols.)
$Me\cdot NH\cdot NO_2$	1·0M-HCl	1·51, 1·43	0·06, 0·05
,, ...	0·5M-H_2SO_4	0·98, 0·98	0·04, 0·07
$Et\cdot NH\cdot NO_2$	,,	1·20	0·07
$Pr^i\cdot NH\cdot NO_2$	,,	1·16	0·06
$(CH_2\cdot NH\cdot NO_2)_2$	,,	1·97, 1·96	0·13, 0·04

To obtained a more precise result a sample of gas (from methylnitramine and sulphuric acid) was collected by the method described in Part II (*J.*, 1951, 1288), though, for convenience, a gas sampling tube was used in place of the bulb *E* (*loc. cit.*). The gas was washed with fuming sulphuric acid to remove methyl alcohol, and then with alkaline pyrogallol; nitrous oxide and nitrogen were determined by sparking with an excess of hydrogen, and measurement of the residual volume. Measurements were made over mercury, but in presence of sufficient water to effect saturation; blank corrections, evaluated by the use of pure nitrous oxide, were made to allow for the dissolution of this gas in sulphuric acid and in alkaline pyrogallol. Values obtained, after the removal of methyl alcohol vapour, were O_2, 1%; N_2O, 98%; N_2, 1%.

Analysis of the Non-gaseous Products of Decomposition.—Quantitative oxidation with chromic acid was carried out by Blank and Finkelbeiner's method (*Ber.*, 1906, **39**, 1326; see also Beckurts, "Die Methoden der Massanalyse," Braunschweig, 1913, p. 398). It was assumed that ethylene glycol and acetaldehyde (from ethylenedinitramine) were converted into oxalic and acetic acid.

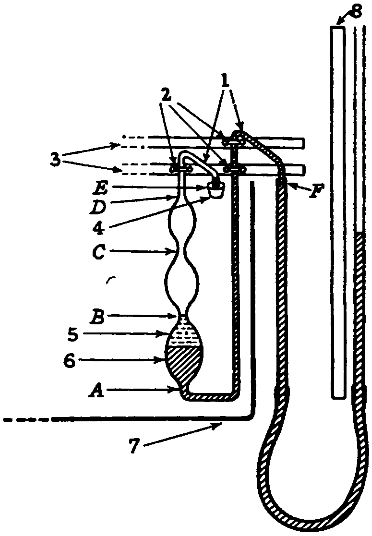
The pure 2 : 4-dinitrophenylhydrazone of acetaldehyde was obtained without difficulty. The solution obtained by the complete decomposition of trimethylenedinitramine in 0·5M-sulphuric acid yielded a crude 2 : 4-dinitrophenylhydrazone, m. p. 146—147° after repeated crystallisation from ethanol, undepressed by mixture with authentic propaldehyde 2 : 4-dinitrophenylhydrazone of m. p. 154° (Found: C, 45·1; H, 4·1. Calc. for $C_9H_{10}O_4N_4$: C, 45·4; H, 4·2%).

Measurement of Reaction Rates.—(a) *Manometric technique.* One of the two containers used is shown in the Figure. In operation the two similar containers were clamped permanently to the frame, and were lowered into, or raised from, the thermostat as a unit. One container held a solution of the nitramine, and the other, filled in a similar manner, the solvent only. The differences in pressure between the two containers were measured, and corrections for variations in (*a*) external pressure and temperature, and (*b*) the vapour pressure of the solvent, were thus unnecessary. A freshly prepared standard solution of the nitramine in dilute sulphuric acid was held, in a small flask, at *E*. A few drops of mercury were expelled from the capillary, and the reservoir was then lowered to draw a known volume (*CE*) of solution into the container. The supply was then removed from *E*, and the reservoir lowered to fill *CE* with air. The outside of the capillary was dried, and the outlet closed with a thick rubber cap (a rubber bung bored half-way through) containing a little mercury, some of which was forced up the capillary tube. The cap was sealed to the tube by "Picein" wax. In this way the solution and gas were confined between mercury "plugs," and any leak was shown by the escape of mercury. The container could be charged in less than 5 min. from the dissolution of the nitramine, and separate experiments showed that no observable decomposition occurred in 20 min. at room temperature. Owing to the low solubility of ethylenedinitramine it was necessary, in this case only, to charge the containers with solutions at 40°.

1, *Capillary tubing*
2, *Clamps*
3, *Rigid frame*
4, *Half-bored rubber bung*
5, *Solution*
6, *Mercury*
7, *Thermostat wall*
8, *Fixed scale*

	Volumes (ml.)	
Container	1	2
AB	19·61	19·30
BC	10·03	9·65
CD	8·38	7·33
DE	0·15	0·15

E *and* F *are bent forward, and lie outside the thermostat*



The containers were lowered into the glass-walled thermostat, and readings of pressure made with the aqueous level in each container at *B*. A flail attached to the stirrer agitated the container holding the nitramine solution.

The decomposition was completed by heating (generally overnight) for at least twice the period required for 90% decomposition, and the final difference in mercury levels (D_f) measured with care. The mercury level from the control container 2 was, owing to mechanical differences such as the permanent position of clamping, slightly higher than that from container 1, even when both contained dilute sulphuric acid at 85°. This constant (C) was measured, and the value of ($D_f + C$) taken to indicate complete decomposition. If, at the time t, the difference in levels was D_t, then the indicated residual nitramine was $(D_f + C) - (D_t + C) = D_f - D_t$.

In operation there was an induction period (*ca.* 10—20 min.) greater than might be reasonably ascribed to thermal equilibration : if, however, the retained gas remained constant, then the slope of the lines obtained by plotting the logarithm of apparent residual concentration against time gave the true rate of reaction (cf. Marlies and La Mer, *J. Amer. Chem. Soc.*, 1935, **57**, 1812). The total quantity of gas evolved in this apparatus was always 10—15% less than that measured by the " sweep-through " technique.

(b) *Acidimetric technique.* Equal volumes (5 ml.) of standard solutions of (*a*) the nitramine in water and (*b*) the mineral acid were mixed to give a solution of the reported concentration. This was heated, under a ground-glass reflux condenser, in a 25-ml. flask immersed to the neck in the thermostat. After cooling, the whole content was titrated (thymolphthalein) to give one point on the decomposition curve. Prolonged heating led, as expected, to disappearance of the nitramine, but retention of the mineral-acid acidity. *tert.*-Butylnitramine was not sufficiently soluble to give a 0·1M-solution in water : portions were weighed individually into the flasks, and dissolved in 1 min. on swirling in the thermostat. Tests showed that the solutions reached thermal equilibrium 3 min. after insertion in the thermostat : this was taken as zero time.

Decomposition of Methylnitramine in Water.—Samples (5 ml.) were heated in sealed tubes for periods of up to 48 hr. at 98° ± 0·2°. A 15—20% reduction in acidity was observed by direct titration. The approximate first-order rate coefficients [10^3k (min.$^{-1}$) at 98°] were 0·08, 0·10, and 0·12, for methylnitramine solutions of, respectively, 0·5, 1·0, and 2·0 molarity at 20°.

Indirect Measurement of the Alkyl Halide Produced.—Solutions were prepared and heated as in the acidimetric technique. After a sufficient time they were cooled, titrated with alkali, acidified with a few drops of acetic acid, and re-titrated with silver nitrate (dichlorofluorescein). The results (Table 2), evaluated from the fall in Cl^- and the fall in acidity over and above that due to the disappearance of the nitramine, would not have been consistent unless decomposition had been essentially complete.

Investigation of the Dinitramines by the Manometric Technique.—Plotting the logarithm of the " residual percentage " (more correctly, the percentage of the total gas still to be evolved) against time did not yield straight lines. Various values were assumed for the first and second unimolecular decomposition coefficients, and the curves so obtained compared with the experimental values. Values in reasonable agreement with the experimental data are given in Table 5; they are probably of the right order but, particularly in the case of the second stage, should not be regarded as more than a rough approximation.

TABLE 5. *Probable rates of decomposition of dinitramines in* 0·5M-*sulphuric acid, at* 85° ± 0·2°.

Compound (initially 0·025M)	First stage of decomp., 10^3k_1 (min.$^{-1}$)	Second stage of decomp., 10^3k_2 (min.$^{-1}$)
$CH_2(NH{\cdot}NO_2)_2$	3·5	7
$(CH_2{\cdot}NH{\cdot}NO_2)_2$	7·5	11·5 *
$CH_2(CH_2{\cdot}NH{\cdot}NO_2)_2$	15	30

* Confirmed directly by use of 2-hydroxyethylnitramine.

Decomposition of Nitramine ($NH_2{\cdot}NO_2$).—The manometric technique was used, though the speed of decomposition was rather high for our apparatus. The unimolecular character of the decomposition led, as expected, to similar reaction rates ($10^3k = 330 \pm 30$ min.$^{-1}$) in 0·5 and in 0·05M-sulphuric acid at 85°. This is more than ten times as fast as the decomposition of any of the primary nitramines investigated; and though the production of $NH_2{\cdot}NO_2$ as an intermediate may lead to a slight delay in the initial production of gas, it cannot have a significant effect upon the slope of the lines obtained by plotting the logarithm of (apparent) residual concentration against time.

Decomposition of Ethylenedinitramine in Water.—We have used, essentially, Tomlinson's method (*loc. cit.*). Solutions were made up, on a w/w basis, by heating and stirring under reflux in the thermostat. Samples (*ca.* 10 ml.) were withdrawn by means of a pre-heated untipped pipette, cooled, and weighed. The precipitated ethylenedinitramine was collected in a sintered-glass crucible, and the mother-liquor titrated with alkali. We found that the titration values increased (from *ca.* 2 to *ca.* 6 ml. of 0·2N-NaOH) during the decomposition.

This was presumably due to the accumulation of water-soluble 2-hydroxyethylnitramine in the system; we have thought it best to employ a uniform correction factor (at least for each concentration of ethylenedinitramine) to allow for the slight solubility of the dinitramine in water. These factors, based on sampling as soon (15—20 min.) as dissolution and thermal equilibration was complete, were 25, 30, 39, and 36 mg. of ethylenedinitramine from 10-g. samples of 2·97, 5·79, 10·74, and 10·88% (w/w) concentration. Standardised conditions of precipitation, filtration, and washing were used: the variations in the correction factor were probably due to the variations in the bulk of material available for dissolution in the washing process. By heating for 48 hr. at 97—98° from 20 to 40% (according to concentration) of the material was decomposed. For solutions containing 2·97, 5·79, 10·74, and 10·88% (w/w) of ethylenedinitramine (*ca.* 0·19, 0·39, 0·72, and 0·73M at 97° by measurement of density to two places of decimals), we found apparent unimolecular " constants " [10^3k (min.$^{-1}$)] of, respectively, 0·07 at 97°, 0·08 at 97°, 0·16 at 97·6°, and 0·17 at 97·2°. Tomlinson reported, in our units, 0·077 for 0·784M-ethylenedinitramine in water at 98°. Though the reaction is probably of fractional order with respect to the dinitramine, little sign of this can be expected to appear in the first 30% of decomposition from any one initial concentration.

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