Nitramines and Nitramides. Part VIII.[*] *Additional Measurements of the Rate of Decomposition of Primary Nitramines, and the Evidence for General Acid-catalysis.*

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(Reprint Order No. 6039.)

Published measurements of rates of decomposition of the compounds $R\cdot NH\cdot NO_2$ by aqueous acids have now been extended to the cases where $R = EtMeCH$, $EtMeCH\cdot CH_2$, or $Me_3C\cdot CH_2$. These decomposed more readily than the simpler alkyl nitramines, and exhibited significant differences between sulphuric and hydrochloric acid solutions of the same hydrogen-ion content. By using *iso*propylnitramine, bisulphate ions have been shown to be catalysts in their own right: other (un-ionised) acids may also act as catalysts, but are too feeble for their influence to be determined with precision.

IN Part IV (*J.*, 1953, 1998) it was shown that, for $R = Me$, Et, Pr^i, or Bu^t, the rate of decomposition of $R\cdot NH\cdot NO_2$ by aqueous acids was proportional to $[H^+][R\cdot NH\cdot NO_2]$. Electron-donation by R seemed to favour decomposition, though *tert.*-butylnitramine was anomalous; and we have therefore prepared and examined *sec.*-butyl-, 2-methylbutyl-, and *neo*pentyl-nitramine. As expected, these decompose more rapidly than the analogues previously investigated; for the complete series the relative rates are $R = Me_3C\cdot CH_2 > EtMeCH > EtMeCH\cdot CH_2 > Pr^i > Et$ or $Bu^t > Me > CH_2\cdot CO_2H$. The ready decomposition of *neo*pentylnitramine and additional evidence, as yet unpublished, show that our formulation of the rate-determining step as $R\cdot NH\cdot NO_2 + H^+ \longrightarrow R^+ + NH_2\cdot NO_2$ is correct as far as the production of alkyl cations is concerned; but the suggestion that nitramine (as such) is set free was possibly overhasty, and is under experimental examination.

The rates of decomposition were determined by the acidimetric technique (Part IV, *loc. cit.*) and are given in Table 1, which is directly comparable with Table 1 of Part IV.

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

1 Run no.	2 R	3 Acid (mole/l. at 20°)	4 First-order rate coeff., 10^3k (min.$^{-1}$)	5 Second-order rate coeff., 10^3k (l. mole^{-1} min.$^{-1}$)
I	MeEtCH	HCl, 0·0514	3·9	78
II	,,	H_2SO_4, 0·0536	5·1	96
III	,,	,, 0·0269	2·6	95
IV	$MeEtCH\cdot CH_2$	,, 0·0266	2·3	85
V	$Me_3C\cdot CH_2$	HCl, 0·0487	4·9	104
VI	,,	,, 0·0249	2·5	103
VII	,,	H_2SO_4, 0·0535	6·3	119
VIII	,,	,, 0·0266	3·1	114

Values in column 5 are those of column 4, divided by the appropriate value of $[H^+]$.

The values of the second-order rate coefficients found for solutions in sulphuric acid seemed to differ significantly from those determined in hydrochloric acid, even when allowance was made for imprecision in the calculation of the hydrogen-ion content of sulphuric acid solutions at 85°. This anomaly could be removed by assuming (1) that the second-order coefficients in hydrochloric acid are the true catalytic constants of the hydrogen ion; and (2) that the observed first-order rates in sulphuric acid are given by $k_{H^+}[H^+] + k_{HSO_4^-}[HSO_4^-]$, where the catalytic constant of the bisulphate ion is of the order of one-tenth of that of the hydrogen ion. We have therefore sought evidence of general acid-catalysis in the case of *iso*propylnitramine, where, from our previous work, k_{H^+} is about 60×10^{-3} l. mole^{-1} min.$^{-1}$.

In our investigation of general acid-catalysis we reverted to the manometric technique (Part IV, *loc. cit.*), since acidimetry was inapplicable. The decompositions were slow,

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[*] Part VII, *J.*, 1954, 2391.

and we were forced to use unduly large concentrations of catalyst: salt effects of unknown extent made it unwise to place too much reliance on individual values. It certainly appears that bisulphate ions have a catalytic action: thus solutions of *iso*propylnitramine (0·05M) in sodium hydrogen sulphate (0·500 and 1·000M at 20°) gave first-order rate coefficients of 7·4 and 13·4 × 10^{-3} min.$^{-1}$ respectively; on the basis of hydrogen-ion content alone the rates would have been about 1·2 and 1·6 × 10^{-3} min.$^{-1}$.

We examined the decomposition in sodium hydrogen sulphate buffers of constant ratio ($NaHSO_4 : Na_2SO_4 = 1 : 1$), using sodium chloride to compensate, to some extent, for changes in salt concentration. The results are given in Table 2. In runs XII, XIII, and XVI, $[Na^+]$ was kept constant, whilst in runs XI, XV, and XIX the total ionic strength was maintained. It appears that, though changes in salt concentration alter the rate (compare runs XVI, XVII, and XVIII), such alterations are small compared with those proportional to the bisulphate content, and no point is far distant from a line giving an intercept of 1·7 × 10^{-3} min.$^{-1}$—of the right order for the hydrogen-ion concentration of these buffers—and a catalytic constant of 8·2 × 10^{-3} l. mole^{-1} min.$^{-1}$ for the bisulphate ion.

TABLE 2. *Decomposition of* iso*propylnitramine, initially* 0·05M, *in sodium hydrogen sulphate buffer solutions at* 85° ± 0·2°.

Run no.	Components (mole/l. at 20°) NaHSO₄ and Na₂SO₄	NaCl	First-order rate coeff., 10^3k (min.$^{-1}$)	Divergence from line $v = 1·7 + 8·2[HSO_4^-]$ (in units of 10^3k, min.$^{-1}$)
XI	1·027	Nil	9·9	−0·2
XII	1·007	Nil	10·2	+0·3
XIII	0·772	0·831	7·3	−0·7
XIV	0·749	0·548	7·9	+0·1
XV	0·619	1·700	7·8	+1·0
XVI	0·385	1·956	4·5	−0·4
XVII	0·380	0·756	4·3	−0·5
XVIII	0·379	2·957	5·0	+0·2
XIX	0·300	2·900	4·8	+0·6

We have also examined the behaviour of *iso*propylnitramine in phosphoric acid, and in phosphate, acetate, and chloroacetate buffers. The results are given in Table 3. In all cases the observed rates are greater than those calculated for the influence of hydrogen ions alone; though positive salt effects may account for part of the increase, they can hardly produce the more than ten-fold increases shown in the buffered solutions.

TABLE 3. *Decomposition of* iso*propylnitramine, initially* 0·05M, *in phosphoric, acetic, and chloroacetic acid solutions at* 85° ± 0·2°.

Run no.	Composition of solutions, at 20°	Calc. value of $10^3[H^+]$ (at 85°)	First-order rate coefficient 10^3k (min.$^{-1}$) Observed	Calc. for $[H^+]$ alone
XX	1·0M-H_3PO_4	50	17·4	3·0
XXI	0·5M-H_3PO_4	34	9·9	2·0
XXII	0·49M-H_3PO_4, and 0·49M-NaH_2PO_4	2·7	5·3	0·16
XXIII	0·25M-H_3PO_4, 0·25M-NaH_2PO_4, and 0·25M-NaCl	2·7	3·1	0·16
XXIV	1·0M-NaH_2PO_4	0·22	0·2	0·013
XXV	1·0M-$CH_3{\cdot}CO_2H$, and 1·0M-$CH_3{\cdot}CO_2Na$	0·01	0·2	0·0006
XXVI	0·97M-$CH_2Cl{\cdot}CO_2H$, and 0·97M-$CH_2Cl{\cdot}CO_2Na$	0·6	1·8	0·035

A buffer of composition 0·5M-NaH_2PO_4 and 0·5M-Na_2HPO_3 gave no observable decomposition at 85°.

We therefore consider that the reaction exhibits general acid-catalysis: in particular, for *iso*propylnitramine at 85°, the catalytic constants [in units of 10^{-3} l. mole^{-1} min.$^{-1}$] are about 60 for H^+, 8 for HSO_4^-, and perhaps of the order of 10 for H_3PO_4, 2 for $CH_2{\cdot}ClCO_2H$, and 0·2 for $CH_3{\cdot}CO_2H$.

EXPERIMENTAL

Reaction rates were evaluated on the basis of natural logarithms. The techniques of measurement have been described in an earlier paper of this series (Part IV, *J.*, 1953, 1998). In calculating hydrogen-ion concentrations at 85° use was made of the work of Hamer (*J.*

Amer. Chem. Soc., 1934, **56**, 860), of Harned and Embree (*ibid.*, p. 1050), and of Nims (*ibid.*, p. 1110). *sec.*-Butylnitramine (van Erp, *Rec. Trav. chim.*, 1895, **14**, 31) was prepared from *sec.*-butylnitrourethane [obtained from *sec.*-butylamine by the general method of Curry and Mason (*J. Amer. Chem. Soc.*, 1951, **73**, 5043)] and purified by distillation at 76°/0·75 mm. (Found: equiv., 119. Calc. for $C_4H_{10}O_2N_2$: equiv., 118).

2-*Methylbutylnitramine*.—Ethyl β-methylvalerate (25 g.) (prepared from *sec.*-butylmalonic ester by hydrolysis, decarboxylation, and esterification) was refluxed for 40 hr. with hydrazine hydrate (15 ml.) in ethanol. After removal of the ethanol by distillation the hydrazide was dissolved in an excess of 2N-hydrochloric acid, ether (125 ml.) added, and sodium nitrite (14·5 g. in 30 ml. of water) run in, with stirring, at <10°. The ether layer was separated, the aqueous layer was re-extracted with ether, and the combined extracts were washed with sodium hydrogen carbonate and dried ($CaCl_2$). Ethanol (80 ml.) was added to this solution of the azide and the residue, after removal of the ether through a fractionation column, was refluxed for 6 hr. Distillation, under reduced pressure, removed excess of ethanol and yielded fractions of b. p. 86—89°/2 mm. and 101—102°/4 mm. The second fraction on redistillation gave N-(2-*methylbutyl*)*urethane* (2·5 g.; b. p. 108—109°/7 mm.) (Found: C, 59·9; H, 10·5. $C_8H_{17}O_2N$ requires C, 60·4; H, 10·7%). On nitration by Curry and Mason's method (*loc. cit.*) the corresponding nitrourethane (3 g., crude) was obtained: passage of ammonia through an ethereal solution of the nitrourethane yielded the ammonium salt of the nitramine, which was collected and decomposed with 2N-hydrochloric acid. Ether-extraction and distillation (98—99°/0·7 mm.), followed by sublimation at 85°/16 mm., yielded 2-*methylbutylnitramine* (1·5 g.) as small flakes of m. p. 32° (Found: C, 45·5; H, 9·2%; equiv., 133. $C_5H_{12}O_2N_2$ requires C, 45·5; H, 9·1%; equiv., 132).

neo*Pentylnitramine*.—*neo*Pentylamine (Walter and McElvain, *J. Amer. Chem. Soc.*, 1934, **56**, 1614) was prepared from trimethylacetic acid by way of the chloride, amide, and nitrile. Treatment by Curry and Mason's method (*loc. cit.*) gave successively the (crude) urethane and nitrourethane in almost quantitative yields. neo*Pentylnitramine*, prepared from the nitrourethane as described in the preceding paragraph, was purified by distillation (92—93°/2·5 mm., 76—77°/0·5 mm.) and was solid at temperatures below 16° (Found: C, 45·0; H, 9·1%; equiv., 133. $C_5H_{12}O_2N_2$ requires C, 45·5; H, 9·1%; equiv., 132).

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[*Received, January 19th*, 1955.]