

*Nitramines and Nitramides. Part IX.\* The Acid-catalysed  
Decomposition of O-Methyl-N-isopropyl nitramine.*

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The *N*- and *O*-methyl derivatives of *N*-isopropyl nitramine have been adequately characterised. The decomposition of the *O*-isomer to yield nitrous oxide, together with methyl and isopropyl alcohol exhibits general acid-catalysis. The rate of decomposition is much greater than that of the parent isopropyl nitramine in identical conditions, and there is no sign of any "build-up" of isopropyl nitramine during decomposition: the process cannot, in any ordinary sense, involve hydrolysis of the *O*-alkyl compound and subsequent decomposition of the parent nitramine.

Values of  $\lambda_{\max}$  and  $\log \epsilon_{\max}$  in the ultraviolet spectra of some *ON*-dialkyl nitramines are given in the Experimental section.

FRANCHIMONT and VAN DISSEL (*Rec. Trav. chim.*, 1894, **13**, 329) treated the potassium salt of methyl nitramine with isopropyl iodide and obtained, by distillation at 40 mm., fractions of b. p. 60—61° and 106—108°. At that time the existence of *ON*-dialkyl nitramines was unsuspected, and the lower-boiling fraction was reported as *N*-methyl-*N*-isopropyl nitramine: it still remains as such in the literature, though the boiling point recorded is anomalous. We have prepared true *N*-methyl-*N*-isopropyl nitramine by methylation of the potassium salt of isopropyl nitramine; the boiling point (108—109°/40 mm.) corresponds with their second fraction, and the constitution has been established by reduction to methyl isopropylamine, isolated as the toluene-*p*-sulphonamide. Franchimont and van Dissel's first fraction was presumably *N*-methyl-*O*-isopropyl nitramine, which we have prepared by treatment of the silver salt of methyl nitramine with isopropyl iodide.

Methylation of the silver salt of isopropyl nitramine with methyl iodide yielded *O*-methyl-*N*-isopropyl nitramine, together with a little (<1 part in 10) of the *N*-methyl isomeride. The use of dimethyl sulphate gave *N*- and *O*-isomers in equal proportions, and diazomethane yielded 7 parts of the *N*- to 3 parts of the *O*-compound.

Early workers (Umbgrove and Franchimont, *Rec. Trav. chim.*, 1898, **17**, 287; Backer, Ahrens Sammlung, 1912, **18**, 359) showed qualitatively that decomposition of  $R \cdot N : NO \cdot OR'$  by 40% sulphuric acid yielded nitrous oxide, together with the alcohols ROH and R'OH; suitable alkyl groups in place of R, but not of R', gave rise to olefins, and the nitrous oxide was said, on fair evidence, to be produced quantitatively. Modern work (Wright *et al.*, *Canad. J. Res.*, 1948, **26**, B, 130; *J. Amer. Chem. Soc.*, 1950, **72**,

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1030) has confirmed the use of sulphuric acid to distinguish *ON*- from *NN*-isomerides, but no detailed investigation of the reaction has been made.

In confirmation of the overall reaction  $R\cdot N:NO\cdot OR' + H_2O \longrightarrow ROH + N_2O + R'OH$  we have found that the gas evolved from *O*-methyl-*N*-isopropyl nitramine contains no elemental nitrogen; and that if the decomposition is carried out in the presence of dichromate, the oxidising agent consumed corresponds to the conversion of methyl alcohol into formic acid, and of isopropyl alcohol into acetone. Olefin formation (see previous paragraph) suggests that *R*, but not *R'*, is liberated as an alkyl cation. We have demonstrated this by the formation, in hydrochloric acid, of *RCl* but not of *R'Cl*; requisite conditions, and results, are dealt with in the Experimental section.

The complete decomposition of *O*-methyl-*N*-isopropyl nitramine to yield nitrous oxide has been found to be much more rapid than that of the parent isopropyl nitramine in identical conditions, and no isopropyl nitramine is formed during the reaction. The suggestion that the process involves hydrolysis to, and subsequent decomposition of, the *aci*-form ( $Pr^i\cdot N:NO\cdot OH$ ) of the primary nitramine (Backer, *loc. cit.*) cannot be maintained, since this would imply that in the competing reactions  $R\cdot NH\cdot NO_2 \rightleftharpoons R\cdot N:NO\cdot OH \longrightarrow R\cdot OH + N_2O$  the rate of decomposition must be much greater than that of equilibration, if the primary nitramine is not to accumulate in a (comparatively) stable form. But if this were so, then acidification of a salt of a primary nitramine (*e.g.*,  $R\cdot N:NO\cdot ONa$ ) would yield  $ROH + N_2O$ , rather than  $R\cdot NH\cdot NO_2$ . The reaction possibly proceeds by a mechanism analogous to ester hydrolysis ( $R\cdot N:NO\cdot OR' \xrightarrow{+H^+} R\cdot N:NO\cdot OHR' \longrightarrow R^+ + N_2O + R'OH$ ) but discussion is deferred until our measurements on a series of *ON*-dialkyl nitramines have been completed.

Rates of decomposition of *O*-methyl-*N*-isopropyl nitramine have been measured manometrically, and by observation of optical density in the ultraviolet region. In all cases the reaction was of the first order with respect to the nitramine. Table 1 shows that the methods of measurement, based respectively on the appearance of the final product (Gas) and the disappearance of the nitramine (U.V.), are in good agreement. The observed rates, in hydrochloric or sulphuric acid, are proportional to the hydrogen-ion content of the solutions, and the average catalytic constant,  $k_{H^+}$ , at 45°, is 3.6 l. mole<sup>-1</sup> min.<sup>-1</sup>. This is 2000—3000 times as large as the value of  $k_{H^+}$  for isopropyl nitramine in aqueous sulphuric acid at the same temperature.

TABLE 1. *Decomposition of O-methyl-N-isopropyl nitramine, initially 0.05M in aqueous acids, at 45° ± 0.1°.*

Run no.	Acid (mole l. <sup>-1</sup> at 20°)	10 <sup>3</sup> [H <sup>+</sup> ] at 45° (calc.)	Method of measurement	First-order rate coefficient, 10 <sup>3</sup> k (min. <sup>-1</sup> )	Catalytic constant $k_{H^+}$ (l. mole <sup>-1</sup> min. <sup>-1</sup> )
I	0.05M-HCl	49.8	U.V.	180	3.6
II	0.025M-HCl	24.9	U.V.	87.8	3.5
III	0.01M-HCl	9.96	U.V.	35.7	3.6
IV	0.0051M-H <sub>2</sub> SO <sub>4</sub>	8.0	Gas	26.0	3.3
V	0.0033M-H <sub>2</sub> SO <sub>4</sub>	5.4	Gas	17.5	3.2
VI	0.005M-HCl	4.98	U.V.	16.5	3.3
VII	0.002M-H <sub>2</sub> SO <sub>4</sub>	3.5	Gas	12.0	3.4
VIII	0.002M-HCl	1.99	Gas	8.0	4.0
IX	0.001M-H <sub>2</sub> SO <sub>4</sub>	1.86	Gas	7.1	3.8
X	0.001M-HCl	0.996	Gas	4.0	4.0
XI	0.001M-HCl	0.996	U.V.	3.5	3.5
XII	0.0005M-H <sub>2</sub> SO <sub>4</sub>	0.97	Gas	4.0	4.1

Runs XIII and XIV.—A solution (0.05M) of *O*-methyl-*N*-isopropyl nitramine in distilled water gave no measurable gas evolution during 4 days at 45°: catalysis by water cannot, therefore, be recognised at this temperature. A solution (0.05M) of isopropyl nitramine in 0.5M-H<sub>2</sub>SO<sub>4</sub> (10<sup>3</sup>[H<sup>+</sup>] = 501 at 45°) gave, by gas evolution at 45°, a first-order coefficient of 0.7 × 10<sup>-3</sup> min.<sup>-1</sup>, indicating a  $k_{H^+}$  value of about 0.0014 l. mole<sup>-1</sup> min.<sup>-1</sup>.

Table 2 extends, for hydrochloric acid, the field of measurement covered by Table 1. Runs XIX—XXII are not fully in accordance with expectation: they show a slight (5%) "drift" and, since a spontaneous (water-catalysed) reaction is observable at 85°, a drift of about the same extent, but in the opposite sense, might be expected. The results,

however, show that, at suitable temperatures, the rate of decomposition is proportional to  $[H^+][Pr-N:NO-OMe]$  to within 10% over a 2000-fold range of concentration of hydrochloric acid. The average values of  $k_{H^+}$  (after allowance, at 85°, for water catalysis) are 0.39 and 89 l. mole<sup>-1</sup> min.<sup>-1</sup> at 25° and 85° respectively. A plot of  $\log k_{H^+}$  against  $1/Temp. (^{\circ}K)$  gives points which are not precisely linear; the observed rate coefficients at 25°, 45°, and 85° are respectively 8% less, 8% more, and 16% less than those values which would give points on what we consider to be the best line. In view of the different methods of measurement, and the wide range of solvent concentration and temperature, these divergences are perhaps to be expected; and the only valid conclusion at present is that the activation energy,  $E$ , is about 20,000 cal.

Catalysis by acetic acid (and therefore, probably, by acids in general) has been demonstrated by the manometric measurements at 85° which are given in Table 3. The values of the first-order rate coefficient are linear with respect to  $[AcOH]$  and show an intercept of  $3.7 \pm 0.2 \times 10^{-3}$  min.<sup>-1</sup> at  $[AcOH] = 0$ . The intercept is greater than might be attributed solely to  $k_{H^+}$  in these solutions, and the remainder of the rate is presumably due to catalysis by water molecules. We tried to verify this by direct observation: the results, though of the right order (runs nos. XXVII—XXIX,  $k = 2.3, 1.1$ , and  $1.6 \times 10^{-3}$  min.<sup>-1</sup>), were not consistent enough for quantitative use. An experiment with 0.01M-sodium hydroxide (Table 3, run XXX) showed that there was no pronounced basic catalysis, and we assumed that, if the hydroxyl ion was ineffective, variations in the

TABLE 2. *Decomposition of O-methyl-N-isopropylnitramine, initially 0.05M in hydrochloric acid, at various temperatures.*

Run No.	Temp. ( $\pm 0.1^{\circ}$ )	Acid (mole l. <sup>-1</sup> at 20°)	$10^3[H^+]$ (calc.)	Method of measurement	First-order rate coefficient, $10^3k$ (min. <sup>-1</sup> )	Catalytic constant, $k_{H^+}$ (l. mole <sup>-1</sup> min. <sup>-1</sup> )
XV .....	25°	0.54	540	U.V.	223	0.41
XVI .....	25	0.108	108	U.V.	40.4	0.37
XVII & XVIII	25	0.05	50	U.V.	19.1	0.38
See Table 1 ...	45	0.05—0.001	—	Gas & U.V.	—	3.6
XIX .....	85	0.001	0.969	Gas	91.6	95 *
XX & XXI .....	85	0.0005	0.485	Gas	45.0	93 *
XXII .....	85	0.00025	0.242	Gas	21.6	89 *

\* Without allowance for catalysis by water.

TABLE 3. *Decomposition of O-methyl-N-isopropylnitramine, initially 0.05M, at 85°  $\pm$  0.1°.*

Run no.	Composition of solvent, at 20°	First-order rate coefficient, $10^3k$ (min. <sup>-1</sup> ) *
XXIII .....	0.1M-AcOH and AcONa	7.6
XXIV .....	0.075M-AcOH and AcONa + 0.025M-NaCl	6.4
XXV .....	0.05M-AcOH and AcONa + 0.05M-NaCl	5.7
XXVI .....	0.025M-AcOH and AcONa + 0.075M-NaCl	4.7
XXX .....	0.01M-NaOH	1.1
XXXV .....	0.1M-AcONa	1.5
XXVI .....	0.025M-AcONa	1.4
XXXVII .....	0.025M-AcONa + 0.075M-NaCl	1.4

\* In all cases by manometric measurements.

concentration of acetate ions would have no significant influence on the rate. Our referees, however, were of the opinion that this assumption should be experimentally investigated, and we have therefore (subsequently) carried out the runs (XXXV—XXXVII) tabulated in Table 3. These (in which hydrolysis does not produce a significant quantity of acetic acid) show that variations in the concentration of acetate ions, or of sodium chloride, do not produce changes outside the probable experimental error; that the spontaneous (water-catalysed) rate is  $1.4 \pm 0.2 \times 10^{-3}$  min.<sup>-1</sup> at 85°; and that the variations in runs XXIII—XXVI may be attributed with confidence to catalysis by acetic acid. For comparison with the  $k_{H^+}$  value of 89,  $k_{AcOH}$  is  $4.0 \times 10^{-2}$  and  $k_{H_2O}$   $2.6 \times 10^{-5}$ , all at 85° and in units of l. mole<sup>-1</sup> min.<sup>-1</sup>. These figures are in agreement with the Brønsted relation between

catalytic coefficient and dissociation constant: probable values being used for the dissociation constants at 85°, the agreement is as good as, if not better than, that found (Brønsted and Guggenheim, *J. Amer. Chem. Soc.*, 1927, **49**, 2582) for the acid-catalysed mutarotation of glucose.

The difference ( $2.3 \pm 0.4 \times 10^{-3} \text{ min.}^{-1}$ ) between the intercept for  $[\text{AcOH}] = 0$  and the spontaneous rate seems not improbable for the catalytic influence of  $[\text{H}^+]$  in the buffer solutions used. No precise figures relevant to 85° were found, but the following approximation is of interest. From MacInnes's figures ("The Principles of Electrochemistry," Reinhold, New York, 1939, pp. 205, 278) the hydrogen-ion content of an acetic acid buffer (AcOH and AcONa, both 0.1N) exceeds the numerical value of the dissociation constant of acetic acid by 0.5, 0.55, and  $0.6 \times 10^{-5}$ , at, respectively, 12°, 25°, and 38°. If this difference is at least maintained, then, from an extrapolated value of  $1.3 \times 10^{-5}$  for the dissociation constant of acetic acid at 85°,  $[\text{H}^+]$  in the buffer of run no. XXIII would be  $1.9 \times 10^{-5}$ ;  $k_{\text{H}^+}$  being taken as 89, the resultant first-order rate would be  $1.7 \times 10^{-3} \text{ min.}^{-1}$ . This approximation makes some attempt to allow for secondary salt effects: the residual difference of  $0.6 \times 10^{-3} \text{ min.}^{-1}$  is scarcely beyond the sum of possible experimental errors, and might well be reduced if primary salt effects were taken into consideration. It may be added that the precise extent of hydrogen-ion catalysis is irrelevant to arguments based on such (run nos. XXIII—XXVI) "isohydric" salt solutions. All that is necessary is to show—as we believe we have done—that any unexplained effect is relatively small.

#### EXPERIMENTAL

Reaction rates were evaluated on the basis of natural logarithms. In calculating hydrogen-ion concentrations in sulphuric acid use was made of Hamer's work (*J. Amer. Chem. Soc.*, 1934, **56**, 860). For other solvents corrections have been made on the assumption that these dilute solutions showed the same expansion as water over the range 20—85°.

All compounds reported as *ON*-dialkylnitramines gave an immediate evolution of gas on treatment with 40% sulphuric acid at room temperature. It appears (p. 4002) that they can also be distinguished spectroscopically from their *NN*-isomerides. The silver salts employed in alkylation were precipitated from water by the action of a slight excess of silver nitrate on the ammonium or *isopropylammonium* salts of the nitramines: they were collected, washed successively with water, acetone, and ether, and "dried" *in vacuo*. Refractive indices were measured with an Abbé refractometer at room temperature (18—21°).

*N-Methyl-N-isopropylnitramine*.—*iso*Propylnitramine (5 g.), potassium hydroxide (2.8 g.), methyl iodide (10 g.), and dry ethanol (75 ml.) were shaken, at room temperature, for two days. The resultant potassium iodide was collected, and the filtrate concentrated by distillation of ethanol at 60°/300 mm. A further small precipitate of potassium iodide was removed, and the residual oil distilled to yield fractions of b. p. 59—60°/40 mm. (0.5 g.) and 107°/40 mm. (3.4 g.). The lower-boiling fraction (*O*-methyl isomer) is obtained in better yield from the silver salt of *isopropylnitramine*. The higher-boiling fraction was washed in ethereal solution with aqueous sodium hydrogen carbonate and distilled, after removal of ether, to yield *N-methyl-N-isopropylnitramine*, b. p. 85—86°/10 mm.,  $n_D$  1.456 (Found: C, 40.4; H, 8.7; N, 23.6.  $\text{C}_4\text{H}_{10}\text{O}_2\text{N}_2$  requires C, 40.7; H, 8.5; N, 23.7%).

*Characterisation of N-Methyl-N-isopropylnitramine*.—The nitramine (1 g.) was heated under reflux for 5 hr. with granulated tin (6 g.) and hydrochloric acid (15 ml. of conc.). Excess of tin was collected, and the filtrate concentrated to 5 ml. The amine was liberated by treatment with sodium hydroxide (20 ml. of 40%) in a semimicro-Kjeldahl apparatus, and was steam distilled into hydrochloric acid. Evaporation yielded crops of the hydrochloride of methyl-*isopropylamine* (0.8 g. of hygroscopic material). The hydrochloride (0.3 g.), dissolved in sodium hydroxide (1 ml. of 20%), was treated with toluene-*p*-sulphonyl chloride (1 g.) in acetone. The resultant precipitate was collected, washed with dilute aqueous sodium hydroxide and with water, dried, and crystallised from acetone to yield stout prisms of *N-methyl-N-isopropyltoluene-p-sulphonamide*, identified by m. p. (78—79°; Boon, *J.*, 1947, **311**, gave 78°) and mixed m. p. with authentic material (Found: S, 13.7. Calc. for  $\text{C}_{11}\text{H}_{17}\text{O}_2\text{NS}$ ; S, 14.1%), prepared from *isopropylamine* by von Braun's method (*Ber.*, 1928, **61**, 1428). The intermediate *N-isopropyltoluene-p-sulphonamide* has been mentioned by Boon (*loc. cit.*) and others, but has not been formally described: it crystallised in stout prisms, m. p. 48—49°, from acetone (Found: C,

56.2; H, 7.1; S, 14.7.  $C_{10}H_{15}O_2NS$  requires C, 56.3; H, 7.0; S, 15.0%). The dialkylsulphonamide, m. p. 78°, was also obtained by direct sulphonylation of methylisopropylamine.

*O-Methyl-N-isopropylnitramine*.—The silver salt of isopropylnitramine (20 g.) was refluxed for 1½ hr. with methyl iodide (20 g.) in ether (100 ml.), and the mixture then shaken, at room temperature, for 24 hr. Silver iodide (18 g.) was collected, and the filtrate, after removal of ether through a fractionating column, was distilled to yield fractions of b. p. 59–61°/40 mm. (5 g.) and 106–108°/40 mm. (0.4 g.). The higher-boiling fraction was the *N*-methyl isomer (see p. 4000). The lower-boiling fraction was redistilled to yield *O-methyl-N-isopropylnitramine*, b. p. 59°/40 mm.,  $n_D$  1.428 (Found: C, 41.2; H, 8.3.  $C_4H_{10}O_2N_2$  requires C, 40.7; H, 8.5%).

*Methylation of isoPropylnitramine by Dimethyl Sulphate and by Diazomethane*.—(a) *isoPropyl-nitramine* (2.5 g.) was dissolved in aqueous potassium hydroxide (1.4 g. in 20 ml. of water), and dimethyl sulphate (3.8 g.) added dropwise with constant shaking. Extraction with ether and subsequent distillation yielded fractions of b. p. 60–61° (0.6 g.) and 108–109° (0.5 g.) at 40 mm., showing a ratio of 6 : 5 for *O*- to *N*-methylation. (b) An ethereal solution of diazomethane (from 20 g. of *N*-methyl-*N*-nitroso-*N'*-nitroguanidine; McKay, *J. Amer. Chem. Soc.*, 1947, 69, 3028) was added portionwise to *isopropylnitramine* (10 g. in 50 ml. of ether) until no further discharge of colour took place. The solution was distilled to remove ether and yield fractions of b. p. 58–65° (2.3 g.) and 108–110° (6.1 g.) at 40 mm., showing a ratio of 23 : 61 for *O*- to *N*-methylation.

*N-Methyl-O-isopropylnitramine*.—The silver salt of methylnitramine (10 g.) was refluxed for 6 hr. with *isopropyl iodide* (10 g.) in ether (200 ml.). Silver iodide (12.4 g.) was collected, and the filtrate, after removal of ether and excess of *isopropyl iodide* through a fractionating column, was distilled (2.5 g. at 57–61°/40 mm.: cf. Franchimont and van Dissel, *loc. cit.*) and redistilled to yield *N-methyl-O-isopropylnitramine*, b. p. 39–40°/20 mm. (Found: C, 40.2; H, 8.4.  $C_4H_{10}O_2N_2$  requires C, 40.7; H, 8.5%).

*O-Methyl- and N-Methyl-N-neopentylnitramines*.—The silver salt of *neopentylnitramine* (8 g.) was refluxed for 4 hr. with methyl iodide (22 g.) in ether (150 ml.). After removal of silver iodide, methyl iodide, and ether, distillation yielded a liquid (2.5 g. of b. p. 69–73°/17 mm.) and a solid residue (b. p. >100°/17 mm.). Redistillation of the liquid yielded *O-methyl-N-neopentylnitramine*, b. p. 63–65°/15 mm. (Found: C, 49.8; H, 9.7.  $C_6H_{14}O_2N_2$  requires C, 49.3; H, 9.6%). The residue of the initial distillation was warmed with 40% sulphuric acid to destroy any remaining *O*-alkyl compound, and extracted with ether. Evaporation and crystallisation from aqueous ethanol yielded the isomeric *N-methyl-N-neopentylnitramine* (0.2 g.) as lustrous needle-like plates, m. p. 65–66° (Found: C, 49.6; H, 9.6%).

*ON-Dimethyl- and ON-Diisopropyl-nitramine*.—These were prepared by methods generally similar to that used for *N-methyl-O-isopropylnitramine*. The dimethyl compound (Found: C, 27.0; H, 6.6. Calc. for  $C_4H_8O_2N_2$ : C, 26.7; H, 6.7%) had b. p. 113–115° (Franchimont and Umbgrove, *Rec. Trav. chim.*, 1896, 15, 218, gave b. p. 112°). The diisopropyl compound (Found: C, 49.6; H, 9.6. Calc. for  $C_6H_{14}O_2N_2$ : C, 49.3; H, 9.6%) had b. p. 58–61°/18 mm. (Thomas, *ibid.*, 1890, 9, 82, gave b. p. 55–57°/10 mm.; for identification as the *ON*-compound see Wright, *Canad. J. Res.*, 1948, 26, B, 292, who gave b. p. 52–53°/10 mm.).

*Gas Evolution from O-Methyl-N-isopropylnitramine: Absence of Elemental Nitrogen*.—A sample of the nitramine was decomposed by means of 0.5M-sulphuric acid. The evolved gas was swept out by a stream of carbon dioxide, and collected over a concentrated solution of potassium hydroxide. Of 0.87 molecular proportion collected, less than 2% was insoluble in ethanol. Details of the method have been given by Barrott, Denton, and Lamberton (*J.*, 1953, 1998).

*Decomposition of O-Methyl-N-isopropylnitramine in Presence of Potassium Dichromate*.—Aqueous potassium dichromate (25 ml. of 0.5N) and sulphuric acid (25 ml. of 40%) were added to a weighed sample (ca. 2 mmole) of the nitramine. Samples (5 ml.) were withdrawn at intervals and run into potassium iodide solution. Similar experiments were carried out with *isopropyl-nitramine*, and with purified methyl and *isopropyl alcohols*. Titration of the liberated iodine with thiosulphate showed final values, in terms of equivalents of oxygen per molecule, of 8.05 for  $Pr^4N:NO\cdot OMe$ , 2.05 for  $Pr^4NH\cdot NO_2$ , 2.00 for  $Pr^4OH$ , and 6.05 for  $MeOH$ ; but no useful conclusions could be drawn from the rate of oxidation.

*Formation of Alkyl Chlorides during Decomposition*.—A weighed sample of the nitramine (ca. 1 mmole) was heated under reflux on a steam-bath with a weighed quantity (ca. 1 g.) of 1.0M-hydrochloric acid. To ensure complete decomposition, *ON*-dialkylnitramines were heated for 2 hr., primary nitramines for 4–6 hr. The resultant solution was diluted, and the condenser washed down, with distilled water; residual acidity was determined by means of standard

potassium hydroxide, and ionisable chlorine by subsequent titration with mercuric nitrate, sodium nitroprusside being used as indicator. Results (Table 4) have been calculated on the basis of the overall equation  $R\cdot N\cdot NO\cdot OR' + HCl \longrightarrow RCl + N_2O + R'OH$  ( $R = \text{alkyl}$ ,  $R' = \text{alkyl or H}$ ). Control experiments with alcohols, and the lack of any halide formation from *O*-alkyl groups, showed that the reaction cannot proceed by formation of alcohol and subsequent esterification. Positive results suggest the formation of alkyl cations, but nil values do not disprove this, except when the same alkyl group produces alkyl chloride from an *N*-, but not from an *O*-linkage. Two factors are involved in the production of  $RCl$ : the formation of  $R^+$ , and its behaviour in its natal environment.

*Evidence Against the Formation of isoPropylnitramine during the Decomposition of O-Methyl-N-isopropylnitramine.*—A solution of *O*-methyl-*N*-isopropylnitramine (initially 0.038M in 0.005M-hydrochloric acid, at 20°) was kept at 45°, and samples (5 ml.) withdrawn at once, and after time intervals known to correspond to 10, 20, 30, 40, 50, 60, 75, and 100% decomposition. These were titrated with standard (*ca.* 0.01M) sodium hydroxide. In all cases the titre was  $2.65 \pm 0.05$  ml. No decomposition of isopropylnitramine can be detected in similar conditions of time, temperature, and acidity; any isopropylnitramine formed should therefore remain

TABLE 4. Formation of alkyl chlorides (conditions given in the relevant experimental section).

Compound	Yield (%) by determ. of:		Compound *	Yield (%) by determ. of:	
	H <sup>+</sup>	Cl <sup>-</sup>		H <sup>+</sup>	Cl <sup>-</sup>
MeN <sup>+</sup> :NO <sup>-</sup> :OMe	45.6, 47.5	45.0, 47.0	C <sub>5</sub> H <sub>11</sub> ·N <sup>+</sup> :NO <sup>-</sup> :OMe	Nil	Nil
MeN <sup>+</sup> :NO <sup>-</sup> :OPr <sup>i</sup>	47.2, 45.4	47.9, 44.7	MeNH·NO <sub>2</sub> †	51	50
Pr <sup>i</sup> N <sup>+</sup> :NO <sup>-</sup> :OMe	3.7	4.3	Pr <sup>i</sup> NH·NO <sub>2</sub> †	3.3	3.7
Pr <sup>i</sup> N <sup>+</sup> :NO <sup>-</sup> :OPr <sup>i</sup>	3.0	4.0	C <sub>5</sub> H <sub>11</sub> ·NH·NO <sub>2</sub>	Nil	Nil

\* C<sub>5</sub>H<sub>11</sub> = *neo*Pentyl.

† In good agreement with earlier work (Barrott, Denton, and Lamberton, *loc. cit.*).

undecomposed, and augment the sodium hydroxide titre. A yield of 1% of isopropylnitramine would have raised the titre by 0.19 ml.

*Measurement of Reaction Rates.*—The manometric technique has been described by Barrott, Denton, and Lamberton (*loc. cit.*). In the optical technique 5 ml. of pre-warmed acid were added to a pre-warmed solution of the nitramine in water to give, on admixture, solutions of the concentrations reported. Samples (0.5 ml.) were withdrawn, run into cold 0.05M-sodium acetate (20 ml.), and then made up to 25 ml. This effectively stops the decomposition, since the optical density was found to remain constant for periods of up to 24 hr. at room temperature. The solutions were examined in a Beckman quartz spectrophotometer. The rates reported are the mean of those derived from separate logarithmic plots of optical density at 230 and 235 mμ. The opacity of sodium acetate prevented readings at the head (213–215 mμ) of the absorption band.

*Measurements of Reaction Rates in Bisulphate and Chloroacetate Buffers.*—In preliminary work some measurements were made by the manometric technique at 45°. The large difference between runs XXXI and XXXII is probably due mainly to catalysis by HSO<sub>4</sub><sup>-</sup>; the difference between runs XXXIII and XXXIV may be due to catalysis, or may be simply a salt effect. Observed first-order rate coefficients are given in units of 10<sup>3</sup>h(min.<sup>-1</sup>): run XXXI in 0.1M-NaHSO<sub>4</sub> and -Na<sub>2</sub>SO<sub>4</sub>, 42.8; run XXXII in 0.01M-NaHSO<sub>4</sub> and -Na<sub>2</sub>SO<sub>4</sub>, 11.2; run XXXIII in 1.0M-CH<sub>2</sub>Cl·CO<sub>2</sub>H and -CH<sub>2</sub>Cl·CO<sub>2</sub>Na, 14.7; run XXXIV in 0.1M-CH<sub>2</sub>Cl·CO<sub>2</sub>H and -CH<sub>2</sub>Cl·CO<sub>2</sub>Na, 8.3.

*Ultraviolet Spectra of ON- and NN-Dialkylnitramines.*—The spectra of the *ON*-compounds showed (in water) maximum absorption at shorter wavelengths (213–215 mμ) than those reported (230–250 mμ; in organic solvents) for *NN*-dialkylnitramines in general (Jones and Thorn, *Canad. J. Res.*, 1949, 27, B, 828): MeN<sup>+</sup>:NO<sup>-</sup>:OPr<sup>i</sup>, λ<sub>max.</sub> (in H<sub>2</sub>O) 213 mμ (log ε 3.81); Pr<sup>i</sup>N<sup>+</sup>:NO<sup>-</sup>:OMe, λ<sub>max.</sub> (in H<sub>2</sub>O) 213 mμ (log ε 3.70); Pr<sup>i</sup>N<sup>+</sup>:NO<sup>-</sup>:OPr<sup>i</sup>, λ<sub>max.</sub> (in H<sub>2</sub>O) 215 mμ (log ε 3.81); *neo*-C<sub>5</sub>H<sub>11</sub>·N<sup>+</sup>:NO<sup>-</sup>:OMe, λ<sub>max.</sub> (in H<sub>2</sub>O) 213 mμ (log ε 3.83); MePr<sup>i</sup>N·NO<sub>2</sub>, λ<sub>max.</sub> (in 16% EtOH) 238 mμ (log ε 3.81).

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