# **348.** *Nitramines and Nitramides. Part XII.* The Base-catalysed Decomposition of Some* ON-*Dialkylnitramines, and Evidence for the Existence of Geometrical Isomers.*

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The alkali-catalysed decomposition of R·N:NO·OR′ (R and R′ being alkyl groups) appears to proceed easily only when two α-hydrogen atoms are present, and an aldehyde can be formed by the reaction $-CH_2·N:NO·OR' \longrightarrow -CHO + N_2 + R'OH$. For R′ = Me, changing R from Me to Et or $Pr^n$ slows the reaction by a factor of about 10; and, for R = Me, changing R′ from Me to Et or $Pr^i$ brings about a slight increase in rate.

These observations apply only to the main bulk of the material prepared by treatment of the silver salt of $R·NH·NO_2$ with the halide R′X; in the majority of cases the behaviour of crude samples was consonant with the presence therein of up to 25% of a less stable geometrical isomer, which can be readily hydrolysed to the parent nitramine.

Purified samples gave rates of acid-catalysed decomposition in agreement with previous work: measurements in Parts IX and XI of this series are therefore not invalidated by the recognition of isomerism in the crude materials.

UMBGROVE and FRANCHIMONT [1,2] decomposed several *ON*-dialkylnitramines by heating them with aqueous potassium hydroxide, and Backer,[3] considering the reaction to be analogous to ester hydrolysis, was puzzled by the formation of nitrogen and an aldehyde

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* Part XI, *J.*, 1957, 4198.

[1] Umbgrove and Franchimont, *Rec. Trav. chim.*, 1897, **16**, 359, 375.

[2] Umbgrove and Franchimont, *Rec. Trav. chim.*, 1898, **17**, 270.

[3] Backer, *Ahrens Sammlung*, 1912, **18**, 359.

in place of the expected primary nitramine. The fact that some primary nitramines are themselves decomposed by alkali[4] does not resolve the difficulty, since we have found that *ON*-dimethylnitramine was broken down, to liberate nitrogen, much more readily than the parent *N*-methylnitramine. The latter cannot, therefore, be an intermediate in the decomposition.

The early workers employed conditions (several hours at 100° in 12% aqueous potassium hydroxide) which were needlessly severe. We found that, at 70°, *O*-alkyl-*N*-methylnitramines were completely decomposed, in a few hours, by means of 0·1M-potassium hydroxide; but the *O*-methyl derivatives of ethyl- and n-propyl-nitramine were more stable by a factor of ten. The *O*-methyl derivatives of isopropyl- and t-butyl-nitramine yielded gas, but the rate of evolution was not significantly altered by changes in the concentration of alkali. Our results (obtained by the measurement of gas pressure at constant volume, with rigorously purified materials) are set out in Table 1.

*Isomeric Forms of Dialkylnitramines.*—The distinction between the *NN*- and *ON*-isomers was recognised[5] in 1894. Signs of a third, unstable, compound were found by Umbgrove and Franchimont,[2] who suggested the possibility of geometrical isomerism. In earlier papers of the present series[6] no sign of isomerism was found; for the materials, purified by repeated distillation *in vacuo*, were kinetically homogeneous on decomposition by means of aqueous acids. On extending this work to decomposition in alkaline solutions we found that crude samples (of most, but not all, of the *ON*-dialkylnitramines examined) did not give a kinetically homogeneous evolution of gas when warmed in aqueous potassium hydroxide. The initial gas evolution was comparatively rapid, and was accompanied by a fall in the concentration of potassium hydroxide. This behaviour was observed even after two or three distillations, though (at least for *O*-ethyl-*N*-methylnitramine) the impurity was to some extent concentrated in the higher-boiling fractions. The materials gave satisfactory elemental analyses; and the kinetic anomalies cannot be due to the *NN*-isomerides, which were shown (*a*) to be present only in very small quantities (<3%), and (*b*) to be relatively stable in alkaline solutions.

*Removal of the Less-stable* ON-*Dialkyl Isomeride.*—The crude materials could be purified by warming for a short time in aqueous alkali,* extraction with ether, and redistillation. After this treatment the decompositions yielded 95—99% of the theoretical quantity of gas, in place of the former 65—95%; and, as judged by the rate of evolution, were kinetically homogeneous. Further, there was now no rapid uptake of hydroxide ion; and the catalytic constants $k_{OH^-}$ (Table 1) were in agreement with the slower, final, rates shown by the crude samples. One example may be given as an illustration. Crude *O*-ethyl-*N*-methylnitramine in 0·025M-potassium hydroxide at 70° gave an initial first-order rate of *ca.* $7{\cdot}2 \times 10^{-3}$ min.$^{-1}$; after 80 min. this had fallen to $4{\cdot}7 \times 10^{-3}$ min.$^{-1}$, and a separate experiment, with 0·0766M-alkali, suggested that at this stage the potassium hydroxide concentration had been reduced to about 0·015M, whence $k_{OH^-} \approx 0{\cdot}3$ l. mole$^{-1}$ min.$^{-1}$ for the final stage of the run. After purification the decomposition was kinetically homogeneous, with $k_{OH^-} = 0{\cdot}37$ l. mole$^{-1}$ min.$^{-1}$. The change in slope, for a first-order plot with the crude material, was thus largely due to a change in the concentration of potassium hydroxide. At faster rates (0·05 and 0·075M-KOH) the anomalous portion of the run was completed before the first observation of gas pressure. The (relative) change in alkali concentration was in these cases smaller; but an anomaly still remained, in that the linear plot, when extrapolated back to the time origin, gave an intercept of less than 100% of the total gas evolved.

*Examination in Detail of the Decomposition of Crude* O-*Ethyl*-N-*methylnitramine.*—

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* Or, probably, by warming in distilled water alone, but this mode of purification has not been examined critically.

[4] Barrott, Gillibrand, and Lamberton, *J.*, 1951, 1282.

[5] Bamberger, *Ber.*, 1894, **27**, 359.

[6] Bruck and Lamberton, *J.*, 1955, 3997; 1957, 4198.

Control experiments showed that the abnormal course of gas evolution was not due to vapour-pressure effects exerted either by the initial nitramine, or by the products of decomposition. Nor was the slowing of the reaction an example of auto-retardation, since a closely similar reaction course was observed when fresh samples of the nitramine were decomposed in the spent solution from a previous run, or in a synthetic mixture containing, besides potassium hydroxide, the products of decomposition (formaldehyde and ethanol) in appropriate concentrations.

Measurements were made, in separate experiments, of (*a*) the course of gas evolution, (*b*) the rise in formaldehyde concentration, and (*c*) the fall in concentration of potassium hydroxide. These measurements were repeated on the material purified by treatment with alkali, and are summarised in Table 5. It can be seen (lines A and B) that the evolution of gas, especially in the initial stages, was faster than the increase in the concentration of formaldehyde: this indicates either a separate source of gas, or (much less likely) the retention of formaldehyde in some intermediate product of decomposition. The removal of formaldehyde by the Cannizzaro reaction can only bear a minor responsibility, since the greater part of the " formaldehyde deficiency " (line C) was observed in the first 20 min., when the concentration of formaldehyde was small, and the rate of the Cannizzaro reaction would be reduced. The changes in " formaldehyde deficiency," after 40 min., are in reasonable agreement with our independent observations of the rate of the Cannizzaro reaction in comparable conditions of concentration and temperature. The concentration of potassium hydroxide (line D) also showed its most rapid fall at the commencement of the run, and the fall in potassium hydroxide concentration at any time was greater (compare lines D and E) than could have been accounted for if the " formaldehyde deficiency " had been due solely to the Cannizzaro reaction. The difference between lines D and E is approximately constant after 40 min.: this suggests that changes in the " formaldehyde deficiency " are then related stoicheiometrically to changes in [KOH], in terms of the relationship $2CH_2O \longrightarrow H{\cdot}CO_2H$.

TABLE 1. *Decomposition of* ON-*dialkylnitramines, initially* 0·05M, *measured by gas evolution in aqueous potassium hydroxide at* 70°. (*First-order rate coefficients,* $k_2$ *in min.*$^{-1}$; *catalytic constants,* $k_{OH^-}$,* *in l. mole*$^{-1}$ *min.*$^{-1}$.)

| Run no. | Compound | Alkali (mole l.$^{-1}$ at 20°) | $10^3k_2$ | $k_{OH^-}$ | Run no. | Compound | Alkali (mole l.$^{-1}$ at 20°) | $10^3k_2$ | $k_{OH^-}$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | MeN:NO·OMe | 0·105 | 24·0 | 0·23 | 12 | EtN:NO·OMe | 0·202 | 4·9 | 0·025 |
| 2 | ,, | 0·0750 | 16·2 | 0·22 | 13 | ,, | 0·150 | 3·6 | 0·025 |
| 3 | ,, | 0·0488 | 11·1 | 0·23 | 14 | ,, | 0·106 | $2{\cdot}0_5$ | 0·020 |
| 4 | ,, | 0·0100 | 2·1 | 0·22 | 15 | Pr$^n$N:NO·OMe | 0·200 | 4·8 | 0·024 |
| 5 | MeN:NO·OEt † | 0·0754 | 25·6 | 0·35 | 16 | ,, | 0·150 | 3·8 | 0·026 |
| 6 | ,, | 0·0500 | 17·9 | 0·37 | 17 | ,, | 0·100 | $2{\cdot}3_5$ | 0·024 |
| 7 | ,, | 0·0250 | 9·0 | 0·37 | 18 | Pr$^i$N:NO·OMe | 0·211 | 0·2 | § |
| 8 | ,, | 0·0100 | 4·0 | 0·41 | 18 | ,, | 0·025 | 0·4 | |
| 9 | MeN:NO·OPr$^i$ | 0·0500 | 23·4 | 0·48 | 20 | Bu$^t$N:NO·OMe | 0·150 ‡ | 24·5 | |
| 10 | ,, | 0·0250 | 11·8 | 0·48 | 21 | ,, | 0·100 ‡ | 29·0 | |
| 11 | ,, | 0·0099 | 4·5 | 0·46 | 22 | ,, | 0·050 ‡ | 25·1 | |

* Catalytic constants have been calculated on the assumption that the hydroxyl-ion concentration at 70° was 98% of that measured at room temperature.

† A plot of the catalytic constants for MeN:NO·OEt against [KOH] suggests a " water-rate " of $0{\cdot}6 \times 10^{-3}$ min.$^{-1}$; but we think this erroneous, in view of the absence of any " water-rate " for the other *N*-methyl compounds.

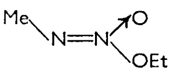
† In $H_2O$–MeOH (75 : 25, v/v).

§ These rates show no relation to [KOH], but are in good agreement, after reasonable allowances for changes in temperature and solvents, with the " water-rates " previously [6] determined.

The simplest and most likely explanation of the figures discussed in the preceding paragraph appears to be that the main reaction, yielding gas and formaldehyde, is accompanied by a more rapid reaction (or reactions) yielding gas and an acid, but no formaldehyde. This behaviour is consonant with the existence, in the crude material, of two isomers of the structure $\mathrm{MeN{:}NO{\cdot}OEt}$, the major constituent being decomposed according to the reaction $\mathrm{MeN{:}NO{\cdot}OEt} \xrightarrow{\mathrm{KOH}} \mathrm{CH_2O + N_2 + EtOH}$, and the minor constituent yielding in part gas ($\mathrm{MeN{:}NO{\cdot}OEt + H_2O \longrightarrow MeOH + N_2O + EtOH}$ ?) and in part the stable nitramine salt by the reaction $\mathrm{MeN{:}NO{\cdot}OEt + KOH \longrightarrow MeN_2O_2K + EtOH}$. Treatment with alkali of a crude (though neutral) sample of *O*-ethyl-*N*-methylnitramine has yielded methylnitramine, isolated as its cyclohexylamine salt.

*Behaviour, in Comparison, of Purified* O-*Ethyl*-N-*methylnitramine*.—These opinions are strongly supported by the results obtained from the purified material (Table 5, lines A′ to E′), when, effectively, the faster reactions had been allowed to run their course, and the residual (isomerically pure) nitramine recovered. In this case formaldehyde concentration is slightly ahead of gas evolution in the early stages—a not unexpected result, since the method of gas measurement tends to show a slight induction period on account of supersaturation. There is no early fall of significant size in the concentration of potassium hydroxide, and the " formaldehyde deficiency " which appears in the later stages is quantitatively related to the fall in alkali concentration: compare lines D′ and E′. Finally, the total yield of gas is now almost quantitative, in place of the 84% obtained from the impure sample. We felt confident, from these results, that we were now dealing with a homogeneous process of decomposition, strictly in accordance with the overall equation $\mathrm{MeN{:}NO{\cdot}OEt \longrightarrow CH_2O + N_2 + EtOH}$, though followed by the Cannizzaro reaction $\mathrm{2CH_2O + KOH \longrightarrow H{\cdot}CO_2K + MeOH}$; and it can be seen that [KOH] is not significantly altered before some 80% of the gas has been evolved.

*Physical Properties of the Crude and Purified Samples, and Structure of the Isomers*.—These properties support the hypothesis that the impure material contains a geometrical isomer of the more stable form. The ultraviolet spectrum of the purified material showed maximum absorption, in water, at a slightly shorter wavelength than for the crude sample; the infrared spectra, observed as smears, were almost precisely identical—with the exception of an absorption band at 1263 cm.$^{-1}$, found only in the crude sample. The refractive index was reduced by purification. The dipole moment of the crude sample was 2·6 D, reduced by purification to 1·8 D; bearing in mind the moments of the *cis*- and the *trans*-form of azoxybenzene (4·7 and 1·7 D, respectively), we think that our more stable isomeride probably has the *trans*-configuration (see inset).



*General Survey of the* ON-*Dialkylnitramines Prepared*.—Purification of the remaining materials (when required) always brought about a fall in the refractive index—a result consonant with the removal of a *cis*-isomer. The proportion of this less stable, presumed *cis*-, isomer in our crude preparations could be estimated by an extrapolation to the time origin of the final, and linear, portion of the first-order " log plot." The relative proportions of the isomerides so indicated cannot be precise, since any removal of alkali by the *cis*-isomer will have retarded the alkali-catalysed decomposition of the *trans*-isomer; but the figures are reasonable approximations. Our crude *O*-ethyl-*N*-methylnitramine contained 15—20% of the less stable isomer.

*ON*-Dimethylnitramine and *O*-methyl-*N*-t-butylnitramine appeared to be pure as first prepared; the volumes of gas evolved were normal, and there were no signs of kinetic inhomogeneity. The aldehyde products from *N*-ethyl-*O*-methylnitramine (crude: 30% of the less stable form) and *O*-methyl-*N*-propylnitramine (crude: 10% of the less stable form) could not be examined quantitatively, on account of the formation of coloured aldehyde resins; these (subsequent) reactions did not seem to give rise to any kinetic anomalies in runs with the purified materials. We have checked the nature of the gas evolved from an alkaline solution of crude *N*-ethyl-*O*-methylnitramine by means of infrared spectroscopic analysis: it was at least 99% nitrogen. Though the crude sample of *N*-isopropyl-*O*-methylnitramine showed an initial kinetic anomaly (corresponding to 20% of an alkali-unstable isomer), the purified material, and also *O*-methyl-*N*-t-butyl nitramine, did not appear to undergo alkali-catalysed decomposition (see Table 1, and notes).

There remains *N*-methyl-*O*-isopropylnitramine (crude: 15—20% of the less stable form). Measurements of formaldehyde, of potassium hydroxide, and of gas evolution are reproduced in Table 6. It can be seen that for the crude sample, whilst the concentration of potassium hydroxide again shows an initial fall, there is no deficiency of formaldehye, in comparison with gas evolution in the early stages. The anomalies are removed by purification, and we conclude that the geometrical isomeride is in this case largely decomposed by the route $\mathrm{MeN{:}NO{\cdot}OPr^i + KOH \longrightarrow MeN{:}NO_2K + Pr^iOH}$, without evolution of gas.

To conclude the discussion of isomerism we point out that the materials termed " crude" are so named for lack of a better term; all " crude " materials used for any measurements had been distilled at least twice, contained less than 3% of the *NN*-isomeride, and gave satisfactory analyses: and that we do not claim, in default of isolation of a pair of isomers, that our evidence as yet constitutes a full proof. The results in Tables 1—3 were all obtained from fully purified materials.

*Activation Energies.*—Some measurements have been made at temperatures other than 70°, and are reported in Table 2. The energies of activation are similar to those found [6] for decomposition by acids; but the frequency factors are somewhat smaller, and lie within the limits prescribed by Hinshelwood and Winkler [7] for bimolecular reactions.

TABLE 2. *The parameters A and E in the kinetic equation* $k = A \exp(-E/\boldsymbol{R}T)$.

| Run nos. and notes | Compound (initially (0·05M) | Values of $k_{\mathrm{OH^-}}$ (l. mole$^{-1}$ min.$^{-1}$) measured by gas evolution at | | | | | | $\log_{10} A$ (l. mole$^{-1}$ sec.$^{-1}$) | $E$ (kcal. mole$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| | | 50° | 51° | 60° | 70° | 75° | 80° | | |
| *a* | $\mathrm{MeN{:}NO{\cdot}OMe}$ | | | | 0·231 | 0·32$_5$ | 0·48 | 9 | 18 |
| *b* | $\mathrm{MeN{:}NO{\cdot}OEt}$ | 0·050 | | 0·123 | 0·34$_5$ | | | 11 | 21 |
| *c* | $\mathrm{MeN{:}NO{\cdot}OPr^i}$ | | 0·094 | 0·204 | 0·49 | | | 10 | 19 |
| *d* | $\mathrm{EtN{:}NO{\cdot}OMe}$ | | | | 0·0246 | 0·038 | 0·057 | 9 | 20 |
| *e* | $\mathrm{Pr^nN{:}NO{\cdot}OMe}$ | | | | 0·0262 | 0·044 | 0·066 | 11 | 22 |

Run nos. are grouped in order of increasing temperature, and concentrations of alkali are given in mole l.$^{-1}$ at 20°. (*a*) 0·0488M-KOH, 3, 23, 24: (*b*) 0·0754M-KOH, 25, 26, 5: (*c*) 0·0488M-KOH, 27, 28, 29: (*d*) 0·202M-KOH, 12, 30, 31: (*e*) 0·150M-KOH, 16, 32, 33. In view of the small number of determinations we do not feel it advisable to quote values of log *A* and *E* to a greater degree of precision.

TABLE 3. *Decomposition of* ON-*dialkylnitramines, initially* 0·05M, *measured by gas evolution in hydrochloric acid at* 45°. (*First-order rate coeff.* $k_1$ *in min.*$^{-1}$; *catalytic constant,* $k_{\mathrm{H^+}}$, *in l. mole*$^{-1}$ *min.*$^{-1}$.)

| Run no. | Compound | Acid (mole l.$^{-1}$ at 20°) | $10^3k_2$ | $k_{\mathrm{H^+}}$ | Average value of $k_{\mathrm{H^+}}$ from ref. 6 |
|---|---|---|---|---|---|
| 34 | $\mathrm{MeN{:}NO{\cdot}OEt}$ | 0·50 | 19·5 | 0·039 | 0·044 |
| 35 | ,, | 0·50 | 20·7 | 0·042 | |
| 36 | $\mathrm{MeN{:}NO{\cdot}OPr^i}$ | 0·50 | 22·0 | 0·044 | 0·038, 0·044 * |
| 37 | $\mathrm{EtN{:}NO{\cdot}OMe}$ | 0·050 | 19·9 | 0·40 | 0·41 |
| 38 | $\mathrm{Pr^nN{:}NO{\cdot}OMe}$ | 0·050 | 25·0 | 0·50 | |
| 39 | ,, | 0·025 | 11·7 | 0·47 | |
| 40 | $\mathrm{Pr^iN{:}NO{\cdot}OMe}$ | 0·0050 | 15·5 | 3·1 | 3·6 |
| 41 | ,, | 0·0025 † | 13·9 | 3·5 | |

* By ultraviolet measurements: attention had already been drawn [6] to the discrepancy between gas evolution and ultraviolet measurements for this compound, and it now appears that the ultraviolet values are the more accurate.

† Sulphuric acid; $\mathrm{H^+}$ (calc.) at 45°, 0·0040M.

*Acid-catalysed Decomposition of Isomerically Pure* ON-*Dialkylnitramines.*—Reasons could be suggested (but cannot now be proved) to account for the apparent homogeneity of the materials examined in earlier papers [6] of this series. We are pleased to find that

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[7] Hinshelwood and Winkler, *J.*, 1936, 371.

any errors in the previous values must be small, and do not in any way invalidate the conclusions drawn from the published figures. In Table 3 we give values of the catalytic constant $K_{H^+}$ which have now been determined on isomerically pure materials. $\mathrm{Pr^nN{:}NO{\cdot}OMe}$ had not been previously examined; the rate found fits normally into the series $\mathrm{R = Me < Et < Pr^n < neo\text{-}C_5H_{11} < Pr^i \ll Bu^t}$ for $\mathrm{R{\cdot}N{:}NO{\cdot}OMe}$.

## EXPERIMENTAL

Reaction rates were evaluated on the basis of natural logarithms, and temperatures were controlled to within 0·1°. Concentrations of alkali or acid have been corrected on the assumption that the solutions showed the same expansion as water over the range 20—80°. The method of rate measurement by a manometric technique has been previously described:[8] we have found it advisable to lengthen (and support, by a rigid connection to the frame) the glass " tail " of the apparatus marked $F$ in the Figure of ref. 8). This alteration ensures a positive internal pressure at the glass-to-rubber joint, and prevents the entry of air which forced us, occasionally, to discard otherwise satisfactory " runs."

*Preparation and Purification of Materials.*—All but one of the *ON*-dialkylnitramines have recently[6] been described. The silver salt of n-propylnitramine (47 g.) was refluxed for 6 hr. with methyl iodide (43 g.) in dry ether (400 ml.), and, after collection of the silver iodide, the filtrate was distilled to yield O-*methyl*-N-*n-propylnitramine* (probably containing some 10% of the *cis*-isomer), b. p. 71—73°/35 mm. (Found: N, 23·4. $C_4H_{10}N_2O_2$ requires N, 23·7%).

*O*-Ethyl-*N*-methylnitramine (19 g.) was purified by dissolution in water (850 ml.), addition of potassium hydroxide (50 ml. of 0·7M), and heating for 1 hr. at 70°. After cooling, the mixture was extracted with ether (4 × 200 ml.), and the extract was washed with water, dried ($Na_2SO_4$), and distilled to yield the residual isomerically pure nitramine of b. p. 40—42°/20 mm. With the exception of $\mathrm{MeN{:}NO{\cdot}OMe}$ and $\mathrm{Bu^tN{:}NO{\cdot}OMe}$, which appeared to be already pure by the test of kinetic homogeneity, all the *ON*-dialkylnitramines were similarly purified: physical properties are summarised in Table 4. The refractive indices were measured with an Abbé refractometer, and the dipole moment of *O*-ethyl-*N*-methylnitramine was determined by standard methods, benzene being used as a non-polar solvent.

*Comparison of Gas Evolution, Formaldehyde Production, and Alkali Concentration.*—The gas evolved (expressed as mmoles per l. of solution) was calculated from observations on the increase in pressure at constant volume, made in the rate-determination apparatus. For formaldehyde, aliquot parts (20 ml.) of a solution of the *ON*-dialkylnitramine in aqueous potassium hydroxide were kept at 70°, cooled rapidly, and treated with a solution (100 ml.) of 2,4-dinitrophenylhydrazine. After 24 hr. at 0°, the precipitate was collected, and dried at 100°. The reagent was prepared by warming 2,4-dinitrophenylhydrazine (10 g.) with hydrochloric acid (2 l. of 2N), filtering off excess of the hydrazine from the cooled solution, and saturating it with the formaldehyde hydrazone by addition of a little formaldehyde; then after 24 hr. at 0°, the suspension was allowed to warm to room temperature, and filtered before

TABLE 4. *Comparison of " crude " and " purified " samples of* ON-*dialkylnitramines.*

| | | Analyses (%) Found | | | Calc. | | | | U.V. Spectra in $H_2O$ | |
|---|---|---|---|---|---|---|---|---|---|---|
| Compound | | C | H | N | C | H | N | $n_D^{25}$ | log $\varepsilon_{max.}$ | mμ |
| $\mathrm{MeN{:}NO{\cdot}OMe}$ | | 26·9 | 6·5 | 30·8 | 26·7 | 6·7 | 31·1 | | 3·94 | 217 |
| $\mathrm{MeN{:}NO{\cdot}OEt}$ | Crude | 34·9 | 7·8 | 27·0 | 34·6 | 7·7 | 26·9 | 1·4320 | 3·76 | 215 |
| | Purified | 34·8 | 7·8 | | | | | 1·4248 | 3·80 | 205 |
| $\mathrm{MeN{:}NO{\cdot}OPr^i}$ | Crude | 40·3 | 8·2 | | 40·6 | 8·5 | | 1·4268 | 3·76 | 212 |
| | Purified | 40·3 | 8·6 | | | | | 1·4245 | 3·78 | 210 * |
| $\mathrm{EtN{:}NO{\cdot}OMe}$ | Crude | 34·8 | 7·5 | | 34·6 | 7·7 | | 1·4293 | 3·74 | 214 |
| | Purified | 34·8 | 7·7 | | | | | 1·4263 | 3·76 | 212 |
| $\mathrm{Pr^nN{:}NO{\cdot}OMe}$ | Crude | | | 23·4 | | | 23·7 | 1·4310 | 3·84 | 212 |
| | Purified | | | 23·9 | | | | 1·4300 | 3·80 | 215 |
| $\mathrm{Pr^iN{:}NO{\cdot}OMe}$ | Crude | | | 24·0 | | | 23·7 | 1·4259 | 3·75 | 212 |
| | Purified | | | 23·5 | | | | 1·4245 | 3·79 | 212 * |
| $\mathrm{Bu^tN{:}NO{\cdot}OMe}$ | | 45·9 | 9·2 | | 45·5 | 9·1 | | | 3·74 | 215 |

* Independently determined[6] as, respectively, 3·81 at 213 and 3·70 at 213 mμ.

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[8] Barrott, Denton, and Lamberton, *J.*, 1953, 1998.

use. Tests showed the precipitation to be >98% of quantitative, even in 0·05M-ethanol (ethanol of this concentration is formed by the complete decomposition of *O*-ethyl-*N*-methylnitramine). The potassium hydroxide concentration was measured by heating aliquot parts (5 ml.) of the nitramine solution, cooling rapidly, and titrating with hydrochloric acid. Our results are given in Tables 5 and 6.

TABLE 5. *Relation of gas evolution, formaldehyde production, and alkali concentration for the decomposition of* O-*ethyl*-N-*methylnitramine at* 70°.

All values in mmole l.$^{-1}$, as at 20°. Initial concentrations: lines A to E crude nitramine (50·5 mmoles l.$^{-1}$) in potassium hydroxide (76·6 mmoles l.$^{-1}$); lines A′ to E′, purified nitramine (50·0 mmoles l.$^{-1}$) in potassium hydroxide (75·0 mmoles l.$^{-1}$).

| | Time (min.) | 10 | 20 | 40 | 60 | 80 | 85 | 160 | 180 |
|---|---|---|---|---|---|---|---|---|---|
| (A) | Gas evolved | 15·5 | 21·8 | 29·8 | 34·3 | 37·7 | | 42·3 | |
| (B) | [$CH_2O$] | | 12·0 | 17·8 | 21·4 | 23·3 | | 27·7 | |
| (C) (= A − B) | Deficiency in [$CH_2O$] | | 9·8 | 12·0 | 12·9 | 14·4 | | 14·6 | |
| (D) | Fall in [KOH] | | 10·8 | 13·1 | 13·5 | 13·9 | | 15·0 | |
| (E) (= C/2) | Fall in [KOH] which could be due to Cannizzaro reaction | | 4·9 | 6·0 | 6·5 | 7·2 | | 7·3 | |
| (A′) | Gas evolved | 11·4 | 19·9 | 31·6 | 38·4 | | 43·2 | | 49·0 |
| (B′) | [$CH_2O$] | 12·4 | 19·2 | 30·0 | 34·5 | | 38·8 | | 38·6 |
| (C′) (= A′ − B′) | Deficiency in [$CH_2O$] | −1·0 | 0·7 | 1·6 | 3·9 | | 4·4 | | 10·4 |
| (D′) | Fall in [KOH] | 0·7 | 0·9 | 1·0 | 1·4 | | 2·3 | | 5·4 |
| (E′) (= C′/2) | Fall in [KOH] which could be due to Cannizzaro reaction | | 0·4 | 0·8 | 2·0 | | 2·2 | | 5·2 |

TABLE 6. *Relation of gas evolution, formaldehyde production, and alkali concentration for the decomposition of* O-*isopropyl*-N-*methynitramine at* 70°.

All values in mmole l.$^{-1}$, as at 20°. Initial concentrations: lines A to E, crude nitramine (51·8 mmoles l.$^{-1}$) in potassium hydroxide (48·9 mmoles l.$^{-1}$); lines A′ to E′, purified nitramine (50·2 mmoles l.$^{-1}$) in potassium hydroxide (48·9 mmoles l.$^{-1}$).

| | Time (min.) | 10 | 30 | 60 | 120 | 240 | 300 |
|---|---|---|---|---|---|---|---|
| (A) | Gas evolved | 15·1 | 19·8 | 28·5 | 36·0 | 39·7 | 40·0 |
| (B) | [$CH_2O$] | 15·4 | 18·4 | 23·8 | 27·6 | 28·8 | 28·2 |
| (C) (= A − B) | Deficiency in [$CH_2O$] | −0·3 | 1·4 | 4·7 | 8·4 | 10·9 | 11·8 |
| (D) | Fall in [KOH] | 3·6 | 5·6 | 6·2 | 8·3 | 10·0 | 9·9 |
| (E) (= C/2) | Fall in [KOH] which could be due to Cannizzaro reaction | | 0·7 | 2·4 | 4·2 | 5·5 | 5·9 |
| (A′) | Gas evolved | 18·5 | 23·8 | 35·6 | 43·7 | 46·7 | 47·0 |
| (B′) | [$CH_2O$] | 17·6 | 22·3 | 31·0 | 36·5 | 34·7 | 34·7 |
| (C′) (= A′ − B′) | Deficiency in [$CH_2O$] | 0·9 | 1·5 | 4·6 | 7·2 | 12·0 | 12·2 |
| (D′) | Fall in [KOH] | 1·1 | 2·0 | 2·6 | 3·9 | 4·9 | 6·7 |
| (E′) (= C′/2) | Fall in [KOH] which could be due to Cannizzaro reaction | 0·5 | 0·8 | 2·3 | 3·6 | 6·0 | 6·1 |

*Fractionation of* O-*Ethyl*-N-*methylnitramine, and Hydrolysis of the Crude Material to yield Methylnitramine.*—An unpurified sample was distilled at 20 mm., and fractions were collected. Kinetic examination at 70° in 0·025M-potassium hydroxide gave the following observed first-order rates at, respectively, 20 and 80 min. from the start of the run: $10^3k$ (min.$^{-1}$) for initial material, 6·8 and 3·9; for fractions of b. p. 35—38°, 6·9 and 5·2; b. p. 38—42°, 6·2 and 5·1; b. p. 42—48°, 7·1 and 3·5. The highest-boiling fraction thus shows the greatest change in rate.

Another sample of *O*-ethyl-*N*-methylnitramine (5·4 g. of b. p. 42—46°/18—20 mm., $n_D^{25}$ 1·4296) was redistilled at 20 mm. to yield the following fractions: (I) 1·5 g., b. p. <42°, $n_D^{25}$ 1·4276; (II) 2·9 g., b. p. 42—44°, $n_D^{25}$ 1·4301; (III) 0·3 g., b. p. >44°, $n_D^{25}$ 1·4371. When 0·05M-solutions of the nitramine were heated in 0·083M-potassium hydroxide at 70°, the fall in alkali (moles per mole of total nitramine) was, respectively, for fractions (I), (II), and (III): 10 min., 0·10, 0·16, 0·36; 20 min., 0·13, 0·22, 0·50; 30 min., 0·16, 0·26, 0·58; and 40 min., 0·17, 0·28, 0·62. The $n_D^{25}$ of fraction (II), when kept for 10 weeks, was found to have fallen to 1·4262 (possibly through decomposition of the less stable isomer); and heating a 0·1M-solution to 70° in 0·136-potassium hydroxide led, in 30 min., to a loss of 0·20 mole of alkali per mole of nitramine.

Fraction (II) (825 mg., now of $n_D^{25}$ 1·4262) was heated at 70° for 70 min. in potassium hydroxide (80 ml. of 0·136M). The cooled solution was washed with ether (4 × 20 ml.), and evaporated on the steam-bath to *ca.* 15 ml.; after re-cooling, it was acidified (13 ml. of 2N-hydrochloric acid) and extracted with ether (2 × 10, and 5 × 5 ml.). The extract was dried ($Na_2SO_4$), then basified by the addition of cyclohexylamine (0·1 ml.), to yield the crude salt (*ca.* 50 mg.); recrystallisation from ethanol–ether gave methylnitramine cyclohexylamine salt (25 mg.), m. p. and mixed m. p. 132° (Found: C, 47·8; H, 9·6. Calc. for $C_7H_{17}N_3O_2$: C, 48·0; H, 9·8%).

*Concentration and Behaviour of the* NN-*Isomers.*—Some of the *NN*-isomer is always produced on alkylation of the silver salts of primary nitramines, but is rapidly removed on fractionation. The residual concentration in our " crude " products (at least twice distilled) was determined by observation of the residual ultraviolet absorption after decomposition of the *ON*-isomers in 2N-hydrochloric acid at 45°; it was generally less than 1%, and never more than 3%. These small quantities of the *NN*-isomers could not cause the anomalies which have been discussed. In addition, for comparison, we prepared *N*-ethyl-*N*-methylnitramine by the alkylation of ethylnitramine with methyl iodide and potassium hydroxide in ethanol, and removed any *ON*-isomers by shaking with 20% sulphuric acid for 1 hr. at room temperature, followed by redistillation; the product had b. p. 100—102°/30 mm. (Found: C, 34·7; H, 7·8. Calc. for $C_3H_8N_2O_2$: C, 34·6; H, 7·7%). Heating this (0·05M) with potassium hydroxide (0·0115M) at 70° had little effect on the alkali concentration, the observed fall (on titration with hydrochloric acid) in moles per mole of nitramine being: in 40 min., 0·006; 80 min., 0·004; 120 min., 0·006; 300 min., 0·008; and 1440 min., 0·020. We have also attempted to follow the decomposition of *NN*-dimethylnitramine by colorimetric determination of the nitrite produced, and by using more drastic conditions (2·07M-potassium hydroxide at 90°) to obtain a measurable rate. No gas was evolved, and only some 50—60% of the expected nitrite was obtained. It seems that the traditional equation $CH_3{\cdot}N(NO_2){\cdot}CH_3 + KOH \longrightarrow CH_2O + KNO_2 + CH_3{\cdot}NH_2$ does not provide a full picture of the decomposition, and that *NN*-dimethylnitramine is much more stable towards alkali than is the *ON*-isomer.

*Behaviour of* O-*Ethyl*-N-*methylnitramine on being heated in Water.*—A solution (0·05M) of the crude nitramine in distilled water at 70° rapidly evolved gas; evolution ceased after about 0·5 hr., when some 0·2 mole had been evolved per mole of total nitramine. The purified material was relatively stable, giving no gas on similar treatment.

*Analysis of the Observed Course of Decomposition for the Unpurified* ON-*Dialkylnitramines.*—Frost and Pearson [9] discuss the resolution of two parallel first-order reactions producing a common product. If $A \xrightarrow{k_1} C$, $B \xrightarrow{k_2} C$, and C is measured, then—if $k_1$ is considerably greater than $k_2$—the value of $k_2$ can be determined from the latter portion of the logarithmic plot of $(C_\infty - C)$ against time, when the reaction $A \longrightarrow C$ is effectively complete. Extrapolation back to the time origin of the line used to determine $k_2$ gives values of B, and hence of A $(= C_\infty - C - B)$. If our samples contained only two isomers, both of which showed first-order (or pseudo-first-order) decomposition to yield one mole of gas per mole of nitramine, then the analysis would fit, it being irrelevant, kinetically, whether the gas measured was nitrogen or nitrous oxide.

Unfortunately, part at least of A gives an acid, but no gas; and the acid reduces the rate of gas evolution from B by neutralisation of the potassium hydroxide. The analysis cannot, therefore, be precise; but good first-order log plots were obtained in three cases out of the four examined: the exception being *O*-isopropyl-*N*-methylnitramine, where there is reason to think that the unstable isomer was converted almost wholly into the acid, methylnitramine. Though we do not consider the numerical values of $k_1$ to be significant, the linear plots show that the observed kinetic anomalies were not due to factors of a random character.

*Infrared Spectra of the* ON-*Dialkylnitramines.*—Smears of the liquids were examined, for wavelengths 2—15 μ, a Grubb–Parsons double-beam spectrometer being used. They showed strong absorption at 1554 ± 10 and 1242 ± 10 cm.$^{-1}$. In several cases the band at 1554 cm.$^{-1}$ was flat-topped, and may represent more than one absorption frequency: it corresponds closely

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[9] Frost and Pearson, " Kinetics and Mechanism," Wiley, New York, 1953, p. 149.

to the *as*-stretching vibration in alkyl nitroparaffins [10] and is within the range suggested by Bellamy [11] for the same vibration in *N*-nitro-compounds. If the second absorption corresponds to the *s*-stretching vibration of the nitro-group, it has been displaced further than had been previously suggested [11] (*viz.*, $\mathrm{C{-}NO_2}$ *ca.* 1380—1340 $\mathrm{cm.^{-1}}$; $\mathrm{N{-}NO_2}$, *ca.* 1300—1250 $\mathrm{cm.^{-1}}$). In interpretation it should be remembered that the *ON*-dialkyl compounds do not have a free, terminal nitro-group; and that the nitramines considered by Bellamy are possibly not typical of the simple alkyl compounds.

All our *ON*-dialkyl compounds showed a medium-to-weak absorption band at 702 ± 5 $\mathrm{cm.^{-1}}$, though in one case ($\mathrm{MeN{:}NO{\cdot}OPr^i}$) this was largely concealed by a more general absorption. The spectra of the " crude " and the " purified " materials were almost identical. The major absorption peaks between 2000 and 1000 $\mathrm{cm.^{-1}}$ were as follows: $\mathrm{MeN{:}NO{\cdot}OMe}$, 1559, 1381, 1245, 1040; $\mathrm{MeN{:}NO{\cdot}OEt}$, 1562, 1444, 1381, 1242, 1032; $\mathrm{MeN{:}NO{\cdot}OPr^i}$, 1545, 1378, 1243, 1102, 1022; $\mathrm{EtN{:}NO{\cdot}OMe}$, 1562, 1460, 1434, 1338, 1240, 1000; $\mathrm{Pr^nN{:}NO{\cdot}OMe}$, 1562, 1463, 1429, 1338, 1239, 1013; $\mathrm{Pr^iN{:}NO{\cdot}OMe}$, 1548, 1465, 1331, 1239, 1009; and $\mathrm{Bu^tN{:}NO{\cdot}OMe}$, 1559, 1460, 1251, 1234, 1009.

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[10] Brown, *J. Amer. Chem. Soc.*, 1955, **77**, 6341.

[11] Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen, London, 1958, Chapter 17.