285. *The Decomposition of Primary Nitramines in Alkaline Solutions.*

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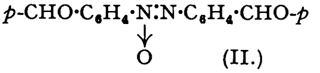
Primary nitramines have generally been considered to be stable towards aqueous alkalis. It has now been found that, in a number of instances, the reaction $RR'CH{\cdot}NH{\cdot}NO_2 \longrightarrow RR'C{=}O + N_2 + H_2O$ occurs on heating in presence of an excess of aqueous sodium or potassium hydroxide. The reaction is not simply the thermal decomposition of the nitramine anion and, though undoubtedly complex, it is often pseudo-unimolecular. It appears to be favoured by (*a*) increasing concentration of hydroxyl ions, (*b*) increasing concentration of sodium or potassium ions, and (*c*) increasing electron-attractive power of the groups R and R′. As the equation indicates, the presence of a hydrogen atom on the α-carbon is apparently essential.

Van Erp (*Rec. Trav. chim.*, 1895, **14**, 45) found that the anions of simple aliphatic nitramines were not attacked by hot 20% aqueous potassium hydroxide. His observations, together with the use of nitramine salts in preparative work, led to the assumption that all primary nitramines showed considerable stability towards aqueous alkalis. This statement must now be qualified.

Hantzsch and Metcalf (*Ber.*, 1896, **29**, 1680) found that nitraminoacetic acid (I; R = H, R′ = CO_2H) was decomposed, with the evolution of nitrogen, by treatment with sodium hydroxide. J. K. N. Jones (private communication) observed that methylenedinitramine was readily decomposed by an excess of caustic alkali; and the existence of a zone of comparative stability around pH 10 suggested that the reaction was not the same as that (around pH 5) previously investigated in some detail (Lamberton, Lindley, and Speakman, *J.*, 1949, 1650). Furthermore, the gas evolved from methylenedinitramine in 1·0M-potassium hydroxide has been found to contain both nitrous oxide and nitrogen: the evolution of nitrogen is not typical of nitramine decompositions which have hitherto been recognised.

$RR'CH{\cdot}NH{\cdot}NO_2$
(I.)



$p\text{-}CHO{\cdot}C_6H_4{\cdot}\underset{\overset{\downarrow}{O}}{N}{:}N{\cdot}C_6H_4{\cdot}CHO\text{-}p$
(II.)

We have confirmed the production of nitrogen from nitraminoacetic acid, and also examined its ethyl ester (I; R = H, R′ = CO_2Et), whose stability as a nitramine was not investigated by Hantzsch. The ester was found by us to decompose much more readily than the acid, nitrogen being evolved with moderate rapidity on heating of solutions of as low a pH as 6·8; and at pH 8·7 hydrolysis was marked by the cessation of gas evolution as the residual ester was converted into the more stable acid. If, as seems likely, the first dissociation constant of nitraminoacetic acid represents the ionisation of the carboxyl group, then the change from ester to acid at pH 8·7 is in fact the replacement of CO_2Et by CO_2^-. The carbethoxyl group is more electron-attractive than the ionised carboxyl group (a statement borne out, incidentally, by a comparison of the dissociation constant of nitraminoacetic ester with the second dissociation constant of the acid), and it was tentatively assumed that electron-attractive groups facilitated the decomposition.

On this hypothesis, and to isolate more easily the non-gaseous reaction products by the use of a nitramine of higher molecular weight, *p*-nitrobenzylnitramine (I; R = H, R′ = *p*-$NO_2{\cdot}C_6H_4$) was next examined. It decomposed readily in the presence of excess of alkali, but secondary reactions also occurred: thus when a 0·1M-solution of the sodium salt in 0·1M-sodium hydroxide was heated the azoxyaldehyde (II) was precipitated in 62% yield (on basis 2 molecules nitramine $\longrightarrow$ 1 molecule dialdehyde). In other respects, also, the behaviour of *p*-nitrobenzylnitramine appeared to be unusual, and has not been fully investigated.

$(p\text{-}C_6H_4R)_2{\cdot}CH{\cdot}NH{\cdot}NO_2$
(III.)

$p\text{-}C_6H_4R{\cdot}CHMe{\cdot}NH{\cdot}NO_2$
(IV.)

In order to avoid secondary reactions associated with *C*-nitro-groups, we turned to the diphenylmethylnitramines. Though showing greater stability, they were completely decomposed—in periods varying from a few hours to a few days—in aqueous 1·0M-potassium hydroxide at 95°. Diphenylmethylnitramine (III; R = H) and its 4 : 4′-dibromo-, 4 : 4′-dimethyl-, and 4 : 4′-dimethoxy-derivatives have been examined. In order to elucidate the reaction, comparable experiments have been made using methyl-, phenyl-, benzyl-, 1-phenylethyl- (IV; R = H), and 1-*p*-bromophenylethyl-nitramine (IV; R = Br).

The corresponding ketones (*e.g.*, benzophenone from III; R = H) have been obtained in good yield by complete decomposition of the diphenylmethylnitramines. Benzaldehyde (as the 2 : 4-dinitrophenylhydrazone) and benzoic acid (presumably as the result of a Cannizzaro reaction) have been obtained from the unstable benzylnitramine. 1-Phenylethyl- and 1-*p*-bromophenylethyl-nitramine could not be completely decomposed in a reasonable time, even by means of stronger (*e.g.*, 4M-)potassium hydroxide; but acetophenone and *p*-bromoacetophenone have been isolated, as 2 : 4-dinitrophenylhydrazones, after partial decomposition of these nitramines. Phenylnitramine was stable, and recoverable. No attempt was made to isolate the decomposition products of methylnitramine. In most cases the gas evolved was tested, qualitatively, for (water-soluble) nitrous oxide: none was observed. A gas sample from diphenylmethylnitramine was collected with complete exclusion of air, and was found by analysis to consist solely of nitrogen. It thus appears that the overall decomposition is

$$>\!\mathrm{CH}\cdot\overset{\ominus}{\overset{\frown}{\mathrm{N}\cdot\mathrm{NO}_2}} \longrightarrow\ >\!\mathrm{C}{=}\mathrm{O} + \mathrm{N}_2 + \overset{\ominus}{\mathrm{O}}\mathrm{H} \quad . \; . \; . \; . \; . \; . \; . \quad (1)$$

though it must be emphasised that an excess of alkali is required, and the process is not simply the thermal decomposition of the nitramine ion.

The progress of decomposition has been followed by measurement of the gas evolved. The total volume of gas produced from benzylnitramine, and from the various diphenylmethylnitramines, corresponded closely with that expected on the basis of equation (1); and the validity of the measurements was further established by the recovery and determination, in a few cases, of the residual nitramine after partial decomposition had taken place. The validity of gas evolution as a measure of the decomposition of methylnitramine, and of the phenylethylnitramines (IV; R = H or Br), has been assumed, though not strictly proven.

TABLE I.

Decomposition of potassium salts of the nitramines $R\cdot NH\cdot NO_2$, *initially* 0·05M., *in aqueous* 1·0M-*potassium hydroxide at* 95°.

Run nos.	R.	Apparent first-order constant, 10^4k min.$^{-1}$, at residual concentration of nitramine salt:		
		90%.	65%.	40%.
I, XIII	Me	0·6	—	—
II	Ph	Stable [1]	—	—
III	$Ph\cdot CH_2$	640	640	640
XLIV	Ph·CHMe	Stable [1]	—	—
XLV, XLVI	p-$C_6H_4Br\cdot CHMe$	Stable [1]	—	—
VI, VII, XIV, XV, XVI	Ph_2CH	16·6	16·6	16·6
XI, XII, XXII	$(p$-$C_6H_4Br)_2CH$	77	105	135
IX, XVII, XVIII	$(p$-$C_6H_4Me)_2CH$	3·7	4·6	4·9
X, XXI	$(p$-$MeO\cdot C_6H_4)_2CH$	2·4	2·4	—

[1] Measurable rates of reaction (see Experimental section) were observed in more concentrated (4M- and 8M-)potassium hydroxide. In the case of phenylnitramine the extremely slow decomposition was clearly of a quite different (oxidative?) type, since it led to a reduction in the volume of the enclosed gas.

Though the overall decomposition presumably represents the summation of several reactions, there often appeared to be a rate-determining step, and the decomposition was then of the first-order with respect to the nitramine. In the case of diphenylmethylnitramine, the individual decompositions showed a close correspondence with the first-order reaction-rate law under a variety of conditions. In other cases, notably di-(*p*-bromophenyl)methylnitramine, the first-order rate "constant" increased as decomposition progressed. The relative stability of the potassium salts of various nitramines in 1·0M-potassium hydroxide at 95°, and the variation of the apparent, instantaneous, first-order constants (obtained from graphs of log residual concentration of nitramine against time), are given in Table I. The small increase in free-alkali content during decomposition (equation 1) is not sufficient to produce a significant change in rate.

Factors affecting the Rate of Reaction.—(a) *Environmental.* Diphenylmethylnitramine was examined under a variety of conditions, and the (first-order) rate of decomposition was found to depend both on the concentration, and on the nature, of the alkali employed. Inspection of Table II shows that, for constant [OH], the rates were proportional to 0·66[Na] and to 0·75[K]. It may be that, if strictly relevant values were known, these variations could be accounted for in terms of the activity coefficients of the ions involved. On the other hand, it appeared, quite empirically, that cationic concentration, rather than " total ionic strength " was the determining factor : thus the presence of M-potassium chloride had quantitatively the same effect as M/3-, not M/6-potassium phosphate; and the nature of the anion seemed to be irrelevant. If allowance was made for the changes in [Na] and in [K], then the rates were proportional, in both hydroxides, to 1·1[OH].

The quantitative significance of these results for other compounds is doubtful. Though a two-fold increase in the concentration of potassium hydroxide brought about a 3·2-fold increase in the rate of decomposition of diphenylmethylnitramine, the corresponding ratios for benzylnitramine and di-*p*-tolylmethylnitramine were *ca.* 2·5 and 1·8.

(b) *Structural.* It appears that the presence of a hydrogen atom on the α-carbon is essential. It is removed in the formation of the ketone (or aldehyde), and when it does not exist (phenylnitramine) stability ensues. An aromatic nitramine, however, cannot be regarded as strictly analogous to the other compounds investigated, and it is hoped to give further consideration to this question.

We have attempted to relate stability to the electron-attractive character of the groups (I; R and R′) attached to the α-carbon of the various nitramines. This property has been measured by the determination of dissociation constants. In view of the different conditions employed in the measurement of stability and of acidity, a quantitative correspondence was not expected; but it was found that, in the case of the closely-related diphenylmethylnitramines, there was some degree of parallelism (as illustrated in Fig. 1) between acidity and rate of decomposition. The relationship was dubious when applied to the unexpectedly stable phenylethylnitramines, and failed in the cases of benzylnitramine and *p*-nitrobenzylnitramine; it may well fail also [see conclusion of section (a), above] when considerable changes are made in the concentration of alkali employed. It does, however, appear that, other factors being equal, the more acidic of a pair of nitramines is likely to exhibit also the faster decomposition.

TABLE II.

Decomposition of alkali-metal salts of the nitramines, $R{\cdot}NH{\cdot}NO_2$, *initially* 0·05M. *in various solvents, at* 95°.

Run nos.	R.	Solvent.	First-order rate constant, 10^4k, min.$^{-1}$.
VIII	Ph_2CH	0·5M-KOH	5·6
VI, VII, XIV, XV, XVI	,,	1·0M-KOH	16·6
V, Va, XL	,,	2·0M-KOH	53·4
XXXIV, XXXV	,,	1·0M-KOH + 1·0M-KCl	23·2
XXXVI	,,	,, + 0·5M-K_2CrO_4	24·4
XXXVII, XXXVIII	,,	,, + 0·16M-K_3PO_4	18·6
XXXIX	,,	,, + 0·33M-K_3PO_4	24·1
XXVIII, XXIX	,,	1·0M-NaOH	13·0
XXXII, XXXIII	,,	2·0M-NaOH	38·1
XXX	,,	1·0M-NaOH + 1·0M-NaCl	16·9
XXXI	,,	,, + 0·5M-Na_2SO_4	17·3
IV	$PhCH_2$	0·5M-KOH	260
III	,,	1·0M-KOH	640
IX, XVII, XVIII	$(p\text{-}Me{\cdot}C_6H_4)_2CH$	1·0M-KOH	{ 3·7 (90%) to 4·9 (40%)
XIX	,,	2·0M-KOH	{ 6·2 (90%) to 9·0 (40%)

We do not postulate, with conviction, any definite reaction mechanism; but some tentative suggestions may be made. The importance of alkali concentration lies possibly in the removal of the α-hydrogen atom as a proton. Sodium and potassium cations facilitate the decomposition, and, unless this is simply an activity-coefficient effect, it might be inferred that the proton is removed from the small proportion of undissociated salt, rather than from the nitramine anion. Alternatively, the proton may shift, by changing a hydrogen bond * into a normal linkage, to an oxygen of the nitro-group; and the importance of hydroxyl-ion concentration may lie in the attack, at a later stage, on the C=N double bond.

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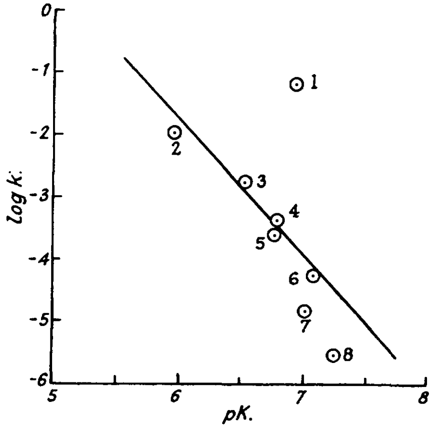
* We are indebted to Professor E. L. Hirst for the suggestion of hydrogen bonding: the C-O distance is probably (from the work of Llewellyn and Whitmore, *J.*, 1948, 1316) about 2·7 A.

By what are essentially anionic migrations, the hybrids (V, VI) might yield structure (VII), and a repetition of the process would give the ketone (in hydrated form) and nitrogen. It may be contended that the oxygen atoms could not readily be removed from the nitro-group in the form of hydroxyl ions; but this must ultimately be the fate of at least one of them, and the formation of molecular nitrogen provides a powerful driving force.

FIG. 1.

Relation between observed first-order constant of decomposition (k, *min.*$^{-1}$) *and acidity* (pK)

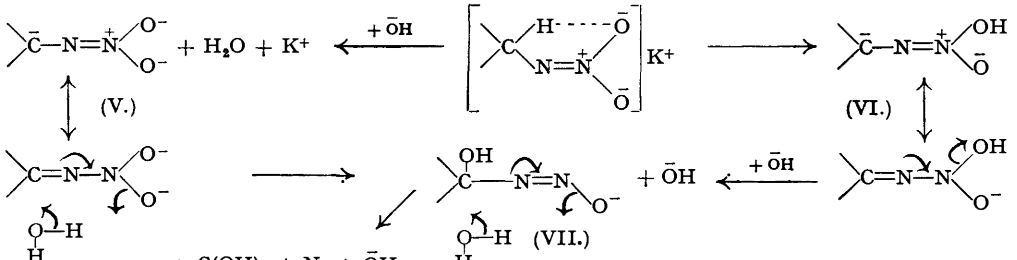


M/20-*solutions of*:

(1) $Ph{\cdot}CH_2{\cdot}NH{\cdot}NO_2$.
(2) $(p\text{-}C_6H_4Br)_2CH{\cdot}NH{\cdot}NO_2$.
(3) $Ph_2CH{\cdot}NH{\cdot}NO_2$.
(4) $(p\text{-}C_6H_4Me)_2CH{\cdot}NH{\cdot}NO_2$.
(5) $(p\text{-}MeO{\cdot}C_6H_4)_2CH{\cdot}NH{\cdot}NO_2$.
(6) $Me{\cdot}NH{\cdot}NO_2$.
(7) $p\text{-}C_6H_4Br{\cdot}CHMe{\cdot}NH{\cdot}NO_2$. } *Estimated, very roughly, as* $\frac{1}{10}$*th of the*
(8) $Ph{\cdot}CHMe{\cdot}NH{\cdot}NO_2$. } (*observed*) *values in* 4M-KOH.

In 1·0M-KOH *at* 95°.

In cases of variation of the " constant " during decomposition, the observed value at 65% *residual nitramine has been used.*



EXPERIMENTAL.

Decomposition of Nitraminoacetic Acid, and of its Ethyl Ester.—One molecular proportion of gas was evolved, in a closed system, when the acid was heated with a large excess of 1·0M-sodium hydroxide, and the ester with a phosphate buffer (2M-H_3PO_4; 2M-NaOH) at pH 7. A sample of the gas evolved appeared in both cases to be wholly insoluble in cold water. The rates of decomposition at 70° were measured, by gas evolution, as previously described (*J.*, 1949, 1654); and the results may be briefly summarised. M/20-Solutions of both ester and acid were used; the phosphate buffers were made from 1·0M-phosphoric acid and 1·0M-sodium hydroxide. Both compounds were stable in 1·0M-nitric acid, and at pH 2·8. The acid was stable, or nearly so, at pH 5·4 and 6·5; it decomposed slowly (13% in one hour) at pH 10·6, and rapidly (complete in 10 minutes) in 1·0M-sodium hydroxide. The ester decomposed slowly, and with moderate speed (15 and 40%, respectively, in 1 hour) at pH 5·5 and pH 6·8. It showed the same rates of decomposition as the acid—probably by reason of prior hydrolysis—at pH 10·6 and in 1·0M-sodium hydroxide. In a borate buffer (1·5M-H_3BO_3; 1·5M-NaOH), at pH 8·7, the acid was stable, whilst the ester showed 30—35% apparent decomposition in 1 hour, but (presumably on account of hydrolysis) only 40—45% apparent decomposition in 2 hours. The rate of decomposition of the ester appeared to depend on the concentration of the phosphate buffers: later work on diphenylmethylnitramine has shown that this may have been caused by changes in [Na] rather than by changes in [PO_4].

Decomposition of p-*Nitrobenzylnitramine.*—The nitramine (0·2 g.) was warmed on a water-bath for 15 minutes with 0·2M-aqueous sodium hydroxide (10 ml.). After cooling, collection of the precipitate yielded 4 : 4′-diformylazoxybenzene (80 mg.) of m. p. 187°, undepressed by mixture with an authentic sample (Kirpal, *Ber.*, 1897, **30**, 1598). Crystallisation from acetic acid–water gave pure material, m. p. 191° (Found : C, 66·5; H, 4·2; N, 10·8. Calc. for $C_{14}H_{10}O_3N_2$: C, 66·1; H, 3·9; N, 11·0%). On decomposition in a closed system, M/20-solutions of the sodium salt in M/20- and M/1-sodium hydroxide yielded, respectively, 0·9 and 0·5 molecular proportion of gas; in the second case no azoxy-compound was precipitated. The gas evolved, in the absence of air, from a M/60-solution of the sodium salt in M/60-sodium hydroxide was found, on sampling, to be soluble in cold water (N_2O content, probably $>90\%$).

Measurement of Decomposition Rates.—The nitramine (1 mg.-mol.) was placed in a suitable container, and brought into solution in 20 ml. of solvent (*e.g.*, for decomposition of a M/20-solution of the potassium salt of diphenylmethylnitramine in 1·0M-KOH + 1·0M-KCl, the solvent was 10 ml. of 2·05M-KOH and 10 ml. of 2·0M-KCl). The container was attached to the long (20 cm.) arm of a glass T-piece of *ca.* 7-mm. bore : this arm was cooled, between the container and the actual T-junction, by a 10-cm. condenser jacket. The arm leading off at right-angles was connected, through pressure tubing, to a gas-burette charged with mercury; and the third arm was drawn out to a capillary. The tightness of the apparatus was first tested by sealing the capillary and maintaining, for 30 minutes, a 15—20-cm. " head " of mercury. If gas-tight, the mercury was re-levelled, and the capillary broken : the container was then swung round and lowered, to a standard depth, into the thermostat. Tests showed that temperature equilibrium was reached in 5 minutes, at which time the capillary was re-sealed, and readings (of gas volume, at atmospheric pressure) commenced. The rate of warming suggested that the reaction time should be measured from 4 minutes after insertion into the thermostat, and the volume readings were extrapolated back to give a true initial volume, unaffected by thermal expansion. The readings were corrected to compensate for changes of pressure of the total volume enclosed, and for changes of temperature of the volume exposed beyond the condenser; the gas was assumed to be saturated with water vapour at the temperature of the cooling water passing through the condenser.

In the earlier experiments (runs I—XII) the container (a glass bulb of *ca.* 30-ml. volume) was sealed to the condenser. This was satisfactory for the more rapid decompositions (half-life 1—4 hours) but was not suitable for the slower reactions. The attack of the alkali on the glass produced, after about 12 hours, small but definite changes in the rate of reaction; and no account has been taken of any result obtained in glass after more than 8 hours' heating. It was, furthermore, impossible to estimate the residual nitramine (by acidification, ether-extraction, and titration) when a glass container had been employed. This was probably because of the presence, in the ethereal extract, of boric acid derived from the glass. In later work silver test-tubes (*ca.* 120 × 18 mm.) were employed. These were attached to the condenser by a rubber bung, and the joint made gas-tight by a film of cellulose acetate. This simple apparatus functioned satisfactorily, and appeared preferable to the more complicated use of a gasket. Apparent decomposition rates after prolonged heating in glass could be reproduced in silver by the initial addition of a few fragments of glass tubing to the solution : no such misleading values are quoted in this paper.

Determination of Residual Nitramine by Titration.—The solutions (in 1·0 M-potassium hydroxide) were cooled rapidly, acidified with aqueous sodium hydrogen sulphate (12·5 ml. of 2·1M.), and submitted to continuous ether-extraction. The extracts were dried (Na_2SO_4) (to remove any traces of aqueous bisulphate carried over), filtered, and evaporated through a fractionating column. The residues were dissolved in alcohol, and titrated, using phenolphthalein as indicator, with standard aqueous sodium hydroxide. The results are given in Table III; the low values for methylnitramine and for di-(*p*-bromophenyl)methylnitramine are not surprising, since methylnitramine is difficult to extract, and the comparatively rapid decomposition of the dibromo-compound probably brought about some loss in the period between the gas measurement and acidification.

TABLE III.

Percentage of residual R·NH·NO_2.

R =	CH_3.	Ph_2CH.	(p-$C_6H_4Me)_2CH$.	(p-$C_6H_4Br)_2CH$.
By gas evolution	84	60, 44	57, 28, 28 *	39
By nitramine recovery	76	59, 46	57, 26, 29 *	35

* In 2·0M-KOH; acidified with adequate $NaHSO_4$.

Decomposition of 1-*Phenylethylnitramine and* 1-p-*Bromophenylethylnitramine in* 4 *and* 8M-*Potassium Hydroxide.*—Apparent first-order constants, 10^4k (min.$^{-1}$), in 4M-potassium hydroxide at 95°, and at, respectively, 90, 65, and 40% residual nitramine were :

For Ph·CHMe·NH·NO_2	0·3	0·3	—
For p-C_6H_4Br·CHMe·NH·NO_2	0·9	1·5	1·5

Similarly, in 8M-potassium hydroxide at 95° :

For Ph·CHMe·NH·NO_2	2·4	3·5	3·5
For p-C_6H_4Br·CHMe·NH·NO_2	1·4	1·9	2·3

It will be noted that in 8M-alkali the unsubstituted compound decomposed the faster, but, in view of the considerable deviations from the first-order rate, it is doubtful if the results are truly comparable.

Decomposition of Di-(p-*bromophenyl*)*methylnitramine.*—The considerable increase in the apparent reaction rate during the progress of the decomposition did not appear to be a simple example of autocatalysis. Solutions initially M/20, M/40, and M/80 in nitramine concentration (in 1·0M-potassium hydroxide, at 85°, for convenience in measurement) gave decomposition curves of a similar type. The prior addition of 4 : 4′-dibromobenzophenone (1 mol. per mol. of nitramine) to M/40- and M/80-solutions apparently caused a slight increase in the initial rate of decomposition, but no acceleration was thereafter observed. Under these conditions—the presence of more than one molecular proportion of (presumably) insoluble solid ketone—the rate of gas evolution was of the first order with respect to the nitramine, and was approx. equal ($k = ca.\ 4 \times 10^{-3}$ min.$^{-1}$) to that shown by the nitramine alone at 60% residual concentration. The influence of the ketone may be physical (surface effect?) rather than chemical. It is doubtful whether the degree of reproducibility of these results warrants their consideration in more than this qualitative fashion, and we refrain at present from further comment.

Measurement of the Dissociation Constants of the Nitramines.—The nitramine (1 mg.-mol.) was dissolved in aqueous alcohol (75 ml. of 50·5% v/v; d_4^{19} 0·933) and titrated potentiometrically at 20° with aqueous 0·1M-sodium hydroxide, using a standard Marconi pH-meter. The dielectric constant of the solvent was taken as 55·88 (by extrapolation of Akerlöf's values, *J. Amer. Chem. Soc.*, 1932, **54**, 4152), leading to a value of 0·9717 for the constant of the Debye–Hückel equation. The apparent thermodynamic dissociation constants are given in Table IV. No correction has been made for the error introduced by the use of a standard meter and glass electrode in aqueous alcohol. This is a constant error in all the results, and is probably less than 0·1 unit of pH (Speakman, *J.*, 1943, 270; Dole, *J. Amer. Chem. Soc.*, 1932, **54**, 3095). The results are, apart from this constant error, probably accurate to within 0·05 units of p*K*; and, for comparison, the values determined for a number of carboxylic acids, in the same manner, are included in the table.

TABLE IV.

Thermodynamic dissociation constants of the nitramines, R·NH·NO$_2$, *and carboxylic acids,* R·CO$_2$H, *in* 50% *v/v aqueous alcohol.*

	p*K* for				p*K* for		
R.	R·NH·NO$_2$.	R·CO$_2$H.	Δp*K*.	R.	R·NH·NO$_2$.	R·CO$_2$H.	Δp*K*.
Me	7·08	5·75	1·33	*p*-C$_6$H$_4$Br·CHMe	7·01	—	—
Ph	5·96	5·55	0·41	Ph$_2$CH	6·53	5·50	1·03
Ph·CH$_2$	6·92	5·56	1·36	(*p*-C$_6$H$_4$Br)$_2$CH	5·95	—	—
p-NO$_2$·C$_6$H$_4$·CH$_2$	6·36	4·99	1·37	(*p*-C$_6$H$_4$Me)$_2$CH	6·79	—	—
Ph·CH·CH$_3$	7·24	—	—	(*p*-MeO·C$_6$H$_4$)$_2$CH	6·77	—	—

The values for nitraminoacetic acid and its ethyl ester were determined in water at 20°, as previously described (Lindley and Speakman, *J.*, 1949, 1657). The ester has pK = 5·3; and the acid pK_1 = 3·2, pK_2 = 6·9. Comparison with methylenedinitramine (pK_1 = 5·0, pK_2 = 6·6; Lindley and Speakman, *loc. cit.*) and with malonic acid (pK_1 = 2·83, pK_2 = 5·69; Gane and Ingold, *J.*, 1931, 2158) is of interest, and suggests that, for power of electron attraction, $CO_2H > NH{\cdot}NO_2 > CO_2Et > \overset{-}{\overbrace{N{\cdot}NO_2}} > CO_2^-$.

Isolation of the Products of Decomposition.—(a) *From diphenylmethylnitramines.* After gas evolution had ceased, the residual alkaline suspension was cooled, and extracted with methylene dichloride. On evaporation, the following ketones were obtained (yields in parenthesis): benzophenone (95%), 4 : 4′-dimethyl- (84%), 4 : 4′-dimethoxy- (88%), and 4 : 4′-dibromo-benzophenone (99%).

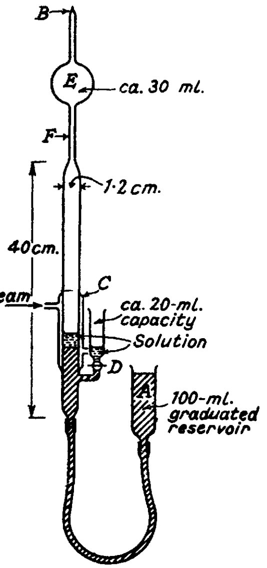
(b) *From benzylnitramine.* Extraction, as in (*a*), gave benzaldehyde (weighed as 2 : 4-dinitrophenylhydrazone) in 31% yield. Acidification of the aqueous layer, and re-extraction with ether, gave crude benzoic acid (identified by mixed m. p.) on evaporation. On the assumption that the acid was produced by the Cannizzaro reaction, the yield corresponded to a further 48% of benzaldehyde.

(c) *From* 1-*phenylethylnitramine and* 1-p-*bromophenylethylnitramine.* The strongly alkaline solutions (8M. and 4M., respectively) were cooled, diluted with water, and extracted with ether. The extracts yielded the 2 : 4-dinitrophenylhydrazones of acetophenone and of *p*-bromoacetophenone (identified by mixed m. p. with authentic specimens) on evaporation and treatment with 2 : 4-dinitrophenylhydrazine in methanol–sulphuric acid.

Stability of Phenylnitramine.—After 20 ml. of a N/20-solution of the potassium salt had been heated for 72 hours at 95° in 1·0M-potassium hydroxide, with no sign of gas evolution, the nitramine was freed by acidification with a slight excess of 2M-hydrochloric acid, and extracted with ether. The ethereal solution was dried, basified with *iso*propylamine, and evaporated to half its volume to remove excess of base. After cooling, the salt was collected; a further crop was obtained by evaporation to dryness, and trituration with ether. The identity of the salt (84% yield) was proved by its m. p. and mixed m. p. with authentic material. In a similar manner 85% and 74% yields of the *iso*propylamine salt were obtained after the nitramine had been heated at 95° for, respectively, 23 days in 4M- and 21 days in 8M-potassium hydroxide. During these runs a portion (*ca.* 2·2 and 5·0 ml., respectively) of the air enclosed in the apparatus was absorbed.

Collection and Analysis of the Gas obtained from Methylenedinitramine, and from Diphenylmethylnitramine.—The apparatus sketched in Fig. 2 was used. The reservoir *A* was raised, with the capillary *B* unsealed, to bring the mercury to the top of *B*. The capillary *B* was then sealed, and *A* lowered to bring the mercury surface within the jacket *C*. The aqueous solution of the nitramine was introduced cautiously through the tap *D*; as a quantitative measurement of the volume evolved was not required, a portion of the solution was left to act as a seal. Decomposition was brought about by passage of steam through *C*. When sufficient gas had been produced—as indicated by the position of *A* required to maintain the aqueous solution within the jacket *C*—the heating was stopped, and the capillary *B* briefly flamed to remove condensate. After a few minutes' drainage, the bulb *E* was sealed at *F* whilst the aqueous solution was still warm (*ca.* 70°). Analyses gave the following results: Sample from diphenylmethylnitramine in 2·5M-potassium hydroxide; water, 15 mg.; nitrogen, 15·5 mg. (100% by vol.): nitrous oxide and oxygen, 0. Sample from methylenedinitramine in 1·5M-potassium hydroxide; water, 13 mg.; nitrogen, 10·8 mg. (54% by vol.); nitrous oxide, 14·2 mg. (45% by vol.); oxygen, 0·1 mg. (1% by vol.). The small apparent percentage of oxygen, obtained by difference of two volumes each measured to 0·05 ml. (≃0·05 mg. of oxygen) is of doubtful significance. No hydrogen, carbon monoxide, nitric oxide, or hydrocarbon was detected in either case.

FIG. 2.



Preparation of Materials.—Nitraminoacetic acid and its ethyl ester were prepared according to Hantzsch and Metcalf (*loc. cit.*); *p*-nitrobenzylnitramine according to Hantzsch (*Ber.*, 1898, **31**, 180); and three of the diphenylmethylnitramines according to Gillibrand and Lamberton (*J.*, 1949, 1883).

*Di-*p*-methoxyphenylmethylnitramine.* 4 : 4′-Dimethoxybenzophenone hydrazone (5·2 g.) (Staudinger and Kupfer, *Ber.*, 1911, **44**, 2210) was shaken for 15 minutes, in an atmosphere of nitrogen, with yellow mercuric oxide (4·8 g.) suspended in ligroin (60 ml.; b. p. 40—60°). Alcoholic potassium hydroxide (2 ml. of 1·5M.) was used as a catalyst. The diazo-compound was dissolved by warming it with additional ligroin (100 ml.), and freed from inorganic material by filtration. On cooling in ice diazodi-*p*-methoxyphenylmethane (3·1 g.; m. p. 99—101°) separated; Staudinger and Kupfer (*loc. cit.*) give m. p. 103—104°. Nitrourethane (1·6 g. in 10 ml. of ether) was added to a solution of the diazo-compound (3·1 g. in 50 ml. of benzene). After effervescence slackened (30 minutes), the reaction was completed at 40°. The mixture was then cooled, and set aside overnight after the addition of *iso*propylamine (2·5 ml.). The *iso*propylamine salt (3·8 g.) was collected, dissolved in water, and acidified with dilute hydrochloric acid. The crude nitramine was then extracted with ether, and purified by precipitation as the ammonium salt, which was collected (2·9 g.), dissolved in cold water (50 ml. at 0°), and acidified with potassium dihydrogen phosphate (24 ml. of 1·0M). The oily precipitate, which slowly solidified, was collected: the ***nitramine*** (1·9 g.) was obtained as fine prisms, m. p. 68°, when a solution in *cyclo*hexane (*ca.* 30 ml.) and sufficiency of ether was allowed to evaporate slowly (Found: C, 62·8; H, 5·6; N, 9·4%; equiv., 284. $C_{15}H_{16}O_4N_2$ requires C, 62·5; H, 5·6; N, 9·7%; equiv., 288).

1-*Phenylethylnitramine.* Acetophenone azine (9·75 g.) (Scholtze and Locht, *J. Amer. Chem. Soc.*, 1926, **48**, 1032) was refluxed with anhydrous hydrazine (5 g.) (Smith and Howard, *Org. Synth.*, **24**, 53) for 30 hours (oil-bath at 130°). Most of the excess of hydrazine was then removed by azeotropic distillation with ligroin (b. p. 90—120°) under reduced pressure. When the overall weight was reduced to that required for the conversion into hydrazone, more ligroin (75 ml.; b. p. 40—60°) was added, and the last traces of hydrazine were destroyed by the addition of mercuric oxide until the colour of the latter persisted. Additional mercuric oxide (17·9 g.) was then added, together with alcoholic potassium hydroxide (0·5 ml. of 1·5M.), and the whole shaken for 1 hour. Filtration yielded a solution (estimated to contain 4·85 g. of diazomethylphenylmethane by Gillibrand and Lamberton's method, *loc. cit.*) to which nitrourethane (4·95 g. dissolved in the minimum volume of ether) was added cautiously. When the reaction had subsided, the resultant nitramide was decomposed by the passage of gaseous ammonia. The ammonium salt of the nitramine was collected, dissolved in water, and acidified with dilute hydrochloric acid. The precipitated ***nitramine*** was collected and crystallised from *cyclo*hexane to yield irregular plates (2·45 g.; 18% calc. on acetophenone azine), m. p. 92° (Found: C, 57·8; H, 6·1%; equiv., 166. $C_8H_{10}O_2N_2$ requires C, 57·8; H, 6·0%; equiv., 166).

p-*Bromoacetophenone azine.* The azine, prepared by Scholtze and Locht's general method (*loc. cit.*), crystallised from methylated spirits in plates (85% yield), and from *cyclo*hexane in needles. Both forms had m. p. 164° (Found: C, 49·4; H, 3·8; N, 7·1. $C_{16}H_{14}N_2Br$ requires C, 48·8; H, 3·6; N, 7·1%). The lack of colour is noteworthy; though the solutions were yellow, the solid had only an extremely faint tinge. An attempt to prepare the hydrazone by Barber and Slack's method (*J.*, 1944, 613) gave material of m. p. 140—150°, crystallisable to yield the azine. It appears that the m. p. (164°) given by these authors is that of the azine, not of the hydrazone.

1-p-*Bromophenylethylnitramine.* *p*-Bromoacetophenone azine (10 g.) and anhydrous hydrazine (2·45 g.), heated as described above, gave on addition of ligroin (b. p. 90—120°) a solid (10·4 g., presumably crude hydrazone) of m. p. 73°. This was suspended in ligroin (100 ml.; b. p. 40—60°) and, after addition of mercuric oxide (10·65 g.) and alcoholic potassium hydroxide (0·5 ml. of 1·5M.), the mixture was shaken, with wet-cloth cooling, for 90 minutes. The solution of diazomethyl-*p*-bromophenylmethane obtained by filtration (estimated content, 5·3 g.) was treated with nitrourethane (3·4 g.) in ether, and the mixture set aside overnight after the addition of *iso*propylamine (2·5 ml.). After collection, the *iso*propylamine salt was dissolved in water, and the *nitramine* precipitated with dilute hydrochloric acid. Crystallisation from *cyclo*hexane yielded fine needles (2·9 g.; 26% calc. on the azine), m. p. 86° (Found: C, 39·3; H, 3·8; N, 11·8%; equiv., 243. $C_8H_9O_2N_2Br$ requires C, 39·2; H, 3·7; N, 11·4%; equiv., 245).

iso*Propylamine salt of phenylnitramine*. Phenylnitramine may be conveniently purified (and stored, if shielded from light) by conversion into the iso*propylamine* salt. The salt, precipitated from a dry ethereal solution of the nitramine by the addition of *iso*propylamine in ether, formed felted needles, m. p. 146° (decomp.) (Found: N, 21·6. $C_9H_{15}O_2N_3$ requires N, 21·3%).

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