357. *Studies on Nitroamines. Part VII. The Decomposition of Methylenedinitroamine in Aqueous Solutions.*

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Methylenedinitroamine decomposes in 11N-mineral acid, in 2N-sodium hydroxide, and at pH in the range 3—8. Considerable stability is exhibited around pH 1 and pH 10.

The decomposition at pH 3—8 leads finally to nitrous oxide and formaldehyde. The primary stage appears to result in the liberation of nitroamine and the conversion of the methylene group into a form oxidisable by alkaline hypoiodite. The decomposition is autocatalytic and is catalysed, though less markedly, by extraneous formaldehyde. It is suggested that the mono-ion shows inherent instability, and the kinetics of the reaction are discussed.

A method of determination has been elaborated which is applicable in the presence of unknown quantities of acid and formaldehyde.

The investigation of the stability of methylenedinitroamine was undertaken originally on account of the possible role of this compound in the synthetic production of cyclonite. Since, however, information has been gained regarding the effect of one nitroamino-substituent on a similar group situated in the α-position to the first, the results are of general interest in the field of nitroamine chemistry.

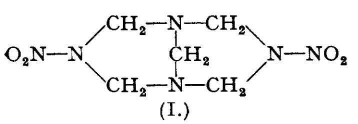
On heating in water, methylenedinitroamine has been shown (Roberts, private communication) to yield, finally, formaldehyde and nitrous oxide, thus :

$$CH_2(NH{\cdot}NO_2)_2 \longrightarrow CH_2O + 2N_2O + H_2O \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

The quantitative production of formaldehyde and nitrous oxide has been confirmed, and preliminary studies were carried out mainly by the measurement of the evolution of gas from heated solutions. However, this method, though convenient and rapid, does not necessarily provide a true measure of the primary stage of decomposition, since products intermediate between the dissolved nitroamine and the evolved gas are conceivable. Supersaturation by gas affects the results in the same sense. In fact (see below), methylenedinitroamine is somewhat, though not markedly, less stable than the results of gas evolution indicate. It has been assumed, by analogy with the behaviour of other primary nitroamines, that complete decomposition in strong mineral acid would give rise to two molecular proportions of gas. A similar volume is produced on heating with aqueous sodium hydroxide, though unpublished work indicates that this is a mixture of nitrogen and nitrous oxide.

Decomposition, as measured by gas evolution, occurred with moderate rapidity (50% in about 1 hour at 70°) on warming in strong (11N.) nitric or sulphuric acid. At lower acid concentrations (N. and 0·1N.), stability was great and appeared, by comparison with trimethylenedinitroamine, to be greater than that shown by an isolated primary nitroamino-group. Tests with phosphate buffers showed that, in contrast with trimethylenedinitroamine, a zone of rapid decomposition (50% in a few minutes at 70°) extended from pH 3 to pH 8; this was succeeded by a second region of stability around pH 10, whilst rapid decomposition was observed again in 2N-sodium hydroxide. These results are presented in Table I (Experimental; section *C*).

The precipitation of 3 : 7-dinitro-1 : 3 : 5 : 7-tetra-*azabicyclo*[3 : 3 : 1]nonane (I) from solutions of monoammonium methylenedinitroamine in aqueous formaldehyde suggested the formation of nitroamine as an intermediate, and the decomposition in water was subjected to a more detailed investigation by acidimetry and the iodometric determination of available formaldehyde.

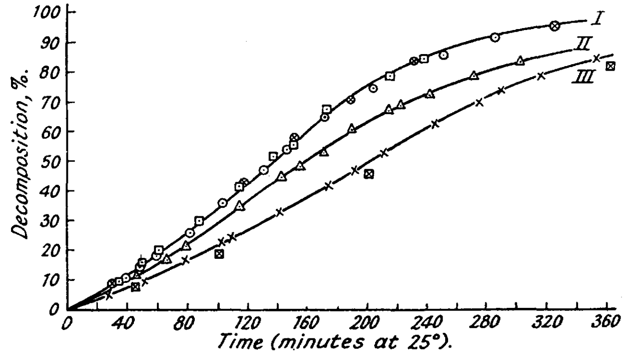


(I.)

Freshly prepared aqueous solutions of methylenedinitroamine could be titrated, using thymolphthalein, to a sharp end-point. As decomposition proceeded, there was a decrease in the volume of sodium hydroxide required to effect neutralisation, but the residual acidity thus determined was not an accurate measure of the methylenedinitroamine content of the solutions. The end-point remained sharp, but thereafter, on standing, the solutions became more alkaline, and the colour of the indicator could no longer be removed by the addition of one drop of 0·1N-hydrochloric acid. In less than 25 minutes, stability was re-established, and the alkali which had been set free could be determined by back-titration with hydrochloric acid. It was thus found that part of the " total acidity " originally determined by direct titration with sodium hydroxide was destroyed on being left for 25 minutes under mildly alkaline conditions; the rest, by contrast, could be termed " permanent." Methylenedinitroamine was shown to be unaffected by the degree of alkalinity employed

(Experimental; section *F*), and the extent of the decomposition calculated from the " permanent acidity " agreed with that found by iodometric determination of available formaldehyde (Experimental; section *D*). At 70°, measurements of " permanent acidity " and formaldehyde (iodometrically) were again consistent, and indicated a greater degree of decomposition than those of " total acidity," gas evolution, or formaldehyde by precipitation as the 2 : 4-dinitrophenylhydrazone (Experimental; section *E*). These phenomena are explicable in terms of the known properties of nitroamine and hydroxymethylnitroamine (Part V, this series). We

FIG. 1.

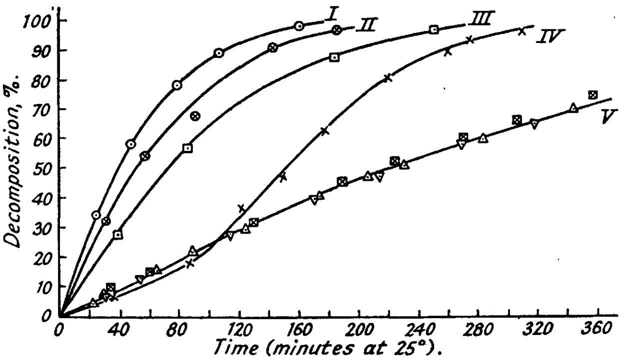


Methylenedinitroamine : M./20 *in acetate buffers* (2·5M-AcOH + 2·5M-NaOH).

I. { *pH* 5·15 → 5·25 ⊙. *pH* 5·25 → 5·35 ⊗. *pH* 5·45 → 5·60 ⊡.
II. *pH* 5·80 → 6·20 △.
III. { *pH* 4·65 → 4·70 ×. *pH* 4·60 → 4·70 *in half-strength buffer* ⊠.

(*pH values to nearest* 0·05 *unit.*)

FIG. 2.



Methylenedinitroamine at pH 4·65 *and* 5·35 : *variations in concentration and solvent.*
(*Acetate buffers,* 2·5M., *unless specified.*)

pH 4·65 {
I. M./20 + 0·195M-CH_2O ⊙.
II. M./5 + 0·195M-CH_2O ⊗.
III. M./20 + 0·045M-CH_2O ⊡.
IV. M./5 ———————— ×.

pH 5·35, *V.* {
M./100 ———————————— △.
M./100 *in half-strength buffer* ⊠.
M./100 *in* 2M-*phosphite buffer* ▽.

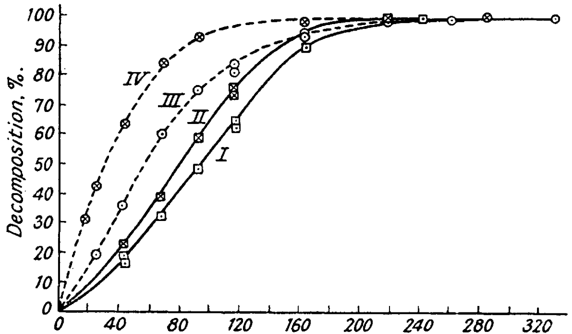
(*pH values to nearest* 0·05 *unit.*)

therefore believe that the first stage of the decomposition in aqueous solution (and by analogy in buffers at pH 3—8) results in the production of nitroamine and/or a simple derivative of nitroamine; the methylene group is also rendered accessible to oxidation by iodine in alkaline solution, thus providing a convenient measure of the extent of decomposition.

In the presence of unknown quantities of acid and formaldehyde, methylenedinitroamine may be determined by precipitation of the barium salt, but this salt is unstable, decomposing with loss of weight on prolonged drying in a vacuum; furthermore, co-precipitation cannot be detected. It is, therefore, preferable to decompose the barium salt and determine the liberated formaldehyde. The method is of diagnostic value (see Part IV).

Factors influencing the Rate of Decomposition at 25°.—(i) *pH of the solution.* The results supported the general conclusions derived from measurements of gas evolution at 70°. Stabilisation by mineral acid or extremely dilute alkali was confirmed (Experimental; section *F*). In acetate buffers the rates of decomposition at pH 5·2, 5·3, and 5·5 were experimentally indistinguishable, and were greater than those observed at pH 4·7 or 6·0; the maximum is thus in the region of pH 5·4 (Fig. 1).

FIG. 3.



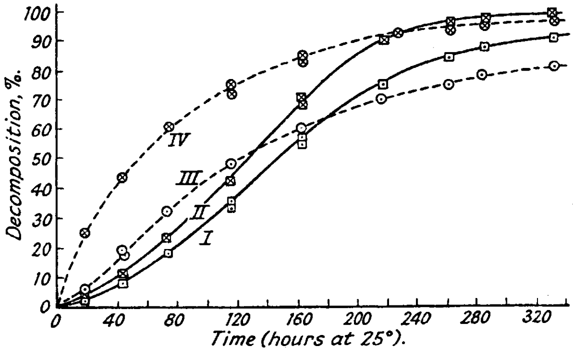
Methylenedinitroamine (unbuffered).

M./20-*solutions.*

M./20 *in water* : ————
Curve I, by " total acidity," ⊡.
Curve II, by iodometric CH_2O ⊠.

M./20 *in* 0·0530M-CH_2O : - - - - - -
Curve III, by " total acidity," ⊙.
Curve IV, by iodometric CH_2O ⊗.

FIG. 4.



Methylenedinitroamine (unbuffered).

M./5-*solutions.*

M./5 *in water* : ————
Curve I, by " total acidity " ⊡.
Curve II, by iodometric CH_2O ⊠.

M./15 *in* 0·2025M-CH_2O : - - - - - -
Curve III, by " total acidity " ⊙.
Curve IV, by iodometric CH_2O ⊗.

(ii) *Concentration of methylenedinitroamine.* In acetate buffers at a given pH, the initial percentage rates of decomposition were similar for M/5-, M/20-, and M/100-solutions; the more concentrated the solution, the more rapid was the subsequent development of the decomposition (compare curves I and III of Fig. 1 with curves V and IV, respectively, of Fig. 2). In water a M/5-solution decomposed more slowly than did a M/20-solution; this may be due to its enhanced acidity.

(iii) *Catalysis.* The S-shape of the curves suggested that the reaction was catalytic, and formaldehyde was found to accelerate markedly the decomposition in a buffer of pH 4·7 (compare curves I and III of Fig. 2 with curve III of Fig. 1; also compare curves II and IV of Fig. 2), in water (Figs. 3 and 4, compare curves II and II with IV and IV), and in 0·1N-hydrochloric acid (Table IV). As expected, the effect was most marked at the start of the reaction. In most cases, additional self-catalysis could be shown by analysis (see General Discussion below); but complexities were clearly indicated by the results for M/5-solutions in water and in M/5-formaldehyde; the initially-greater rate of decomposition in formaldehyde was later surpassed by that of the powerfully self-catalysed decomposition in water (Fig. 4, curves II and IV).

In the case of M/100-solutions at pH 5·35, dilution of the acetate buffer with an equal volume of water, or its replacement by a phosphate buffer, had little effect on the course of decomposition (Fig. 2, curve V). The slight decrease in rate on dilution of the buffer with water in the case of an M/20-solution at pH 4·7 may be due simply to the enhanced drift in pH arising from the lowered buffering capacity (Fig. 1, curve III).

GENERAL DISCUSSION.

Kinetics.—The decomposition of methylenedinitroamine does not appear to follow any simple kinetic course, but our experiments warrant the following comments.

(*a*) The generally S-shaped reaction–time curves (Figs. 1, 2, 3, and 4) suggest that the reaction is autocatalytic, and the finite initial rate further suggests that there must also be a spontaneous reaction.

(*b*) If (i) the catalytically active product is formaldehyde and (ii) the spontaneous reaction is of the first order, the overall kinetics should be expressed by the equation :

$$-\,d[CH_2(NH{\cdot}NO_2)_2]/dt = k_s[CH_2(NH{\cdot}NO_2)_2] + k_c[CH_2(NH{\cdot}NO_2)_2][CH_2O]$$

$$i.e., \quad \frac{-\,d[CH_2(NH{\cdot}NO_2)_2]/dt}{[CH_2(NH{\cdot}NO_2)_2]} = k_0 = k_s + k_c[CH_2O] \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

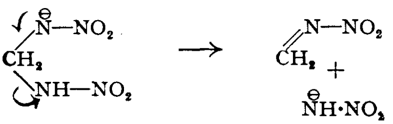
k_s and k_c being the specific rate constants of the spontaneous and autocatalysed reactions, and k_0 the apparent, instantaneous, first-order constant obtainable at any stage from the slope of the reaction–time curve. According to equation 2, a plot of k_0 against formaldehyde concentration should give a straight line which intersects the axis at k_s and has a slope of k_c. Within experimental error, this relation appears to hold for the experiments on the decomposition of methylenedinitroamine in water or in buffer solutions at pH 4·7 and 5·2.

(*c*) However, the reaction is more complex than this, for, according to equation 2, results for M/20-, M/5-, and M/100-methylenedinitroamine at a given pH should yield points lying on the same straight line, whereas in fact they do not. Moreover, when extraneous formaldehyde is present, the decomposition is indeed initially accelerated, but not to the extent to be anticipated from equation 2.

(*d*) From the known dissociation constants (Part VIII, this series), the proportion of methylenedinitroamine mono-ion at a given pH and infinite dilution could be calculated. If it is borne in mind that, in the application of these results to actual solutions, no correction was made for salt-concentration effects, the values of k_s and k_c [subsection (*b*)] at pH 4·7 and 5·2 and in water are consistent with the suggestion that the rates of both the spontaneous and autocatalytic reactions are proportional to the concentration of the mono-ion; and the observation that maximum overall rate of decomposition occurs at about pH 5·4 is consistent with the (uncorrected) calculation that the maximum concentration of mono-ion occurs at pH 5·8.

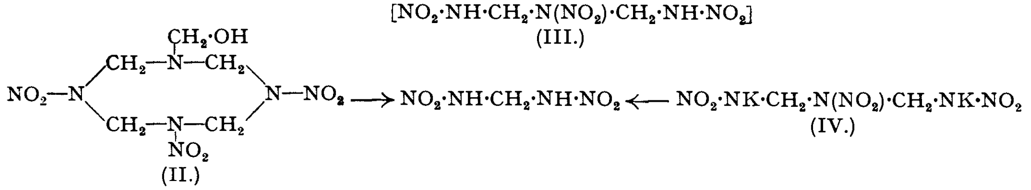
Applications to Nitroamine Chemistry.—Though the observed stability of the un-ionised and of the doubly ionised material at pH 1 and 9, respectively, does not guarantee their stability at intermediate pH values, the hypothesis that decomposition proceeds specifically through the mono-ion is favoured (preceding section).

It may be that, in the spontaneous reaction, one nitroamino-group cannot facilitate the ejection of the other as a nitroamine anion; but, after mono-ionisation has taken place, the relatively greater availability of electrons permits this rupture, thus :



In the doubly ionised material there is electron availability from both nitroamino-nitrogen atoms, but there remains no relatively attractive grouping to promote migration. It is not considered that our present knowledge permits the formulation of any mechanism for the catalytic reaction.

Whatever theories of decomposition may be advanced, it appears that the system $NO_2{\cdot}NR{\cdot}CH_2{\cdot}\overset{\ominus}{N}{\cdot}NO_2$ is unstable in aqueous solution, and there is no obvious reason to limit this instability to the case of R = H. Furthermore, when R is not ionisable, the possibility of stabilisation in alkali by formation of the di-ion is removed. This may explain why, in two cases, methylenedinitroamine has been isolated in place of a higher nitroamino-methylene homologue. For example, workers at Bristol (private communication) prepared a compound which they believed to be (II), by nitrolysis of (I). It yielded nitrous oxide and methylenedinitroamine, and not (III), on treatment with alkali. Again, Canadian workers (private communication) have prepared the compound (IV) which, though formally a salt of (III), yielded methylenedinitroamine on neutralisation with acid.



$[NO_2{\cdot}NH{\cdot}CH_2{\cdot}N(NO_2){\cdot}CH_2{\cdot}NH{\cdot}NO_2]$ (III.)

(II.) $\longrightarrow NO_2{\cdot}NH{\cdot}CH_2{\cdot}NH{\cdot}NO_2 \longleftarrow NO_2{\cdot}NK{\cdot}CH_2{\cdot}N(NO_2){\cdot}CH_2{\cdot}NK{\cdot}NO_2$ (IV.)

EXPERIMENTAL.

A. General.—Determinations of formaldehyde were made iodometrically unless otherwise stated. In acidimetry a methyl alcoholic solution of thymolphthalein was used as indicator. The methylenedinitroamine (Part II, this series) was recrystallised from ether. pH values were measured with the glass electrode; those at 70° are derived by an admittedly speculative extrapolation from data at 18° and 40°, but are held to be correct to within the limits stated. The pH ranges quoted indicate the probable change during the decomposition of the methylenedinitroamine.

B. Total Gas Evolution from Methylenedinitroamine.—0·1M-, 0·05M-, and 0·025M-aqueous methylenedinitroamine evolved 1·96, 1·97, and 2·08 molecular proportions of gas on maintenance at 70° in a closed system. 0·05M-Solutions in 2N-sodium hydroxide evolved 1·96 and 1·95 molecular proportions under the same conditions.

C. Measurement of the Rate of Gas Evolution.—Consistent results could not be obtained by the addition of solid methylenedinitroamine to preheated buffer solutions in a closed system. The presumed supersaturation was overcome, and a reasonable agreement between individual experiments obtained, by the following technique.

TABLE I.

(All solutions initially M./20 with respect to dinitroamine.)

Solvent.	pH during decomposition (estimated at 70°).	Time, in minutes, for 50% decomposition (by gas evolution) on rapid heating (20° → 70° in 5 minutes) and maintaining at 70°. Methylenedinitroamine.	Trimethylenedinitroamine.
11·2N-HNO_3		70 *	**4·5**
10·8N-H_2SO_4		110	**5**
1·0N-HNO_3		>1500 †	120
2·0M-H_3PO_4		>1000 †	180
0·1N-HNO_3		> 500 †	> 500 †
Phosphate buffers : 2·0M-H_3PO_4 2·0N-NaOH	**2**	60	>1000 †
	3	**8**	
	4·7 → 5·2	2·**5**	
	5·6 → 5·9	3	stable
	6·4 → 6·6	6	
	7·5 → 7·8 ‡	50	
	10·0	> 500 †	
	11·0 11·6	130	
2·0N-NaOH		**4·5**	

* Fume-off occurred at *ca.* 70 minutes.

† Estimated by extrapolation.

‡ pH 7·8 at 50% decomposition; the rate of gas evolution fell rapidly thereafter as, with lowered buffering capacity, the pH rose above 8.

The reaction vessel (a tube of *ca.* 20 ml. capacity, with a tap, giving access to the air, sealed to a side arm) was loosely filled with glass wool. A 50-ml. dropping funnel, the stem of which was jacketed to form a small condenser, was attached, and the reaction vessel, with its tap open to the air, was immersed in the thermostat. The freshly prepared solution under investigation was introduced into the dropping funnel, and connection made from the mouth of the dropping funnel to the nitrometer. With the nitrometer-tap partly removed to give access to the air, the solution was run into the reaction vessel, and the clock started. After 15 seconds, drainage was expressed from the dropping funnel by manipulation of the rubber tube leading to the nitrometer; after 30 seconds, the tap of the reaction vessel was closed and the nitrometer tap inserted in position. The liquid thus introduced was found to rise in temperature to approximately 45° after 1 minute, 60° after 2 minutes, and 70° after 5 minutes. In blank experiments a consistent increase in gaseous volume was observed after closing the tap. The crude volumes of gas evolved were appropriately corrected. Results are recorded in Table I.

D. Measurement of the Degree of Decomposition ; Relation between Available Formaldehyde, Total Acidity, and Permanent Acidity for Methylenedinitroamine Solutions in Water or Dilute Formaldehyde.—Solutions of methylenedinitroamine were maintained at 25°, and the apparent percentage decomposition measured by the following methods. (*a*) " Total acidity " : an aliquot was titrated directly with standard sodium hydroxide; time required for titration about 2 minutes. (*a'*) " Permanent acidity " : the titrated aliquot from (*a*) was set aside for 25 minutes at room temperature, and then back-titrated with standard hydrochloric acid. The " permanent acidity " was found by subtracting the titre of hydrochloric acid from that of sodium hydroxide required in operation (*a*). (*b*) " Formaldehyde without destruction of nitroamine " : the titrated aliquot from (*a*) was determined immediately [a treatment alternative to (*a'*)]. (*b'*) " Formaldehyde after destruction of nitroamine " : the back-titrated aliquot from (*a'*) was analysed. For results see Table II.

TABLE II.

Concentration; solvent; run no.	Time (hours) at 25°.	Apparent % decomposition by method : (*a*.)	(*a'*.)	(*b*.)	(*b'*.)
M./20 in water; I	0	1	1	—	2
	49	21, 21	27	29	—
	51	23, 21	28	29	30
M./20 in 0·0527M-formaldehyde; II ...	0	0	0	—	2
	47	41, 41	69	70	69
	50	43	72	—	73

E. Relation between Available Formaldehyde, Acidity, and Gas Evolution for Solutions of Methylenedinitroamine in Water at 70°.—To methylenedinitroamine was added sufficient distilled water, at 70°, to give a M/20-solution which was maintained at 70° in a thermostat. Aliquots were run into ice, and thereafter determined, as in section *D*, by methods *a*, *a'*, *b*, and *b'*; formaldehyde was also determined by means of Brady's reagent. The gas-evolution results (admittedly less accurate) were obtained graphically from separate experiments in which methylenedinitroamine was added to water, at 70°, in a closed system. Results are recorded in Table III.

TABLE III.

Run nos.	Time (minutes) at 70°.	Apparent % decomposition. Method (see Section *D*). (*a*.)	(*a'*.)	(*b*.)	(*b'*.)	Brady.	Gas.
III & IV	5	5	—	18	—	—	2
	10	16	29	—	32	21	10
	15	29	—	47	—	—	25
	20	42	59	—	61	46	39
	22	45	—	65	—	—	45
	27	58	—	78	—	—	58
	30	66	83	—	85	67	65
	33	72	—	91	—	—	72
	43	88	—	100	—	—	87
	63	98	—	102	—	—	95
	85	100	—	101	—	—	96

F. Stabilisation by Acid and by Alkali.—(*a*) Solutions of methylenedinitroamine (M/20 in N/10-hydrochloric acid) were maintained at 25°, and the apparent percentage decomposition (see Table IV) measured by methods (*a*) and (*b*) (section *D*).

TABLE IV.

Concentration; solvent.	Run no.	Method of determination.	Apparent % decomposition. Hours at 25°. 19·5	116	265	407	524	*ca.* 600; then heated for 45 min. at 80° with buffer of pH 5·2.
M./20 in M/10-HCl	V	(*a*)	1	1	2	3	4	
		(*b*)	0	1	3	4	6	100
M./20 in M/10-HCl + 0·0509M-CH_2O	VI	(*a*)	1	2	5	7	9	
		(*b*)	1	4	8	12	17	100

(*b*) Methylenedinitroamine was over-neutralised with standard sodium hydroxide to give the disodium salt (M./20) in an excess (*ca.* 0·0012—0·0013M.) of alkali. On keeping the mixture at 25°, the alkalinity increased very slowly; after 459 hours, the mixture of run VII was 0·0032M., and that of run VIII (in which free formaldehyde was added initially) 0·0045M. with respect to free sodium hydroxide. In run VII, free formaldehyde, equivalent to the decomposition of 1% of the methylenedinitroamine, had appeared after 72 hours, but the amount did not increase thereafter; in run VIII the original concentration of formaldehyde remained unchanged. Since these results probably included the effect of the Cannizzaro reaction, the residual methylenedinitroamine was determined (Table V) by the difference between the total formaldehyde present after complete decomposition (heating for 25 to 30 minutes at 80° in a buffer of pH 5·2) and the free formaldehyde present in a separate aliquot.

TABLE V.

Concentration of disodium methylenedinitroamine; solvent.	Run no.	% Decomposition. Hours at 25°.			
		1	72	240	459
M./20 in 0·0012M-NaOH	VII	0	1	1	4
M./20 in 0·0013M-NaOH + 0·0532M-CH_2O	VIII	1	2	4	6

G. Decomposition in Acetate Buffers.—Solutions of methylenedinitroamine in acetate buffers (2·5N-acetic acid–sodium hydroxide, with two exceptions) were maintained at 25°, and the amount of decomposition was determined by method (*b*) (section *D*). The results of these runs (IX to XXIX) are given in Figs. 1 and 2. Curve II of Fig. 1 shows clearly the decrease in the rate of decomposition with increased pH, but is not strictly comparable on account of the lowered buffering capacity. Some results in a phosphate buffer (2M-H_3PO_4—2N-NaOH) are recorded by curve V of Fig. 2.

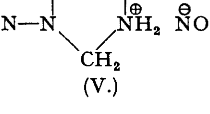
H. Further Investigation of the Decomposition in Unbuffered Solutions.—Solutions of methylenedinitroamine in water or dilute formaldehyde were maintained at 25°, and the decomposition was determined by methods (*a*) and (*b*) (section *D*). The results (of runs XXXII to XXXIX) represent an extension of section *D* to yield decomposition curves, which are given in Figs. 3 and 4. The difference between the upper and the lower line in each pair of curves provides an approximate measure of the nitroamine content of the solutions.

Preparation of 3 : 7-*Dinitro*-1 : 3 : 5 : 7-*tetra-aza*bicyclo[3 : 3 : 1]*nonane* (I) *from Methylenedinitroamine.*—Methylenedinitroamine (0·34 g. in 4 ml. of water) was partly neutralised with 2N-ammonia solution (1·2 ml.), and 38% formaldehyde (0·6 ml.) was added. After 24 hours, the precipitate (0·18 g.), m. p. 202° (decomp.), was collected and crystallised from nitromethane. 3 : 7-Dinitro-1 : 3 : 5 : 7-tetra-aza*bicyclo*[3 : 3 : 1]nonane (0·07 g.), m. p. 208—209° (decomp.), undepressed by admixture with an authentic specimen (Richmond, Myers, and Wright, *J. Amer. Chem. Soc.*, in press), was obtained. If no formaldehyde was added a small yield (0·03 g.) of material, m. p. 210°, was precipitated.

Determination of Free Methylenedinitroamine in the Presence of Acid and Formaldehyde.—To 10 ml. of solution, containing 0·1—0·4 g. of methylenedinitroamine, were added, successively, 9N-ammonia solution (5—6 ml.; note 1), M-barium chloride (5 ml.), and 90% methyl alcohol (30 ml.; note 2). After cooling for 1 hour in ice, the precipitate was collected on a sintered-glass funnel (the last traces were transferred with two 5-ml. portions of cold 60% methyl alcohol) and washed with, successively, cold 60% methyl alcohol (5 ml.), 90% methyl alcohol (5 ml.), and ether (15 ml.). Without being dried, the precipitate was then decomposed by stirring on the filter with an acetate buffer of pH 5·0 (25 ml.; 5—3 volumes of 2·5N-acetic acid and sodium hydroxide) and sucked through into a 100-ml. flask having a ground-glass neck. The solution and washings (25 + 15 ml. of water) were heated under reflux for 20 minutes at 80°, cooled, and made up to 250 ml. Formaldehyde (1 mol., equivalent to 1 mol. of methylenedinitroamine) was then determined iodometrically (note 3) in suitable (50 or 100 ml.) aliquots. An empirical correction (the addition of 11 mg. to the apparent weight of methylenedinitroamine in the original 10 ml. of solution) was required for accurate results.

Notes. (1) Added rapidly: pH at precipitation was >10. (2) All the methyl alcohol was purified by hypoiodite (Bates, Mullaly, and Hartley, *J.*, 1923, 403). A small quantity of ethyl alcohol (indicator solvent) in the original solution was not detrimental. (3) Blank determinations on the acetate buffer are recommended. 10—15 Minutes were ample for complete reaction when one-third of the iodine was available for back-titration, and an excess (*ca.* 1/20th of the total volume) of 2·5N-sodium hydroxide was added after decolorisation. Although ammonia interferes with the determination, any earlier coprecipitation of ammonium salts may be detected by the formation of nitrogen tri-iodide on the addition of sodium hydroxide.

In the following record of results, the empirical addition of 11 mg. is included and the true weight of methylenedinitroamine is given in parentheses. Mg. in 10 ml.: 402 (400); 199 (200); 115, 112 (114); 100 (100); 50, 54 (50). The following additional results were obtained after precipitation with 20 ml. of methyl alcohol, and washing with 50% methyl alcohol, the cooling time being 1—1½ hours. Mg. in 10 ml.: 403 (400); 199 (200); 100 (100); 47 (50).


(V.)

Determination of Potential Methylenedinitroamine.—(i) A suitable quantity of material was weighed into a small tared sintered-glass crucible, and decomposed by the addition of 6N-ammonia solution (7 ml.). After 5 minutes, with occasional stirring, the resultant liquid was sucked into a conical flask, and the crucible washed twice with 0·5N-ammonia solution (4 + 4 ml.). The insoluble material was weighed after vacuum-desiccation, and the methylenedinitroamine determined in the filtrate by addition of barium chloride etc., as previously detailed. (ii) Alternatively, if the material is wholly soluble, it may be decomposed in the precipitation flask by the addition of 3N-ammonia solution (15 ml.).

Samples (0·6—0·75 g.) of a specimen of 1 : 3-dinitrohexahydro-1 : 3 : 5-triazine nitrate (V) (Vroom and Winkler, *Canadian J. Res.*, in the press; also Bristol workers, private communication) were used. Method (i): Found: insoluble material, 0·5, 0·3%; potential methylenedinitroamine in soluble portion, 55, 56%. Method (ii): Found: potential methylenedinitroamine in total weight, 56, 55%. Calc. for (V): insoluble material, 0; potential methylenedinitroamine, 56·7%.

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