ertheless, what appeared to be best values of the limiting equivalent conductance, Λ_0, and the ion-pair dissociation constant, *K*, were obtained, and the results are given in Table II.

TABLE II

LIMITING EQUIVALENT CONDUCTANCE AND ION-PAIR DISSOCIATION CONSTANT OF SOME SALTS IN ACETIC ACID AT 30°

Salt	Λ_0	$K \times 10^7$
Potassium bromide	41	1.1
Sodium bromide	37	1.3
Lithium bromide	29	7.2
Potassium formate	35	1.1
Sodium formate	31	0.65
Lithium formate	23	0.87
Potassium acetate	24	3.6
Sodium acetate	20	2.1
Lithium acetate	13	6.0

In Table III is presented a comparison of the numerical values of the equilibrium constant, *K*, for the postulated ion-pair exchange reaction (a), as previously obtained[4] from solubility data by equation 1, with the corresponding constants, S_0K', calculated from the dissociation constants in Table II and the previously reported value of $S_0 = 0.01837$ *m*.

In view of the uncertainties involved in determining the individual dissociation constants from the conductance data, the agreement shown in Table III would appear to be rather surprisingly good. The fact that the constants obtained from the two very different types of measurement are of the same order of magnitude lends considerable further support to the hypothesis previously advanced that reactions of type (a) may be of major importance in accounting for salt effects on solubility in those solvents in which both the solvent salt and the solute salt exist largely as ion-pairs.

TABLE III

COMPARISON OF ION-PAIR EXCHANGE CONSTANTS OBTAINED FROM SOLUBILITIES AND FROM CONDUCTANCE MEASUREMENTS

Added salt	*K* eq. 1	$K'S_0$ eq. 4
Sodium acetate	0.0114	0.0090
Sodium formate	.0102	.0092
Lithium acetate	.00250	.0047
Lithium formate	.00328	.0022

Returning to the results presented in Table II, it is of interest to note that in a series of salts possessing a common anion the limiting equivalent conductances are observed to decrease in the order potassium > sodium > lithium, which, of course, corresponds to the order observed in water solutions, and may very probably be attributed to a similar cause, namely, a progressively increased degree of solvation.

LAWRENCE, KANSAS

[CONTRIBUTION FROM ARTHUR D. LITTLE, INC.]

The Thermal Decomposition of Methylenedinitramine

BY MARVIN C. TOBIN, JOHN P. FOWLER, HENRY A. HOFFMAN AND CHARLES W. SAUER[1]

RECEIVED SEPTEMBER 18, 1953

Data are presented for the thermal decomposition of molten and solid methylenedinitramine and solid methylenedinitramine inhibited with picric acid. It is shown that the course of the decomposition of the solid is similar to that of other materials. A theory of the phenomena observed in the decomposition of solids is presented. Infrared spectra are presented for methylenedinitramine and its solid decomposition product.

In contrast to the tremendous amount of research carried out on the kinetics of decompositions taking place in the gas or solution phases, relatively little has been done with pure liquids or solids. Yet the decomposition of liquids or solids is often of the greatest practical interest, especially in connection with the storage of unstable materials. In addition, many phenomena appear in connection with the decomposition of solids which are absent in the gas or liquid phases, due to the mobility of the molecules of the latter. Methylenedinitramine makes a good subject for this type of study, due to its low melting point and comparative ease of decomposition.

It is well known[2] that the decomposition of methylenedinitramine is catalyzed by its products. Since it was desired to examine the primary decomposition process, the decompositions were carried out by heating the material in open tubes to allow escape of volatile products, and following the progress of weight loss with respect to time. This procedure was considered feasible in view of the lack of any sign that the compound reacted with the atmosphere. Trial tests showed that the rate of sublimation of the solid was very small.

This paper also reports the existence of a stabilizer for methylenedinitramine–picric acid. The discovery of this arose from a search for a way to inhibit the decomposition of methylenedinitramine.

Experimental

Samples.—The methylenedinitramine[3] was twice recrystallized from freshly distilled 2-nitropropane, by saturating the solvent at room temperature, and chilling in a full, stoppered bottle in a deep-freezer chest. In this way, possible decomposition during recrystallization was prevented. The pure material was dried under suction on a sintered glass filter, the crystals crushed and dried under vacuum; m.p. 105–106° dec.

To prepare the sample of methylenedinitramine–picric

---

(1) This work was done under Contract DA-19-020-ORD-47 with the Office of the Chief of Ordnance and has been released by the War Department for publication.

(2) A. H. Lamberton, C. Lindley and J. C. Speakman, *J. Chem. Soc.*, 1650 (1949).

(3) This sample was from an experimental batch prepared by the Atlas Powder Co., Tamaqua, Penna.

acid, a 0.5168-g. portion of methylenedinitramine was intimately mixed with 2% its weight of picric acid. Enough benzene was added to form a slurry, the mixture stirred for one minute and dried under vacuum. The pure material dried sample was carefully crushed to reduce agglomerates. It had previously been found that methylenedinitramine is quite insoluble in benzene.

Procedure.—Weight loss was followed by two methods. Above 90°, the sample tube was suspended from a pan attached to a Westphal balance into an oven. At the start of a run, the tube containing the weighed sample was suspended from a pan, and sufficient weight added to bring the balance to equilibrium. As weight was lost, weights were added to the pan to restore equilibrium, so that weight loss as a function of time could be followed. The temperature control was to ±1°. The balance was found to be sensitive to 0.002 g.

Below 90° the tubes were heated in an oven. They were removed at intervals ranging from 4-72 hours, cooled, weighed and replaced in the oven. Temperature control was to ±1°, weighing to 0.0001 g. The data given are corrected for the time used in cooling, weighing and reheating the samples.

All samples for experiments on the solid were taken from the same batch of powder, so as to standardize the variable of particle size. The mean crystallite size is estimated at 0.5 mm.

Results

It was found feasible to follow decomposition of the melt to essentially complete decomposition. The samples melted readily, but solidified after some three hours of heating. Decomposition was complete in all cases at about 45% weight loss. The residue was a white powdery solid which decomposed at about 208°. This solid was found to be insoluble in water, benzene, acetone, alcohol or Skellysolve. No quantitative analysis of the escaping gases was made; but infrared analysis showed them to contain HCHO, N_2O and H_2O. The solid samples at 70, 80 and 100° showed no evidence of fusion at any time during the heating period.

The logarithm of the amount undecomposed (a = weight loss at complete decomposition) as a function of time is shown in Fig. 1,[4] for methylenedinitramine melt at 110, 115, 120 and 130°. Since we measure weight loss rather than amount decomposed, we assume that the weight loss at any time bears the same relation to the amount decomposed as the weight loss at complete decomposition bears to the sample weights. It is easily shown, for a first-order reaction, that these assumptions lead to the equation $dw_0/dt = k(a_0 - w_0)$ where the zero subscript corresponds to the observed quantities. The points fall quite well on straight lines, so the decomposition apparently follows the first order law. A plot of the logarithms of the rate constants against the inverses of the absolute temperatures (Fig. 2) leads to the expression for the rate constant

$$k = 10^{15.6} e^{-35.4 \text{ kcal./mole}/RT} \text{ sec.}^{-1} \quad (1)$$

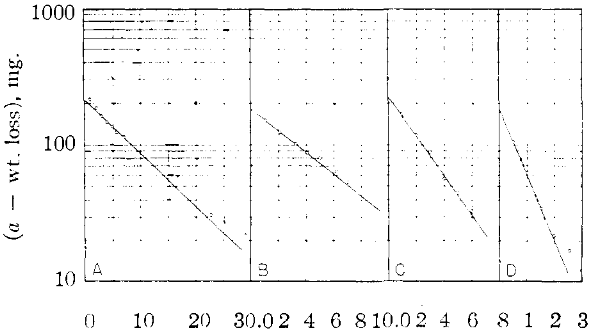

Fig. 1.—Amount undecomposed *vs.* time for methylenedinitramine melt: A, 110°, sample wt. 0.5124 g., a = 213 mg., k = 0.10 hour^{-1}. B, 115°, sample wt. 0.4404 g., a = 189 mg., k = 0.17 hour^{-1}. C, 120°, sample wt. 0.5136 g., a = 235 mg., k = 0.33 hour^{-1}. D, 130°, sample wt. 0.4121 g., a = 197 mg., k = 1.10 hour^{-1}.

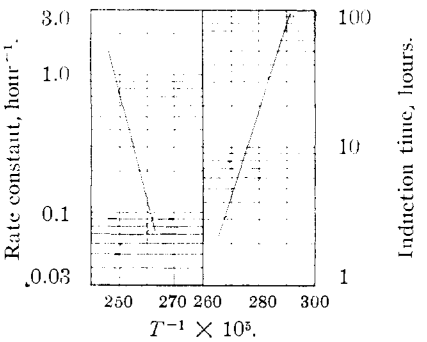

Fig. 2.—Log k *vs.* $1/T$ for methylenedinitramine melt and log τ *vs.* $1/T$ for solid methylenedinitramine.

The plot of weight loss *vs.* time at 70, 80 and 100° in Fig. 3 reveals several interesting features. The decomposition may be divided into three regions. First comes a region of decreasing rate of decomposition, complete at some 1% decomposed. This region is herein referred to as the induction period. This is followed by a region where the rate of decomposition increases with time (the auto-accelerative period). Finally, a region is reached where the rate again decreases with increasing time (the degressive period). The duration of the induction period may be defined quite precisely by taking it as the time at which the first inflection point (second derivative of weight loss with respect to time equals zero) is reached. It is seen in Fig. 2 that there is a linear relationship between the logarithm of the induction time and the reciprocal of the absolute temperature.

Two curves are shown in Fig. 4 at 80°, one for pure methylenedinitramine and one for methylenedinitramine–picric acid. It is obvious that neither the duration of the induction period nor the course of the decomposition after the induction period is affected by the picric acid. However, the picric acid does visibly reduce the percentage of material decomposed during the induction period, and thus acts as an inhibitor. The similarity of the two 80° curves during the auto-accelerative periods may be shown by plotting the logarithm of the weight loss minus a constant (5.5 for pure methylenedinitramine, 0.1 for methylenedinitramine–picric acid[5] against the logarithm of the time. Both sets of points fall on the same straight line, so that during

---

[4] While the graphs only show data to 60% decomposition in some cases, all decompositions were carried to 100%.

[5] The figures 0.1 mg. and 5.5 mg. represent the total weight loss due to the first-order process discussed below. The data are normalized to the same sample weight of 0.4958 g. See equations (5) and (6) below.

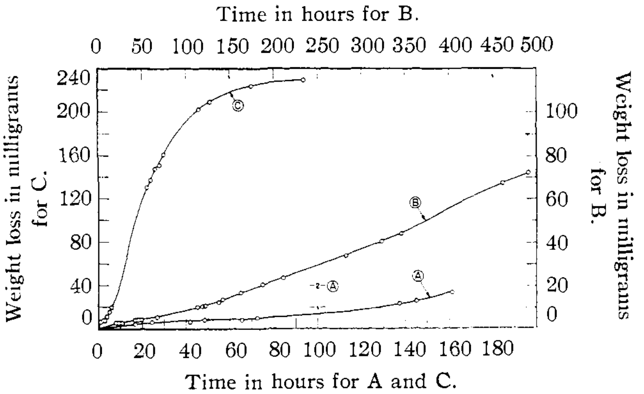

Fig. 3.—Weight loss *vs.* time for solid methylenedinitramine: A, 70°, sample wt. 0.4202 g. B, 80°, sample wt. 0.3936 g. C, 100°, sample wt. 0.5883 g.

this period (weight loss − constant) = $0.00192 \times t^{1.76}$. It is thus found that the weight loss for 0.4958 g. of methylenedinitramine at 80° may be expressed by the equation

$$w = 5.5\,(1 - e^{-0.16t}) + 0.00192t^{1.76}$$

mg. during the first two periods. The constant 0.16 was evaluated by means of equations 6 and 8, using the measured induction time of 30 hours.

Discussion

Melt.—The thermal decomposition of the melt shows no unusual features, except the production of a large amount of solid product. The activation energy is typical of nitramines, although the frequency factor is high. It is quite improbable that the reaction is truly unimolecular, but no attempt was made to work out the mechanism.

Solid.—Some rather detailed studies of the decomposition of crystals have been made, including microscopic examination of single crystals.[6-10] It was found, in general, that decomposition proceeds from discrete nuclei, mainly on the crystal surfaces. The nuclei tended to grow at a rate linear in the radius, but the rate of initial nucleus formation generally increased with time. The course of the decomposition followed identically the same course as did methylenedinitramine, the induction period following the law[11]

$$\log \tau = (E/T) + B \qquad (2)$$

However, during the auto-accelerative period, the exponent of the time ran as high as eight.

That the decomposition of methylenedinitramine starts primarily on the crystal surfaces is apparent from the inhibitive effect of picric acid, which was added in such a manner that it could deposit only on the surfaces of the methylenedinitramine crystals.

Although Garner, Gomm and Hailes[7] have developed an approximate expression for the auto-accelerative portion of the decomposition (see Appendix I), no satisfactory explanation for the presence of the induction period has been put forward. It has been attributed to slow formation of the nuclei[9] but this fails to explain both the immediate onset of decomposition and the initial decrease in reaction rate. It is obvious from an examination of the experimental curves that the first two periods may be represented by a very rapid first-order decomposition of a small quantity of material, superimposed on a slower auto-accelerative process.

This may be illustrated by the following model.[12] Consider a surface containing X_0 strains or other imperfections. These decompose with the large rate constant k_1, according to a first-order law. Each nucleus loses a weight z in this rapid decomposition. Subsequently, each nucleus loses weight according to a power law, with the rate constant $k_2 << k_1$. We consider a second-power law for simplicity. In the following, we use the abbreviations "weight of nucleus" for "weight loss at the site of a nucleus" and "weight of nuclei" for "total weight loss at the sites of nuclei." We let

$\mathrm{d}X = k_1(X_0 - X)\,\mathrm{d}\theta$ = no. of nuclei formed in time interval $\mathrm{d}\theta$

$w = (z + k_2(t - \theta)^2)$ = wt. of nucleus, formed at time θ at later time t

The total weight of nuclei, formed in $\mathrm{d}\theta$, at a later time t, is given by

$$\mathrm{d}W = k_1(X_0 - X)(z + k_2(t - \theta)^2)\mathrm{d}\theta \qquad (3)$$

which leads to

$$W(t) = k_1 z X_0 \int_0^t e^{-k_1\theta}\,\mathrm{d}\theta + X_0 k_1 k_2 \int_0^t e^{-k_1\theta}\,(t - \theta)^2\mathrm{d}\theta$$

$$= zX_0(1 - e^{-k_1 t}) + X_0 k_1 k_2 \int_0^t e^{-k_1\theta}\,(t - \theta)^2\mathrm{d}\theta$$

$$= zX_0(1 - e^{-k_1 t}) + X_0 k_2(t^2 - \frac{2t}{k_1} + \frac{2}{k_1{}^2}\,(1 - e^{-k_1 t})) \qquad (4)$$

Since $k_1 >> k_2$, we may write as a good approximation

$$W(t) = X_0\left(z + \frac{2k_2}{k_1{}^2}\right)(1 - e^{-k_1 t}) + X_0 k_2 t^2 \qquad (5)$$

which is of the form of the experimental expression given just preceding Discussion.

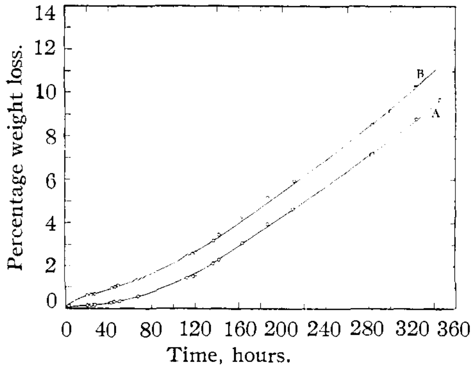

Fig. 4.—Percentage weight loss *vs.* time at 80° for methylenedinitramine and methylenedinitramine coated with picric acid: A, methylenedinitramine, sample wt. 0.3936 g. B, methylenedinitramine–picric acid, sample wt. 0.4958 g.

---

(6) A. Wischin, *Proc. Roy. Soc.* (*London*), **172A**, 314 (1939).

(7) W. E. Garner, A. S. Gomm and H. R. Hailes, *J. Chem. Soc.*, 1393 (1933).

(8) W. E. Garner and D. J. B. Marke, *ibid.*, 657 (1936).

(9) N. F. M. Bright and W. E. Garner, *ibid.*, 1872 (1934).

(10) W. E. Garner and W. R. Southon, *ibid.*, 1705 (1935).

(11) N. Semenoff, "Chemical Kinetics and Chain Reactions," Oxford Univ. Press, New York, N. Y., 1935, p. 437.

(12) Compare J. Y. McDonald, *J. Chem. Soc.*, 839 (1936).

For a more general growth law, we may write

$$W = W_0(1 - e^{-k_1t}) + kt^n \qquad (6)$$

and

$$W'' = -W_0k_1^2e^{-k_1t} + kn(n - 1)t^{n-2} = 0 \qquad (7)$$

Then

$$e^{k_1\tau} = \frac{W_0k_1^2}{kn(n - 1)\tau^{n-2}} \qquad (8)$$

Taking logarithms twice

$$\ln k_1 + \ln \tau = \ln \ln (W_0k_1^2/kn(n - 1)\tau^{n-2}) \qquad (9)$$

Setting

$$k_1 = b_1\, e^{-E_1/RT} \qquad (10)$$

We have finally

$$\ln \tau = E_1/RT + \ln (\ln(W_0k_1^2/kn(n - 1)\tau^{n-2})/b_1) \qquad (11)$$

The second term on the right-hand side of 11 is temperature dependent, but since it is a log–log function, it may be treated as essentially constant.

Finally

$$\log \tau = \frac{E_1}{2.303RT} + B \qquad (12)$$

in agreement with the experimental expression 2. From Fig. 2, $E_1 = 27.8$ kcal./mole for methylenedinitramine. It may be seen from Fig. 4 that the duration of the induction period is quite insensitive to the amount decomposed during the induction period. This is in agreement with equations 11 and 12, since the terms controlling this amount, W_0 and k_1, are found in the log–log term. It should be noticed that this model requires that $E > 2E_1$, that is, that the energy of activation for growth be more than twice that for nucleation; otherwise 11 will lead to imaginary induction times.

In the cases observed by other workers, where new nuclei are formed *continuously*, it is necessary to assume that lumped into the growth term is a quantity which expresses slow formation and growth of nuclei on the perfect areas of the crystal. This point is discussed in Appendix I.

The end of the auto-accelerative period is assumed to be the time at which the surface area of the crystals is completely covered. The final decrease in rate of decomposition is ascribed to the reduced surface area as the decomposition penetrates radially into approximately spherical particles, and may be due to either reduction of area, or surface blocking by reaction product.

The idea of two essentially different mechanisms of nucleation being present is supported by the action of picric acid as a stabilizer, since this material affects only the induction period.

Acknowledgments.—The authors wish to express their thanks to Mr. James H. Orr, Jr., for preparing the illustrations, to Mrs. Ruth M. Gerow for typing the manuscript, and to Mrs. Elaine Blanton for taking the infrared spectra.

Appendix I

Garner, Gomm and Hailes[7] have given an expression for the rate of decomposition of a crystal surface on which N nuclei are produced in unit time, the rate of growth being proportional to r^2.

They give

$$dp/dt = k \sum^{t} t^2 = \frac{k}{6}(2t^3 + 3t^2 + t)$$

where p = pressure of evolved gas. This treatment neglects the fact that N as defined by them will decrease with time, due to the fact that growth of nuclei formed at early times will decrease the area available for new nucleation. Let

N_0 = nuclei formed/unit time/unit free area[13]
A_0 = initial area of surface
t = time as boundary condition
θ = time as variable
N = number of nuclei formed to time θ
$k(t - \theta)^2$ = area covered by nucleus, formed at time θ at later time t
$A(\theta)$ = area covered by all nuclei at time θ

For the sake of clarity, it may be mentioned that our nucleus is assumed to be hemispherical, so that. in the following, by the "area covered by a nucleus" is meant the circular cross sectional area of the nucleus.

The "total area covered by nuclei" is the sum of all these cross sections. Since nuclei form only on the surface, the rate of formation of fresh nuclei, and the rate of growth of a hemispherical nucleus may be derived from a consideration of the two-dimensional features of the phenomena.

The number of nuclei formed in time dθ at θ is

$$\mathrm{d}N = N_0(A_0 - A(\theta))\mathrm{d}\theta \qquad (1)$$

The area covered by nuclei formed in time interval dθ around θ at a later time t is

$$\mathrm{d}A = k(t - \theta)^2\mathrm{d}N \qquad (2)$$

The area covered by all nuclei at time t is

$$\int_0^A \mathrm{d}A = A(t) = N_0k\int_0^t (t - \theta)^2(A_0 - A(\theta))\mathrm{d}\theta$$
$$= \frac{A_0N_0kt^3}{3} - N_0k\int_0^t A(\theta)(t - \theta)^2\mathrm{d}\theta \qquad (3)$$

This integral equation (Volterra's integral equation of the second kind) may be solved by the method of iteration given by Lovitt.[14] Taking $A_0(\theta) = A_0N_0k\theta^3/3$, to terms in t^9

$$A(t) = \frac{A_0N_0kt^3}{3} - \frac{A_0(N_0kt^3)^2}{180} + \frac{A_0(N_0kt^3)^3}{45{,}360} - \dots \qquad (4)$$

$(A(t) \leq A_0)$

An alternate method of solution is to differentiate triply equation 3 with respect to t. This leads to the differential equation

$$A'''(t) + 2kN_0A(t) = 2kN_0A_0$$
$$A''(0) = A'(0) = A(0) = 0 \qquad (5)$$

The solution is readily found[15] as

$$A(t) = A_0\left(1 - \frac{1}{3}e^{-Bt} - \frac{2}{3}e^{Bt/2}\cos\frac{\sqrt{3}}{2}Bt\right) \qquad (6)$$

where $B = (2N_0k)^{1/3}$, $A(t) \leq A_0$. Equation 6 is the closed form of the series 4.

Assuming radial growth of the nuclei, the loci of decomposition are hemispheres, and the volume (weight) of decomposed material is given by

---

(13) This quantity is not the same as the N_0 defined earlier!

(14) W. Lovitt, "Linear Integral Equations," Dover Publications, New York, N. Y., p. 15.

(15) H. Phillips, "Differential Equations," John Wiley and Sons, Inc., New York, N. Y., 1934, Chapter IV.

$$V = K\int_0^t (t - \theta)^3 \mathrm{d}\, N$$
$$= N_0Kk\int_0^t (t - \theta)^3(A_0 - A(\theta))\mathrm{d}\theta \quad (7)$$

where k and K are related in an obvious manner.

From 6, we may estimate N_0k, since when $A(t) = A_0$, we have

$$e^{-3Bt/2} + 2\cos\frac{\sqrt{3}}{2}Bt = 0 \quad (8)$$

which may be solved to give $Bt = 1.842$ for the smallest root. This figure may be used to estimate B from the observed time at which the auto-accelerative period ends. It should, however, be emphasized that the treatment holds only for the particular growth law assumed.

It may be seen by inserting $N_0kt^3 = 3.11$, the value at $A(t) = A_0$, into 4 that the effect of terms in the series past the first is small. The second term is only 5% of the first when the surface is completely decomposed. This means that the effect of the reduction of area available for fresh nucleation will become noticeable only at late times.

It should be pointed out that our treatment neglects the effect of overlapping of centers of decomposition. This will become important at late times, and will tend to slow down the rate of reduction of undecomposed surface.

The effect on nucleation of blocking of surface may be illustrated by setting $A(\theta) = N_0A_0k\theta^3/3$ into 1 and integrating between 0 and t. We find

$$N(t)/N_0A_0 = t(1 - N_0kt^3/12) \quad (9)$$

When $A = A_0$, $N(t)/N_0A_0 \simeq 0.75t$, since, $N_0kt^3 = 3.11$

Had no blocking taken place, we would have had $N(t)/N_0A_0 = t$. It is thus seen that the effect of blocking is to reduce the number of nuclei formed by the time when $A = A_0$ by only 25%.

The smallness of this decrease is a consequence of the rapid increase of reaction rate with time.

If we call t_0 the time when $A = A_0$, then

$$A_0 = N_0kt_0^3/3 \quad (10)$$

When $1/n$ of the surface has been used up

$$A_0/n = N_0kt_n^3/3 \quad (11)$$

These give

$$t_n/t_0 = n^{-1/3} \quad (12)$$

It is thus seen that when 50% of the total reaction time has elasped, only $^1/_8$ of the surface has been used. This is a verification of the statement made above that blocking is important only at late times.

Appendix II. Infrared Spectra

The infrared spectra of methylenedinitramine and the solid decomposition product were obtained in Nujol mull on a Perkin–Elmer automatic recording infrared spectrophotometer at Arthur D. Little, Inc. The region from 1400–4000 cm.$^{-1}$ was covered with a CaF_2 prism, that from 650–1400 cm.$^{-1}$ with a NaCl prism. The spectra are recorded in Table I. A detailed assignment of frequencies is not possible with these limited data, but one may reasonably identify the broad band at 3100–3400 cm.$^{-1}$ with N–H stretching, and the bands at 1580 and 1310–1380 cm.$^{-1}$ with NO_2 stretching, in methylenedinitramine. The breadth of the 3100–3400 cm.$^{-1}$ band is believed to be due to bonding of the hydrogens on one nitramine group with another nitramino group. The band at 3500 cm.$^{-1}$ in the decomposition product is probably due to a small number of isolated OH groups. It does not seem possible reasonably to assign it to a combination tone or overtone, and its sharpness precludes its being representative of hydrogen-bonded OH.

From the spectra, one may conclude about the decomposition product that: 1. It contains no N–H groups. This is shown by the absence of bands around 3200 cm.$^{-1}$. 2. NO_2 groups are probably present. This is shown by the strong, broad band at 1540–1590 cm.$^{-1}$ and the strong bands at 1335 and 1345 cm.$^{-1}$. 3. There may be a small number of OH groups present.

CAMBRIDGE, MASSACHUSETTS

TABLE I

THE INFRARED SPECTRA OF METHYLENEDINITRAMINE AND ITS DECOMPOSITION PRODUCT, IN CM.$^{-1}$

Methylenedinitramine	Decomposition product
3100–3400 br. with structure	3500 m
3000 } s[a]	3140 w
2950 }	3090 w
2900 s	2970 s[a]
1580 v. br	2890 s
1450 m-br[a]	1540–90 v. br
1420 m-br	1460 s[a]
1380 m-br[a]	1440 s
1310 s	1425 s
1275 s	1390 m[a]
1130 s	1370 m
1085 s	1345 s
918 m	1335 s
785 } m	1260 s br
780 } m	1180 m
698 m br	1130 m
	1090 s
	1070 s
	1030 s
	965 w
	930 s br
	910 m
	862 m
	850 sh
	768 s
	760 w
	680 w br

[a] Region of Nujol bands.