## THE THERMAL DECOMPOSITION OF NITROMETHANE UNDER HIGH PRESSURE

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The thermal decomposition of nitromethane has been studied under approximately 40 atm pressure and over the temperature range of 312-340°C, and shown to be approximately first order with a rate constant given by

 $k = 10^{13.73} \exp(-49200/RT) \sec^{-1}$ .

The main products are nitric oxide, hydrogen cyanide, carbon dioxide, formaldehyde and water, with some carbon monoxide and small quantities of methane and nitrous oxide. In addition to this, a solid of the empirical formula  $C_{10}H_{10}N_4O_2$  accumulated as the reaction proceeded. The amount of hydrogen cyanide produced was found to depend on the initial pressure.

The initial step in the decomposition is considered to be the same as in the low pressure range:

$$CH_3NO_2 \rightarrow CH_3 + NO_2,$$
  
$$CH_3NO_2 \rightarrow CH_3NO + O$$

and not

Oxygen increases the rate of decomposition and decreases the quantity of hydrogen cyanide obtained. Nitrogen dioxide inhibits the decomposition reaction, and nitric oxide in small quantities does not have any significant influence on the rate of the decomposition.

The thermal decomposition of nitromethane in the low-pressure range from 5 to 400 mm has been studied by a number of workers.<sup>2-6</sup> The only previous study in the high pressure range (12 to 20 atm) has been carried out by Mueller,<sup>1</sup> who postulated the primary step

$$CH_3NO_2 \rightarrow CH_3NO + O.$$

Such a reaction, however, appears energetically unlikely. Mueller investigated the influence of oxygen, nitric oxide and nitrogen dioxide on the rate of disappearance of nitromethane, but did not investigate the dependence of the rate constant on the temperature. Since he does not give the value of the activation energy for the reaction, and since his results concerning the influence of oxygen on the rate of decomposition of nitromethane do not agree with those obtained in the low-pressure range,<sup>2, 6</sup> a re-investigation of the reaction was undertaken.

#### EXPERIMENTAL

## MATERIALS

Nitromethane (Messrs. Commercial Solvents Corporation) was purified by distillation. The fraction employed for the decomposition experiments had a constant boiling point of 101°C at 760 mm pressure and  $n_D^{20}$  1·3818. Its infra-red spectrum agreed with that published by Smith, Pan and Nielsen.<sup>7</sup>

Nitric oxide was prepared by heating a dry powder of potassium nitrite, potassium nitrate, chromic oxide and ferric oxide to  $300^{\circ}$ C. The nitric oxide produced was collected over dilute sodium hydroxide solution, and contained only a fraction of 1 % of

nitrogen as impurity. For purification, the nitric oxide was solidified in liquid air, and the nitrogen pumped off.

Nitrogen dioxide was obtained by heating lead nitrate, and was separated from oxygen by condensation.

Oxygen was prepared from potassium chlorate by heating it with manganese dioxide. Formaldoxime was prepared by condensation of hydroxylamine with formaldehyde according to the method described by Scholl.<sup>8</sup> The solid trimer of formaldoxime obtained after distillation was used in our experiments.

Diacetyl peroxide was prepared by the method of Rembaum and Szwarc.<sup>9</sup> The peroxide was used in the form of a solution in nitromethane, as the pure compound is dangerous. The concentration of the solution was determined by the iodometric method of Wagner, Smith and Peters.<sup>10</sup>

Carbon dioxide was prepared by heating analytically pure magnesium carbonate at  $600^{\circ}$ C and was not further purified.

#### APPARATUS AND METHOD

Pyrex ampoules of approximately 4 ml capacity were filled with a weighed amount of nitromethane, frozen in dry ice and sealed under a vacuum of  $10^{-5}$  mm Hg. As the volume of the ampoule was known and all experiments were carried out above the critical temperature of nitromethane, its initial pressure could be determined by assuming the validity of the ideal gas laws. The ampoules were immersed in a heating bath which was held at constant temperature ( $\pm 0.2^{\circ}$ C). The temperature was controlled by means of a Thyratron phase shift control unit operated by a platinum resistance thermometer in a Wheatstone bridge. A calibrated copper-constantant thermocouple was used for the temperature measurements. If a gas was to be added, a measured amount of it was condensed into an ampoule containing a weighed quantity of nitromethane.

#### ANALYTICAL PROCEDURE

At various stages of the decomposition the reaction was quenched, the ampoule opened at  $-180^{\circ}$ C (liquid-air temperature), and the amount of carbon monoxide and nitrogen present determined volumetrically. The carbon monoxide was absorbed in ammoniacal cuprous chloride solution and the amount of nitrogen determined by difference. The temperature was then raised to  $-140^{\circ}$ C (m.p. of petrol ether) and the combined amount of methane and nitric oxide determined, the nitric oxide by absorption in alkaline sodium sulphite solution and the methane by difference. The temperature was further raised to  $-70^{\circ}$ C (dry ice), and the amount of nitrous oxide and carbon dioxide determined, the latter by absorption in soda-lime and the former by difference.

After the removal of the permanent gases at  $-70^{\circ}$ C, the residue was dissolved in 0.1 N potassium hydroxide. The quantity of nitromethane that had remained undecomposed, was determined polarographically by the method of De Vries <sup>11</sup> with a Leeds and Northrup Electrochemograph. A volumetric determination of nitromethane with hypochlorite <sup>12</sup> gave the same results. The free hydrocyanic acid was titrated with N/100 silver nitrate <sup>13</sup> or determined colorimetrically by the pyridine + benzidine method <sup>14</sup> with the same results. Part of the hydrocyanic acid appeared in the reaction products as glycolonitrile, formed by condensation with formaldehyde which is also a product of the reaction. This "bound " hydrocyanic acid was set free by alkali and determined as above. The amount of formaldehyde was calculated from the amount of bound hydrocyanic acid found. The alkali insoluble solid which remained, had the empirical formula C<sub>10</sub>H<sub>10</sub>N<sub>4</sub>O<sub>2</sub> and was determined colorimetrically. The water produced in the decomposition reaction was determined colorimetrically by means of standardized solutions of cobaltous chloride in dry methanol.<sup>15</sup>

#### RESULTS

#### DISTRIBUTION OF PRODUCTS

The distribution of products obtained at various stages of the decomposition reaction of nitromethane at approximately 40 atm and  $340^{\circ}$  is given in fig. 1.

The main products of the reaction are water, carbon dioxide, hydrocyanic acid, nitric oxide and formaldehyde. In addition to this, a solid of the empirical formula  $C_{10}H_{10}N_4O_2$  accumulated as the reaction proceeded. The amounts of this solid at various stages of the decomposition of nitromethane are given in table 1.

### **DECOMPOSITION OF NITROMETHANE**

When these results are compared with those obtained by Taylor and Vesselovsky,<sup>2</sup> and by Cottrell, Graham and Reid,<sup>4</sup> it is found that the main difference lies in the amount of hydrogen cyanide produced. The first authors found in some cases small quantities of hydrogen cyanide, but Cottrell and collaborators, though they noted occasionally the faint odour of hydrogen cyanide, were unable to detect this compound analytically. Gray, Joffe and Roselaar <sup>4</sup> found also hydrogen cyanide, but they report only qualitative tests on the cyanide in.



FIG. 1.—Plot of decomposition products against nitromethane decomposed at 340°C.

Table 1.—Amount of solid product (calculated as  $C_{10}H_{10}N_4O_2)$  at various stages of the decomposition of nitromethane

at 340°		at 330°		
% nitromethane decomposed	w/w % of solid product	% nitromethane decomposed	w/w % of solid product	
10	0.61	5	0.21	
20	1.09	10	0.46	
40	2.2	20	<b>0</b> ·89	
50	2.77	30	1.46	
70	4.13			

Since the mechanism proposed by Mueller for the initial step of the decomposition reaction under high pressure is based on the fact that hydrocyanic acid is one of the major carbon-containing compounds, we studied the influence of the initial pressure in the reaction vessel on the amount of hydrocyanic acid produced. It was found that the amount of hydrogen cyanide increased with the initial pressure of nitromethane. In one case the initial pressure in the reaction vessel was increased by adding carbon dioxide; this also increased the amount of hydrogen cyanide produced. The results obtained are summarized in table 2.

TABLE 2.—HYDROCYANIC ACID PRODUCED AT VARIOUS INITIAL PRESSURES, AT 330°C

initial pressure of nitromethane atm	pressure of carbon dioxide atm	time min	% nitromethane decomposed	mole HCN produced per 100 mole nitro- methane decomposed
0.714	—	35	9	8.5
1.22		35	9	11.0
8.2		35	13.6	19.2
0.935	12.2	35	12.4	20.4

In fig. 2 the percentage of nitromethane decomposed is plotted against time at various temperatures. The plot of log [a/(a - x)] against time shows the decomposition reaction to be of the first order.

From the plot of log k against the reciprocal value of the absolute temperature the following parameters were obtained for the Arrhenius equation  $k = A \exp(-E/RT)$  by the method of least squares :

 $\log A = 13.73 \pm 0.28$ ;  $E = 49.200 \pm 0.600$  kcal/mole.



FIG. 2,-Plot of the percentage of nitromethane decomposed against time.

#### ADDITION OF NITRIC OXIDE

Table 3 shows the effect of nitric oxide on the rate of decomposition of nitromethane. It is seen that the rate is not affected significantly by the addition of a small amount of nitric oxide, which is in agreement with the results obtained by Mueller in the highpressure range, and by Cottrell and collaborators at low nitromethane pressures.

Frejacques <sup>3</sup> who investigated the influence of nitric oxide on the decomposition rate of nitromethane in the pressure range from 4-40 mm observed a slightly inhibitory effect in the lower range and an increase in the rate of decomposition at pressures near 40 mm.

Table 3.—Effect of added nitric oxide on the decomposition rate of nitromethane, at  $330^\circ\mathrm{C}$ 

of nitromethane atm	nitric oxide mole %	duration min	% nitromethane decomposed	
41		10	5.4	
39	8.4	10	5.6	
40		10	5.1	
39		35	18.0	
41	9	35	17.4	
41		35	17.6	

#### **DECOMPOSITION OF NITROMETHANE**

We determined also the effect of added nitric oxide on the amount of hydrogen cyanide produced. From table 4 it can be seen that the quantity of hydrogen cyanide increases slightly and that the ratio of bound and free hydrogen cyanide changes. This might be due to the oxidation of part of the formaldehyde formed, by nitric oxide.

Table 4.—Effect of added nitric oxide on the amount of hydrogen cyanide produced, at  $330^{\circ}C$ 

initial pressure of nitromethane atm	nitric oxide mole %	duration min	hydrogen cyanide (bound) mole HCN/100 mole nitro- methane decomposed	hydrogen cyanide (free) mole HCN/100 mole nitro- methane decomposed
38.4	13	10	6.5	29.6
37		10	13.2	21.0

#### ADDITION OF NITROGEN DIOXIDE

Table 5 shows the influence of addition of nitrogen dioxide on the rate of decomposition of nitromethane. These values show a higher inhibitory effect than those already reported by Mueller,<sup>1</sup> and it seems reasonable to ascribe them to the depletion of methyl radicals by the reversal of step II (see below).

The alternative suggestion that inhibition could be due to the interaction of nitrogen dioxide with methane to yield nitromethane is untenable since this reaction has been shown to be considerably slower than step IX,<sup>16</sup> all the more, since the concentration of methane is very much smaller than that of nitromethane. Consequently, on the basis of these two steps alone, nitrogen dioxide would lead to catalysis rather than inhibition.

# Table 5.—Effect of added nitrogen dioxide on the decomposition rate of nitromethane, at $330^\circ$ C

initial pressure of nitromethane atm	nitrogen dioxide mole %	duration min	% nitromethane decomposed
35.5	10.5	10	3.6
38.1	9.8	35	10.4
24.8	36.0	10	3.1
26.5	37.5	35	8.7
41		10	5.6
39		35	18.0

#### ADDITION OF OXYGEN

Oxygen was reported to increase the rate of decomposition of nitromethane under low pressures.<sup>2</sup>, <sup>3</sup>, <sup>6</sup> Mueller, who investigated the effect of oxygen on the thermal decomposition of nitromethane under high pressures (12-17 atm), reported that oxygen does not increase the rate of decomposition of nitromethane, but reduces the amount of hydrogen cyanide among the reaction products.<sup>17</sup> From our experimental results it can be seen (table 6) that oxygen increases the rate of decomposition of nitromethane in addition to reducing the amount of hydrocyanic acid.

Table 6.—Effect of added oxygen on the decomposition rate of nitromethane, and on the amount of hydrogen cyanide present, at  $330^{\circ}C$ 

initial pressure of nitromethane atm	oxygen mole %	duration min	% nitromethane decomposed	mole HCN/100 mole nitromethane decomposed
38.3	8.5	35	23.2	—
42.5	18.5	35	25.8	
46.5	34.6	35	24.2	20
35		35	19.6	41

#### ADDITION OF DIACETYL PEROXIDE

The effect of methyl radicals on the decomposition of nitromethane under low pressures had been studied by addition of di-*tert*. butyl peroxide.<sup>6</sup> In our experiments addition of 25 mole % of diacetyl peroxide caused nitromethane to decompose even at 250°C; after 10 min, 4 % of the nitromethane had decomposed. Under similar conditions nitromethane alone does not decompose at all. FORMATION OF HYDROGEN CYANIDE FROM FORMALDOXIME

The amount of hydrogen cyanide produced by the decomposition of formaldoxime at 450 mm Hg and 922 mm Hg, at 330°C, was determined. After 35 min, the amount of hydrogen cyanide produced was 78 % and 83 % of the theoretical value, respectively.

## DISCUSSION

Taylor and Vesselovsky <sup>2</sup> proposed as initial step in the thermal decomposition of nitromethane

$$CH_3NO_2 \rightarrow CH_3NO + O.$$
 (I)

Cottrell, Graham and Reid determined experimentally an activation energy of 53.6 kcal for the decomposition reaction of nitromethane. They concluded that reaction (I) is unlikely on energetic grounds and suggested the following alternative reaction sequence:

$$CH_3NO_2 \rightarrow CH_3 + NO_2$$
 (II)

$$CH_3 + CH_3NO_2 \rightarrow CH_4 + CH_2NO_2$$
 (III)

$$CH_2NO_2 + NO_2 \rightarrow CH_2O + NO + NO_2$$
 (IV)

$$CH_2O + NO_2 \rightarrow CO + NO + H_2O$$
 (V)

$$CH_3 + CH_3 \rightarrow C_2H_6.$$
 (VI)

Mueller sees in the fact that large quantities of hydrogen cyanide are formed when nitromethane decomposes under high pressure, a strong argument in favour of reaction (I). He reasons as follows. It is known that nitrosomethane isomerizes readily into formaldoxime which decomposes into hydrogen cyanide and water.<sup>18</sup> There are two plausible ways in which nitrosomethane may be produced in this case :

$$CH_3NO_2 \rightarrow CH_3NO + O$$
 (I)

$$CH_3 + NO \rightarrow CH_3NO.$$
 (VII)

If (VII) were significant then addition of nitric oxide would have inhibited the decomposition reaction by slowing down reaction (III). As it was found that nitric oxide does not inhibit the reaction, one must conclude that nitrosomethane is produced by (I). Mueller believes, therefore, that the following reaction scheme represents more accurately the initial sequence in the decomposition of nitromethane :

$$CH_3NO_2 \rightarrow CH_3NO + O$$
 (I)

 $O + CH_3NO_2 \rightarrow products$  (VIII)

$$CH_3NO_2 \rightarrow CH_3 + NO_2$$
 (II)

$$CH_3 + CH_3NO_2 \rightarrow CH_4 + CH_2NO_2 \tag{III}$$

$$CH_3 + CH_3 \rightarrow C_2H_6. \tag{IV}$$

Further reactions taking place between the initial products lead to the formation of carbon dioxide, carbon monoxide, hydrogen cyanide, etc.

It seems to us that on the basis of the results presented in table 2 one can explain the production of large quantities of hydrogen cyanide in the high-pressure range without postulating reaction (I). One can assume that nitrosomethane is produced by reaction (VII). The efficiency of the reaction between methyl radicals and nitric oxide depends on the pressure inside the reaction vessel. The higher the pressure the higher will be the efficiency of this reaction owing to third-body effects.<sup>19</sup> The rise in the quantity of nitrosomethane produced under high pressure will also raise the quantity of hydrogen cyanide amongst the reaction products.

#### **DECOMPOSITION OF NITROMETHANE**

This mechanism is supported by the fact that the amount of hydrogen cyanide produced is raised even when the pressure inside the reaction vessel is increased by the addition of an inert material such as carbon dioxide, and further by the fact that nitrosomethane when decomposed even under low pressure gives almost the theoretical amount of hydrogen cyanide. That reaction (VII) occurs can be seen from the fact that by introducing nitric oxide into the reaction vessel the amount of hydrogen cyanide produced increases.

The contribution of reaction (III) to the rate of decomposition of nitromethane will be significant under low pressures or at the initial stages of the high-pressure decomposition reaction. Under these conditions the amount of nitric oxide is small and does not influence reaction (III) which proceeds as a very short chain.

When nitromethane decomposes under high pressure, reaction (VII) predominates and reaction (III) is suppressed, in parallel with the accumulation of the nitric oxide in the reaction vessel. This mechanism is supported by the fact that nitric oxide inhibits the decomposition of nitromethane if it is present in large quantity at the beginning of the decomposition reaction.<sup>1</sup> The contribution of the reaction (III) to the decomposition of nitromethane at the initial stage of the reaction, and the possibility of the reaction,

$$NO_2 + CH_3NO_2 \rightarrow products$$
, (IX)

might be the reason for the low activation energy obtained (49.2 kcal/mole) which is less  $^{20,21}$  than the bond dissociation energy  $D(CH_3-NO_2)$  of 57 kcal/mole.\*

Comparison of tables 2 and 3 shows that the "first-order" rate constant is slightly but definitely pressure-dependent. It appears that increase of pressure from 1-40 atm increases the rate constant by a little more than a factor of 2.

One may conclude that the same mechanism applies to the initial steps of the decomposition in the high- and low-pressure range. The only difference lies in the rate of the methyl + nitric oxide reaction which influences the amount of hydrocyanic acid present among the reaction products. An increase in rate is observed in the high-pressure range owing to third-body effects.

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\* It has been pointed out by a referee that this value is in some doubt. On the basis of recent thermochemical results  $^{22}$  it appears that the bond dissociation energy may be as low as 53 kcal.