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The Thermal Decomposition of Nitromethane at High Pressures

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The thermal decomposition of nitromethane was studied at 355° and in the pressure range from 180 to 300 p.s.i.a. Because of the presence of large quantities of hydrogen cyanide among the products of the reaction, the mechanisms proposed previously were re-examined. Evidence was obtained that the initial decomposition of nitromethane occurs in two ways: $CH_3NO_2 \rightarrow CH_3NO + O$ (1) and $CH_3NO_2 \rightarrow CH_3 + NO_2$ (2). Reaction (1) appears to predominate at high nitromethane pressures and reaction (2) at low nitromethane pressures. Relatively large quantities of nitric oxide inhibit the rate of disappearance of nitromethane, which is in agreement with a non-chain radical mechanism.

Introduction

The homogeneous thermal decomposition of nitromethane in the pressure range from 54 to 400 mm. has been studied by a number of workers.[1-4] The present investigation was undertaken to obtain information about the reaction at nitromethane pressures of 180 to 300 p.s.i.a. It is the purpose of this paper to discuss the following aspects of the high pressure reaction: (1) product distribution, (2) effect of nitric oxide, (3) effect of nitrogen dioxide, and (4) evidence for the initial step of the decomposition.

Experimental

Materials.—Nitromethane obtained from the Commercial Solvents Corporation was purified by steam distillation and stored. Before use it was distilled through an Oldershaw column. The fraction employed for the decomposition experiments had a constant boiling point of 100° at 750 mm. pressure. It was found to contain less than 0.03% water when tested with Karl Fischer reagent, and its infrared spectrum agreed with that published by Smith, Pan and Nielsen.[5]

Nitric oxide with a stated purity of 98% was obtained from the Mathieson Chemical Corporation. Only the portion volatile at −155° was used. No impurity could be detected in its mass spectrum or infrared spectrum.

Nitrogen dioxide (98% pure) and carbon dioxide (99.8% pure) were also obtained from the Mathieson Corp. and used without further purification.

Apparatus and Method.—The tests were carried out in sealed ampoules of approximately 3-ml. capacity, which were made of 12-mm. standard Pyrex tubing. The ampoules were immersed in a Blue-Temp heating bath whose temperature could be controlled to ±0.5°. A Chromel–Alumel thermocouple, previously calibrated at the melting point of tin (Bureau of Standards sample), was employed for the temperature measurements. The ampoule reached the temperature of the heating bath in less than 20 sec. after immersion; at the conclusion of a test, the ampoule was removed from the furnace, exposed to the air for 20 sec., and quenched in water at room temperature.

The test samples were prepared as follows: After an accurate determination of the volume of the ampoule, the ampoule was fitted with a stopcock and adapter. It was then evacuated to a pressure of approximately 10^{-5} mm. and weighed on an analytical balance. A quantity of nitromethane that had been thoroughly degassed was then introduced. After being reweighed, the ampoule was frozen in liquid nitrogen and sealed under vacuum. Assuming the validity of the ideal gas laws (all experiments were carried out above the critical point of nitromethane[6]), the initial pressure of nitromethane under the test conditions could be computed. In the case of an additive, a measured quantity of the added gas was passed into the ampoule after the nitromethane had been weighed in.

Analysis.—Separate decomposition tests were conducted for determining the product distribution and the extent of the decomposition.

The mixture containing products and undecomposed nitromethane was separated into three fractions by obtaining the volatile portions at −195, −50° and at room temperature. Each fraction was analyzed in a General Electric analytical mass spectrometer. The presence of formaldehyde was checked by a modified Schryver colorimetric method, described by Matsukawa.[7]

The extent of the decomposition was determined by a polarographic analysis of the nitromethane remaining at the conclusion of the test. The analysis was carried out in a Sargent Type III Polarograph, according to the method of De Vries and Ivett.[8]

Results and Discussion

Homogeneity.—The homogeneity of the reaction was investigated by determining the percentage nitromethane decomposed in packed and unpacked ampoules.[9] The results obtained with a fourfold increase in surface-to-volume ratio are presented in Table I. They indicate that not more than 2% of the reaction in the unpacked ampoules takes place on the surface.

TABLE I

EFFECT OF SURFACE-TO-VOLUME RATIO

Temperature 355°, duration 31 min.

Initial pressure of nitromethane, p.s.i.a.	Decomposed, %	Relative surface-to-volume ratio
274	32.1	4-fold increase
245	29.0	3.5-fold increase
250	26.0	No increase

Product Distribution.—The products obtained from the thermal decomposition of nitromethane at approximately 250 p.s.i.a. and at 355° after 2, 5, 15, 31 min., and 24 hr. are listed in Table II. The reliability of these analyses is considered to be good, since the ratio of C:N:O:H among the products is very close to that in nitromethane. The average ratio for three 5-min. runs is 1.0:1.0:2.2:2.9. Furthermore, the percentage nitromethane decomposed, as derived from a mass balance, agrees well with that computed from polarographic determinations (Table III).

The most significant result of the product analyses is the fact that in the early stages of the decomposition, hydrogen cyanide is the major carbon-containing compound. This has an im-

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[1] H. A. Taylor and V. V. Vesselovsky, *J. Phys. Chem.*, **39**, 1095 (1935).

[2] T. L. Cottrell, T. E. Graham and T. J. Reid, *Trans. Faraday Soc.*, **47**, 584 (1951).

[3] M. C. Fréjacques, *Compt. rend.*, **231**, 1061 (1950).

[4] L. J. Hillenbrand, Jr., and M. L. Kilpatrick, *J. Chem. Phys.*, **21**, 525 (1953).

[5] D. G. Smith, Chi-Yuan Pan and J. R. Nielsen, *ibid.*, **18**, 706 (1950).

[6] D. N. Griffin, THIS JOURNAL, **71**, 1423 (1949).

[7] D. Matsukawa, *J. Biochem.* (*Japan*), **30**, 385 (1939).

[8] T. De Vries and R. W. Ivett, *Ind. Eng. Chem.*, *Anal. Ed.*, **13**, 339 (1941).

[9] The surface area was increased by placing into the ampoule several polished glass rods whose surface area had been determined.

TABLE II

PRODUCT ANALYSES, MOLES PRODUCT PER MOLE NITROMETHANE DECOMPOSED

Temperature 355°

Pressure, p.s.i.a.	179	215	242	249	221	201	249	234
Time, min.	2	5	5	5	15	31	3.5 hr.	24 hr.
Product								
CO_2	0.08	0.19	0.19	0.20	0.20	0.27	0.30	0.34
CO	.17	.21	.17	.21	.18	.20	.22	.19
CH_4	.09	.10	.09	.10	.08	.07	.05	.06
HCN	.35	.36	.39	.40	.39	.37	.31	.22
CH_3CN	.05	.01	.01	.01	.03	.06	.07	.09
C_2H_5CN	.04	.03	.03	.01	trace	....	....	....
CH_2O[a]	.06	.04	.03	.04	.01	....	....	....
NO	.42	.53	.53	.54	.35	.28	.14	.02
N_2O	.02	....	.03	.04	.07	.05	.06	....
N_2	.04	.03	.03	.01	.06	.07	.16	.35
H_2O[b]	1.01	.94	1.00	.94	1.00	.90	.91	1.11

[a] Schryver's color test gave 0.07 mole after 5 min. [b] In some cases a deficiency of water was noted. Since the mass-spectrometer analysis of water is often uncertain, a correction was made based on the C:O:H ratio in the products.

TABLE III

PERCENTAGE DECOMPOSITION

Temperature, 355°, duration, 5 min., initial pressure of nitromethane, 215–244 p.s.i.a.

Run no.	Mass spectrometer analysis of products[a]	Run no.	Polarographic analysis of nitromethane
237	5.8	118	5.1
238	4.8	144	7.0
182	6.7	177	3.4
mean	5.8	198	5.4
		218	3.8
		mean	5.1

[a] Based on the average of total carbon and total nitrogen in the products.

portant bearing on the proposed mechanisms for the initial reaction sequence, and will be discussed in a later section. Hydrogen cyanide disappears only very slowly; after 24 hours, when virtually all nitromethane had reacted, 22% of the carbon remains in the form of hydrogen cyanide.

Nitric oxide is the major nitrogen-containing product, and its concentration decreases as the reaction proceeds. Although the ratio of $CO:CH_4:CO_2$ appears to vary somewhat for different percentages of decomposition, the ratios after 5% decomposition (5 min.) and after complete decomposition (24 hr.) seem to be representative for the early and late stages of the reaction. These ratios are 10:5:10 and 10:3:18, respectively.

These results will be compared with the product distribution in the low pressure thermal decomposition of nitromethane (50 to 400 mm.) in static systems.[10] Taylor and Vesselovsky[1] identified the following products after complete decomposition had occurred: nitric oxide, carbon monoxide, methane, carbon dioxide, nitrogen, water, small amounts of hydrogen and an unsaturated hydrocarbon. They also obtained evidence for the formation of formaldoxime, and in some cases found hydrogen cyanide.

Cottrell, Graham and Reid[2] report that the following products are formed during the decomposition: nitric oxide, nitrous oxide, carbon monoxide, methane, carbon dioxide, water, small amounts of ethylene and ethane, and a trace of nitrogen dioxide. Although the authors state that they noted occasionally the faint odor of hydrogen cyanide, they were unable to detect this compound.[11] They observed that nitric oxide is the major nitrogen-containing compound, and that its concentration decreases as the decomposition proceeds. This is in agreement with the behavior of nitric oxide at high nitromethane pressures. Cottrell and co-workers also found that the concentrations of carbon monoxide, methane and carbon dioxide remain constant after approximately 5% decomposition, and that the ratio of these products is 10:6.2:1.4.

During another investigation in this Laboratory,[12] one mass spectrometer analysis of the products from a low pressure nitromethane run, representing approximately 42% decomposition, was performed, and the results are listed in Table IV. The ratio of carbon monoxide to methane to carbon dioxide agrees closely with that observed by Cottrell, Graham and Reid, and in this case also nitric oxide is the major nitrogen-containing compound. However, in addition to the products identified by Cottrell and co-workers, hydrogen cyanide and nitrogen also were detected.

TABLE IV

PRODUCT ANALYSIS

Initial pressure of nitromethane, 158 mm.; temperature, 418°; duration 28 min.[a]

Product	Moles product/mole nitromethane decompd.	Product	Moles product/mole nitromethane decompd.
CO_2	0.07	CH_3CN	Some
CO	.51	NO	0.56
CH_4	.27	N_2O	.02
C_2H_6	.02	N_2	.10
HCN	.15	H_2O	.78

[a] Under these conditions 42% of the nitromethane had decomposed.

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(10) Préjacques (ref. 3) studied the thermal decomposition of nitromethane in the pressure range of 4 to 40 mm. Because of the extremely low pressures employed, it is believed that the results of his investigation are not directly comparable to those discussed.

(11) Since Cottrell and co-workers used only the products volatile at −78° for mass spectrometer analyses, hydrogen cyanide may have been missed.

(12) Unpublished.

Hillenbrand and Kilpatrick[4] studied the thermal decomposition of nitromethane in a flow system using an atmosphere of nitrogen as the carrier gas. The mole fraction of nitromethane was varied from 0.06 to 0.13. Comparing the products for 40% decomposition, the authors obtained a formaldehyde yield of 0.4 at 473° and of 0.2 at 420°. The yield of formaldehyde increases with decreasing percentage decomposition to 0.9 at 473° and to 0.5 at 420°. The methane yield was found to be 0.15, and it appears to be independent of the extent of decomposition and of temperature. It is believed that the conditions of the flow experiments may have been sufficiently different from the low pressure studies carried out by Cottrell, Graham and Reid, and in this Laboratory, to account for the variations in product distribution.

Although high initial pressures of nitromethane appear to favor greatly the formation of hydrogen cyanide, significant amounts of the compound seem also to be produced during the low pressure decomposition of nitromethane. A further effect of high initial pressures appears to be that more carbon dioxide, but less methane, is formed.

Addition of Nitric Oxide.—Table V shows the effect of nitric oxide on the rate of disappearance of nitromethane. It is seen that the rate is not affected by the addition of a small amount of nitric oxide, which is in agreement with the work at low nitromethane pressures.[2] Relatively large amounts of nitric oxide, however, appear to inhibit the decomposition at high nitromethane pressures. It is not known whether this also holds true in the low pressure region.

TABLE V

EFFECT OF NO ON THE RATE OF DECOMPOSITION

Temp., 355°; duration, 31 min.

Initial pressure of nitromethane	Mole %	Decomp., %	Initial pressure of nitromethane	Mole %	Decomp., %
180		26.5	181	11.3 NO	20.8
270		28.8	274	18.9 NO	14.4
289	0.9 NO	29.5	264	20.8 NO	18.4
273	1.0 NO	28.5	166	20.7 CO_2	28.1
188	12.0 NO	18.5	178	17.7 CO_2	28.5

In order to determine whether the inhibition by nitric oxide may be the result of an inert gas effect, an equivalent amount of carbon dioxide was also employed as an additive (Table V). Because carbon dioxide does not affect the rate, it may be concluded that the inhibitory action of nitric oxide at high nitromethane pressures is specific. It is difficult to assess the role of added nitric oxide as a radical chain inhibitor in the case of the thermal decomposition of nitromethane, since nitric oxide is an important decomposition product. In this connection it should be pointed out that during another investigation in this Laboratory,[13] it was observed that 43 mole % propylene does not affect significantly the rate of decomposition of nitromethane at approximately 70 mm. initial pressure. One explanation for the inhibitory action of nitric oxide in relatively large concentrations may be that the decomposition proceeds by very short chains, requiring a considerable quantity of nitric oxide for effective inhibition. This is in accord with the non-chain radical mechanism proposed by Cottrell, Graham and Reid, which will be discussed in a later section.

Addition of Nitrogen Dioxide.—Harnsberger[14] studied the reaction between methane and nitrogen dioxide, and found that it yields nitromethane. He also reports that the latter reacts further with nitrogen dioxide to form carbon dioxide and nitric oxide. On the basis of his experiments Harnsberger derives the following rate laws

$$\frac{-\mathrm{d}(\mathrm{NO_2})}{\mathrm{d}t} = 1.5k_\mathrm{a}(\mathrm{NO_2})(\mathrm{CH_4})$$

and

$$\frac{-\mathrm{d}(\mathrm{NO_2})}{\mathrm{d}t} = 2.5k_\mathrm{b}(\mathrm{NO_2})(\mathrm{CH_3NO_2})$$

where

$$k_\mathrm{b}/k_\mathrm{a} = 10$$

$$k_\mathrm{b} = 10^7 \exp(-21{,}000/RT)(\text{mole/liter})^{-1}\ \text{sec.}^{-1}$$

However, when 20 mole % nitrogen dioxide was added to nitromethane at 250 p.s.i.a. pressure (Table VI) its rate of disappearance remained unaffected in the early stages of the decomposition and, in the later stages, an inhibition was noted. This indicates that the reaction between nitromethane and nitrogen dioxide is not important under the conditions of the present investigation. It is not likely that the inhibition is caused by the interaction between methane and nitrogen dioxide to form nitromethane, because in addition to the difference in the rate constants of the two reactions, the concentration of methane is only about 0.005 times that of nitromethane. Because in the presence of added nitrogen dioxide a large quantity of nitric oxide is found among the products, this compound is probably responsible for the inhibitory effect.

TABLE VI

EFFECT OF NITROGEN DIOXIDE ON THE RATE OF DECOMPOSITION (TEMP., 355°)

Initial pressure of nitromethane, p.s.i.a.	NO_2, mole %	Duration, min.	Amt. decompd., %
ca. 230		5	5.1[a]
217	11.9	5	5.6
192	11.7	5	4.8
175		15	14.4
211		15	16.0
221	12.0	15	10.9
182	12.1	15	8.8
200		31	26.9[b]
192	11.1	31	20.5
230	12.1	31	19.2

[a] Mean of 5 runs. [b] Taken from a plot of per cent. decomp. *vs.* initial pressure of nitromethane.

Initial Step in the Thermal Decomposition of Nitromethane.—Taylor and Vesselovsky proposed that the initial step in the thermal decomposition of nitromethane occurs as

$$\mathrm{CH_3NO_2} \longrightarrow \mathrm{CH_3NO} + \mathrm{O} \qquad (1)$$

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(13) Unpublished.

(14) H. F. Harnsberger, Dissertation, University of California, 1951.

Cottrell, Graham and Reid suggested the reaction sequence

$$CH_3NO_2 \longrightarrow CH_3 + NO_2 \tag{2}$$

$$CH_3 + CH_3NO_2 \longrightarrow CH_4 + CH_2NO_2 \tag{3}$$

$$CH_2NO_2 + NO_2 \longrightarrow CH_2O + NO + NO_2 \tag{4}$$

$$CH_2O + NO_2 \longrightarrow CO + NO + H_2O, \text{ etc.} \tag{5}$$

$$CH_3 + CH_3 \longrightarrow C_2H_6 \tag{6}$$

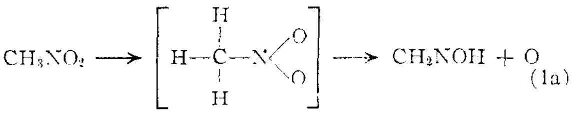
They assign an energy of more than 73 kcal. to reaction (1) and 53 kcal. to reaction (2). Since their experimentally determined activation energy is 53.6 kcal., they conclude that reaction (1) is unlikely on energetic grounds. The value of 52.3 kcal. for the heat of reaction (2) is probably correct, but it is by no means certain that the energy necessary for reaction (1) is as high as 73 kcal. Cottrell and co-workers arrive at this value by using published data for the heats of formation of nitromethane and atomic oxygen, and an estimated value of at least 2 kcal. for the heat of formation of nitrosomethane. In making this estimate they had to employ a number of assumptions, which may have caused an error of several kilogram calories in the value for the heat of reaction (1). It is believed, therefore, that this reaction should not be excluded solely on the basis of the energy considerations presented by Cottrell, Graham and Reid. Furthermore, the fact that large quantities of hydrogen cyanide are formed is a strong argument in favor of reaction (1). It is known that nitrosomethane isomerizes readily into formaldoxime,[15] which decomposes into hydrogen cyanide and water. The latter reaction is catalyzed appreciably by nitric oxide.[16] There are two plausible ways in which nitrosomethane or formaldoxime may be produced

$$CH_3NO_2 \longrightarrow CH_3NO + O \tag{1}$$

and

$$CH_3 + NO \longrightarrow CH_3NO \tag{7}$$

In both cases nitrosomethane would be formed first and, after isomerization into formaldoxime, the latter would decompose into hydrogen cyanide and water. Since nitric oxide is a major product in the thermal decomposition of nitromethane, the formation of hydrogen cyanide from formaldoxime should occur very rapidly. Reaction (1) may also take place as



$$CH_3NO_2 \longrightarrow \left[H{-}\underset{H}{\overset{H}{C}}{-}N{\lessgtr}^{O}_{O} \right] \longrightarrow CH_2NOH + O \tag{1a}$$

In this case formaldoxime would be formed directly, and it is difficult to say which path is actually followed. It should not be inferred, however, that such a reaction would necessarily be intramolecular. If the only reactions causing the decomposition of nitromethane are those suggested by Cottrell, *et al.*, and if no other reactions besides (1) and (7) are assumed to lead to hydrogen cyanide, the following reaction sequence would have to be written

$$CH_3NO_2 \longrightarrow CH_3 + NO_2 \tag{2}$$

$$CH_3 + CH_3NO_2 \longrightarrow CH_4 + CH_2NO_2 \tag{3}$$

$$CH_3 + NO \longrightarrow CH_3NO \longrightarrow HCN + H_2O \tag{7}$$

$$CH_3 + CH_3 \longrightarrow C_2H_6 \tag{6}$$

It was found that in the high pressure decomposition of nitromethane, 40% of the nitromethane leads to hydrogen cyanide and 10% to methane. If these values are substituted in the above reaction scheme, only 60% of the nitromethane that has disappeared can be accounted for. In the low pressure decomposition, 15% leads to hydrogen cyanide, 30% to methane, and 2% to ethane. If these values are substituted, only 79% of the nitromethane consumed is accounted for. In order to make up for the deficiency, one must assume either that nitromethane undergoes additional reactions or that the methyl radical participates in reactions other than the ones listed. There is no evidence that either of these possibilities occurs to any large extent.

It is believed, therefore, that the following reaction scheme represents more accurately the initial sequence in the decomposition of nitromethane

$$CH_3NO_2 \longrightarrow CH_3NO + O \tag{1}$$

$$O + CH_3NO_2 \longrightarrow \text{Products} \tag{9}$$

$$CH_3NO_2 \longrightarrow CH_3 + NO_2 \tag{2}$$

$$CH_3 + CH_3NO_2 \longrightarrow CH_4 + CH_2NO_2 \tag{3}$$

$$CH_3 + CH_3 \longrightarrow C_2H_6 \tag{6}$$

If the experimentally determined values for the concentrations of hydrogen cyanide, methane and ethane are substituted in this reaction scheme, it is found that all the nitromethane that has disappeared can be accounted for in the high pressure decomposition, and 94% in the low pressure decomposition.

On the basis of the evidence presented, it is believed that both reactions (1) and (2) occur over the pressure range studied, but that reaction (2) predominates at low nitromethane pressures, and that reaction (1) is the principal initial reaction at high pressures.

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(15) C. S. Coe and T. F. Doumani, THIS JOURNAL, **70**, 1516 (1948).

(16) H. A. Taylor and H. Bender, *J. Chem. Phys.*, **9**, 761 (1941).