ALIPHATIC NITRO COMPOUNDS

UNTIL recently only the higher nitrated paraffins were considered to have explosive properties or to be of use in explosive compositions. It was only quite recently that nitromethane was discovered to possess powerful explosive properties, although it requires a strong initiator. Among other nitro compounds tetranitromethane deserves special attention. Due to its high oxygen content it may be considered as an oxygen carrier.

NITROMETHANE

Nitromethane, CH_3NO_2, is a volatile liquid. It may be obtained by direct vapour phase nitration of paraffinic hydrocarbons either with nitric acid vapours (Hass et *al.* [l-8]) or with nitrogen dioxide (T. Urbanski and Slebodzinski [9]). It may also be prepared by the action of sodium- or potassium nitrite on chloroacetic acid (Kolbe [10]):

$$NaNO_2 + ClCH_2COOH \rightarrow NaCl + CH_3NO_2 + CO_2 \qquad (1)$$

or by reacting dimethyl- or methylsodium sulphate with sodium nitrite (Krause Elm:

$$2NaNO_2 + (CH_3)_2SO_4 \rightarrow 2CH_3NO_2 + Na_2SO_4 \qquad (2)$$

$$NaNO_2 + CH_3NaSO_4 \rightarrow CH_3NO_2 + Na_2SO_4 \qquad (2a)$$

A method consisting in reacting silver nitrite with methyl iodide or bromide is of value as a laboratory method only.

In 1951 Médard [12] found that nitromethane could be detonated by means of a strong initiator.

As a combustible with a rather high oxygen content nitromethane, alone or in various mixtures, has been gaining even increasing use as a rocket fuel. This great interest in nitromethane provided an incentive for the investigation of its physical and chemical properties.

PHYSICAL PROPERTIES

According to Toops [13], the boiling point of nitromethane at 760 mm is 101.2°C and the temperature coefficient of pressure dp/dt is 0.0427°/mm, its freezing point is -28.55°C and its density at 20° and 30° is 1.13816 g/cm^3 and 1.12439 g/cm^3 respectively.

The temperature coefficient of density dd/dt = 0.001377.

A number of authors have determined vapour pressures of nitromethane (Hodge [14]; W. M. Jones and Giauque [15]). More recent data are given by McCullogh, Scott *et al.* [16]:

Temperature, °C   55.71 61.30 72.56 83.92 95.41 101.19 112.83 124.56 136.40
Vapour pressure, mm Hg 149.4 187.6 289.1 433.6 634.0 760.0 1074.6 1486.1 2026.0

Vapour pressure can be expressed by the Antoine equation:

$$\log p = 7.274170 - 1441.610 / (t + 226.939) \qquad (3)$$

Cox [17] suggested another equation:

$$\log P = A (1 - 374.347 / T) \qquad (4)$$

Here $\log A = 0.845118 - 6.1497 \times 10^{-4}T + 6.0541 \times 10^{-7}T^2$, p is in mm Hg, P in atm, t in °C, T in °K.

McCullogh, Scott et al. [16] pointed out that Cox's equation also holds true beyond the usual experimental temperature range: 55 - 136°C.

Pitzer and Gwinn [18] and later McCullogh, Scott et al. [16] determined the heat of vaporization of nitromethane:

$$\text{at } 45.3°C \ \Delta H_v = 8883 \pm 1 \ \text{cal/mole}$$
$$\text{at } 101.4°C \ \Delta H_v = 8120 \pm 1 \ \text{cal/mole}$$

The following empirical equation has been given by McCullogh and his colleagues :

$$H_v = 11730 - 4.9977 T - 1.24 \times 10^{-2}T^2 \ \text{cal/mole} \qquad (5)$$

The heat capacity of the vapour is given approximately by eqn. (6):

$$C_p = C_p^0 - PT\left(\frac{d^2B}{dT^2}\right) + 2[P^2/R]\left[B\left(\frac{d^2B}{dT^2}\right)\right]\left[1 - 3\frac{BP}{RT}\right] \qquad (6)$$

C_p^0 is the heat capacity in the ideal gaseous state and B is the second virial coefficient. The last term in eqn. (6) is usually neglected, but for a highly polar molecule, such as that of nitromethane, it should be retained.

C_p^0 and B are given by the following equations:

$$C_p^0 = 2.352 + 4.288822 \times 10^{-2}T - 1.694 \times 10^{-5}T^2 \ \text{cal deg}^{-1} \text{ mole}^{-1} \qquad (7)$$

$$B = -300 - 12.97 \exp (1700/T) \ \text{cm}^3 \text{ mole}^{-1} \qquad (8)$$

McCullogh, Scott et al. also give the values of thermodynamic functions such as entropy, standard heat, standard free energy etc., at temperatures from 0° to 1500°K.

The heat of combustion of nitromethane at atmospheric pressure and 20°C is 169.4 kcal/mole, according to Kharasch [19].

The standard heat of formation of liquid nitromethane H_f^0 (liq.) is -27.03± 0.15 kcal/mole at 298.16°K.

The standard heat of formation in the gaseous state ΔH_f^0 (gas.) is -17.86 kcal/mole at 298.16°K (McCullogh, Scott et al. [16]).

The other physical constants are:

<div align="center">

Viscosity at 15°C 0.694 cP

at 30°C 0.595

(according to Tikmermans and Hennalt-Roland [20])

Surface tension at 15°C 37.74 dynes/cm

at 30°C 35.48

(according to Hennaut-Roland and Lek [21]).

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STABILITY

When stored in glass apparatus at a temperature slightly higher than room temperature (30°C) nitromethane was found to develop a partial vacuum (0.2 atm) (Bellinger, Friedmann, Bauer, Eastes, Bull [22]). This indicates an absorption of oxygen insufficient, however, to change the appearance or other physical properties of the substance. On long storage at 48.9°C or more, nitromethane undergoes slight decomposition with the evolution of traces of nitrogen dioxide.

The thermal stability of nitromethane can be improved by adding a small amount of boric acid. It reduces the tendency of nitromethane to decompose on distillation (Lippincott [23]). The addition of a small amount (0.2-1.0%) of phenolic anti-oxidants, such as hydroquinone, has also been suggested, i.e. substances having a critical oxidation potential as low as the air oxidation potential of α− naphthol (Senkus [24]).

IGNITION AND BURNING

Nitromethane can be ignited by an open flame. Corelli [25] reported, that the "flash point" in the Abel-Pensky apparatus is 35-37°C and the temperature of auto-ignition is 440°C (Constam and Schlaepfer's method).

The flash point (by Marcusson's method) is 42-43°C. Makovky and Lenji [26] report that nitromethane has a threshold explosion temperature of 312°C.

The problem of ignition is very important when nitromethane is to be used as rocket monofuel. Ignition of nitromethane with oxygen is not reliable (Bellinger, Friedmann, Bauer, Eastes, Goss [22]) and very often leads to ignition failure and explosion. The presence of oxygen makes nitromethane more sensitive to detonation.

There is very little danger that burning nitromethane will explode. The following test, described by Commercial Solvents Corporation [27], is rather significant from this point of view. A 55-gallon sealed drum filled with nitromethane, was enclosed in a concrete chamber in a mass of pine wood which was ignited quickly throughout by charges of smokeless powder. Although the temperature inside the chamber was higher than 700°C the heat merely caused the drum to burst, after which the contents burned quietly for about 30 min.

Since nitromethane should be considered as an oxidizing agent and since at elevated temperatures the oxidation processes can assume a rapid rate, it is recommended that nitromethane should not be heated in the presence of hydrocarbons or other combustible substances in a confined space. Thus explosion may occur during the heating of nitromethane-lubricating oil mixtures to high temperature under pressure.

The possible use of nitromethane as a liquid monofuel for rocket propulsion has aroused interest in the problem of its thermal decomposition.

Although this has come about only recently, the first experiments on the subject were carried out as long ago as 1935 by H. A. Taylor and Vesselovsky [28]. The experiments were related to the temperature range of 380-420°C and 200 mm pressure. The reaction was found to be of the first order, with an activation energy of 61.0 kcal/mole.

Subsequently, Frejacques [29] and Cottreh, Graham and Reid [30] continued the experiments within the ranges of 310-440°C and 380-430°C, under 4-40 mm and 200-400 mm pressures respectively. They confirmed the previous statement that the reaction is of the first order, with activation energies of 42.8 and 53.6 kcal/mole respectively. The reaction constant, *k,* may be calculated, according to Cottrell et *al.,* from the equation

$$\textbf{\textit{k}} = 10^{14.6} \exp \frac{-53,600}{TR} \sec^{-1} \tag{9}$$

Hillenbrand and Kilpatrick [31] investigated the same problem at 420-480°C. They confirmed the previous results and obtained a value of 50,000 for the activation energy.

Gray, Yoffe and Roselaar [32] examined the decomposition of nitromethane at 447°C.

Experiments by Müller [33] and Makovky and Günwald [34] on the decomposition of nitromethane under pressures of 12.2-20.2 and 40 atm and at temperatures of 355°C and 312-340°C respectively are particularly interesting. The reaction constant, according to these investigators, was

$$k = 5.4 \textbf{\textit{x}} 10^{13} \exp \frac{-49,200}{R_T} \sec^{-1} \tag{10}$$

T. Urbanski and Pawelec [351] found the activation energy to be 45.0 kcal/mole for the range 460-570°C.

The products of decomposition at low pressures were: NO, N_2O. H_2O, CO, CO_2, CH_4, small amounts of ethylene and ethane, and trace of NO_2 (Cottrell ef al. [30]). Nitrogen oxide was the principal nitrogen-containing compound.

Decomposition under pressure led to the formation of N_2, NO, H_2O, CO, CO_2, CH_4, HCN and small quantities of CH_3CN, C_2H_5CN, CH_2O, N_2O (Müller [33]).

The main difference between decomposition at high pressure and at low pressure is the presence of hydrogen cyanide as the principal carbon compound in the former case.

In addition to gaseous products, solid (ill-defined) compounds formed, particularly when decomposition took place at high pressure.

The presence of oxygen accelerated decomposition, whereas hydrogen slowed it down. Addition of small amounts of nitrogen oxide or nitrogen dioxide had no influence on the rate of decomposition under high pressure, although high concentrations of these-gases had an inhibiting effect.

With regard to the mechanism of decomposition, some authors (Taylor and Vesselovsky [28]) suggest N-O bond fission
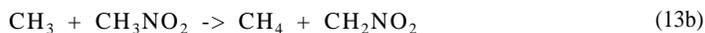
$$CH_3NO_2 \rightarrow CH_3NO + \mathbf{O} \tag{11}$$

while others (Frkjacques [29], Cottrell et al. [25], Gray et al. [32]) assume the rupture of C-N bond:

$$CH_3NO_2 \rightarrow CH_3 + NO_2 \tag{12}$$

More recently Müller, and also Makovky have reported both mechanisms taking place at elevated pressure.

Hillenbrand and Kilpatrick [31] suggested that the decomposition was partly due to intramolecular rearrangement. Makovky assumes that it proceeds by a radical chain mechanism with very short chains.

The following scheme has been suggested by Taylor and Vesselovsky [28] for the initial steps of the reaction at low pressure:

$$CH_3NO_2 \rightarrow CH_3 + NO_2 \tag{13a}$$

$$CH_3 + CH_3NO_2 \rightarrow CH_4 + CH_2NO_2 \tag{13b}$$

$$CH_2NO_2 + NO_2 \rightarrow CH_2O + NO + NO_2 \tag{13c}$$

$$CH_2O + NO_2 \rightarrow CO + NO + H_2O \tag{13d}$$

$$CH_3 + CH_3 \rightarrow C_2H_6 \tag{13e}$$

At high pressure the following radical reactions also take place:

$$CH_3NO_2 \rightarrow CH_3NO + O \tag{14a}$$

$$O + CH_3NO_2 \rightarrow CH_2O + HNO_2 \tag{14b}$$

$$CH_3 + CH_3NO_2 \rightarrow CH_4 + CH_2NO_2 \tag{14c}$$

It is possible that the presence of hydrocyanic acid in the product of decomposition at high pressure may be ascribed to the formation of CH_3NO:

$$CH_3NO + CH_2=NOH \rightarrow HCN + H_2O \tag{15}$$

(reaction described by Mitchell and Hinshelwood [36]).

Nitrosomethane is likely to be formed as a result of N-O fission or from the CH_3 radical :

$$CH_3 + NO \rightarrow CH_3NO \tag{16}$$

EXPLOSIVE PROPERTIES

Reliable evidence that nitromethane possesses properties characteristic of an explosive has been provided relatively recently. In particular two disastrous railway accidents which occurred in 1958 in the U.S.A. (one at Niagara Junction and the other at Mount Pulaski, Ill.) gave decisive proof that nitromethane should be considered as an explosive and classified as such when subjected to transportation. Both accidents occurred with nitromethane in tank cars. Since then nitromethane has been the only nitroparaffin which is not allowed to be shipped in tank cars but only in smaller containers, such as drums.

Bellinger, Friedmann, Bauer, Eastes and Bull [22] brought about the detonation of nitromethane confined in a heavy-walled container by the severe impact produced by firing 0.50 caliber ammunition at it. When a thin-walled container was substituted for the heavy-walled one, no detonation occurred. According to Cass [37], nitromethane subjected to an impact test exploded under the impact of a 2 kg weight falling from a height greater than 1.95 m. Nitroglycerine explodes under similar conditions when the dropping height is only 35 cm. According to Commercial Solvents Corporation [27], liquid nitromethane can detonate under a sudden impact of compressed air ca. 2000 lb/in^2. Apparently air compressed to 1200 lb/in^2 may be applied safely.

Nitromethane will detonate only when a very strong initiator is used. According to Makovky and Lenji [26], 10 g of hermetically sealed nitromethane can be detonated by 2.5 g of tetryl initiated in turn by 0.5 g of lead azide.

According to T. Urbanski and Pawelec [35], nitromethane could not be detonated completely by means of a No. 8 detonating cap alone or with addition of 1-8 g of tetryl, when nitromethane was confined in copper tubes of 13.6/14.8 mm and 23/25 mm diameter and 15 cm length.

The sensitivity of nitromethane to detonation increases with increase in temperature. The following figures (Table 122) were obtained by Kaplan, Johnston, Sill, and Peebles [38]. Nitromethane was confined in 3 in. stainless-steel tubing and explosion was initiated by No. 8 detonator.

The addition of certain compounds can render nitromethane more sensitive to detonation by a No. 8 cap, for instance strong bases and acids, such as aniline, ethylenediamine, methylamine, aqueous NH_3, KOH, Na_2CO_3, formic, nitric, sulphuric and phosphoric acids.

TABLE 122

°F	°C	Number of tests	Number of explosions
60-90	15.6-32.2	numerous	0
100-110	31.8-43.3	25	1
120-125	38.9-51.7	13	4
130-140	54.4-60	10	5
160-180	71.1-82.2	18	13

The data on the rate of detonation of nitromethane have been obtained only recently.

Médard [12] found the rate to be 6600±132 m/sec when in a glass tube 30 mm in diameter and 1.8 mm thick, or in an aluminium tube of the same diameter and 2.5 mm thick. A particularly strong initiator was used. Nachmani and Manheimer [39] reported lower figures (Table 123 and 124).

TABLE 123

NITROMETHANE CONFINED IN PAPER

Diameter mm	Detonation rate m/sec
44	6280
34	6260
29	6150
26.5	partial detonation
25	no detonation

TABLE 124

NITROMETHANE CONFINED

Tubes made of:	Internal diameter mm	Wall thickness mm	Detonation rate m/sec
iron	40	4	6320
	27	3	6300
	25	17	6280
brass	7	0.8	6060
polyvinyl chloride	7.5	1.0	no detonation
rubber	8	2	,,
	10	3	,,
polyester	8	7	,,

According to T. Urbanski and Pawelec [35], the rate of detonation of nitro-
methane can be expressed by the following figures (Table 125).

TABLE 125

Tubes made of:	Diameter mm	Initiation	Rate of detonation average values m/sec	Method
copper	18/20	No. 8 detonator and 1-5 g tetryl	6190	Dautriche
copper steel	23/25 22/27			
copper	18/20	No. 8 detonator and 6.2g tetryl	6405	Electric Chronograph

Van Dolah, Herickes, Ribovich and Damon [40] found values of 6275 and
6285 m/sec in steel and aluminium tubes respectively of 27 mm internal diameter.
The same authors confirmed that addition of small quantities of various substances
significantly affects the susceptibility to detonation of the resulting solution.

Bases (ethylenediamine, triethylamine, pyridine) were found to be strong sen-
sitizers. Acids (sulphuric acid, acetic acid) were found to be much weaker sensitiz-
ers. Dibutyl phthalate, benzene, cyclohexane were found to be weak desensitizers.

According to Médard [12], in the lead block test nitromethane gives figures
similar to picric acid. T. Urbanski and Pawelec [35] found 325-360 cm^3, averaging
345 cm^3, i.e. 110% of that of picric acid. The same authors determined the lead
block expansion when nitromethane was detonated by means of a No. 8 detonator
and 1 or 5 g of tetryl. The expansion given by tetryl was deducted from the
bulk expansion (Table 126).

TABLE 126

Charge			Expansion	
nitromethane 8 -	detonator No.	tetryl g	total c m^3	after deduction of tetryl expansion c m^3
10	8	1	445	420
-	8	1	25	
10	8	5	640	
-	8	5	145	495

Salts of nitromethane are extremely sensitive to flame and bum readily. They
are also sensitive to friction, impact and electric discharge. Mercuric salt can
be transformed into mercuric fulminate (Vol. III).