NITROMETHANE

PHYSICAL PROPERTIES, THERMODYNAMICS, KINETICS OF DECOMPOSITION, AND UTILIZATION AS FUEL

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CONTENTS

I. INTRODUCTION

The chemical properties, structure, and methods of preparation of nitromethane and other nitroparaffins have been reviewed many times in the last twenty years (2, 8, 12, 18, 19, 20, 21, 23, 24, 29, 34, 35, 36, 44, 51, 55, 59, 60, 61, 62, 65, 70, 75, 77). The present review is concerned only with certain aspects of the physical chemistry of nitromethane and its physical properties. The data gathered and discussed here are of special interest for the use of nitromethane as fuel for rockets.

II. PHYSICAL PROPERTIES OF NITROMETHANE

A. GENERAL PHYSICAL PROPERTIES

Table 1 summarizes the physical constants of nitromethane which are important when one considers its utilization as a fuel.

A good critical review of data concerning the vapor pressure, heat of vaporization, and vapor heat capacity of nitromethane is given in the literature (52).

TABLE 1
Physical properties of nitromethane

		Reference
Boiling point (760 mm.), °C.	101.20	(73)
Temperature coefficient of pressure (dt/dp), °C./mm.	0.0427	(73)
Freezing point, °C.	−28.55	(73)
Density, g./cc.:		
20°C.	1.13816	(73)
25°C.	1.13128	(73)
30°C.	1.12439	(73)
Temperature coefficient of density (dd/dt)	0.001377	(73)
Critical density, g./cc.	0.352 ± 0.004	(28)
Refractive index:		
20°C.	1.38188	(73)
25°C.	1.37964	(73)
30°C.	1.37738	(73)
Temperature coefficient of refractive index (dn/dt)	0.000450	(73)
Viscosity, centipoises:		
15°C.	0.694	(72)
25°C.	0.632	(41)
30°C.	0.595	(72)
Surface tension, dynes/cm.:		
15°C.	37.74	(37)
20°C.	36.97	(37)
30°C.	35.48	(37)
Temperature coefficient of surface tension (dγ/dt)	0.150	(37)
Total surface energy at 25°C., ergs cm.$^{-2}$.	77.11	(5)
Temperature of autoignition, °C. (method of Constam and Schlaepfer)	440	(13)
Flash point (Abel-Pensky method), °C.	35–37	(13)
Flash point (Tag open cup), °F.	112	(11)
Lower limit of flammability (per cent by volume in air)	7.3	(11)
Fire point (Marcusson method), °C.	42–43	(13)
Critical temperature, °C.	315 ± 1	(28)
Critical pressure, p.s.i.a.	915 ± 15	(28)
Cubical expansion coefficients, $\beta \times 10^3$ at 25°C.:		
$\left(\beta = \frac{1}{V_0} \cdot \frac{\mathrm{d}V}{\mathrm{d}t}\right)$	1.427	(43)
(The data have been fitted to the equation: $V_t = V_0 (1 + at + bt^2 + ct^3)$)		
$a \times 10^3$	1.29302	
$b \times 10^5$	0.69944	
$c \times 10^8$	1.32026	
Solubility at 20°C.:		(10)
Milliliters of nitromethane in 100 ml. of water	9.5	
Milliliters of water in 100 ml. of nitromethane	2.2	

The vapor pressure of nitromethane is accurately represented by both the Antoine equation (73),

$$\log_{10}p = 7.274170 - 1441.610/(t + 226.939) \tag{1}$$

and the Cox equation (16),

$$\log_{10}P = A(1 - 374.347/T) \tag{2}$$

where

$$\log_{10}A = 0.845118 - 6.1497 \times 10^{-4}T + 6.0541 \times 10^{-7}T^2$$

p is in millimeters, P in atmospheres, t in °C., and T in °K.

Although the Cox equation is more cumbersome to use for numerical calcula-

tions, it is more reliable in extrapolation beyond the temperature range in which most of the experiments were performed (55–136°C.) (52).

The results of the determination of the heat of vaporization of nitromethane (52) in the temperature range 318–374°K. can best be represented by the following empirical equation:

$$\Delta H_v = 11730 - 4.9977T - 1.2400 \times 10^{-2}T^2 \text{ cal. mole}^{-1} \qquad (3)$$

The vapor heat capacity can be represented with satisfactory approximation by:

$$C_p = C_p^{\circ} - PT(d^2B/dT^2) + 2[P^2/R][B(d^2B/dT^2)][1 - 3BP/RT] \quad (4)$$

The exact relationship is:

$$C_p = C_p^{\circ} - RT^2(d^2B/dT^2)/V + R[B - T(dB/dT)]^2/[V^2 + 2BV] \quad (5)$$

In these equations V is the molal volume of the vapor, B is the second virial coefficient, and C_p° is the heat capacity in the ideal gaseous state. The last term in equation 4 is usually neglected, but for the highly polar nitromethane molecule B is large, and the last term of equation 4 must be retained to represent accurately the vapor heat capacity data.

C_p° and B are given by the following equations:

$$C_p^{\circ} = 2.352 + 4.2882 \times 10^{-2}T - 1.694 \times 10^{-5}T^2 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$
$$B = -300 - 12.97 \exp(1700/T) \text{ cc. mole}^{-1}$$

### B. THERMODYNAMIC DATA AND SOME OTHER PROPERTIES

Values of the thermodynamic functions at selected temperatures from 0° to 1500°K. are presented in table 2 (52).

TABLE 2

The molal thermodynamic properties of nitromethane*

T	$-(F^{\circ} - H_0^{\circ})/T$	$(H^{\circ} - H_0^{\circ})/T$	$H^{\circ} - H_0^{\circ}$	S°	C_p°	ΔH_f°†	F_f°†	$\log_{10} K_f$†
°K.	cal. deg.⁻¹	cal. deg.⁻¹	kcal.	cal. deg.⁻¹	cal. deg.⁻¹	kcal.	kcal.	
0	0	0	0	0	0	−14.55	−14.55	+∞
273.16	54.49	10.07	2.751	64.56	12.95	−17.62	−2.90	2.32
298.16	55.39	10.34	3.083	65.73	13.70	−17.86	−1.66	1.22
300.00	55.45	10.36	3.108	65.81	13.76	−17.88	−1.56	1.14
400	58.59	11.60	4.640	70.19	16.80	−18.69	+4.02	−2.20
500	61.32	12.92	6.460	74.24	19.56	−19.32	9.77	−4.27
600	63.79	14.22	8.532	78.01	21.92	−20.11	15.73	−5.73
700	66.08	15.47	10.83	81.55	23.90	−20.11	21.56	−6.73
800	68.23	16.63	13.30	84.86	25.56	−20.33	27.51	−7.52
900	70.25	17.70	15.93	87.95	26.97	−20.45	33.51	−8.14
1000	72.16	18.69	18.69	90.85	28.17	−20.48	39.52	−8.64
1100	73.98	19.60	21.56	93.58	29.19	−20.46	45.52	−9.04
1200	75.73	20.44	24.53	96.17	30.07	−20.37	51.50	−9.38
1300	77.39	21.21	27.57	98.60	30.82	−20.26	57.49	−9.66
1400	78.99	21.92	30.69	100.91	31.48	−20.11	63.48	−9.91
1500	80.53	22.58	33.87	103.11	32.05	−19.94	69.43	−10.12

* To form an internally consistent set of values of the thermodynamic properties and to retain a higher accuracy of increments with temperature of a given property, the values in this table are given to more significant figures than are justified by their absolute accuracy.

† The standard heat, standard free energy, and common logarithm of the equilibrium constant for the formation of nitromethane by the reaction:

$$C(\text{graphite}) + \tfrac{3}{2}H_2(\text{gas}) + O_2(\text{gas}) + \tfrac{1}{2}N_2(\text{gas}) \rightarrow CH_3NO_2(\text{gas})$$
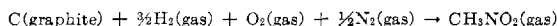
The standard heat of formation of liquid nitromethane from the elements, ΔH_f° (l), has recently been found to be -27.03 ± 0.15 kcal. mole^{-1} at 298.16°K. (52).

The standard heat of formation in the ideal gaseous state, ΔH_f° (gas), as computed from ΔH_f° (l) by addition of the standard heat of vaporization (9.171 kcal. mole^{-1}) is -17.86 kcal. mole^{-1} at 298.16°K.

The heat of combustion of nitromethane at atmospheric pressure and 20°C. is 169.4 kcal. mole^{-1} (42).

Among the properties which greatly determine the suitability of a fuel for use as a propellant are its stability, its corrosiveness, its sensitivity to shock, and its toxicity.

C. STABILITY

Nitromethane was found (3) to develop a partial vacuum (0.2 atm.) when stored in glass apparatus at 30°C. This result indicates absorption of oxygen, but it is not of sufficient magnitude to change the appearance or other physical properties. On long storage at 48.9°C. or more, nitromethane undergoes a slight decomposition with the evolution of traces of nitrogen dioxide. A small percentage of boric acid (45) in the distillation flask reduces the tendency of nitromethane to decompose during distillation. This tendency might be attributed to the elution of alkali from the glass of the distillation flask.

The thermal stability of nitromethane can be improved by mixing it with 0.2–1 per cent of hydroquinone or other phenolic antioxidants having a critical oxidation potential at least as low as the air oxidation potential of α-naphthol (64). Another way to improve the thermal stability is the incorporation of a small amount (0.01–1.5 per cent) of sulfuric acid, phosphoric acid, acidic salts of easily hydrolyzable amphoteric bases such as the aluminum salts of such acids, or easily hydrolyzable esters of such acids (63).

D. CORROSIVENESS

The rates of corrosion of nitromethane are low. Nitromethane attacks commonly used stainless steel and aluminum alloys at rates less than 0.0001 in. per year and mild steel at the rate of only about 0.0005 in. per year.

Most other common metals and alloys are attacked at rates too low to cause structural failure. Nitromethane was found to be relatively noncorrosive to the following materials (3): 464 stainless steel, 2S aluminum, W.D. 1010 cold rolled steel, the coating of the standard shipping drum (Ohio Kote No. 37), and phenol-formaldehyde coating. Plastics such as bakelite, chlorinated rubber, and polyethylene resist the attack of nitromethane very well.

The slight corrosive tendencies of nitromethane are enhanced in the presence of water because of the formation of the tautomer, which is weakly acidic. The corrosive action of nitromethane in the presence of water when stored in steel containers can be inhibited by the addition of small proportions of phosphoric acid or monobutyl phosphate.

It has been found that certain types of lead pigments in contact with nitro-

methane cause slow development of pressure in storage cans, whereas other lead pigments are entirely satisfactory. The lead compounds which do not react with nitromethane are white basic lead carbonate and basic lead sulfate, whilst compounds such as litharge and lead shavings react with nitromethane.

E. SENSITIVITY TO HEAT

The danger of the explosion of nitromethane from fire is negligible, as was demonstrated by the following test (11). A 55-gallon sealed drum was enclosed in a mass of highly combustible material (pine wood), which was ignited quickly throughout by a length of double-base military smokeless powder. Although the temperature was more than 700°C. inside the bombproof concrete chamber, the heat merely ruptured the heavy rim of the drum head, and the contents burned quietly for about 30 min.

Since nitromethane is a mild oxidizing agent, and since at elevated temperatures the oxidation processes may be accelerated, it is generally recommended that it should not be heated in the presence of hydrocarbons to elevated temperatures in a confined space. Tests made to determine the stability of nitromethane when heated in combination with lubricating oils in rocking bomb experiments indicate that an explosion may result during the cooling of nitromethane–hydrocarbon mixtures which had been heated under pressure to high temperatures.

F. SENSITIVITY TO SHOCK

Nitromethane is the only mononitroparaffin which can be detonated by severe impact. It is necessary to confine the nitromethane in a heavy-walled container in order to cause a detonation by shock. For example, 0.50 caliber ammunition fired into ordinary containers filled with nitromethane did not cause a detonation of the material (3). If heavy-walled containers are substituted for ordinary containers, 0.50 caliber gun fire can produce detonation. Shock and detonation tests of the well-known type were made with loads up to 2 kg. and a fall height of 1.95 m., but nitromethane remained stable up to these limits (9). Nitroglycerol under similar conditions explodes when the drop height is only 35 cm. As a matter of fact, it was found that in order to detonate 10 g. of nitromethane in a hermetically sealed bomb, it was necessary to use 2.5 g. of tetryl together with 0.5 g. of lead azide.

Liquid nitromethane can be detonated by a sudden impact of air under high pressure (∼2000 p.s.i.) (11). Pressures of 1200 p.s.i. can apparently be applied safely. It is not certain whether the initiation of the detonation is accomplished by the shock alone or by its combination with local overheating.

Nitromethane can be detonated by forcing it rapidly through empty pipes which terminate in a closed end or constricted fittings. Extreme force is necessary to cause detonation under such conditions.

The following compounds render nitromethane sensitive to detonation by a No. 8 blasting cap: aniline, ethylenediamine, morpholine, methylamine, ammonium hydroxide, potassium hydroxide, sodium carbonate, and acids such as formic, nitric, sulfuric, and phosphoric.

Compounds which inhibit the propagation of the explosion of nitromethane are higher nitroparaffins, benzene, xylene, n-butyl alcohol, methyl alcohol, n-butyl acetate, amyl acetate, di-n-butyl phthalate, and di-n-butyl sebacate.

G. TOXICITY

The maximum allowable vapor concentration of nitromethane is 100 p.p.m. by volume in air (11). It is suggested that precautions, such as supplying fresh air, be used when handling nitromethane. Because of the high heat of adsorption of nitromethane, respirators of the activated-carbon type should not be used. Hopcalite present in certain types of respirators for converting carbon monoxide to carbon dioxide is also known to affect nitromethane to such an extent that a fire may result. Nitromethane is not significantly absorbed by the skin.

H. VELOCITY OF DETONATION

The velocity of detonation of nitromethane has been measured for charges of varying radii and for various confining materials (53, 58). The influence of the initial temperature of nitromethane on its detonation velocity and sensitivity (as measured by the failure diameter) has also been studied (7).

Tables 3 and 4 (58) give, respectively, the velocity of detonation of unconfined nitromethane in tubes of impregnated paper and of nitromethane in containers of various materials.

TABLE 3

Detonation of unconfined nitromethane

Diameter	Detonation Velocity	Remarks
mm.	*m./sec.*	
44	6280	
34	6260	Mean of two measurements
29	6150	Mean of four measurements; spread of results = ±50 m./sec.
27		Detonation failed in tube with measuring probes; complete detonation with no probe
26.5		Partial detonation with no probes
25		Detonation failed; result of three measurements

TABLE 4

Detonation of nitromethane in containers of various materials

Material	Internal Diameter	Wall Thickness	Weight of Casing per Unit Length / Weight of Explosive per Unit Length	Detonation Velocity
	mm.	*mm.*		*m./sec.*
Iron...............	40	4	2.7	6320
	27	3	3.0	6300
	25	17	18.6	6280
Brass..............	7	0.8	3.4	6060
Aluminum..........	6.4	0.5	0.7	Detonation failed after first probe
	6.4	0.5	0.7	Complete detonation; no probe
Polyvinyl chloride..	7.5	1.0	0.7	
	6.5	2.5	1.9	
Natural rubber......	8	2	0.8	No detonation; no probes
	10	3	1.3	
Polyester...........	8	7	6.7	

The measurement of the velocity of detonation of nitromethane by the Dautriche method (53), using a glass tube 30 mm. in diameter and 1.8 mm. thick, or an aluminum tube of a similar diameter and 2.5 mm. thick, gave the value of 6600 ± 132 m./sec. This value is higher than the highest value found by Nachmani (58).

Measurement of the velocity of detonation of nitromethane in brass tubes for different initial temperatures (7) showed that nitromethane exhibits a temperature dependence of this velocity of −3.7 m./sec./°C. (figure 1). A study of the effect of temperature on the failure diameter of nitromethane in glass showed that the failure diameter increases by more than a factor of 2 as the initial temperature is lowered approximately by 60°C. (figure 2).
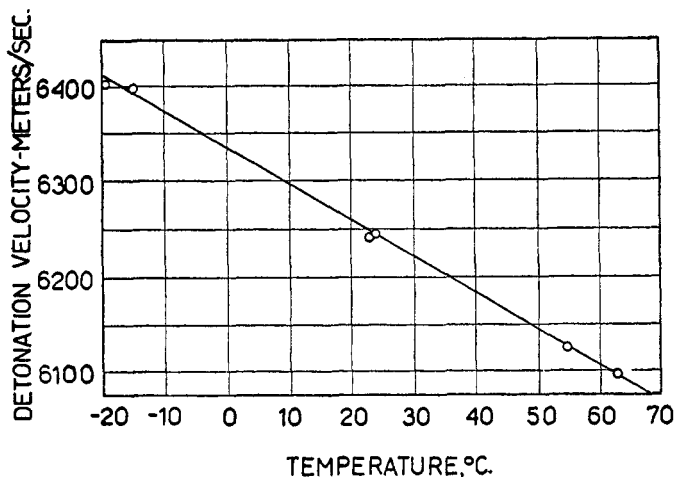

FIG. 1. Effect of temperature on the velocity of detonation of nitromethane in brass tubes (inside diameter, 1.75 in.; ⅛ in. wall).
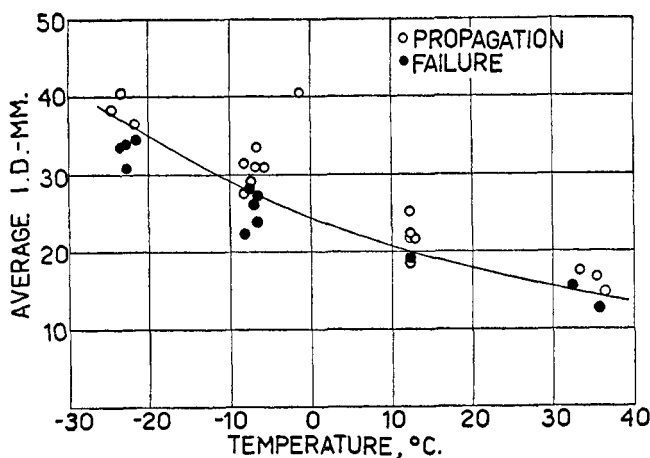

FIG. 2. Effect of temperature on the failure diameter of nitromethane confined in glass tubes.

III. The Decomposition of Nitromethane

A. THERMAL DECOMPOSITION

The kinetics of the thermal decomposition of nitromethane were investigated by static methods (15, 22, 49, 57, 69) and by flow methods (27, 38, 39), at various temperatures, and at low (4–400 mm.) (15, 22, 27, 38, 39, 69) and high pressures (12–20 atm.; 40 atm.) (49, 57). The reaction was found to be of first order in both cases (15, 22, 49, 69). At low pressures (4–400 mm.) there is a slight increase in the order with the temperature (22).

The influence of the addition of the following gases on the rate of decomposition at low pressures was investigated: helium, nitrogen, nitric oxide, carbon dioxide, oxygen, water (22, 69). Most of them were found to be ineffective; however, oxygen accelerates the decomposition (22, 69) and hydrogen (22) slows it down. Addition of nitric oxide or nitrogen dioxide did not have any influence on the rate of decomposition in the high-pressure range, except when present in high concentrations; then these gases had an inhibiting effect (49, 57). Oxygen when added to nitromethane decomposing under high pressure did not influence the velocity of reaction, but changed the distribution of the reaction products (56).

Free radicals produced by the decomposition of di-*tert*-butyl peroxide (27) and acetyl peroxide (49) lower the temperature of the decomposition of nitromethane.

There is a significant difference in the products of the decomposition reaction depending on the initial pressure.

At low pressures, from 200 to 400 mm., in the temperature range of 280–430°C. the following products were found during the decomposition reaction (15): nitric oxide, nitrous oxide, water, carbon monoxide, methane, carbon dioxide, small amounts of ethylene and ethane, and a trace of nitrogen dioxide. Although the faint odor of hydrogen cyanide was occasionally noted, this compound was not detectable. Nitric oxide was the major nitrogen-containing compound, and its concentration decreased as the decomposition proceeded. The ratio of carbon monoxide, methane, and carbon dioxide (10:6.2:1.4) remained constant after approximately 5 per cent of the nitromethane had decomposed.

At pressures of 12–20 atm. and a temperature of 355°C. the following major products of the decomposition reaction were identified (57): carbon dioxide, carbon monoxide, methane, hydrogen cyanide, nitric oxide, nitrogen, water, and minor amounts of methyl cyanide, ethyl cyanide, formaldehyde, and nitrous oxide. At 5 per cent decomposition the molar ratio of carbon monoxide: methane: carbon dioxide was 10:5:10; at complete decomposition it was 10:3:18.

Analysis of the decomposition products obtained at 40 atm. also indicated the presence of large quantities of hydrocyanic acid (49). An increasing amount of a solid product, not mentioned by authors who investigated the decomposition reaction at lower pressures, accumulated as the reaction proceeded at this pressure. The ratio of carbon monoxide: methane: carbon dioxide was found (49) to be:

| At 330°C.	At 340°C.
After 5% decomposition 10:10:23.5 After 30% decomposition 10:10:50	After 5% decomposition 10:9:25 After 30% decomposition 10:9:50 After 70% decomposition 10:8.5:62

The difference between the distribution of products at 40 atm. and that at 12–20 atm. is that at the former large quantities of the solid product are formed, and in the beginning of the reaction carbon dioxide is prevalent.

The most obvious difference between the decompositions at high pressures and at low pressures is the presence of hydrocyanic acid as a major carbon compound in the initial stages of decomposition in the first case.

For the first step of the decomposition of nitromethane at low pressures two mechanisms have been proposed. The rupture of the N→O bond (69),

$$CH_3NO_2 \rightarrow CH_3NO + O \tag{I}$$
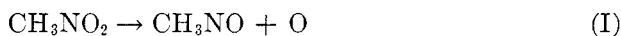
and the rupture of the C—N bond (15, 22, 27, 38, 39):

$$CH_3NO_2 \rightarrow CH_3\cdot + NO_2 \tag{II}$$
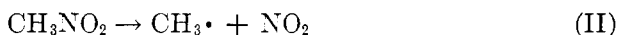
One study attributes a small part of the decomposition to intramolecular rearrangement (38, 39).

In view of the product distribution, mechanism I can hardly be applicable to low pressures, as it is in contradiction to the well-known fact that nitrosomethane decomposes to hydrocyanic acid and water according to the following equation (54):
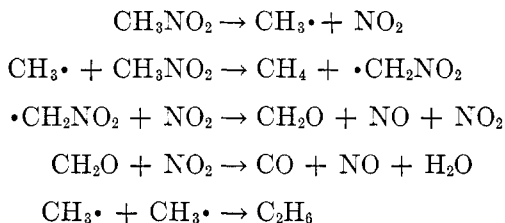
$$CH_3NO \rightarrow HCN + H_2O$$
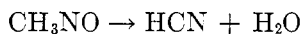
On the other hand, the existence of free radicals and nitrogen dioxide during the decomposition reaction has been demonstrated (27, 39), facts which support mechanism II. The values of the energy of activation found by the various investigators were in the range of 50–53 kcal./mole except in two cases in which figures of 41 and 61 kcal./mole were reported. The value of 41 kcal. may be attributed to the very low range of pressures (4–40 mm.) (22) in which the study has been conducted. At this pressure, the collisions may not suffice to maintain a first-order reaction, and a low activation energy and frequency factor would result. Surface effects may also cause the rate parameters to be low.

The energy of the C—N bond is 57 kcal., a value which is higher than most of the activation energies found. This seems to indicate that some radical mechanism also applies. The fact that nitric oxide, which is known to inhibit reactions proceeding by radical chain mechanisms, does not have any significant influence in this case seems to contradict this conclusion. However, one can assume that the decomposition proceeds by very short chains, so that only a considerable quantity of nitric oxide could be effective as an inhibitor (49, 57).

The following scheme has been suggested (15) for the initial steps of the de-

composition reaction at low pressure:

$$CH_3NO_2 \rightarrow CH_3\cdot + NO_2$$

$$CH_3\cdot + CH_3NO_2 \rightarrow CH_4 + \cdot CH_2NO_2$$

$$\cdot CH_2NO_2 + NO_2 \rightarrow CH_2O + NO + NO_2$$

$$CH_2O + NO_2 \rightarrow CO + NO + H_2O$$

$$CH_3\cdot + CH_3\cdot \rightarrow C_2H_6$$

Further reactions taking place between the initial products lead to the formation of water, carbon dioxide, carbon monoxide, nitrous oxide, etc. (15, 22, 38, 39).

A combination of mechanisms I and II has been proposed for the initial steps of the decomposition reaction at high pressures. The energy of activation obtained (49.2 kcal. (49)) is less than the bond dissociation energies $D(CH_3\!-\!NO_2)$ and $D(CH_3NO\!-\!O)$. This is attributed to the following radical reactions also taking place:

$$O + CH_3NO_2 \rightarrow CH_2O + HNO_2$$

$$CH_3\cdot + CH_3NO_2 \rightarrow CH_4 + \cdot CH_2NO_2$$
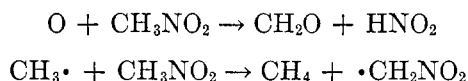
which lower the overall activation energy for the reaction.

Further reactions occurring between the initial products lead to the formation of water, carbon dioxide, carbon monoxide, nitrous oxide, etc. (49, 57).

Reaction I is supported by the large quantity of hydrocyanic acid formed at high pressure. This acid can be produced by the reaction (54):

$$CH_3NO \rightarrow CH_2\!\!=\!\!NOH \rightarrow HCN + H_2O$$

CH_3NO might be formed by either reaction I or reaction III:

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

$$CH_3\cdot + NO \rightarrow CH_3NO \qquad\qquad (III)$$

If reaction III were significant, addition of nitric oxide to nitromethane should inhibit the rate of disappearance of nitromethane by the reaction

$$CH_3\cdot + CH_3NO_2 \rightarrow CH_4 + \cdot CH_2NO_2$$
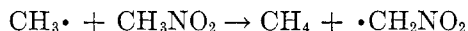
which is not the case. That methyl radicals react with nitromethane is proven by the observation that acetyl peroxide decomposes nitromethane even at 250°C. Under similar conditions, nitromethane by itself does not decompose (49). Hydrocyanic acid must then be formed mainly as a consequence of reaction I.

It seems therefore that there is a difference between the mechanism of the decomposition of nitromethane at high pressure and the mechanism at low pressure. At low pressure nitromethane decomposes by the following mechanism:
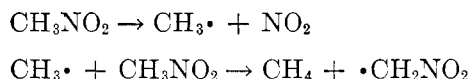
$$CH_3NO_2 \rightarrow CH_3\cdot + NO_2$$

$$CH_3\cdot + CH_3NO_2 \rightarrow CH_4 + \cdot CH_2NO_2$$

TABLE 5

Results obtained and mechanisms proposed by various investigators
for the thermal decomposition of nitromethane

Investigators	Year	Temperature Range	Initial Pressure of Nitromethane	Method	Mechanism	E	K
		°C.					
Taylor and Vesselovsky.........	1935	380–420	200 mm.	Static	N→O bond fission	61,000	
Cottrell, Graham, and Reid........	1950–51	380–430	200–400 mm.	Static	C—N bond fission	53,600	$10^{14.5}e^{-53,600/RT}$ sec.$^{-1}$
Fréjacques.........	1950	310–440	4–40 mm.	Static	C—N bond fission	42,800	$2.5 \times 10^{11}e^{-42,800/RT}$ sec.$^{-1*}$
Hillenbrand and Kilpatrick.......	1953	420–480		Flow	Partly intramolecular	50,000	$2.7 \times 10^{13}e^{-50,000/RT}$ sec.$^{-1}$
Gray, Yoffe, and Roselaar.........	1956	447	—	Flow	C—N bond fission	—	—
Mueller...........	1955	355	12.2–20.2 atm.	Static	N→O bond fission and partly C—N bond fission	—	—
Makovky and Gruenwald......	1957	312–340	40 atm.	Static	N→O bond fission and partly C—N bond fission	49,200	$5.4 \times 10^{12}e^{-49,200/RT}$ sec.$^{-1}$

* At 10 mm. initial pressure.

At higher pressures (12–40 atm.) the following reactions also contribute to the decomposition reaction:

$$CH_3NO_2 \rightarrow CH_3NO + O$$
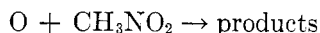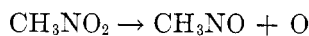
$$O + CH_3NO_2 \rightarrow products$$

Table 5 summarizes the mechanisms proposed by various investigators for the decomposition of nitromethane at different initial conditions.

B. INFLUENCE OF CATALYSTS ON THE THERMAL DECOMPOSITION OF NITROMETHANE

A study of the influence of various metallic oxides on the ignition temperature of nitromethane (50) showed that basic oxides catalyze the reaction, whereas acidic oxides do not. It seems that the aci-form of the nitromethane plays an important role in the mechanism of the catalytic ignition reaction, probably because of its reaction with the basic oxides.
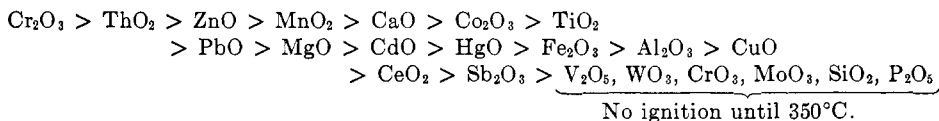
Table 6 gives the order of catalytic influence of the various oxides examined.

C. PHOTOLYSIS OF NITROMETHANE

The study of the photochemical decomposition of nitromethane (40) was carried out by the irradiation of nitromethane vapors with a mercury lamp, the wavelengths responsible for the decomposition lying between 2000 and 3000 A.

TABLE 6

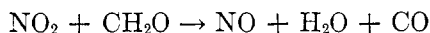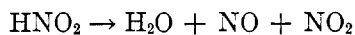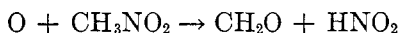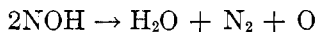*Order of catalytic influence of oxides on the thermal decomposition of nitromethane*

$Cr_2O_3 > ThO_2 > ZnO > MnO_2 > CaO > Co_2O_3 > TiO_2$
$> PbO > MgO > CdO > HgO > Fe_2O_3 > Al_2O_3 > CuO$
$> CeO_2 > Sb_2O_3 > \underbrace{V_2O_5, WO_3, CrO_3, MoO_3, SiO_2, P_2O_5}$
No ignition until 350°C.

After prolonged irradiation (58–62 hr.) two fractions [(a) at −180°C. and (b) at −80°C.] were separated, having the following compositions (volumes being given in milliliters at N.T.P.).

	Total volume	N_2	CO	NO	CO_2	Residue
		Experiment I (58 hr. irradiation)				
	ml.	*ml.*	*ml.*	*ml.*	*ml.*	*ml.*
Fraction a..................	28.1	14.9	5.7	7.5	—	—
Fraction b.................	6.7	—	—	3.3	2.2	2.2
Total.....................	34.8	14.9	5.7	10.8	2.2	2.2
		Experiment II (62 hr. irradiation)				
Fraction a.................	20.1	13.5	2.8	3.8	—	—
Fraction b.................	12.9	—	—	7.5	3.2	3.2
Total.....................	33.0	13.5	2.8	11.3	3.2	3.2

It was concluded that the primary reaction is

$$CH_3NO_2 \rightarrow CH_2O + NOH$$

which is followed by

$$2NOH \rightarrow H_2O + N_2 + O$$

$$O + CH_3NO_2 \rightarrow CH_2O + HNO_2$$

$$HNO_2 \rightarrow H_2O + NO + NO_2$$

$$NO_2 + CH_2O \rightarrow NO + H_2O + CO$$

A similar mechanism has been suggested previously for the photolysis of nitroso compounds (1) and nitrites (71).

Nitroso compounds   Nitro compounds
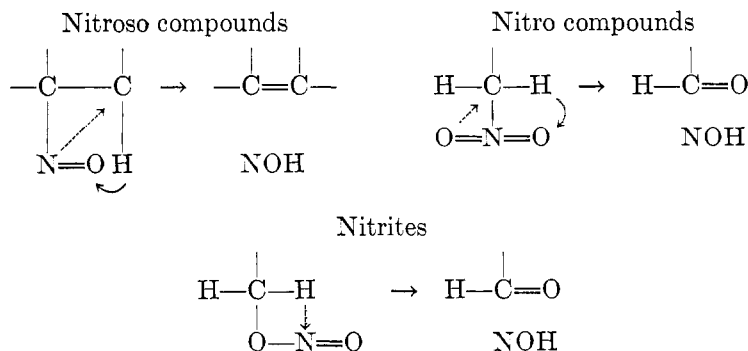
Nitrites

A more recent investigation (25) has shown, however, that nitrite photolysis proceeds by the same mechanism as nitrite pyrolysis, viz., via O—N bond fission, and that subsequent reactions of the radicals formed can account for all the products observed:

$$C_2H_5ONO + h\nu \rightarrow C_2H_5ONO^*$$

$$C_2H_5ONO^* \rightarrow C_2H_5O + NO$$
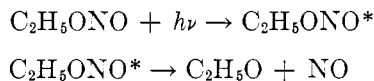
A similar explanation can be given for the photolysis of nitromethane, which is in agreement with the products observed (40):

$$CH_3NO_2 + h\nu \rightarrow CH_3\cdot + NO_2$$
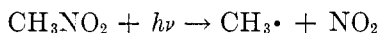
Here too, the initial reaction would be identical with the first step postulated for the thermal decomposition of nitromethane at low pressures (see page 636).

The subsequent reactions of the alkyl radicals with nitrogen dioxide (26) can account for the formation of the observed products, especially when one bears in mind that both the nitrogen dioxide and the aldehydes formed themselves undergo photochemical reactions during prolonged irradiation (40).

IV. Nitromethane as Fuel

A. THE UTILIZATION OF NITROMETHANE AS MONOPROPELLANT

The first suggestion to use nitromethane as a liquid monopropellant came from Crocco and Corelli (17).

Nitromethane can develop the type of pressure–time relationship required in rocket motors when used alone (48) or applied in combination with oxygen. Nitromethane is regarded as a very good propellant from the point of view of its physical properties and handling in the field; however, the following problems were found still to exist when one tried to develop a rocket motor based on nitromethane: (1) positive ignition of nitromethane; (2) explosion hazards (especially in the cooling ducts of regeneratively cooled motors); (3) the high chamber pressure needed to sustain combustion.

1. Ignition

It is possible to ignite nitromethane with or without gaseous oxygen. However, the methods of ignition that are carried out with an addition of oxygen are not reliable (4), almost 25 per cent of the experiments having led to ignition failure and explosion. Also, oxygen makes nitromethane more sensitive to detonation, and its injection simultaneously with that of nitromethane complicates the injection system. Nitromethane when used together with oxygen can be ignited with a spark plug (68) or by an igniter developed by the U. S. Army Chemical Warfare Service for use in flame throwers (4).

The ignition of nitromethane in the rocket combustion chamber can be accomplished without using oxygen by the following methods:

    (1) Starting the motor by the use of a solid propellant, e.g., cordite (48). When nitromethane is then allowed to enter the combustion chamber under the prevailing conditions of high pressure and high temperature,

it alone will be able to sustain combustion. The disadvantage of the cordite method is that the length of the cordite stick necessary is dependent upon the temperature of the surroundings and the motor used.

(2) Injection of a small amount of nitromethane into the combustion chamber and ignition by a black powder igniter (48). The high pressure and temperature thus created will then permit further nitromethane to burn alone. This method requires a careful regulation of the amount of nitromethane injected prior to ignition; otherwise the ignition would not be smooth and would degenerate into an explosion.

(3) It has been claimed that nitromethane alone is ignited by pumping it at 70–100 atm. into the combustion chamber in which magnesium oxide is electrically preheated (14).

(4) Nitromethane can be ignited by a simultaneous injection of a complex organometallic compound of the general formula RMeX, in which R is a methyl or ethyl radical, Me is aluminum or zinc, and X is at least one halogen from the group consisting of iodine or bromine (74). These compounds are apt to burn, with a very small delay, upon contact with the fuel, bringing the combustion chamber into temperature and pressure conditions necessary for the initial decomposition of nitromethane.

Methods 1, 2, and 3 do not require elaborate mechanisms for the injection, whilst method 4, which has the advantage of making re-ignition possible, requires special injection devices.

2. Explosion hazard

Nitromethane when not used with oxygen needs for stable operation motors of high characteristic length, L^* ($L^* = V_c/At$, where V_c = volume of combustion chamber and At = throat area). It seems that the occurrence of sporadic explosions in the regenerative cooling coils is related to the use of high L^* motors, which cause a large temperature rise of nitromethane in the coils.

When pure nitromethane is heated, it has a threshold explosion temperature of 312°C. Addition of a small amount (from a trace to 2 per cent by weight of the total fuel) of an alkyl or alicyclic chromate or dichromate, or an acetylacetonate of various metals, modifies the explosion characteristics of nitromethane (33). In general it has been found that chromium or uranium are the two most effective metals, but tungsten and molybdenum may also be used. When approximately 1 per cent by weight of the pyridine compound of uranyl acetylacetonate is added to nitromethane, the threshold explosion temperature is increased to 323.9°C., whilst 1 per cent by weight of dicyclohexylammonium chromate increases the explosion temperature to 366.5°C.

Under certain conditions nitromethane has the ability to propagate detonations. Since the speed of detonation is much greater than that of the flame, the detonation can travel upstream through the injector and pipelines to the storage tank and thus cause severe explosions. The danger of flashback can be reduced by the addition of ammonium nitrite or polychlorofluoromethanes (32) or by mechanical means. A tube of polyester resin reinforced with fiber glass (in order

to withstand the pressure of the injected fuel) acts as a safety valve, detonation being interrupted when it reaches the tube (48). The reason for this effect has been explained elsewhere (Section II,H).

Attempts have been made to reduce the explosion hazard in the cooling coils by reduction of the minimum L^* necessary for stable combustion; a 25 per cent reduction of L^* minimum (from 6 to 4.5 m.) was achieved by the addition of combustion catalysts like ferric or chromic acetylacetonates (48) to the nitromethane. This is, however, not sufficient to ensure safe regenerative cooling, so that ceramic lining of the motor should be adopted as a means for protecting the wall of the combustion chamber.

3. Lowering the working pressure

When nitromethane is used in a combustion chamber together with oxygen, stable operation is possible when the prevailing pressure is 20 atm.; without oxygen the necessary working pressure is around 30 atm. This is a disadvantage, because it raises the dead weight of the rocket by necessitating the use of heavier containers for the fuel, so that they will be able to withstand higher injection pressure. The problem can be solved by the addition of combustion catalysts, like ferric or chromic acetylacetonates, to the fuel. These catalysts ensure stable operation even at 20 atm. without the use of oxygen (48).

4. Performance characteristics

Table 7 summarizes the calculated performance characteristics of nitromethane and mixtures of nitromethane and gaseous oxygen as rocket propellants (68).

B. FUEL MIXTURES CONTAINING NITROMETHANE

Several fuel mixtures containing nitromethane as the main compound have been patented. One composition (30) contains roughly equal parts of nitromethane, tetranitromethane, and water. An emulsifying agent such as triethanolamine stearate is added. The water lowers the flame temperature and the rate of flame propagation. Another composition (32) consists of liquid nitroparaffins containing not more than one nitro group per carbon atom, tetranitromethane as oxidizer in no more than 10 per cent by weight of the fuel, and a flashback preventer such as polychlorofluoromethane or ammonium nitrite. A further com-

TABLE 7

Calculated performance characteristics of (a) nitromethane and (b) nitromethane + gaseous oxygen

Propellant	Chamber Pressure	Exhaust Velocity	Specific Impulse	Chamber Temperature	Mean Molecular Weight	Specific Heat Ratio
	p.s.i.	*f.p.s.*	*sec.*	*°F.*	*lb./mole*	
CH_3NO_2............................	300	7010	218	3950	20	1.25
CH_3NO_2 + 5 per cent oxygen....	270	7300	227	4500	21	1.23

position (31) contains 55.5 per cent nitromethane and 44.5 per cent tetranitromethane with p-phenylenediamine or sym-diethyldiphenylurea as stabilizers.

Nitromethane can be used in a mixture with nitroethane or nitropropane (48). The addition of the higher nitroparaffins lowers the combustion temperature, but the specific impulse does not change much, because of the simultaneous reduction of the mean molecular weight of the combustion products. Addition of about 2 per cent of chromic or ferric acetylacetonate makes possible an addition of as much as 50 per cent of nitroethane to nitromethane. Addition of the higher nitroparaffins also lowers the sensitivity of nitromethane to detonation.

A method for preparing a gel of nitromethane by blending it with 10–50 per cent of nitrocellulose has been described (46). Ignition of the gel is made easier by the use of a small amount (up to 3 per cent by weight) of chromic acetylacetonate. These gels can be used either as rocket fuels or as explosives. In the latter case a sensitizer in form of an organic amine has to be added.

Nitromethane as a fuel for piston engines increases the output of the engine by 20 per cent (66). For a small reciprocating two-cylinder engine, 20 per cent nitromethane in methyl alcohol is the best blend. Above that concentration knocking occurs. Mixed with castor oil (25 per cent), methyl alcohol (37 per cent), and (1 to 2 per cent of) 2,2-dinitropropane as additive, nitromethane has been proposed as fuel for model engines (6).

The use of nitromethane as fuel in average cars is not practical because of its price and its tendency to cause knocking.

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