Physical and Chemical Properties of Hexanitroethane

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Recent developments in the synthesis of hexanitroethane (HNE) have renewed interest in its use as a possible high energy oxidizer. The chemical reactivity and the physical properties of hexanitroethane have been extensively studied and are presented in this report. Hexanitroethane is a solid, high energy oxidant, melting at about 150°C and containing 92% NO_2, by weight. It has a crystalline density of 2.25 g/cm^3 and a vapor pressure of 0.5 mm Hg at 25°C. The heat of formation of hexanitroethane was determined to be +28 kcal/mole.

THE synthesis of hexanitroethane (HNE) was first reported by Will (1)[6] in 1914 but has received little attention until recently. It is synthesized in poor yield by coupling bromopicrin with base and potassium nitrite giving dipotassium tetranitroethane, which is nitrated to HNE with white fuming nitric acid and concentrated sulfuric acid. Recently new synthetic developments have made HNE available in pilot-plant quantities,[7] more economically attractive, and have renewed interest in HNE as a possible solid oxidizer.

Physical Properties of Hexanitroethane

Hexanitroethane is a colorless crystalline solid melting with decomposition at approximately 150°C, depending upon method and rate of heating, and contains 92% NO_2 by weight. It has a theoretical crystalline density of 2.25 g/cm^3 and has been compressed into pellets giving a density of 1.88 g/cm^3. Hexanitroethane has a low vapor pressure and is not impact-sensitive. The principal physical properties are summarized in Table 1.

Preliminary kinetic studies of the thermal decomposition of hexanitroethane show that the decomposition is apparently first order. At 60°C, the rate is too slow for convenient measurement, but at 70°C, the half-life is about 400 hr. Vapor phase fractometry indicates that the products are nitrous oxide, nitric oxide, carbon dioxide, and nitrogen dioxide. This study is still in progress, and complete results will be published separately.

Crystal Structure and Density

Crystals of hexanitroethane appear to be optically isotropic under polarized light and, therefore, belong to the isometric system. Investigation of the crystals at room temperature in an x-ray diffraction spectrometer with a copper-nickel target system yields the diffraction data in Table 2. Analysis of these data shows that the crystal structure is probably a body-centered cubic lattice. The density of the crystal calculated from the three strongest lines and assuming four molecules in the unit cell is 2.25 g/cm^3, which is consistent with a value of 1.88 g/cm^3 obtained by compression into pellets at 2000 psi.

Vapor Pressures

The experimental values for the vapor pressure of HNE from 20° to 70°C are given in Table 3; the data are represented by the equation

$$\log_{10} P(\text{mm Hg}) = 5.0244 - (1590/T°\text{K}) \qquad [1]$$

In the lower temperature range, this equation is precise only to ±15% because of the difficulty in measuring the low pressures. At 70°C, the thermal decomposition becomes appreciable and, therefore, vapor pressures above this temperature have no real significance; Eq. [1], of course, is not applicable. The computed heat of sublimation for HNE, making the usual Clausius-Clapeyron assumptions, is 7.2 kcal/mole.

The hexanitroethane used for the vapor pressure measurements was purified by triple vacuum sublimation of crystals obtained from methylene chloride.

The vapor pressures were measured using a modified glass isoteniscope with mercury as a manometer fluid (Fig. 1). It had been found that hexanitroethane reacted slowly with mercury at room temperature to form an extremely thin protective surface. This film offered sufficient protection against further reaction; however, extreme care was taken to prevent breaking of the film during the measurements. Halocarbon high-temperature stopcock grease[8] was used for both the sample holder spherical joint and the connecting stopcock. To insure against leakage, the stopcock and spherical joint were held with spring clamps. Prior to a run, the isoteniscope U-tube was partially filled with mercury, and the empty sample holder was positioned. With the connecting stopcock opened, the isoteniscope was pumped out to remove occluded gas from the mercury. The isoteniscope was then equilibrated with the atmosphere, and the sample was introduced in the holder. After reassembling, the apparatus was allowed to stand for 30 min. During this period the exposed mercury surface was sufficiently deactivated for pressure measurements.

The entire isoteniscope was then immersed in a magnetically stirred water bath, and the system was pumped down to 1 μ on a vacuum line with the connecting stopcock open. After reaching 1 μ, the connecting stopcock was closed and remained so for the entire run. A period of 1 hr was found sufficient to achieve thermal equilibrium. Vapor pressures were obtained by reading, through a telescope, the mercury level differences against a scale clamped to the U-tube.

Thermochemical Data

Young (2) has derived the following empirical equation for estimating the value of the heat of combustion of nitroparaffins:

$$-\Delta H_c = 50.3s \qquad [2]$$

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[6] Numbers in parentheses indicate References at end of paper.

[7] American Cyanamid Company, Bound Brook. N. J.

[8] Halocarbon Products Corporation, Hackensack, N. J.

Table 1 Properties of hexanitroethane[a]

Melting point	150°C (decomposition)
Density, crystalline	2.25 g/cm^3
Compressed, 2000 psi	1.88 g/cm^3
Crystal structure	Body-centered cubic, free flowing crystals at 5°C, waxy at ambient temperatures
Impact sensitivity	77 cm (2 kg wt)
Shock sensitivity	Initiated by no. 8 detonator (can be inhibited by additive)
Vapor pressure	$\log P$(mm Hg) = 5.0244 − (1590/T°K) 20.7°C, 0.4 mm 29.8°C, 0.6 mm
Heat of formation	+28.0 kcal/mole
Heat of sublimation	7.2 kcal/mole
Rate of decomposition	First order 70°C, 400-hr half-life
Toxicity (5), inhalation	Very toxic
Skin	Nontoxic
Ingestion	Slightly toxic

[a] Data obtained by Materials Sciences Laboratory, Lockheed Missiles and Space Company, except where noted.

where s is the number of oxygen atoms necessary for complete combustion. For HNE, $s = 4$ and ΔH_c is 201.2 kcal/mole. The heat of formation is then estimated:

$$\Delta H_f = 201.2 - 2(94.4) = +12.4 \text{ kcal/mole} \qquad [3]$$

Roth and Isecke (3) give +8.8 kcal/mole for the standard heat of formation of tetranitromethane. Using this as a reference, the heat of formation of HNE can be estimated by bond energy considerations. The replacement of hydrogen by an NO_2 group is calculated as 8.97 kcal. Combining this value with the heat of formation of ethane and the heat of sublimation of HNE determined experimentally, the heat of formation of HNE is estimated as +26.4 kcal/mole.

The heat of combustion of hexanitroethane was determined experimentally by combustion in a Parr calorimeter under 45 atm of oxygen. To insure complete combustion, the HNE was mixed with benzoic acid and pressed into a pellet at 20,000 psi prior to combustion. The heat of combustion of HNE was obtained by subtracting the heat due to the combustion of the benzoic acid from the total heat liberated. Mass spectrometric analysis of the gaseous products showed principally carbon dioxide and nitrogen. The small amount of dissolved nitric acid was titrated and the heat of combustion corrected in the usual manner. Table 4 summarizes the values obtained for five runs and gives an average value for the heat of formation of +28.6 kcal/mole.

Chemical Reactivity of Hexanitroethane

Hexanitroethane is a strong oxidizing agent and, as such, will react with most organic materials. Will (1) reports that hexanitroethane oxidizes hydroquinone to quinone more rapidly than tetranitromethane. The reactions of hexanitroethane with aromatic compounds has also been studied by Allsop and Kenner (4). They report the replacement of activated hydrogen by a nitro group in most cases.

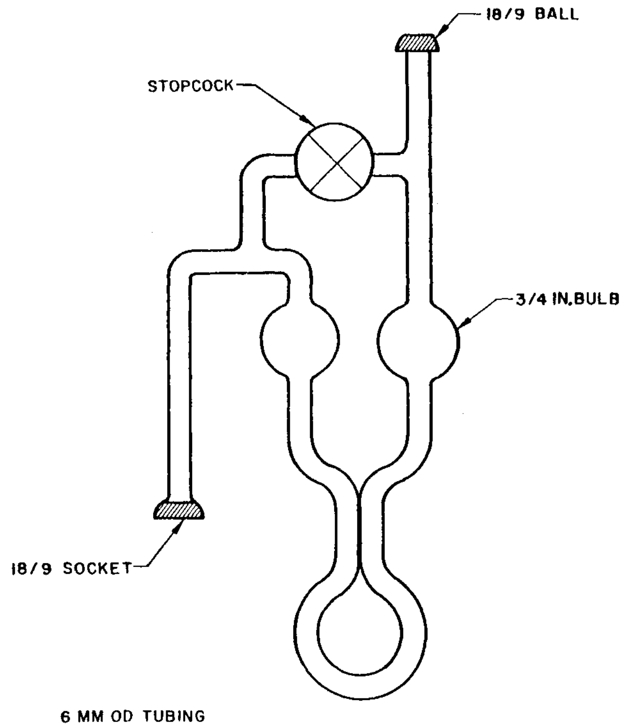

Fig. 1 Isoteniscope

Addition compounds with aromatic compounds are also formed and are presumed to be molecular complexes similar to those formed by tetranitromethane. Most of the complexes are not stable, but their color may be used for identification. In fact, an analytical method was developed in connection with the toxicity studies (5), based upon the spectrophotometric determination of the acenaphthene complex.

Hexanitroethane reacts with olefinic compounds forming unidentified nitro compounds and other highly oxidized fragments. It reacts rapidly with vinyl ethers and 1,4-dimethylbutadiene but only slowly with allyl acetate and maleic anhydride. Hexanitroethane is hypergolic with UDMH and other strongly basic amines.

A study of the reactivity of hexanitroethane with compounds containing different functional groups reveals that hexanitroethane reacts with almost all classes, although at widely different rates. Exceptions seem to be the straight chain hydrocarbons, which contain few tertiary hydrogen atoms, and highly halogenated materials, such as Teflon. Table 5 summarizes the qualitative results of the compatibility studies at 50°C.

Toxicity of Hexanitroethane

The toxicological properties of hexanitroethane have been extensively studied (5). The evaluation was carried out by a series of repeated vapor exposures at three concentration

Table 2 X-ray diffraction assignments for hexanitroethane

2θ, deg	Relative intensity	Assignment	d, Å	$h^2 + k^2 + l^2$	l_0, Å	$V = a_0^3$	$\rho = \frac{300.07 \times 4}{V}$
15.48	Very strong	110	5.7192	2	8.0881	529.10	2.27
22.2	Weak	200	4.0008	4	8.00		
26.89	Strong	211	3.3127	6	8.1158	534.56	2.25
31.10	Medium	220	2.8732	8	8.1266	536.69	2.24
34.7	Medium	310	2.583	10	8.168	544.94	2.20
41.5	Very weak	222	...	...	...	...	...
44.5	Very weak	321	...	...	...	...	...
47.5	Very weak	400	...	...	...	...	...

Table 3 Vapor pressure of hexanitroethane

T, °C	Pressure, mm Hg		Deviation
	Observed	Calculated[a]	
20.7	0.40	0.42	+0.02
36.1	0.80	0.77	−0.03
48.0	1.15	1.20	+0.05
62.0	2.00	1.94	−0.06
70.2	2.50	2.50	0.00
50.0	1.50	1.39	−0.11
29.8	0.60	0.60	0.00
44.3	1.00	0.96	−0.04
55.0	1.50	1.50	0.00
22.8	0.40	0.45	+0.05
40.6	0.80	0.90	+0.10
30.6	0.80	0.62	−0.18
45.5	1.20	1.05	−0.15

[a] Calculated from Eq. [1].

Table 4 Heat of formation of hexanitroethane

HNE, g	Benzoic acid, g	Ratio of HNE/benzoic	ΔH_c, kcal/mole	ΔH_f, kcal/mole
0.9403	0.3564	2.64	−215.4	+27.3
1.5302	0.4919	3.11	−217.0	+28.9
1.0578	0.8513	1.24	−221.2	+33.1
1.2579	0.5152	2.44	−214.4	+26.3
1.9446	0.2166	8.96	−215.4	+27.3
			−216.7 (avg)	+28.6 ± 1.9 (avg)

levels to four species of animals. High toxicity at repeated exposure to 3.0 ppm was reported. However, adequate ventilation during handling and the low vapor pressure of hexanitroethane essentially minimize the toxicity problem in actual usage.

Discussion

Higher energy oxidizers all have problems associated with their practical use in propellants (6). Their very chemical constitution predicts most problem areas. Those oxidizers in which the difficulties can be most easily minimized will eventually make significant contributions to advance the state of the art.

Some of the advantages of hexanitroethane as an oxidizer are 1) high oxygen content, 2) low vapor pressure and high melting point, 3) high density, 4) low impact sensitivity, 5) nonhygroscopicity, and 6) potential availability at low cost. The disadvantages that accompany the use of hexanitroethane as an oxidizer are 1) high chemical reactivity, and 2) marginal thermal stability at temperatures near 70°C.

Although the thermal stability is the problem of most concern, the overall properties of hexanitroethane compare favorably with any of the high energy solid oxidizers currently under consideration. All have their own specific disadvantages. Perhaps the proper formulation of hexanitroethane with as yet unknown binders will lead to its acceptance for special applications. A kinetic study of the thermal decomposition of hexanitroethane is currently underway. An understanding of the mechanism of this decomposition, including catalytic and inhibiting effects, may help to improve the stability problem.

Table 5 Reaction of HNE with functional groups at 50°C

Functional group[a]	Time, hr	Results
Hydrocarbons		
Nujol	0.25	NO_2 gas
Heavy white 0:1	0.5	NO_2 gas
Micro wax	2	Dark yellow
Para wax	1	Light yellow, NO_2 at 4 hr
Hexadecane	68	White solution, no reaction
Eicosane	20	White, no reaction
Polybutene-8[b]	4	Dark yellow
Polyethylene[c]	60	No reaction
Polyisobutylene[d]	20	No reaction; no reaction at 10 hr[e]
Alcohols		
Ethanol	68	Very pale yellow; light straw at 1 hr[e]
i-propanol	68	Very pale yellow
1,4-butanediol	100	Light yellow
1,3,6-hexanetriol	68	Light yellow
Polyethyleneglycol[f]	6	Light yellow; NO_2 in 1 hr[e]
Polypropyleneglycol	16	Light to dark yellow
Esters		
Ethyl acetate	2	Yellow-brown, NO_2 at 3 hr
Ethyl methylcarbamate	4	Light yellow, explodes violently at 6 hr[e]
Ethyl nitrate	4	White solution, slight NO_2 at 48 hr
Tricresyl phosphate	0.5	NO_2 gas
Isocyanates		
Toluene diisocyanate	3	Dark brown
Hexamethylene diisocyanate	3	Brown precipitate
Ethers		
Diethyl	8	Yellow
Amides		
Dimethylformamide	0.1	Brown
Acetamide	16	Slightly yellow
Polymers		
PBAA[g]	8	Yellow, foam
Butarez[h]	8	Yellow, foam
Estane[i]	8	Yellow, foam
Miscellaneous		
Al powder	8	No reaction[e]

[a] Concentration: 20% to 25% HNE in compound, except where noted.[e]

[b] Oronite Chemical Company.

[c] E. I. du Pont de Nemours & Company.

[d] Vistanex, Enjay Chemical Company.

[e] Concentration: 0.1-g compound + 0.5 g HNE.

[f] Carbowax 4000, Carbide and Carbon Chemicals Company.

[g] Polybutadiene-acrylic acid copolymer.

[h] Polybutadiene, Butarez 15, Phillips Petroleum Company.

[i] Polyurethane, B. F. Goodrich Chemical Company.

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