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DEKAZENE

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A HIGH ENERGY FUEL CANDIDATE
FOR
LIQUID BN SYSTEMS (C)

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REPORT NO. 25

DEKAZENE

A High Energy Fuel Candidate for Liquid BN Systems (C)

by

M. FREDERICK HAWTHORNE

and

ANTHONY R. PITOCELLI

Approved:

Ben F. Aycock

Ben F. Aycock
Head, Synthetic Chemistry Section

Allen R. Deschere

Allen R. Deschere
General Manager

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ABSTRACT

Dekazene was shown to be a member of the $B_{10}H_{12}X_2$ class of decaborane derivatives ($X = NH_2$) and therefore of known structure. Physical properties of dekazene were measured.

Dekazene can be prepared in four ways, and can undergo a number of interesting reactions.

Specific impulse calculations indicated that a liquid monopropellant composed of a solution of dekazene in anhydrous hydrazine would deliver a specific impulse of 275-285 lb._f-sec./lb._m at 1000 psi. Flame temperatures of the monopropellant would be low. Solution of dekazene in aqueous hydrazine could also be used as monopropellant with some sacrifice in specific impulse. Solubility of dekazene in several aqueous hydrazine solutions was measured.

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DEKAZENE

A High Energy Fuel Candidate for Liquid BN Systems (C)

In June, 1958 the reaction of hydrazine with bis-acetonitrile decaborane was found by this Division to give a product in high yield which analyzed sufficiently well, considering the standards of the period, for $B_{10}H_{12} \cdot N_2H_4$. This material was found to be extremely stable toward air-oxidation and hydrolysis. The structure of this material was not known and it was assigned the trivial name "dekazene". Treatment of dekazene with additional hydrazine resulted in the formation of another stable material which was named "dekadiazene" and analyzed for $B_{10}H_{12} \cdot 2 N_2H_4$. At that time dekazene was hopefully considered to be an N-N bridged member of the $B_{10}H_{12}X_2$ family of ligand displacement products which result from the treatment of bis-acetonitrile decaborane with relatively non-basic nucleophiles.¹ This thesis was modified² when it became apparent that no N-N bond was present in dekazene.

Due to the fact that dekazene could be dissolved in anhydrous hydrazine this system was given cursory consideration as a storable liquid monopropellant which employed the BN thermochemical concept.³ The results of an actual liquid motor firing are now well known to those concerned with high energy propellants.⁴ Dekazene has been produced in pilot plant quantities and is available for further examination.

¹ M. F. Hawthorne and A. R. Pitochelli, J. Am. Chem. Soc., **80**, 6485 (1958).

² Rohm & Haas Company, Quarterly Progress Report on Synthetic Chemistry, P-59-18, September 1959, Part I, Metallo-Organic Chemistry, page 1.

³ Rohm & Haas Company, Quarterly Progress Report on Synthetic Chemistry, P-58-25, December 1958, Part I, Metallo-Organic Chemistry, page 11.

⁴ Rocketdyne Research Report No. 59-37.

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I. STRUCTURE

Recently acquired evidence,¹ which is summarized below, shows dekazene to be a member of the bis-acetonitrile decaborane family of $B_{10}H_{12}X_2$ compounds. In dekazene, ammonia plays the role of the ligand, X. Since the structure of bis-acetonitrile decaborane is known from X-ray diffraction work,² the structure of dekazene is described by Fig. 1.

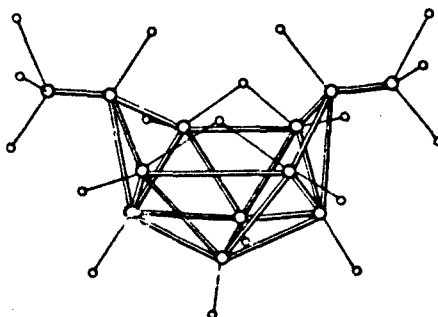


Fig. 1 Structure of dekazene.

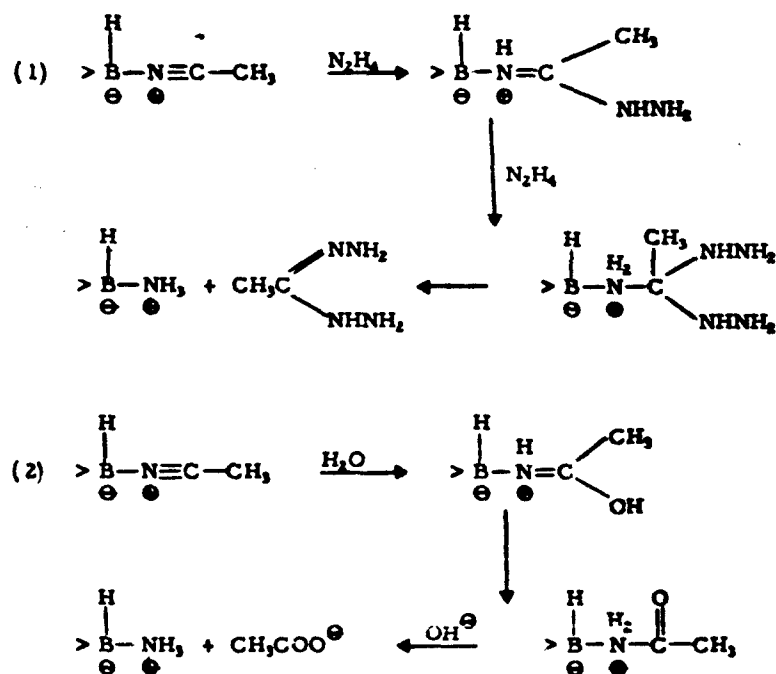
The structure of dekazene was assigned on the basis of reactions which led to its formation. These reactions are: (1) the reaction of bis-acetonitrile decaborane with hydrazine.³ (2) the basic hydrolysis of bis-acetonitrile decaborane with aqueous-alcoholic sodium hydroxide.¹ (3) the reaction of bis-diethylsulfide decaborane with ammonia¹ and (4) the reaction of decaborane with ammonia.¹ Reaction (1) was employed in the original preparation while reaction (2) afforded insight as to the structure of dekazene and the mechanism of reaction (1).

¹ Rohm & Haas Company, Quarterly Progress Report on Synthetic Chemistry, P-59-18, September 1959, Part I, Metallo-Organic Chemistry, page 1.

² W. N. Lipscomb and J. M. Reddy, *J. Am. Chem. Soc.*, **81**, 754 (1959).

³ Rohm & Haas Company, Quarterly Progress Report on Synthetic Chemistry, P-58-18, October 1958, Part I, Metallo-Organic Chemistry, page 13.

Treatment of bis-acetonitrile decaborane with a warm solution of sodium or potassium hydroxide in aqueous methanol resulted in the formation of dekazene in 79% yield. Since the only nitrogen present in the reaction system was contained in the acetonitrile ligands, dekazene cannot be formulated as a hydrazine derivative. These results indicated that the original reaction (1) was merely a hydrazinolysis as shown in equation (1) while reaction (2) involved hydrolytic cleavage of the acetonitrile ligand (equation 2).



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With these observations available, reaction (3) was successfully carried out in 85% yield.



In this case, the saturated ligand, diethylsulfide, was displaced by ammonia¹ from the 6 and 9 positions of the decaborane cage without the loss of hydrogen. This reaction is a further example of many such ligand displacement reactions which occur with members of the $B_{10}H_{12}X_2$ series.²

Reaction (4) is an example of the direct conversion of decaborane to a member of the $B_{10}H_{12}X_2$ series² with ammonia playing the role of the ligand, X.



This reactor promises to be the most economical method for the preparation of dekazene pending a thorough process study. Yields of 94% have been obtained with this method.

The infrared spectrum of dekazene is shown in Fig. 2

¹ Rohm & Haas Company, Quarterly Progress Report on Synthetic Chemistry, P-59-18, September 1959, Part I, Metallo-Organic Chemistry, page 1.

² M. F. Hawthorne and A. R. Pitochelli, J. Am. Chem. Soc., **80**, 6685 (1958).

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Fig. 2 Infrared spectrum of dekazene.

II. REACTIONS OF DEKAZENE

A. Anion Formation. - As predicted on the basis of its structure, dekazene reacted with sodium hydride in tetrahydrofuran solution to produce hydrogen and a soluble sodium salt.¹



Attempts to alkylate or acylate this salt with alkyl or acyl halides were unsuccessful. However, the products desired from these reactions may be obtained by other known paths.

¹ Rohm & Haas Company, Quarterly Progress Report on Synthetic Chemistry, P-58-18, October 1958, Part I, Metallo-Organic Chemistry, page 14.

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B. Dehydrodekazene. - Treatment of dekazene with an alcoholic solution of boron trifluoride etherate¹ produced copious amounts of hydrogen and an ether soluble product (m. p. 160°) known as dehydrodekazene. This material was later shown to be a B₉ derivative by its direct synthesis from ethylsulfide nonaborane and ammonia.²



The role of the alcoholic boron trifluoride in the original preparation of dehydrodekazene was that of a solvolytic medium required for B₁₀ to B₉ degradations.³ Dekazene is stable toward normal alcoholysis and hydrolysis.

C. Dekazene-Hydrazine Complex. - Perhaps the most unusual reaction of dekazene is the formation of a relatively stable hydrogen-bonded complex (dekadiazene) with hydrazine. When dekazene is dissolved in hydrazine, ethanol added to the warmed solution, and the solution allowed to cool, crystals of a 1:1 complex of dekazene and hydrazine separate. The process may be reversed by heating the complex in vacuo to 110° or by recrystallization from water.



The hydrazine complex is a relatively stable solid having approximately the same impact sensitivity as RDX. It may be heated to at least 250°C. in the air without decomposition.

III. PROPERTIES OF DEKAZENE

Dekazene is a crystalline white solid which does not melt below 280° C., and is not impact sensitive. Dekazene is soluble in boiling water, tetrahydrofuran, acetone, aqueous hydrazine, and anhydrous hydrazine. The solubility of dekazene in hydrazine-water solution was

- ¹ Reaction Motors Div., Thiokol Chemical Corp., Report 210-Q4, page 73.
- ² Rohm & Haas Company, Quarterly Progress Report on Synthetic Chemistry, P-59-18, September 1959, Part I, Metallo-Organic Chemistry, page 16.
- ³ Rohm & Haas Company, Quarterly Progress Report on Synthetic Chemistry, P-59-12, June 1959, Part I, Metallo-Organic Chemistry, page 37.

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determined (Table I); all solutions seemed to be permanently stable at room temperature, and no gassing was observed after the first day.

Table I
Solubility of Dekazene in Aqueous Hydrazine

Temp., °C.	Grams Solute ^b / Gram Solvent		
	100% N ₂ H ₄ ^a	93.0% N ₂ H ₄	86.9% N ₂ H ₄
15	0.660	0.573	0.498
20	0.669	0.579	0.495
25	0.676	0.576	0.493
30	0.742	0.596	0.479

^a These were the only solutions which would fire on impact (20 in. with 1 kilogram weight).

^b The corresponding weight of dekazene-hydrazine complex, the phase which actually separates, may be obtained by increasing the reported solute weight by a factor of 1.21.

The thermal stability of pilot plant dekazene was examined at 120°. After seven hours in contact with air, infrared spectra gave no evidence of degradation. In another experiment pilot plant dekazene was heated at 110° in a closed system. Hydrogen was initially evolved at a low rate which decreased with time to an insignificant rate. These results suggest "thermal soaking" as a simple method for removing thermally unstable impurities. Analysis of these relatively crude samples of dekazene by the phase solubility¹ method in anhydrous acetone indicated an impurity concentration of 1.8%.

Specially purified dekazene showed much less hydrogen evolution at 110° C.

The infrared spectrum of the dekazene-hydrazine complex is shown in Fig. 3.

¹ J. Mitchell, Jr., I. M. Kolthoff, E. S. Proskauer, and A. Weissberger, "Organic Analysis," Vol. II, Interscience Publishers, Inc., New York, N. Y.

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Fig. 3 Infrared spectrum of the dekazene-hydrazine complex.

IV. THERMOCHEMISTRY OF DEKAZENE

A precise value for the heat of formation of dekazene is not available. However, RMD¹ has recently measured the heat of combustion from which a heat of formation of -110 ± 10 Kcal./mole was obtained. Combustion products were determined.

The heat of explosion of a saturated solution of dekazene (7.12 moles N_2H_4 /mole of dekazene) was approximately 1400 cal./gram. As hydrazine is removed from this system the heat of explosion increases to near 2000 cal./gram.

Pending a rigorously proven value for the heat of formation of dekazene, a series of calculations were carried out which express the theoretical specific impulse (frozen flow $\approx$ equil. flow) of a saturated solution of dekazene in anhydrous hydrazine as a function of assumed values of the heat of formation of dekazene. These results are shown in Fig. 4 and are based on a chamber pressure of 1000 psi expanded

¹ Private communication, Dr. Stanley Tannenbaum, Reaction Motors Division, Thiokol Chemical Corp.

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to 14.7 psi. Low flame temperatures, characteristic of the BN system, are obtained. It is seen that a ΔH_f of -110 Kcal./mole and a realizable monopropellant solution gives a predicted impulse of 285 lb._F-sec./lb._m at 1000 psi.

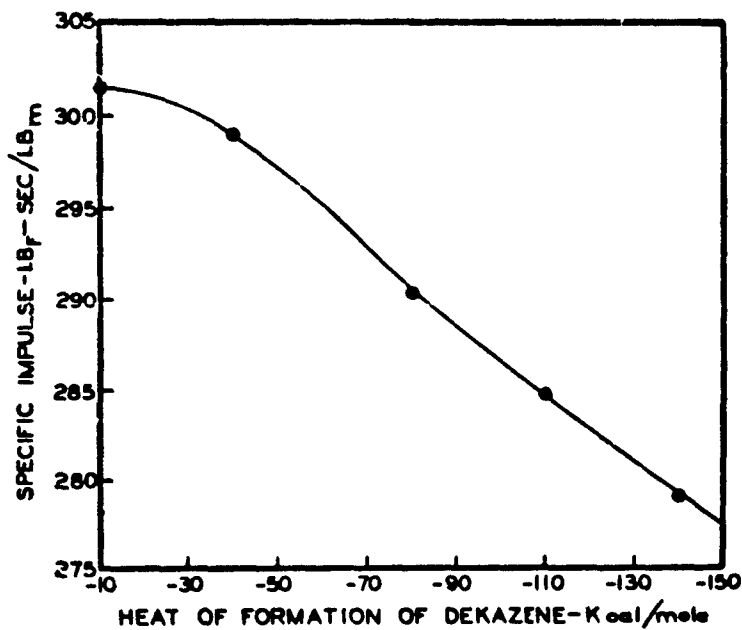


Fig. 4 Theoretical specific impulse of a saturated solution of dekazene in anhydrous hydrazine as a function of assumed values of the heat of formation of dekazene.

The effect of increasing the hydrazine to dekazene ratio with a ΔH_f value of -110 Kcal./mole for dekazene was investigated. At a mole ratio of 8.5 the specific impulse dropped to 279 lb._F-sec./lb._m, while at a ratio of 11.0 the specific impulse became 271 lb._F-sec./lb._m.

The saturated solution obtained in 93% hydrazine-7% water gave a calculated specific impulse of 276 lb._F-sec./lb._m ($\Delta H_f = -110$ Kcal./mole) at 1000 psi.

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V. PREPARATION OF DEKAZENE AND THE DEKAZENE-HYDRAZINE COMPLEX

In a typical preparation, 100 gm. BAND is suspended in 300 cc. benzene in a 3-necked 2-liter flask fitted with a water condenser, mechanical stirrer, dropping funnel, and drying tube. A 180 cc. portion of Eastman 95% hydrazine is added dropwise to the stirred suspension, maintained at 0-5° by means of an ice-water bath (BAND dissolves exothermically in hydrazine). After addition is completed, the ice bath is replaced by a mantle and the stirred solution heated to reflux and maintained at reflux for at least two hours. The mantle is then removed and the two-phase system allowed to cool somewhat before continuing. (Normally, at this point, the benzene layer will take on a deep red coloration due to a compound resulting from reaction of acetonitrile with hydrazine).

At this point, the procedure varies, depending on which compound is desired. If dekadiazene is the desired product, the benzene layer is decanted off and the hydrazine layer poured into a large Erlenmeyer flask on a steam bath and 1.5-2 l. 95% ethanol added portionwise. The suspension resulting is allowed to cool, the crystals are filtered and washed with ethanol and ether, and air dried. When the suspension is refrigerated overnight before the crystals are isolated, yields of 88-90% $\text{NDN} \cdot \text{N}_2\text{H}_4$ are obtained. Normally, a water soluble organic by-product floats to the top of the suspension and may be removed manually before filtration. $\text{NDN} \cdot \text{N}_2\text{H}_4$ may be recrystallized by dissolving it in 95% N_2H_4 and precipitating the product from the heated solution with ethanol.

To obtain dekazene, water instead of ethanol is added to the warm hydrazine layer. Very finely divided white crystals precipitate immediately. Ice may be added to the suspension to increase the yield. By using 2-3 liters of ice water for isolations, yields of 95% NDN may be effected. To rid the NDN of the pink organic by-product, it is

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washed with warm water until white. It may then be washed with ethanol and ether and air dried.

Dekazene may also be obtained by conversion of dekaliazene. Recrystallization of $\text{NDN} \cdot \text{N}_2\text{H}_4$ from boiling water gives NDN in 89% yield. The overall yield of NDN from BAND by this route is approximately 80%. Consequently, if dekazene is the desired product, the first method outlined is recommended. However, the conversion method does yield dekazene as very pure, well-defined crystals.

Dekazene may be recrystallized either from boiling water alone, or, more rapidly, by dissolving it in hydrazine and adding water to the solution.

Acknowledgments. - The authors are indebted to Dr. Kenneth Wilde for the specific impulse calculations and to Mr. Earl D. Bosserman and Mr. R. Donald Strahm for the solubility, thermal stability, and analytical data.

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