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RESEARCH PROJECT TERMINATION

Date: 10 Aug 1971

Project Title: Synthesis, Stability, and Energetics of High Energy Rocket Propellant Ingredients at Cryogenic Temperatures.

Project No: E-19-606 (old B-518)

Principal Investigator: Dr. Henry A. McGee

Sponsor: Air Force Office of Scientific Research; Arlington, Va.

Effective Termination Date: 6-30-71 (Final Report due 7-30-71)*

Clearance of Accounting Charges: by 7-31-71

*Final Report submitted 7-26-71.

Grant Closeout Items Remaining: Final Fiscal Report due by 9-30-71.

Note: This project continued work under AFOSR Grant No. AF-AFOSR-1308-67 after 7-1-70. Work under the grant before that time was on Project No. B-516, which terminated 6-30-70.

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GEORGIA INSTITUTE OF TECHNOLOGY
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Date: 28 July 1970

RESEARCH PROJECT INITIATION

Project Title: Synthesis, Stability, and Energetics of High Energy Rocket Propellant
Ingredients at Cryogenic Temperatures

Project No.: B-518

Project Director: Dr. Henry A. McGee

Sponsor: Air Force Office of Scientific Research, Arlington, Va.

Agreement Period: From 1 July 1970 until 30 June 1971

Type Agreement: Modification No. AFOSR-67-1308C to
AF-AFOSR-1308-67

Amount: \$34,000 AFOSR Funds (B-518)
9,410 GIT Contribution (E-508)
\$43,410

Grant Administrators

Scientific Matters:
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Reports Required

Interim Scientific - by 31 Aug 70, six (6)
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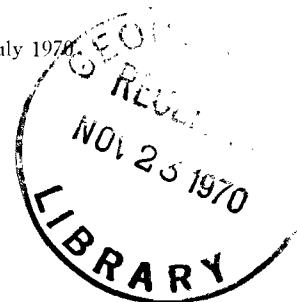
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Cryogenic Stability of Small Boron Compounds and Their Energetics Using the MINDO Method*

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(Received 27 March 1970)

Borane from the pyrolysis of BH_3CO survives quenching to 65–67°K and revaporization, but its isolation as a cryoreagent is unlikely since it dimerizes at temperatures corresponding to vapor pressures of about 10^{-6} torr. The reaction intermediate B_4H_8 produced in the pyrolysis of B_4H_{10} also survives a cryogenic quench and revaporization. The MINDO molecular orbital method has been successfully applied to some B–H–F compounds, and computational results both affirm the accuracy of earlier energetic data and suggest further fruitful synthetic chemistry.

I. INTRODUCTION

The possible existence of borane, BH_3 , as a stable cryochemical reagent has been a puzzling question in this laboratory for several years. In the study of this question, molecular energetic data were developed¹ which cast serious doubt on some aspects of the then accepted thermodynamic and kinetic character of both B_2H_6 and BH_3CO . We should like to now report new cryogenic observations of BH_3 and show how a new MO calculational scheme, the MINDO method, unifies and supports our electron-impact-based energetic data. A legitimate criticism of all molecular energetic arguments based upon electron-impact data concerns the possible production of excited ions. To resolve this uncertainty, we have searched for a possible excited BH_3^+ in the dissociative ionization of B_2H_6 .

B_4H_8 has been observed as a reaction intermediate in the pyrolysis of B_4H_{10} .² Such unusual boron species, normally classified as intermediates, may exist as manipulatable reagents at cryogenic temperatures, and hence an effort to stabilize B_4H_8 by extreme cooling has also seemed reasonable.

II. EXPERIMENTAL

High concentrations of borane are obtained in the pyrolysis of BH_3CO .¹ To study the cryogenic stability of BH_3 , pyrolysis and rapid quenching experiments were performed in a cryogenic reactor and inlet system attached to a mass spectrometer.³ The quartz furnace was mounted inside and concentric with the monel walls of the quenching space that were maintained at 65–67°K. The minimum distance from the furnace outlet port to the cold surface was about 2.5 mm, and the

quenching space was maintained below 10^{-6} torr by fast through-pumping. Refrigeration capacities limited experiments to about 40 min duration with furnace inlet pressures of BH_3CO of $1\text{--}100 \times 10^{-3}$ torr and temperatures of 280–350°C over a 4-cm-long by 4-mm-i.d. heated space. The mass-spectrometric arrangement allowed analysis to occur at the ambient temperature of the quench reactor with no warmup.³ This is, of course, crucial.

Similar experiments were performed to study the cryogenic stability of B_4H_8 , but the parent B_4H_{10} was pyrolyzed at 220–250°C, at pressures near 5×10^{-3} torr, and the furnace effluent was quenched to 77°K.

In dissociative ionization, the total excess energy of an ion has been shown to correlate well with its translational excitation,⁴ and the latter is readily determined from measurements of peak widths at half-height as a function of electron energy.⁵ In the appearance of $^{11}\text{BH}_3^+$ from B_2H_6 , these measurements were made as described by Franklin *et al.*⁵ at a series of electron energies and at different gate widths. Similar measurements were made for the parent ions of He, H_2O , N_2 , and Ar, which are known to be produced with no excess translational energy. By comparisons with these known ions, the excess energy of $^{11}\text{BH}_3^+$ at its appearance potential from B_2H_6 was determined.

III. RESULTS

BH_3 , B_2H_6 , and CO were observed as having passed completely through the quenching space during pyrolysis and quench experiments with BH_3CO . For such observation, the furnace effluent must pass through a tubular quenching space $\frac{1}{2}$ -in. i.d. by $4\frac{1}{8}$ -in. long and a

$\frac{1}{8}$ -in.-i.d. by $1\frac{1}{8}$ -in.-long tube all at 67°K before emerging into the ion source at a point $\frac{3}{8}$ in. from the ionizing electron beam to yield mass spectra like that of Table I. There were no slits or other obstructions between the cold inlet port and the electron beam.

After the pyrolysis was completed and the furnace had been turned off, the quenching space could be maintained at 65°K for about 16 min, during which time BH_3 , B_2H_6 , and a small amount of CO were continually observed in spectra like that of Table I. As the quench reactor then slowly warmed from 65°K, the spectra gradually became that of authentic B_2H_6 , and BH_3CO was observed above 90°K. This total sequence of observations was repeated in three separate experiments.

In the pyrolysis and quench of B_4H_{10} , spectra like that of Table II were also reproducibly observed in three separate experiments. There was never any evidence of higher boranes in these spectra.

For optimum study, ions should possess a total excitation of 0.5 eV or more, and for such ions, both the accuracy and precision of the measurement should be $\pm 5\%$.⁴ Application of the technique revealed no excitation of BH_3^+ from the electron bombardment of B_2H_6 .

IV. DISCUSSION

B_2H_6 has insufficient vapor pressure at 65–67°K to be detectable in this cryogenic mass-spectrometric inlet system. At sufficiently high temperatures to be seen, authentic B_2H_6 is characterized by an m/e 13 to m/e 27 ratio of about 0.2 as shown in Table I. In these experiments, not only is B_2H_6 seen, but the 13/27 ratio is 0.35 to 0.6 at 67°K and 0.7 to 0.8 at 65°K. We conclude that free BH_3 survives both transport through the quench reactor and condensation and revaporization at 65–67°K, and that the observed low-temperature spectra are due to free BH_3 and B_2H_6 formed by recombination in the quench reactor and in the ion source (which is at room temperature). The activation energy for recombination thus seems very nearly equivalent to that for vaporization, and hence the isolation of pure BH_3 as a cryogenic reagent unfortunately seems not very probable.

Similarly, from the enhancement, particularly of

TABLE I. Relative intensities of BH_n^+ ions for B_2H_6 and for the equilibrium vapor over the cold composite solid from the pyrolysis and quench of BH_3CO .

m/e	$T=65^\circ\text{K}$	$T=67^\circ\text{K}$	Diborane at 90°K
27	100	100	100
13	72	35.5	19.5
12	44	47.5	14.5
11	26.6	21	18.7
10	6	5	4.1

TABLE II. Relative intensities of ions in the B_4 region for B_4H_{10} and for the equilibrium vapor over the cold composite solid from the pyrolysis and quench of B_4H_{10} .

m/e	B_4H_{10} at 163°K	Quenched product at 149°K
52	12	11
51	26.5	25
50	100	100
49	84.5	99.5
48	72	80
47	54	61
46	41.5	44.5
45	26.5	29.5

m/e 48 and 49, in the spectrum of the quenched material over that of authentic B_4H_{10} , we conclude that B_4H_8 must have survived the quench and revaporization. But the vapor pressures are too similar to allow a separation of these B_4 species by simple distillation alone at very low temperatures.

V. ENERGETICS

The absence of excitation in BH_3^+ from B_2H_6 further supports our earlier energetic arguments. If excitation had occurred in the appearance of BH_3^+ from B_2H_6 , the observed A.P. would have exceeded the true value by the amount of this excitation, and the deduced value of $D(\text{BH}_3\text{--BH}_3)$ would have been correspondingly too large by this same amount.

But to further authenticate these energetic arguments from a theoretical perspective, we have calibrated the new MINDO molecular orbital method⁶ for B–H and B–F bonds. The MINDO method was selected because of its demonstrated superior accuracy in calculations of heats of formation and ionization potentials for a wide variety of compounds. In the MINDO approximation, the one-center repulsion integrals are written in terms of the Slater–Condon parameters which, along with the one-center attraction integrals, are input data and are listed in the program as a block data subroutine. The MINDO approximation for the one-electron resonance integral is

$$\beta_{\mu\nu} = S_{\mu\nu}(I_\mu + I_\nu)(\beta_{\text{AB}}^{\text{I}} + \beta_{\text{AB}}^{\text{II}}/R_{\text{AB}}^2),$$

where Φ_μ and Φ_ν are atomic orbitals of atoms A and B, respectively, I_μ and I_ν are the corresponding valence-state ionization potentials, $S_{\mu\nu}$ is the overlap integral, R_{AB} is the internuclear separation of the atoms, and $\beta_{\text{AB}}^{\text{I}}$ and $\beta_{\text{AB}}^{\text{II}}$ are empirical parameters for A–B-type bond which we must now evaluate for B–H and B–F bonds. This was accomplished for B–H by temporarily setting $\beta_{\text{BH}}^{\text{II}} = 0$, setting R_{BH} of single-bonded BH equal to the measured value of 1.2325 Å,⁷ and evaluating $\beta_{\text{BH}}^{\text{I}}$ by fitting $\Delta H_f(\text{BH}) = 104$ kcal/mol.⁸ In the MINDO method, standard bond lengths rather than

TABLE III. Summary of bond lengths and optimum β parameters for the calculation of one-electron resonance integrals.

Molecule	Bond	Standard bond length (\AA)	β_{AB}^I	β_{AB}^{II}	Bond type
BH	B-H	1.2325	0.1765	0.005	Single
BH ₃	B-H	1.19	0.1765	0.005	sp^2 hybrid
BF	B-F	1.30	0.2495	0	sp^2 hybrid
BF ₃	B-F	1.30	0.2495	0	sp^2 hybrid
BHF ₂ , and	B-H	1.19	0.1765	0.005	sp^2 hybrid
H ₂ BF	B-F	1.30	0.2495	0	sp^2 hybrid

experimental values are used, but these values were not significantly different from the actual ones for small hydrocarbons, and hence the experimental R_{BH} was used. The resulting value of β_{BH}^I and using $R_{BH} = 1.19 \text{ \AA}$ ⁹ in sp^2 hybridized BH₃ permitted a computation of the $\Delta H_{\text{atom}}(\text{BH}_3) = 256 \text{ kcal/mol}$, which is in very good agreement with the electron-impact-based value of 257 kcal/mol. Since BH and BH₃ have different kinds of bonds, β_{BH}^{II} was given a value greater than zero, and then both β_{BH}^I and β_{BH}^{II} were adjusted to obtain an optimum consistency in both cases (see Tables III and IV). Calibrating on larger values of $\Delta H_f(\text{BH})$, but within the experimental uncertainty, yields values of $\Delta H_{\text{atom}}(\text{BH}_3)$ somewhat smaller than 257 kcal/mol; for example, at $\Delta H_f(\text{BH}) = 106 \text{ kcal/mol}$, $\Delta H_{\text{atom}}(\text{BH}_3)$ is computed to be 250 kcal/mol. Thus, to achieve optimum consistency the MINDO computation permits a selection of heat of formation data from within the stated experimental uncertainties. A change in bond length in BH₃ of 0.01 \AA still yields energetic quantities within the experimental uncertainties.

We have been unsuccessful in applying the MINDO technique to the three-center-two-electron bonds of B₂H₆.

A. B-H-F Compounds

It is instructive to inquire whether the parameters which correlate our experimental results on BH and BH₃ will correctly predict the heat of formation of BHF₂. Since BHF₂ has the same sp^2 hybrid B-H bond as found in BH₃, a "standard" bond length of 1.19 \AA was used for the calculation. The parameters for the sp^2 hybridized B-F bond were obtained by setting $R_{BF} = 1.3 \text{ \AA}$, the experimental value in BF₃,¹⁰ and evaluating β_{BF}^I from fitting $\Delta H_f(\text{BF}_3)$ (see Tables III and IV). β_{BF}^{II} was set equal to zero since all of the compounds considered here have the same kind of B-F bond, and a "standard" bond length was used. One then calculates $I(\text{BF}_3) = 15.45 \text{ eV}$, which may be compared with $I(\text{BF}_3) = 15.55 \pm 0.04 \text{ eV}$ from photoionization experiments,^{11,12} $\Delta H_f(\text{BHF}_2) = -176.805 \text{ kcal/mol}$, which may be compared with an experimental value of $-175.7 \pm 1.5 \text{ kcal/mol}$,¹³ and $I(\text{BHF}_2) = 13.80 \text{ eV}$ for which there is no experimental value.

These parameters were also used to calculate $\Delta H_f(\text{BF})$ and $I(\text{BF})$. The assumption of a two-electron bond and the use of the measured bond distance of 1.265 \AA ¹⁴ yields poor agreement with experiment. However, use of an sp^2 hybrid bond,¹⁵ and a "standard" bond length of 1.3 \AA as in BF₃, yields very good agreement with experiment, as is evident from Table IV. The theoretical $I(\text{BF})$ is about 0.7 eV higher than the median experimental value, but this latter value is questionable since it was measured at about 1300°.

No data are available on the final member of this family, BH₂F, since it has not yet been synthesized, but MINDO predicts $\Delta H_f(\text{BH}_2\text{F}) = -70.6 \text{ kcal/mol}$ and $I(\text{BH}_2\text{F}) = 12.08 \text{ eV}$. The molecules BH₃ and BH₂F are the lowest-energy configurations of the four atoms. The next lowest potential minimum is 72.3 kcal/mol higher for BH₃ and 99.6 kcal/mol higher for BH₂F; hence we conclude that BH₂F is the more stable species, and if the kinetic characteristics of the fluoride are not

TABLE IV. A comparison of theoretical and experimental heats of formation and ionization potentials.

Molecule	ΔH_f (kcal/mol)	ΔH_f (kcal/mol)	I.P. (eV)	I.P. (eV)
	Theoretical ^a	Experimental	Theoretical	Experimental
BH	104.028	106 ± 2 ^b	9.71	9.77*
BH ₃	35.964	34.5 ± 2 ^c	11.92	12.24 ± 0.1 ^c
BF	-26.915	-29.0 ± 2.6 ^d	12.19	11.5 ± 0.4 ^b
BF ₃	-270.513	-270.10 ± 0.24 ^e	15.45	15.55 ± 0.04 ^f
BHF ₂	-176.805	-175.7 ± 1.5 ^f	13.80	
BH ₂ F	-70.614		12.08	

^a This MINDO calculation.^b Reference 8.^c Reference 1.^d J. Blauer, M. S. Greenbaum, and M. Farber, J. Phys. Chem. **68**, 2332 (1964).^e S. Wise, J. Margrave, H. Feder, and W. Hubbard, J. Phys. Chem. **65**,

2157 (1961).

^f Reference 13.^g S. H. Bauer, G. Herzberg, and J. W. C. Johns, J. Mol. Spectry, **13**, 256 (1964).^h D. L. Hildenbrand and E. Murad, J. Chem. Phys. **43**, 1400 (1965).ⁱ Reference 11.

too unlike those of BH_3 , we expect BH_2F to be synthesizable if perhaps only at very low temperatures.

A thorough study of the efficacy of the MINDO method with B-H-F compounds is limited by the small number of compounds with no three-center-two-electron bonds.

B. Energetics of B_2H_6 and BH_3CO

The heat of atomization of BH_3 is 256.5 kcal/mol and 257.5 kcal/mol from completely independent sets of data on B_2H_6 [$D(\text{BH}_3\text{-BH}_3) = 59$ kcal/mol] and BH_3CO [$D(\text{BH}_3\text{-CO}) = 33.7$ kcal/mol], respectively.¹ In both calculations only the values of $D(\text{BH}_3\text{-BH}_3)$ and $D(\text{BH}_3\text{-CO})$ are significantly questionable, as is evident from

$$\Delta H_{\text{atom}}(\text{BH}_3) = \Delta H_f(\text{B}) + 3\Delta H_f(\text{H}) + \Delta H_f(\text{CO}) \\ - \Delta H_f(\text{BH}_3\text{CO}) - D(\text{BH}_3\text{-CO}).$$

Other experimental techniques have yielded

$$D(\text{BH}_3\text{-CO}) = 23.1 \text{ kcal/mol}^{16}$$

and

$$D(\text{BH}_3\text{-BH}_3) = 35 \text{ kcal/mol},^{17}$$

both of which values yield a heat of atomization of BH_3 of about 269 kcal/mol. Using $R_{\text{BH}} = 1.19 \text{ \AA}$, a value of β^{I} fit to 269 kcal/mol, and $\beta^{\text{II}} = 0$, $\Delta H_f(\text{BH})$ is calculated to be 100.5 kcal/mol, which is outside of the experimental range. Nonzero values of β^{II} yield even poorer agreement.

MINDO underestimated the adiabatic ionization potential of BH by only 0.06 eV (see Table IV). The difference between the calculated (11.92 eV) and the electron impact (12.24 ± 0.1 eV) ionization potential of BH_3 can be attributed to the difference between the adiabatic and vertical ionization potentials of the molecule.

All of the above suggests that viewed through the

lens of the MINDO approximation there is a consistency in our earlier energetic arguments¹ that cannot be developed using other data. The successful application of MINDO to these B-H-F compounds demonstrates the broader applicability of the method.

* Research sponsored by the Air Force Office of Scientific Research, Office of Aerospace Research, U.S. Air Force, under Grant AF-AFOSR-1308-67.

¹ J. H. Wilson and H. A. McGee, Jr., *J. Chem. Phys.* **46**, 1444 (1967); P. S. Ganguli and H. A. McGee, Jr., *ibid.* **50**, 4658 (1969).

² A. B. Baylis, G. A. Pressley, Jr., M. E. Gordon, and F. E. Stafford, *J. Am. Chem. Soc.* **88**, 929 (1966).

³ H. A. McGee, Jr., T. J. Malone, and W. J. Martin, *Rev. Sci. Instr.* **37**, 561 (1966).

⁴ M. A. Haney and J. L. Franklin, *J. Chem. Phys.* **48**, 4093 (1968).

⁵ J. L. Franklin, P. M. Hierl, and D. A. Whan, *J. Chem. Phys.* **47**, 3148 (1967).

⁶ N. C. Baird and M. J. S. Dewar, *J. Chem. Phys.* **50**, 1262 (1969); N. C. Baird, M. J. S. Dewar, and R. Sustman, *ibid.* **50**, 1275 (1969), and in a continuing series of papers. We are grateful to Professor Dewar for supplying us with a program listing and for discussions concerning the MINDO method. The program used here was obtained from the Quantum Chemistry Program Exchange, Chemistry Department, University of Indiana, Bloomington, and was designated MINDO 4. The heat of formation of the fluorine atom was changed to 15.45 kcal/mol rather than 18.86 kcal/mol, V. H. Dibelar, J. A. Walker, and K. E. McCulloh, *J. Chem. Phys.* **51**, 4230 (1969).

⁷ G. M. Almy and R. B. Horstall, *Phys. Rev.* **51**, 491 (1937).

⁸ A. C. Hurley, *Proc. Roy. Soc. (London)* **A261**, 237 (1961).

⁹ A theoretical value obtained by F. P. Boer, M. D. Newton, and W. N. Lipscomb, *J. Am. Chem. Soc.* **88**, 2361 (1966). The same bond distance was obtained in this laboratory from an INDO calculation on an assumed plane BH_3 molecule.

¹⁰ A. H. Nielson, *J. Chem. Phys.* **22**, 659 (1954).

¹¹ V. H. Dibelar and S. K. Liston, *Inorg. Chem.* **7**, 1742 (1968).

¹² The efficacy of MINDO in calculations of ionization potentials is discussed by M. J. S. Dewar and S. D. Worley, *J. Chem. Phys.* **50**, 654 (1969).

¹³ R. F. Porter and S. K. Wason, *J. Phys. Chem.* **69**, 2208 (1965).

¹⁴ R. Onaka, *J. Chem. Phys.* **27**, 374 (1957).

¹⁵ C. Edmiston and K. Ruedenberg, *J. Chem. Phys.* **43**, S97 (1965).

¹⁶ A. B. Burg and Y. C. Fu, *J. Am. Chem. Soc.* **88**, 1147, (1966).

¹⁷ T. P. Fehlner and W. S. Koski, *J. Am. Chem. Soc.* **87**, 409 (1965).

SYNTHESIS, STABILITY, AND ENERGETICS OF HIGH ENERGY
ROCKET PROPELLANT INGREDIENTS AT CRYOGENIC TEMPERATURES

June 1971

Final Scientific Report

AF-AFOSR-1308-67

Research conducted between
May 1, 1967 and June 30, 1971

by

Henry A. McGee, Jr.

Principal Investigator



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Synthesis, Stability, and Energetics of High Energy
Rocket Propellant Ingredients at Cryogenic Temperatures

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- I. Introduction and rationale
- II. Brief technical summary
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- V. Associates
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I. INTRODUCTION AND RATIONALE

Weapons delivery depends primarily on chemical rocket propulsion. Present limitations on range, speed and payload can be overcome if new, more energetic propellant ingredients can be found. The most productive search will be by novel, more imaginative, techniques for synthetic and kinetic chemical studies, such as are embodied in this research.

A mutually complementary experimental and theoretical program has been conducted. This study involved uniquely combined plasma or pyrolysis activation and cryoquench techniques to yield small molecules, generally of the first row elements, which exhibit unusual reactivity or high energy behavior. A new semi-empirical and accurate molecular orbital computer program was used to aid in the selection of the candidate molecules most likely to be successfully synthesized. Experimental successes permitted improvement of the theory, theory guided experiment, and thereby the total program was optimized. The underlying objectives were then synthesis and the subsequent characterization of products from a molecular energetic and kinetic perspective.

This research program was one of basic chemistry, but it has been conducted in the chemical engineering department by research engineers. In a sense, therein lies a clue to the distinction between this AFOSR program and a perhaps similar appearing program sponsored by e.g., NSF. And that is, the efforts herein were motivated by a primary interest in the ultimate application or use of this science and not merely as a stimulating intellectual exercise. This motivation permeated the research and strongly influenced the day-to-day decisions in the laboratory. For example,

synthetic chemistry is a large part of this effort, but we employed only those synthetic methods that seemed to be generalizable, at least in principle, to large scale production. Without this capability, of course, the product species, no matter how interesting, will remain a laboratory curiosity.

The results will benefit the Air Force in the areas of high energy propulsion, in energy storage and conversion, and in new materials, particularly inorganic polymers for high temperature service.

II. BRIEF TECHNICAL SUMMARY

Equipment and Technique:

Much of our success in chemical synthesis can be traced to the design and development of a versatile cryogenic reactor-mass spectrometric inlet arrangement which we feel to be a significant contribution both to mass spectrometric technique and to the technology of cryochemical research and development.¹ For the increased emphasis on novel synthetic procedures and chemical reactivity studies that has characterized this program, it was desirable to translate, to the greatest possible extent, all of the common operations of bench-scale chemistry to the point of their convenient utilization at cryogenic temperatures. Our earlier reactor designs, which in fact proved to be very useful in their own right, were essentially glorified traps with built-in, but very carefully designed, mass spectrometric probes.² The new design employs any sort of reactor, followed by any simple processing, and continuous mass spectrometric monitoring at any point with no attendant warm-up from the cryogenic operating temperature level. All three functions of reaction, processing, and analysis are effectively immersed in a liquid refrigerant (usually a 2:1 mixture of isopentane and 2-methyl pentane respectively which is useful to -168° , or a mixture of Freons, or other liquids) which can be automatically thermostated at any desired temperature level. In this facility we have successfully employed gaseous discharge reactors, pyrolysis reactors, submerged arc reactors, and exploding wire reactors, each of unusual design and each operating completely at cryogenic temperatures. These cryo-

¹J. K. Holzhauser, and H. A. McGee, Jr., Anal. Chem. 41, 24A (1969).

²H. A. McGee, Jr., T. J. Malone and W. J. Martin, Rev. Sci. Instr. 37, 561 (1966).

reactors, in varying degree, physically superimpose the operations of high energy excitation and cryogenic quench.

The design and development of instrumentation and techniques for the automatic recording of ionization efficiency data represents a significant and generally useful advance in mass spectrometry. The ion intensity and corresponding electron energy signals are impressed upon the y and x channels respectively of an X-Y recorder to automatically produce characteristic ionization efficiency curves. Since the output is so rapid (typically 2 to 3 min.) it is possible to run appearance potentials "on-line" during the course of an experiment such that this threshold energy measurement has become a working analytical datum for control of an experiment. Appearance potential, relative volatility, and cracking pattern are the three "handles" most frequently used in this laboratory for the separation and identification of these usually previously unobserved cryochemical species.

Noble Gas Compounds:

Experimental efforts to form noble gas compounds have a very long history, and the advantages of such species as propellants were discussed by McGee in 1958³. The molecular energetics are such that an excited helium atom, either alone or stabilized by combination with an H or F atom, would represent the most energetic chemical propellant even theoretically possible. Although theoretically exciting, the data and conclusions from all of the experimental research have been poor or equivocal. But the scientific community was shocked when Neil Barlett in 1962 produced a white solid from red gaseous PtF_6 and colorless Xe. It was XePtF_6 -- the first confirmed noble gas compound.

³A lecture by H. A. McGee, Jr., given at the Southeastern Regional ACS Meeting, Gainesville, Florida, December 1958, and reported in Chemical and Engineering News 36, No. 52, 26 (1958).

As part of this AFOSR program, a number of novel synthesis experiments aimed principally at postulated neon, argon, and krypton oxides and fluorides were conducted. These experiments involved such things as exploding wires immersed in liquid argon-fluorine solutions, similar submerged DC arcs, and cryoquenched low pressure gaseous discharges. There was never even a hint of successful synthesis except in the production of KrF_2 .⁴ This compound had been reported previously, but it was possible to develop its molecular energetics from ionization efficiency measurements.⁴

This noble gas compound phase of our research program was reluctantly discontinued.

Boron Hydrides:

From a purely energetic perspective, the lower boron hydrides, BH and BH_3 , have significant attributes as propellants. Also both species are ground state singlets, that is, they are not free radicals, and hence we expect that it may be possible to isolate these species at very low temperatures.

Earlier work on the isolation and characterization of BH_3 as a cryo-chemical reagent⁵ was expanded with considerable success.⁶ Pyrolysis of BH_3CO proved to be a convenient source of BH_3 . The analysis of precise ionization efficiency measurements permitted the development of the molecular energetics of BH_3CO , and, together with other data, a verification of our earlier energetic results on the BH_3 ; B_2H_6 system. The symmetric dissociation energy of B_2H_6 was established as 59 kcal/mole, and thus the specific enthalpy of, e.g., the $\text{BH}_3\text{-OF}_2$ flame gas will be greater than from the similar combustion of B_2H_6 by 59 kcal/mole. Unfortunately, our cryogenic rate data suggest that borane, BH_3 ,

⁴P. A. Sessa and H. A. McGee, Jr., J. Phys. Chem. 72, 2078 (1969).

⁵J. H. Wilson and H. A. McGee, Jr., J. Chem. Phys. 46, 1444 (1967).

⁶P. S. Ganguli and H. A. McGee, Jr., J. Chem. Phys. 50, 4658-4660, (1969).

is lost by dimerization at temperatures where its vapor pressure is only about 10^{-5} torr, and hence its practical utility is minimal. Research on this very interesting species was then discontinued. In a similar vein, B_4H_8 , normally considered to be a reaction intermediate, was also stabilized at very low temperatures.⁷

B-N Chemistry:

Our interest in the chemistry of boron prompted a series of exploratory experiments to produce and characterize the simplest B-N based hydrocarbon analogs. These explorations were successful, thus opening a whole new component of this initially solely energetic program to also include certain basic issues in a new family of materials.

It has long been recognized and elaborately discussed that BN should exhibit a similar chemistry to that of its isoelectronic counterpart C_2 . A large number of BN compounds corresponding to their isosteric hydrocarbon analogs have been made, but the basic building blocks of such a chemistry, iminoborane, HBNH, and aminoborane, H_2BNH_2 , have eluded synthesis because of their extreme reactivity. One expects these two compounds to be acetylene-like and ethylene-like respectively. Using our combined cold-plasma and cryogenic quench technique, we have been able to synthesize, isolate, and characterize H_2BNH_2 but HBNH has continued to elude our synthetic procedures.⁸

It has also been possible to synthesize and partially characterize the substituted compound Cl_2BNH_2 and possibly $HClBNH_2$.⁹ These compounds are simply made from the gas phase reaction of BCl_3 and NH_3 .

⁷P. S. Ganguli, L. P. Gordon, and H. A. McGee, Jr., J. Chem. Phys. 53, 782 (1970).

⁸C. T. Kwon and H. A. McGee, Jr., Inorg. Chem. 9, 2458 (1970).

⁹C. T. Kwon, H. A. McGee, Jr., and R. M. Parikh, unpublished work.

H_2BNH_2 and $HClBNH_2$ are isoelectronic with ethylene and vinyl chloride respectively, and our results suggest that both of these B-N species polymerize to form materials presumably similar to polyethylene and polyvinylchloride. A thorough characterization of these new polymers has not been completed, but it is possible that these discoveries will permit major advances in new materials development, particularly for high temperature service.

N-O-F Compounds:

Energetic arguments from many perspectives confirm that certain N-O-F compounds offer the greatest potentialities as high energy or improved oxidizers.

All five of the heretofore known N-O-F compounds have been synthesized in good yield and characterized by their heretofore essentially unknown mass spectra.¹⁰ The molecular energetics of each compound has been developed from ionization efficiency measurements on the principle ions produced by electron impact dissociative ionization.¹⁰ With only one exception these mass spectra were previously unknown as was the bulk of the energetic information. In addition, a new compound, O_2NNF_2 , was synthesized in good yield and mass spectrometrically and energetically characterized. Studies of both this new compound and the related $ONNF_2$ would have been impossible without a cryogenic reaction facility since both are too reactive to exist except at very low temperatures. Several theoretical models including both the double-quartet idea and the MINDO molecular orbital scheme have been applied to the N-O-F family of known and postulated compounds with encouraging results. Thus it has been possible to predict the heats of formation and ionization potentials

¹⁰P. A. Sessa and H. A. McGee, Jr., Inorg. Chem., in press, expected appearance, June, 1971.

of numerous conceivable, but presently unknown, N-O-F compounds. These data then permit arguments as to the probable synthetic success with these hypothetical high energy N-O-F compounds.

Theoretical Research:

The theoretical component of this AFOSR research program has included basically two elements: the use of principally semi-empirical LCAO-MO-SCF computational techniques to calculate heats of formation and ionization potentials, and the development of a generally applicable approach to predicting reaction kinetics in unusual high energy systems at cryogenic temperatures.

The so-called MINDO (Modified Intermediate Neglect of Differential Overlap) technique has been under continuous development by Professor M. J. S. Dewar and his associates at the University of Texas for several years.¹¹ This work (also under AFOSR sponsorship) is of great practical significance since for the first time it allows one to make quantum chemical calculations of thermodynamic quantities to within chemically significant accuracies. The theory was developed for organic compounds, but we have successfully applied the ideas and approximations to B-H-F compounds as well.¹² We have also applied the MINDO technique to the calculation of the thermodynamic properties of both the known as well as many postulated N-O-F compounds, but the results have not as yet been completely salutary.¹³

A new general theory of chemical kinetics has been developed for the entire field of cryochemistry. The essential ideas here were the existence of a weakly coupled activated complex and the use of the MINDO or INDO techniques to estimate the total energy of a pair of colliding molecules as a function

¹¹M. J. S. Dewar and E. Haselbach, J. Amer. Chem. Soc. 92, 590 (1970).

¹²P. S. Ganguli, L. P. Gordon, and H. A. McGee, Jr., J. Chem. Phys. 53, 782 (1970).

¹³P. S. Ganguli and H. A. McGee, Jr., unpublished work.

of orientation and separation, that is, to estimate the potential energy surface for the reaction.¹⁴ These notions have been specifically applied to the dimerization of borane where the activation energy was predicted to be 1.86 kcal¹⁵ before it was independently measured in another laboratory to be 0±2 kcal.¹⁶

¹⁴P. S. Ganguli, Ph.D. Thesis in chemical engineering, Georgia Institute of Technology, Atlanta, Georgia, August, 1970.

¹⁵P. S. Ganguli and H. A. McGee, Jr., unpublished work.

¹⁶G. W. Mappes, S. A. Fridmann, and T. P. Fehlner, J. Phys. Chem. 74, 3307 (1970).

III. GENERAL

The increasing interest within the scientific community in cryochemistry has been evidenced in a number of ways. For example, two Symposia were presented during the ACS national meeting in Minneapolis in April, 1969. The first of these was entitled "Spectroscopic Methods in Cryochemistry," it was arranged by Dr. Henry A. McGee, Jr., and it was jointly sponsored by the Divisions of Physical and Inorganic Chemistry. The second was entitled "Reactions of High Temperature Species," it was arranged by Dr. John Margrave and Dr. Phil Skell, and it was jointly sponsored by the Divisions of Petroleum and Fuel Chemistry. Since they were so closely interrelated, the chairmen worked closely together arranging these Symposia. Here we see four Divisions of the ACS involved in discussions of chemical phenomena at very low temperatures.

Of the hundreds of papers presented at the Minneapolis ACS meeting, our presentation was one of that handful judged of sufficient general interest and importance to warrant a news story in Chemical and Engineering News.¹⁷ This presentation dealt largely with accomplishments under this AFOSR sponsored research program.

Though this research program has had a strong orientation in basic chemistry, the parallel pragmatic orientation toward propulsion, energy storage and conversion, and new materials has provoked considerable interest in the engineering community as well. The principle investigator will be an invited tour speaker for the American Institute of Chemical Engineers during the 1971-72 year. His invitation and his lectures will be based very largely on this research done under AFOSR sponsorship.

¹⁷see Chemical and Engineering News 47, No. 17,50 (1969).

IV. PUBLICATIONS AND THESES

The detailed technical results under this program have been presented in a series of journal articles and PhD theses during the tenure of the grant. These publications have been sent to AFOSR as they were developed, but for completeness, we also include here a list of these items. The three PhD thesis research programs listed below were completely supported by this grant.

Publications

1. P. S. Ganguli and H. A. McGee, Jr., "Molecular Energetics of Borane Carbonyl and the Symmetric Dissociation Energy of Diborane," J. Chem. Phys. 50, 4658 (1969).

Large concentrations of borane, BH_3 , are produced upon the pyrolysis of borane carbonyl. Ionization efficiency measurements using a fast inlet mass spectrometric technique, have led to $I(BH_3)$ as well as $A(B^+)$, $A(BH^+)$, $A(BH_2^+)$ and $A(BH_3^+)$ from BH_3CO . These numbers permit a complete development of the molecular energetics of BH_3CO and a confirmation of the symmetric dissociation energy of diborane of 59 kcal/mole. Earlier equilibrium data on the BH_3CO decomposition, combined with these electron impact data also confirm $D(BH_3 - BH_3) = 59$ kcal/mole. Earlier kinetic studies that suggest a very much lower dissociation energy are shown to be equivocal at best.

2. J. K. Holzhauer and H. A. McGee, Jr., "A Facility for Chemical Reaction Research and Mass Spectrometric Analysis at Cryogenic Temperatures," Anal. Chem. 41, 24A (1969).

Chemical research at cryogenic temperatures is impeded by the prerequisite for the design and development of new cryogenic apparatus and technique. The facility described here provides for a variety of reactor designs, and features continuous mass spectrometric analysis at cryogenic temperatures with no associated sample warm-up.

3. P. S. Sessa and H. A. McGee, Jr., "Mass Spectrum and Molecular Energetics of Krypton Difluoride," J. Phys. Chem. 73, 2078 (1969).

KrF₂ was produced in an all metal discharge reactor immersed in liquid nitrogen and fed with a reactant gas mixture of Kr:F₂ ratio of 1:5. Ionization efficiency measurements yielded $A(\text{Kr}^+, \text{KrF}_2) = 13.21 \pm 0.25$ eV and $A(\text{KrF}^+, \text{KrF}_2) = 13.71 \pm 0.20$ eV.

4. P. S. Ganguli, L. P. Gordon, and H. A. McGee, Jr., "Cryogenic Stability of Small Boron Compounds and Their Energetics Using the MINDO Method," J. Chem. Phys. 53, 782 (1970).

Borane from the pyrolysis of BH₃CO survives quenching to 65° - 67°K and revaporization, but its isolation as a cryoreagent is unlikely since it dimerizes at temperatures corresponding to vapor pressures of about 10⁻⁵ torr. The reaction intermediate B₄H₈ produced in the pyrolysis of B₄H₁₀ also survives a cryogenic quench and revaporization. The MINDO molecular orbital method has been successfully applied to some B-H-F compounds, and computational results both affirm the accuracy of earlier energetic data and suggest further fruitful synthetic chemistry.

5. C. T. Kwon and H. A. McGee, Jr., "Cryochemical Preparation of Monomeric Aminoborane," Inorg. Chem. 9, 2458 (1970).

Borazine vapor was subjected to a radiofrequency discharge in a low-pressure, fast-flow system followed by an immediate quench to -196°. Unidentified solid products were deposited in the discharge tube, and all gaseous products except nitrogen and hydrogen were trapped by the cryoquench. Upon slow warming of the trap, diborane, aminoborane (H₂BNH₂), unreacted borazine, and probably borazanaphthalene and diborazinyl were evolved at -170°, -160°, -130°, -40°, and -30°, respectively. Aminoborane was identified by (a) its relative volatility, (b) its mass spectrometric fragmentation pattern, (c) its ionization potential, $I(\text{H}_2^{11}\text{BNH}_2) = 11.0 \pm 0.1$ eV, which was unchanged when observing the compound in the effluent from the discharge, in the cold subliming vapor or over the

purified solid product, and (d) its infrared spectrum at various temperatures down to 4.2°K. Mass spectrometric data were obtained using cryogenic inlet techniques to prevent premature loss of reactive or unstable species. Solid aminoborane begins to polymerize between -196° and -155° to yield an inert, white material. However, this reaction does not rapidly go to completion since the mass spectrum of H_2BNH_2 is continuously observed during warming the polymerizing material from -155° to -64° over an approximately 100-min period.

6. Chin T. Kwon, PhD thesis in chemical engineering, August, 1970, "Preparation of Aminoborane and Low Temperature Mass Spectrometric Studies of its Reactivity and Energetics."
7. Partha S. Ganguli, PhD thesis in chemical engineering, August, 1970, "Cryosynthesis and Energetics of Some Highly Reactive Small Boron Compounds and General Theoretical Reaction Kinetics at Cryogenic Temperatures."
8. H. A. McGee, Jr., editor, "Abstracts of Papers," 11th AFOSR Contractors' Meeting on Kinetics of Energy Conversion, Georgia Institute of Technology, 3, 4 Sept. 1970, AFOSR-70-2232-TR.
9. Paul A. Sessa, PhD thesis in chemical engineering, December, 1970, "Mass Spectrometric Investigation of the Synthesis and Molecular Energetics of Nitrogen-Oxygen-Fluorine Compounds."
10. P. A. Sessa and H. A. McGee, Jr., "Nitrodifluoramine and the Mass Spectral and Energetic Characterization of all Known N-O-F Compounds at Cryogenic Temperatures," Inorg. Chem., in press, expected June, 1971.

All five of the heretofore known N-O-F compounds (ONF , NO_2F , NO_3F , $ONNF_2$ and ONF_3) have been synthesized and mass spectrometrically characterized. Their positive ion cracking patterns are sufficiently different to allow unambiguous assignments. Appearance potential measurements have permitted the derivation of several heats of formation, and the ionization potential of nitryl fluoride was directly measured. Extensive synthesis studies with N_2F_4 and O_2F_2 as principle reagents were disappointing, but one additional N-O-F compound, nitrodifluoramine, O_2NNF_2 , was produced and mass spectrometrically and energetically

characterized. The compound was made from the reaction of NO_2 and NF_2 free radicals. O_2NNF_2 is a white solid at -196° which decomposes to N_2F_4 and NO_2 even at -130° . The temperatures at which the vapor pressures of ONNF_2 and O_2NNF_2 are 1 torr were estimated to be $-141 \pm 2^\circ$ and $-123 \pm 2^\circ$, respectively. The mass spectral characterization of both ONNF_2 and O_2NNF_2 is impossible without cryogenic inlet techniques due to the instability of these compounds.

11. C. T. Kwon, H. A. McGee, Jr., and R. M. Parikh, "Synthesis, Characterization, and Elementary Chemistry of Dichloroaminoborane," in preparation.
12. C. T. Kwon and H. A. McGee, Jr., "Diazaboracyclopropane," in preparation.
13. C. T. Kwon and H. A. McGee, Jr., "A New Family of B-N Polymers," in preparation.

V. ASSOCIATES

The excellent scientific accomplishments of this research program would have been impossible without the innovativeness and diligence of the following associates.

1. Chin T. Kwon, predoctoral fellow, March, 1967 to August, 1970, and post-doctoral fellow, August, 1970 to present.
2. Arnold F. Stalder, post-doctoral fellow, July, 1967 to July, 1968.
3. Linda P. Gordon, research associate, October, 1967 to September, 1969.
4. Juergen K. Holzhauser, predoctoral fellow, October, 1967 to September, 1969.
5. Paul A. Sessa, predoctoral fellow, October, 1967 to December, 1970.
6. George B. Oglesby, research associate, February, 1968 to June, 1970.
7. Wolfgang K. Lutzhoft, post-doctoral fellow, December, 1968 to September, 1969.
8. Partha S. Ganguli, predoctoral fellow, July, 1969 to August, 1970, and post-doctoral fellow, August, 1970 to present.
9. Ramesh M. Parikh, research associate, October, 1970 to February, 1971.

VI. ADMINISTRATIVE

This grant (AF-AFOSR-1308-67) was initially awarded effective May 1, 1967 for a period of 24 months, but this original grant period was later extended to 26 months, or until June 30, 1969, at no additional cost. The grant was renewed for one year effective July 1, 1969 and again for one more year effective July 1, 1970. This report is a final summary of this 50-month program which ended on June 30, 1971.

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) GEORGIA INSTITUTE OF TECHNOLOGY School of Chemical Engineering Atlanta, Georgia 30332		2a. REPORT SECURITY CLASSIFICATION Unclassified	
		2b. GROUP	
3. REPORT TITLE Synthesis, Stability, and Energetics of High Energy Rocket Propellant Ingredients at Cryogenic Temperatures			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Final Scientific Report (May 1, 1967 to June 30, 1971)			
5. AUTHOR(S) (First name, middle initial, last name) Henry A. McGee, Jr.			
6. REPORT DATE June 1971	7a. TOTAL NO. OF PAGES 16	7b. NO. OF REFS 17	
8a. CONTRACT OR GRANT NO. AF-AFOSR-1308-67	9a. ORIGINATOR'S REPORT NUMBER(S) Project No. B-518		
b. PROJECT NO. 9750-01	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)		
c.			
d.			
10. DISTRIBUTION STATEMENT			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY Air Force Office of Scientific Research 1400 Wilson Boulevard Arlington, Virginia 22209	
13. ABSTRACT Uniquely combined high energy excitation and cryogenic quenching arrangements were employed to synthesize unusual molecules of importance in chemical energy storage, high energy propulsion, and inorganic high temperature polymers. Cryogenic reaction and instrumentation facilities were designed and developed using principally mass spectrometric and infrared techniques. The molecular energetics of all interesting product species were developed from controlled energy electron bombardment techniques, and several recent LCAO-MO-SCF computational procedures were successfully modified and applied to the prediction and correlation of the energetics of both proposed and successfully synthesized product species. Attention was centered when postulated hydrides and fluorides of the light noble gases, the lower boron-hydrides, nitrogen-oxygen-fluorine compounds, and the boron-nitrogen isoelectronic analogs of acetylene, ethylene, and their halogenated derivatives. A listing with brief individual resumes of the 13 journal articles containing the detailed technical results of this project are presented in this final report.			

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Cryogenics Plasma Synthesis Labile species Molecular energetics Mass spectrometry Kinetics Inorganic polymers						