[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

Energetics of the Boranes. V. Prediction of Heats of Formation. Interconversion of the Hydrides of Boron

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An empirical system of molecular enthalpies has been set up for the hydrides of boron. Predictions of standard heats of formation so made are compared with a similar set prepared by Prosen, based on average bond dissociation energies, assigned to four types of bonds, by means of which the known structure of the boranes can be represented. Also, an empirical curve is proposed for the standard, ideal gas entropies. Free energy increments for the interconversion of these hydrides have been deduced. The values are consistent with the available qualitative observations on the interconversion reactions.

A System of Molecular Enthalpies.—A compilation of average single and multiple bond energies, wherein a value is assigned to the energy which is to be associated with the bond between two adjacent atoms, has proved useful for predicting the heats of formation of the hydrocarbons and of some of their derivatives. In general, such a system appears to work well for compounds in which there are enough electrons to furnish a pair for each line drawn to connect the atoms. It should be generally recognized that a primary requisite for any system of "bond energies," which implies localized bonds between the atoms in a molecule, is that each species of atom in the unknown compound have the same number of ligands as it has in the calibrating compound. Otherwise, the heat of formation of the gaseous atoms from their elements will not cancel out from the computed heat of formation of the unknown compounds. Obviously, this cannot be extended to the hydrides of boron and to other similar systems without extensive modifications.

In the boranes a large variety of bonding occurs. Since four experimental magnitudes are available[1]
[ΔH_f^0 (300) for BH_3, B_2H_6, B_5H_9 and $B_{10}H_{14}$]
it is possible to deduce energy values for, at the most, four bond types. If this is done, none remains for a check on the system. The validity of such a method will thus depend on the accuracy of values so predicted and checked by heats of formation to be obtained in the future.

Prosen[2] proposed the following procedure based on the theoretical analysis of bonding in the hydrides, as given by Eberhardt, Crawford and Lipscomb.[3] Briefly, he defined four types of bonds; they are

	Av. bond dissociation energy (abde) deduced from ΔH_f^0's kcal./bond
B–H (electron pair; 2 center)	93.1
B–B (electron pair; 2 center)	83.1
$\mathrm{B}\underbrace{\mathrm{-H-}}\mathrm{B}$ (one electron pair for 2 ligands; 3 center)	107.2
$\mathrm{B}\underbrace{\mathrm{-B-}}\mathrm{B}$ (one electron pair for 2 ligands; 3 center)	97.7

Herein each hydrogen has a total of one bond, either B–H or $\mathrm{B}\underbrace{\mathrm{-H-}}\mathrm{B}$; each boron has a total of four bonds, involving B–H, B–B or $\mathrm{B}\underbrace{\mathrm{-B-}}\mathrm{B}$. The deduced four *abde*'s are cited above [based on ΔH_{sub} (B) = −140 kcal]. Values for B–B and $\mathrm{B}\underbrace{\mathrm{-B-}}\mathrm{B}$ were obtained by solving simultaneously assignments for pentaborane-9 and decaborane.

Prosen expressed the bonding in the other known and postulated hydrides in terms of these four values and predicted their heats of formation; *i.e.*, the unknown heat of formation of the gaseous compound plus the sum of these bond energies must equal the known heat of vaporization of an equivalent amount of boron plus the production of an equivalent number of hydrogen atoms. These will be compared below with another empirical procedure. However, a practical difficulty may arise for the higher boranes, the compositions of which have been established, but not their structures; Prosen's representations may not be unique unless the arrangement of boron atoms is specified. No specific allowance was made for resonance energies, whereas the structures as drawn are clearly single representations of a number of energetically equivalent structures. The simultaneous procedure for solution probably compensates for this. However, one must argue that the energies per B–B–B and per B–B are the same in all the hydrides, irrespective of the number of equivalent structures which can be written involving these bonds.

An alternate approach to this problem[4] is to treat the available data in a strictly empirical fashion; this places a minimum of dependence on postulated bond structures. Actually, the procedure discussed below was a consequence of qualitative theoretical considerations of bonding in the hydrides of boron, as suggested by the "valence cone" of Platt[5] and the "smoothed potential" theory of Arnold.[6]

Consider the standard enthalpy for the reaction

$$50\mathrm{B(s)} + 75\mathrm{H_2(g)} = \frac{50}{n}\,\mathrm{B}_n\mathrm{H}_{n+p}\mathrm{(g)} + 25\left(2 - \frac{p}{n}\right)\mathrm{H_2(g)}$$

This corresponds to the hydrogenation of one mole of unit cells of the element. The enthalpy increments for this reaction have been measured for three cases: $n = 2, p = 4$; $n = 5, p = 4$; $n = 10, p = 4$. A plot of these ΔH^0 values *vs.* $50\,(1 + p/n)$ is given in Fig. 1. In this plot the origin

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[1] W. H. Evans, D. D. Wagman and E. J. Prosen, N. B. S. report no. 4943, August 31, 1956.

[2] E. J. Prosen, Symposium on Hydrides, Spring 1955 American Chemical Society meeting (Abst. No. 68, Division of Physical and Inorganic Chemistry).

[3] W. H. Eberhardt, B. Crawford, Jr., and W. N. Lipscomb, *J. Chem. Phys.*, **22**, 989 (1954).

[4] S. H. Bauer, Spring 1955 American Chemical Society meeting, (Abstract No. 88, Division of Physical and Inorganic Chemistry).

[5] (a) J. R. Platt, *J. Chem. Phys.*, **22**, 1448 (1954); (b) for the most recent topological approach, refer to R. F. Dickerson and W. N. Lipscomb, *ibid.*, **27**, 212 (1957).

[6] J. R. Arnold, *ibid.*, **22**, 757 (1954).

($\Delta H^0 = 0$) was taken to be the origin of the function $50\,(1 + p/n)$. Note that the four points given by boron, decaborane, pentaborane-9 and diborane fall on a smooth curve. All other hydrides of boron can be fitted onto this curve, and hence the corresponding heats of formation may be interpolated. Values for the other hydrides which have been identified or surmised are listed in Table I; the predictions made by Prosen are included for comparison.

One should not be surprised that the two diverse procedures lead to such closely similar values since both are essentially empirical and both start with the same measured values (designated by *a*). One slight argument in favor of the latter procedure is that predictions are made directly of standard heats of formation and not in terms of the operationally unattainable *abde's*. Checks made by comparing abde's often prove misleading, since small relative errors in these may lead to very large errors relative to heats of formation. Prosen's procedure clearly does not suffer from this difficulty.

The fact that the four known points do fall on a smooth curve (Fig. 1) is significant and is subject to interpretation. In elementary boron the structural unit consists of four icosahedra, in which each boron is connected to five other atoms within its icosahedron and with another boron either in an adjacent icosahedron or to one of two distinctive tetra-coördinated boron atoms. There are a total

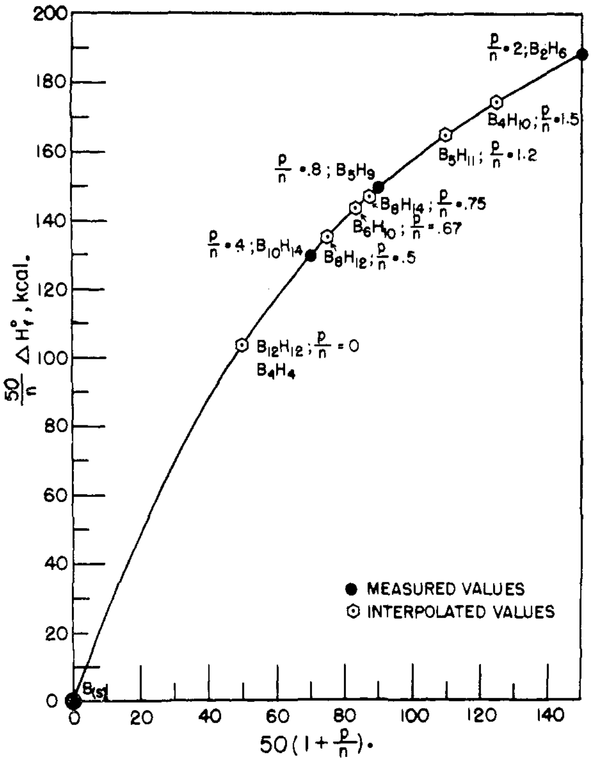

Fig. 1.—Empirical curve relating heats of formation of the hydrides of boron (B_nH_{n+p}) to their relative H:B content.

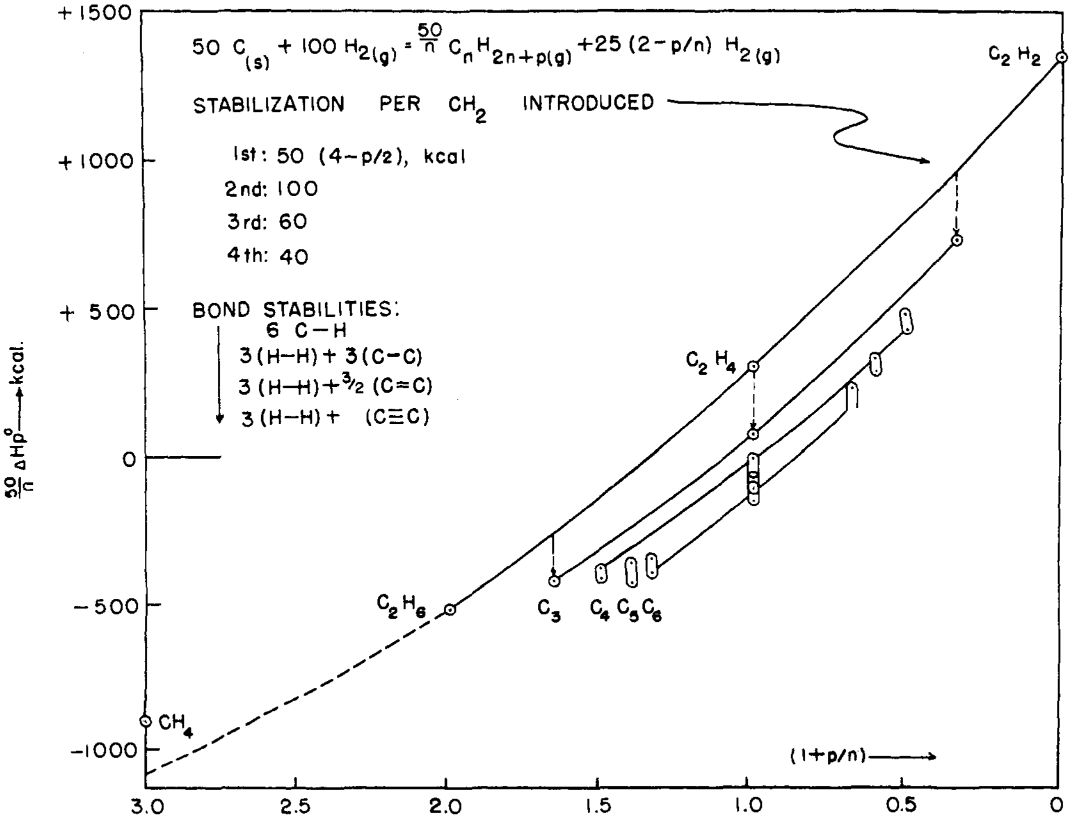

Fig. 2.—Empirical curves relating heats of formation of selected hydrides of carbon (C_nH_{2n+p}) to their relative H:C content.

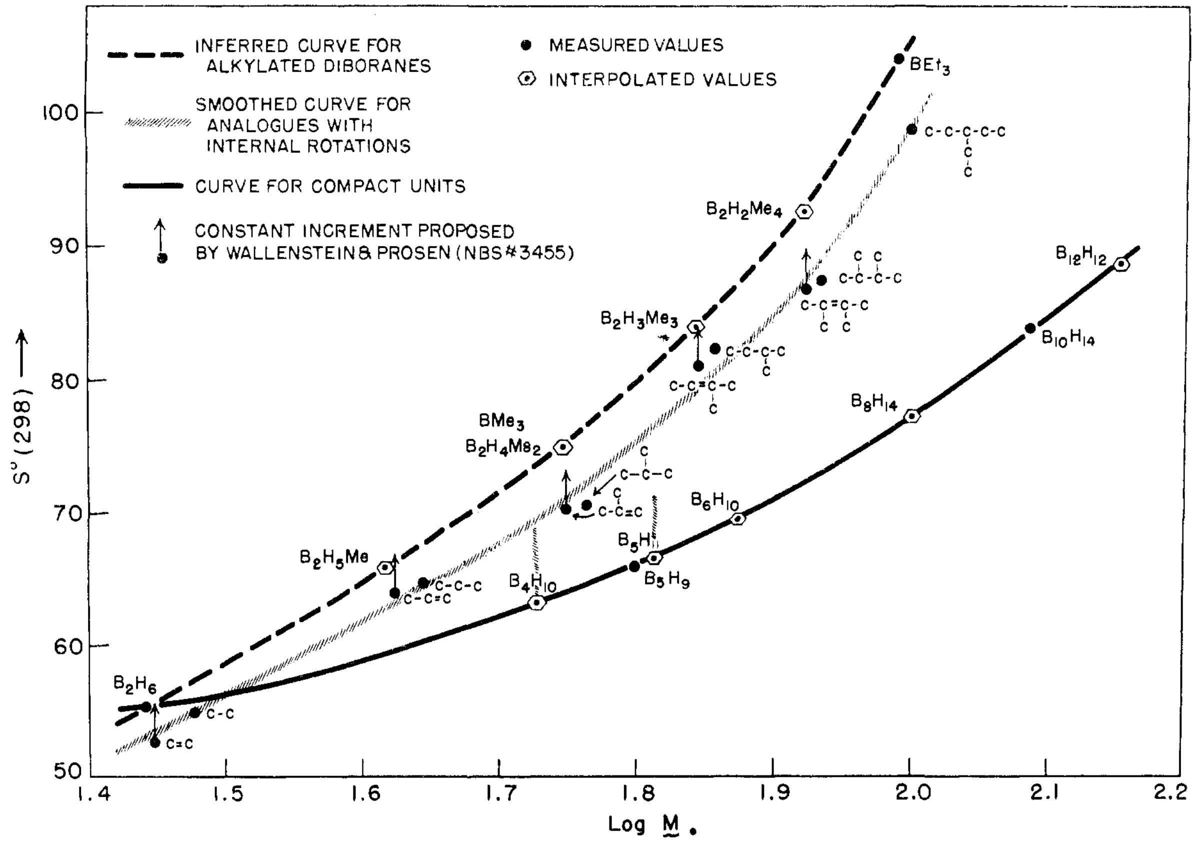

Fig. 3.—Empirical curves relating standard entropies of some ideal gases at 298°K. to their molecular weights.

of 148 bonds per unit cell. On the basis of the most recent value for the heat of sublimation of boron,[7] this leads to (129.5 × 50)/148 = 43.8 kcal. for the average energy of rupture per bond. Further, since there are only 150 electrons per unit cell, the deduced value for the average dissociation energy for $(B{:}B)_{n=1}$ is 88.8 kcal. Alternatively, the deduced value for the average dissociation energy of $B\text{–}H_{(sp^3)}$ is 89.3 kcal, based on the estimated heat of formation of $BH_3(g)$ (+18 kcal. mole^{-1}). Were H atoms available, hydrogenation of elementary boron might be slightly favored not only energetically but also by the fact that the entering atoms would permit retention to some extent of the type of electron distribution prevalent in the element, as is roughly indicated by Platt's valence cone. A hydrogen atom can establish only two ligancies in the formation of a bridge, whereas boron atoms have as many as six; but the disruption of the well distributed electron atmosphere in elementary boron is just about compensated by the new bonds formed with the hydrogen atoms. Hence, one may argue that the positive enthalpy of formation is essentially due to the *loss of H–H bonding*, $25(1 + p/n)$ being equal to the number of H_2 units lost.

One point remains to be demonstrated—that a similar smooth curve does not result for a system in which the bonds formed are best described in terms of electron pairs. Consider, for instance

$$50C(s) + 100H_2(g) = \frac{50}{n}\,C_nH_{2n+p} + 25\left(2 - \frac{p}{n}\right)H_2(g)$$

with $p = 2, 0, -2$. Inspection of Fig. 2 shows that plotting $(50/n)\ \Delta H_f^0$ against any simple function of (p/n) will not give a smooth curve; in particular $p/n = 0$ for all the olefins, while appreciable differences appear between alkene homologs. Only by drawing individual curves for each value of n can the various points be placed on parallel smooth functions. We have made further tests to determine whether compounds of carbon and hydrogen in which there is extensive resonance would fit into a scheme such as is suggested by Fig. 1. The general conclusion is that for a properly selected group of conjugated hydrocarbons such a scheme might apply.

Interconversion of the Boron Hydrides.—Before one is able to predict free energy increments for the interconversion of the boranes, some empirical procedure must be utilized to estimate the entropies. It is generally recognized that for a homologous series of compounds the entropy per mole of the ideal gas at one atmosphere plotted against log M (mol. wt.) gives a fairly smooth curve. Typical curves are shown in Fig. 3. Note that the branched alkanes and alkenes fall on one curve. Furthermore, diborane, pentaborane-9 and decaborane form a lower smooth curve. This difference is a striking confirmation of the fact that in the hydrocarbons there is considerable internal rotation whereas in the hydrides of boron this is lacking due to the compact nature of the structures. We

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[7] W. Chupka, private communication. For comparison, see A. W. Searcy and C. E. Myers, *J. Phys. Chem.*, **61**, 957 (1957).

TABLE I

ESTIMATED ENTHALPIES OF FORMATION AND IDEAL GAS ENTROPIES

Substance	$\Delta H_f^\circ(298)_{\text{kcal.}}$(g) Bauer		Prosen	$50(1 + p/n)$	Log M	S° (298)
B_2H_6		7.53[a]		150	1.441	55.32[a]
B_4H_4	8.3		9	50	1.675	61.5
B_4H_{10}	13.9		14	125	1.726	63 → 70
B_5H_{11}	16.5		15 5	110	1.813	67 → 71
B_5H_9		15.02[a]		90	1.799	65.95[a]
B_8H_{14}	23.5			87.5	2.002	77.30
B_6H_{10}	17.2		16	83.3	1.874	69.60
$B_{10}H_{14}$		27.0[a]		70	2.086	85.09[a]
$B_{12}H_{12}$	24.7			50	2.152	88.80
H_2(g)		....		....	.....	31.21[a]
BH_3(g)		18[a]		[150]	[1.140]	44.9
B_5H_9(l)		7.72[a]		....	.....	44.03[a]
$B_{10}H_{14}$(s)		8[a]		....	.....	42.20[a]
$B_{12}H_{12}$(s)		7		....	.....	44
B(c)		....		....	.....	1.4[a]

[a] Designates a measured value; the others are either interpolated or estimated.

TABLE II

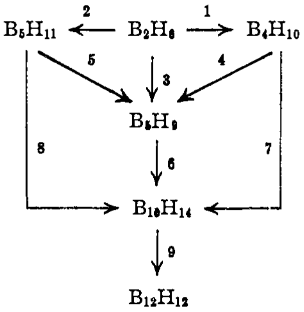
APPROXIMATE EXPRESSIONS FOR: FREE ENERGY INCREMENTS (KCAL.) FOR THE INTERCONVERSION OF BORANES

(1)	$25B_2H_6(g) = \frac{50}{4}B_4H_{10}(g) + \frac{25}{2}H_2(g)$	$\Delta F^0 = -14 + (0.203 \text{ to } 0.118)T$
(2)	$25B_2H_6(g) = 10B_5H_{11}(g) + 20H_2(g)$	$= -23 + (0.093 \text{ to } 0.049)T$
(3)	$25B_2H_6(g) = 10B_5H_9(g) + 30H_2(g)$	$= -38 - 0.212T$
(4)	$\frac{50}{4}B_4H_{10}(g) = 10B_5H_9(g) + \frac{35}{2}H_2(g)$	$= -24 - 0.415T$
(5)	$10B_5H_{11}(g) = 10B_5H_9(g) + 10H_2(g)$	$= -15 - 0.306T$
(6)	$10B_5H_9(g) = 5B_{10}H_{14}(g) + 10H_2(g)$	$= -15 - 0.078T$
(7)	$\frac{50}{4}B_4H_{10}(g) = 5B_{10}H_{14}(g) + \frac{55}{2}H_2(g)$	$= -39 - (0.496 \text{ to } 0.408)T$
(8)	$10B_5H_{11}(g) = 5B_{10}H_{14}(g) + 20H_2(g)$	$= -30 - (0.380 \text{ to } 0.340)T$
(9)	$5B_{10}H_{14}(g) = \frac{50}{12}B_{12}H_{12}(g) + 10H_2(g)$	$= -32 - 0.257T$
(3a)	$25B_2H_6(g) = 10B_5H_9(l) + 30H_2(g)$	$= -111 + 0.006T$
(6a)	$10B_5H_9(l) = 5B_{10}H_{14}(s) + 10H_2(g)$	$= -37.2 - 0.083T$
(9a)	$5B_{10}H_{14}(s) = \frac{50}{12}B_{12}H_{12}(s) + 10H_2(g)$	$= -10.8 - 0.284T$
(10)	$5B_{10}H_{14}(s) = 50B(c) + 35H_2(g)$	$= -40 - 0.951T$
(11)	$\frac{50}{12}B_{12}H_{12}(s) = 50B(c) + 25H_2(g)$	$= -29.2 - 0.667T$

have therefore interpolated values for the other boranes from this curve (Table I). For tetraborane and pentaborane-11 the predictions are somewhat ambiguous since these molecules have relatively open structures and the relative contributions of the vibrational entropies to the total may exceed that of the other boranes. This is indicated on the graph (cross hatched vertical lines) and by the range of values given in the table.

From the values in Table I one can estimate the free energy increments for the following conversions (all components ideal gases at 1 atmosphere, at 25°); these are summarized in Table II.

It is interesting to note that in spite of the uncertainty in the *magnitude* of the entropy increments for the first two reactions, their *signs* are unambiguous; *i.e.*, ΔS_1^0 and ΔS_2^0 are both negative. Were it not for the concurrent reactions (5,8,4,7), these two reactions would reach equilibrium, and the driving force from diborane toward tetraborane and pentaborane-11 might be reversed at a sufficiently high temperature. The thermodynamic estimates are thus in accord with the observed decline in the yields of tetraborane and pentaborane-11 with increasing temperature of the hot zone, during the pyrolysis of diborane.



From the above approximate computations it is clear that when all of the reactants are in the gas phase the most stable compounds are those with the lowest value of p/n [$p/n = 0$ for $B_{12}H_{12}$: the minimum value is $p/n = -1$, for B(s) + H_2(g)]. When the reactants are in condensed phases, the drive toward loss of H_2, as measured by the corresponding free energy increment, is reduced. Thus, given a reaction in the form

$$\alpha A(g) = \beta B(c) + \gamma H_2(g);\ \Delta F^0(g) \quad \begin{pmatrix} T \text{ specified;} \\ p = 1 \text{ atm.} \\ \text{for } A(g) \end{pmatrix}$$

Then for

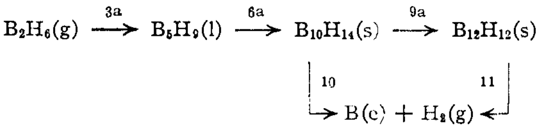
$$\alpha A(s) = \beta B(c) + \gamma H_2(g);\ \Delta F^0(s)$$

where A(s) designates the pure condensed phase of substance A, at T under an external pressure of 1 atm.

$$\Delta F^0(s) = \Delta F^0(g) - \alpha RT \ln(\text{v.p.})_{A,\text{ at }T}$$

Since compounds characterized by small (p/n)

values generally have low vapor pressures, there will be a reduced drive toward loss of H_2 from the condensed phase. This tendency also will be reduced by an appropriate selection of solvents for A. We have, therefore, included in Table II estimated free energy increments for the reactions



$$\begin{tikzcd}
B_2H_6(g) \arrow[r, "3a"] & B_5H_9(l) \arrow[r, "6a"] & B_{10}H_{14}(s) \arrow[r, "9a"] \arrow[d, "10"] & B_{12}H_{12}(s) \arrow[dl, "11"] \\
 & & B(c) + H_2(g) &
\end{tikzcd}$$

Ithaca, N. Y.

[Contribution from the National Bureau of Standards]

Ionization and Dissociation of Hydrazoic Acid and Methyl Azide by Electron Impact

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Relative abundances, appearance potentials and kinetic energy studies are reported for the principal positive and negative ions of hydrazoic acid and methyl azide. Probable ionization dissociation processes are outlined consistent with the observed and computed energetics and with adiabatic correlation rules. Bond dissociation energies and heats of formation of radicals and radical ions are calculated and compared with previously reported values. A 37 kcal./mole activation energy barrier to decomposition at room temperature is indicated for hydrazoic acid by the observed low value for $D(HN\text{-}N_2)$. Consideration of the various trinitrogen species results in the conclusions that both N_3^+ and N_3^- ions are stable entities whereas N_3 must be very unstable if it exists at all.

Introduction

Although the literature of electron impact phenomena includes mass spectrometric studies of a variety of organic and inorganic nitrogen compounds, it does not include data on the azides. These interesting compounds are generally unstable and frequently capable of explosive decomposition. The simplest azide, hydrazoic acid, is reported by Rice and co-workers[2,3] to undergo decomposition thermally or by electric discharge to give the imine radical, NH. The significance of the latter as a component in ultra-energy rocket fuels has been investigated by Baum, *et al.*,[4] although these workers find no evidence for the imine radical from HN_3. For these reasons, and as a preliminary step in the mass spectrometric study of the decomposition of hydrazoic acid, it was considered of interest to examine the bond strengths and ion energetics of certain simple azides. Accordingly, the present study was undertaken.

Experimental

Apparatus.—Measurements were made by means of a modified General Electric 60° sector-field mass spectrometer with a 6-inch radius of curvature. The modified Nier-Type ion source included a heavy-walled, relatively gas-tight ionization chamber designed for improved temperature distribution in the ionizing region and a favorable pressure differential between ionizing region and filament region. Temperature of the ion source was not regulated other than by maintaining constant filament temperature.

The filament emission was manually controlled and maintained constant by a regulated d.c. power supply. The electron beam was collimated by a source magnet field of about 150 gauss. The ionizing voltage (electron accelerating voltage) was selected by means of a precision voltage divider providing minimum voltage increments of 0.01 v. in the range of 0 to 100 v.

The analyser tube was operated at high voltage while the ion source was maintained near ground potential. A variable biasing voltage applied to the source permitted observations of stopping potentials for ions formed with excess kinetic energy. Necessary changes in the ion collector assembly essentially followed the suggestions of Fox and Hipple.[5]

The ion detection circuit included an Applied Physics Corporation Vibrating Reed Electrometer, Model 31, and a Leeds and Northrup Speedomax recorder. Minimum reproducible ion currents of 10^{-14} amp. were recorded using a 10^{11} ohm input resistor.

Procedure.—Conventional mass spectrometric techniques and procedures were used in sample introduction. Mass spectra were obtained for 70 v. electrons by continuously varying the ion deflecting magnetic field while maintaining constant ion accelerating voltage. Appearance potentials of the positive ions were evaluated from semi-log plots of ion current *versus* ionizing voltage for the unknown ion and the calibrating gas, argon. Curves were normalized and uncertainties estimated as previously described.[6] Appearance potentials of negative ions were evaluated from linear plots of ion current *versus* ionizing voltage. The latter scale was calibrated by measuring the maximum of the resonance attachment peak for the unknown ion compared with the maximum of the resonance attachment peak for the Cl^- ion of HCl.[7]

Materials.—Hydrazoic acid was prepared by the reaction of 60–80% sulfuric acid with solid or aqueous sodium azide using vacuum techniques. The product vapors were collected in a sample bulb fitted with a stopcock and demountable standard taper for attachment to the mass spectrometer. Mass spectrometric analysis indicated a high purity material (~99%). However, the use of concentrated sulfuric acid on dry sodium azide almost invariably resulted in a product grossly contaminated with impurities not easily separable by simple bulb-to-bulb distillation.

Methyl azide was prepared by the reaction of dimethyl sulfate and aqueous sodium azide using vacuum techniques. Mass spectrometric analysis of the product vapors indicated dimethyl ether as a major impurity. To avoid the possible danger of handling the relatively large amounts required for fractional distillation, the purification was accomplished by passing the crude material through a gas chromatograph. The effluent vapors desorbed from the column easily were diverted to collection bulbs when the detector indicated evolution of the methyl azide fraction. Mass spectrometric analysis gave no indication of impurities in the separated fraction other than a trace of water vapor.

Results

Tables I and II give the relative abundances of ions from hydrazoic acid and methyl azide, respectively, together with the appearance potentials of

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[1] Guest Scientist on leave from the Humble Oil and Refining Co., Baytown, Texas.

[2] F. O. Rice and M. Freamo, This Journal, **73**, 5529 (1951).

[3] F. O. Rice and C. Grelecki, *ibid.*, **79**, 1880 (1957).

[4] L. Baum, H. Graff, E. I. Hormats and G. Moe, Air Force Office of Scientific Research, Report No. 1149, July, 1956.

[5] R. E. Fox and J. A. Hipple, *Rev. Sci. Instr.*, **19**, 462 (1948).

[6] V. H. Dibeler and R. M. Reese, *J. Research Natl. Bur. Standards*, **54**, 127 (1955).

[7] R. E. Fox, *J. Chem. Phys.*, **26**, 1281 (1957).