plexity of the system and is beyond the scope of this study.

Pyrolysis and Photolysis of CF_3OCl. Since CF_3OF appears to be a good precursor for generating $CF_3O\cdot$ radicals,[29] CF_3OCl, having an even weaker O–halogen bond, was studied. The photolytic gas-phase decomposition of CF_3OCl producing CF_3OOCF_3 and Cl_2 in high yields[8] indicates the formation of an intermediate $CF_3O\cdot$ radical. However, photolysis of CF_3OCl at 13°K in Ar matrix was ineffective, and photolysis in the gas phase during sample deposition and pyrolysis produced COF_2 as the only new product. The lack of evidence for a $CF_3O\cdot$ radical indicates either that the $CF_3O\cdot$ radical is very short lived, decomposing rapidly to COF_2, or that CF_3OCl decomposes under the given conditions in a reversal of its formation reaction

$$CF_3OCl \longrightarrow COF_2 + ClF \qquad (7)$$

The presence of ClF as by-product could not be established; however, ClF is known to be an extremely weak infrared absorber, and, hence, may have escaped detection.

Acknowledgment. We are indebted to Mr. R. D. Wilson for his help in assembling the experimental set-up. This work was sponsored by the Air Force Rocket Propulsion Laboratory, Research and Technology Division, Edwards, California, Air Force Systems Command, USAF.

[29] W. A. Shepard and C. M. Sharts, "Organic Fluorine Chemistry," W. A. Benjamin, New York, N. Y., 1969, p 220.

Chemical Ionization Mass Spectrometry of Borazine

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Abstract: Chemical ionization mass spectra of borazine in methane, ethane, *n*-butane, and ammonia have been obtained. Protonation of borazine to form $H_3B_3N_3H_4^+$ and fragmentation by loss of H to form $H_2B_3N_3H_3^+$ are the major processes observed when methane is used as the source of reactant ions. Protonation reactions become relatively more important than fragmentation in the borazine–ethane system. The mass spectrum of borazine in *n*-butane consists almost exclusively of the ion species $H_3B_3N_3H_4^+$. A lower limit of 7.7 eV is set for the proton affinity of borazine. Borazine undergoes addition reactions with $C_2H_5^+$, $C_3H_7^+$, and $C_4H_9^+$ to form complexes assumed to be protonated *B*-alkylborazine ions. A complex species, $(NH_3)H_2B_3N_3H_3^+$, is observed in the borazine–ammonia system.

Borazine ($H_3B_3N_3H_3$) is frequently referred to as "inorganic benzene"[1] because of its structural similarity to benzene. However, the chemical behavior of the two compounds differs in many respects. One of the unique features of borazine, owing to the heterocyclic nature of the B–N ring, is its tendency to form adducts readily by addition of simple acids or bases. As a new approach to the study of this feature of borazine chemistry, we have employed the procedure referred to by Field[2] as chemical ionization mass spectrometry to investigate gas-phase ion–molecule reactions of borazine. The sources of ion reactants include CH_4, C_2H_6, n-C_4H_{10}, and NH_3.

Experimental Section

The mass spectrometer used in these experiments was a 10-in., 60° direction-focusing instrument. The chemical ionization source was constructed by modifying the ion box associated with a Nier-type source used for electron bombardment work. The ion box was sealed except for a 0.002 × 0.4 in. exit slit and a tapered opening on the side to accept a $^5/_{20}$ male joint from a glass delivery tube. This tube was joined by a small piece of flexible Teflon tubing to another glass tube that passed out the vacuum wall through a Swagelok-type fitting to the gas source. The analyzer and source compartments of the mass spectrometer were separated by a 0.007 × 0.4 in. slit, and each section was pumped with a 4-in. diffusion pump using Dow Corning 705 silicone pump fluid. Our ion source differs in several respects from those of other workers, and some differences in operating conditions should also be noted.

In initial experiments, iridium filaments were used for the source of electrons for ionization, but these were destroyed at high source pressures, apparently due to the presence of boron compounds. Tungsten filaments were found to be dependable up to source pressures of 3 mm and, for short periods, at source pressures as high as 4.5 mm. For most of the experimental observations the electron energy was maintained at 80 V. It was noted in test runs with methane that the CH_5^+/CH_4^+ ratio decreased for a constant source pressure as the electron energy was reduced to 50 V. The two drawing-out plates located above the source slit could be maintained at potentials of between 0 and −280 and 0 and −450, respectively. Variation in these potentials affected greatly the overall ion sensitivity but did not have a marked effect on the CH_5^+/CH_4^+ ratios. A small residual CH_4^+ signal was noted at source pressures as high as 2 mm. The ion accelerating voltage was maintained at 2800 V.

Gas mixtures were prepared by measuring the partial pressure of a sample of borazine in a 2-l. bulb with a silicone oil manometer and then adding a quantity of the reagent gas to bring the final pressure to a desired value from which the composition could be obtained. Gas flow to the ion source from the sample bulb was regulated through a Nupro fine metering valve with vernier handle. The gas pressure in the ion-source delivery tube was measured with a McLeod gauge. In a different series of experiments, a small quantity of borazine was injected through a metering valve into the hydrocarbon gas stream in front of the source entrance. With this procedure the hydrocarbon gas pressure could be maintained at a constant level while the effect of chemical ionization could be noted by comparing relative ion intensities before and after the addition of borazine. Borazine was prepared from *B*-trichloroborazine by the procedure of Hohnstedt and Haworth.[3] Methane, ethane, butane,

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(1) A. Stock in "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933, p 97.

(2) M. S. B. Munson and F. H. Field, *J. Amer. Chem. Soc.*, **88**, 2621 (1966).

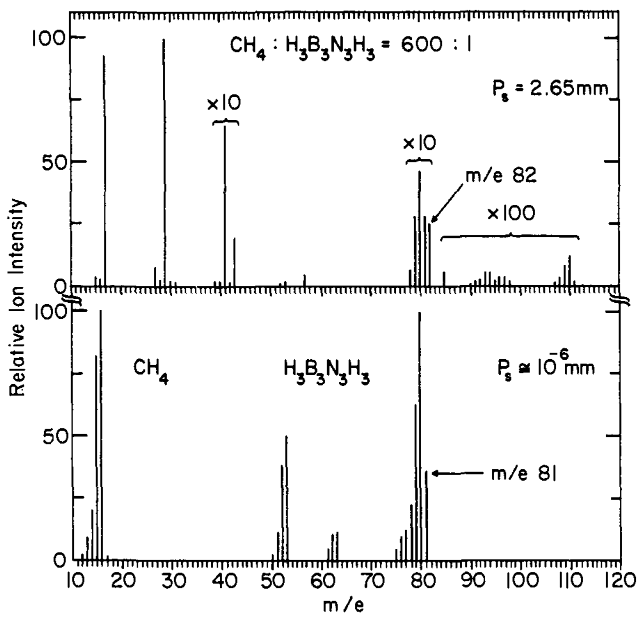

Figure 1. Mass spectral displays of low-pressure system of borazine and methane (lower figure) and the chemical ionization mass spectrum at a high source pressure (upper figure).

and ammonia were obtained from commercial sources. The purity of the gases was checked by mass spectral analysis. Traces of hydrocarbon impurities were found in the methane and butane; these did not cause serious problems in interpretation of the chemical ionization data. The ethane used was purified by repeated condensation and distillation in a liquid-nitrogen-cooled trap.

Results

Chemical ionization mass spectra obtained from CH_4-borazine, C_2H_6-borazine, n-C_4H_{10}-borazine, and NH_3-borazine mixtures are indicated in Table I. As shown in Figure 1, evidence that reaction is occurring between hydrocarbon ions from methane and borazine is clearly indicated from the increase in intensity of parent + 1 ion ($H_3B_3N_3H_4^+$) in the borazine spectrum as the source pressure is increased. The normal electron-impact spectrum of borazine (Figure 1) shows a large fragmentation contribution in the range m/e 51–53 ($H_3B_2N_2^+$) with an intensity ratio for m/e 53:80 of about 0.5. In the chemical ionization spectrum of borazine, low-mass ion fragments are almost totally absent and the ion spectrum is clustered in the region from about m/e 77 to 82. A weaker spectrum of complex ion species also appears at higher masses. The dependence of chemical ionization of borazine on the hydrocarbon reactant and the source pressure is shown in Table II. In the CH_4-borazine spectrum a significant intensity of the parent − 1 peak ($H_2B_3N_3H_3^+$) is obtained over the entire pressure range studied. The intensity ratio of $H_3B_3N_3H_4^+/H_2B_3N_3H_3^+$ is enhanced in the ethane spectrum, and in butane $H_3B_3N_3H_4^+$ is produced exclusively at the highest pressures.

Results of experiments in which borazine was added to the hydrocarbon gas stream before it entered the ion source are shown in Table III. Since the source pressure remained nearly constant while these measurements were taken, the decrement in I_i/I_t for the hydrocarbon ion reactants should be balanced by the increment in I_i/I_t for product ions. How close this approximation holds for each system studied is indicated by summations at the bottom of the column of data in Table III.

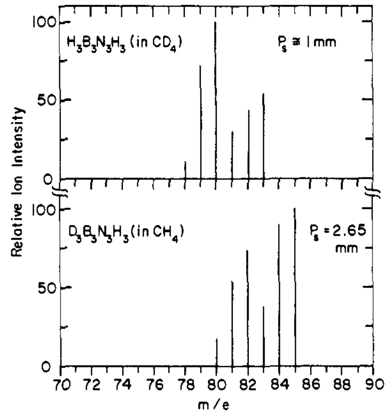

Figure 2. Chemical ionization mass spectrum of $H_3B_3N_3H_3$ in CD_4 and $D_3B_3N_3H_3$ in CH_4.

Discussion

Before proceeding with a discussion of the energetics or kinetics of ion–molecule reactions involving borazine, we must establish simple reaction paths. The data in Table III are the most helpful for this purpose. One obvious feature in comparing the parent + 1/parent − 1 ratios in mass spectra of alkane–borazine mixtures is that CH_5^+ must be efficient in removing a H atom from borazine. We can express, for the general case of dissociative proton transfer

$$RH^+ + H_3B_3N_3H_3 \longrightarrow R + H_2 + H_2B_3N_3H_3^+ \qquad (1)$$

Mass spectral patterns for CH_4-$D_3B_3N_3H_3$ and CD_4-$H_3B_3N_3H_3$ mixtures are shown in Figure 2. It is apparent from these spectra that the hydrogen atom removed from borazine was originally bound to the B atom. Field and coworkers[2] have observed that CH_5^+ can undergo both dissociative and nondissociative proton-transfer reactions. The protonation of borazine may be expressed by the general equation

$$RH^+ + H_3B_3N_3H_3 \longrightarrow R + H_3B_3N_3H_4^+ \qquad (2)$$

To identify the ion reactants that are proton donors to borazine it is convenient to consider first the n-C_4H_{10}-borazine system. In this case $H_3B_3N_3H_4^+$ is the major product ion and, as the data in Table III show, the large increment in $I_{H_3B_3N_3H_4^+}/I_t$ is nearly balanced by the decrement in $I_{C_4H_9^+}/I_t$, indicating that $C_4H_9^+$ is a reactant according to reaction 2. In the C_2H_6-borazine system, several hydrocarbon ions including $C_2H_5^+$ and $C_2H_4^+$ appear to be effective protonating agents for borazine. Some fraction of the change in hydrocarbon ion intensities when borazine is present must result from the production of $H_2B_3N_3H_3^+$, but most of the product ion is $H_3B_3N_3H_4^+$ under those conditions. For $C_2H_4^+$ the dissociative proton-transfer reaction (reaction 1) is unlikely because of energy restrictions (see later discussion).

In the CH_4-borazine system, reactions 1 and 2 are of about equal importance. Since, as we noted above, CH_5^+ must be effective in removing H from borazine, a significant fraction of the protonated borazine species must be due to reaction through $C_2H_5^+$. It is also possible that $C_2H_5^+$ could react with borazine through

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(3) L. F. Hohnstedt and D. T. Haworth, *J. Amer. Chem. Soc.*, **82**, 89 (1960).

Table I. Chemical Ionization Mass Spectra of Alkane–Borazine and NH_3–Borazine Mixtures

	CH_4 + borazine[a]		C_2H_6 + borazine[b]		n-C_4H_{10} + borazine[c]		NH_3 + borazine[d]		
m/e	Intensity	Ionic species	Intensity	Ionic species	Intensity	Ionic species	Intensity	Ionic species	m/e
13	19.0		4.0						13
14	38.0		10.0	CH_2^+	3.0				14
15	174.0	CH_3^+	27.0	CH_3^+	31.0	CH_3^+	15.0		15
16	137.0	CH_4^+	4.0				50.0	NH_2^+	16
17	889.0	CH_5^+	8.0				226.0	NH_3^+	17
18	19.0		4.0				1000.0	NH_4^+	18
19	19.0		4.0				3.0		19
26	19.0		38.0				0.3		26
27	231.0	$C_2H_3^+$	150.0	$C_2H_3^+$	50.0	$C_2H_3^+$	1.0		27
28	134.0	$C_2H_4^+$	1000.0	$C_2H_4^+$	13.0		1.5		28
29	1000.0	$C_2H_5^+$	738.0	$C_2H_5^+$	31.0	$C_2H_5^+$	1.3		29
30	42.0		244.0	$C_2H_6^+$	31.0		0.9		30
31	82.0	$C_2H_7^+$	31.0				0.8		31
32			13.0				0.9		32
33							0.3		33
35							0.2		35
36							0.4		36
37							1.1		37
38							1.0		38
39			24.0		62.0	$C_3H_3^+$			39
40			6.0		6.0				40
41	132.0	$C_3H_5^+$	167.0	$C_3H_5^+$	31.0	$C_3H_5^+$	0.1		41
42			13.0		13.0		0.6		42
43	49.0	$C_3H_7^+$	150.0	$C_3H_7^+$	130.0	$C_3H_7^+$	1.2		43
44			11.0				0.2		44
45							0.8		45
46							0.2		46
47							0.1		47
50							0.2		50
51	9.0						1.0		51
52	14.0						3.6		52
53	19.0	$B_2N_2H_3^+$					5.6	$B_2N_2H_3^+$	53
54							0.1		54
55			17.0		9.0				55
56			13.0		94.0				56
57	19.0	$C_4H_9^+$	124.0	$C_4H_9^+$	1000.0	$C_4H_9^+$			57
58			13.0		130.0		0.1		58
59							0.1		59
60							0.3		60
61							0.5		61
62							0.7		62
63							0.5		63
65							0.1		65
66							0.4		66
67							1.1		67
68							1.7		68
69					3.0		0.4		69
70					2.0		0.8		70
71	14.0	$C_5H_{11}^+$	4.5	$C_5H_{11}^+$	16.0	$C_5H_{11}^+$			71
72			1.2		3.0				72
73			2.4						73
75							0.2		75
76							0.7		76
77			3.0				1.8		77
78	52.0		7.2				2.9		78
79	177.0		18.9		2.0		3.3		79
80	259.0	$H_2B_3N_3H_3^+$	33.9		20.0		4.2	$H_2B_3N_3H_3^+$	80
81	207.0		39.0		75.0		0.3		81
82	238.0	$H_3B_3N_3H_4^+$	41.7	$H_3B_3N_3H_4^+$	103.0	$H_3B_3N_3H_4^+$	0.2		82
83			0.7		1.0				83
85			0.7	$C_6H_{13}^+$	1.56	$C_6H_{13}^+$			85
86			0.3		0.13				86
89	1.4		0.3		0.09				89
90	1.7		0.5		0.26		0.1		90
91	5.7	$C_7H_7^+$	0.9	$C_7H_7^+$	3.20	$C_7H_7^+$	0.2		91
92	1.7		0.1		0.26		0.6		92
93	2.4		0.2		0.22		0.7		93
94	4.0	$CH_3HB_3N_3H_3^+$	0.2		0.20		0.5		94
95	2.8		0.3		0.45		2.0		95
96	4.0		0.2		0.13		6.4		96
97	4.0		0.3		0.32		8.9	$(NH_3)H_2B_3N_3H_3^+$	97
98	3.8	$(OH_2)H_2B_3N_3H_3^+$	0.2		0.26		0.2		98
99			0.1		0.20				99
105			0.2		0.05				105
106	1.7		0.4		0.13				106
107	2.4		1.1		0.50				107

Table I (*Continued*)

m/e	CH_4 + borazine[a] Intensity	CH_4 + borazine[a] Ionic species	C_2H_6 + borazine[b] Intensity	C_2H_6 + borazine[b] Ionic species	n-C_4H_{10} + borazine[c] Intensity	n-C_4H_{10} + borazine[c] Ionic species	NH_3 + borazine[d] Intensity	NH_3 + borazine[d] Ionic species	m/e
108	6.1		2.3		0.58	$(C_2H_3)H_2B_3N_3H_4^+$			108
109	15.5		4.0		0.14				109
110	20.5	$(C_2H_5)H_2B_3N_3H_4^+$	3.9	$(C_2H_5)H_2B_3N_3H_4^+$	0.17				110
111	3.1		0.8		0.41				111
112	2.6		0.5		0.47				112
113					0.45	$C_8H_{17}^+$			113
114					0.05				114
119					0.14	$C_9H_{11}^+$			119
120			0.2		0.04				120
121			0.5		0.09				121
122			0.7	$(C_3H_5)H_2B_3N_3H_4^+$	0.20				122
123			0.3		0.41				123
124			0.3	$(C_3H_7)H_2B_3N_3H_4^+$	0.56	$(C_3H_7)H_2B_3N_3H_4^+$			124
125					0.05				125
132					0.05				132
133					0.09				133
134					0.16				134
135					0.41				135
136					0.72				136
137					1.39				137
138					1.78	$(C_4H_9)H_2B_3N_3H_4^+$			138
139					0.13				139

[a] $CH_4:B_3N_3H_6$ = 160:1, P_s (source pressure) = 2.96 mm. [b] $C_2H_6:B_3N_3H_6$ = 462:1, P_s = 2.50 mm. [c] n-$C_4H_{10}:B_3N_3H_6$ = 210:1 P_s, = 2.05 mm. [d] $NH_3:B_3N_3H_6$ = 466:1, P_s = 1.50 mm.

Table II. Mass Spectra of Borazine Obtained by Chemical Ionization in Methane, Ethane, and *n*-Butane at Various Source Pressures

Reaction composition	P_s, mm	m/e 82	81	80	79	78	77
$CH_4/H_3B_3N_3H_3$ = 160	2.40	68.5	76.4	100.0	57.9	19.7	9.2
	3.48	100.0	85.2	96.5	60.0	16.9	4.2
	4.10	100.0	80.2	63.0	39.3	11.3	4.2
$C_2H_6/H_3B_3N_3H_3$ = 460	1.15	38.5	80.5	100.0	53.1	16.1	6.2
	1.95	92.6	100.0	92.6	53.2	16.9	8.1
	2.55	100.0	84.0	68.0	37.6	13.0	∼0
n-$C_4H_{10}/H_3B_3N_3H_3$ = 210	0.95	100.0	93.9	62.5	50.0	31.2	20.3
	1.15	100.0	84.6	29.2	12.3	4.6	∼0
	1.45	100.0	74.6	21.6	2.5	0.0	0.0
	2.05	100.0	71.5	23.1	2.4	0.0	0.0
	∼4	100.0	77.2	18.5	1.9	0.0	0.0
Calculated isotopic distribution for $H_3B_3N_3H_4^+$		100.0	74.56	18.61	1.55	0.00	0.00

Table III. Ion Balance Relationships in the Chemical Ionization Mass Spectra of Alkane–Borazine Mixtures[a]

Ion	CH_4–borazine[b] $\Delta(I_i/I_t)$	Ion	C_2H_6–borazine[c] $\Delta(I_i/I_t)$	Ion	n-C_4H_{10}–borazine[d] $\Delta(I_i/I_t)$
CH_3^+	−2.81	$C_2H_2^+$	−0.89	$C_3H_5^+$	−0.67
CH_4^+	−3.44	$C_2H_3^+$	−5.39	$C_3H_7^+$	−3.34
CH_5^+	−20.72	$C_2H_4^+$	−12.37	$B_2N_2H_3^+$	+0.49
H_3O^+	−1.07	$C_2H_5^+$	−11.66	$C_4H_7^+$	−0.59
$C_2H_3^+$	−2.40	$C_2H_6^+$	−4.12	$C_4H_8^+$	−3.44
$C_2H_4^+$	−1.00	$C_3H_5^+$	−2.17	$C_4H_9^+$	−47.59
$C_2H_5^+$	−13.09	$C_3H_6^+$	−0.78	$C_4H_{10}^+$	−6.13
$B_2N_2H_3^+$	+3.10	$C_3H_7^+$	−0.46	*m/e* 76–82	+54.16
$C_4H_{11}^+$ [e]	+1.55	$B_2N_2H_3^+$	+2.27	*m/e* > 82	+7.83
m/e 76–82	+30.13	*m/e* 76–82	+27.28		
m/e > 82	+9.59	*m/e* > 82	+6.71		
Summation	−0.16		−1.58		+0.72

[a] $I_t = \Sigma_i I_i$. Values given are in per cent. [b] P_s = 2.6 mm. [c] P_s = 1.8 mm. [d] P_s = 1.4 mm. [e] May be due to C_4H_{10} impurity.

hydride abstraction to form C_2H_6 and $H_2B_3N_3H_3^+$. The primary ions CH_3^+ and CH_4^+ which have not been completely removed by reaction with CH_4 may be reacting with borazine, but the data in Table III indicate these effects are not of major importance.

Ions of the types $(C_nH_{2n+1})H_3B_3N_3H_3^+$ and $(C_nH_{2n-1})H_3B_3N_3H_3^+$ can occur by simple addition reactions

$$C_nH_{2n\pm1}^+ + H_3B_3N_3H_3 \longrightarrow (C_nH_{2n\pm1})H_3B_3N_3H_3^+ \quad (3)$$

or by dissociative proton-transfer reactions

$$C_nH_{2n+3}^+ + H_3B_3N_3H_3 \longrightarrow (C_nH_{2n+1})H_3B_3N_3H_3^+ + H_2 \quad (4)$$

and

$$C_nH_{2n+1}^+ + H_3B_3N_3H_3 \longrightarrow (C_nH_{2n-1})H_3B_3N_3H_3^+ + H_2 \quad (5)$$

The complex species $(C_2H_5)H_3B_3N_3H_3^+$, $(C_3H_7)H_3$-

$B_3N_3H_3^+$, and $(C_4H_9)H_3B_3N_3H_3^+$ are observed under conditions where the intensity of $C_nH_{2n+3}^+$ ions necessary for reaction 4 is very low. This indicates reaction 3 rather than 4 is occurring in a number of cases. For reaction 4 only the cases with $n = 1$ or 2 have been observed.

Energetics of Ion–Molecule Reactions. Based on the principle that exothermic ion–molecule reactions require small activation energies and are more probable than endothermic reactions under most ion source conditions, we can set minimal energy limits for reactions 1 and 2. The enthalpy (ΔH_1) for reaction 1 is given by

$$\Delta H_1 = \mathrm{PA(R)} + \mathrm{AP}(H_2B_3N_3H_3^+) - \mathrm{IP(H)} - D_0^0(H_2)$$

where PA(R) is the proton affinity of R, $\mathrm{AP}(H_2B_3N_3H_3^+)$ is the minimum appearance potential of $H_2B_3N_3H_3^+$ from borazine, and IP(H) and $D_0^0(H_2)$ are the ionization potential of H and the dissociation energy of H_2, respectively. Using well-established values[4] for the latter two quantities and a value of 11.5 eV[5] for the appearance potential of $H_2B_3N_3H_3^+$, we obtain for the reaction criterion, $\Delta H_1\ (\mathrm{eV}) = \mathrm{PA(R)} - 6.6 \leq 0$. Neglecting uncertainty in $\mathrm{AP}(H_2B_3N_3H_3^+)$, which is probably of the order of a few tenths of an electron volt, this energy relationship indicates that dissociative proton transfer is possible if the proton affinity of R is less than about 6.6 eV. Of the possible ions listed in Table IV, CH_5^+ will easily meet this boundary condition for reaction 1, while $C_2H_3^+$, $C_2H_6^+$, and $C_4H_9^+$ are somewhat marginal and $C_2H_4^+$, $C_2H_5^+$, $C_3H_5^+$, and $C_3H_7^+$ are expected to be unreactive. Thermochemical data[6] indicate for the reaction

$$C_2H_5^+ + H_3B_3N_3H_3 \longrightarrow C_2H_6 + H_2B_3N_3H_3^+ \qquad (6)$$

a value of $\Delta H_6 = -1.3$ eV. This suggests that in both the CH_4–borazine and C_2H_6–borazine systems reaction 6 is likely. Based on the high proton affinity of NH_3 (~9.4 eV),[4] reaction 1 with $R = NH_3$ is considered highly improbable. In the NH_3-borazine system hydride abstraction may occur by reaction of a primary ion with borazine. A reaction that is energetically favorable is

$$NH_2^+ + H_3B_3N_3H_3 \longrightarrow NH_3 + H_2B_3N_3H_3^+ \qquad (7)$$

Table IV. Minimum Proton Affinity of Borazine Based on Reactions of Hydrocarbon Ions With Borazine (Reaction 2)

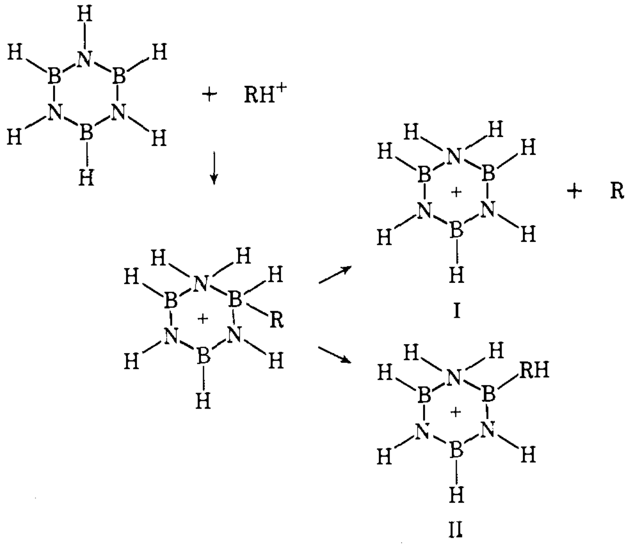
Possible reactant RH^+	PA(R),[a] eV
CH_5^+	5.0–5.2
$C_2H_3^+$	6.56
$C_2H_4^+$	7.72
$C_2H_5^+$	6.92
$C_2H_6^+$	6.33
$C_3H_3^+$	
$C_3H_5^+$	8.43–8.50
$C_3H_7^+$	7.02–8.18
$C_4H_9^+$	6.24–8.52

[a] Data for CH_5^+ taken from M. S. Munson and F. H. Field, *J. Amer. Chem. Soc.*, **87**, 3294 (1965). All other data taken from ref 6.

Calculations using the appearance potentials of NH_2^+ from NH_3,[7] and $H_2B_3N_3H_3^+$ from borazine indicate ΔH_7 to be −4.3 eV. The $H_2B_3N_3H_3^+$ intensity is diminished at high source pressures; this may reflect loss of NH_2^+ reactant by competing processes.

The exothermicity condition for reaction 2 is $\Delta H_2 = \mathrm{PA(R)} - \mathrm{PA}(H_3B_3N_3H_3) \leq 0$. A lower limit on the proton affinity of borazine can be established provided ion reactants for reaction 2 are known. From the reactants $C_4H_9^+$, $C_2H_5^+$, and $C_2H_4^+$ identified earlier and the information in Table IV, lower limits on the proton affinity of borazine are set at 6.2, 6.9, and 7.7 eV, respectively. The last value, of course, is the most significant. Other ions listed in Table IV that should also meet the boundary condition for reaction 2 are CH_5^+, $C_2H_3^+$, $C_2H_6^+$, and $C_3H_7^+$.

Proton attachment to borazine is expected to occur at an N atom, since this is the more basic reaction site in the molecule. Following a simple analogy with a reaction in which an acid like HCl adds to borazine,[8] we can visualize a simple mechanism that will account both for protonation and for complex formation by hydrocarbon ions through the following scheme



The implication of this mechanism is that for $R = C_2H_4$, C_3H_6, and C_4H_8 product II has the alkyl group bound to a boron atom and corresponds in the ground state to a protonated *B*-alkylborazine species. In general, the yields of product II are one to two orders of magnitude below that for I. This may be accounted for by a mechanism that requires a third body for II but not for I. More than one structure for the product of reaction 3 with $C_3H_5^+$ or $C_2H_3^+$ as reactants is possible. In these cases structure II would have an unsaturated group bound to a boron atom. However, other species

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(4) V. I. Vedeneev, L. V. Gurvich, V. N. Kondrat'yev, V. A. Medvedev, and Ye. L. Frankevich, "Bond Energies, Ionization Potentials and Electron Affinities," Edward Arnold Ltd., London, 1966.

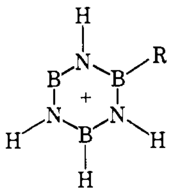
(5) E. D. Loughran, C. L. Mader, and W. E. McQuistion, Atomic Energy Commission Report LA-2368, 1960.

(6) J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions," NSRDS-NBS 26, U. S. Government Printing Office, Washington, D. C., 1969.

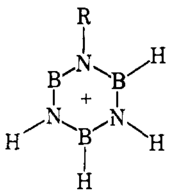
(7) M. M. Mann, A. Hustrulid, and J. T. Tate, *Phys. Rev.*, 58, 340 (1940).

(8) A. W. Laubengayer, O. T. Beachley, and R. F. Porter, *Inorg. Chem.*, 4, 578 (1965). (Note: HCl adds to borazine in a 3:1 proportion, while only one hydrocarbon ion adds to form the complexes observed in the present work.)

that are probably more stable are



or

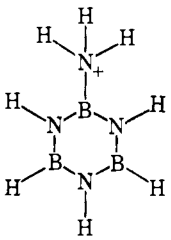


These correspond to the parent − 1 ion of the *B*-alkylborazine or *N*-alkylborazine, respectively.

The species $(NH_3)H_2B_3N_3H_3^+$ observed in the NH_3–borazine system is most probably the protonated form of *B*-monoaminoborazine formed by the reaction

$$NH_4^+ + H_3B_3N_3H_3 \longrightarrow (NH_3)H_2B_3N_3H_3^+ + H_2 \qquad (8)$$

A reasonable structure for the product is



In this case it is unlikely that a proton is transferred to the borazine ring.

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Lowest Excited States of Ketene[1]

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Abstract: Analysis of the vibrational progression evident in the absorption spectrum of ketene suggests the absorption is due to a singlet–singlet transition and indicates the energy of the lowest singlet state is less than 61 kcal/mol (2.65 eV) above the ground state. Reasonable singlet–triplet energy splittings place the energy of the lowest triplet at less than 55 kcal/mol (2.39 eV). This conclusion is in agreement with recent results which demonstrate that ketene quenches the triplet state of biacetyl. Attempts to directly observe the triplet state of ketene by a variety of spectroscopic methods, including gas- and liquid-phase absorption spectroscopy, oxygen enhancement techniques, and triplet ← triplet absorption spectroscopy, were unsuccessful.

Recent spectroscopic data from our laboratory in combination with a reinterpretation of the published results of other workers[2] have led us to conclude that the lowest excited singlet level of ketene is below 61 kcal/mol (2.65 eV) and the lowest triplet level is below 55 kcal/mol (2.39 eV). The values are *much* lower than the commonly accepted values[2] of E_S = 74 kcal/mol (3.21 eV) and E_T = 61 kcal/mol (2.65 eV).

Ketene has been widely used as a photochemical source of triplet and singlet methylene radicals. Recent evidence, primarily based upon product analysis and quenching data, has suggested that both spin states of methylene are formed by photolysis of ketene at all wavelengths less than 3660 Å.[3,4] Spin conservation requires the postulating of triplet ketene as the precursor to triplet methylene. Direct evidence for triplet ketene is sparse, but a spectroscopic investigation has positioned the lowest triplet state of ketene at 61 kcal/mol (2.65 eV) above the ground state.[2] Using the sensitized phosphorescence of triplet biacetyl as a test for triplet ketene, Grossman, *et al.*,[2a] observed that ketene quenched rather than enhanced emission from biacetyl.

A recent redetermination of $\Delta H_f°(CH_2CO)$ = -11.4 ± 0.4 kcal/mol,[5] together with $\Delta H_f°(CH_2) \leqslant 94$ kcal/mol,[6] and $\Delta H_f°(CO) = -27.2$ kcal/mol,[7] suggests a bond dissociation energy in the neighborhood of 78 kcal/mol (3.38 eV). This value is in agreement with the fact that only photons with energy in excess of 3.38 eV photodissociate ketene and suggests that predissociation is not important in excited states of energy less than 3.38 eV. This is in contrast to the results of Dixon and Kirby,[2b] who have suggested the triplet state of ketene is predissociated, setting an upper limit for the bond dissociation energy of ketene as 61 kcal/mol. Interest in our laboratory in the mechanism of photodissociation and the thermodynamic values of ketene has prompted us to reinvestigate the absorption spectrum of this molecule. Our studies included (a) gas- and liquid-phase absorption spectra, (b) search for absorption from metastable states following flash photolysis, and (c) investigation of the oxygen-intensification technique which is known to enhance weak singlet–triplet transitions.[8]

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[1] Work supported in part by the United States Atomic Energy Commission.

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