in a 1-cm cell varied from 0.400 with $[IO_3^-] = 0.0$ to 0.445 with $[IO_3^-] = 0.070$ M. With an extinction coefficient of 92 $M^{-1}\ cm^{-1}$ for $IrCl_6^{3-}$,[14] the extinction coefficient of the proposed species, $IrCl_6{\cdot}IO_3^{4-}$, would be 114 $M^{-1}\ cm^{-1}$ at 415 nm.

Discussion

If the denominator term in $[IO_3^-]$ does indeed arise from a complex formation reaction, one possible mechanism for the $IrCl_6^{3-} + IO_3^-$ reaction is given by eq 10–13. This mechanism

$$HIO_3 \overset{K_a}{\rightleftharpoons} IO_3^- + H^+ \qquad (10)$$

$$IrCl_6^{3-} + IO_3^- \overset{K_f}{\rightleftharpoons} IrCl_6{\cdot}IO_3^{4-} \qquad (11)$$

$$IrCl_6{\cdot}IO_3^{4-} + H^+ \xrightarrow{k_1} Ir(IV) + I(IV) \qquad (12)$$

$$IrCl_6{\cdot}IO_3^{4-} + 2H^+ \xrightarrow{k_2} Ir(IV) + I(IV) \qquad (13)$$

$$4Ir(III) + I(IV) \overset{\text{fast}}{=\!=} 4Ir(IV) + I(0) \qquad (14)$$

is consistent with those proposed for the ClO_3^- and BrO_3^- reactions, although several differences are apparent. In this mechanism, k_1, k_2, and K_a have the values given above and $K_f = B''$. There are numerous possible variations on this mechanism which are kinetically indistinguishable and equally consistent with the evidence at hand.[15,16] The absence of a first-order dependence on $[H^+]$ in the B'' term indicates that binuclear complex formation cannot involve HIO_3. However, the existence of a binuclear complex does not necessarily implicate its involvement as a reactant. Steps 12 and 13 could involve instead reactions between $IrCl_6^{3-}$ and HIO_3 (or $H_2IO_3^+$). The same form of rate law would be involved in each case although the identity of the parameters in the equation would differ. If the sum of terms in the denominator did not arise from binuclear complex formation, it would be necessary to devise a steady-state mechanism.[15,16] This does not seem very likely since such a mechanism would require $IrCl_6^{3-}$ to exist in two different forms with the second form participating as a steady-state intermediate.[16]

The existence of binuclear complexes of metal ions and iodate has some precedence. Complexes have been identified with the metal ions $Cr(H_2O)_6^{3+}$ (first and second formation constants 3.3 M^{-1} and 40 M^{-2}),[17] $Cr(NH_3)_5OH_2^{3+}$ (formation constant 11 M^{-1}),[18,19] *cis*-$Co(en)_2(H_2O)_2^{3+}$ (formation constant 2.3 M^{-1}),[19] and VO^{2+} (formation constants of 1.7 M^{-1} and 0.4 M^{-2}).[20] The formation of $H(IO_3)_2^-$ from HIO_3 and IO_3^- has also been proposed,[9] with a formation constant of 4.0 M^{-1} determined by potentiometric measurements and 3.0 M^{-1} by cryoscopic measurements. Thus it is not unreasonable to suggest the formation of a binuclear complex from $IrCl_6^{3-}$ and IO_3^-, although a formation constant of 27 M^{-1} does seem somewhat high considering the ionic charges of these species.

First-order and second-order hydrogen ion dependences are consistent with previous results on reactions of iodate. The reduction by $Fe(CN)_6^{4-}$ had a $[H^+]$ dependence identical with that observed here,[21] while the oxygen exchange between iodate and water follows a rate law containing these terms[22] as well as others.[23] The formation of $Cr(NH_3)_5IO_3^{2+}$ and of *cis*-$Co(en)_2(H_2O)IO_3^{2+}$ is first order in $[H^+]$,[19] and the reduction of IO_3^- by I^- is second order in $[H^+]$.[10,24] These results are all consistent with the general expectation for reactions of oxyanions,[2] as well as with the general observation[25] that when reactant and product differ in the number of protons, some of the protons are gained or lost prior to the rate-determining step.

The halate oxidations of $IrCl_6^{3-}$ all seem to have unique mechanistic features, although the occurrence of a net activation process

$$XO_3^- + IrCl_6^{3-} + 2H^+ \xrightarrow{k} \{H_2XO_3IrCl_6^{2-}\}^{\ddagger}$$

is a common feature of all three mechanisms. It is not possible to ascertain whether these activation processes all involve the same detailed steps or whether all the activated complexes have the same structures. Values of k calculated from appropriate combinations of rate parameters, with approximate corrections for the different conditions in the ClO_3^- study,[3] are 5×10^{-5}, 50, and 5 $M^- s^{-1}$ for X = Cl, Br, and I, respectively. These results are consistent with the general observation that IO_3^- and BrO_3^- oxidations are more facile than ClO_3^- oxidations, probably due to easier substitution on the larger and softer halogens.[2]

Acknowledgment. Partial support of this work by the Faculty Grant-in-Aid program at Arizona State University is gratefully acknowledged.

Registry No. IO_3^-, 15454-31-6; $IrCl_6^{3-}$, 14648-50-1; H^+, 12408-02-5.

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Contribution from the Department of Chemistry,
Cornell University, Ithaca, New York 14853

Acidity of $B_5H_9^+$ and Stability of the B_5H_8 Radical

Jia-Shen Wang, Anthony J. DeStefano, and Richard F. Porter*

Received September 1, 1977

A relatively unexplored area of boron chemistry is that concerned with the role of free radical intermediates. Especially scarce is information on the nature of radicals formed when a B–H bond is broken. The purpose of this paper is to report results of an experimental investigation of the stability of B_5H_8. Structural features of the B_5H_8 radical and the relevance of this species in the photochemistry of B_5H_9 will be noted.

Equilibrium studies of proton-transfer reactions in the gas phase have provided proton affinity data for a large number of stable molecules. For measurements of proton affinities of short-lived intermediates equilibrium techniques are gen-

0020-1669/78/1317-1374$01.00/0

erally difficult or impossible. However, through rate measurements for a series of proton-transfer reactions involving an unstable species, it is possible to place boundaries on its proton affinity.[1] In this paper we present thermochemical data for the reactive B_5H_8 radical from observations of a series of proton-transfer reactions

$$B_5H_9^+ + R \rightarrow RH^+ + B_5H_8 \qquad (1)$$

where R is a stable molecule with known proton affinity. The validity of this indirect method of relative proton-transfer rates relies on the assumption that the rates for exothermic proton-transfer reactions are in general fast, and the bimolecular rate constants fall in the range of 10^{-10}–10^{-9} cm^3 molecule^{-1} s^{-1}. Thus if $k(1)$ is significantly less than 10^{-10} cm^3 molecule^{-1} s^{-1}, it is possible to infer that process 1 requires an activation energy and is probably endothermic. By measuring the rate constants for reaction 1 for different species R and knowing the proton affinity of each R, PA(R), boundaries may be set on PA(B_5H_8). From this value and the use of the appropriate thermochemical cycle it should be possible to obtain a value for the dissociation energy of B_5H_9 to B_5H_8 and H. The success of the bracketing procedure depends on the reliability of the proton affinity data for the reference compounds and the availability of accurate ionization energies for the neutral precursors of the reactant ions. The Bronsted bases selected for this study include a number of organic molecules for which proton affinity data have recently been evaluated.[2]

Experimental Section

The mass spectrometer and photon impact ion source used in this study have been described previously.[3] The reaction chamber consisted of a 0.375 in. cubical cavity in a 0.75 × 0.5 × 0.40 in. block of type 304 stainless steel. Light entered the source through a 0.030 × 0.250 in. slit centered 0.477 cm from the base of the cavity. This slit was covered by a 1 mm thick LiF window held in place with Dow Corning 732 RTV adhesive. The source was equipped with a repeller which maintained a field strength of 14.8 V/cm. The ion exit slit was 0.003 × 0.250 in. The draw out potential was 400 V negative with respect to the reaction chamber, and the ion acceleration potential was held at +2000 V. The light source was a hydrogen resonance lamp similar to that described by Ausloos and Lias.[4] It was powdered by a Ratheon Model PGM-10 microwave power generator. Under normal operating conditions the principal source of radiation was the 10.2 eV Lyman α line of hydrogen. The LiF window used is an effective filter for radiation above 11.9 eV,[5] and in test experiments with xenon (ionization potential 12.1 eV), Xe$^+$ was not detectable.

Pentaborane(9) was obtained from the Callery Chemical Corp. Pentaborane-*1-d* was prepared by deuterium exchange of pentaborane with deuterium chloride in the presence of aluminum chloride.[6]

Results

Under our reaction conditions only the parent ion mass grouping for B_5H_9 is observed. The photoelectron spectrum[7] of B_5H_9 shows a first band onset at 9.87 eV with a maximum at 10.53 eV. Electronic excitation to the first electronic state of the cation required a threshold photon energy of 11.84 eV. This energy is essentially excluded by the LiF filter. Thus $B_5H_9^+$ ions in our experiment are formed in the electronic ground state with a small degree of vibrational excitation.

In Figure 1 is shown the effect of change in source pressure on the relative intensities of the ions for the B_5H_9–CH_3CN system. Radiation at 10.2 eV is insufficient to ionize CH_3CN (ionization potential 12.2 eV),[8] leaving $B_5H_9^+$ the only ionic species present at low source pressures. The major ion–molecule reaction products are the protonated species CH_3CNH^+ and the species $(CH_3CN)_2H^+$, $CH_3CNB_5H_7^+$, and $CH_3CNHB_5H_7^+$. At low source pressures we observe onset of the process

$$B_5H_9^+ + CH_3CN \rightarrow CH_3CNH^+ + B_5H_8 \qquad (2)$$

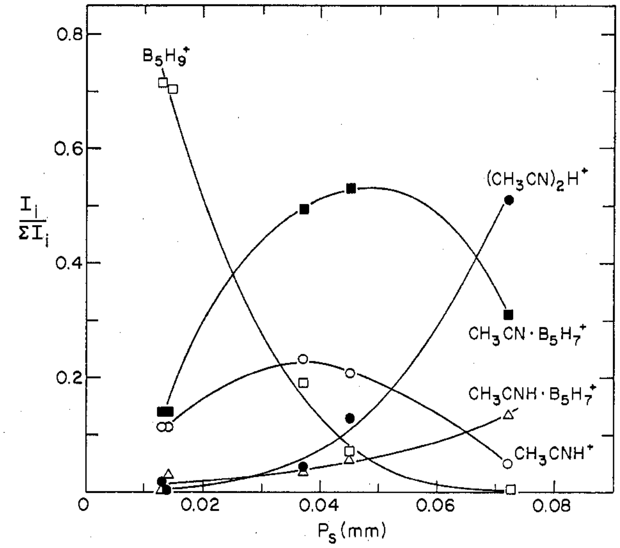

Figure 1. Dependence of $B_5H_9^+$–CH_3CN reaction products on source pressure. Source gas composition B_5H_9:CH_3CN:CH_4 = 1:4.2:3.4.

The bimolecular rate constant for this reaction was calculated assuming that the only other reaction $B_5H_9^+$ undergoes is the competitive reaction

$$B_5H_9^+ + CH_3CN \rightarrow CH_3CNB_5H_7^+ + H_2 \qquad (3)$$

and that all other ionic reaction products result from secondary reactions of CH_3CNH^+. With data obtained at low source pressures we can obtain the integral rate constant k_{int} which is the sum of the bimolecular rate constants k_2 and k_3 for the branching steps, reactions 2 and 3, respectively. From pseudo-first-order kinetics which apply to these processes we have the expression

$$k_{\text{int}} = -\frac{1}{\eta_R \tau} \ln \{I_{B_5H_9^+}/\Sigma I_i\}$$

where η_R is the number density of CH_3CN at 300 K, τ is the ion residence time for $B_5H_9^+$, and $\sum I_i = I_{B_5H_9^+} + I_{CH_3CNH^+} + I_{CH_3CNB_5H_7^+}$. Using a free-flight residence time, $\tau_{ff} = 2.0 \times 10^{-6}$ s, we obtain from the onset data (Figure 1) $k_{\text{int}} = 7.4 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. Using the branching ratio $k_2/k_3 = \{I_{CH_3CNH^+}/I_{CH_3CNB_5H_7^+}\} \simeq 1.0$ then gives $k_2 \approx 3.7 \times 10^{-10}$ cm^3 molecule indicating that (2) is a fast reaction. This implies PA(B_5H_8) ≤ PA(CH_3CN) = 187.3 kcal/mol.[2] Since proton transfer between $B_5H_9^+$ and B_5H_9 is not observed,[9] we set PA(B_5H_8) > PA(B_5H_9) > 170 ± 3 kcal/mol.

Photoionization spectra of C_6H_6–B_5H_9 mixtures consist of $C_6H_6^+$ and $B_5H_9^+$. The only other ion species observed for conditions indicated in Table I were the dimer ions $(C_6H_6)_2^+$ and $(B_5H_9)_2^+$ which were generally less than 1% of the total ion intensity. The net ion signal of $C_6H_7^+$ that could have resulted by proton transfer from $B_5H_9^+$ to C_6H_6, after correction for the ^{13}C isotopic species in $C_6H_6^+$, was infinitesimal. From this observation and our instrument sensitivity we can place the rate constant for this reaction less than 3×10^{-11} cm^3 molecule^{-1} s^{-1}. Thus we conclude that the proton affinity of B_5H_8 is greater than that of benzene (183.4 kcal/mol).[2]

An additional series of measurements was made with mixtures of an organic base and pentaborane-*1-d* (deuterium in the apical position). The purity of the B_5H_9D used was conveniently checked by its photoionization spectrum. For each set of measurements a blank spectrum of the base was obtained for the same range of source pressures used for investigating base–B_5H_9 mixtures. This was necessary in order to correct for possible enhancement of the RH^+ intensity due to protonation of the base by its cation. Results of this phase of the study are summarized in Table I. From these measurements we are able to place the proton affinity of B_5H_8

Table I. Reaction Sequences Involving the Pentaborane(9) Cation

					Exptl data		Expected I_{RD^+}/I_{RH^+} for various proton-transfer sites in $B_5H_9^+$	
Reacn mixture	Reacn compn	Press range, mmHg	Pertinent observn of reacn 1	$PA(B_5H_8)$,[a] kcal/mol	I_{RD^+}/I_{RH^+}	No. of points	Positions 1-9	Positions 1-5
$B_5H_7D_2/B_5H_8D/B_5H_9/NH_3$	0.12/0.69/0.19/1.0	0.01-0.03	Occurs	<200.7	0.14 ± 0.03	11	0.12	0.24
B_5H_8D/B_5H_9/ethyl acetate	0.33/0.67/1.0	0.017-0.032	Occurs	<198.0	0.027 ± 0.016	12	0.038	0.071
B_5H_8D/B_5H_9/ethyl acetate	0.33/0.67/1.0	0.016-0.031	Occurs	<198.0	0.035 ± 0.015	9	0.038	0.071
B_5H_8D/B_5H_9/acetone	0.33/0.67/1.0	0.012-0.030	Occurs	<194.6	0.036 ± 0.012	15	0.038	0.071
$B_5H_8D/B_5H_9/i\text{-}C_4H_8$	0.33/0.67/1.0	0.011-0.024	Occurs	<193.0	0.038 ± 0.020	11	0.038	0.071
$B_5H_7D_2/B_5H_8D/B_5H_9/i\text{-}C_4H_8$	0.03/2.34/0.63/1.0	0.013-0.018	Occurs	<193.0	0.12 ± 0.03	9	0.10	0.20
$B_5H_7D_2/B_5H_8D/B_5H_9$/ethyl formate	0.01/0.78/0.21/1.0	0.010-0.036	Occurs	<191.2	0.031 ± 0.022	12	0.10	0.20
$B_5H_7D_2/B_5H_8D/B_5H_9$/ethyl formate	0.01/0.78/0.21/1.0	0.011-0.025	Occurs	<191.2	0.038 ± 0.011	20	0.10	0.20
$B_5H_7D_2/B_5H_8D/B_5H_9/CH_3CN$	0.01/0.78/0.21/1.0	0.01-0.016	Occurs	<187.4	0.047 ± 0.020	16	0.10	0.20
$B_5H_8D/CH_3CN/CH_4$	1.0/4.2/3.3	0.022-0.046	Occurs	<187.4	0.038 ± 0.011	5	0.12	0.25
$B_5H_7D_2/B_5H_8D/B_5H_9/C_2H_5OH$	0.01/0.78/0.21/1.0	0.014-0.018	Occurs	<186.8	0.044 ± 0.011	8	0.10	0.20
$B_5H_7D_2/B_5H_8D/B_5H_9/CH_3CHO$	0.01/0.78/0.21/1.0	0.010-0.020	Occurs	<185.4	0.038 ± 0.014	20	0.10	0.20
$B_5H_9/C_6H_6/CH_4$	1.0/0.23/4.2	0.020-0.080	Not obsd	>183.4				
B_5H_9	Neat	0.003-0.054	Not obsd	>170				

[a] Proton affinity taken from ref 1.

below that of acetaldehyde (185.4 kcal/mol). From the appropriate thermochemical cycle ΔH for the reaction

$$B_5H_9(g) \rightarrow B_5H_8(g) + H(g) \tag{4}$$

is given by

$$\Delta H = PA(B_5H_8) + IP(B_5H_9) - IP(H) \tag{5}$$

Using $IP(B_5H_9) = 9.87$ eV, $PA(B_5H_8) = 184 \pm 2$ kcal/mol from our measurements, and $IP(H) = 13.595$ eV we obtain for reaction 4 $\Delta H(4) = 98.4 \pm 2$ kcal mol^{-1}. Using the heat of formation of $B_5H_9(g)$ ($\Delta H_f° = 17.5$ kcal/mol)[10] and $\Delta H_f° = 52$ kcal/mol for H(g) we obtain $\Delta H_f°(B_5H_8) = 63.8 \pm 3$ kcal mol^{-1}.

The data in Table I provide some insight into the reaction mechanism for the proton-transfer reactions of $B_5H_9^+$. For each reaction mixture containing deuterium-labeled pentaborane it was possible to calculate the proportion of RD^+ and RH^+ expected if the hydron transferred from $B_5H_8D^+$ originated at the apical position exclusively or from any of the five terminal sites or from all nine sites in the cation. The last two columns of Table I give calculations assuming the hydron has an equal chance of coming from all nine sites (positions 1-9) or only from the apical and basal sites (positions 1-5), respectively. We assume that $B_5H_8D^+$, following its formation, does not have sufficient internal energy for H-D rearrangement since it is produced at an energy close to the adiabatic ionization potential of the precursor molecule. Furthermore, if the ion rearranged prior to its reaction with R we would expect to observe a statistical distribution of RD^+ and RH^+ product ions regardless of the nature of R. We note, for example, that the RD^+:RH^+ ratio observed in the $B_5H_8D^+ + CH_3CN$ reaction is well below the calculated statistical value based on all nine reaction sites. On the other hand the RD^+:RH^+ ratio observed in the reaction with the strong base NH_3 is very close to statistical. Our interpretation of these isotope effects is that the least activation energy required is for removal of a basal proton from $B_5H_9^+$ in its reactions with the weaker bases investigated. However, in the more exothermic reactions of $B_5H_9^+$ with strong bases isotope rearrangement probably occurs through the reaction intermediate. Recent photochemical studies with B_5H_9[11] have shown that the preferred product of a Hg-photosensitized reaction is the 2,2-$B_{10}H_{16}$ decaborane, indicating that H was abstracted from a basal B-H bond in forming the B_5H_8 radical intermediate. These photochemical observations are compatible with our thermodynamic measurements for a B_5H_8 radical formed by loss of a basal proton from $B_5H_9^+$. The value for the (B_5H_8)-H dissociation energy obtained in this study is close to that for the process $HBF_2(g) \rightarrow BF_2(g) + H(g)$ (97.5 ± 6.0 kcal/mol)[10] but is substantially less that for rupture of a B-H bond in borazine (112 ± 3 kcal/mol).[12] The energy required to separate a H atom from B_5H_9 is well below that which could be provided by the $Hg(^3P_1)$ state in photosensitization (111 kcal/mol).

Acknowledgment. We are grateful for support of this work by the National Science Foundation through Grant No. CHE 7602477.

Registry No. B_5H_8, 65930-58-7; $B_5H_9^+$, 65982-52-7; CH_3CN, 75-05-8; $CH_3CNB_5H_7^+$, 65982-51-6.

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Contribution from Oak Ridge National Laboratory,
Oak Ridge, Tennessee 37830

Preparation and Structure of Anhydrous Zinc Chloride[1]

J. Brynestad*[2] and H. L. Yakel[3]

Received October 18, 1977

Structures of three crystalline modifications of anhydrous zinc chloride were reported by Brehler[4] and by Oswald and Jaggi.[5] All three are based on pseudo-close-packed anion lattices in which zinc ions occupy tetrahedral interstices. In