reductase.[29] It may also affect the photodynamics of its nickel hydrocorphinoid chromophore as it does for nickel porphyrin reconstituted hemoglobins.[15,30,31] This aspect of nickel hydrocorphinoid photodynamics is currently being explored in our laboratories.

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Hydride Binding Energies of Boranes

Sir:

Ion/molecule reactions and gas-phase equilibrium measurements have provided an extensive body of accurate thermochemical information for organic and inorganic ions.[1-6] Gas-phase thermochemical data for borohydride negative ions are conspicuously absent, despite the widespread practical significance of borohydride ion chemistry in solution[7-10] and the relative ease of formation of simple borohydride negative ions in mass spectrometer ion sources.[11,12] The reason for this, in part, is the present lack of suitable ion/molecule reactions involving borohydride ions and well-characterized reference species that are necessary for evaluating their heats of formation.

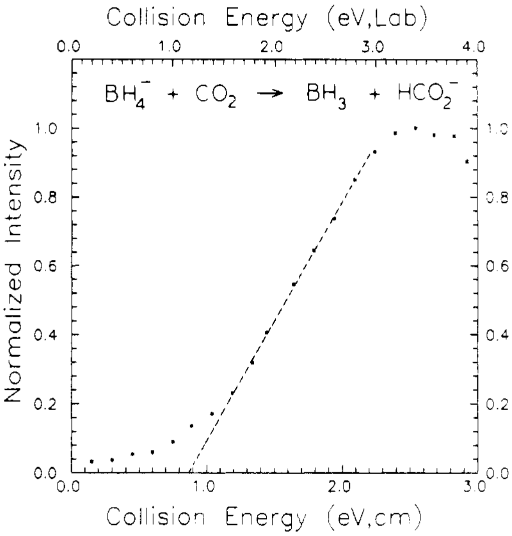

Figure 1. Plot of normalized HCO_2^- ion intensity as a function of BH_4^- ion kinetic energy in the center-of-mass frame (lower scale) and the laboratory frame (upper scale). The dashed line represents a linear fit of the steeply rising portion of the appearance curve.

As part of our ongoing studies of hydride affinities and gas-phase hydride transfer reactions,[13-16] we recently developed a method for estimating hydride binding energies of neutral compounds from endothermic H^- transfer reactions in a flowing-afterglow–triple-quadrupole apparatus. We report here our measurements of the hydride affinity (HA) of BH_3, B_2H_6, and a few of their common derivatives, along with gas-phase heats of formation for the corresponding borohydride negative ions.

All experiments were carried out at 298 ± 2 K in a tandem flowing afterglow–triple-quadrupole instrument recently constructed in our laboratory.[17] Borohydride ions can be synthesized in the helium flow reactor by several different methods. Borane–methyl sulfide (Me_2S^+–BH_3^-, BMS) provides a convenient alternative to diborane for the gas-phase synthesis of BH_4^-.[11,12] This volatile Lewis acid–base complex reacts with a variety of pregenerated negative ions (X^-) to yield monosubstituted borohydride ions (XBH_3^-) that undergo further reactions with additional BMS to yield BH_4^- and polyborohydride cluster ions (eq 1). Other substituted borohydride ions can be synthesized from

$$X^- \xrightarrow{\text{BMS}} XBH_3^- \xrightarrow{\text{BMS}} BH_4^- \xrightarrow{\text{BMS}} \rightarrow B_2H_7^-, B_3H_8^- \qquad (1)$$

the corresponding neutral boranes by reactions with hydride donor anions such as $C_5H_{11}SiH_4^-$ [16] or c-$C_6H_7^-$ [18] (eq 2).

$$n\text{-}C_5H_{11}SiH_4^- + BR_3 \rightarrow HBR_3^- + n\text{-}C_5H_{11}SiH_3 \qquad (2)$$

$$R = \text{Et, OMe, O-}i\text{-Pr, F}$$

The BH_4^- and $B_2H_7^-$ ions and most all of the substituted borohydride ions described above are completely unreactive in the

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presence of simple aliphatic carbonyl compounds, substituted olefins, CO_2, and other potential H^- acceptor reagents.[19] Neither hydride transfer *nor adduct formation* occur in the relatively high-pressure flow reactor (0.5 Torr). Furthermore, reactions between neutral, monomeric boranes such as BEt_3 or $B(OMe)_3$ and potential hydride donor anions such as CH_3O^-, $CH_3CH_2O^-$, CH_3CHCHO^-, $PhCHCH_3^-$, and CH_3CHCN^- produce exclusively the corresponding adduct ions by efficient termolecular (or radiative[20]) association. This behavior precludes the use of conventional ion/molecule equilibrium and bracketing experiments for determining the relative hydride affinities of neutral boranes under flowing afterglow conditions.[14] However, we have found that endothermic hydride transfer reactions between mass-selected, translationally excited borohydride ions and certain reference hydride-acceptor compounds can be observed in the triple-quadrupole collision chamber. From careful analysis of the energy thresholds for appearance of the H^--transfer products, estimates of the hydride binding energies of the borohydride reactant ions can be obtained.

For the present experiments, we chose CO_2 as a convenient reference H^--acceptor compound since it has a well-established hydride affinity ($HA(CO_2) = 51.6 \pm 2.5$ kcal/mol).[13] Figure 1 illustrates a typical data set for the endothermic hydride transfer between BH_4^- and CO_2 carried out under single-collision conditions in the triple-quadrupole instrument[21-23] (eq 3). Shown in the

$$BH_4^- \text{ (KE)} + CO_2 \xrightarrow{E_T} HCO_2^- + BH_3 \qquad (3)$$

figure is the normalized intensity of the formate ion product (*m/z* 45) plotted against the nominal center-of-mass collision energy. Parent ion retarding potential analysis carried out in the absence of CO_2 locates the energy origin and shows a BH_4^- kinetic energy distribution of approximately 0.7 eV (fwhm).[24]

A linear fit of the steeply rising portion of the appearance curve in Figure 1 gives a line intersecting the energy axis at 0.87 eV. Addition of the Doppler correction for thermal motion of CO_2 (0.15 eV)[25] yields a threshold energy for this experiment of 1.02 eV (23.5 kcal/mol).[26] Several replicate measurements provide a final value and precision of 22.6 ± 1.2 kcal/mol, which may be combined with $HA(CO_2)$ to give $HA(BH_3) = 74.2 \pm 2.8$ kcal/mol. Combining our hydride affinity estimate with $\Delta H_f[BH_3,g] = 24.7 \pm 3.5$ kcal/mol[27] gives $\Delta H_f[BH_4^-,g] = -14.8 \pm 4.5$ kcal/mol. The actual error in E_T is likely to be somewhat higher (ca. ±5 kcal/mol) due to uncertainty in the true energy scale and the approximate fitting procedures. Also, while appearance measurements necessarily yield upper limits for reaction endothermicities, the good agreement between our results and the computed hydride affinity of borane reported by Eisenstein et al. (79.4 kcal/mol)[28] and Dewar (82 kcal/mol)[29] and an older estimate by Altshuller (80 ± 5 kcal/mol) based on lattice energy calculations for alkali-metal borohydride salts[30] strongly suggests that the interconversion of translational and internal energy is efficient for this system and that the kinetic shift, if any, must be small.[23]

Table I. Thermochemical Data for Gas-Phase Borohydride Ions

reactant ion, HBR_3^-	E_T	$HA(BR_3)^{c,f}$	$\Delta H_f[BR_3,g]^{d,f}$	$\Delta H_f[HBR_3^-,g]^{e,f}$
BH_4^-	0.98 ± 0.05^a	74.2 ± 2.8	24.7 ± 3.5	-14.8 ± 4.5
$HBEt_3^-$	0.77 ± 0.02^a	69.4 ± 2.5	-36.5 ± 1.2	-71.2 ± 2.8
$B_2H_7^-$	$(1.71 \pm 0.05)^b$	74.0 ± 7.1	9.8 ± 4.0	-29.5 ± 5.8
BH_3CN^-	1.94 ± 0.11^a	96.3 ± 3.5	43.0 ± 5.8	-18.6 ± 4.6

[a] Doppler-corrected threshold energy for occurrence of hydride transfer to CO_2 in units of eV. Uncertainty indicates the overall precision from at least four measurements. [b] Doppler-corrected CID threshold and precision (eq 4) in units of eV. [c] Hydride affinity of the corresponding neutral borane in units of kcal/mol; $HA(CO_2) = 51.6 \pm 2.5$ kcal/mol, ref 13. [d] Heat of formation of neutral borane in units of kcal/mol: BH_3, ref 30, 31; BEt_3, ref 38; B_2H_6, ref 31; BH_2CN, this work, see text. [e] Heat of formation derived for the borohydride ion in units of kcal/mol; $\Delta H_f[H^-, g] = 34.7 \pm 0.5$ kcal/mol, ref 33. [f] Uncertainty represents the root mean sum of the component uncertainty intervals.

Similar experiments were carried out with $HBEt_3^-$ and BH_3CN^-[32] with the results summarized in Table I. The heat of formation for BH_3CN^- was derived from the measured threshold for collision-induced dissociation (CID) of this ion to $BH_3 + CN^-$ (2.65 ± 0.09 eV $= 61.1 \pm 2.1$ kcal/mol) and the known heats of formation for BH_3 and CN^- (17.8 ± 2.1 kcal/mol).[33] The hydride binding energy and heat of formation for BH_3CN^- combine to yield $\Delta H_f[BH_2CN,g] = 43.0 \pm 5.8$ kcal/mol. The large increase in hydride affinity between BH_3 and BH_2CN is in accord with recent ab initio calculations[34] and the attenuated reducing power of $NaBH_3CN$ compared to $NaBH_4$ in solution.[35]

The threshold energy for hydride transfer to CO_2 from $B_2H_7^-$ could not be determined reliably due to the apparently low cross section for this reaction and the facile dissociation of $B_2H_7^-$ to BH_4^- and BH_3 (eq 4). However, from the measured threshold

$$B_2H_7^- \rightarrow BH_4^- + BH_3 \qquad (4)$$

for reaction 4 with Ar and CH_4 target gases (1.71 ± 0.05 eV $= 39.4 \pm 1.2$ kcal/mol) combined with the known heats of formation for the products, we can establish $\Delta H_f[B_2H_7^-,g] = -29.5 \pm 5.8$ kcal/mol. Our measured energy for reaction 4 is in good agreement with results from high-level ab initio calculations (35.4 kcal/mol)[36] and an older calorimetric estimate (31 ± 8 kcal/mol).[37] We can combine $\Delta H_f[B_2H_7^-,g]$ with $\Delta H_f[B_2H_6,g] = 9.8$ [illegible] 4.0 kcal/mol[31] to derive the hydride affinity of diborane, $HA(B_2H_6) = 74.0 \pm 7.1$ kcal/mol. The essentially identical hydride affinities of BH_3 and B_2H_6 are a direct consequence of the fact that $D[BH_3-BH_3] \simeq D[BH_3-BH_4^-]$.

While $HA(B(OMe)_3)$ could not be measured with confidence due to poor threshold behavior in its reaction with CO_2, it is apparent from our experiments that it is significantly less than that of BEt_3 (ca. 60 kcal/mol). This is consistent with the relative Lewis acidities of these boranes toward other anions reported by Larson and McMahon.[2]

Additional gas-phase borohydride ion thermochemistry and its relationship to borohydride-based reduction mechanisms in solution

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will be presented in a future publication.

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Registry No. BH_4^-, 16971-29-2; $B_2H_7^-$, 27380-11-6; BEt_3H^-, 75338-98-6; BH_3CN^-, 33195-00-5; BH_3, 13283-31-3; B_2H_6, 19287-45-7; BEt_3, 97-94-9; BH_2CN, 31139-16-9.

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First Example of a Mixed-Spin Trinuclear Manganese(II) Complex: $[MnN_6(S = {}^1/_2)][MnO_6(S = {}^5/_2)][MnN_6(S = {}^1/_2)]$

Sir:

Polynuclear manganese complexes in N,O coordination are of current interest.[1] Species of this family are believed to be active in photosystem II.[2] Herein we report the first example of a novel situation: a trinuclear N,O-coordinated complex in which manganese(II) is discretely present in both low-spin ($S = {}^1/_2$) and high-spin ($S = {}^5/_2$) configurations.[3]

Scheme I

A. Synthesis :

$$3Mn(ClO_4)_2 + 6HL \xrightarrow{(i)} Mn_3L_6 + 6HClO_4$$

B. Cleavage :

$$Mn_3L_6 + 2KOH \xrightarrow{(ii)} 2K[MnL_3] + Mn(OH)_2$$

C. Reassembly :

$$2K[MnL_3] + Mn(ClO_4)_2 \xrightarrow{(iii)} Mn_3L_6 + 2KClO_4$$

(i) 3 moles KOH, MeOH, stir. (ii) 15:1 Me_2CO-H_2O, warm, stir. (iii) MeOH, boil.

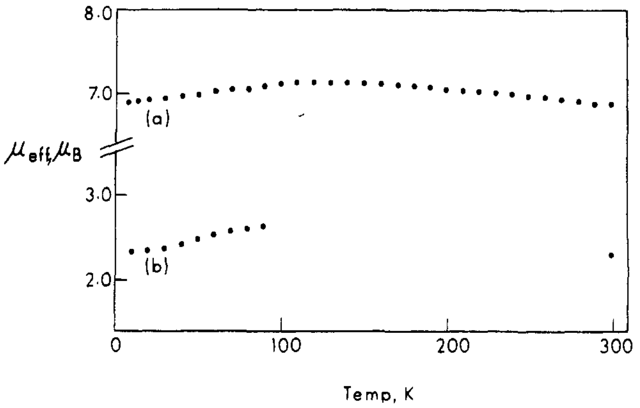

Figure 1. Variable-temperature magnetic moments of (a) Mn_3L_6 and (b) $[Ph_4As][MnL_3]$.

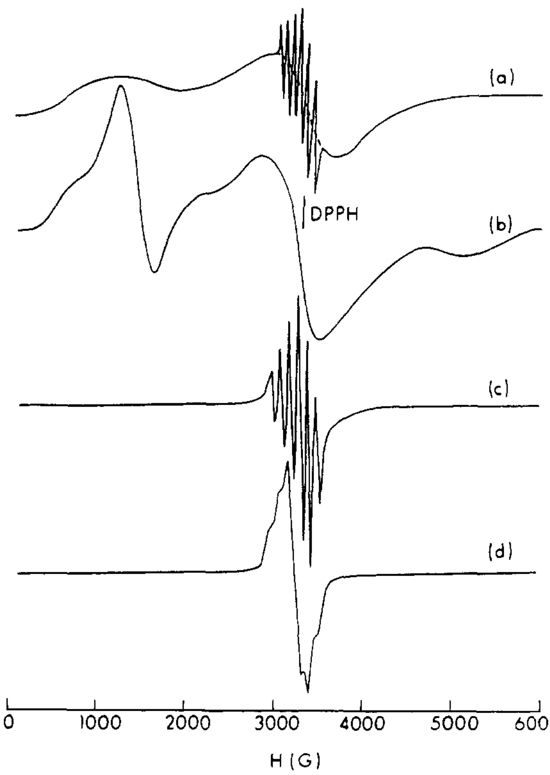

Figure 2. EPR spectra (X-band, 9.13 GHz) at 298 K: (a) Mn_3L_6 in dichloromethane; (b) Mn_3L_6 in polycrystalline form; (c) $[Ph_4As][MnL_3]$ doped (1%) into $[Ph_4As][FeL_3]$ in polycrystalline form; (d) $[Ph_4As][MnL_3]$ in polycrystalline form.

The concerned complex is Mn_3L_6 in which (phenylazo)benzaldoxime, PhN=NC(=NOH)Ph (HL), acts as the ligand in the deprotonated form, L^-. Synthesis and reactions are stated in Scheme I. The complex Mn_3L_6 obtained directly from Mn^{2+} and HL occurs as a dark solid[4a] (green in solution) and is quantitatively cleaved by 2 equiv of KOH. One equivalent of the manganese is precipitated,[5] as hydroxide and the other 2 equiv remains in

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