The discussion by Chong and Franklin regarding the breakup of $C_2H_7^+$ by the process

$$C_2H_7^+ \longrightarrow C_2H_5^+ + H_2 \qquad (6)$$

must also be questioned. Our lower limit of PA-($C_2H_7^+$) makes the free energy change for reaction 6 positive. It is, therefore, unnecessary to invoke an activation energy for reaction 6 to explain the observation of $C_2H_7^+$ in gas-phase, ion-molecule reactions.

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Reaction of the Decahydrodecaborate(2−) Ion with Benzoylating Agents. The Effect of Acid

Sir:

We wish to report the results of some mechanistic studies on the reaction of $B_{10}H_{10}^{2-}$ with benzoyl halides. Equations 1 and 2 summarize the pertinent reactions in

$$B_{10}H_{10}^{2-} + C_6H_5COX \longrightarrow \underset{\text{I}}{2\text{-}B_{10}H_9COHC_6H_5^-} + X^- \qquad (1)$$

$$X = Cl, Br$$

$$\underset{\text{I}}{2\text{-}B_{10}H_9COHC_6H_5^-} \rightleftharpoons \underset{\text{II}}{2\text{-}B_{10}H_9COC_6H_5^{2-}} + H^+ \qquad (2)$$

this system.[1] Using benzoyl chloride or bromide in anhydrous acetonitrile, isolated yields of recrystallized II in the 80–90% range can be obtained with no evidence for the presence of other isomers. The high conversion of $B_{10}H_{10}^{2-}$ to product was also verified by ^{11}B nmr and visible spectroscopy. Figure 1A presents ^{11}B nmr spectra which show the essentially complete conversion of $B_{10}H_{10}^{2-}$ to I within 5 min using C_6H_5COBr as the benzoylating agent. Spectrophotometric examination of the reaction using the 435-nm absorption of I as a probe[2,3] also showed a high conversion (from 75–99% yield) when the concentration of reagents was greater than 0.01 *M* as in the nmr studies or in the preparative reactions.[4] In the kinetic studies, data were collected based on the absorption of I but integrated rate equations were used only at reagent concentrations which gave yields of I greater than 90%. In these cases, conditions pseudo first order in $B_{10}H_{10}^{2-}$ were achieved using a large excess of benzoylating reagent. At concentrations of reagents which gave lower yields, kinetic data were obtained using the initial rate method. The results were the same by either method and the average k agreed to within 5%.

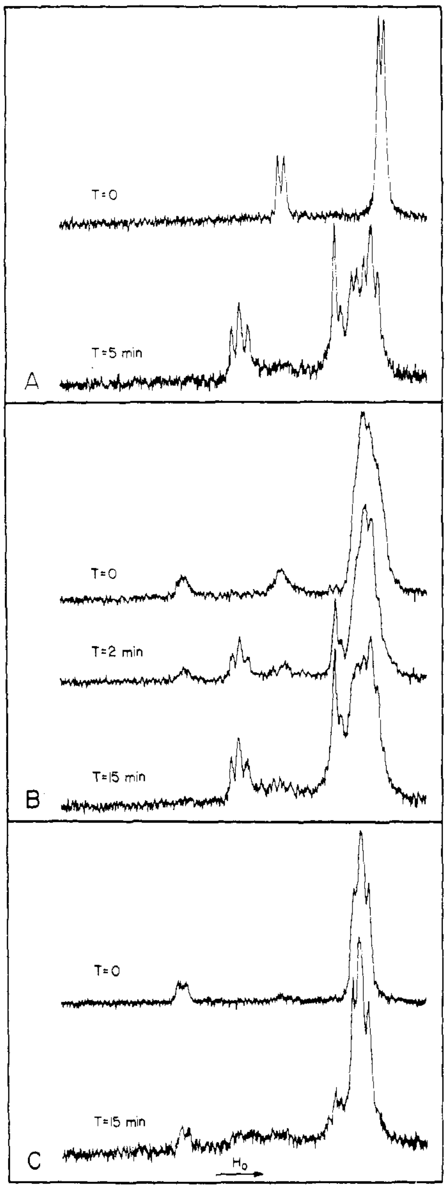

Figure 1. The 80.5-MHz ^{11}B nmr spectra of the reaction of C_6H_5COBr with (A) $B_{10}H_{10}^{2-}$, (B) a mixture of $B_{10}H_{10}^{2-}$ and $B_{10}H_{11}^-$, and (C) $B_{10}H_{11}^-$ in acetonitrile.

Some kinetic data obtained by the initial rate method using benzoyl chloride are presented in Table I. The rate law shown in eq 3 was obtained from these data and

$$\frac{d[I]}{dt} = k[B_{10}H_{10}^{2-}][C_6H_5COCl] \qquad (3)$$

the same rate law was also observed in the case of benzoyl bromide which reacted substantially faster ($k_{Br}/k_{Cl} = 318$). For benzoyl chloride the activation parameters of the reaction are $\Delta H^{\ddagger} = 16.3$ kcal/mol and $\Delta S^{\ddagger} = -19.8$ cal/(deg mol) while a very small deuterium isotope effect $k_H/k_D = 1.23$ was observed using $[(C_4H_9)_4N]_2B_{10}D_{10}$ as the substrate.

The most surprising kinetic result concerned the effect of strong acid on the rate of formation of I. Entries 1 and 10–17 in Table I clearly indicate a decrease in the reaction rate upon the addition of acid. The

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[1] W. H. Knoth, J. C. Sauer, D. C. England, W. R. Hertler, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **86**, 3973 (1964).

[2] A value of ϵ 9000 was determined for I using a Beer's law plot which compares with a value ϵ 7800 reported in ref 1.

[3] Since K for eq 2 was determined to be substantial (pK 2.3 ± 0.2), the reaction samples in the yield and also the kinetic studies were diluted with 0.05 *M* CF_3CO_2H in acetonitrile before recording the spectrum to ensure that all benzoylation product was indeed present as I.

[4] Below about 0.010 *M* $B_{10}H_{10}^{2-}$ or C_6H_5COX (X = Cl or Br) even at high concentrations of the other reagent, the yield fell to 50% or lower. It is not clear whether the apparent decrease in yield as determined spectrophotometrically is due to the presence at low concentrations of reagents of an alternative reaction of $B_{10}H_{10}^{2-}$ or to an artifact of the method. A number of potential causes have, however, been eliminated. The decrease in the yield of I is not due to the reaction of I with excess starting reagents or solvent nor is it due to prior depletion of $B_{10}H_{10}^{2-}$ by the acid catalyzed (the source of the acid in this case being the product itself) reaction of $B_{10}H_{10}^{2-}$ with CH_3CN to yield $B_{10}H_9NCCH_3^-$.

Table I. Initial Rate Data[a] on the Formation of $B_{10}H_9COHC_6H_5^-$

No.	$B_{10}H_{10}^{2-}$ [b]	C_6H_5COCl	CF_3CO_2H	10^6k_i, M sec^{-1}	10^4k, M^{-1} sec^{-1}
1	0.075	0.45		17.32	4.99
2	0.075	0.225		8.67	5.13
3	0.075	0.075		2.92	5.19
4	0.075	0.045		1.69	5.01
5	0.075	0.0075		0.267	4.75
6	0.0375	0.045		0.832	4.93
7	0.0375	0.225		4.26	5.05
8	0.0075	0.045		0.0165	4.89
9	0.0075	0.225		0.816	4.84
10	0.075	0.45	0.05	12.87	
11	0.075	0.45	0.10	11.59	
12	0.075	0.45	0.20	9.25	
13	0.075	0.45	0.30	7.64	
14	0.075	0.45	0.40	6.27	
15	0.075	0.45	0.50	5.20	
16	0.075	0.45	0.60	4.63	
17	0.075	0.45	0.70	3.93	

[a] At 308°K, CH_3CN solvent. [b] $(C_4H_9)_4N^+$ salt.

nature of the acid effect was examined by 80.5-MHz ^{11}B nmr and was shown to be a consequence of the equilibrium protonation of $B_{10}H_{10}^{2-}$ to yield a new species, probably $B_{10}H_{11}^-$.[5] In Figure 1B both $B_{10}H_{10}^{2-}$ and $B_{10}H_{11}^-$ are present in the initial reaction mixture, and substantial formation of I occurs within 2 min after addition of C_6H_5COBr. However, some $B_{10}H_{10}^{2-}$ and $B_{10}H_{11}^-$ clearly remain. After 16 min, the reaction is essentially complete and the spectrum is principally that of I. In the absence of acid the reaction would be complete in less than 3 min. In Figure 1C all the $B_{10}H_{10}^{2-}$ is initially present as $B_{10}H_{11}^-$ and after 15 min, within the limits of nmr detection, little reaction has occurred with C_6H_5COBr. The apparent inertness of $B_{10}H_{11}^-$ to benzoylation is even more striking in the case of the less reactive benzoyl chloride. Under conditions equivalent to those of Figure 1C, the nmr spectrum of the acid form is unchanged even after 1 hr. This evidence is supported by the 40% recovery of $B_{10}H_{10}^{2-}$ from reaction mixtures of C_6H_5COCl and $B_{10}H_{11}^-$ after a 1-hr reaction period. In the absence of acid the same reaction mixture proceeds to greater than 80% yield.

A mechanism consisting of eq 4 and 5 yields an initial

$$B_{10}H_{10}^{2-} + H^+ \overset{K}{\rightleftharpoons} B_{10}H_{11}^- \tag{4}$$

$$B_{10}H_{10}^{2-} + C_6H_5COCl \xrightarrow{k_2} B_{10}H_9COHC_6H_5^- + Cl^- \tag{5}$$

rate law which agrees with both the kinetic and spectroscopic data (eq 6). In the absence of acid eq 6 reduces to the observed rate law (eq 3). With acid present eq 6

$$\left(\frac{d[I]}{dt}\right)_0 = k_i = \frac{k_2[B_{10}H_{10}^{2-}]_0[C_6H_5COCl]_0}{1 + K[H^+]} \tag{6}$$

requires a plot of $[B_{10}H_{10}^{2-}]_0[C_6H_6COCl]_0/k_i$ *vs.* $[H^+]$ to be linear with an intercept equal to $1/k_2$ and a slope equal to K/k_2. Using the kinetic results of Table I, the expected linear plot was obtained and from this plot a value of $K = 4.6 \pm 0.5$ M was extracted. An independent evaluation[5] of K from ^{11}B nmr data yields a value of $K = 0.8 \pm 0.2$ M. Closer agreement between the independently determined values is unlikely because of the nonideality of the solutions for all determinations of K and the absence of C_6H_5COX in the ^{11}B nmr determinations.[5]

The substitution chemistry of $B_{10}H_{10}^{2-}$ [6] is not well understood and the results reported here suggest that some of the complexity may be due to the presence of two species of different reactivity: $B_{10}H_{10}^{2-}$ and a protonated form $B_{10}H_{11}^-$. This is especially relevant since the preponderance of the synthetic studies of $B_{10}H_{10}^{2-}$ was carried out under strongly acidic conditions. Moreover, the apparent inertness of $B_{10}H_{11}^-$ toward electrophilic attack coupled with the electrophilic properties of the proton may imply an intermediate in electrophilic substitution at $B_{10}H_{10}^{2-}$ which resembles $B_{10}H_{11}^-$. An electrophile (E) may attack $B_{10}H_{10}^{2-}$ to produce $B_{10}H_{10}E^{2-}$ where E takes the place of the additional proton in $B_{10}H_{11}^-$. We are examining this possibility.

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[5] P. A. Wegner, R. Unger, R. Wiersema, M. F. Hawthorne, unpublished results. The equilibrium formation of $B_{10}H_{11}^-$ from $B_{10}H_{10}^{2-}$ and CF_3CO_2H in acetonitrile has been studied quantitatively using ^{11}B nmr spectroscopy. These studies regarding the structure and reactivity of $B_{10}H_{11}^-$ will be reported later.

[6] E. L. Muetterties and W. Knoth, "Polyhedral Boranes," Marcel Dekker, New York, N. Y., 1968, includes an extensive discussion of the substitution chemistry of $B_{10}H_{10}^{2-}$.

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$C_2B_6H_{10}$, a New *nido*-Carborane

Sir:

The heretofore unknown *nido*-carborane, $C_2B_6H_{10}$, has been synthesized,[1] isolated, and identified from the reaction between $C_2B_3H_5$ and B_2H_6 in a heated stainless steel flow reactor. Yields of <5% based upon the stoichiometric equation (1) were obtained.[2]

$$C_2B_3H_5 + {}^3/_2B_2H_6 \longrightarrow C_2B_6H_{10} + 4H_2 \tag{1}$$

The product $C_2B_6H_{10}$ is an air-sensitive clear liquid which is relatively unstable in the liquid phase, decomposing at ambient temperatures primarily to $C_2B_6H_8$ and $C_2B_5H_7$; it can be stored in the gas phase for extended periods of time with no apparent decomposition.

Reaction conditions consisted of a flow system (~20 sec nominal residence time) of equimolar quantities of diborane and $C_2B_3H_5$ (preparation reported previously[3]) at 0.5 atm in a 0.75 in. × 12 in. stainless steel tube reactor heated to 300°. The effluent from the

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[1] J. F. Ditter, J. D. Oakes, and E. B. Klusmann, Abstracts of the 160th National Meeting of the American Chemical Society, Chicago, Ill., 1970.

[2] For general information on carborane structures, properties, and reactions see (a) R. E. Williams, "Progress in Boron Chemistry," Vol. 2, Pergamon Press, Oxford, England, 1970, Chapter 2; (b) R. N. Grimes, "Carboranes," Academic Press, N. Y., 1970.

[3] J. F. Ditter, E. B. Klusmann, J. D. Oakes, and R. E. Williams, *Inorg. Chem.*, 9, 889 (1970).