cence caused by cooling precluded measurement of the spectrum. Several of the most likely excitation mechanisms involving strain include phase transitions which halve the dimensions of the unit cell by changing the P–C–P bond angles or which allow formation of an intermolecular double bond. These possibilities are currently being investigated

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(10) Contribution No. 3217.

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Preferred Direction of Proton Transfer between $C_2H_7^+$ and CO, CH_4, N_2O, and C_2H_4 at 300°K[1]

Sir:

In a recent publication,[2] Chong and Franklin purport to have observed thermodynamic equilibrium at 340°K for the proton transfer reaction

$$CH_5^+ + C_2H_6 \rightleftharpoons C_2H_7^+ + CH_4 \tag{1}$$

The reaction was studied in a single ion source with p_{CH_4} maintained at 384 μ and $p_{C_2H_6}$ varied from 101 to 291 μ. The product to reactant ion ratios yielded an average value for the equilibrium constant of 4.94 ± 0.33 and a difference in proton affinities, $PA(C_2H_6) - PA(CH_4)$ of about 1 kcal mol^{-1}. From well-established values for the heats of formation of the other species involved in reaction 1, they calculate $PA(C_2H_6) = 127.0 \pm 1.05$ kcal mol^{-1}. This result does not agree with recent observations in our laboratory using the flowing afterglow technique.[3]

We have been employing this technique to study proton transfer reactions of the type

$$XH^+ + Y \rightleftharpoons YH^+ + X$$

starting in each direction. Thermalization of the protonated reactant is ensured by allowing it to undergo thousands of collisions prior to entry into the reaction region. Determination of the preferred direction of the reaction under these conditions establishes the relative proton affinity of X and Y.

Such studies, both in the forward and reverse directions, of the following reactions showed that proton transfer at 300°K occurs preferentially in the direction in which the reactions are written

$$N_2OH^+ + C_2H_6 \rightleftharpoons C_2H_7^+ + N_2O \tag{2}$$

$$COH^+ + C_2H_6 \rightleftharpoons C_2H_7^+ + CO \tag{3}$$

$$C_2H_7^+ + C_2H_4 \rightleftharpoons C_2H_5^+ + C_2H_6 \tag{4}$$

Experimental details will be reported elsewhere.[4] For each of the reactions (2–4) it was observed that $k_f/k_r \gg 1$. The identity of the product ion ($m/e = 31$) in reactions 2 and 3 was established as $C_2H_7^+$ by isotope analysis. Values of $PA(N_2O) = 134^{+5}_{-2}$ kcal mol^{-1} and $PA(CO) = 138^{+5}_{-2}$ have both been determined in our laboratory,[5a] from equilibrium studies of proton transfer involving CH_4, N_2O, and CO and the value of $PA(CH_4) = 126^{+5}_{-1}$ of Chupka and Berkowitz.[5b] Our value for PA(CO) is in good agreement with Harrison's value[6] of 137^{+12}_{-3}. $PA(C_2H_4)$ has been calculated to be 159 kcal mol^{-1} from the known heats of formation[7] of $C_2H_5^+$, H^+, and C_2H_4. Our observations of reactions 2–4 therefore imply $136 < PA(C_2H_6) < 159$ kcal mol^{-1}. The lower limit is 9 kcal mol^{-1} higher than the value reported by Chong and Franklin,[2] which implies a value for the equilibrium constant of reaction 1 of at least 8×10^5 compared with their observation of 4.9.

One theoretical value is available for comparison. Lathan, Hehre, and Pople[8] have made *ab initio* molecular orbital calculations of the geometry and energy of $C_2H_7^+$. Their theoretical value of $PA(C_2H_6) = 140.1$ kcal mol^{-1} at 0°K (not corrected for zero point vibrations) lies within our limits. Thus it appears that, although the high-pressure, ion source technique has correctly assigned the order of the proton affinities, *viz.* $PA(C_2H_6) > PA(CH_4)$, it has not provided the correct value for the proton affinity difference. There are several possible reasons for this. (1) Mass discrimination in the ion detection system. Chong and Franklin do not comment on this possible source of error. (2) Thermodynamic equilibrium may not have been established. The range in $p_{C_2H_6}$ of less than a factor of 3 may have been insufficient to test this. (3) Probably the most important possibility is the failure to achieve thermalization of the protonated species prior to reaction in either direction. This can lead to steady-state conditions which do not reflect true thermodynamic equilibrium. Since the rate in the forward direction is close to the collision rate, while the rate in the reverse direction is much ($\sim 10^6$) slower, the latter is likely to be affected by ion excitation to a greater extent than will the forward rate. This will result in a measured equilibrium constant lower than the true value. Such effects may also have led to a low value for the equilibrium constant reported by Kasper and Franklin[9] for the reaction

$$CO_2H^+ + CH_4 \rightleftharpoons CH_5^+ + CO_2 \tag{5}$$

although the disagreement with our flowing afterglow studies[10] in this case was less severe, perhaps because the rate constants of the forward and reverse reactions do not differ to so large an extent.

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(1) This work was supported in part by the National Research Council of Canada.

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(10) R. S. Hemsworth, H. W. Rundle, D. K. Bohme, H. I. Schiff, D. B. Dunkin, and F. C. Fehsenfeld, *J. Chem. Phys.*, **59**, 61 (1973).

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%.

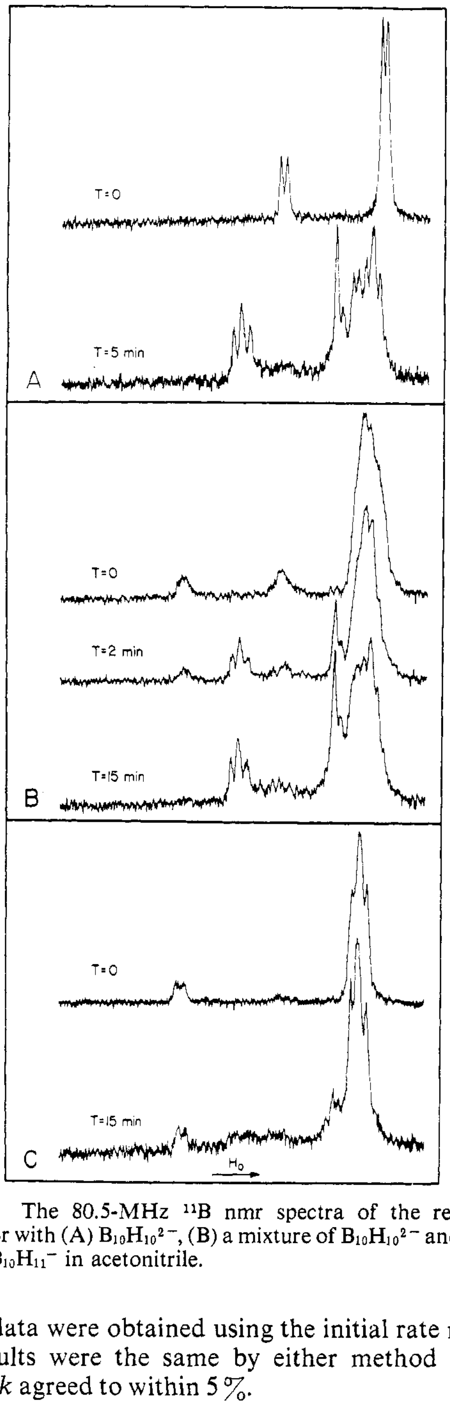

Figure 1. The 80.5-MHz ^{11}B nmr spectra of the reaction of C_6H_5COBr with (A) $B_{10}H_{10}^{2-}$, (B) a mixture of $B_{10}H_{10}^{2-}$ and $B_{10}H_{11}^-$, and (C) $B_{10}H_{11}^-$ in acetonitrile.

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 (p*K* 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 $B_{10}H_9NCCH_3^-$.