the distributions of the electrons. They found that the Coulomb energies of the halogen molecules are negative, and therefore contribute to the stabilization of the molecules; the values calculated were -30.2 kcal/mole for I_2, -37.6 for Br_2, -42.8 for Cl_2, and -10.3 for F_2. The Coulomb energy for F_2 is clearly very small compared to the others, and it was concluded that "the source of the anomaly [in the dissociation energy of F_2] does indeed lie here."[8]

This conclusion can now be put on a more quantitative basis, and also given a somewhat different interpretation. If the calculated Coulomb energies are plotted against $1/R$, the usual extrapolation leads to a value of 62.5 kcal/mole for F_2; the deviation is therefore $62.5 - 10.3 = 52$ kcal/mole, which is essentially the same as that observed in the dissociation energy of the fluorine molecule (54 kcal/mole). This strongly supports the idea that the anomaly in the Coulomb energy is responsible for the deviation in the dissociation energy.

It is suggested, however, that the accepted interpretation of this anomaly, as arising from the unusually strong repulsion of the unshared outer-shell electrons on one fluorine atom for those on the other, should be reexamined. It has been shown in this work that a destabilizing effect of essentially the same magnitude, per fluorine atom, as that found in F_2 occurs in a number of other diatomic species, in which the fluorine atom is associated with various other atoms. Such an effect also occurs in the formation of the *free* fluoride ion, in the absence of any second atom.

It does not seem justifiable, therefore, to attribute this destabilization to an interaction associated with a specific molecule or bond. It appears rather that the anomaly involves the fluorine atom, in whatever circumstances, and its interaction with an external electron which enters its outer shell. This external electron may be provided, for example, by an alkali metal atom, in forming an "ionic" bond, or it may be provided by a nonmetal atom, as part of a "covalent" bond, or it may simply be involved in an attachment process, $F + e^- \rightarrow F^-$. In any case, it is suggested that because of the exceptionally small size of the fluorine atom (see Table I), the entering electron feels unusually large forces of attraction from the nucleus and repulsion from the electrons already associated with the atom. It appears that the magnitude of the anomaly in the repulsive forces is greater than in the attractive forces. Thus, although the attractive forces are by far the dominant ones and the electron does enter the outer shell of the fluorine atom, the energy of the interaction is less, by about 26 kcal/mole, than what it would be if there were no anomalous effects present. It is suggested, therefore, that the Coulomb energies calculated by Caldow and Coulson reflect primarily the interaction of each fluorine atom with the electron provided to the bond by the other fluorine.[11]

(11) A very interesting treatment of bond energies has been presented by R. T. Sanderson, *J. Inorg. Nucl. Chem.*, 30, 375 (1968), whose qualitative interpretation of the anomaly in the F_2 bond energy also deemphasizes the role played by repulsion between the unshared electrons on one fluorine atom and those on the other.

Homogeneous Exchange of Iodine with Methyl Iodide in the Single-Pulse Shock Tube[1,2]

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Abstract: The homogeneous gas-phase exchange of iodine with methyl iodide was studied in a single-pulse shock tube in the temperature range 870–1105°K. Tracer quantities of the γ-ray emitter, ^{131}I, were introduced in the iodine. The observed exchange rates were consistent with the mechanism $M + I_2 \rightleftharpoons 2I + M$ and $I + CH_3I \rightleftharpoons CH_3 + I_2$ (where M is the inert carrier gas, argon), with a rate $k_1 = 10^{13.2} \exp(-17.4 \text{ kcal}/RT)$ cm^3 mole^{-1} sec^{-1}.

The gas-phase exchange of iodine with methyl iodide has not been successfully studied in the past because of complications caused by surface-catalyzed exchange. Clark, Pritchard, and Trotman-Dickenson[4] found the exchange rate extremely sensitive to changes in the surface–volume ratio of the reaction vessel. For an unpacked vessel they found the exchange to proceed by the rate law $R = k(I_2)^{1/2}(CH_3I)$. Only a lower limit of 32 kcal for the over-all activation energy of this exchange could be inferred from this work. They proposed the exchange to proceed by an SN2 inversion of the methyl iodide by atomic iodine.

However, in a consideration of the reaction between methyl iodide and hydrogen iodide

$$CH_3I + HI \longrightarrow CH_4 + I_2 \tag{1}$$

Flowers and Benson[5] as well as Sullivan[6] have convincingly argued that the reaction occurs primarily *via* the radical mechanism

$$I_2 \underset{k_r}{\overset{k_d}{\rightleftharpoons}} 2I \qquad K_{equil} \tag{2}$$

$$I + CH_3I \underset{k_2}{\overset{k_1}{\rightleftharpoons}} CH_3 + I_2 \tag{3}$$

$$HI + CH_3 \rightleftharpoons +CH_4 + I \tag{4}$$

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(1) Work was performed in the Ames Laboratory of the Atomic Energy Commission. Contribution No. 2509.

(2) Based on a Ph.D. Thesis by A. J. Kassman submitted 1969 to Iowa State University, Ames, Iowa.

(3) Pratt & Whitney Aircraft, AMRDL, Middletown, Conn.

(4) D. Clark, H. O. Pritchard, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 2633 (1954).

(5) M. C. Flowers and S. W. Benson, *J. Chem. Phys.*, 38, 882 (1963).

(6) J. H. Sullivan, *ibid.*, 46, 73 (1967).

Table I. Details of the CH_3I–I_2 Isotopic Exchange Experiments

p_1, mm	I_2 concn, mole %	CH_3I concn, mole %	Inc shock velocity, km sec^{-1}	T_5,[a] °K	Dwell time, msec	Fraction exchange	Compression ratio ρ_5/ρ_1[a]	Log k_1, cm^3 mole^{-1} sec^{-1}
220	0.209	2.85	0.591	954	2.10	0.492	4.15	9.23
224	0.299	2.85	0.581	929	2.11	0.474	4.05	9.35
187	0.208	2.85	0.608	997	1.46	0.466	4.34	9.27
239	0.242	2.16	0.561	870	2.16	0.117	3.69	9.02
235	0.185	2.15	0.571	893	2.08	0.152	3.78	9.00
235	0.112	2.15	0.581	917	2.10	0.262	3.88	9.10
215	0.233	2.15	0.586	934	1.86	0.155	3.96	8.90
197	0.302	2.15	0.591	949	1.58	0.187	4.05	9.04
236	0.166	3.15	0.566	889	2.16	0.198	3.89	8.97
237	0.290	3.15	0.571	905	2.14	0.175	3.98	8.90
228	0.172	3.15	0.576	915	1.82	0.237	4.02	9.01
235	0.195	3.15	0.561	877	2.18	0.135	3.84	8.82
136	0.312	3.15	0.638	1079	1.10	0.748	4.76	9.56
165	0.308	3.15	0.620	1032	1.37	0.740	4.56	9.51
158	0.369	1.94	0.650	1105	1.48	0.787	4.66	9.53
188	0.181	1.94	0.625	1035	1.57	0.666	4.35	9.46
193	0.186	1.94	0.609	989	1.72	0.496	4.15	9.37
195	0.198	1.94	0.603	974	1.74	0.528	4.10	9.45
197	0.236	1.94	0.625	1036	1.61	0.745	4.35	9.53
198	0.256	1.94	0.614	1005	1.79	0.622	4.24	9.44

[a] Subscript 5 on T and density, ρ, refers to the temperature behind the reflected shock. Subscript 1 refers to the initial conditions.

Reaction 3 is especially significant since it provides for the isotopic exchange of iodine between methyl iodide and elementary iodine. Values of the k_1 are available from the experimental work of Flowers and Benson in the range of 530–590°K.

The present study was undertaken in the belief that surface reaction would be negligible in the short reaction times accessible in the shock tube. It was hoped that possibly the relative contribution of the radical process (reaction 3) and the bimolecular inversion could be evaluated.

Experimental Section

Apparatus. The single-pulse shock tube used was similar to that described by Lifshitz, Bauer, and Resler[7] with the addition of a plunger to mechanically puncture the diaphragms. The driven section was a 1-in. diameter Pyrex tube, and metal parts were fabricated from stainless steel. The ratio of length (from the diaphragm to end wall) to diameter was 76. The dump tank which was located 6 cm before the diaphragm had a volume of 3.9 l. The driver end of the tube was fitted with a piston, sealed with O rings for tuning the shock tube to achieve the maximum cooling rate with each set of operating conditions. A ball valve was located 4 in. from the end wall to isolate a reactant sample for analysis after each experiment. Two Kisler quartz pressure transducers, Model 601A, were fixed in the 4-in. end section with a separation of 2.625 in. Helium was used as the driver gas and the reactants were diluted with argon. Diaphragms were 0.5-mil Mylar film.

The outputs of the transducers were recorded with a Tektronix Type 535 oscilloscope modified with a raster sweep circuit. The time intervals for the incident shock to traverse the distance between two piezoelectric transducers could be measured with the aid of a time mark generator to *ca.* ±1.5 μsec.

Materials. Methyl iodide, AR grade, was treated by passage through a column of anhydrous silica gel. It was stored in a darkened vessel containing a fresh strip of copper wire. A basic solution of ^{131}I was procured from Cambridge Nuclear Corp. Tagged iodine was prepared by the addition of carrier potassium iodide, AR grade, to the carrier-free active iodide. Nitric acid was added until the precipitation of elementary iodine was complete, and then the solid was filtered and sublimed. The argon was supplied as >99.995% pure by Air Products and Chemicals.

Procedure. For each condition of operating pressures in the driver and driven sections, the shock tube was tuned from observations of the oscilloscope traces by adjusting the location of the piston in the driver section to provide the maximum cooling rate which is obtained by convergence of the reflected shock, the contact surface, and the leading edge of the reflected cooling wave. The oscilliscope trace from a transducer located 19 mm from the end wall of the driven section is shown in Figure 1. This figure illustrates the very rapid pressure rise in the shock wave and the presence of a single cooling wave indicated by the nearly exponential reduction in pressure following a dwell time at high pressure and temperature of 2.1 msec. It is estimated that the cooling rate amounts to 0.4 deg/μsec.

To prepare for an exchange experiment, a sample of methyl iodide which had been frozen at liquid nitrogen was expanded into a 45-l. evacuated tank. The pressure of the methyl iodide vapor was next measured at room temperature by means of a Wallace and Tiernan absolute pressure gauge, Model FA 160, which had a 50-mm full-scale graduated in 0.2 mm. Argon was next introduced into the mixing tank and the pressure measured with a Hg manometer. This mixture was prepared at least 1 day prior to use. These measurements provided the mole fraction of the mixture.

Next, a sample of the tagged solid I_2 was weighed into a 10-ml bulb fitted with a capped standard taper and a stopcock for attachment to a 3-l. sample bulb. The iodine was permitted to expand into the large bulb, and its partial pressure was calculated from the weight of the I_2, the known volume, and the measured temperature by the ideal gas law. Next, the argon–CH_3I mixture was expanded into the sample bulb from the mixing tank. The pressure in the system was measured at this time indirectly by means of a "click" gauge. This click gauge, a small bulb with a flattened section blown at the end of a short length of glass tubing, gives an audible click with visible motion of the diaphragm at a calibrated pressure difference across the gauge. In this way the iodine-containing vapors did not contact mercury. To prevent the deposit of solid iodine, the sample bulb, the click gauge, and the driven section of the shock tube were heated to 62°. These measurements provided the mole fractions of the components in the shocked gas. These components were expanded into the driven section of the shock tube. The pressure of this gas, p_1, was measured just before the shock by means of the click gauge and a mercury manometer. This initial pressure and components of the systems are included with the experimental data in Table I.

Following the shocks in which a satisfactory oscilloscope trace was obtained, the products were pumped into a cold trap at liquid nitrogen temperature. After they were warmed, the contents of the trap were dissolved in acetone following the procedure of Clark, *et al.*[4] The solution was then shaken until colorless with a small drop of mercury, forming a precipitate of mercuric iodide. The organic fraction was distilled off and diluted to volume with acetone. The mercuric iodide was dissolved in 10% NaI solution and diluted to volume with water. The γ rays of the methyl iodide and the iodine fractions were individually counted by a scintillation spectrometer with a 3-in. NaI(Tl) crystal operated in conjunction with a RIDL 400 channel analyzer. Mass spectrometric analysis of

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(7) A. Lifshitz, S. H. Bauer, and E. L. Resler, Jr., *J. Chem. Phys.*, **38**, 2056 (1963).

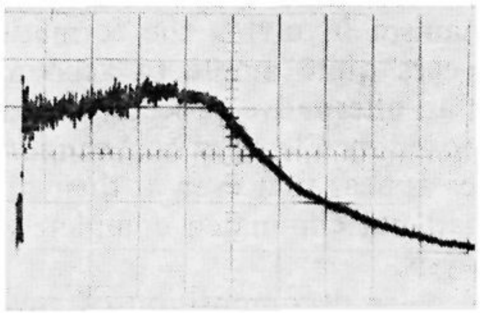

Figure 1. Oscilloscope trace from the transducer located 1.9 cm from the reflecting wall of the shock tube for a shock in argon illustrating the effectiveness of the tuning to attain a single cooling wave. The sweep velocity is 0.5 cm/msec.

shocked methyl iodide samples indicated no significant iodine formation from the decomposition of methyl iodide.

Calculations. Reflected shock temperatures were computed from the incident shock velocities with an IBM 360/65 digital computer by means of the usual conservation equations for shock tubes and the ideal gas law.[8] Thermodynamic parameters for argon, iodine, and iodine atoms were taken from the JANAF[9] tables. Enthalpies and heat capacities for methyl iodide were tabulated at 100° intervals using the classical partition functions without anharmonicity corrections. Vibrational frequencies for methyl iodide were taken from Sponer.[10] The endothermic dissociation of iodine was considered directly in the conservation equations, and no correction was necessary for the temperature.

Results

Results of the shock-tube experiments are included in Table I. The dwell times of column 6 are the space averages for the reactant section. These have been increased 5% to correct for expansion of the gases in the cooling fan.

The fraction of exchange in each experiment was determined by the γ-ray analysis of the separated fractions with the following definitions. A_Z is the activity of the component, Z, in counts per minute (cpm), and S_Z is the specific activity of that component, cpm (moles of I)$^{-1}$. S^∞, the specific activity at isotopic equilibrium, cpm (moles of I)$^{-1}$, is the total activity divided by the total moles of iodine atoms. The fraction exchange, F, was defined by the expression

$$F = S_{\mathrm{CH_3I}}/S^\infty = A_{\mathrm{CH_3I}}(X_{\mathrm{CH_3I}} + 2X_{\mathrm{I_2}})/(A_{\mathrm{CH_3I}} + A_{\mathrm{I_2}})X_{\mathrm{CH_3I}} \quad (5)$$

where the X's are the mole fractions of the corresponding components.

The rate constants for the dissociation of iodine and the recombination of iodine atoms in the presence of a third body (reaction 2) were taken from the work of Britton, *et al.*[11]

$$\frac{-2\mathrm{d}[\mathrm{I_2}]}{\mathrm{d}t} = \frac{\mathrm{d}[\mathrm{I}]}{\mathrm{d}t} = 2(R_\mathrm{d} - R_\mathrm{r}) = 2k_\mathrm{d}[\mathrm{M}][\mathrm{I_2}] - 2k_\mathrm{r}[\mathrm{M}][\mathrm{I}]^2 \quad (6)$$

Upon the decomposition of the I_2 molecules at the reaction temperature behind the reflected shock wave, the exchange with methyl iodide can proceed by reaction 3. With the steady-state approximation applied to methyl radical concentrations, the rate of formation of active methyl iodide in the high-temperature gas system is given by

$$\frac{\mathrm{d}}{\mathrm{d}t}(A_{\mathrm{CH_3I}}) = R_1(S_{\mathrm{I_2}} - S_{\mathrm{CH_3I}}) \quad (7)$$

Since there are three exchanging species, I, I_2, and CH_3I, a second differential equation is necessary to describe the exchange. The rate of change of activity in I is

$$\frac{\mathrm{d}(A_\mathrm{I})}{\mathrm{d}t} = 2R_\mathrm{d}S_{\mathrm{I_2}} - 2R_\mathrm{r}S_\mathrm{I} + R_1(S_{\mathrm{I_2}} - S_\mathrm{I}) \quad (8)$$

where S_I is the specific activity of iodine atoms at the reaction temperature. $S_{\mathrm{I_2}}$, S_I, and $S_{\mathrm{CH_3I}}$ are functions of $A_{\mathrm{CH_3I}}$ and A_I; so eq 7 and 8 are simultaneous differential equations in these variables. These equations could be solved in closed form if the iodine equilibrium reaction were established rapidly in comparison with the total contact time. Since at the lower temperatures the relaxation period for the iodine dissociation was as high as 30% of the total dwell time in the shock tube, it was desirable to include the rate of iodine dissociation in the exchange expressions. The equations were solved numerically by a fourth-order Runge–Kutta procedure.[12] For each experiment a value of k_1 was found which gave the observed fraction of exchange. These values are also included in Table I, and they have been plotted in Figure 2. The solid points represent the values of Flowers and Benson[5] in their study of the methyl iodide–hydrogen iodide reaction.

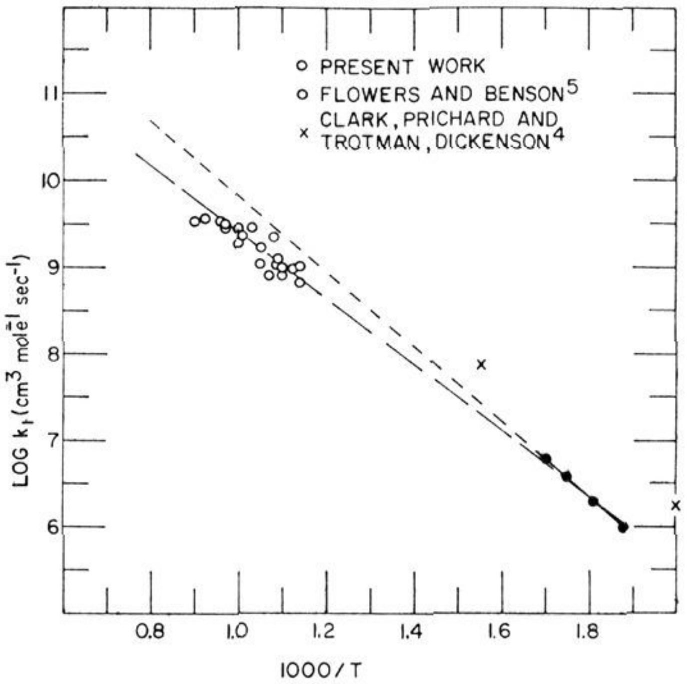

Figure 2. Arrhenius plots for the isotopic exchange of iodine with methyl iodide. The upper line is the line for $k_1 = 10^{14.2}\exp(-20.0\ \mathrm{kcal}/RT)$ as determined by Flowers and Benson. The solid portion indicates the temperature range of their experiments. The lower line represents $k_1 = 10^{13.2}\exp(-17.4\ \mathrm{kcal}/RT)$.

A plot of the function $k_1 = 10^{14.2}\exp(-20.0\ \mathrm{kcal}/RT)$, which characterized the results of Flowers and Benson,[5] is plotted in Figure 2. Their values have also been supported by a study of the approach to equilibrium in the reaction between CH_4 and I_2.[13] The rate constants for unpacked vessels, reported by Clark, *et al.*,[4] are also shown in Figure 2 where they lie significantly above the Flowers–Benson line. The data for the present shock tube studies involve an extrapolation of 300–500° from the region studied by Flowers and Benson. The values

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(8) J. N. Bradley, "Shock Waves in Chemistry and Physics," John Wiley & Sons, Inc., New York, N. Y., 1962, p 21.

(9) "JANAF Thermochemical Tables," Dow Chemical Co., Midland, Mich., 1965.

(10) H. Sponer, "Molekülspektren," Julius Springer, Berlin, 1935.

(11) D. Britton, N. Davison, W. Gehman, and G. Schott, *J. Chem. Phys.*, **25**, 804 (1956).

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(13) C. A. Goy and H. O. Pritchard, *J. Phys. Chem.*, **69**, 3040 (1965).

of k_1 cluster in an area centered about $10^{-0.3}$ lower than the extrapolation. The statistical variation for the shock tube data prevents an accurate evaluation of E_1 by themselves. However, an Arrhenius plot from the mean of the Flowers–Benson data to the mean of the shock tube data yields the equation: $k_1 = 10^{13.2} \exp(-17.4\ \text{kcal}/RT)$. These low values in k_1 may reflect in part a somewhat lower temperature behind the reflected shock wave than is predicted by simple shock wave theory. Studies[14,15] of reflected shocks for argon in the region 1500–3000°K, considerably higher than in the present work, have indicated temperatures 30–60° lower than the predicted values. Still, standard deviation in log k_1 for the points amounts to 0.12 which will correspond to 0.8 kcal in the E_1. This E_1 therefore lies within 3σ of the value given by Flowers and Benson. They indicated that their value of $E_1 = 20.0$ kcal gave a value for the bond dissociation energy of CH_3I about 1–2 kcal higher than other estimates, and the preexponential factor was somewhat high in view of the calculated collision number. Hence the present equation which makes use of the high-temperature data perhaps represents a better description of the kinetic behavior.

The mechanism involving the formation of methyl radicals appears quite ample to account for the exchange, and an alternative process such as the SN2 inversion proposed by Clark, *et al.*,[4] cannot play a major role. It does appear that even at their highest temperature they had not eliminated completely the effect of the wall catalysis.

The bimolecular decomposition of methyl iodide by argon was also tested as an alternative means for the methyl radical formation. With a preexponential factor of 10^{14} sec^{-1} cm^3 mole^{-1} as a limit for the expected collision frequency, an activation of only 35 kcal mole^{-1} would be required to provide even 10% of the reaction. Since this activation energy is 20 kcal below the bond dissociation energy, the contribution of this mechanism does not appear significant over the temperature range studied. Also, the bimolecular reaction of I_2 with methyl iodide was eliminated since a collision frequency for a reasonable activation energy would be much in excess of theoretical values.

The experimental data appear therefore to be consistent with a mechanism involving the formation of a methyl radical in the collision between an iodine atom and methyl iodide which now has been rather well established for several recent kinetics studies.[5,6,13,16]

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The Rate of Bridge–Terminal Proton Exchange in μ-Dimethylamino-diborane

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Abstract: The intramolecular hydrogen exchange in μ-dimethylamino-diborane has been studied by fitting the line shape of the ^{11}B nmr spectrum as a function of temperature. Relaxation matrix theory was used to establish a model for the line shape, and it was found necessary to consider the temperature dependence of both the exchange rate constant and the line-width parameter in order to reproduce the observed spectra over the full temperature range studied (213–373°K). A nonlinear least-squares program was used to extract values of these parameters from the spectra. The boron–bridge hydrogen and the boron–terminal hydrogen coupling constants were found to be 33.0 and 129.3 Hz, respectively. They are of the same sign and temperature independent. The exchange process was studied in solution in 1,2-dimethoxyethane, tetrahydrofuran (four concentrations), methylcyclohexane (two concentrations), and the neat liquid. The rate constant is found to have two components and may be written $k(T,C) = k_1(T) + Ck_2(T)$, where k_1 is the rate constant in inert solvents and in the neat material, k_2 is the rate constant for the ether-catalyzed exchange process, and C is the concentration of the ether. The results obtained were $\Delta S^{\ddagger} = 0.4 \pm 0.3$ cal/deg and $\Delta H^{\ddagger} = 16.9 \pm 0.1$ kcal/(deg mole) in methylcyclohexane and the neat liquid, $\Delta S^{\ddagger} = -25.5 \pm 0.1$ cal/deg and $\Delta H^{\ddagger} = 6.1 \pm 0.4$ kcal/(deg mole) for the catalyzed process in tetrahydrofuran, and $\Delta S^{\ddagger} = -28.7 \pm 0.4$ cal/deg and $\Delta H^{\ddagger} = 6 \pm 1$ kcal/(deg mole) in 1,2-dimethoxyethane. The ranges are standard errors.

The ^{11}B nmr spectrum of μ-dimethylamino-diborane is strongly temperatured ependent due to intramolecular exchange of the bridge and terminal hydrogens (see Figure 1).[1,2] Gaines and Schaeffer[2] reported the rate of exchange in ether solutions to increase with increasing base strength of the ether, and they estimated an activation energy of 3.7 kcal/mole for the process in 1,2-dimethoxyethane. They also discuss the mechanism of this exchange and conclude that it probably proceeds by cleavage of a boron–bridge hydrogen bond followed by rotation of the $-BH_3$ group and reestablishment of the bridge bond. If this mechanism is correct, the observed acceleration of exchange by Lewis bases

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(2) D. F. Gaines and R. Schaeffer, *ibid.*, 86, 1505 (1964).