verse step, the dissociation of the inner sphere complex is a simple first order involving the same form of the activated complex for both mechanisms. The entropy of activation for the dissociation step (−17.7 e.u.) is in agreement with the idea that the activated complex has a greater charge separation than the reactant, and such would be the case if waters entered the inner sphere and displaced the sulfate ion. The value would seem to indicate that the sulfate ion is just displaced and not completely eliminated from the coördination sphere.

It appears that at high acidity, low chromium(III) and sulfate ion concentrations, only three chromium species, Cr^{+3} ion, outer-sphere association (ion pair) complex ion $(Cr^{+3}SO_4^{=})^+$ and inner sphere complex ion $CrSO_4^+$, are necessary to explain the behavior of chromium(III) sulfate solutions.

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[CONTRIBUTION FROM THE N.M.R. DEPARTMENT, THE WEIZMANN INSTITUTE OF SCIENCE, REHOVOT, ISRAEL]

The Activation Energies of Proton Transfer Reactions in Water[1]

BY A. LOEWENSTEIN AND A. SZÖKE

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The rate constants of the acid and base catalyzed proton transfer reactions in water were measured in the temperature range of 20–80°, by the n.m.r. technique. The pH was controlled through the use of buffers. The Arrhenius activation energies obtained are: 2.6 ± 0.3 kcal./mole in the acidic range and 4.8 ± 0.5 kcal./mole in the basic range. In addition transverse and longitudinal relaxation times (T_2 and T_1) were measured at very low and high pH values.

Introduction

The study of proton transfer reactions in water is of importance to the understanding of the anomalous conductivities of hydronium and hydroxyl ions. Furthermore, in aqueous solutions of acids and bases, fast proton transfer in the water may be involved as part of the reaction scheme.

Three mechanisms are supposed to contribute to proton transfer in water

$$H_2O + H_3O^+ \overset{k_1}{\rightleftarrows} H_3O^+ + H_2O \tag{1}$$

$$H_2O + OH^- \overset{k_2}{\rightleftarrows} OH^- + H_2O \tag{2}$$

$$H_3O^+ + OH^- \overset{k_R}{\rightleftarrows} H_2O + H_2O \tag{3}$$

The recombination rate of hydronium and hydroxyl ions (reaction 3) was measured by Eigen and de Maeyer[2] using chemical relaxation methods. It was found that $k_R = (1.4 \pm 0.2) \times 10^{11}$ sec.$^{-1}$ M^{-1} at 25°, and its temperature dependence is described by an activation energy of 2–3 kcal./mole. Preliminary measurements on water, using the nuclear magnetic resonance (n.m.r.) technique, were reported by Meiboom, Luz and Gill.[3] Recently these measurements were extended and reinterpreted by Meiboom.[4] The rate constants thus obtained for reactions 1 and 2 were: $k_1 = (10.6 \pm 4) \times 10^9$ sec.$^{-1}$ M^{-1} and $k_2 = (3.8 \pm 1.5) \times 10^9$ sec.$^{-1}$ M^{-1} at 25 ± 1°. A measurement, performed with water containing the natural abundance of O^{17}, of the activation energy of reaction 1 was reported by Weiss,[5] who obtained a value of $0.7 < \Delta E < 8$ kcal/mole.

In the present work, measurements of these rate constants by the n.m.r. technique are reported over the temperature range of 20–80°. The results at room temperature reproduce those given by Meiboom,[4] under better controlled chemical conditions. From the dependence of the rates on temperature, the Arrhenius activation energies were evaluated.

Another problem studied was the apparent decrease[3] in T_2 (the transverse relaxation time) at pH values below 3 or above 10. It is shown that this decrease is accompanied by a similar decrease in T_1 (the longitudinal relaxation time) and thus has no significant connection with the exchange reactions.

Experimental Procedure

All n.m.r. measurements were performed at a proton frequency of 31.65 Mc./sec. Transverse relaxation times (denoted henceforth by T_2 in H_2O^{17} enriched water and T_2' in ordinary water) were measured by the modified Carr–Purcell method.[6] The accuracy of T_2 measurements was estimated to be ± 0.1 sec. T_1 was measured by the 180°–90° pulses method.[7] The values of T_1 were close to those obtained (in degassed samples) by Simpson and Carr[8] and were measured with an accuracy of ± 0.1 sec.

Temperature control was accomplished by passing a heated air current of constant flow around the sample. The temperature was measured with the aid of a Copper–Constantan thermocouple inserted in the air gap near the coils. The accuracy of the temperature data is estimated to be ± 1°.

Solutions were prepared in H_2O^{17} enriched water containing between 0.6 and 1.2 atom per cent of O^{17}. The concentration of O^{17} was determined by a mass-spectrometer.[9]

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[1] A preliminary report of this work was presented at the 29th meeting of the Israeli Chemical Society and was published in the *Bull. Res. Counc. of Israel*, **10A**, No. 3, 28 (1961).

[2] M. Eigen and L. de Maeyer, *Naturwissenschaften*, **42**, 413 (1955).

[3] (a) S. Meiboom, Z. Luz and D. Gill, *J. Chem. Phys.*, **28**, 1611 (1957); (b) D. Gill, Thesis, The Hebrew University, Jerusalem, 1959.

[4] S. Meiboom, *J. Chem. Phys.*, **34**, 375 (1961).

[5] K.-H. Weiss, private communication.

[6] S. Meiboom and D. Gill, *Revs. of Scient. Instr.*, **29**, 688 (1958).

[7] H. Y. Carr and F. M. Purcell, *Phys. Rev.*, **94**, 630 (1954).

[8] J. H. Simpson and H. Y. Carr, *ibid.*, **111**, 1201 (1958).

[9] The authors are indebted to the Isotope Department of the Weizmann Institute for kindly supplying the H_2O^{17} enriched water and for the mass spectrometer determinations of the O^{17} concentration.

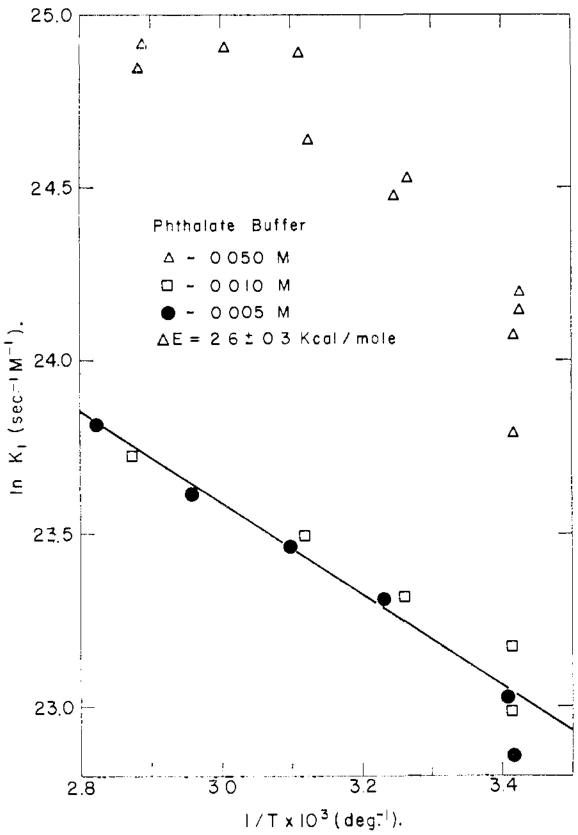

Fig. 1.—Plot of the natural logarithm of the rate constant of the reaction $H_3O^+ + H_2O$, k_1, as a function of the reciprocal value of the absolute temperature, for different KH phthalate buffer concentrations.

The water was carefully distilled *in vacuo* prior to preparation of the solutions.

In order to achieve precise control of the *p*H, buffer solutions were used. In the acidic range (*p*H 5.53–5.90) a KH Phathalate–NaOH buffer was used at concentrations of 0.05, 0.01 and 0.005 *M*. In the basic range two buffers were used: diethylbarbiturate–HCl (*p*H 7.88–8.61) and Borax–HCl (*p*H 8.42–8.77), the concentrations being 0.05, 0.01 and 0.002 *M*. Since the buffering compounds may be involved in exchange reactions and thus have an effect on the broadening of the water lines, the following procedures were used: (1) Measurements were taken at diminishing buffer concentrations until further dilution had no effect. As will be shown later, this procedure is superfluous with the two basic buffers used. (2) It has been shown[4] that all changes in T_2 in *pure* water are due to the H_2O^{17} present. Any possible effects arising from direct exchange between the water and buffer molecules were eliminated by replacing $1/T_1$ by $1/T_2'$ in the expression for the rate constant (eq. 3 of ref. 4), where T_1 is the longitudinal relaxation time of the O^{17} enriched solutions and T_2' is the transverse relaxation time of a buffer solution of the same concentration in water containing the natural abundance of O^{17} (0.037%). The O^{17} contribution to $1/T_2'$ in these solutions was always negligible in comparison to the same quantity $(1/T_2)$ measured in the O^{17} enriched solutions. It should be noted that the contribution to $1/T_2$ of an exchange reaction in water that is catalyzed by the buffer is not eliminated by this procedure; however, it is assumed to be small and is in any case corrected for by procedure 1.

The changes in the *p*H of the buffer solutions with temperature were measured with a Metrohm type E 184C *p*H-meter equipped with a combined (glass-calomel) type H electrode. The *p*H meter was calibrated at different temperatures by using Borax 0.01 *M* and KH Phthalate 0.05 *M* buffers whose *p*H-temperature dependence is known.[10]

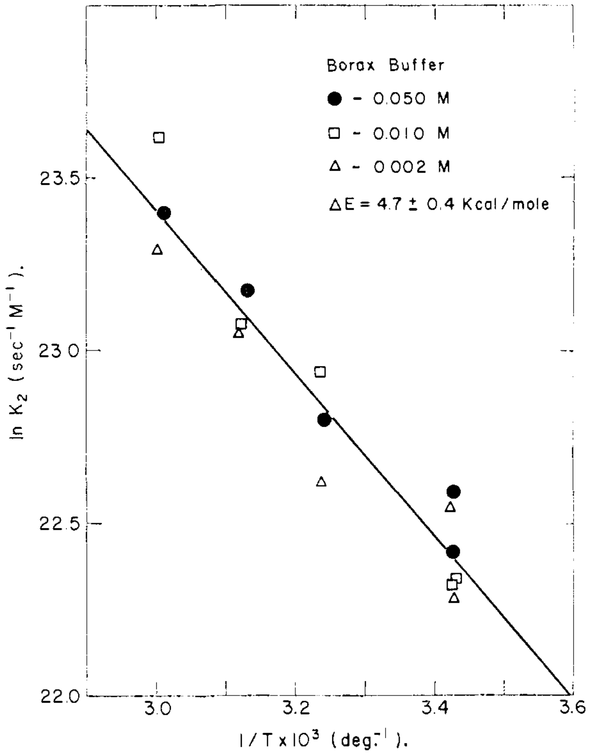

Fig. 2.—Plot of the natural logarithm of the rate constant of the reaction $H_2O + OH^-$, k_2, as a function of the reciprocal value of the absolute temperature, for different borax buffer concentrations.

Results and Discussion

The values of the rate constants k_1 and k_2 were calculated from the measured values of T_2 and T_2' (replacing T_1) by eqs. 3 and 9 of ref. 4. The value δ = 290 rad./sec. (spin–spin coupling constant between O^{17} and H) was accepted from ref. 4. Values of K_w at different temperatures were taken from Dorsey.[11] A correction taking into account the change of T_1 of O^{17} with temperature was applied, assuming inverse proportionality to the viscosity. The value of T_1 at 25° was taken from ref. 4 (T_1^{-1} = 230 sec.$^{-1}$) and viscosities from ref. 11, p. 183. This correction was never greater than 20% of the rate constants.

Figs. 1–3 show plots of the natural logarithm of the rate constants as a function of the reciprocal of the absolute temperature. The straight lines were drawn using the least squares method and the errors in the slopes are the probable errors.[12] The values of the activation energies thus obtained were: 2.6 ± 0.3 kcal./mole for the reaction $H_3O^+ + H_2O$ and 4.7 ± 0.4 or 5.0 ± 0.5 kcal./mole for the reaction $H_2O + OH^-$ (for the two basic buffers). From Figs. 2 and 3 it is seen that the rates are almost independent of buffer concentration for the case of Borax and diethylbarbiturate buffers. However, the results for the phthalate

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(10) "Symposium on *p*H Measurement," ASTM Technical Publication No. 73, p. 38.

(11) N. E. Dorsey, "Properties of Ordinary Water Substance," Reinhold Publishing Corp., New York, N. Y., 1941, p. 378.

(12) H. Margenau and G. M. Murphy, "Mathematics of Physics and Chemistry," D. Van Nostrand Co., New York, N. Y., 1943, p. 502.

buffers (Fig. 1) show a marked deviation for the highest buffer concentration (0.05 *M*). This may indicate an exchange reaction in water involving the protons of the carboxylic groups of the phthalate. At lower phthalate concentrations, the contribution of this reaction becomes less important, and it seems that the dilution limit was reached. Figs. 1–3 indicate that the rate constants may not obey an Arrhenius equation and that ΔE may be a function of the temperature.

The values of the rate constants k_1 and k_2 at 25° were evaluated from the graphs and the results are

$k_1 = (11.0 \pm 1.1) \times 10^9$ sec.$^{-1}$ M^{-1} (Phthalate buffer)

$k_2 = (5.0 \pm 0.7) \times 10^9$ sec.$^{-1}$ M^{-1} (Barbiturate buffer)

$k_2 = (6.0 \pm 0.9) \times 10^9$ sec.$^{-1}$ M^{-1} (Borax buffer)

The inaccuracy in δ (taken from ref. 4) may introduce an additional error of about 30% in the absolute values of the rate constants at any temperature. However, this correction introduces only a very small error (less than 3%) in the values of the activation energies, since it appears only through the correction applied for the change of T_1 of O^{17}.

The rate constants for reactions 1 and 2 were calculated[4] from the anomalous mobilities of H^+ and OH^- and are in good agreement with the experimental values measured at room temperature. However, the temperature dependence of the anomalous mobility of these ions differs significantly from the temperature dependence of the rate constants. The values of the apparent activation energies for the anomalous mobilities of H^+ and OH^- are lower,[13,14] especially for the OH^- ion, than the corresponding activation energies of the transfer reactions. Furthermore, the activation energies of the mobilities decrease with increasing temperature whereas those of the transfer reactions seem, if anything, to increase very slightly with temperature. Bjerrum[14] calculated the true activation energies for the mobilities and transfer, assuming that the same mechanism is responsible for both and taking into account a correction due to the change of the number of hydrogen bonds with temperature. He obtained the values of 2.5 and 4.7 kcal./mole for reactions 1 and 2 respectively, which is in excellent agreement with the results given in this work. This correspondence however may be fortuitous since we believe that the change of water structure with the temperature may be involved in a similar way both in transfer and mobility reactions.

Another point is that for both mobilities and proton transfer, the activation energies for OH^- are higher than those for H_3O^+. This fact was explained by Gierer and Wirtz[15] by considering the charge distribution in the transition state. However, the difference in the case of the transfer reactions seems too high to be accountable on this basis alone.

The activation energies of proton transfer reactions for ammonium and methylammonium ions in aqueous solutions were measured by Connor and Loewenstein[16] and were found to be near zero for the predominant reactions. The values of the free energies, heats and entropies of activation for these processes ($\Delta F^{\ddagger}$, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, respectively) were given in Table III of ref. 15 and may be compared with the analogous values for the transfer reactions in water. The computed[17] figures are recorded in Table I, which also includes the measured activation energies and the calculated frequency factors A (pre-exponential factors of the Arrhenius equation). The interesting features in Table I are that the values of $\Delta F^{\ddagger}$ are of approximately the same magnitude in both cases whereas the values of $\Delta S^{\ddagger}$ are considerably lower in water. This may indicate that the steric factor or the mutual orientation of the molecules taking part in the proton transfer plays a less important role in water than in the ammonium salts.

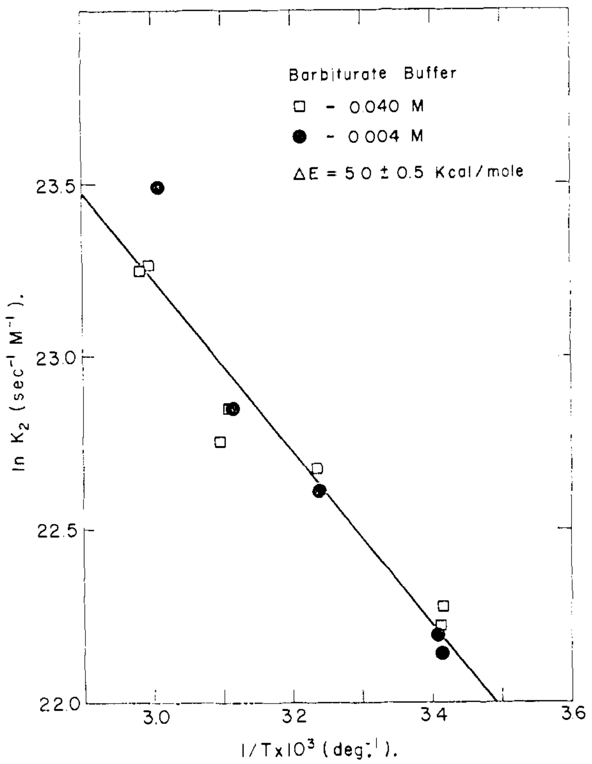

Fig. 3.—Plot of the natural logarithm of the rate constant of the reaction $H_2O + OH^-$, k_2, as a function of the reciprocal value of the absolute temperature, for different diethylbarbiturate buffer concentrations.

Measurements at Extreme *p*H Values.—It was mentioned in the introduction that the T_2 of water shows an 'anomalous' decrease at *p*H values below 3 or above 10. This behavior could not be explained in terms of salt effects.[3b] An attempt[5] to explain it as being due to the presence of Mn^{++} (a misinterpretation of Meiboom's work[4]) also failed. We therefore reinvestigated this *p*H range and found that T_2 is in fact equal to T_1 within the

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[13] M. Eigen and L. deMaeyer, *Proc. Royal Soc.*, **247A**, 505 (1958).

[14] N. Bjerrum, *Dan. Mat. Fys. Medd.*, **27**, No. 1 (1951).

[15] A. Gierer and K. Wirtz, *Ann. Phys. Lps.*, [6] **6**, 257 (1949).

[16] T. M. Connor and A. Loewenstein, *J. Am. Chem. Soc.*, **83**, 560 (1961).

[17] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 523.

TABLE I

VALUES OF ΔE, $\Delta H^{\ddagger}$, $\Delta F^{\ddagger}$, $\Delta S^{\ddagger}$, (AT 300°K.) FOR PROTON TRANSFER IN WATER

Reaction	ΔE (kcal. mole^{-1})	$\Delta H^{\ddagger}$ (kcal. mole^{-1})	$\Delta F^{\ddagger}$ (kcal. mole^{-1})	$\Delta S^{\ddagger}$ (e.u.)	A (sec.$^{-1}$)
$H_3O^+ + H_2O$	+2.6	+2.0	+3.8	−5.8	9.4×10^{11}
$OH^- + H_2O$	+4.7	+4.1	+4.1	−0.1	1.7×10^{13}
	+5.0	+4.4	+4.3	+0.5	2.3×10^{13}
$H_3O^+ + OH^-$[a]	+2.5	+1.9	+2.3	−1.3	9.0×10^{12}

[a] Approximate values calculated from ΔE and k_R given by Eigen and deMaeyer.[2]

TABLE II

VALUES OF T_1 AND T_2 (IN SEC.) IN VERY ACIDIC OR BASIC WATER (25°)

	*p*H	T_1 (meas.)	T_2 (meas.)	T_1 (calcd.)
Ordinary water	~ 0	2.54	2.52	2.52
Ordinary water	~14	2.24	2.17	2.11
H_2O^{17} enriched water (0.6%)	0.86	2.39	2.36	

limits of experimental error and that the two decrease together. Table II summarizes some of the results. The decrease of T_1 and T_2 at high acid and base concentrations is due to the increase of the viscosity under these conditions. Table II includes values of T_1 calculated by the formula $T_1 = T_1(\max)/\eta$ where $T_1(\max)$ is equal[3b,8] to 2.6 and η is the specific viscosity. Thus, this effect is not related in any way to the proton transfer reaction since the latter would give rise to a difference between T_2 and T_1.

Acknowledgments.—The authors wish to thank Dr. S. Alexander for very helpful discussions and suggestions in the early stages of this work and Mr. M. Sasson for his excellent care of the n.m.r. instrument.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY, CAMBRIDGE, MASSACHUSETTS]

An Electron Impact Investigation of Some Organoboron Difluorides[1,2]

BY W. C. STEELE,[3] L. D. NICHOLS[4] AND F. G. A. STONE

RECEIVED SEPTEMBER 11, 1961

The appearance potentials of the major positive ions in the mass spectra of methyl-, vinyl-, ethyl- and iso-propylboron difluoride have been measured. The boron–carbon bond dissociation energy has been calculated in each of the four cases, and an indirect measurement of the boron–hydrogen bond dissociation energy in the HBF_2 molecule is reported. The heat of formation of methylboron difluoride has been calculated, and estimates are given for the other three compounds. The various processes for dissociation under electron impact are discussed.

Continued interest in preparative boron chemistry during the last two decades has emphasized the lack of molecular thermodynamic data for boron compounds in general. In particular, little information[5] concerning the strength of the boron–carbon bonds in organoboron compounds is available, and this has limited our understanding of the bonding in these substances and the factors governing the course of their reactions. To remedy this situation in the case of the lower organoboron difluorides RBF_2 (R = CH_3–, C_2H_5–, CH_2:CH– and $(CH_3)_2CH$–), a mass spectrometric study of these halides was made. The appearance potentials obtained in this work, taken in conjunction with the appropriate free radical ionization potentials, allowed a direct calculation of boron–carbon bond strengths without many of the difficulties attendant upon a calorimetric investigation of compounds containing both boron–carbon and boron–halogen bonds.

Experimental

The organoboron difluorides used in this work were prepared by treating the appropriate tetraorganotin compound with boron trifluoride.[6] The compounds were manipulated in a high vacuum system, and their purity was determined from their infrared and mass spectra. A small amount of boron trifluoride was the most common impurity, but was easily reduced to below 1%.

Appearance potentials were measured using a Consolidated Electrodynamics Corporation Model 21-103C mass spectrometer, modified to allow magnetic scanning. All measurements of ions containing boron were made on the peak corresponding to the ^{11}B isotope. The data were evaluated by the vanishing current method,[7] using semi-log plots where possible. Some of the ionization efficiency curves failed to yield semi-log plots parallel to the standard curves, in which case the appearance potentials were obtained by a conventional extrapolation to zero intensity on linear paper or by the essentially equivalent "extrapolated voltage difference" method. Argon (I = 15.76 e.v.) and krypton (I = 14.00 e.v.) were used as standards and were introduced simultaneously with the sample in each case.

Since organoboron difluorides are highly reactive towards water, it was necessary to thoroughly flush the mass spectrometer and sample system with sample material prior to its final introduction, in order to prevent a build-up of hydrolysis products during the appearance potential determinations. Fortunately, the occurrence of this hydrolysis could be detected immediately in the mass spectrum.

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(1) (a) Part VII of the series "Organoboron Halides." For Part VI see J. R. Phillips and F. G. A. Stone, *J. Chem. Soc.*, in press; for Part V see S. L. Stafford and F. G. A. Stone, *J. Am. Chem. Soc.*, **82**, 6238 (1960). (b) Also Part VII of the series "Spectroscopic Studies on Organometallic Compounds"; for Part VI see E. Pitcher and F. G. A. Stone, *Spectrochim. Acta*, **17**, 1244 (1961).

(2) This research was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research.

(3) Postdoctoral Fellow, Harvard University.

(4) Fellow of the General Electric Educational and Charitable Fund, 1959–1961.

(5) (a) The thermochemical bond energy term E has been calculated for the boron–carbon bond in several trialkylboron compounds from their heats of combustion, the most recent refinements being those of W. H. Johnson, M. V. Kilday and E. J. Prosen, *J. Research Natl. Bureau Standards*, **65A**, 215 (1961); (b) The appearance potentials of trimethyl- and triethyl-boron have been measured by R. W. Law and J. L. Margrave, *J. Chem. Phys.*, **25**, 1086 (1956), but no attempt was made to interpret results in terms of bond dissociation energies.

(6) F. E. Brinckman and F. G. A. Stone, *J. Am. Chem. Soc.*, **82**, 6218 (1960).

(7) See F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, Inc., New York, N. Y., 1957.