

liminary study¹⁶ indicated that proton irradiation of pentaborane-9 produced higher boron hydrides which consisted of smaller boron hydride polyhedra coupled together. In fact, in more recent work,¹⁷ it is found that deuterium irradiation of pentaborane produced decaborane-16 with no detectable amounts of decaborane-14 and irradiation of decaborane-14 resulted in the coupling of two of these units ($B_{10}H_{18}$) to produce icosaborane-26.

Carboranes, carbon-boron-hydrogen compounds with delocalized electron-deficient skeletons, have been prepared by electric discharge through mixtures of a boron hydride, such as pentaborane, and an unsaturated hydrocarbon, such as acetylene.¹⁸ The tracing of the mechanism of these reactions while more complex than that of $B_{10}H_{18}$ synthesis is closely related to it, since $B_{10}H_{16}$ is found among the products of these reactions.

Acknowledgments.—The authors wish to thank Dr. L. Edwards of Callery Chemical Company for arranging to have the experimental aspects of this research run at Callery. The authors also wish to thank Mr. Sol James, Chief of Automatic Computations, Martin Computing Center, for his generous cooperation and Mrs. Jane

(16) H. Schmied and W. S. Koski, Abstracts of Papers, 135th National American Chemical Society Meeting, 1959, p. 38M.

(17) L. H. Hall and W. S. Koski, *J. Am. Chem. Soc.*, **84**, 4205 (1962).

(18) R. E. Williams, C. D. Good and I. Shapiro, paper presented before the Division of Inorganic Chemistry, 140th National American Chemical Society Meeting, Chicago, Ill., September 1961.

TABLE IV
COMPARISON OF B_5H_9 AND B_5D_9 MONOISOTOPIC
FRAGMENTATION PATTERNS

Species	$B^{11}_2H_n^+$ (calcd. using 1.17% B^{10})	Species	$B^{11}_2D_n^+$ (calcd. using 1.17% B^{10} and 1.529% H)
B_5H_9	100.18	B_5D_9	99.90
B_5H_8	0.74	B_5D_8	0.63
B_5H_7	100.00	B_5D_7	100.00
B_5H_6	6.90	B_5D_6	4.17
B_5H_5	133.75	B_5D_5	108.80
B_5H_4	25.51	B_5D_4	16.14
B_5H_3	26.50	B_5D_3	17.03
B_5H_2	27.80	B_5D_2	18.83
B_5H	23.43	B_5D	15.07
B_5	30.40	B_5	17.62
B_4H_9	0.45	B_4D_9	1.63
B_4H_8	0.04	B_4D_8	-0.01
B_4H_7	0.06	B_4D_7	0.07
B_4H_6	5.00	B_4D_6	5.33
B_4H_5	11.08	B_4D_5	9.92
B_4H_4	41.01		
B_4H_3	27.91		
B_4H_2	20.81		
B_4H	13.59		
B_4	7.65		

Hebel for the actual programming of the fragmentation pattern problem.

[CONTRIBUTION OF THE DEPARTMENT OF CHEMISTRY OF ARGONNE NATIONAL LABORATORY, ARGONNE, ILL.]

Reaction Constants of the Hydrated Electron^{1a}

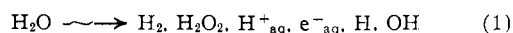
BY SHEFFIELD GORDON, EDWIN J. HART, MAX S. MATHESON, JOSEPH RABANI^{1b} AND J. K. THOMAS

RECEIVED FEBRUARY 14, 1963

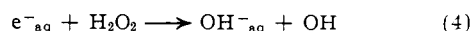
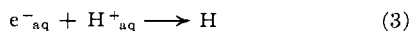
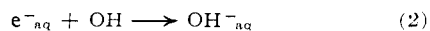
Intense pulses of energetic electrons produce an absorption in the visible in aqueous solutions which is attributed to the hydrated electron, e^-_{aq} . By following the decay of this absorption at 5780 Å., rate constants for a number of reactions of the hydrated electron have been measured. The effect of ionic strength on the rate constant for $e^-_{aq} + \text{ferricyanide ion}$, as well as the fact that some of the added reactants are known electron scavengers, confirms that the absorption is due to e^-_{aq} . Among the rate constants measured are: $e^-_{aq} + H^+_{aq}$, $2.36 \pm 0.24 \times 10^{10} M^{-1} \text{sec}^{-1}$; $e^-_{aq} + H_2O_2$, $1.23 \pm 0.14 \times 10^{10} M^{-1} \text{sec}^{-1}$; $e^-_{aq} + O_2$, $1.88 \pm 0.2 \times 10^{10} M^{-1} \text{sec}^{-1}$; and $e^-_{aq} + e^-_{aq}$, $1 \times 10^{10} M^{-1} \text{sec}^{-1}$; all rate constants being for $-d(e^-_{aq})/dt$.

The discovery² of the broad optical absorption band of the hydrated electron in irradiated water makes it possible to observe directly a primary radiation chemical species in water. We have now used the technique of pulsed radiolysis to measure rate constants for reactions of the hydrated electron. The apparatus used was developed by Matheson and Dorfman³ and has been described elsewhere.⁴ Generally, the decay of absorption at 5770–5790 Å. was followed, but a few experiments at 6850 Å. gave similar results.

The species formed by irradiation of water are given in eq. 1.



The hydrated electron is a very reactive species and possible reactions with other species in 1 are

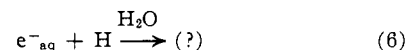
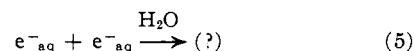


(1) (a) Based on work performed under the auspices of the U. S. Atomic Energy Commission. (b) Post Doctoral Fellow from the Hebrew University, Jerusalem, Israel.

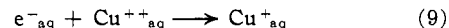
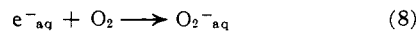
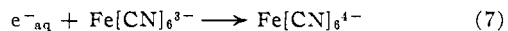
(2) E. J. Hart and J. W. Boag, *J. Am. Chem. Soc.*, **84**, 4090 (1962); J. W. Boag and E. J. Hart, *Nature*, **197**, 45 (1963).

(3) M. S. Matheson and I. M. Dorfman, *J. Chem. Phys.*, **32**, 1870 (1960).

(4) I. M. Dorfman, I. A. Taub and R. E. Bühler, *ibid.*, **36**, 3051 (1962).



The hydrated electron may also react with water in a first-order reaction, but Czapski and Schwarz⁵ set this rate constant as probably less than 10^4sec^{-1} (our results show an upper limit of $4 \times 10^4 \text{sec}^{-1}$) so that in our experiments with e^-_{aq} concentrations of 2 to 30 micromolar and second-order rate constants about $10^{10} M^{-1} \text{sec}^{-1}$, second-order reactions predominate. The rate constants for 3 and 4 were measured by adding sufficient H_2SO_4 or H_2O_2 that the decay of e^-_{aq} absorption became pseudo-first order with first-order rate constants proportional to $[H^+_{aq}]$ or $[H_2O_2]$. These rate constants as well as those for reactions 7, 8 and 9 are given in Table I. The constants for 7, 8 and 9 were



measured in the presence of potassium ferricyanide, oxygen or cupric sulfate.

The reactions of Table I are consistent with the idea that the absorption decay followed is that of the hy-

(5) G. Czapski and H. A. Schwarz, *J. Phys. Chem.*, **66**, 471 (1962).

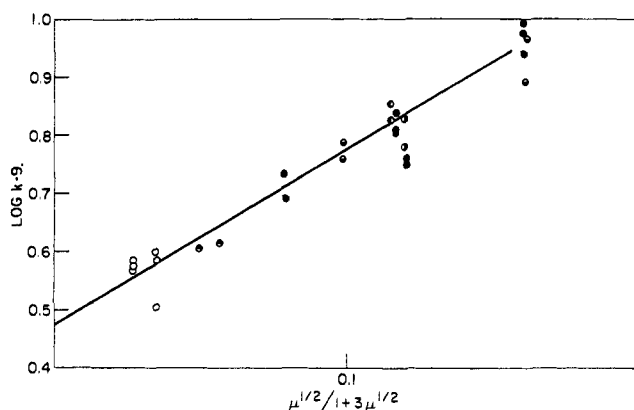


Fig. 1.— k_7 as a function of ionic strength μ at pH 10.30–10.47; except where specified, $MeOH = 2.5 \times 10^{-2} M$ to scavenge OH was added: \circ , no salt added to $K_3Fe(CN)_6$; \bullet , Na_2SO_4 ; \ominus , $KClO_4$; \odot , $NaOH$ (pH 12.45); \ominus , $K_4Fe(CN)_6$; no $MeOH$: \bullet , $K_4Fe(CN)_6$ as added salt and OH scavenger, pH 7 (OH^- formed scavenges H^+).

drated electron. In addition the ratios of $k_3:k_4:k_8$ given by Czapski and Allen⁶ are 1.0:0.54:1.0 from competition experiments while the ratios from Table I are 1.0:0.52:0.80. Reaction 7 was used to obtain supporting evidence that the hydrated electron is involved by determining k_7 in the presence of added salts. Czapski and Schwarz⁵ used the expression

$$\log \frac{k}{k_0} = 1.02Z_aZ_b \frac{\mu^{1/2}}{1 + \alpha\mu^{1/2}}$$

derived from the Debye-Hückel theory and the Brönsted model of ionic reactions to provide evidence for e^-_{aq} as an intermediate in water radiolysis. Here k_0 is the rate constant at zero ionic strength for reaction between a and b with charges, respectively, Z_a and Z_b . They took α as unity⁵ which amounts to choosing a distance of closest approach of ions of 3 Å. If the radius of the hydrated electron is about 10 Å, then α might be taken as 3. The line in Fig. 1 corresponds to $\alpha = 3$, $Z_a = -1$ and $Z_b = -3$. However, no quantitative significance is attached to the line in view of the known difficulties in applying the Debye-Hückel theory at high ionic strengths. Added salt also gave a smaller and opposite effect on k_3 .

TABLE I

RATE CONSTANTS^a OF THE HYDRATED ELECTRON AT 21–23°

	Rate constant	Reaction	pH
k_3^b	2.36 ± 0.24	$e^-_{aq} + H^+_{aq}$	4.0 to 4.6
k_4	$1.23 \pm .14$	$e^-_{aq} + H_2O_2$	7
k_7^c	$0.30 \pm .04$	$e^-_{aq} + Fe(CN)_6^{3-}$	7 and 10.3
k_8^d	$1.88 \pm .2$	$e^-_{aq} + O_2$	7
k_9	$3.3 \pm .3$	$e^-_{aq} + Cu^{++}_{aq}$	7

^a In units $10^{10} M^{-1} sec^{-1}$. ^b L. M. Dorfman and I. A. Taub of this Laboratory independently find $2.26 (\pm 0.21) \times 10^{10} M^{-1} sec^{-1}$. ^c For zero ionic strength by extrapolation. ^d J. P. Keene⁹ obtained $1.5 \times 10^{10} M^{-1} sec^{-1}$.

For first-order reactions whose products do not absorb the analyzing light, the rate constants k are equal to the slopes of the $-\ln D$ vs. t plots, where D is the optical density of the solution at time t . For a second-order reaction, plots of $1/D$ vs. t will be linear, yielding slopes $k/\epsilon l$, where l is the light path in the cell and ϵ the molar extinction coefficient. To obtain ϵ the energy input into the reaction cell was measured with the modified ferrous sulfate dosimeter saturated with oxygen⁷ ($G = 15.6 Fe^{3+}/100$ e.v.). From this energy input and an assumed G for electrons, $G_{e^-_{aq}}$, of 2.5.⁸

(6) G. Czapski and A. O. Allen, *J. Phys. Chem.*, **66**, 262 (1962).

(7) J. K. Thomas and E. J. Hart, *Radiation Research*, **17**, 408 (1962).

the initial concentration of electrons was estimated for an aqueous system pulse irradiated similarly to the dosimeter. This initial concentration combined with the initial optical density gave $\epsilon = 11,400 (\pm 30\%)$ including 12% uncertainty in $G_{e^-_{aq}}$ liter/mole cm. at 5770–5790 Å. for the decadic molar extinction coefficient. Our $G_{e^-_{aq}} \times \epsilon$ at 5770–5790 is 28,500, while Keene reports 18,700 at 5430 Å. and his data can be extrapolated to give 23,500 at 5770–5790 Å.⁹

When reactions 2 and 3 were suppressed by adding methanol (0.005 to 0.1 M) to scavenge OH radicals and sodium hydroxide (pH 10 to 13) to scavenge H^+_{aq} ions, the decay of absorption followed second-order kinetics until about 65% of the electrons had reacted. The second-order rate constant of $2.05 \times 10^{10} M^{-1} sec^{-1}$ is independent of methanol concentration, is somewhat lower at higher pH 's, and independent of a fourfold variation in the initial electron concentration. The evidence is that we are dealing principally with second-order reactions between species produced by the radiation. After the observed rate constant of $2.05 \times 10^{10} M^{-1} sec^{-1}$ is corrected for reaction 4 (taking $G_{H_2O_2} = 0.7^{10}$), a residual rate constant of $1.70 \times 10^{10} M^{-1} sec^{-1}$ remains. This may be due to the reaction of e^-_{aq} with $\cdot CH_2OH$ or to reactions 5 or 6 or to a combination. A small salt effect suggests participation of a reaction of the electron with another negative species as in 5. Replacing methanol with ethanol or diethyl ether gave similar rate constants.

In alkaline ferrocyanide solutions a second-order rate constant of $2.95 \times 10^{10} M^{-1} sec^{-1}$ ($2 \times 10^{-3} M K_4Fe(CN)_6$) was found. If OH^- + ferrocyanide gives ferricyanide directly, $G_{OH} = 2.4$,¹⁰ and $k_7 = 0.6 \times 10^{10} M^{-1} sec^{-1}$ at this ionic strength (Fig. 1), we subtract 0.58×10^{10} for reaction 7 and 0.35×10^{10} for reaction 4 to obtain $2.02 \times 10^{10} M^{-1} sec^{-1}$ residual rate constant. This is experimentally the same as the methanol result except that correction has been made for the reaction of e^-_{aq} with the product of OH plus scavenger. This suggests that the residual rate constant in both cases may be due to reactions 5 and 6.

As to the possibility of reaction 6, we note only that the electron affinity of H is 18 kcal., and that since the maximum G_H estimate is 0.6¹¹ only a fraction of the electrons could react with H atoms.

With regard to reaction 5 it may be noted that it has been suggested that the dimer $(e^-)_2$ exists in equilibrium with e^- in potassium-ammonia solutions.¹² Also there is the small salt effect noted above. Our evidence provides support for reaction 5 with a rate constant¹³ of about $1.7 \times 10^{10} M^{-1} sec^{-1}$.

In alkaline solution at pH 10.5 (no OH scavenger) the apparent second-order rate constant is $6.3 \times 10^{10} M^{-1} sec^{-1}$. (A long-lived transient is noted if carbonate is present in the alkali, which transient is suppressed by methanol.) This rate should be largely due to reaction 2 and gives $k_2 \sim 4.2 \times 10^{10} M^{-1} sec^{-1}$ or $\sim 6 \times 10^{10} M^{-1} sec^{-1}$ depending on whether the rate in the alkaline methanol solution is principally due to reaction 5 or to $e^-_{aq} + \cdot CH_2OH$.

We are continuing work on the reactions of the hydrated electron.

(8) Mean value between 2.3 and 2.8; see references M. S. Matheson, *Ann. Rev. Phys. Chem.*, **13**, 77 (1962), pp. 98–99.

(9) J. P. Keene, *Nature*, **197**, 47 (1963).

(10) A. O. Allen, "The Radiation Chemistry of Water and Aqueous Solutions," D. Van Nostrand Co., Inc., New York, N. Y., 1961, p. 46.

(11) (a) J. T. Allan and G. Scholes, *Nature*, **187**, 218 (1960); (b) J. Rabani and G. Stein, *J. Chem. Phys.*, **37**, 1865 (1962).

(12) C. A. Hutchison, Jr., and D. E. O'Reilly, *ibid.*, **34**, 163 (1961).

(13) NOTE ADDED IN PROOF.—Experiments with $\sim 0.1 M H_2$ and pH 13 give $k_5 = 1 \times 10^{10} M^{-1} sec^{-1}$ at this pH . This result and other recent experiments suggest reaction 6 accounts for an appreciable part of the rate constant $1.7 \times 10^{10} M^{-1} sec^{-1}$.

Acknowledgment.—We wish to acknowledge the invaluable support of B. E. Cliff in the operation of the linear accelerator, of W. A. Mulac in carrying out

experiments, S. Petrek in improvement of apparatus as well as very helpful discussions with R. L. Platzman, L. M. Dorfman and I. A. Taub.

[CONTRIBUTION No. 1471 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, LOS ANGELES 24, CALIF.]

Proton Magnetic Resonance in Stannane, the Methylstannanes and Related Compounds¹

BY N. FLITCROFT AND H. D. KAESZ

RECEIVED DECEMBER 28, 1962

Proton magnetic resonances in SnH_4 , the methylstannanes $[(\text{CH}_3)_n\text{SnH}_{4-n}]$, $(\text{CH}_3)_3\text{Sn}^- \cdot \text{Li}^+$ and $(\text{CH}_3)_3\text{PbH}$ have been obtained. Chemical shift of the protons as well as spin-spin coupling between the various magnetically active nuclei in these molecules has been determined. The protons bonded to tin or lead are less shielded than those bonded to carbon in these derivatives. The trends observed in tin-proton spin-spin coupling constants are discussed in the light of possible structural changes occurring in the stannanes.

Introduction

We have studied proton magnetic resonance in SnH_4 , the series of methylstannanes and $(\text{CH}_3)_3\text{PbH}$ to determine the chemical shift of protons bonded directly to a heavy atom of the main group metals, and to compare this with the unusually high chemical shift of protons bonded to transition metals.² The only reports of the chemical shift of tin-bonded protons in the literature are incomplete references to unpublished work, such as footnote 12 in the review by Green^{2b} or the paper by Duffy, Feeney and Holliday.³ For $(\text{CH}_3)_3\text{PbH}$, our results and interpretations are not entirely in keeping with the results nor with the interpretation of the spectrum previously reported for this compound.³

We have also determined the constants for the spin-spin interaction between the metal-bonded hydrogen with magnetically active isotopes of the metal, and with other protons in the molecule, which serve to indicate that no appreciable exchange of metal-bonded protons was occurring. The tin-proton spin-spin coupling constants in SnH_4 , the methylstannanes and $(\text{CH}_3)_4\text{Sn}$ were compared to see whether any systematic trend was occurring in that series of compounds, similar to trends observed in the methyltin halides.⁴

Experimental

Sample Preparation.—The volatile and air-sensitive compounds were handled and sealed into sample tubes on a chemical high-vacuum line.⁵ SnH_4 was prepared and purified by the method of Emelús and Kettle.⁶ $(\text{CH}_3)_2\text{SnH}_2$ and $(\text{CH}_3)_3\text{SnH}$ were prepared by the reduction of the corresponding chlorides with LiAlH_4 ,⁷ $(\text{CH}_3)_2\text{SnCl}_2$ was purchased from the Metal & Thermit Co., and $(\text{CH}_3)_3\text{SnCl}$ prepared in 93% yield from $(\text{CH}_3)_4\text{Sn}$ and SnCl_2 by an adaptation of the method reported by Anderson.⁸ $(\text{CH}_3)_3\text{PbH}$ was prepared from $(\text{CH}_3)_3\text{PbCl}$, after Becker and Cook.⁹

The reduction of CH_3SnCl_3 by LiAlH_4 was found to give extremely poor yields of CH_3SnH_3 . A milder reducing medium, the aqueous borohydride method of Schaeffer and Emilius,¹⁰ was used to obtain that hydride from $\text{K}(\text{CH}_3\text{SnO}_2)$; NaBH_4 (1.5 g.) was added to a solution of $\text{K}(\text{CH}_3\text{SnO}_2)$ (prepared

according to Pfeiffer and Lehnardt¹¹ from $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (15 g.), excess KOH (30 g.) and CH_3I) which was then added over 0.5 hour to a well-stirred solution of 6 *M* HCl (150 ml.) in a three-necked flask. The resulting evolved gas was collected at -78° under reduced pressure, and subsequently fractionated on the vacuum line giving approximately 3 g. of CH_3SnH_3 ; v.p. found 268 mm., required⁷ 273.5 mm., at -23° .

Solutions of the alkyltin anions were prepared in CH_3NH_2 by reduction of $(\text{CH}_3)_3\text{SnCl}$ or $(\text{CH}_3)_2\text{SnCl}_2$, with the calculated amount of Li . N.m.r. tubes containing samples were stored at reduced temperature. At room temperature irreversible decomposition occurs; hence such tubes should be handled carefully as the pressures developed (due to solvent and, perhaps, some H_2) can lead to explosions.

Apparatus and Procedures.—Proton magnetic resonances were measured on a Varian A-60 spectrometer both for neat liquids and solutions in neopentane and cyclopentane. Neat samples of SnH_4 and of $(\text{CH}_3)_3\text{PbH}$ and its cyclopentane solution were not stable at room temperature, and were scanned at -50° on a Varian 4300B spectrometer (at fixed frequency, 40,000 Mc. at 9,396 gauss) equipped with a temperature-regulating probe. Only the low field satellites of the tin-bonded proton resonances fell within the normal operating range of the A-60 spectrometer, but the high-field satellites could be brought within range and the tin-proton spin-spin coupling measured by the side-band technique, using a calibrated Hewlett-Packard model 200 D audiofrequency oscillator. The spectra obtained on the 4300B spectrometer were measured and also calibrated by this audiofrequency oscillator. A complete set of spectra will be sent to the Chemical and Petroleum Research Laboratory (Carnegie Institute of Technology, Pittsburgh 13, Pa.) for publication in the catalog of nuclear magnetic resonance spectral data of the A.P.I. Research Project 44.

Results and Discussion

The results of our measurements are summarized in Table I. Data for the tetramethyl derivatives were repeated for purposes of comparison; these were in good agreement with previous reports. The values reported here are believed to be accurate to within 1%, or better, especially when obtained on the A-60 spectrometer. The solutions of the hydrides in hydrocarbons contained traces (*ca.* 0.5 to 1%) of dimethyl ether or dioxane from the reaction mixtures from which the hydrides were obtained. Separate experiments on solutions of these hydrides at concentrations up to 50% ether by volume showed that the chemical shift between the methyl protons and the metal-bonded protons varied only up to 0.14 p.p.m., with no change in the spin-spin coupling.

The data for $(\text{CH}_3)_3\text{PbH}$ are only partially in agreement with previously reported work.³ The absolute τ -values for the chemical shifts of Pb-H and Pb-CH_3 appear to be in poor agreement with our values, but this is only because of differences in the standards being used in the two experiments. In fact, the difference between the resonance of the methyl protons and one of the resonances at $\tau = 2.98$ (Table I) taken as the PbH proton in the previous work is in good agreement with the difference between these two resonances

(1) This work was supported by Grant no. 1073-A1 from the Petroleum Research Fund.

(2) (a) G. Wilkinson and J. M. Birmingham, *J. Am. Chem. Soc.*, **77**, 3421 (1955); (b) see also the recent review by M. L. H. Green, *Angew. Chem.*, **72**, 719 (1960).

(3) R. Duffy, J. Feeney and A. K. Holliday, *J. Chem. Soc.*, 1144 (1962).

(4) (a) J. R. Holmes and H. D. Kaesz, *J. Am. Chem. Soc.*, **83**, 3903 (1961);

(b) G. P. Van der Kelen, *Nature*, **193**, 1069 (1962).

(5) R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

(6) H. J. Emelús and S. F. A. Kettle, *J. Chem. Soc.*, 2444 (1958).

(7) A. E. Finholt, A. C. Bond, K. E. Wiltzbach and H. I. Schlesinger, *J. Am. Chem. Soc.*, **69**, 2692 (1947).

(8) H. H. Anderson, *Inorg. Chem.*, **1**, 648 (1962).

(9) W. E. Becker and S. E. Cook, *J. Am. Chem. Soc.*, **82**, 6264 (1960).

(10) (a) G. W. Schaeffer and Sr. M. Emilius, *ibid.*, **76**, 1203 (1954);

(b) see also, W. L. Jolly, *ibid.*, **83**, 335 (1961).

(11) P. Pfeiffer and R. Lehnardt, *Ber.*, **36**, 1057 (1903).