[CONTRIBUTION FROM THE ROHM AND HAAS CO., REDSTONE ARSENAL RESEARCH DIVISION, HUNTSVILLE, ALA.]

The Nature of the Electrophilic Deuterium Exchange Reaction of Decaborane with Deuterium Chloride[1]

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Treatment of decaborane with deuterium chloride in carbon disulfide solution and in the presence of aluminum chloride results in deuterium-protium exchange at the 1, 2, 3 and 4 positions of decaborane. Deuterium chloride in dioxane solution is a useful reagent for the preparation of bridge and 5, 6, 7, 8, 9 and 10-d_{10} decaborane. The aluminum chloride-catalyzed exchange reaction proceeds in such a manner that the four entering deuterium atoms are kinetically indistinguishable. The mechanistic and preparative aspects of these observations are discussed.

Among the many reactions of decaborane which have been reported in the literature, the replacement of a proton by an electrophile is perhaps the most thoroughly documented. Such re-

$$B_{10}H_{14} + E^{\oplus} \longrightarrow B_{10}H_{13}E + H^{\oplus}$$

actions have led to the preparation of halogen[2] and alkyl[3] substituted decaboranes.

As a portion of a program aimed at the elucidation of the chemistry of decaborane, it was important to identify the boron atoms in the decaborane molecule which were labile to electrophilic attack. Since deuterium chloride in the presence of aluminum chloride has been shown to be an effective reagent for the deuteration of aromatic hydrocarbons,[4] it was reasonable to expect a similar exchange between decaborane and this reagent. The selection of the deuterium nucleus as the electrophilic species presented three advantages. (1) The position of exchange could be easily recognized with the use of B^{11} nuclear magnetic resonance spectroscopy.[5] (2) The results obtained could be correlated with the results of previous studies of the base-catalyzed deuterium exchange.[6,7] (3) The decaborane produced from electrophilic deuterium exchange would serve as a useful tool for further studies of decaborane chemistry.

As reported in a previous communication,[8] decaborane and deuterium chloride do indeed enter into an exchange reaction in the presence of aluminum chloride and carbon disulfide solvent. These earlier experiments were carried out under equilibrium conditions for extended periods of time. Four consecutive exchanges at room temperature resulted in the introduction of approximately six deuterium atoms per mole of decaborane. Examination of the B^{11} and H^1 spectra of these deuterated samples led to the conclusion that substitution had occurred at the 2, 4 and 5, 7, 8 and 10 positions.[9] Samples prepared at a later date, however, indicated a preponderance of substitution at the 2, 4 and 1, 3, 6 and 9 positions. These inconclusive preliminary results suggested that the exchange system in question could be handled more profitably under reaction conditions of a kinetic nature.

Results

Carbon disulfide solutions of decaborane were treated at 26 ± 0.1° with a large excess of deuterium chloride in a constant pressure flow system. As described in the Experimental section, the reaction cell was equipped for the periodic removal of aliquots of reaction mixture which were subsequently examined by B^{11} n.m.r. spectroscopy[5] and direct deuterium analyses.[6]

In the presence of a 0.66 mole equivalent of aluminum chloride catalyst, decaborane readily exchanged four of the fourteen available protons with deuterium chloride. Table I presents the data obtained in a typical exchange experiment. A first-order plot of this rate data produced an acceptable fit to 90% completion when four kinetically indistinguishable exchange sites were considered. A plot based on three or five sites no longer produced a straight line.

TABLE I

THE ALUMINUM CHLORIDE CATALYZED EXCHANGE BETWEEN DEUTERIUM CHLORIDE AND DECABORANES

Time (hr.)	2	4	6	10	12	14	16	36
Average no. D atoms/mole of $B_{10}H_{14}$	1.43	2.10	2.72	3.40	3.56	3.69	3.82	4.23

In order to prove that the cessation of exchange after the introduction of four deuterium atoms was not the result of slow catalyst poisoning, a sample of exchanged decaborane was treated with fresh catalyst and deuterium chloride. No further exchange was observed.

Figure 1 illustrates the B^{11} n.m.r. spectra obtained after various time intervals during an aluminum chloride catalyzed exchange reaction. The observed resonances are assigned in Fig. 1 to the ten boron atoms of decaborane in accord with the observations of Williams and Shapiro.[5] It is seen in Fig. 1 that the high field doublet undergoes total collapse to a singlet during exchange. This indicates essentially complete deuteronation at the 2,4 positions. It is evident from the unaltered shape of the high field portion of the triplet that exchange at the 5,7,8 and 10 positions does not occur. In addition, the H^1 n.m.r. and infrared spectra of the final exchange product showed no

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* Department of Chemistry, The University of California, Riverside, California.

[1] Presented in part at the 138th Meeting of the American Chemical Society, New York, N. Y., Sept. 11-16, 1960, p. 47-N.

[2] M. Hillman, *J. Am. Chem. Soc.*, **82**, 1096 (1960).

[3] R. L. Williams, I. Dunstan and N. H. Blay, *J. Chem. Soc.*, 5006 (1960).

[4] M. Brullman, H. J. Gerber and D. Meier, *Helv. Chim. Acta.*, **41**, 1831 (1958).

[5] R. E. Williams and I. Shapiro, *J. Chem. Phys.*, **29**, 677 (1958).

[6] M. F. Hawthorne and J. J. Miller, *J. Am. Chem. Soc.*, **80**, 754 (1958).

[7] I. Shapiro, M. Lustig and R. E. Williams, *ibid.*, **81**, 838 (1959).

[8] J. A. Dupont and M. F. Hawthorne, *ibid.*, **81**, 4998 (1959).

[9] The nomenclature used is that accepted by the Boron Nomenclature Committee as described by G. Schaeffer, Abstracts of Papers of the 133rd Meeting of the American Chemical Society, San Francisco, Calif., April 13-18, 1958, p. 2-L.

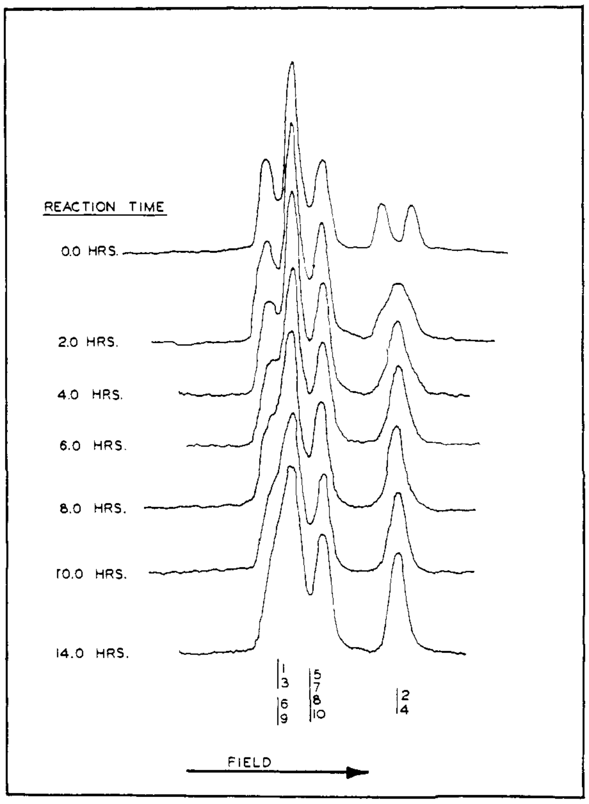


Fig. 1.—Changes in the B^{11} spectrum of decaborane during $DC/AlCl_3$ exchange.

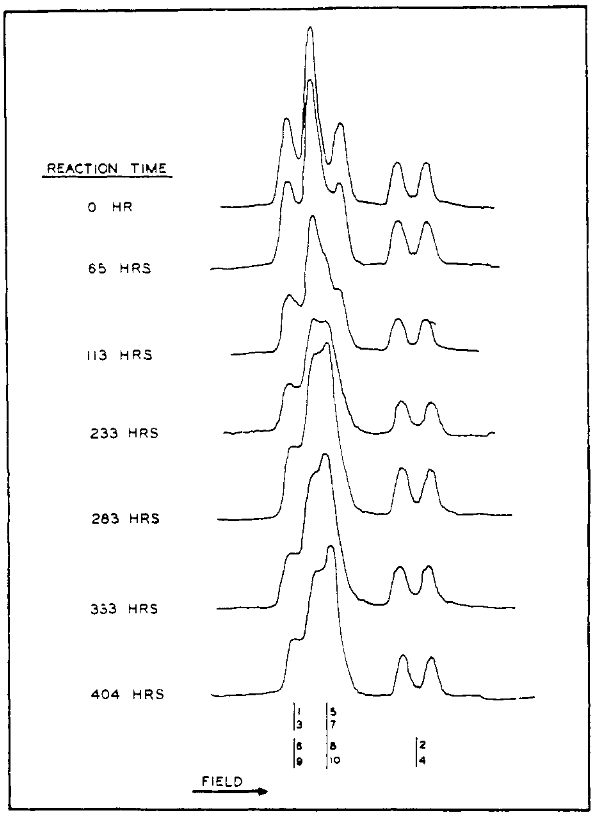


Fig. 2.—Changes in the B^{11} n.m.r. spectrum of decaborane during DC/dioxane exchange.

evidence for exchange in the bridge positions. Thus, of the four deuterium atoms which enter the decaborane molecule under electrophilic conditions, two may be unequivocally assigned to the 2 and 4 positions while the remaining two must enter either the 1 and 3 or the 6 and 9 positions. Substitution at either of the later pairs of boron atoms is readily apparent from the over-all change observed in the low field portion of the triplet. The fact that the low field member of the doublet representing the remaining unexchanged positions is not observed can be attributed mainly to the coincidental coalescence of peaks brought about by serious overlap. Further consideration on this point will be taken up below.

The problem of ascertaining if the 1 and 3 or the 6 and 9 positions were electrophilic exchange sites was attacked in the following manner. Shapiro, Lustig and Williams[7] had previously shown that the course of the base-catalyzed exchange of decaborane with deuterium oxide involved rapid exchange of the bridge protons followed by a slow exchange at the 5, 6, 7, 8, 9 and 10 positions. Thus, if the $B_{10}H_{10}D_4$ material obtained from electrophilic exchange with deuterium chloride contained deuterium at the 1 and 3 and not the 6 and 9 positions, retro-exchange under base-catalyzed conditions should not alter the material. Similarly, further exchange of the $B_{10}H_{10}D_4$ product with deuterium oxide under base-catalyzed conditions would lead to the formation of $B_{10}D_{14}$. Experimentally, base-catalyzed exchange reactions of decaborane in aqueous media leave much to be desired. These exchange reactions occur with great rapidity resulting in complicating exchange at the 1,3 and 2,4 positions over extended reaction times. Furthermore, considerable losses of decaborane result through hydrolysis. Thus, a new and less vigorous method of accomplishing base-catalyzed exchange reactions was sought.

Previous work in this Laboratory illustrated that deuterium chloride in the presence of anhydrous dioxane would affect base-catalyzed exchange of decaborane.[6] The dioxane solvent apparently functioned as an effective base catalyst. Nearly quantitative recoveries of decaborane were achieved. This method of base-catalyzed exchange was adapted to the problem at hand and the course of this mode of exchange was followed by B^{11} and H^1 n.m.r. techniques.[7] All exchanges were carried out with 5.0 M deuterium chloride and 5×10^{-2} M decaborane in dioxane at room temperature. As in the electrophilic exchange experiments described above, small aliquots of reaction mixture were withdrawn at intervals and analyzed by nuclear magnetic resonance and direct deuterium analyses of recovered decaborane. After 45 hr. essentially complete exchange of the bridge protons had occurred as shown by the H^1 n.m.r. and infrared spectra as well as deuterium analysis. The B^{11} n.m.r. spectrum of this sample showed no perceptible evidence for exchange at terminal positions. After 404 hr. essentially complete exchange of the bridge and 5, 6, 7, 8, 9 and 10 terminal positions had occurred as shown by the same methods. The decaborane contained 8.6 deuterium atoms per molecule at this point. An equilibrium value of 9.1 deuterium atoms per molecule was calculated for the experimental conditions employed and without consideration of an equilibrium isotope effect. Figure 2 illustrates the observed B^{11} n.m.r. spectra obtained after the denoted time intervals. It is seen that these spectra agree generally with the previously reported spectra of Shapiro, Lustig and Williams[7] obtained with samples from aqueous exchange media. It is to be noted in Fig. 2, however, that no exchange occurs involving the 2 and 4 positions. Furthermore, the readily distinguishable detail of the lowest field peak shows that the 1, 3 positions are also not involved in exchange. The fact that some detail of the non-participating doublet is observed here and not in the case of electrophilic substitution (Fig. 1) can be explained by considering the fact that 5, 7, 8 and 10-exchange occurs only in this case. Therefore, the collapse of the 5, 7, 8 and 10 peaks moves the center of gravity of the observed spectrum further toward higher field. This shift greatly reduces the net overlap in the lowest field portion of the spectrum thereby allowing partial resolution of the 1, 3 doublet. The possibility also exists that the slight non-equivalency between the 1, 3 and 6, 9 doublets[5] might augment this same effect. Thus, if the 6, 9 doublet occurs at highest field, partial resolution of the 1, 3 doublet would most likely be observed in the base-catalyzed exchange spectra. Likewise, resolution of the 6, 9 doublet would not be expected in the case of electrophilic exchange.

The identification of the electrophilic deuteration sites as the 1, 2, 3 and 4 positions was readily apparent from the following results. Treatment of $B_{10}H_{10}D_4$ samples obtained from the aluminum chloride-catalyzed exchange with hydrogen chloride in dioxane for 400 hr. resulted in no significant change of the B^{11} n.m.r. spectrum or deuterium analysis of the sample. Similar treatment of the electrophilically exchanged samples with deuterium chloride–dioxane for 400 hr. resulted in essentially complete replacement of all fourteen protium atoms by deuterium atoms (12.6 atoms D per molecule). This analysis was confirmed by the B^{11} n.m.r. spectrum of the sample which contained the three singlets expected for $B_{10}D_{14}$.[10] In addition, the reaction of an aluminum chloride catalyzed exchange sample with acetonitrile gave only hydrogen.[11]

Discussion

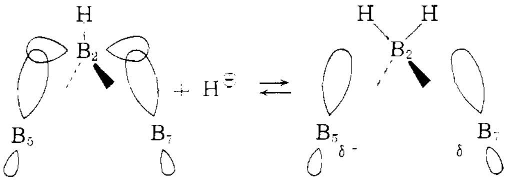
The results presented above clearly illustrate that preferential electrophilic deuterium exchange occurs at the 1, 2, 3 and 4 positions of decaborane. This work coupled with earlier studies of the halogenation[2] and alkylation[3] reactions firmly establishes the enhanced reactivity of these positions in electrophilic substitution reactions.

Williams and co-workers[3] have presented evidence for the preferential methylation of decaborane at the 2, 4 over the 1, 3 positions.[12] These results were rationalized[3] in terms of the charge distributions calculated for the decaborane molecule by Lipscomb.[13] More recent molecular orbital calculations by Moore, Lohr and Lipscomb[14] are in agreement with these results in that the electron densities decrease in the order 2 > 1 > 5 > 6.

In contrast to the results of the methylation study,[3] the deuterium exchange reaction does not exhibit preferred substitution of deuterium at the 2 and 4 over the 1 and 3 positions in decaborane. This anomaly might be rationalized in two ways.

If the deuteron supplied by the aluminum chloride–deuterium chloride reagent is extremely reactive relative to an incipient methyl carbonium ion, lower selectivity between the 2, 4 and the 1, 3 positions would prevail.[15]

The valence bond description[12] of decaborane indicates that the apical boron atoms are hybridized sp^2 with the p-orbitals participating in open three-center bonds. It appears to be more than coincidental that the most reactive sites for electrophilic substitution have such hybridization. The possibility exists that the substitution at the apical positions proceeds through an unstable intermediate in which these apical boron atoms have increased in coördination number. Thus in the deuterium exchange reaction, the 2 (or 4) position of decaborane could change from sp^2 to sp^3 upon deuteronation. The positive charge introduced by deuteronation could be redistributed among the boron atoms which are near neighbors to the apices. The following diagram illustrates this point.



A

If the formation of the intermediate A were rate-determining in the deuterium exchange reaction and if A were in rapid internal equilibrium with a similar cationic intermediate having a BH_2 group on the 1 or 3 boron atoms, the rates of exchange at the 1, 3 and 2, 4 positions would be identical as observed. The deuterium exchange reaction might well represent a special case due to the well known intramolecular mobility of hydrogen atoms in certain boron hydride derivatives.

Experimental

Materials.—Decaborane was purified by sublimation followed by recrystallization from *n*-hexane. Carbon disulfide was purified by stirring with anhydrous magnesium sulfate

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(10) Operating at a higher frequency (16.2 mc.), Williams and Shapiro (ref. 5) were able to obtain partial resolution of the composite 1, 3, 6, 9 peak in $B_{10}D_{14}$ spectra thereby giving a spectrum which consists of four distinct peaks.

(11) R. Schaeffer, *J. Am. Chem. Soc.*, **79**, 1006 (1957).

(12) As an example, Williams, Dunstan and Blay (ref. 3) report that the aluminum chloride catalyzed methylation of decaborane produced a 3:1 preponderance of 2-methyldecaborane over 1-methyldecaborane.

(13) W. N. Lipscomb, "Advances in Inorganic Chemistry and Radiochemistry," Vol. I, Academic Press, Inc., New York, N. Y., 1959, p. 118.

(14) Private communication from Prof. Lipscomb regarding a paper in press by E. B. Moore, Jr., L. L. Lohr, Jr., and W. N. Lipscomb. The following charge distributions were found after correction for bridge hydrogen charges of −0.2e each: 1, 3(+0.046e); 2, 4(−0.254e); 5, 7, 8, 10(+0.069e) and 6, 9(+0.468e).

(15) This statement is based upon the postulate of Hammond (G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955)) which states that the more energetic the reagent, the less selectivity it will exhibit between similar and competitive reactions.

and mercury for 24 hr. followed by distillation. The middle cut from this distillation was used. The aluminum chloride was Baker and Adamson anhydrous, sublimed, reagent grade. Dioxane was purified according to the method of Vogel.[16]

Deuterium chloride was prepared by the reaction of phosphorus trichloride with deuterium oxide in the following manner: Into a dry 3 liter stainless steel Hoke cylinder previously purged with dry nitrogen, was placed 100 g. (4.99 moles) of 99.82 mole% deuterium oxide (Bio-Rad Laboratories). After attaching a suitable valve, the tank was cooled with liquid nitrogen and evacuated. Two hundred ml. (314.8 g., 2.29 moles) of phosphorus trichloride (Baker and Adamson reagent grade) were transferred *in vacuo* to the tank. The tank was then removed from the liquid nitrogen and immersed directly into cold water, where it was allowed to remain undisturbed for 24–48 hr. The deuterium chloride produced was purified by passage through two −78° traps followed by two passes through three consecutive −135° traps. Finally, the gas was condensed into a separate 3 liter Hoke cylinder at −196°. Approximately 3.8–4.0 moles (76–80% of theory) of deuterium chloride were obtained. Infrared analysis showed less than 2% hydrogen chloride. This method, in theory, utilizes only one-half of the available deuterium in contrast to other methods. Nevertheless, of the methods investigated, it was found to be the most expedient laboratory technique for preparing moderately large quantities of deuterium chloride.

Hydrogen chloride, anhydrous (99.9% min. purity), was supplied by Matheson Co., Inc.

Deuterium Chloride–Aluminum Chloride Exchange. (a) **Apparatus.**—The system used for this study consisted essentially of the following component sections in order of their sequence: (a) a solvent-gas saturator; (b) a suitable reaction vessel (described below); (c) an electrically operated manostat; (d) a flow rate indicator, and (e) a gas receiving tank.

In order to prevent loss of solvent (carbon disulfide) from the reaction solution during the course of the reaction, it was necessary to saturate the deuterium chloride gas stream with solvent vapor prior to passage through the reactor. This was accomplished satisfactorily by first passing the gas stream through refluxing carbon disulfide and then through a glass-bead carbon disulfide scrubber maintained at room temperature (approx. 25°). The small temperature difference between the scrubber and the reaction vessel caused no noticeable solvent depletion in the reactor.

The reactor employed is illustrated in Fig. 3. All attempts to pass the deuterium chloride directly into the reaction solution proved unsatisfactory. Clogging of the gas entrance tube invariably occurred. The method of introduction shown below proved to be as efficient as any of the solution dispersion methods investigated. The manostat employed was a magnetically operated, Teflon-glass valve (normally closed) which was activated through a relay operating off of contacts in a mercury manometer. Using this device the pressure in the reactor section could be controlled within 1 mm. The flow rate of gas was measured simply by collecting the effluent gas in a large known volume and following the pressure rise per unit time. The observed volume was necessarily corrected for the partial pressure of carbon disulfide.

Except when measuring the flow rate, the effluent gas stream was normally allowed to pass through a −78° trap to remove most of the carbon disulfide and then condensed in a 3 liter stainless steel tank maintained at −196°.

(b) **Procedure.**—Within a nitrogen filled dry box, 7.34 g. (0.060 moles) of decaborane, 5.34 g. (0.04 moles) of aluminum chloride, 60 ml. of carbon disulfide and a Teflon coated magnetic stirring bar were placed in the reactor. This was stoppered, removed from the dry box, and then quickly attached to the system at joint C (Figure 3). The reactor was cooled to −78° and evacuated through stopcock A along with the total "downstream" section of the system. The remaining portion of the system (from stopcock B to DCl storage tank), previously purged with dry nitrogen, was evacuated by intermittant pumping which allowed carbon disulfide vapor to sweep most of the air from the system. Following evacuation the reactor was warmed to room temperature and thermostated at 26 ± 0.1°. Stirring was commenced and stopcocks A and B were opened. Deuterium chloride was admitted to the system until a pressure of 60 mm. (relative to atmospheric pressure, 754 mm.) was obtained. The manostat was then set at this pressure and the flow rate adjusted to approximately 2.0–2.5 liters per hour by means of a neddle valve located on the deuterium chloride storage tank. In lieu of a suitable reducing valve the storage tank was maintained at −78° in order to provide a constant tank pressure.

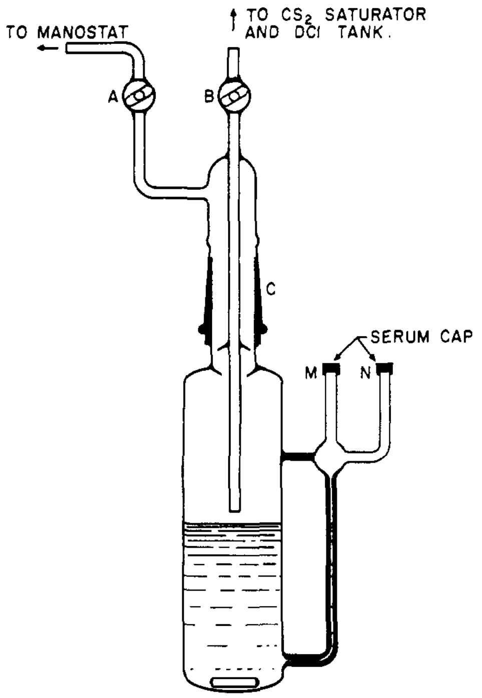

Fig. 3.—Reaction cell employed in the deuterium chloride–aluminum chloride exchange.

(c) **Preparation of Samples.**—Sampling of the reaction solution was accomplished in the following manner: The solution was caused to flow up into the capillary side tube of the reactor (Fig. 3) by allowing expansion of the inside pressure into a syringe attached to the rubber serum cap, N. This sample was forced back into the reactor and replaced by a fresh aliquot. Using a separate syringe, approximately a 0.5 cc. sample of the solution was withdrawn through the remaining serum cap, M. The sample was then injected into a specially designed vacuum filtration apparatus which permitted collection of the filtrate directly into an n.m.r. tube and provided for the subsequent sealing and removal of the sample tube under a dry nitrogen atmosphere. The B^{11} n.m.r. spectrum of each sample was recorded immediately after filtration. In those cases where an H^1 n.m.r. spectrum was also desired, the n.m.r. tube was stored at −78° until the spectrum could be obtained.

Elemental analysis of the final product from a typical exchange reaction revealed no detectable amount of chlorine and only a trace amount of carbon.

Deuterium Chloride–Dioxane Exchange.—Approximately 200 ml. of dioxane was saturated with deuterium chloride at 0° under carefully controlled anhydrous conditions. The resulting solution was warmed to room temperature and allowed to stir for approximately 1 hr. Titration of an aliquot showed the solution to be 5.0–5.1 *M* in deuterium chloride. A 100 ml. (0.5 mole) aliquot of this solution and 0.610 g. (0.005 mole) of decaborane were placed in a 200 ml. round-bottomed flask, equipped with a 19/38 ₸ joint and a stopcock located on the neck, through which was admitted a stream of dry nitrogen. The flask was stoppered and allowed to stir at room temperature. Periodically a 10 cc. sample was withdrawn and the DCl–dioxane removed under vacuum at approximately 25°. The resulting decaborane was sublimed with moderate heating,[17] dissolved

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[16] "Practical Organic Chemistry," Arthur I. Vogel, Longmans, Green and Co., New York, N. Y., 1948, p. 175.

[17] The conditions employed in the sublimation of the various ex-

in carbon disulfide, filtered and n.m.r. spectra recorded. Preparation of the sample for analysis was accomplished by removing the carbon disulfide under vacuum and resubliming the isolated decaborane into an appropriate receiver. Larger scale reactions, employing 0.05 mole of decaborane, were carried out with the same procedure. Elemental analysis of the final exchange product revealed only a trace amount of chlorine and less than 1% carbon.

The dioxane exchanges of tetradeuteriodecaborane with deuterium and hydrogen chloride were carried out in the same manner as described above using approximately the same molar ratios of reactants.

Deuterium Analyses.—The percentage of deuterium in any given decaborane sample was determined using the pyrolysis method previously described.[6,18]

The mass spectrometer (Consolidated Engineering Corporation, type 21-620) was calibrated using equilibrium mixtures of H_2, HD and D_2 prepared by the decomposition of known mixtures of water and deuterium oxide on zinc at 400°.[19] The precision of the above method was approximately 1% and the accuracy was estimated to be within 2%.

N.m.r. Spectra.—The B^{11} and H^1 n.m.r. spectra were obtained with a Varian High Resolution Spectrometer operating at 12.8 and 40 mc., respectively. All B^{11} n.m.r. spectra in any given series were recorded at essentially the same sweep rate and chart speed.

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change samples produces no detectable amount of internal H-D exchange. This is readily apparent from the fact that exclusively bridge deuteronated decaborane is obtained by sublimation of a 45 hr.-DCl/dioxane exchange sample. Furthermore, no detectable change in either the H^1 or B^{11} n.m.r. spectra is observed after sublimation of the various electrophilic exchange-samples.

(18) J. Graff and David Rittenberg, *Anal. Chem.*, **24**, 878-881 (1952).

(19) "Physical Properties and Analysis of Heavy Water," Isidor Kirshenbaum, McGraw-Hill Book Co., Inc., New York, N. Y., 197-201 (1951).

[Contribution from the Frick Chemical Laboratory, Princeton University, Princeton, N. J.]

The Dielectric Relaxation of Dibromodichloromethane, Succinonitrile and Several Camphor Derivatives in the Solid State[1,2]

By Donald E. Williams and Charles P. Smyth

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The dielectric constant and loss at 3.2 cm. wave length have been measured over a wide range of temperature for *dl*-camphene, *d*-camphor, *dl*-camphor, *d*-camphoric anhydride, *dl*-isoborneol, dibromodichloromethane and succinonitrile in the solid state. All of them show molecular orientational freedom in the crystal lattice over a considerable range of temperature. Dielectric relaxation times have been obtained for all of the solids and heats and entropies of activation have been calculated for five of them. The rotational freedom of these molecules in the crystal lattice between the freezing point and a transition point is comparable to that in the liquid state.

Very extensive dielectric investigations have been carried out on the rotational or orientational freedom of molecules in the solid state.[3] Most of the molecules investigated have fallen into one of two categories. Either they have been fixed so rigidly in the crystal lattice that they could not orient at all in the electric field used in the measurements, or they have possessed sufficient rotational freedom to orient in radio frequency fields without appreciable relaxation effects. Measurements of dielectric constant and loss at 3.22 cm. wave length carried out in this Laboratory upon *d*-camphor[4] and upon six tetrasubstituted methanes[5] gave information concerning the relaxation of the molecules in the crystal lattice. This paper reports similar measurements with some improvements in technique upon five bicyclic terpenes, dibromodichloromethane and succinonitrile, all save two of which had previously been measured at radio frequencies.[6-8]

Purification of Materials.—*dl*-Camphene, supplied by The Matheson Company, Inc., was twice recrystallized from ethyl alcohol and then repeatedly melted and frozen under a 3 cm. vacuum; m.p. 50°; literature[9] m.p. 51-52°, transition temperature −108°.

d-Camphor, supplied by Eastman Kodak Co., was twice recrystallized from ethyl alcohol and then sublimed; m.p. 176°; literature m.p. 177.6°,[6] 179.75°[9]; transition temperature 28°; literature,[6] 28°.

dl-Camphor (synthetic), supplied by The Matheson Company, Inc., was measured as received; m.p. 178.0°; literature[10] m.p. 178.8°; transition temperature −67°, literature[9] −66°.

d-Camphoric anhydride, supplied by The Matheson Company, Inc., was recrystallized from ethyl alcohol and vacuum dried for three days; m.p. 218°; literature 216-217°, 223.5°[11]; transition temperature 133°; literature[11] 135°.

dl-Isoborneol, supplied by The Matheson Company, Inc., was recrystallized twice from ethyl alcohol and then sublimed; m.p. (sealed tube) 212°; literature[12] m.p. (sealed tube) 212°; transition temperature 8-9°.

Dibromodichloromethane from The Matheson Company, Inc., was recrystallized from the melt four times and measured immediately, m.p. 22°; literature 22°.

Succinonitrile, supplied by Matheson, Coleman and Bell, Inc., was vacuum distilled. The middle fraction was taken; f.p. 57.2°; literature 57.15-57.20°.[13]

Methods of Measurement.—Dielectric constants and losses were measured at a wave length of 3.19 cm. by methods described in part in a previous paper[5] and in full in the thesis

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(1) This research was supported in part by the Office of Naval Research. Reproduction, translation, publication, use or disposal in whole or in part by or for the United States Government is permitted.

(2) This paper represents a part of the work submitted by Donald E. Williams to the Graduate School of Princeton University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., New York, N. Y., 1955, Chap. V.

(4) J. G. Powles, *J. Chem. Phys.*, **20**, 1648 (1952).

(5) J. G. Powles, D. E. Williams and C. P. Smyth, *ibid.*, **21**, 136 (1953).

(6) W. A. Yager and S. O. Morgan, *J. Am. Chem. Soc.*, **57**, 2071 (1935).

(7) A. H. White and W. S. Bishop, *ibid.*, **62**, 8 (1940).

(8) A. H. White and S. O. Morgan, *J. Chem. Phys.*, **5**, 655 (1937).

(9) "The Merck Index," 6th Ed., Merck and Co., Inc., Rahway, N. J., 1952, p. 194.

(10) I. Heilbron and H. M. Bunbury, "Dictionary of Organic Compounds," Eyre and Spottiswoode, London, 1953.

(11) L. O. Fisher, *Bull. soc. chim. belges*, **49**, 129 (1940).

(12) Ref. 9, vol. III, p. 65.

(13) J. Timmermanns and Mme. Hennaut-Roland, *J. chim. phys.*, **34**, 693 (1937).