other runs on the purified specimens the coefficient was close to 55×10^{-6}. To indicate this variation, Fig. 1 shows a shaded band including the two extreme values but the curve is drawn to represent the results of the other concordant runs.

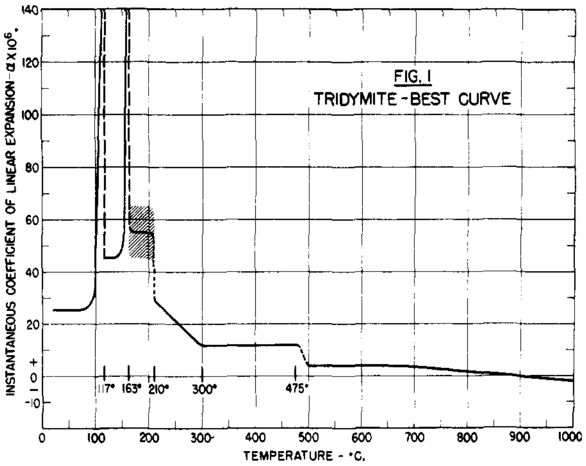

Fig. 1.—Instantaneous coefficient of linear thermal expansion of tridymite.

At about 210°, however, the coefficient for all specimens showed a virtually discontinuous decrease, after which there was a substantially linear decrease to about 300°. From this temperature to about 475° the coefficient was practically constant. At approximately 475° there was another small, though definite, break in the curve. Above 500° there is a continuous decrease in the coefficient until it becomes negative in the range above 900°.

Discussion

The marked change in the expansion coefficient at 210° is believed to correspond to the thermal effect reported by Mosesman and Pitzer, although it occurs at a temperature slightly lower than that which they observed. There is, likewise, a smaller change at 475°, but this is beyond the range of temperature investigated by these authors.

The extended transitions which occur at 117 and 163° are interpreted by Mosesman and Pitzer in terms of the rotation of oxygen atoms in the lattice structure. But they point out that this interpretation leaves no room for a third transition just over 200°. In line with this view, it is evident from the expansion data that the change which takes place at 210° must be of a totally different type. It is difficult to determine, however, just what its origin may be. Indeed, the whole course of the coefficient curve above 200° is puzzling. There appears, however, to be little hope of interpreting this behavior on the basis of expansion measurements alone. Additional data on lattice structure and thermal effects are needed. It should be noted, however, that these effects are presumably not due to the presence of impurity since they occur in careful purified samples as well as in relatively impure material.

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Hydrolysis of Pentaborane

BY I. SHAPIRO[1] AND H. G. WEISS[1]

The rate of hydrolysis of pentaborane had been reported[2] to be very slow at room temperature with prolonged heating with water at *ca.* 90° required to achieve complete hydrolysis. On the basis of hydrogen measurements the reaction is given as

$$B_5H_9 + 15H_2O \longrightarrow 5B(OH)_3 + 12H_2 \qquad (1)$$

In our laboratories we have found that the slowness of the rate of hydrolysis of pentaborane is only apparent, and can be attributed to the poor miscibility of pentaborane and water. Pentaborane can be shaken with water[3] at room temperature with very little noticeable reaction. After cessation of shaking, the two liquids separate, and some gas bubbles and a white solid form at the interface. The situation is entirely different when one adds an inert mutually miscible solvent, such as dioxane, to the mixture. In this case the rate of reaction becomes too rapid to measure in glassware by the usual techniques of freezing with subsequent warming of the mixture, or by using breakoff tubes to introduce one liquid into another liquid.

Several experiments on measuring the rate of hydrolysis have been attempted in metal equipment in which the pressure of the system was recorded by means of a statham gage connected to a brush oscillograph. In these experiments a vial containing known amounts of pentaborane (usually 15 cc. gas at S.C.) was crushed beneath the surface of a (50 ml.) solution of dioxane containing 20% water after the system had been evacuated of noncondensable gases and then brought to a constant temperature (30°). A perforated disk connected to a hand-operated plunger served as a means of crushing the vial and stirring the solution. After the crushing of the vial the pressure of the system increased rapidly (25% of maximum pressure rise in 7.2 sec.; 50%, in 16.3 sec.; 70%, in 41.5 sec.), and attained within several minutes a maximum pressure rise corresponding to that expected from Eq. 1.[4] The rate of stirring has a profound effect on the rate of increase in pressure of the system. By alternately stirring and resting the solution during the course of the reaction, one obtains plateaus on the pressure–time trace. Consequently, better mixing will be necessary in order to distinguish the rate of hydrolysis of pentaborane from the rate of mixing of the reactants.

The use of an inert solvent in hydrolyzing pentaborane simplifies the time required for its analysis. In a typical experiment carried out in glassware, 31.2 cc. of B_5H_9 (gas at S.C.) shaken for five minutes with excess water in dioxane yielded 375 cc. of H_2 (gas at S.C.). Titration of the resulting boric acid with standard base after the addition

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(1) Research Department, Olin Mathieson Chemical Corporation Pasadena, California.

(2) A. Stock, "Hydrides of Boron and Silicon," Cornell Univ. Press, Ithaca, N. Y., 1933, p. 71.

(3) In order to avoid ignition of pentaborane these experiments were carried out in the absence of air—the usual high-vacuum techniques were employed.

(4) Equation 1 has been found applicable for the case of excess water. Studies on the hydrolysis of pentaborane in the presence of excess pentaborane will be reported later.

of mannitol gave a boron content equivalent to 31.0 cc. of B_5H_9. The calculated H_2/B_5H_9 ratio was 12.1. In another experiment 6.56 cc. of B_5H_9 (by titration) yielded 78.4 cc. of H_2 to give a ratio of 11.9.

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Dissociation of Quaternary Ammonium Polyhalides in Trifluoroacetic Acid[1]

BY ROBERT E. BUCKLES AND JACK F. MILLS

RECEIVED JULY 19, 1954

During the investigation of quaternary ammonium dichloriodides[2] and of the quaternary ammonium tetrachloroiodides[3] it was found that the visible and ultraviolet absorption spectra of the salts in trifluoroacetic acid were identical with those of the halogens expected from the complete dissociation of the polyhalide ion. In Table I are summarized similar results for other quaternary ammonium halides. In each case the hydrogen halide derived from the most electronegative halogen atom present in the polyhalide ion must have been formed also. Little ionization of the hydrogen halide would be expected in trifluoroacetic acid, which is such a strong proton donor that the trifluoroacetate ion present would show little tendency to act as a proton acceptor, and the acid itself would show even less. Consequently it is not unreasonable that the concentration of the halide ion in each case would be so low that the molecular halogen present in the dilute solution used would not interact to give any detectable amount of polyhalide ion. The dissociation cannot be explained by competitive complexing of the molecular halogen with the solvent since such acidic solvents as trifluoroacetic acid show[4] little tendency to enter into such complex formation.

TABLE I

MOLAR ABSORBENCY INDICES OF ABSORPTION SPECTRA PEAKS OF HALOGENS AND QUATERNARY AMMONIUM POLYHALIDES IN TRIFLUOROACETIC ACID

Compound	Concn., $M \times 10^3$	λ, mμ	a_m
I_2	1.44	512	815
Me_4NI_3	1.55	513	806
Bu_4NI_3	1.40	513	805
Me_4NI_5	0.64	512	1624
$Me_4NI_4Cl^a$	0.72	512	1682
Br_2	13.9	411	160
Me_4NBr_3	14.2	410	159
Bu_4NBr_3	12.8	410	157
IBr	11.1	487	308
Me_4NIBr_2	7.7	487	314
$Me_4NIBrCl$	7.4	486	294

[a] Iodometric analysis showed this compound to be impure. The percentage of reducible halogen was 3% high.

The addition of excess tetramethylammonium chloride, which showed little absorption in the region studied, had little effect on the spectrum of tetramethylammonium tetraiodochloride. It did lower the iodine bromide peak shown by tetramethylammonium iodobromochloride at 486 mμ from a molar absorbancy index (molar extinction coefficient) of 294 to 258. Absorption in the region 260–400 mμ was increased at the same time. Such changes might indicate some suppression of the dissociation and formation of the iodobromochloride ion especially since a peak of molar absorbency index around 3.5×10^4 near 240 mμ and one of molar absorbency index about 400 near 355 mμ have been observed[5] for this ion in ethylene chloride and in acetonitrile.

Attempts to suppress the dissociation in a 7.08×10^{-4} M solution of tetramethylammonium triiodide with tetramethylammonium iodide (3.4×10^{-3} M) led to the disappearance of the violet color and the precipitation of the triiodide salt. When 2.5 ml. of water was present with the trifluoroacetic acid in 50 ml. of solution a red-violet solution was obtained. The absorption spectrum showed an iodine peak of molar absorbency index 706 at 500 mμ and very high absorption at wave lengths below 400 mμ which would be expected of triiodide ion.

In the course of the investigation it became necessary to re-examine the absorption spectra of iodine, bromine and iodine chloride in trifluoroacetic acid. It was observed that the values for the molar absorbency indices reported[4a] for these halogens were consistently too low. Evidently a combination of difficulties encountered in making up the stock solutions and standardizing them had not been completely surmounted in the earlier investigation. The higher values obtained in the present investigation and given in Table I actually are more consistent with the conclusions reached in the earlier work than are the values which were reported at that time. That is, the solutions of the halogens in trifluoroacetic acid behave spectrophotometrically like those in non-complexing solvents. This general relationship is shown in Fig. 1 for iodine bromide, which was not included in the original study.

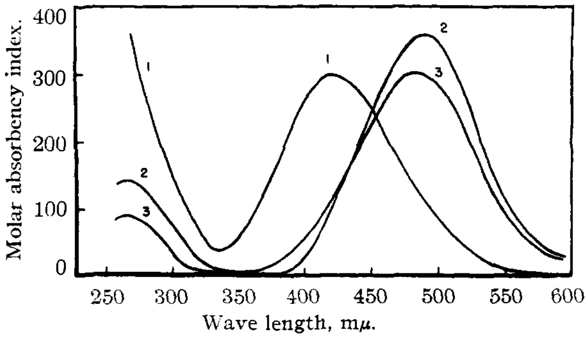

Fig. 1.—Absorption spectra of iodine bromide (1) 5.3×10^{-3} M in anhydrous acetic acid, (2) 6.6×10^{-3} M in carbon tetrachloride and (3) 1.11×10^{-2} M in trifluoroacetic acid.

Experimental Part

Materials.—The solvents and the halogens were purified as described[4a] for the earlier investigation. The polyio-

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[1] Work carried out under Contract No. AT(11-1)-72, Project No. 7 with the U. S. Atomic Energy Commission.

[2] R. E. Buckles and J. F. Mills, THIS JOURNAL, **76**, 4845 (1954).

[3] R. E. Buckles and J. F. Mills, *ibid.*, **76**, 3716 (1954).

[4] (a) R. E. Buckles and J. F. Mills, *ibid.*, **75**, 552 (1953); (b) J. G. Bower and R. L. Scott, *ibid.*, **75**, 3583 (1953); (c) L. I. Katzin and J. J. Katz, *ibid.*, **75**, 6057 (1953).

[5] A. I. Popov and R. F. Swenson, private communication.