Wavelength (μ).

Fig. 1.—Infrared spectra: A, saturated solution of Ia in benzene (benzene peaks at 5.09 μ and 5.51 μ); B, after addition of 1 equiv. of t-butyl hypochlorite and 0.5 equiv. of potassium t-butoxide; C, after addition of 1 equiv. of potassium t-butoxide; D, after addition of slightly more than 1 equiv. of potassium t-butoxide; E, after evaporation of solution of curve C to dryness and extraction of solids with pentane; F, mixture of curve E after two weeks in freezer. Curves A-D were determined for chloroform sloutions, curves E and F for pentane solutions.
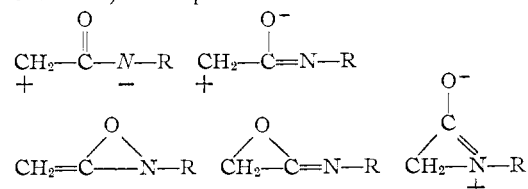
An intermediate absorbing at 1843 cm.$^{-1}$ (CHCl$_3$) was observed as a mixture with other materials from the reaction of N-t-butyl-N-chloroacetamide (Ic) with potassium t-butoxide.

One reasonable explanation of these observations is that the reaction follows the path I → V and that the band at 1847 cm.$^{-1}$ is due to the aziridinone intermediate IIIa.[5] Attempts to isolate this intermediate by addition of slightly less than one equivalent of potassium t-butoxide in IIa have not been successful. However, a roughly 1:1 mixture (based on relative intensities of the ν(C=O) bands) of two products thought to be IIIa and α-t-butoxy-N-t-butylphenylacetamide (VIIa) has been obtained. Attempts to separate the two substances have resulted in destruction of the component absorbing at 1847 cm.$^{-1}$. The latter (as a mixture with VIIa) is very short-lived in the

(5) Estimated ν(C=O) for α-lactams is 1830–1850 cm.$^{-1}$.

presence of water or hydroxylic solvents at room temperature but may be kept in the solid state or in dry pentane solution in the freezer for several weeks with only gradual loss of the high frequency component. The position of the 1847 cm.$^{-1}$ band is little affected by the dielectric constant of the solvent, being essentially unchanged in *cold* chloroform, methylene chloride, benzene, pentane, acetonitrile or methanol. The band disappears completely in methanol after 20 minutes at 5° and after 5 minutes at room temperature. If the mixture is allowed to stand at room temperature for one day in t-butyl alcohol, the principal product is VIIa (m.p. 107–108°, ν(C=O) 1669 cm.$^{-1}$, ν(N—H) 3398 cm.$^{-1}$ (CHCl$_3$); found for C$_{16}$H$_{25}$NO$_2$: C, 73.20; H, 9.41; N, 5.00)).

Although it appears reasonable that the intermediate in this new rearrangement may have the aziridinone structure (III), a number of resonance forms can be written for III, of which five (other than III) are reproduced below.

$$\underset{+}{CH_2}-\overset{\overset{O}{\|}}{C}-\overset{-}{N}-R \quad \underset{+}{CH_2}-\overset{\overset{O^-}{|}}{C}=N-R$$

$$CH_2=\overset{\overset{O}{/\backslash}}{C}----N-R \quad CH_2-\overset{\overset{O}{/\backslash}}{C}=N-R \quad CH_2-\underset{+}{\overset{\overset{O^-}{\underset{}{C}\backslash\!\!\backslash}}{N}}-R$$

Examination of these forms (the spectral properties of which may be difficult to predict) will suggest that further evidence will be required before the appropriate structure can be selected. The similarity of the present situation to that encountered in the Favorskii rearrangement will be obvious.[6,7] The difference in behavior of the intermediate toward t-butyl alcohol and toward t-butoxide ion is also characteristic of the Favorskii rearrangement.[6,7]

(6) H. O. House and W. F. Gilmore, J. Am. Chem. Soc., 83, 3972, 3980 (1961).

(7) A. W. Fort, Abstracts of Papers, Meeting of the American Chemical Society, Sept. 4, 1961, Chicago, Ill., p. 19-Q.

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EXCHANGE OF HYDROGEN BETWEEN WATER AND THE HYDROBORATE ION

Sir:

We wish to report evidence for the exchange of hydrogen between hydroborate ions and water in aqueous hydroborate solutions. Exchange takes place by two different paths. The exchange rate corresponding to one path is independent of pH and is measurable at elevated temperatures in solutions of very high pH (~14). The exchange corresponding to the other path is acid-catalyzed and is detectable in solutions undergoing hydrolysis at ordinary temperatures.

The pH-independent exchange reaction was studied by measuring the exchange between D$_2$O (99.82%) and potassium hydroborate (0.4 M) in solutions which were 1, 3 and 5 M in sodium deuteroxide and in which the ionic strength was brought to 5.4 M with sodium chloride. These solutions were held in a thermostated bath and

aliquots were removed at various times. Each aliquot was cooled, diluted 1:200 with ordinary water, and then hydrolyzed with excess sulfuric acid. The evolved hydrogen was analyzed mass-spectrometrically. We assumed that the percentage of H_2 was equal to the percentage of unexchanged hydrogen in the hydroborate and that the percentage of HD was equal to the percentage of deuterium in the hydroborate.[1] There are two reasons why the rate of appearance of deuterium in the hydroborate may not exactly equal the rate of the reaction $BH_4^- + D_2O \rightarrow BH_3D^- + HDO$. (1) Hydrolysis occurred concurrently with the exchange; and since the species BH_4^- and BH_3D^- probably do not hydrolyze at the same rate, the relative amounts of these species is not an accurate indication of the extent of exchange. (2) The deuterium atoms in species such as BH_3D^- and $BH_2D_2^-$ may exert secondary isotope effects such that the hydrogen atoms in these species undergo exchange at a different rate than those in BH_4^-. We believe both of these effects are of minor importance in our experiments because exchange was allowed to proceed only about 20% toward completion and because, in the runs with 5 M OD^-, the hydrolysis consumed only 10–25% of the hydroborate.

Therefore, in Fig. 1 we have plotted the logarithm of the percentage of unexchanged hydrogen in the hydroborate against time for solutions 1, 3, and 5 M in OD^- at 95.8° and for solutions 5 M in OD^- at 73.7°. Since all the points for a given temperature fall on one straight line, it is clear that the exchange reaction is first order in hydroborate and zero order in hydroxide. From the slopes of the straight lines for 95.8° and 73.7°, we calculate a heat of activation of 26 kcal./mole and an entropy of activation of −10 cal./deg. mole.

The acid-catalyzed exchange reaction was first suspected during a study of the acid hydrolysis of deuterioborate in ordinary water. The compositions of the hydrogen samples obtained from complete hydrolyses at three different temperatures are given in Table I. The presence of D_2

TABLE I

ACID HYDROLYSES OF DEUTERIOBORATE IN ORDINARY WATER

	0°	22.6°	50.0°
% H_2	3.92	3.10	2.99
% HD	94.92	95.62	95.63
% D_2	1.16	1.28	1.38
% H	51.38	50.91	50.80

in the hydrogen is a phenomenon which will be discussed elsewhere. The fact that the % H_2 was always greater than the % D_2 may be explained partially by the presence of some hydrogen in the deuterioborate. The significant fact for this discussion is that the % H varied with the temperature during hydrolysis. This variation derives from a variation in the extent of exchange of hydrogen between the water and either the hydroborate

(1) The hydrogen from samples which had undergone no exchange contained only about 0.5% HD, presumably the ca. 0.5% deuterium in the hydrolyzed solution. Other data indicate that completely exchanged hydroborate (pure BD_4^-) would give about 1-2% H_2 when hydrolyzed in ordinary water. Our solutions were followed only to about 20% exchange, so it is unlikely that the calculated percentages of reaction are inaccurate by more than 0.5%.
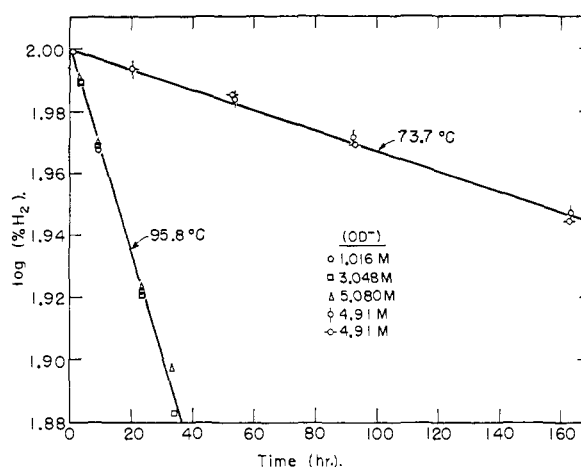

Fig. 1.—First-order plots for the exchange of D_2O with hydroborate.

ion, an intermediate in its hydrolysis, or both. To determine definitely whether or not the hydroborate was undergoing exchange, we then examined the hydrogen evolved at different times in the hydrolyses of solutions of hydroborate in D_2O. In a hydrolysis at pH 7, the hydrogen evolved during the first 60% of reaction contained 7.94% H_2, 83.30% HD, and 8.76% D_2, and the hydrogen evolved during the last 40% of reaction contained 6.82% H_2, 75.40% HD, and 17.78% D_2. In a hydrolysis at pH 9, the hydrogen evolved while the reaction proceeded from 6% to 12% toward completion contained 5.59% H_2, 91.75% HD, and 2.66% D_2; that evolved while the reaction proceeded from 47% to 54% toward completion contained 5.64% H_2, 89.28% HD, and 5.08% D_2; and that evolved while the reaction proceeded from 79% to 84% toward completion contained 5.59% H_2, 87.36% HD, and 7.05% D_2. The ratio of the exchange rate to the hydrolysis rate was approximately the same for both hydrolyses, even though the solutions differed in pH by two units. If the % D_2 is plotted against the average percentage of hydrolysis for the run at pH 9, the points fall on a straight line of slope 0.060. These data indicate that the exchange rate has the same dependencies (first order) on the concentrations of H^+ and BH_4^- as does the acid hydrolysis rate. At 25°, the rate constant for the exchange is about 6% of that for the hydrolysis. The data of Table I indicate that the activation energy for exchange is less than that for hydrolysis.

The fact that Girardot and Parry[2] found no exchange during 17.5 hours at room temperature in a hydroborate solution of pH 12 is completely consistent with our findings.

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(2) P. R. Girardot and R. W. Parry, J. Am. Chem. Soc., 73, 2368 (1951).