and that this diffusion is hindered by the helium, thus increasing the rate. The fact that the first packing we used lowered the rate in some of the runs might be considered as confirmation of this, but it is probable that the effect of packing is due to condensation of material on the surface,[27] as is indicated by the fact that the first packing became darker with use than the second packing, which gave more normal rates. In any event, if the chain length depended upon the number of collisions of a methyl radical with azomethane molecules before hitting the wall, it would rapidly approach 1 at low pressures; with a chain length less than 2 at 150 mm it would surely be reduced to practically 1 at pressures around 5 mm, and if the sole effect of the helium were to reduce the diffusion of methyls to the wall, one would not then expect the addition of 5 or 10 mm of helium to 1 mm of azomethane to have any effect; it does, however, have an appreciable effect, indicating, we believe, that the effect of the helium is actually due to activation. We believe that the constancy of α over a range of pressures and two temperatures is strong evidence in favor of the view that the azomethane decomposition is not a chain reaction, or at least that the chain length is independent of temperature and pressure over that range. The falling off of the rate constant at low pressures must then be caused by lack of activating collisions, and the reaction is a satisfactory one to use as a test for the theory.

[27] Compare Winkler and Hinshelwood, Proc. Roy. Soc. **A149**, 355 (1935).

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Reaction Products of Ethyl Alcohol and Sodium Hydroxide

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A study has been made of the products formed when sodium hydroxide and ethyl alcohol react in the absence of water. Evidence has been found which indicates a reaction in which sodium ethylate and water are produced. Three types of tests have been made to determine the amount of water formed. The copper acetylide method, a volumetric method, and a method involving infrared absorption measurements all indicate a reaction which goes from 75 to 100 percent toward completion.

ALTHOUGH ethyl alcohol is usually regarded as a neutral liquid like water, in certain types of reactions it can be shown to act as a weak acid and in still others as a weak base. Thus, when ethyl alcohol reacts with an active metal such as sodium or potassium, hydrogen is given off and a salt is formed which is readily hydrolyzed by water. When treated with strong acids, alcohol forms addition compounds, which in general are unstable at ordinary temperatures.[1]

Engel and Lescoeur[2] have reported the following reaction between alcohol and the alkali hydroxides at high temperatures in the absence of water:

$$C_2H_5OH+KOH\rightarrow C_2H_5OK+H_2O.$$

In this reaction the alcohol obviously acts as an ordinary acid. However, owing to the difficulties involved in making an analysis, Engel and Lescoeur were unable to make any quantitative measurement of the extent of the reaction. For the case of potassium hydroxide Engel reports that, after the alcoholic solution of the hydroxide has been prepared at room temperature, subsequent cooling causes the deposition of needle-like crystals. Although these crystals when dried decompose rapidly at 60°C, Engel believes that they have the composition of $C_2H_5OK\cdot C_2H_5OH$. The mechanism of this reaction is shown by the following equation:

$$KOH+2C_2H_5OH\rightarrow C_2H_5OK\cdot C_2H_5OH+H_2O.$$

[1] H. J. Lucas, *Organic Chemistry* (Am. Book Co. 1935), p. 123.

[2] M. Engel, Comptes rendus **103**, 156 (1886); H. Lescoeur, Comptes rendus **121**, 692 (1895).

The complex form of the ethylate probably decomposes rapidly at high temperatures into ordinary potassium ethylate and alcohol. No quantitative tests on these crystals were possible.

It was the purpose of this investigation to make a study of this reaction by means of the infrared absorption of the reaction products. In order to do this it was necessary to find some part of the composite spectrum which would change in a manner depending upon the amount of one of the products formed. The bands in the spectrum of a solution arise from two sources:

(1) from the molecules of the components of the solution and
(2) from interactions between the molecules of different kinds.

The range 4μ to 5μ was chosen as the region for the observation of spectral changes. Weniger[3] has shown that compounds containing the ethyl group do not have strong characteristic absorption within this range, and Grantham[4] has shown that the band characteristic of inorganic hydroxides appears at a different wave-length (2.30μ). Thus, the alcohol, the ethylate, and the hydroxide by themselves are incapable of producing intense absorption between 4μ and 5μ. Water[5] in the liquid state, on the other hand, has a very strong absorption band at 4.7μ, and Williams and Plyler[6] have shown that this band is present in water-alcohol mixtures and that its intensity is a measure of the water content of the mixture. This 4.7μ water band is suitable for use as a measure of the amount of water formed in the reaction to be studied, unless other bands arising from association appear in the same position.

As for the existence of associational bands near 4.7μ, previous studies of binary mixtures of the compounds involved have shown that no appreciable associational bands are to be found near this point. A broad band with maximum at 5.2μ is present in aqueous solutions of hydroxides, while alcoholic solutions of hydroxides have a small, sharp band at this same point.[7, 8] In water-alcohol mixtures[6] the interaction bands occur at wave-lengths far removed from 4.7μ. As for associational bands in which ethylate-alcohol interactions are involved, the general experience has been that the bands arising from association of such similar organic compounds are either very weak or appear at wave-lengths much longer than 4.7μ. Thus, on the assumption that there are no tertiary associational compounds producing absorption in the 4μ–5μ region, it was decided that the 4.7μ band could be used as a means of testing for water formed in the reaction.

The alcoholic solution of sodium hydroxide was prepared by dissolving 11.1 grams of previously dried NaOH (Baker's C.P.) in 100 cc of anhydrous ethyl alcohol. The alcohol had been dried over lime, distilled, then dried over anhydrous copper sulphate, distilled again, and finally distilled from metallic sodium. The resulting alcohol gave only a faint color when tested by the copper acetylide method of Weaver[9] and of Hartley and Raikes.[10] The NaOH was fused in the usual manner.

The mixture was heated for one hour under a reflux provided with glass stoppers and ground glass joints. All apparatus had been heated to remove surface moisture before the reagents were introduced. The system was protected with a $CaCl_2$ tube. After an hour a sample was drawn, cooled, and immediately examined for the 4.7μ water band.

The remaining portion was distilled from the apparatus and collected in a receiver protected from the air by a $CaCl_2$ tube. Ground glass joints were used throughout in the apparatus. The distillate was tested for water by the aforementioned method of Weaver and others. A dense precipitate of copper acetylide was produced, indicating that a considerable amount of water had been formed in the reaction. This result was checked by means of a volumetric method involving a reaction between the water produced and calcium carbide with the production of acetylene.

In measuring the infrared absorption of the solutions a large type Hilger spectrometer with a fluorite prism was used as a resolving instrument. The effective slit-width was 0.04μ at 4.5μ. The

[3] W. Weniger, Phys. Rev. **31**, 388 (1910).
[4] G. E. Grantham, Phys. Rev. **18**, 339 (1921).
[5] E. K. Plyler and C. J. Craven, J. Chem. Phys. **2**, 303 (1934).
[6] Dudley Williams and E. K. Plyler, J. Opt. Soc. Am. (in press).
[7] E. K. Plyler and Walter Gordy, J. Chem. Phys. **2**, 470 (1934).
[8] E. K. Plyler and Dudley Williams, J. Chem. Phys. **2**, 565 (1934).
[9] E. R. Weaver, J. Am. Chem. Soc. **36**, 2462 (1914).
[10] H. Hartley and H. R. Raikes, J. Chem. Soc. **127**, 524 (1925).

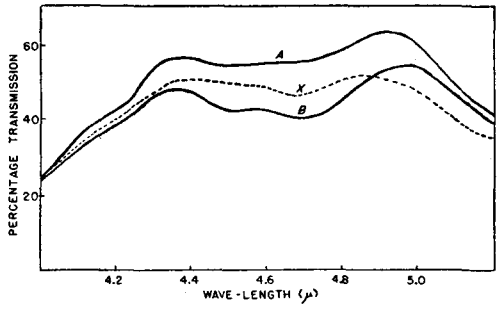

FIG. 1. The percentage transmission of absolute alcohol and two solutions. *A*, absolute alcohol, *B*, five percent water in alcohol. *X*, cell of unknown water content.

cell windows were of fluorite, and the cells were prepared by placing mica washers 0.05 mm in thickness between the fluorite plates. The fluorite plates, the mica washers, and all instruments used in preparing the cells were kept in a desiccator with P_2O_5 for several hours before being used. This minimized the possibility of difficulties arising from water adsorbed on the plates.

In Fig. 1 are shown the results obtained in the absorption measurements. Curve *A* represents the percentage transmission of the anhydrous alcohol used in preparing the solution. Curve *B* shows the transmission of a solution of five percent (by volume) of water in this same sample of anhydrous alcohol. It will be noted that near 4.7μ there appears a broad depression, which indicates the presence of water. The dotted curve *X* represents the results obtained with the solution of unknown water content. It will be noted that in general this dotted curve lies between the other two curves, showing that there is no strong characteristic absorption in this region arising from substances other than the water, which produces the broad depression near 4.7μ. Beyond 4.9μ, however, the curve *X* lies much deeper than the other two. This absorption arises from associations in which the remaining NaOH molecules are involved. The broadness of the 5.2μ band indicates that the solvation effect probably involves chiefly the NaOH and water rather than the NaOH and alcohol, since the NaOH-alcohol band is much narrower than this band. By a comparison of the intensities of the bands observed near 4.7μ it is estimated that the unknown solution probably contains from one-half to two-thirds as much water as the 95 percent solution. This calculation corresponds to a reaction which goes from 75 to 100 percent toward completion.

The results obtained in this study indicate the possibility of using infrared absorption measurements in still other cases where ordinary analytical methods are not readily applicable.

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The Structure of Ice III

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The stability of the high pressure ice forms discovered by Tammann and Bridgman at very low temperatures and atmospheric pressure has made it possible to obtain x-ray diffraction photographs of these forms. Since ice III is extracted from the press by taking it through the ice II region the precautions taken to avoid consequent misinterpretation of the ice III films are given. The analysis of the ice III diffraction patterns leads to a body-centered orthorhombic structure, and a unit cell of dimensions $a=10.20$A, $b=5.87$A, and $c=7.17$A. The unit cell contains sixteen molecules, has the symmetry of space group V_h^{26}-Ibam, and leads to a value for the density of 1.105 g per cc. Each oxygen ion is surrounded by a distorted tetrahedron of oxygen ions in a manner similar to that of ice I. An arrangement of the hydrogen atoms is proposed which makes the ice III lattice ionic. The volume decrease in the ice I–ice III transition is shown to be the result of a rearrangement of the oxygen ions. A simple transition mechanism is described, which is used to interpret some of the phenomena observed by Bridgman. The nature of the ice II–ice III transition is also discussed. A correlation between the latent heat of the solid-solid reactions involving ice I, ice II, ice III and the H−O−H bond angles is suggested. Some remarks are made concerning the liquid-solid reaction at high pressure. A brief description of some qualitative results obtained from the unanalyzed ice V and ice VI films is made. A summary of all the conclusions drawn from the high pressure ice investigations is made.

* Now at The United Drug Co., Boston.