suffer spontaneous decomposition accompanied by a rapid rise of temperature, at a temperature characteristic for each mixture.

2. This acceleration is due to the exothermal nature of the decomposition.

3. Pressure of oxygen exerts a marked effect on the decomposition of potassium chlorate.

AMES, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF OREGON]

THE IONIZATION OF ALCOHOLS

BY ROGER J. WILLIAMS AND R. W. TRUESDAIL[1]

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Since early in the history of organic chemistry, esterification has been compared to neutralization and alcohols have been said to play the role analogous to that of bases. Current statements can be found, however, to the effect that alcohols are not bases, and the analogy of esters and salts though used by many is probably accepted as satisfactory by few. The purpose of this work was to contribute to our knowledge of the extent of ionization of alcohol in either of the two ways, as a base into ethyl and hydroxyl ions or as an acid into hydrogen and ethylate (OC_2H_5) ions. In an article published since this work was completed, Danner and Hildebrand,[2] have measured the ionization of alcohol by two methods, considering the ionization as an acid as predominant and assuming the ionization of alcohol as a base to be negligible in comparison.

Approximate Measurement of the Degree of Ionization of Alcohol into Hydrogen and Ethylate Ions

An attempt was first made to determine the degree of ionization of ethyl alcohol into hydrogen and ethylate, by determination of the equilibrium point in the reaction, $C_2H_5OH + NaOH \rightleftharpoons C_2H_5ONa + H_2O$. At the time the work was started, knowledge of the equilibrium point in this reaction was exceedingly scant, so even approximate results were thought desirable. When sodium hydroxide is dissolved in absolute alcohol some water is formed by reaction. A dynamic method was devised, accurate to about 10%, for determining very small amounts of water in alcohol, in such a way that equilibrium would not be appreciably disturbed. This method was then applied to the determination of the amount of water formed by the addition of a known amount of solid sodium hydroxide of

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[1] The experimental work concerned with metallic nitrides and hydrides was done by R. W. Truesdail, and a report of this work was incorporated in a thesis submitted by him at the University of Oregon, in partial fulfilment of the requirements for the degree of Master of Science.

[2] Danner and Hildebrand, THIS JOURNAL, 44, 2824, 2832 (1922).

known purity to a known quantity of alcohol of nearly 100% purity, with known water content.

The method of determining the water in the alcohol without shifting the equilibrium, if such were present, consisted in rotating a known amount of the sample to be tested with a sample of known weight of especially prepared granules of calcium carbide, for a definite length of time, so that only a small amount (about 4%) of the water actually present was used up. This amount was sufficient to allow a nephelometric determination of the calcium in suspension as calcium hydroxide, and from this by comparison with the action of samples of similar carbides on alcohol containing known amounts of water, the amount of water actually present was determined.

From results obtained in this way, alcohol was calculated to be about 8% as highly ionized as water. It was not certain that the other substances in the solution did not interfere somewhat with the determination of the water and it was also probable that the acid properties of the acetylene formed caused the results to be too high. For these reasons and also because of the recent, more satisfactory work of Danner and Hildebrand it was thought best not to take space for full experimental details of this work.

The results have some value in confirming the results of Danner calculated from electromotive-force measurements. The errors in the method used above were probably of such a nature as to make the results high, and on this basis alcohol would be expected to be ionized *less* than 8% as much as water. The value of the degree of ionization of alcohol obtained by Danner and Hildebrand by the conductivity method (55% as highly ionized as water) must, therefore, be too high, but their value obtained by potential measurements (1% as highly ionized as water) is not an unreasonable figure in the light of the measurements reported here.

Calculation of the Degree of Ionization of Alcohol as a Base from the Equilibrium Point of Esterification Reactions

The knowledge of the equilibrium point in an esterification reaction, assuming the reaction to be neutralization, makes possible the calculation of the degree of ionization of the alcohol, just as in the preceding case. Values for these equilibrium constants were available,[3] so that further experimental work was not necessary. In the reaction, $C_2H_5OH + HCl \rightleftarrows C_2H_5Cl + H_2O$, Euler found that the relation, $\frac{[C_2H_5OH]\ [HCl]}{[C_2H_5Cl]\ [H_2O]} = 1$, held approximately.

When equimolecular quantities of ethyl alcohol and hydrochloric acid were mixed, all 4 substances concerned would be present in the same concentration at equilibrium. If the alcohol acts as a base the reaction is ionic and the following relation holds.

$$\frac{\alpha_{\text{alc.}}\ [C_2H_5OH]\ \alpha_{HCl}\ [HCl]}{\alpha_{\text{ester}}\ [C_2H_5Cl]\ \alpha_{H_2O}\ [H_2O]} = 1, \text{ or } \frac{\alpha_{\text{alc.}}\ \alpha_{HCl}}{\alpha_{\text{ester}}\ \alpha_{\text{water}}} = 1$$

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[3] Euler, *Z. physik. Chem.*, **36,** 405 (1901).

If 1 be substituted for α_{HCl} and 2×10^{-9} for α_{H_2O}, then,

$$\alpha_{alc.} = \alpha_{ester} \times 2 \times 10^{-9}$$

The degree of ionization of ethyl chloride is so small as practically to defy detection, and since the ionization of alcohol as a base is about one five-hundred millionth the ionization of ethyl chloride, the basic strength of alcohol is nil, as determined by this method.

Reaction of Alcohols with Metallic Nitrides and Hydrides

To attack the problem of the ionization of alcohols in another way, specific reactions were chosen in which alcohols might act either as bases or acids and were carried out to see which course the reaction takes. For this work methyl alcohol was chosen as typical of the alcohols, because some work along this line had been done previously with methyl alcohol, and its reactions with magnesium nitride and calcium hydride were studied.

With magnesium nitride methyl alcohol might react typically in either of two ways: (1) $Mg_3N_2 + 6CH_3OH = 3Mg(OH)_2 + 2(CH_3)_3N$; or (2) $Mg_3N_2 + 6CH_3OH = 3Mg(OCH)_2 + 2NH_3$.

Szarvasy,[4] gives the following equation for the reaction: $Mg_3N_2 + 6\,CH_3OH = 3Mg(OH)OCH_3 + NH_3 + (CH_3)_3N$. However, his work is not conclusive, as he fails to give the details of his procedure, or information as to the amount or purity of the nitride and alcohol used, or the amount recovered, or how ammonia was differentiated from trimethylamine. Nothing precludes the possibility that the presence of trimethylamine was merely inferred from a low chloride or nitrogen content of the salt procured. He states in the first part of his paper that he expected to obtain all of the nitrogen as trimethylamine. His work does not check with the fact that with calcium nitride, methyl alcohol is reported to yield ammonia.

Magnesium nitride was prepared in a porcelain combustion tube by heating magnesium powder at red heat in a stream of ammonia gas. The ammonia gas was generated from a Dewar flask of liquid ammonia. To regulate the flow of ammonia a wire gauze was fixed in the flame of a Meker burner, and its distance from the Dewar flask was varied at will. A weighed sample of magnesium nitride, Mg_3N_2, was heated with absolute methyl alcohol for 30 minutes in a small distilling flask in an atmosphere of dry nitrogen under such conditions that the volatile bases, ammonia and trimethylamine, after passing through a reflux condenser were caught in a known volume of standard sulfuric acid solution. The vapors remaining in the flask and condenser were then driven over into the acid with a gentle stream of dry nitrogen admitted through the side opening of the distilling flask. The reflux condenser was then replaced by a stopper and the condenser attached for distilling over the alcohol. The alcohol was practically all driven over into the same standard acid used to absorb volatile bases. The acid was then titrated back with standard alkali solution and the amount of basic nitrogen (ammonia and trimethylamine) was determined. The neutral solution was acidified and evaporated to dryness on a water-bath and made up to 100 cc. The nitrogen from ammonia was then determined as gas in the Van Slyke apparatus for determining amino nitrogen. The apparatus was used exactly as for determination of amino nitrogen except that

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[4] Szarvasy, *Ber.*, **30**, 305 (1897).

it was necessary to keep the reaction mixture at a temperature of about 60° for about 30 minutes by immersing the container in a water-bath, in order to obtain a quantitative yield of nitrogen. Blank determinations were made and suitable corrections applied.

The following table gives some of the results obtained with the purest samples of nitride. All results indicated clearly that the methyl alcohol acted exclusively to form ammonia in each case and that no trimethylamine was formed, since nitrogen is not evolved from trimethylamine by treatment with nitrous acid as in the Van Slyke method.

Table I

Nitrogen Obtained from the Reaction of Methanol or Magnesium Nitride

Sample of Mg_3N_2	Mg_3N_2 G.	Total N G.	N by the Van Slyke method G.	G.
I	0.3394	0.0921	0.0920	0.0926
II	.3448	.0932	.0937	.0937

Subsequently, it was shown that no organic base, primary, secondary or tertiary is produced. The reaction product of 0.150 g. of magnesium nitride in an excess of methanol was evaporated to dryness and the dry salt was mixed with powdered cupric oxide and heated to red heat. The issuing gases were run through lime water, and only the faintest trace of calcium carbonate was precipitated, showing the absence of practically all organic matter.

Methanol might act in either of two ways with metallic hydrides. Using calcium hydride as an example the reactions would be: (3) $CaH_2 + CH_3OH = Ca(OH)_2 + CH_4$; (4) $CaH_2 + CH_3OH = Ca(OCH_3)_2 + H_2$. As no record was found of experimental work on this point, the reaction was carried out, to determine in which of the two possible ways it proceeds. Calcium hydride was used because of its comparative ease of preparation. Reaction 3 would plainly indicate basic properties for methanol. Reaction 4 would indicate that methanol has at least weak acid properties.

Calcium hydride was prepared by heating calcium shavings in an iron muffle in a lead bath at 340°, in an atmosphere of hydrogen for about 2 hours. The preparation was not very pure as subsequent results showed, partly due to the presence of the original calcium. It was, however, brittle and easily ground, and unlike metallic calcium in physical properties. Time did not permit the preparation of a purer sample, but the results seem to be conclusive as they stand. A weighed sample of calcium hydride was placed in a 10cc. test-tube fitted with a 2-holed stopper carrying a dropping funnel and a capillary outlet tube leading to a gas buret filled with mercury. A little of the alcohol was admitted through the dropping funnel and the evolved gas was collected in the buret, while the test-tube was kept warm by a pilot flame. After many hours, when the action had practically ceased, sufficient alcohol was admitted through the dropping funnel to fill the test-tube completely and extend into the capillary. The sample of gas was then run into a Hempel pipet over a strong alkaline permanganate solution to oxidize alcohol vapor present. After some time the gas was returned to a fresh buret (containing no alcohol) and was analyzed for hydrogen and methane by the explosion method.

Methane was absent in every case (see Table II) showing that the alcohol acts exclusively according to the equation, $CaH_2+2CH_3OH = Ca(OCH_3)_2 +$

$2H_2$. The amount of hydrogen liberated by the alcohol was just a little less than that liberated by water from the same amount of hydride, due to the fact that the reaction with alcohol had not reached completion.

The results with both magnesium nitride and calcium hydride confirm the results given in the first part of the paper, and the conclusion seems justified that alcohols have very weak acidic properties and their basic properties are entirely negligible. In reacting with Grignard reagents and with calcium carbide at high temperature, also, alcohols fail to show basic properties. Alcohols act, so far as is known, exclusively according to Equations 5 and 7, and not as they would be expected to if they were basic, or in part if they were amphoteric, as would be represented by Equations 6 and 8.

$$R\text{—}Mg\text{—}Br + H\text{—}OCH_3 = R\text{—}H + Mg(OCH_3)Br \qquad (5)$$

$$R\text{—}Mg\text{—}Br + CH_3OH = R\text{—}CH_3 + Mg(OH)Br \qquad (6)$$

$$CaC_2 + 2HOC_2H_5 = C_2H_2 + Ca(OC_2H_5)_2 \qquad (7)$$

$$CaC_2 + 2C_2H_5OH = (C_2H_5)_2C_2 + Ca(OH)_2 \qquad (8)$$

TABLE II

GASES FROM ACTION OF METHANOL ON CALCIUM HYDRIDE

		CaH_2 sample			
		1	1		2
CaH_2, g.		0.0550	0.0434		0.0661
Total vol. of gas after CH_3OH ox. cc.		56.7	49.7		60.0
Vol. of gas for explosion, cc.	(a)	10.0	10.0	(a)	10.0
	(b)	10.1		(b)	10.2
	(c)	10.3			
Total vol. air and gas, cc.	(a)	34.1	41.9	(a)	39.1
	(b)	35.4		(b)	38.5
	(c)	40.1			

		CaH_2 sample			
		1	1		2
Vol. after expl. cc.	(a)	24.9	32.8	(a)	28.4
	(b)	26.5		(b)	27.6
	(c)	30.9			
Vol. after KOH ab., cc.	(a)	24.9	32.8	(a)	28.4
	(b)	26.5		(b)	27.6
	(c)	30.9			
Vol. of CO_2, cc.	(a)	0	0	(a)	0
	(b)	0		(b)	0
	(c)	0			
Total vol. of H_2, cc.		29.8	28.5		31.1

Sample 1 of calcium hydride liberated 59.2% of the calculated amount of hydrogen when treated with water and in two experiments gave 52.6% and 57.6% when treated with methanol. Sample 2 liberated 58.27% when treated with water and 51.89% when treated with methanol.

Discussion

Evidence has thus been presented to show that alcohols have weak acid but no basic properties. In addition, in the classification and understanding of the properties of the esters, there are marked advantages to be gained by discarding the conception of alcohols as bases and by laying emphasis on their acidic character. Esters, then, may be classified with mixed acid anhydrides, in which one of the "acids" involved is alcohol. Esters do, in fact, show marked similarities to acid anhydrides such as are listed below, and the analogy with salts is relatively remote and useless. (1) Esters and anhydrides of strong acids generally hydrolyze *more* completely than esters or anhydrides of weak acids, in this respect acting just the opposite from salts. Hydrolysis of esters and anhydrides (especially those of weak acids) is generally a rather slow reaction, while the hydrolysis of salts takes place instantaneously. (2) Esterification resembles in some respects the formation of acid anhydrides from acids, as both types of reactions are slow and therefore are not ionic in the ordinary sense, and both take place under dehydrating conditions. (3) Esters and anhydrides are alike in being poor conductors of electricity. (4) They are alike in the less fundamental but rather striking respect, that both are generally volatile, while salts are characteristically non-volatile, especially if they are not decomposed by heat. This classification of esters and like substances with acid anhydrides makes possible a better correlation of certain parts of organic with inorganic chemistry.[5]

We wish to thank our colleagues especially for the valuable criticisms and suggestions they have made.

Summary

1. Results were obtained which appear roughly to confirm those of Danner and Hildebrand on the ionization of alcohol into hydrogen and ethylate ions.

2. Assuming that esterification is a neutralization reaction, the degree of ionization of alcohol into ethyl and hydroxyl ions is shown by calculation to be nil.

3. Experimental chemical evidence is presented indicating that alcohols ionize in only one way, namely, as weak acids.

4. The advantages to be gained in the study of organic chemistry from emphasis on the acidic character of the alcohols are briefly pointed out.

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COMPLEXES IN SOLUTIONS OF COPPER AND COBALT SALTS

BY HENRY GEORGE DENHAM AND STUART WORTLEY PENNYCUICK

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In a recent paper by Watkins and Denham,[1] further evidence has been put forward concerning the presence of auto-complexes in solutions of copper halides. The evidence is mainly derived from migration experiments and is held to support the theory of complexes suggested by Donnan and Bassett[2] to explain the color changes exhibited by solutions of the

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[5] An elaboration and extension of this point of view by one of us, entitled "The Classification of Carbon Compounds and Their Correlation with Compounds of Other Elements" will appear shortly as a University of Oregon Publication.

[1] Watkins and Denham, *J. Chem. Soc.*, **115**, 1269 (1919).

[2] Donnan and Bassett, *ibid.*, **81**, 939 (1902).