[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

DECOMPOSITION OF DIACETONE ALCOHOL BY SODIUM HYDROXIDE IN WATER MIXTURES OF ORGANIC SOLVENTS

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Introduction

This paper gives a preliminary orientation toward a study of the decomposition velocity of diacetone alcohol in non-aqueous solutions. The measurements have been carried out with varying water mixtures of a number of different aliphatic alcohols as solvents. Some other solvents were used but they were either very difficult to purify or the solubility of the alkali hydroxides in their pure state was very small. Therefore the measurements with water mixtures of these solvents do not have any greater interest and will not be given here. As catalyst 0.1 N sodium hydroxide was added. The complete lack of any data regarding the thermodynamical properties of the catalyst in these solutions makes it very difficult to give a reasonably safe interpretation of the results obtained.

Experimental Methods and Materials

The method[1] used to measure the reaction velocity was the same as previously described. Errors due to evaporation of the solvent are discussed in the preceding paper[2] on measurements with weaker bases. All the different solvents used, except methyl and ethyl alcohol and glycerine, were obtained from the Eastman Kodak Co. Ethyl alcohol was refluxed and redistilled twice over burnt lime. All the others were delivered as solvents practically free from water. For a first orientation in this field further drying and fractional redistillation were regarded as entirely unnecessary. Methyl alcohol was dried over burnt lime and redistilled but no difference was found for the reaction velocity in solutions prepared with the dried or undried alcohol.

Experimental Results

A summary of the measurements is given in Table I. Their graphical representation is shown in Fig. 1. The amount of organic solvent used is always given in weight percentage (w. p.). The solutions for a weight percentage of 99 were obtained through the dilution of a weighed amount of a very concentrated aqueous solution of sodium hydroxide with the pure solvent. An allowance of 0.5% is made for water in the pure solvent. In the last column of Table I are given some measurements with mixtures of methyl and n-propyl alcohol. These solutions were made up from

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[1] Åkerlöf, THIS JOURNAL, **48**, 3046 (1926); *ibid.*, **49**, 2955 (1927).

[2] Åkerlöf, *ibid.*, **50**, 733 (1928).

the pure solvents. The sodium hydroxide concentration represents the normality in 1000 g. of the solvent. The velocity constants are given with the minute as unit of time. They have about the same accuracy as the results published in preceding papers.

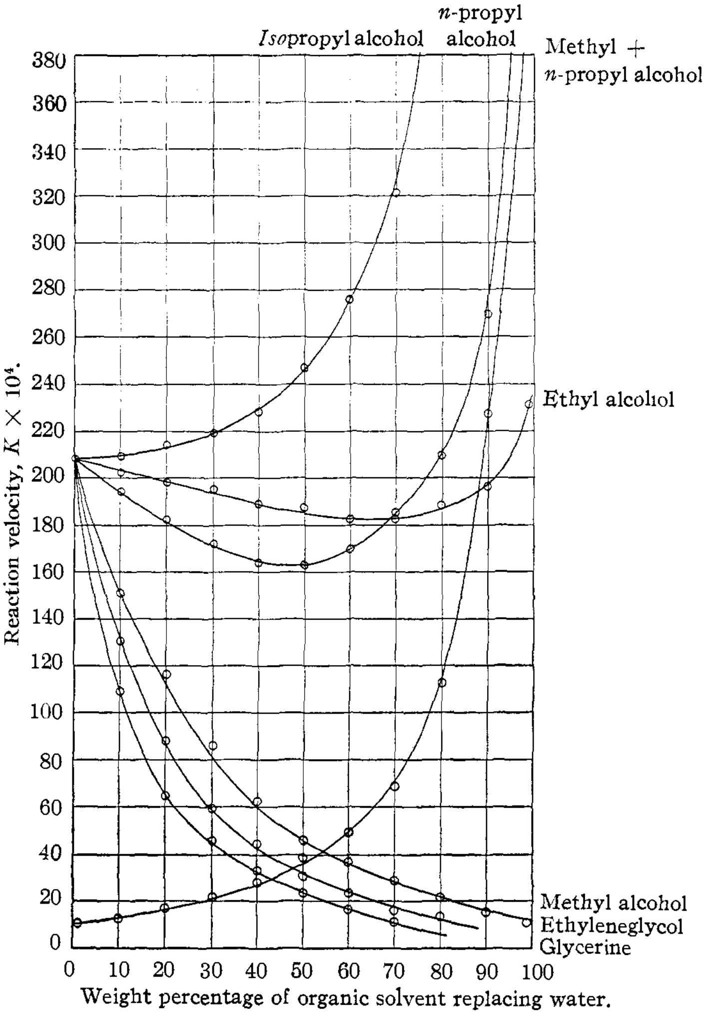

Fig. 1.—Curves for the decomposition velocity of diacetone alcohol in water-aliphatic alcohol mixtures with 0.1 *N* sodium hydroxide added as a catalyst.

The results seem to be rather remarkable. The differences in velocity for solutions in pure methyl, ethyl and *n*-propyl alcohol are relatively quite large. In these solutions only few hydroxyl ions might be present on account of the formation of alkali metal alcoholates. The function of

TABLE I

DECOMPOSITION VELOCITY OF DIACETONE ALCOHOL WITH 0.1 N SODIUM HYDROXIDE AS CATALYST IN SOLUTIONS OF WATER–ALIPHATIC ALCOHOL MIXTURES

	Values of $K \times 10^4$						
W. p.	Glycerine	Ethylene-glycol	Methyl alcohol	Ethyl alcohol	*n*-Propyl alcohol	*Iso*propyl alcohol	Methyl + *n*-propyl alcohol
0	208	208	208	208	208	208	10.3
10	109	130	151	202	194	209	12.5
20	64.4	88.0	116	198	182	214	17.2
30	45.8	59.2	86.3	195	172	219	21.9
40	32.8	44.6	62.4	189	164	228	28.0
50	23.8	30.3	46.0	187	163	247	38.7
60	16.2	21.6	38.4	182	170	276	50.8
70	10.9	15.8	28.7	182	185	321	68.4
80	...	13.2	21.6	188	209	900[a]	112
90	...	...	15.4	196	270	..	227
99	...	...	10.3	231	500[b]	..	500[b]

[a] Approximate value. The solution parted in two phases, one very small, around 1% of the total volume, contained more than 50% of the sodium hydroxide added.

[b] Value that may have a larger error (the true value most probably higher).

the hydroxyl ion is then taken over by the alcoholate ions. With an increase in their weight and therefore also in size an increase in reaction velocity apparently follows. Thermodynamically this result was to be expected because the solubility of sodium hydroxide in the primary alcohols decreases rapidly with increasing molecular weight of the alcohol. At the saturation point the activity of the hydroxide in solution is constant and equal to the activity of the solid. At corresponding concentrations the activity coefficient of the alkali hydroxide must therefore increase with decreasing solubility. In preceding papers it was shown that the decomposition velocity of diacetone alcohol was proportional to the mean activity coefficient of the alkali hydroxide.

Conclusions

A comprehensive study of the literature regarding reactions catalyzed in non-aqueous solutions has been given by Walden.[3] Therefore in this place we will not attempt any extensive discussion of the results obtained. Only the more obvious facts will be stated.

The velocity for the decomposition of diacetone alcohol at 25° with 0.1 N sodium hydroxide as a catalyst has been measured in varying water mixtures of a number of different alcohols. The velocity in pure primary alcohols as solvents increases with increasing molecular weight of the solvent. This is the opposite of the rule found by Goldschmidt[4] and co-workers for the formation of an ester, catalyzed by one of the halide acids

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[3] Walden, "Elektrochemie nichtwässriger Lösungen," J. A. Barth, Leipzig, **1924.** The literature is covered to July, 1923.

[4] Goldschmidt and co-workers, *Z. physik. Chem.*, **81,** 30 (1912); **94,** 233 (1920); **114,** 1 (1924); **117,** 312 (1925); **121,** 153 (1926); **124,** 23 (1926).

in the same alcohols. The monomolecular reaction velocity decreased with increasing molecular weight of the solvent.

The reaction velocity in the pure alcohols decreased with increasing number of oxy groups in the alcohol. The velocity was very much higher in ethyl alcohol than in ethylene glycol solutions. The addition of dextrose with five oxy groups decreased the velocity very rapidly to values too small to be measured accurately. The velocity in solutions of isomeric alcohols is greatest for the form with the most compact alkyl group. Again Goldschmidt and co-workers found the contrary. The velocity of formation of an ester catalyzed by one of the halide acids is highest for the normal form.

The reaction velocity in solutions of some of the pure alcohols is largely influenced by the presence of small amounts of water. This influence decreases with decreasing molecular weight of the alcohol or with increasing number of oxy groups. It seems to be rather small for methyl alcohol, ethylene glycol and polyvalent alcohols. The curves for the reaction velocity in water–alcohol mixtures showed in all cases a continuous variation. Sharp bends or other peculiarities did not seem to be present.

Summary

The decomposition velocity of diacetone alcohol at 25° with 0.1 *N* sodium hydroxide as catalyst has been measured in varying water mixtures of a number of different alcohols. A short discussion of the results has been given.

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[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY AND SOILS, DEPARTMENT OF AGRICULTURE]

THE COMPRESSIBILITY ISOTHERMS OF HYDROGEN, NITROGEN AND A 3:1 MIXTURE OF THESE GASES AT TEMPERATURES BETWEEN 0 AND 400° AND AT PRESSURES TO 1000 ATMOSPHERES

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This report is the fourth of a series from this Laboratory concerning the physical properties of hydrogen, nitrogen and their mixtures at high pressures.[1] In it are presented the results of a continuation of a study of compressibility phenomena of hydrogen and nitrogen through the temperature range from 0 to 400°.

Method.—A quantity of gas at known pressure and temperature is confined in a heavy steel pipet of known capacity. This gas is allowed to expand into a gas buret maintained at constant temperature and the

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[1] (a) Bartlett, THIS JOURNAL, **49**, 65 (1927); (b) **49**, 687 (1927); (c) **49**, 1955 (1927).