an increase in viscosity with increasing concentration of formamide from 20 to 91 weight per cent. The viscosity then decreases to the value of pure formamide.

4. The results indicate a negligible change in volume on mixing the two associated liquids.

5. The formation of the compound $C_6H_8O_2\cdot 5HCONH_2$ is indicated by the maximum in the viscosity curves.

KINGSTON, RHODE ISLAND RECEIVED JULY 28, 1941

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

The Electron-Sharing Ability of Organic Radicals. XIV. The Effect of the Radicals on the Ionizing Power of Organic Solvents

BY FRANK J. MOORE AND I. B. JOHNS

In a general way the greater the dielectric constant of a solvent the greater is its ionizing power. This fact was observed independently by Nernst and by Thomson and has been formulated into the rule which bears their names. The fact that other effects beside that of the dielectric constant must be considered in accounting for ionizing power has been recognized by many experimenters.

The factors determining the degree of ionization of weak acids have been summarized by Wynne-Jones.[1] They are three. First, the electrostatic action between the solvated proton and the acid ion depends in part upon the dielectric constant of the solvent. Second, the chemical potentials of the solvated proton and the acid ion may vary with the solvent. Though this variation is difficult to estimate, Wynne-Jones concludes, in agreement with Bjerrum and Larsson,[2] that the chemical potentials of the two ions should undergo the same variation with change of solvent. Third, the basicities or proton accepting powers of the various solvents are different. This factor is the subject of the present paper.

The measurement of the basicities of the various solvents is complicated by several difficulties. First, in order that the solute be not an ion aggregate and hence subject to treatment of the type which Debye and Hückel have given, one is limited to the weak acids. Thus one is forced to make measurements on weak electrolytes in solvents possessing much less ionizing power than does water. In the present work picric acid was the solute chosen.

The second complication arises from the fact that once ionization takes place the attractions between the ions will depend upon the dielectric constant of the solvent. This effect will, of course, be included in the ionization constants which are used for comparing the ionizing powers of the solvents. Accordingly in the present study solvents having nearly identical dielectric constants were used.

Finally, a suitable scale is needed for measuring the electronic properties of the radicals attached to the polar group of the solvent molecule. In earlier papers in this series[3] such a scale has been given. The radicals are arranged in the order of their effect on the ionization constant of the carboxyl group. Since the constants were determined in one solvent for any given series of acids it is certain that the scale by which the radicals are compared is free from any effect of dielectric constants.

A later paper[4] has shown that the normalizing power of a series of ketones depends in a regular way on this electron-sharing ability of the radicals attached to the carbonyl group. From this one may conclude that the attraction of the solvent molecule for the proton is a function of the electron-sharing ability of the radicals attached to the polar group. As the electron-sharing ability of the radical increases the donor power of the functional group decreases with a corresponding weakening of the proton-solvent bond resulting in decreased ionization.

Ketones and nitriles were chosen as solvents in the present work because their functional groups have neither so high nor so low an inherent basicity that variations due to the radicals should be too small for convenient measurement. Fur-

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[1] W. F. K. Wynne-Jones, *Proc. Roy. Soc.* (London), **A140**, 440 (1933).

[2] N. Bjerrum and E. Larsson, *Z. physik. Chem.*, **127**, 358 (1927).

[3] R. M. Hixon and I. B. Johns, THIS JOURNAL, **49**, 1786 (1927); L. D. Goodhue and R. M. Hixon, *ibid.*, **56**, 1329 (1934); **57**, 1688 (1935).

[4] F. A. Landee and I. B. Johns, *ibid.*, **63**, 2895 (1941).

thermore these liquids do not undergo self-association to any marked extent, a reaction that would interfere with the bonding of the proton with the solvent. The ionization of acids in strongly associated liquids doubtless takes place in spite of the association rather than because of it.

In the experimental part are given the conductances and the ionization constants of picric acid in acetone, methyl ethyl ketone, and acetophenone as well as in propionitrile and benzonitrile.

Experimental

The measurements of the ionization constants were made by the conductance method. The apparatus used employed the circuit designed by Jones and Josephs[5] including the modified Wagner ground recommended by them. A vacuum tube oscillator was used which gave a good sinusoidal current at a frequency of a thousand cycles per second and at constant voltage.

The cells were of the Kohlrausch type having cell constants of the order of 0.18. This is approximately the figure for the cells designed by Washburn[6] and approved by Morgan and Lammert[7] for solutions of moderate conductance. They proved very satisfactory, having a particularly low capacitance. During measurements they were kept in a thermostat controlled to 25 ± 0.05°.

The electrodes were not platinized. While platinization of the electrodes is an advantage in overcoming polarization, it has certain disadvantages which prohibit its use with many non-aqueous solvents. Partington[8] has shown that the catalytic effects of the platinum may cause chemical changes in the solvent. These effects are minimized by using bright platinum electrodes.

The solvents were purified by repeated fractional distillations using their conductances as a measure of purity. Reasonable agreement was found between the measured values and those reported by other investigators.

The solutions at all the concentrations were made up in stoppered flasks which had been cleaned, washed with water and then with purified acetone, and dried in a current of dry nitrogen. The conductance cells were cleaned and dried in the same manner. The most concentrated solution was prepared first and the others prepared from it by successive 1:1 dilutions. All transfers were made with pipets filled with dry nitrogen into flasks which were also filled with dry nitrogen. This method avoided contact with the atmosphere. This precaution is necessary as the absorption of small amounts of moisture causes material changes in the conductances of the solutions, especially those at low concentration. The solutions were allowed to stand until equilibrium had been reached.

The solutions varied widely in the time required for the ionization to reach equilibrium. The reason for this is not entirely clear. It was noticed, however, that ionization was slow in reaching equilibrium in all those solvents containing a methylene group adjacent to the functional group. In these solvents upwards of two days were required for the conductance to reach its maximum value. In acetonitrile the ionization was so slow, apparently incomplete after four weeks, as indicated by the continually increasing conductance of the solution, that determinations in this solvent had to be given up. In benzonitrile, where no methylene group is present, ionization was complete in three hours.

Calculations of the conductances of the solutions at infinite dilution were made by the two usual methods. From a graph of $1/\Lambda$ against $C\Lambda$, which is a straight line in the region in which the law of mass action holds, the value of $1/\Lambda$ at infinite dilution was read from the intercept $C\Lambda = 0$. As this method is subject to reading error, especially when Λ_0 is large, the value was checked by the method of Washburn.[9] The latter method is very sensitive in the evaluation of Λ_0 especially when this value is large.

The data obtained from the study of picric acid in these solvents are presented in Tables I and II.

TABLE I

EQUIVALENT CONDUCTANCE, Λ_0 AND K OF PICRIC ACID IN KETONES, AT 25°

Molar concentration	Acetone	Methyl ethyl ketone	Acetophenone
0.10	0.2525	0.0829	0.00394
.05	.388	.1259	.00498
.025	.547	.1662	.00660
.0125	.740	.2300	.00995
.00625	1.040	.3150	.01744
.00312	1.400	.4325	...
.00156	1.925	...	...
Λ_0	7.5	1.95	.33
$K \times 10^4$	1.38	1.98	.15

TABLE II

EQUIVALENT CONDUCTANCE Λ_0 AND K OF PICRIC ACID IN PROPIO- AND BENZONITRILE, AT 25°

Molar concentration	Propionitrile	Benzonitrile
0.10	...	3.59
.005	27.2	5.22
.0025	39.1	7.32
.00125	52.5	9.85
.000625	65.9	13.11
.000312	80.4	16.90
.000156	94.0	21.60
.000078	107.5	26.25
Λ_0	120	39.6
$K \times 10^4$	4.25	1.02

Discussion

In Table III are given the ionization constants of picric acid in each of the solvents investigated, together with the electron-sharing abilities of the radicals and the dielectric constants of the solvents.

It is obvious from the data in this table that the ionization constants do not depend in any regular way upon the dielectric constants of the solvents.

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(5) G. Jones and R. C. Josephs, THIS JOURNAL, **50**, 1049 (1928).

(6) E. W. Washburn, *ibid.*, **38**, 2431 (1916).

(7) J. L. R. Morgan and O. M. Lammert, *ibid.*, **45**, 1692 (1923).

(8) J. R. Partington, *J. Chem. Soc.*, **99**, 1937 (1911).

(9) E. W. Washburn, THIS JOURNAL, **40**, 122 (1918).

TABLE III

IONIZATION CONSTANTS OF PICRIC ACID IN SOLVENTS OF THE TYPES R-CO-CH_3 AND RCN

Solvent	Dielectric constant, 20°	Specific conductance at 25° × 10^7	Electron-sharing ability of R, (3)	$K \times 10^4$ of picric acid
Methyl ethyl ketone	17.8	1.65	−1.45	1.98
Acetone	21.5	1.46	−1.40	1.38
Acetophenone	18.1	0.97	+4.2	0.15
Propionitrile	27.0	3.00	−1.45	4.25
Benzonitrile	26.5	0.66	+4.2	1.02

On the other hand, in both types of solvent as the electron-sharing ability of the radical increases the ionizing power decreases. The order of magnitude of the constants found in the nitriles is the same as that for those found in the ketones. This is to be expected from the fact that the ability of the —CN group to associate with active hydrogens is about the same as that of the carbonyl group.

Summary

The conductances and the ionization constants of picric acid in acetone, methyl ethyl ketone, acetophenone, propionitrile and benzonitrile have been determined. The ionization constants depend on the electron-sharing ability of the radicals in the solvent molecule rather than on the dielectric constant of the solvent.

AMES, IOWA RECEIVED AUGUST 20, 1941

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

The Electrolytic Preparation of Ethyl Glyoxylate[1]

BY WILLIAM OROSHNIK AND PAUL E. SPOERRI

During the course of investigations concerning the synthesis of amino-heterocyclics a ready source of pure ethyl glyoxylate became necessary. The literature revealed only one preparation with a reported yield, that of Traube,[2] who reduced ethyl oxalate with sodium amalgam in absolute ethanol obtaining 20% yields of the alcoholate of ethyl glyoxylate. Since a German patent[3] claims "very good" yields of glyoxylic esters are obtained by the electrolytic reduction of oxalic esters in aqueous sulfuric acid, it was decided to investigate the electrolytic method as a source of ethyl glyoxylate.

Ethyl oxalate was reduced to ethyl glyoxylate in ethanol, ethanol–water, and water media at mercury, lead, and lead amalgam cathodes, using sulfuric acid as the electrolyte. The best yields, 53 and 50%, were obtained in ethanol solution at lead amalgam and mercury cathodes. When aqueous alcohol was used the yield dropped in proportion to the amount of water present, and the poorest yields were obtained in purely aqueous solution.

The ethyl glyoxylate was obtained as the alcoholate. This was converted into the free aldehyde in 98% yields, by means of phosphorus pentoxide by modifying the method of Traube.[2]

Experimental

Apparatus.—Two types of cells were used. The first cell consisted of a mercury cathode, porous porcelain diaphragm, and a circular lead anode in the porcelain cup. The second cell varied only in that the cathode was a circular strip of lead which surrounded the porous cup. C. P. mercury and C. P. lead (National Lead Company) were used as cathodes. The lead amalgam cathode was made by allowing a clean lead cathode to stand in a saturated mercuric chloride solution for an hour, washing it free of solution, and drying and polishing with a dry cloth.

Electrolysis.—The current used in this work was 110 d. c. After the apparatus was assembled and placed in an ice–salt-bath, the catholyte was put in and the anode chamber was filled with 30% aqueous sulfuric acid to the same level. With the catholyte at 10°, the current was turned on, and on becoming constant, was adjusted to the desired value. The voltage drop across the cell was adjusted by varying the distance between anode cup and cathode. The temperature of the catholyte was kept at 10–15° in all experiments.

In using the lead amalgam and mercury cathodes, and with ethanol solutions, there was no escape of hydrogen until about three-quarters of the theoretical amount of current was consumed. With the lead cathode there was a constant escape of hydrogen.

Electroendosmosis was prevalent in all cases, a total of 60 cc. of anolyte migrating to catholyte every four hours.

(a) Isolation of Product from an Alcohol Solution.—The reduction mixture, neutralized with an excess of sodium bicarbonate, was filtered free of solids and made acid to litmus with oxalic acid. (When alcoholic sodium hydroxide or sodium ethoxide are used to neutralize the sulfuric acid the resulting sodium sulfate is very slimy and extremely difficult to filter off). Benzene equal in volume to half the solution was added and the solution was frac-

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(1) This paper was presented at the Baltimore meeting of the American Chemical Society, April, 1939. Original manuscript received April 9, 1940.

(2) Traube, *Ber.*, **40**, 4953 (1907).

(3) German Patents 163,842, 210,693.