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Precise Conductance Measurements and the Determination of Rate Data[1]

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The conductances of 10^{-4} to 10^{-3} molar solutions of hydrochloric acid in water and in some ethanol–water mixtures have been determined by precise techniques. The results are in good agreement with data obtained by earlier workers. A technique based on precise conductance measurements has been elaborated for the determination of the first-order rate coefficient for the solvolysis of an alkyl chloride with a precision of 0.03%.

Introduction

As part of a general investigation directed toward elucidating the causes of the secondary deuterium isotope rate effect and establishing this effect as a criterion of mechanism, the measurement of the influence of structure and solvent changes on the α- and β-deuterium isotope rate effects in solvolysis reactions was undertaken. For these purposes one is interested in differential isotope effects and the small differences involved made it apparent at an early stage that it would be necessary to determine the isotope effects with some precision.

Isotope rate effects may be determined by competition experiments in which the reaction is interrupted and the isotopic fractionation in a reactant or product determined by mass spectrometric or radioactivity analysis. However, the competition type experiment is generally undesirable in the case of β-deuterium isotope effects due to the multiplicity of products formed in steps subsequent to the rate-determining step of solvolysis. Further, mass spectrometric analysis of hydrogen isotopes is generally less precise than for other elements. Secondary deuterium isotope effects usually are determined by direct measurements of the reaction rates of the pure isotopic compounds (however, *cf.* Seltzer[4]). Of the techniques available for the determination of solvolysis rate coefficients the conductometric method seemed to hold the most promise for obtaining the desired precision.

In calculating reaction rate constants from conductivity measurements, the approximation usually is made that the conductivity is a linear function of the concentration. The error introduced by this approximation depends on the solvent, the electrolyte and the concentration range over which measurements are made. Calculations based on existing conductance data for hydrochloric acid in ethanol–water mixtures indicated that point by point first-order rate constants would vary 3–5 per cent. through a run if calculated on the basis of the linear conductivity–concentration approximation in the concentration range of 10^{-4} to 10^{-3} molar.

Robertson has obtained a precision of 0.1–0.3% in the measurements of the rate coefficient for solvolysis of tosylates in water, and he has shown that the linear conductivity–concentration approximation does not introduce an error greater than 0.2% in the case of *p*-toluenesulfonic acid in dilute aqueous solution.[5] However, Hyne and Robertson[6] have found that the linear conductivity–concentration simplification is quite unsatisfactory for measurements in ethanol. They have developed an ingenious technique which employs the conductance apparatus as a null indicator between two conductance cells, one of which contains the solvolysis solution and the other the solvent to which a standard solution of the electrolyte generated in the reaction is added periodically from a precision buret. With this arrangement the null point is determined with the usual precision of a conductance measurement but the observations related to the concentration are read from the buret. It seemed preferable to us to obtain the observations directly from the conductance bridge, if possible, to reduce the possible sources of error and give greater precision. This approach has the disadvantage of requiring the conductance parameters, but does enable one to demonstrate the validity of the assumptions on which the kinetic computations are based. While our method was developed for the precise determination of deuterium isotope rate effects, it should be useful in many other applications. Λ_0 and S_α must be measured in separate experiments. Consistent conductance data check apparatus and techniques.

Experimental[7]

Materials.—Conductivity water of specific conductance 1 to 2×10^{-7} mho was prepared by passing distilled water through a column packed with Analytical Grade Amberlite MB-1.

Conductivity ethanol was prepared by a modification of the phthalate method.[8] Commercial absolute ethanol was dried preliminarily for two days with Drierite. The alcohol was fractionally distilled through a 100 × 2 cm. vacuum-jacketed distillation column packed with 10-mm. stainless steel helices and fitted with an automatic total condensation, variable take-off head which had an inlet-tube for dry purified nitrogen. A continuous stream of nitrogen was necessary to maintain ethanol of low conductance (3.7–4.5 ×

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[1] (a) Taken from the thesis submitted by B. L. Murr, Jr., to the Graduate School of Indiana University in partial fulfillment of the requirements for the Ph.D. degree. (b) Presented in part before the Division of Physical Chemistry at the 139th National Meeting of the American Chemical Society, St. Louis, Missouri, March, 1961. (c) Supported in part by Grant G 5062 from the National Science Foundation, Washington, D. C. (d) Supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

[2] University Fellow, 1957–1958, Dow Fellow, 1958–1959.

[3] Alfred P. Sloan Research Fellow.

[4] S. Seltzer, *J. Am. Chem. Soc.*, **83**, 1861 (1961).

[5] R. E. Robertson, *Can. J. Chem.*, **33**, 1536 (1955).

[6] J. B. Hyne and R. E. Robertson, *ibid.*, **35**, 623 (1957).

[7] For complete experimental details and a presentation of the statistical treatment, see B. L. Murr, Ph.D. Thesis, Indiana University, 1961. One contemplating the use of these methods should obtain a copy of the thesis, which is available from University Microfilms, Inc., Ann Arbor, Michigan.

[8] A. M. El-Aggan, D. C. Bradley and W. Wardlaw, *J. Chem. Soc.*, 2092 (1958).

10^{-8} mho) and a magnetic stirrer was used in the still pot to prevent bumping.

Dry nitrogen for the distillation and manipulation of ethanol was purified by leading H. P. Dry Nitrogen successively through Ascarite, 10% sulfuric acid (Kraus–Parker tower[9]), concentrated sulfuric acid using sintered-glass bubblers, a spray trap, indicating silica gel, Drierite and magnesium perchlorate. A second nitrogen system omitting the drying agents but using a gas-washing bottle with sintered-glass bubbler filled with solvent was used for solvent saturated nitrogen.

Reagent potassium chloride was purified by a standard method.[10]

Reagent silver nitrate was used without further purification.

Reagent concentrated hydrochloric acid was diluted with conductivity water to a specific gravity of 1.10, carefully distilled in a suitably protected all-glass apparatus[11] and analyzed by potentiometric titration immediately before use.

Conductance Apparatus.—Conductances were determined by means of a Jones–Josephs bridge manufactured by the Leeds and Northrup Company. It was operated and calibrated as described by Dike[12] using resistors certified by the National Bureau of Standards. The ratio arms were balanced to equality. Measurements were made at an oscillator output of 1 volt or less. Solvent resistance was determined by shunting the cell with three of the 10 K. resistors of the bridge in series.

Temperature Control.—The conductance bridge, thermostat, nitrogen purification systems, ethanol still and water purification column were set up in a room with temperature controlled at 26 ± 2° and humidity maintained between 50 and 60%. Temperature fluctuations in the thermostat were ±0.003° at most. The bath temperature was set periodically at 25 ± 0.005° by means of a platinum resistance thermometer calibrated by the National Bureau of Standards and a Mueller Temperature Bridge which was calibrated at the time of use.

Conductance Cells.[7]—Cells of the type described by Daggett, Bair and Kraus[10] were used with the following modifications. Contact between the electrodes and the bridge leads was made with platinum wire gold-soldered to the electrode assembly and each cell was fitted at the neck with a gas-inlet stopcock.

Platinization and Electrode Pretreatment.—Electrodes were lightly platinized by electrolysis of a 0.025 *M* solution of hydrochloric acid containing 0.3% platinic chloride and 0.025% lead acetate[13] for 20 sec. per electrode. The cell was cleaned and the frequency dependence of the resistance of a 10^{-3} *N* potassium chloride solution was determined. If the difference between the resistances determined at 500 and 2000 c.p.s. exceeded 0.02% of the resistance the platinization procedure was repeated. This extent of platinization rendered a frequency dependence correction unnecessary for kinetic measurements.

Daggett, Bair and Kraus[14] found that when a cell had been dried, e.g., for weighing, it was necessary to treat the cell with hot nitric acid before conductance measurements in order to obtain reproducible results. Our observations were similar. It was also necessary prior to measurements in aqueous ethanol to stir a 10^{-3} *N* solution of hydrochloric acid in the solvent to be studied in the cell for several hours. The symptoms of insufficient electrode preconditioning are a rapid fluctuation of the resistance and a high, variable frequency dependence. After pretreatment and rinsing the solvent conductance came to a steady value indicating that there was no slow desorption of electrolyte.

Cell Calibration.—Conductivity water used for cell calibration was prepared in an all-glass, 5-l. round-bottomed flask fitted with a gas-inlet tube, a syphon and a water inlet. This flask was cleaned with hot nitric acid, rinsed, swept out with purified nitrogen and filled with conductivity water from the ion-exchange column. The water was equilibrated for one hour with purified nitrogen entering through the syphon. Water was drawn from this reservoir under pressure of purified nitrogen.

A sample of potassium chloride (*ca.* 75 mg.) was weighed on the microbalance into a tared glass cup fashioned from 8 mm. Pyrex tubing. Cups were cleaned with boiling nitric acid, rinsed, boiled in conductivity water several times, wrapped in aluminum foil and dried in the oven. The cups were manipulated with forceps.

The cell (previously weighed dry with a cap and a seamless 5-cm. Teflon-covered magnetic stirring bar) was cleaned with boiling nitric acid, rinsed, steamed and allowed to cool in a stream of purified, water-saturated nitrogen entering through a tube reaching to the bottom of the cell. The cooled cell was rinsed with conductivity water from the 5-l. reservoir, filled through a tube extending to the bottom of the cell, weighed and placed in the thermostat. The conductance of the water was followed for one hour with moderate stirring. If the conductance did not reach a steady, low value ($1-2 \times 10^{-7}$ mho) the cell was recleaned.

After the solvent conductance had been recorded, the cell cap was carefully removed and, with nitrogen entering the gas-inlet of the cell, the cup containing the salt was added quickly.[15] It was shown by adding an empty cup that the solvent conductance was not changed by more than 0.3% during this procedure for which the cell was open for about 10 seconds. The solvent conductance was always less than 1% of the conductance of the salt solution. The resistance was measured at 500, 1000 and 2000 c.p.s. The corrected resistance was obtained by extrapolation of a plot of R against $1/\sqrt{f}$ to infinite frequency. The tedium of weighing an exact quantity of potassium chloride was avoided by employing the equation proposed by Lind, Zwolenik and Fuoss[16] to calculate the equivalent conductance for the solution. The solvent conductance was allowed for. It was found that there was no Parker effect[13] over the range of potassium chloride concentrations from 10^{-4} to 10^{-3} *M* if extrapolated resistance values were used.

Preparation and Standardization of Hydrochloric Acid Solutions.—Constant-boiling hydrochloric acid was prepared by the method of Foulk and Hollingsworth.[11] A quantity of acid was added from a weight buret to an Erlenmeyer flask and diluted gravimetrically to approximately 0.2 *N* with conductivity water under protection of purified nitrogen.

Potentiometric Titration.[17]—Reagent silver nitrate (0.2 eq.) was weighed and transferred to a tared 1-l. glass-stoppered Erlenmeyer flask. The salt was dissolved in 1 l. of conductivity water and the total weight of the solution was recorded. The chloride titer was determined by potentiometric titration of weighed samples of potassium chloride. With the exception of the use of a weight buret, the apparatus, technique and procedure were essentially those described by Shiner and Smith.[18] A portion of the solution was diluted gravimetrically in an amber-glass Erlenmeyer flask to less than 0.01 *N*. A glass cup containing *ca.* 5 meq. of potassium chloride was placed in a 100-ml. beaker with a 1.9-cm. Teflon-covered magnetic stirring bar, 14 ml. of water, 6 ml. of 2.5 *N* acetate buffer and 6 drops of "Tergitol Non-Ionic, NPX" detergent. Silver nitrate (0.2 *N*) was added dropwise from a weight buret to the stirred solution to a point within 0.3% of the equivalence point. The indicator electrode, salt bridge and microburet containing the dilute silver nitrate were put in the beaker and 20 drops more of the detergent were added. After a steady potential had been reached (*ca.* 5 min.) the titration was completed by adding 0.1 ml. increments of dilute silver nitrate solution with stirring, the potential being recorded after each increment. The equivalence point was determined from the

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(9) C. A. Kraus and H. C. Parker, *J. Am. Chem. Soc.*, **44**, 2429 (1922.)

(10) H. M. Daggett, E. J. Bair and C. A. Kraus, *ibid.*, **73**, 799 (1951).

(11) C. W. Foulk and M. Hollingsworth, *ibid.*, **45**, 1220 (1923).

(12) P. H. Dike, *Rev. Sci. Instr.*, **2**, 379 (1931).

(13) G. Jones and D. M. Bollinger, *J. Am. Chem. Soc.*, **57**, 280 (1935).

(14) Private communication from Dr. E. J. Bair.

(15) A superior procedure involves the use of a cup storage and dropping device developed in the laboratory of Dr. R. L. Kay of Brown University. This device, which allows the addition of an increment of solute without opening the cell, has been used successfully in the laboratory of Dr. C. G. Swain at M.I.T. Private communication from D. F. Evans.

(16) J. E. Lind, J. J. Zwolenik and R. M. Fuoss, *J. Am. Chem. Soc.*, **81**, 1557 (1959).

(17) I. M. Kolthoff and N. H. Furman, "Potentiometric Titrations," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1931, p. 148.

(18) V. J. Shiner, Jr., and M. L. Smith, *Anal. Chem.*, **28**, 1043 (1956).

maximum in the plot of $\Delta E/\Delta V$ against volume of titrant added. Duplicate titrations agreed to within 0.005%.

A weighed sample (*ca.* 25 g.) of the 0.2 *N* hydrochloric acid solution was added from a weight buret to a 100-ml. beaker containing 8 ml. of 2.5 *N* acetate buffer and 6 drops of detergent. The solution was titrated exactly as described above for the standardization of silver nitrate.

Ethanol–Water Mixtures.—The composition of binary mixtures used in the study of solvolytic reactions is commonly reported in volume per cent. The solvents used in this investigation were prepared by weight methods, although they are referred to in volume per cent. The composition in weight per cent. of each volume per cent. solution was calculated using the densities of water and ethanol at 25° given in the "International Critical Tables." Mixtures were prepared under protection of purified nitrogen by weighing water in a 1- or 2-l. Erlenmeyer flask and adding ethanol to the calculated total weight for the desired composition. Mixtures could not be prepared in the cell itself owing to liberation of air at the electrodes on mixing water and ethanol. The mixture was stirred at 26° for 30 minutes to facilitate expulsion of air. Transfers were made under pressure of purified, solvent-saturated nitrogen through an all-glass syphon.

Conductance of Hydrochloric Acid in Water and in Ethanol–Water Mixtures.—For runs in water, standardized 0.2 *N* hydrochloric acid (80–100 g.) was transferred by weight buret and diluted gravimetrically to *ca.* 0.02 *N* in a 1-l. Erlenmeyer flask with conductivity water. For runs in ethanol–water mixtures, standardized 0.2 *N* acid was weighed into a clean, dry 1-l. Erlenmeyer flask and ethanol was added to a predetermined total weight to yield the desired composition (60, 70 or 80 vol. % ethanol). The solution was diluted gravimetrically to *ca.* 0.02 *N* by addition of previously prepared solvent mixture.

The weighed and pretreated cell, containing a magnetic stirring bar, was rinsed with solvent, either water or aqueous ethanol, swept out with purified, solvent-saturated nitrogen, filled with solvent, weighed and placed in the thermostat. Carefully weighed quantities of hydrochloric acid (0.02 *N* in the appropriate solvent) were added to the cell using a weight buret similar to that of El-Aggan, Bradley and Wardlaw.[8] During the addition the solutions were protected from the atmosphere by the use of solvent-saturated nitrogen. The resistance was followed for 15 minutes after each addition although it usually was constant after two minutes. During this time the cell was agitated gently to wash down any solution which might have splashed onto the cell wall. The resistance was measured at 500, 1000 and 2000 c.p.s. Five to ten such additions were made during a run.

Conductance values reported in this paper are those of stirred solutions. Lind and Fuoss[19] report lower resistances for stirred salt solutions in dioxane–water than for unstirred solutions and report the unstirred values. Daggett, Bair and Kraus[10] report similar observations for potassium chloride in water and chose the stirred values as correct since the discrepancy became less for larger electrode chambers, the unstirred value approaching the stirred value. We have followed Daggett, Bair and Kraus.

Treatment of Conductance Data.—The concentration (mole/l.) after each addition was calculated assuming the density of the solution to be that of the pure solvent. The resistance used was that observed at 2000 c.p.s. except for the more concentrated solutions in water for which a correction (less than 0.015%) was obtained from a plot of *R* against $1/\sqrt{f}$. The solvent conductance for solutions of strong acids is negligible if the only impurity is carbon dioxide. The equivalent conductivity Λ is given by equation 1.

$$\Lambda = \Lambda_0 - S_\alpha c^{1/2} \qquad (1)$$

The plots of Λ *vs.* $c^{1/2}$ were linear for all hydrogen chloride solutions in the concentration ranges in the solvents employed in this work. From these plots values of Λ_0 and S_α were obtained as intercept and slope, respectively.

Kinetic Measurements.—The cell was filled with ethanol-water mixture (50, 60, 70 or 80 vol. %) in the same manner as for the conductance measurements and placed in the thermostat. After thermal equilibrium had been established and the conductance of the solvent found to be satisfactory, alkyl chloride (*ca.* 0.95 meq./l. of solvent) was added. The bridge resistance was set to a value corresponding to a hydrochloric acid concentration of about 10^{-4} *N*. The time (t_0) was noted when the resistance of the solution in the cell equaled this value (R^0). Thereafter readings were taken at roughly equal intervals of time over a period of two to three half-lives. All observations were made in the manner described for R^0. The time was kept by a device consisting of a 60 r.p.m. Bodine synchronous motor which drove a small, five-digit Veeder Root Reset Counter. The time was direct-reading in seconds. The clock was checked periodically against Radio Station WWV. For reactions with half-lives of less than two hours a stopwatch was used in conjunction with the clock. The time for complete mixing in fast reactions was reduced considerably by temporarily placing a glass elbow attached to a glass rod in the lower connecting tube of the electrode chamber so that the circularly moving solution was directed into the chamber.

Readily miscible chlorides such as *t*-butyl chloride were injected below the surface of the solvent by means of a 0.25 ml. syringe with a 10-cm. needle. Due to the volatility of *t*-butyl chloride it was necessary to have a minimum of air space above the solution. This was accomplished by using a cell cap which occupied all but a few milliliters of air space. The cell was filled with solvent to within a few millimeters of the bottom of the cap. The liquid level in the cell was below the level of the oil of the thermostat.

For more difficultly soluble materials such as 1-phenylethyl chloride the halide was weighed into a small glass-stoppered tube and 11 ml. of solvent was added. While the mixture remained in two layers the tube was placed in the thermostat to attain thermal equilibrium. It was then mixed by shaking vigorously and 10 ml. of the solution was transferred to the cell with a pipet. For the relatively non-volatile 1-phenylethyl chloride the observed rate constant was shown to be independent of the volume of air space above the solution but this was not the case with *t*-butyl chloride.

Treatment of Kinetic Data.—The rate data were treated by the method of least squares assuming errors in both time and resistance. The method used is similar to that used by DeTar[7,20,21] except that the error in resistance is not a constant but is proportional to the resistance (constant percentage error). Equation 2 gives the form of the first-order rate equation which was fitted using *a*, *b* and *k* as parameters; Λ^∞ is the equivalent conductance of hydrochloric acid in the solution at infinite time, Λ^0 is that at zero time, Λ_i that at t_i and *k* the rate coefficient.[21a]

$$1/\Lambda_i R_i = a - be^{-kt_i} \qquad (2)$$

$$a = 1/\Lambda^\infty R^\infty \text{ and } b = (1/\Lambda^\infty R^\infty - 1/\Lambda^0 R^0)$$

The necessary values of Λ_i were calculated from the corresponding resistance R_i and concentration c_i, which was computed by solving equation 3 (obtained by combining equation 1 with the cell constant equation, $\Lambda_i = 10^3\,K/c_iR_i$, where *K* is the cell constant, to eliminate Λ_i) by the Newton–Raphson method.

$$S_\alpha c_i^{3/2} - \Lambda_0 c_i + 10^3\,K/R_i = 0 \qquad (3)$$

The statistical treatment was programmed for an IBM 650 Data Processing Machine.[7]

Preparation of 1-Phenylethyl Alcohol.—Redistilled acetophenone (14 g., 0.116 mole) was allowed to react with a 10% excess of lithium aluminum hydride suspended in ether. The alcohol was distilled using a spinning-band column to give 11 g. (78%) of product (b.p. 46–48°, 0.3 mm.).

Preparation of 1-Phenylethyl Chloride.—Commercial tank hydrogen chloride was led into a 1–2 g. sample of 1-phenylethyl alcohol in a 5 ml. centrifuge tube cooled in an ice bath. After *ca.* two hours, the water ceased to separate and the sample was allowed to warm to room temperature. The chloride was separated after centrifugation and dried over 40-mesh C.P. anhydrous calcium chloride. The dried alkyl chloride was introduced into a high-vacuum line.

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(19) J. E. Lind and R. M. Fuoss, *J. Phys. Chem.*, **65**, 999 (1961).

(20) D. F. DeTar, *J. Am. Chem. Soc.*, **77**, 2013 (1955).

(21) W. E. Deming, "Statistical Adjustment of Data," John Wiley and Sons, Inc., New York, N. Y., 1943, p. 128.

(21a) The symbol Λ_0 (equivalent conductance at infinite dilution) persists in the conductance literature contrary to the recommendation of Λ^∞ for this quantity [*J. Am. Chem. Soc.*, **82**, 5521–5522 (1960)] In order to aviod confusion we have kept Λ_0 as used in the conductance literature. This required the symbol $\Lambda^{\circ 0}$ for the equivalent conductivity at zero time.

Hydrogen chloride was removed by degassing and the halide purified by two vacuum transfers, leaving a small residue each time.

***t*-Butyl Chloride.**—Commercial *t*-butyl chloride was distilled from anhydrous potassium carbonate through a 100 × 2 cm. vacuum-jacketed column packed with glass helices. This *t*-butyl chloride gave the same kinetic results as a sample prepared from *t*-butyl alcohol using the procedure described above for 1-phenylethyl chloride.

Conductance Results.—Cell constant determinations agreed to within 0.003% if the salt samples were weighed on the same microbalance and 0.006% if samples were weighed on different microbalances.

The potentiometric chloride titration was reproducible to 0.005% using 0.15 *N* silver nitrate and 0.003% using a 0.2 *N* solution. These figures also apply to the titration of 0.15 *N* and 0.2 *N* hydrochloric acid solutions. The uncertainty in the concentration of the hydrochloric acid stock solutions was of the order of 0.007%. The effects of non-conducting impurities in the potassium chloride have been minimized by using the same salt for both cell constant determinations and for the standardization of the hydrochloric acid stock solution.

The measurements of the conductance of hydrochloric acid in dilute aqueous solution (10^{-4} to 10^{-3} *N*) were carried out in two different cells with three different samples of distilled hydrochloric acid. The results of the three determinations were in good accord.

The results for the conductance of hydrochloric acid in water are summarized in Table I.

TABLE I

CONDUCTANCE OF HYDROCHLORIC ACID IN WATER AT 25°

$c \times 10^4$	Λ	Λ_0[a]	$c \times 10^4$	Λ	Λ_0
0.9561	424.71	426.25	3.3034	423.38	426.24
0.9672	424.60	425.15	4.0442	423.08	426.25
1.1663	424.46	426.16	4.0877	423.05	426.25
1.8285	424.09	426.22	4.6021	422.83	426.21
1.8311	424.14	426.27	5.0050	422.74	426.26
2.1113	423.92	426.21	5.9302	422.40	426.23
2.5640	423.74	426.26	6.7211	422.14	426.23
2.5747	423.77	426.29	7.6809	421.87	426.24
3.0069	423.50	426.23	8.3744	421.65	426.21
3.1824	423.44	426.25	9.4224	421.38	426.22

Av. Λ_0 = 426.23. Graphical slope = 157.6. Onsager slope = 157.9

[a] Λ_0 calculated from the equation $\Lambda_0 = \Lambda_{\text{obs}} + S_\alpha c^{1/2}$.

The value of Λ_0 associated with each point was calculated from the simple Onsager equation using the theoretical slope of 157.9 (calculated for Λ_0 = 426.2).

The conductance data for hydrochloric acid in ethanol-water mixtures given in Table II were determined in the same manner as those in water. The two procedures differ only in the necessity of preparing the mixed solvent.

TABLE II

CONDUCTANCE OF HYDROCHLORIC ACID IN ETHANOL-WATER MIXTURES

$c \times 10^4$	Λ	Λ_0	$c \times 10^4$	Λ	Λ
A. 60 vol. % Ethanol					
0.9790	113.55	113.55	6.3491	111.40	113.59
1.8978	112.39	113.59	7.3288	111.22	113.57
2.7772	112.15	113.60	8.1657	111.08	113.56
3.8992	111.89	113.59	8.1657	111.08	113.56
4.9941	111.65	113.59	9.0419	110.94	113.56
Av. Λ_0 = 113.57. Graphical slope = 87.0. Onsager. slope = 86.8					
B. 70 vol. % Ethanol					
0.8902	90.000	90.940	5.3384	88.743	91.030
1.7572	89.686	91.032	6.2901	88.544	91.027
2.4194	89.475	91.014	7.2790	88.356	91.027
3.1720	89.265	91.027	8.2361	88.183	91.024
3.8785	89.087	91.036	9.1534	88.028	91.023
4.6726	88.891	91.030	9.9602	87.904	91.028
Av. Λ_0 = 91.027. Graphical slope = 99.0. Onsager slope = 91.0					
C. 80 vol. % Ethanol					
1.0774	70.442	71.603	5.8409	68.935	71.642
2.0234	70.050	71.643	6.7724	68.725	71.639
2.6112	69.832	71.642	7.9534	68.485	71.643
3.5135	69.542	71.641	8.9209	68.303	71.648
4.4589	69.277	71.642	9.9156	68.127	71.653
5.0722	69.119	71.641			
Av. Λ_0 = 71.642. Graphical slope = 112.0. Onsager slope = 98.9					

Discussion.—During preliminary measurements some difficulty was experienced with a basic impurity in the solvent. The cause of the low conductance values in the neighborhood of 10^{-4} *N* was originally supposed to be adsorption. Our test of this supposition was based on the suggestion of Randall and Scott[22] that adsorbed electrolyte is not easily removed by rinsing with solvent. Their evidence indicates that the amount of electrolyte adsorbed from a dilute solution is practically independent of the concentration. These ideas lead one to expect that, if adsorption of electrolyte were the cause of our preliminary low conductance values, pretreatment of the cell with hydrochloric acid and rinsing prior to a conductance determination would result in significantly higher conductance values. However, such an equilibration did not alter the results. The difficulty was eventually overcome by including in the nitrogen line more gas-scrubbing bottles containing aqueous sulfuric acid, indicating that the error was caused by some basic impurity and not by adsorption.

The average value of Λ_0 for HCl in water is 426.24 ± 0.02, which agrees well with the value of 426.16 obtained by Shedlovsky,[23] the value of 426.27 obtained by Saxton and Langer[24] and the value of 426.2 preferred by Owen and Sweeton[25] (all values are adjusted to the Jones and Bradshaw standard[16,26]). There is less spread in our data than in the earlier data. This probably is due to the superiority of the cells and stirring technique of Daggett, Bair and Kraus[10] and to the inherent efficiency afforded by the ion-exchange method of water purification.

Our data when treated according to the Fuoss-Onsager equation[27] give a value for Λ_0 of 426.29 using Stokes' values for *J* (606) and *E* (203.6).[28] This Λ_0 differs from the value of 426.50 recently reported by Stokes[28] by more than the combined experimental errors (*ca.* 0.01%) of the two sets of data. Possible sources of the discrepancy are different temperature standards, different cell types and the use in our measurements of continuous stirring. Our experiments indicate that an adsorption error is unlikely. El-Aggan, Bradley and Wardlaw[8] found that the addition of powdered

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[22] M. Randall and G. N. Scott, *J. Am. Chem. Soc.*, **49**, 636 (1927).

[23] T. Shedlovsky, *ibid.*, **54**, 1411 (1932).

[24] B. Saxton and T. W. Langer, *ibid.*, **55**, 3638 (1933).

[25] B. B. Owen and F. H. Sweeton, *ibid.*, **63**, 2811 (1941).

[26] G. Jones and B. C. Bradshaw, *ibid.*, **55**, 1780 (1933).

[27] R. M. Fuoss, *ibid.*, **81**, 2659 (1959).

[28] R. H. Stokes, *J. Phys. Chem.*, **65**, 1242 (1961).

glass to a dilute solution of hydrochloric acid in ethanol did not cause a change in the resistance of the solution and one would expect adsorption to be a more serious problem with ethanol than with water.

A simple Onsager-type equation has been used to represent the data on the conductance of hydrochloric acid in the ethanol–water mixtures. This is sufficient for purposes of the kinetic calculations because all that is required is some accurate analytical representation of the conductance–concentration relationship. Our conductance measurements do not cover a sufficient concentration range to allow the accurate determination of the ion-size and ion-association parameters in these solvents; however, some qualitative comments are possible. In 60 vol. % ethanol (dielectric constant 46.7[29]) the slope of the $\Lambda - c^{1/2}$ plot is in agreement with the Onsager value (87.0 observed, 86.7 calculated), while for 70% ethanol (dielectric constant 40.8) and 80% ethanol (dielectric constant 34.9) the observed slopes are 99.0 (calculated 91.0) and 112.0 (calculated 98.9), respectively. The fact that both these observed values are appreciably larger than the calculated Onsager values indicates some association. The composition above which we find deviations from the Onsager limiting slope compares qualitatively with that found by Shedlovsky and Kay for hydrochloric acid in methanol–water mixtures.[30]

Results of Kinetic Measurements.—Our direct conductometric method for the determination of first order rate parameters yields strikingly reproducible results. This is true provided one exercises the same precautions which are necessary to obtain satisfactory conductance data. Errors due to solvent composition, temperature, resistance and time measurements have been kept to 0.01% so that the factor limiting the precision is probably the condition of the electrode surface and/or the compound purity.

For all five independent measurements of the rate coefficient for solvolysis of 1-phenylethyl chloride in 60% ethanol the average deviation is 0.02%. These results are summarized in Table III. Table IV lists the rate constants obtained for α-phenylethyl chloride and *t*-butyl chloride in various aqueous-ethanol solutions.

TABLE III

REPRODUCIBILITY OF THE RATE CONSTANT FOR 1-PHENYLETHYL CHLORIDE IN 60 VOL. % ETHANOL AT 25°

Run	$k \times 10^4$, sec.$^{-1}$	St. error, % k	R^{∞}, obsd.	R^{∞}, calcd.	R^0, obsd.	R^0, calcd.
626	1.0871	0.010	3634.0	3633.6	33000	32970
627	1.0866	.006		4140.6	33000	33003
628	1.0865	.012	3961.4	3962.0	33000	32999
629	1.0865	.013		4474.0	33000	33001
630	1.0866	.010	4244.5	4243.4	33000	33001

Discussion.—If the first run in Table III, which gave a coefficient significantly higher than the average of the remaining four, is ignored, the average deviation is 0.005%. The several runs were carried out in different volumes of solvent and at various initial concentrations of the alkyl chloride, a new solvent batch being prepared for each run. The results are independent of these factors, suggesting the absence of catalysis by the glass surface. Rate coefficients determined in cells with unplatinized electrodes are indistinguishable from those obtained in cells with platinized electrodes as long as the electrodes were properly equilibrated by pretreatment. Thus there is no apparent catalysis by the electrode surface.

TABLE IV

COMPARISON OF RATE CONSTANTS OBTAINED CONDUCTOMETRICALLY AND TITRIMETRICALLY

Solvent vol. %	Conductometric, $k \times 10^5$ sec.$^{-1}$	Titrimetric,[a] $k \times 10^5$ sec.$^{-1}$	Δ,[b] % of k
A. 1-Phenylethyl chloride at 25°			
50	36.203	34.2	5.0
60	10.867	10.35	4.6
70	3.4386	3.35	2.6
80	1.0019	0.987	1.5
B. *t*-Butyl chloride at 25°			
60	12.498	12.32	1.5
70	3.7295	3.65	2.2
80	0.93764	0.926	1.2

[a] Data of Fainberg and Winstein (refs. 32 and 33). [b] $\Delta = (k_{\text{con.}} - k_{\text{tit.}}) \times 100/k_{\text{con.}}$.

In our statistical treatment the resistance at zero time and the resistance at infinite time are treated as parameters to be chosen along with the rate coefficient to give the best fit of the data in the least squares sense. The calculation is begun with estimates of the parameters which are subsequently refined. The final values were shown to be independent of the original estimates. From seventy observations made over the first two half-lives the statistical treatment yields the resistance at infinite time (value at 13 half-lives) to within 0.02%. The calculated resistance at zero time is within 0.1% of the observed value. The agreement of the calculated and observed values of the zero resistance is, in general, not as good as for the infinity resistance since the zero resistance is ten times larger and is derived from the constant b of equation 2 (see Experimental).

If one uses only the first forty-nine observations in the statistical treatment the calculated rate constant and the infinity resistance are higher by 0.05–0.2% than that obtained using all seventy of the observations. If the last forty-nine observations are used, lower values of the parameters are obtained. The expected chlorine isotope effect is too small to account for this apparent fall in the rate. A mass-law effect appears to be the only chemical cause for the rate decrease. This discrepancy may well be due simply to an inability to predict the parameters from data taken over a narrow portion of the reaction. As would be expected the standard error is larger the fewer points used.

It was found that point-by-point rate coefficients for the entire run using the a and b parameters statistically computed from the early points show no trend. The same is true using the parameters computed from the later points and those computed

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[29] The dielectric constant values were obtained by interpolation of the data for ethanol–water mixtures given in the "International Critical Tables."

[30] T. Shedlovsky and R. L. Kay, *J. Phys. Chem.*, **60**, 151 (1956).

from all observations. In the extreme, the difference between the coefficients based on early and late points is as much as 0.3% even though the average deviation of the point by point rate coefficients based on a given set of parameters is of the order of 0.03%. Thus it cannot be concluded that rate data are correct only on the basis of a lack of trend in the point by point rate coefficients.

One of the time consuming aspects of this technique is the independent determination of the conductance parameters Λ_0 and S_α. As one might expect, the parameters derived from the rate data are not very sensitive to the value of Λ_0 but they are much more sensitive to the value of S_α, the limiting slope of the Λ *vs.* $c^{1/2}$ plot. It is primarily S_α which determines the correction to the rate data as is evident from equation 4 obtained by rearranging equation 3 (see Experimental).

$$10^3\, K/Rc = \Lambda_0 - S_\alpha c^{1/2} \qquad (4)$$

If the left hand side of (4) were a constant then obviously no correction would be necessary. If data of the optimum precision are not required one can often estimate the value of Λ_0 from data in the literature and calculate S_α from Onsager's relation.[31] We used this procedure to treat the rate data obtained in 50% ethanol, but one cannot use this approach unless ion association is negligible. It seems feasible to derive the conductance values from the rate data but we have not pursued this.

Table IV gives a comparison of the rate constants obtained by the conductometric technique with those determined titrimetrically by Fainberg and Winstein.[32,33] The reliability of the titrimetric values is estimated to be 1–2%. The conductometric values are all higher than the titrimetric values.[34] With *t*-butyl chloride the agreement is probably within the experimental error; but in the case of 1-phenylethyl chloride, while there is good agreement between the values in 80% ethanol, the difference increases in the more aqueous solvents. Since these two compounds solvolyze at comparable rates, the discrepancies cannot be due to some error which is proportional to the rate. The difficulty probably is due to the decreasing solubility of 1-phenylethyl chloride in the more aqueous solvents. The concentration of alkyl halide used by Fainberg and Winstein was from ten to thirty-five times that in our conductometric determinations.

To summarize, we have applied the techniques of precise conductance measurements to the problem of rate determination. The reproducibility study of the solvolysis of 1-phenylethyl chloride indicates that the rate coefficient can be determined with a precision of 0.02% if one exercises the utmost care and carries out a number of runs. In the absence of great care the limits of reproducibility may rise to 0.1% but no higher in our experience if the solvent and compound are pure. It is expected that, with further experience with this method, improvements will be forthcoming in defining more precisely the factors governing precision, if not in the precision itself.

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[31] H. S. Harned and B. B. Owen, "Electrolytic Solutions," Third Edition, Reinhold Publishing Corp., New York, N. Y., 1958.

[32] A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **78**, 2770 (1956).

[33] A. H. Fainberg and S. Winstein, *ibid.*, **79**, 1597 (1957).

[34] Often rate constants determined conductometrically are higher than the titrimetric values. See W. M. Schubert and R. G. Minton, *ibid.*, **82**, 6188 (1960).

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Proton Exchange Rates and Hydrogen-Bonding for Water in Organic Solvents[1a]

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The chemical behavior of water protons in a series of organic solvents has been studied by nuclear magnetic resonance and infrared techniques. The shifts in the OH stretching frequencies and the n.m.r. chemical shifts of the water protons have been measured in various solvents and correlated with each other, and with hydrogen bond energies. A theory of chemical shifts due to hydrogen bonding is discussed. The equilibrium constants for water dimer formation in these solvents have been estimated from the n.m.r. data. The n.m.r. spectral line shape has been studied as a function of solvent, temperature, water concentration, and added acid, for dilute solutions of H_2O–D_2O mixtures with a hydrogen to deuterium ratio of one. The rate of inter-water proton exchange was determined by this technique. At room temperature, the mean exchange rate τ^{-1} for 1.1 formal water in various solvents is (in sec.$^{-1}$): 6.7 (nitromethane), 0.91 (acetonitrile), 1.0 (acetone), 1.6 (dioxane), 25 (pyridine), 8.3 (dimethylsulfoxide), 100 (triethylamine). The apparent activation energy is less than 1.5 kcal./mole for the weakly basic solvents and the reaction is approximately second order in water. The dominant mechanism in the first five solvents is thought to be a direct proton exchange in a ring formed by three water molecules. The trimer concentration decreases and the direct exchange rate increases with increasing temperature; the net result is an exchange rate which is almost temperature independent. The trimer concentrations in dimethylsulfoxide and triethylamine are too low to account for the observed rates but the concentrations of OH^- and protonated solvent SH^+ are high in these two solvents and, hence, mechanisms that depend upon OH^- and SH^+ can become important. The activation energy for the process involving OH^- is probably lower than for the one in which SH^+ partakes; therefore, the OH^- mechanism dominates.

Introduction

Very little is known about the behavior of water as a solute rather than as a solvent. This study represents a preliminary investigation of water dis-

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