at 19°. The 625 cm.$^{-1}$ band appears and disappears sharply when passing through the transition temperatures and the 638 cm.$^{-1}$ band changes correspondingly, Fig. 4.

Two explanations suggest themselves. The first attributes this effect to a shift in the wagging frequency with the relaxation of the spiral. This would require the 638 cm.$^{-1}$ band to be absent above 20°. Since, in addition to the crystalline component, there is an amorphous contribution to the 638 cm.$^{-1}$ band, the persistence of this band above 20° is not immediate proof that this explanation is wrong. The second explanation relates the splitting to the change from triclinic to hexagonal packing. In the hexagonal crystal, the 15 CF_2 groups in the unit cell are divided into 5 sets of 3 identical CF_2 groups. This regular perturbation, not present in the triclinic form, may be responsible for the splitting. Further studies are in progress to determine the cause of these variations and the temperature dependence of the infrared spectrum in general.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

Acid Ionization Constants of Alcohols. I. Trifluoroethanol in the Solvents H_2O and D_2O[1]

BY P. BALLINGER AND F. A. LONG

RECEIVED JUNE 18, 1958

The equilibrium constants for the reaction of trifluoroethanol with hydroxide and deuteroxide ion in water and in deuterium oxide, respectively, have been determined by a conductivity method. Combination of the results with data on the ion products for the solvents leads to values of the thermodynamic ionization constants of the acids. The values for 25° are $K_a(H_2O) = 4.3 \times 10^{-13}$ and $K_a(D_2O) = 0.95 \times 10^{-13}$. The method should have general utility for uncharged acids with pK_a values in the range of from 10 to 15 and experimental details are given.

The ordinary aliphatic alcohols are well known to be very weak acids in aqueous solution. However, only a few quantitative measurements of their ionization constants have been reported, although the problem has been discussed and some useful relative data are available. For example, a recent study by Hine and Hine[2] gives relative data on the acidities of a number of alcohols in the solvent isopropyl alcohol. Although the relative strengths in this solvent will probably not be quantitatively the same as for the solvent water, there very probably will be a qualitative correlation. Hence the conclusions that water and ethanol are of very similar acid strength but that most glycols are much more acidic are of considerable interest.

The only quantitative data for the acidities of alcohols in water appear to be those for halogen derivatives, particularly for the highly fluorinated alcohols. Table I lists representative data. The pK_a values of this table clearly indicate the weakness of these acids. However it seems safe to conclude that the actual ionization constants are known only very approximately. There are several reasons for this. All of the data of Table I have been obtained by pH measurements with a glass electrode, usually of a "half-neutralized" solution of the alcohol. The difficulties of accurate measurement of pH values as high as 11 are well known. Furthermore, all of these acids are so weak that there is real doubt about the adequacy of the method itself. Finally, except for the studies of Roberts, McBee and Hathaway,[4] no attempt has been made to correct for ionic strength effects, etc.[7]

TABLE I

Alcohol	Solvent	pK_a	Ref.
CF_3CH_2OH	Water	11.4	3
CF_3CH_2OH	Water	12.43	4
CF_3CH_2OH	50% aq. ethanol	11.3	5
$CF_3CH(OH)CH_3$	Water	11.8	3
$C_3F_7CH_2OH$	50% aq. methanol	11.4	6
$(C_3F_7)_2CHOH$	50% aq. methanol	10.6	6
CCl_3CH_2OH	50% aq. ethanol	11.8	5

An analysis of these various difficulties has made it evident that measurement of the conductivity of aqueous solutions which contain the alcohol together with some alkali offers several advantages.[8] Consider for example an alcohol (abbreviated as SH) with $K_{SH} = 1 \times 10^{-12}$. In an aqueous solution which contains some sodium hydroxide and an excess of SH there will be transformation of NaOH to NaS by the reaction

$$SH + OH^- = S^- + H_2O \qquad (1)$$

The equilibrium constant for this reaction is $K = K_{SH}/K_w$ and for our example $K = 100$ at 25°. With stoichiometric concentrations of 0.01 M

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[1] Work supported by a grant from the Atomic Energy Commission.

[2] J. Hine and M. Hine, THIS JOURNAL, **74**, 5266 (1952).

[3] A. L. Henne and R. L. Pelley, *ibid.*, **74**, 1426 (1952).

[4] C. W. Roberts, E. T. McBee and C. E. Hathaway, *J. Org. Chem.*, **21**, 1369 (1956); see also E. T. McBee, W. F. Marzluff and O. R. Pierce, THIS JOURNAL, **74**, 444 (1952).

[5] R. N. Haszeldine, *J. Chem. Soc.*, 1757 (1953).

[6] A. L. Henne and W. C. Francis, THIS JOURNAL, **75**, 991 (1953).

[7] The basic difficulty of applying this method to very weak acids is well illustrated by the report in ref. 4 that the pK_a for ethanol in water is 12.70, only 0.3 unit larger than the value for trifluoroethanol. Preliminary conductivity studies indicate that the pK for ethanol is at least two units larger than that for the fluoroalcohol and on general grounds it is likely that the difference is in the order of four units. Evidently the pH method becomes quite inadequate for very weak acids.

[8] *Cf.* G. H. Twigg, W. S. Wise, H. J. Lichtenstein and A. R. Philpotts, *Trans. Faraday Soc.*, **48**, 699 (1952).

SH and 0.002 M NaOH, almost 50% of the NaOH would be transformed to NaS. Since the equivalent conductivities of these two electrolytes are about 245 and 80, respectively, there would be a large, easily measured change in conductivity. As a result conductivity data permit determination of K and hence ultimately of K_{SH} with considerable accuracy.

One of the favorable aspects of this procedure is that only minor approximations are needed to give the thermodynamic value of the ionization constant. The true value of K is given by

$$K = \frac{C_{S^-}\gamma_{S^-}}{C_{SH}C_{OH^-}\gamma_{SH}\gamma_{OH^-}}$$

where the γ's are activity coefficients. At the low concentrations which are feasible for this method none of the activity coefficients will differ greatly from unity. In particular γ_{SH} will remain close to unity until comparatively high concentrations of SH and electrolyte are attained.[9] More importantly, to the approximation of the Debye–Hückel limiting law, $\gamma_{S^-} = \gamma_{OH^-}$. Hence to a good approximation the measured value of K for sensible concentrations is also the thermodynamic value. Multiplication of this by K_w for pure water then gives the thermodynamic value of K_{SH}.

This first communication gives details on the experimental procedures and gives the results for studies of trifluoroethanol in the solvents H_2O and D_2O.

Experimental

A sample of trifluoroethanol, kindly supplied by Pennsalt Chemicals, proved to be better than 99.9% pure when subjected to vapor phase chromatography, the sole contaminant being a little water. The material was refractionated (b.p. 72.4° at 738 mm.) over anhydrous calcium sulfate to which had been added a little sodium bicarbonate to remove any trace of strong acid.

Solutions of the volatile trifluoroethanol were prepared by introducing the appropriate amount of the substance into a dry, carbon dioxide-free volumetric flask of known tare, weighing, and immediately cooling the flask to *ca.* −20°. The air drawn into the flask by this cooling had been treated to remove carbon dioxide. After adding most of the solvent, the solution was allowed to reach room temperature before making up to the mark.

All vessels were flushed with dry carbon dioxide-free air before any solutions were introduced. Distilled water and deuterium oxide (99.5% D_2O) were freed as much as possible from carbon dioxide by flushing with dry carbon dioxide free air for an hour or more. The specific conductivity of water treated in this way was $1\text{–}2 \times 10^{-6}$ ohm^{-1}cm.$^{-1}$.

A stock solution of sodium hydroxide (0.5 N) was prepared from concentrated sodium hydroxide solution and carbon dioxide-free water. Stock sodium deuteroxide solution was prepared by passing dried carbon dioxide-free air through deuterium oxide and then over sodium until the reaction was complete; the concentrated material was diluted with deuterium oxide and standardized by weight against 0.1 N hydrochloric acid.

The conductivity cell was of conventional design, with lightly platinized electrodes and had a capacity of 12 ml. The cell constant, determined with carefully prepared solutions of potassium chloride, was 0.5083 cm.$^{-1}$. The electrical apparatus comprised a 1 Kc. oscillator, Campbell-Shackleton ratio bridge, Leeds and Northrup precision a.c. resistance box, amplifier and earphones. The cell was maintained at 25.0 ± 0.005° in a bath of kerosene.

Measurement of the Equilibrium Constant.—In a typical experiment, 25-ml. portions of 0.0075 N sodium hydroxide were pipetted into a series of dry 50-ml. volumetric flasks and various known volumes of 0.2160 M trifluoroethanol added. The solutions were then made up to the mark with carbon dioxide-free water. The conductivity cell was rinsed four times with each solution before filling and the resistance was measured over a period of time until it reached a constant value. This usually occurred within 15 minutes. In one experiment, the alkaline solution of trifluoroethanol was left in the cell for 10 hr. The resistance decreased by less than 0.02% during that time, showing that fluoride ion is liberated only very slowly under these conditions.[10]

Preliminary experiments with other substituted ethanols had shown that part of the change in resistance which they cause when added to sodium hydroxide solutions is due to a decrease in ionic mobilities caused by the increased viscosity of these mixtures. For example, ethanol itself produces an almost identical percentage increase in the resistance of both potassium chloride and sodium hydroxide and the increase is proportional to the viscosity of the mixture over the concentration range studied (0–0.25 M). Table II lists the effect of trifluoroethanol on the conductivity of potassium chloride solution. The observed conductivities of the alkaline solutions have been increased by the same factor. This assumes that the effect of viscosity is the same for a solution of sodium hydroxide as for one of potassium chloride; it also assumes that the effect of the salt, sodium trifluoroethoxide, on viscosity is the same as that of the alcohol itself. On the basis of data for acetic acid and sodium acetate, this last is a fairly good assumption. Furthermore its effect is minimized by the fact that only a small fraction of the alcohol is ever transformed into the salt.

Table II

Conductivity of 0.00375 N Sodium Hydroxide Solutions Containing Excess Trifluoroethanol at 25°

Soln.	CF_3-CH_2OH (M)	R (ohm)	Viscosity cor.	10^4 Conductivity	10^4 Cond. (cor.)	R(cor.)
1	0.0	572.9	1.00000			R_0 = 572.9
2	.0216	830.7	1.00308	12.0380	12.0751	828.2
3	.0432	998.7	1.00616	10.0126	10.0743	992.6
4	.0648	1117.7	1.00924	8.9467	9.0294	1107.5
5	.1080	1276.2	1.01540	7.8357	7.9564	1256.9
6[a]	.0	707.4	1.00000	14.136	14.136	707.4
7[a]	.1080	718.3	1.01540	13.922	14.136	707.4

[a] 0.005N potassium chloride solution.

In the reaction

$$Na^+ + OH^- + CF_3CH_2OH \overset{K}{\rightleftarrows} Na^+ + OH^-(1 - \alpha) + \alpha CF_3CH_2O^- + \alpha H_2O$$

the equivalent conductivity of the solutions at equilibrium is given by $\Lambda_c = \lambda_c Na^+ + \lambda_c OH^-(1 - \alpha) + \alpha\lambda_c CF_3CH_2O^-$ where α is the degree of dissociation and the λ's are the ionic mobilities of the various ions at the prevailing total electrolyte concentration, c. Since the resistance of the solution is inversely proportional to Λ we have

$$\frac{R_{(cor.)}}{R_0} = \frac{\Lambda_c NaOH}{\lambda_c Na^+ + \lambda_c OH^-(1 - \alpha) + \alpha\lambda_c CF_3CH_2O^-}$$

where R_0 and Λ_cNaOH are the resistance and equivalent conductivity, respectively, of the sodium hydroxide solution by itself.

In the experiments of Table II a value of 48.1 was chosen for $\lambda_c Na^+$ (c = 0.00375 M) based on the literature value[11] for $\lambda_0 Na^+$ and the known variation with concentration of the equivalent conductivity of sodium chloride. The value of Λ_cNaOH was calculated from the measured resistance of the solution and in all of our experiments was from 2 to 3% below the best literature value. This decrease is doubtless due to a slight, apparently unavoidable contamination by atmospheric carbon dioxide. It was shown, however, that the presence of as much as 10% of bicarbonate ion would cause an error of only 0.5% in K; therefore no correction for this slight contamination was made. $\lambda_c OH^-$ was taken as the difference between the measured Λ_cNaOH and $\lambda_c Na^+$.

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(9) F. A. Long and W. F. McDevit, *Chem. Revs.*, **51**, 119 (1952).

(10) E. J. P. Fear, J. Thrower and J. Veitch, *J. Chem. Soc.*, 1322 (1958).

(11) Except where otherwise indicated, conductivity data are taken from H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publ. Corp., New York, N. Y., 1950.

The value of $\lambda_c CF_3CH_2O^-$ was calculated to be 31.2 ±0.1 by the procedure described below.

For each of solutions 2 to 5 of Table II a value of α was obtained from the expression

$$\frac{R_{(\text{cor.})}}{572.9} = \frac{236.6}{48.1 + 188.5(1 - \alpha) + 31.2\alpha}$$

The equilibrium constant for the reaction is then given by

$$K = \frac{\alpha}{(1 - \alpha)(CF_3CH_2OH)}$$

where (CF_3CH_2OH) is the equilibrium concentration of unreacted substrate.

The value (31.2) for $\lambda_c CF_3CH_2O^-$ was obtained by plotting $1/K$ for each solution against a series of arbitrary values (ranging from 25 to 40) of $\lambda_c CF_3CH_2O^-$. A family of straight lines was obtained which intersected at or very near a point corresponding to $\lambda_c CF_3CH_2O^- = 31.2$.

The results of several experiments are given in Table III. We believe that greater weight should be given to the first series of results for the reason that difficulties from incursion of carbon dioxide were relatively more serious for the 0.00125 N sodium hydroxide.

TABLE III

EQUILIBRIUM CONSTANT FOR THE REACTION OF TRIFLUOROETHANOL WITH SODIUM HYDROXIDE IN WATER AT 25°

Initial NaOH concn. (M)	CF_3CH_2OH concn. (M)	R	$R_{(\text{cor.})}$	α	K
0.00375	0.004301^c	626.5	626.1	0.1437	44.6
	.008601^c	676.2	675.4	.2424	41.6
	.02150^c	820.1	817.6	.4602	43.1
	.02160^b	830.7	828.2	.4636	43.5
	.04301^c	990.7	984.7	.6358	43.0
	.04320^b	998.7	992.6	.6360	42.8
	.06480^b	1117.6	1107.5	.7260	42.7
	.08601^c	1202.2	1187.6	.7826	43.3
	.1080^b	1276.2	1256.9	.8185	43.0
	.2150^c	1476.8	1432.9	.9046	44.8
	.....	R_0 = 572.9^b	....	Mean =	43.2
	.....	R_0 = 565.9^c			
0.00125	0.01164	2163.4	2159.2	0.3089	40.4
	.02788	2517.4	2509.2	.4777	41.1
	.05720	3195.3	3169.4	.6950	40.5
	.....	R_0 = 1721.2	....	Mean =	40.7

[b,c] Two separate experiments, each with fresh solutions and a small difference in R_0.

Measurement of K in Deuterium Oxide.—The method was the same except that 10–ml. portions of 0.0102 N sodium deuteroxide were made up to 25 ml. in volumetric flasks after adding measured volumes of a solution (0.1119 M) of trifluoroethanol in deuterium oxide.

The appropriate value (26.9 ± 0.1) of $\lambda_c^{(D_2O)}CF_3CH_2O^-$ was determined by the graphical method described above. $\lambda_c^{(D_2O)}Na^+$ was chosen as 39.8 using the relationship[12]

$$\left(\frac{\lambda_c Na^+}{\lambda_0 Na^+}\right)_{D_2O} = \left(\frac{\Lambda_c NaCl}{\Lambda_0 NaCl}\right)_{D_2O} = \left(\frac{\Lambda_c NaCl}{\Lambda_0 NaCl}\right)_{H_2O}$$

where $\lambda_0^{(D_2O)}Na^+ = 41.6$.[13]

TABLE IV

EQUILIBRIUM CONSTANT FOR THE REACTION OF TRIFLUOROETHANOL-*d* WITH 0.00408 N SODIUM DEUTEROXIDE IN 99.5% DEUTERIUM OXIDE AT 25°

Soln.	CF_3-CH_2OD (M)	R	R(cor.)	α	K
1	0.0	814.7	814.7 = R_0[14]	....	..
2	.008952	994.8	993.7	0.3196	61.4
3	.02238	1186.8	1183.4	.5527	61.4
4	.06714	1493.1	1480.3	.7979	61.7
				Mean	K = 61.5

The viscosity factor in solvent deuterium oxide was slightly less (1.0140 for a 0.108 M soln. of CF_3CH_2OD) than the corresponding factor in water owing to the higher viscosity of deuterium oxide itself. Results for a series of solutions appear in Table IV.

Discussion

The acid dissociation constant of trifluoroethanol is given by

$$K_a = \frac{[CF_3CH_2O^-][H^+]}{[CF_3CH_2OH]}$$

where the brackets indicate activities. The value of K_a follows directly from the measured K given in Tables III and IV since

$$K_a = \frac{[CF_3CH_2O^-]}{[CF_3CH_2OH][OH^-]} \times [H^+][OH^-]$$

Using for the ion product of water the values 1.01×10^{-14} for H_2O and 0.154×10^{-14} for D_2O[17] we arrive at ionization constants of 4.3×10^{-13} and 0.95×10^{-13} for trifluoroethanol in water and deuterium oxide, respectively. (The latter value is actually for 99.5% D_2O but within limit of error it can also be considered correct for the pure solvent.)

The ratio $K_a^{(H_2O)}/K_a^{(D_2O)} = 4.5$ is consistent with an extrapolation of Fig. 2 of Rule and LaMer[18] which shows that there is a substantial increase in this ratio for progressively weaker acids. Our results for the two solvents are also in agreement with the discussion by Gurney.[19] Furthermore, the agreement between our value of K_a in water and the values given in Table I is good, although as was pointed out in the introduction, the method by which the latter were obtained may make the agreement somewhat fortuitous.

There are several possible sources of error in our experiments. One of these is the presence of "strong" acid impurity in the material studied. This can be very serious with the less acidic substituted ethanols but the extent of reaction of trifluoroethanol in alkaline solution is so high that the amount of an acid such as acetic or trifluoroacetic which is sufficient to cause a large error in the value of K would certainly be large enough to be detected by vapor phase chromatography or by lowering of the electrical resistance of neutral potassium chloride solutions.

The viscosity correction that has been applied to the measured conductivities of the solutions is only approximate since it is made on the assumption that the viscosity-induced change in conductivity caused by the organic substance or its anion is the same for potassium chloride and sodium hydroxide. However, this correction is so small compared with the degree of dissociation that a substantial error in the former will cause a negligible change in the value of K. Lastly, the value of the mobility of the trifluoroethoxide anion is not very firmly established. The value that we have chosen does lead to K values which are constant over a wide

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(12) J. P. Chittum and V. K. LaMer, THIS JOURNAL, **59**, 2425 (1937).

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(14) This leads to $\lambda_c^{(D_2O)}OD^- = 113.1$ at $c = 0.00408$ M, a value which is in good agreement with those from previous studies.[15,16]

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(16) A. Gierer, *Z. Naturforsch.*, **5A**, 577 and 581 (1950).

(17) R. W. Kingerly and V. K. LaMer, THIS JOURNAL, **63**, 3256 (1941).

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(19) R. W. Gurney, "Ionic Processes in Solution," McGraw-Hill Book Co., New York, N. Y., 1954.

range of substrate concentrations, and we believe that this value is accurate.

We estimate the accuracy of the results for the individual ionization constants to be ±10%, but the ratio $K_a(H_2O)/K_a(D_2O)$ is probably more accurate as many of the errors in the individual constants will cancel.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Halogen, Iron and Vanadium Potentials in Lithium Chloride–Potassium Chloride Eutectic[1]

BY H. A. LAITINEN AND J. W. PANKEY

RECEIVED AUGUST 4, 1958

Electrode potentials of chlorine, bromine, iodine, iron and vanadium systems were measured in a lithium chloride–potassium chloride eutectic at 450°. Platinum foils in contact with solutions of platinum(II) were used as reference electrodes. Halogen electrodes were prepared by the passage of vapors of the halogen around graphite indicator electrodes in eutectic solutions of the halide in question. Iron(II) and vanadium(II) ions were produced by anodic dissolution of the respective metals. The massive metals served as indicator electrodes to measure potentials at various concentrations of divalent ions. Iron(III) and vanadium(III) solutions were prepared by anodic oxidation with graphite rods of eutectic solutions of the respective divalent ions. Potentials at the graphite rods were measured at various ratios of trivalent to divalent ion concentrations. Standard potentials are given for molarity, molality and mole fraction concentration scales.

In a recent publication[2] of an electromotive force series in molten lithium chloride–potassium chloride eutectic at 450°, the potential of the chlorine–chloride electrode was included. In the present paper, the experimental details of the evaluation of this electrode are given, and several additional entries to the e.m.f. series are made.

Halogen electrodes have been studied in pure and mixed molten halides by a number of investigators[3–8] beginning with Salstrom and Hildebrand. In most studies, reversible behavior was described, although the time necessary to reach equilibrium was often of the order of one to two hours. Drossbach,[7] however, noted small overvoltages upon anodization of carbon electrodes in molten chlorides, and interpreted impedance measurements on the basis of a slow heterogeneous reaction, probably $Cl + Cl \rightarrow Cl_2$. Smirnov and co-workers[5] anodized the carbon rod electrodes to saturate them with chlorine but did not remove hydrogen chloride from the melt prior to the anodic pretreatment. Little attention has been paid to corrections for variations of the pressure. Various measurements also have been made of the decomposition potentials of halide melts. These data are not directly of concern here and are mainly of interest for comparison with values calculated from thermodynamic data for pure metal chlorides.[9] For references, the reader is referred to the thesis of the junior author.[1]

The behavior of the iron(II)–iron(0) electrode has received study in alkali metal chloride–aluminum chloride systems,[10–12] in similar bromide mixtures[13] and in sodium bromide–potassium bromide melts.[14] Iron(III) has been found to exhibit two reduction steps,[15] presumably to iron(II) and the metal.

No previous reports of the potential of the vanadium(II)-vanadium(0) electrode have apparently been made, although the electrolytic reduction of vanadium(V) oxide has been described, yielding spinels of the type $V_2O_3 \cdot MO$ where M was Fe, Mn, Co or Zn,[16] and vanadium(IV) oxide.[17] Anodization of ferrovanadium in $AlBr_3 \cdot KBr$ melts showed evidence for anodic dissolution of vanadium, but the oxidation state was not established.[17]

Experimental

Materials and Equipment. Physical Equipment.—The furnace, temperature controller, polarograph, potentiometer, constant-current source and electrolytic cell have been previously described.[2,18–20] An auxiliary furnace, operating at 500° served where required to treat equipment before insertion into the solvent. The electrolysis cell and auxiliary equipment that was used to measure the electrode potentials is illustrated in Fig. 1. All portions were of Pyrex (Corning 774) glass except as noted. Side-arm tube A was the cell, which protruded from the furnace above the level A-A.

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[1] Sponsored in part by Office of Ordnance Research, U. S. Army. Abstracted from the Ph.D. thesis of J. W. Pankey, 1958.

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