[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Potentiometric Titration of Fluorinated Alcohols in Aqueous and Non-Aqueous Systems

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The pK_a values for 3-amino-1,1,1-trifluoro-2-propanol and 3-diethylamino-1,1,1-trifluoro-2-propanol have been determined in aqueous solution. Butylamine enhances the acidity of trifluoroethanol to cause an inflection in the titration curve corresponding closely to the theoretical equivalence point.

DISCUSSION

Several authors[2] have determined ionization constants for alcohols containing an adjacent perfluoroalkyl group and have found a marked enhancement of acidity due to the $-I_s$ effect of the fluorine in the molecule. As part of a study of the isomer distribution from cleavage reactions of fluorinated epoxides, a method was desired which would quickly indicate the location of a hydroxyl group relative to a perfluoroalkyl group in a bifunctional alcohol. Ionization constant data for fluorinated carboxylic acids[3] indicate a marked decrease in acid strength as the fluorine atoms are moved further down a hydrocarbon chain. A similar phenomenon should exist in the fluorinated alcohols and hence an alcohol with an adjacent perfluoroalkyl group should show a much lower pK_a value. To establish the range of pK_a values for bifunctional alcohols containing an adjacent trifluoromethyl group, the ionization constants for 3-amino-1,1,1-trifluoro-2-propanol (I) and 3-diethylamino-1,1,1-trifluoro-2-propanol (II) have been determined. These were calculated both by the half-equivalence method[4] and the method of Glasstone[5] which corrects for ionic strength deviations. Inasmuch as an alcohol containing a perfluoroalkyl group displaced by one methylene group was not readily available for standardization purposes, ethanol was assumed to be a representative compound and was titrated under similar conditions. The pK_a values obtained in the aqueous system are summarized in Table I as determined from the data in Figure 1.

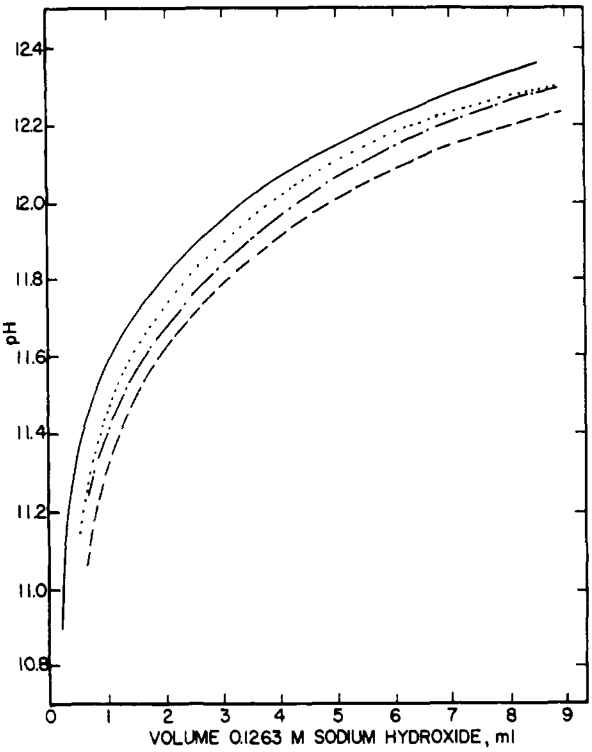

FIGURE 1. TITRATION CURVES IN WATER: ———, ethanol; ....., 3-diethylamino-1,1,1-trifluoro-2-propanol; -.-.-, trifluoroethanol; ---, 3-amino-1,1,1,-trifluoro-2-propanol.

The narrow range in pK_a of 0.27 unit shown by the first three alcohols should encase the upper limit of pK_a values for molecules containing adjacent perfluoroalkyl and carbinol groupings since the substituent amino groups on the *alpha* carbon atom should raise the pK_a to the highest possible value for this type of molecule. As would be expected, the diethylamino alcohol is less acidic than the unsubstituted aminoalcohol. The pK_a for ethanol appears to be outside the upper limit imposed by II.

Though determination of ionization constants in aqueous solutions potentially will allow identification of the position of a hydroxyl group in a pure compound, quantitative estimation of isomer distribution in mixtures of compounds with similar physical properties requires a potentiometric

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(1) A portion of a thesis submitted by C. E. Hathaway to Purdue University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, January, 1956.

(2) (a) E. T. McBee, W. F. Marzluff, and O. R. Pierce, *J. Am. Chem. Soc.*, **74**, 444 (1952); (b) A. L. Henne and R. L. Pelley, *J. Am. Chem. Soc.*, **75**, 1426 (1953); (c) A. L. Henne and W. C. Francis, *J. Am. Chem. Soc.*, **75**, 991 (1953).

(3) A. L. Henne and C. J. Fox, *J. Am. Chem. Soc.*, **73**, 2323 (1951).

(4) Henne and Fox[3] have suggested the extension of the half-equivalence technique beyond the usual pH limits of 4 to 10 to include the fluorinated alcohols and have obtained reasonable agreement with the corrected values.

(5) S. Glasstone, *Introduction to Electrochemistry*, D. Van Nostrand Co., Inc., New York, N. Y., 1942, p. 322.

TABLE I

pK_a VALUES FOR FLUORINATED ALCOHOLS

Alcohol	pK_a Half-equivalence method	Corrected[5]
Trifluoroethanol	11.82	12.43
3-Amino-1,1,1-trifluoro-2-propanol	11.78	12.29
3-Diethylamino-1,1,1-trifluoro-2-propanol	11.84	12.56
Ethanol	11.94	12.70

method which shows a sharp equivalence point exclusively for the more acidic alcohol.

The acidity of phenol is enhanced sufficiently when mixed with a carboxylic acid in butylamine solvent to obtain a sharp equivalence point for each acid.[6] Extension of this technique to the slightly less acidic fluorinated alcohols should allow a quantitative determination of the system with adjacent perfluoroalkyl and carbinol groups exclusive of any other fluorinated structural isomer.

The titration curve for the butylamine solvent system has been reproduced in Figure 2. Though trifluoroethanol shows no sharp break, the middle of the inflection occurs at 94% of the theoretical equivalence value and further refinement of the technique should allow the desired quantitative isomer determination.

EXPERIMENTAL

Starting materials. Trifluoroethanol from the catalytic reduction of trifluoroacetic acid was purified by rectification from a small amount of calcium hydride. The ethanol was commercial grade absolute alcohol. 3-Amino-1,1,1-tri-2-propanol and 3-diethylamino-1,1,1-trifluoro-2-propanol were obtained from 1,1,1-trifluoro-2,3-epoxypropane.[7] The butylamine was dried over potassium hydroxide pellets, decanted, and rectified. The ethanolamine was rectified. The ethylene diamine was dried over sodium hydroxide pellets and rectified from sodium. All distillations were carried out in a system protected from the atmosphere with an Ascarite tube. Sodium aminoethoxide was prepared by the addition of sodium to ethanolamine.

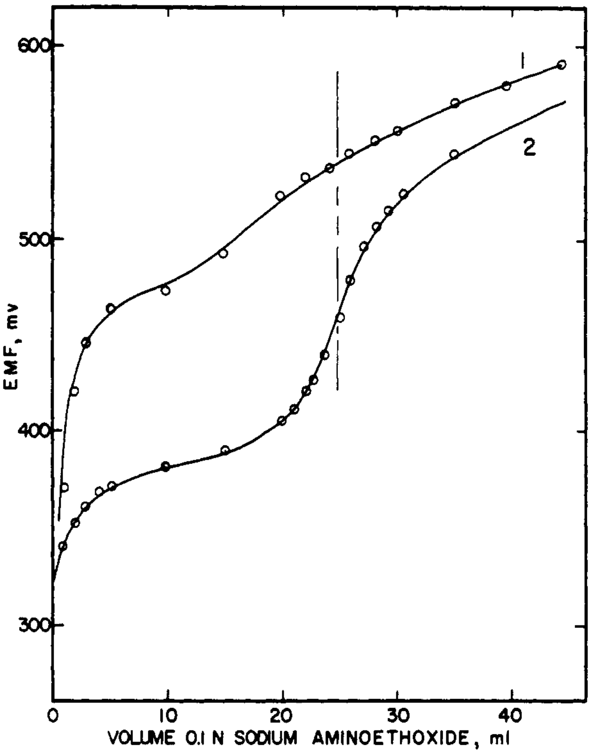

FIGURE 2. TITRATION CURVES IN ETHYLENE DIAMINE–BUTYLAMINE: 1, Trifluoroethanol; 2, Phenol.

Measurement of ionization constants in aqueous solutions. A solution (25 ml.) of the alcohol of known concentration was titrated with carbon dioxide-free 0.1263 *N* sodium hydroxide. The titration was followed with a Beckman *p*H meter, model H2, equipped with a special glass electrode, No. 4990-75, for high *p*H and calibrated with a standard solution at *p*H 11.80 prepared from a Coleman buffer tablet. Titration data are reproduced in Figure 1. The method of calculation was essentially that of Glasstone,[5] the corrected pK_a values listed in Table I being obtained by plotting apparent pK_a values for various ionic strengths and extrapolating back to zero ionic strength.

Titration of trifluoroethanol and phenol in butylamine. A solution of 0.103 *N* trifluoroethanol in butylamine (25 ml.) was titrated with a 0.11 *N* solution of sodium aminoethoxide in an ethanolamine–ethylene diamine solvent by the method of Fritz and Lisicki.[6] The system was flushed with a slow stream of nitrogen to exclude carbon dioxide and moisture. A solution of 25 ml. of 0.098 *N* phenol in butylamine was similarly titrated and the data are recorded in Figure 2. The titration was followed with an antimony-glass electrode combination using the same *p*H meter used with the aqueous systems.

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(6) J. S. Fritz and N. M. Lisicki, *Anal. Chem.*, **23**, 589 (1951).

(7) E. T. McBee, C. W. Roberts, and C. E. Hathaway, *J. Am. Chem. Soc.*, **78**, 3851 (1956).