Heating the adducts with dilute acids or bases regenerated the phthalan and hexahydrophthalan.

Preparation of Hexahydrophthalan.—Phthalan, 106 g. (0.9 mole), was hydrogenated over 4 ml. of Raney nickel catalyst at 150–160° for 12 hours with an initial cold pressure of 1700 p.s.i.g. The product was fractionated through a column of 50 theoretical plates. The yield of hexahydrophthalan with a strong menthol odor was 107 g. (96%), b.p. 179° (740 mm.), $n^{25}\text{D}$ 1.4683, d^{25}_4 0.9727, f.p. glass.

Anal. Calcd. for $C_8H_{14}O$: C, 76.14; H, 11.18; molar refraction, 36.40. Found: C, 76.13; H, 11.27; molar refraction, 36.08.

Hydrogenolyses of Phthalan.—The hydrogenolyses of phthalan were run at reaction temperatures of 250, 300 and 350 ± 5° for 12 hours in a 1080-ml. stainless steel rocking autoclave which was heated by an external electric furnace. In all three runs 5 g. of copper–chromium oxide catalyst, 80 g. of phthalan (0.67 mole) and 1625–1725 p.s.i.g. of hydrogen pressure were charged to the autoclave. Hydrogen absorptions corresponded to 1.6, 2.9 and 4.0 moles of hydrogen per mole of phthalan at 250, 300 and 350°, respectively. The bomb was cooled to room temperature after reaction and the products filtered free of catalyst and fractionated in a column of 50 theoretical plates. The fractions were then analyzed quantitatively by means of their infrared spectra and other physical properties; a summary of the yields of the various products is presented in Table I.

Preparation of *o*-Methylbenzyl Alcohol.—A mixture of 185 g. (1 mole) of *o*-xylyl bromide and 123 g. (1.5 moles) of fused sodium acetate dissolved in a minimum volume of boiling glacial acetic acid was refluxed for 24 hours. Without isolating the resulting *o*-xylyl acetate, the crude reaction mixture was neutralized and then made alkaline with an excess of 400 ml. of 20% sodium hydroxide solution. After refluxing 8 hours the product was steam distilled; the distillate was extracted with ether, the ethereal extract was dried over anhydrous potassium carbonate and the ether distilled off. On refrigeration the *o*-methylbenzyl alcohol crystallized after which it was filtered free of oil and recrystallized from pentane: yield 105 g. (86% yield) of white needles, m.p. 36–37°; *o*-tolylcarbinyl-N-phenylcarbamate, m.p. 79–80°.[10]

Anal. Calcd. for $C_8H_{10}O$: OH, 14.0. Found: OH, 14.3, 14.0.

Preparation of 2-Methylcyclohexanemethanol.—(a) Hydrogenation of *o*-methylbenzyl alcohol over Raney nickel or palladium-on-charcoal gave high yields of *o*-xylene and 1,2-dimethylcyclohexane and only minor amounts of this compound.

(b) A mixture of 2-methylcyclohexanol and excess zinc chloride–hydrochloric acid reagent (1:1 molar ratio) was refluxed for 4 hours and cooled to room temperature. The upper phase was removed and washed with concentrated sulfuric acid, a saturated solution of sodium bicarbonate and then water and dried over anhydrous calcium chloride. The product, 2-methylchlorocyclohexane, was fractionated, b.p. 153–154° (735 mm.).

Into the ethereal solution of a Grignard reagent prepared from 148 g. (1.12 moles) of the halide, formaldehyde vapor from the thermal depolymerization of paraformaldehyde at 180–200° was bubbled until a negative Gilman test was obtained. After hydrolysis and steam distillation the reaction product was fractionated in a column of 50 theoretical plates and the yield was 70 g. (50% yield) of 2-methylcyclohexanemethanol, b.p. 194° (733 mm.), $n^{25}\text{D}$ 1.4610.

Anal. Calcd. for $C_8H_{16}O$: C, 75.00; H, 12.50; OH, 13.28. Found: C, 75.27; H, 12.66; OH, 13.22.

Only one isomer was isolated in the fractionation; this appears to be the form previously designated as *trans* by Skita.[11]

Acknowledgment.—We wish to express our thanks to Messrs. Joseph B. Simsic and Daniel T. Muth for their assistance. Absorption spectra were run on the Baird Infrared and Cary Ultraviolet Recording Spectrophotometers of the Mellon Institute, Pittsburgh, Pennsylvania, and microanalyses were performed by the Huffman Microanalytical Laboratories, Denver, Colorado.

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(10) E. H. Huntress and S. P. Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1941, p. 412.

(11) A. Skita, *Ann.*, **431**, 9, 20 (1923).

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The Ionization Constants of Some Fluorine-containing Alcohols[1,2]

By E. T. McBee, W. F. Marzluff and O. R. Pierce

Diols of the general formula $HOCH_2(CF_2)_nCH_2OH$ where n is 1, 2, 3 or 4 were synthesized. The pK_a values of 2,2,3,3-tetrafluoro-1,4-butanediol were measured and found to be 12.1 ± 0.1 and 13.7 ± 0.2 while those of 2,2,3,3,4,4,5,5-octafluoro-1,6-hexanediol were determined as 12.1 ± 0.1 and 12.8 ± 0.2. In addition, the pK_a value of 2,2,2-trifluoroethanol was measured and found to be 12.3 ± 0.05. The inductive effect of fluorine substitution beta to hydroxyl groupings can be calculated by empirical methods.

Discussion

Fluorine-containing diols were prepared for use in quantitative determinations of the effect of fluorine substitution on the acidity of hydroxyl groupings. Alcohols containing fluorine beta to the hydroxyl group were first prepared by Swarts[3a,b] who reported 1,1,1-trifluoro-2-propanol to be more acidic than phenol.[3a] Since work in this Laboratory had demonstrated that 2,2,2-trifluoroethanol was not acidic in nature, the ionization constants of 2,2,2-trifluoroethanol and diols containing fluorine were measured.

Diols of the general formula $HOCH_2(CF_2)_n$-CH_2OH, where n is 1, 2, 3, 4, were synthesized from the respective fluorine-containing acids. Octafluoroadipic acid was prepared by the oxidation of 1,2-dichloroöctafluorocyclohexene and hexafluoroglutaric acid was obtained by the oxidation of 1,2-dichlorohexafluorocyclopentene (Hooker Electrochemical Co.) using potassium permanganate.[4] The yield of the acid in each case was from 40 to 50%. Hexafluorocyclobutene was oxidized with potassium permanganate at autogenous pressures to give the desired tetrafluorosuccinic acid.[5] The

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(2) Presented, in part, before the Fluorine Symposium, 118th Meeting of the American Chemical Society, Chicago, Illinois, September, 1950.

(3) (a) F. Swarts, *Bull. soc. chim. Belg.*, **38**, 99 (1929); (b) *Compt. rend.*, **197**, 1261 (1933).

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TABLE I

FLUORINE-CONTAINING DIOLS AND ETHERS

Compound	M.p., °C.	B.p., °C. 745 mm.	Yield, %	Composition, % Carbon Found	Carbon Calcd.	Hydrogen Found	Hydrogen Calcd.
$HOCH_2CF_2CH_2OH$	52.53		85	32.1	32.1	5.51	5.4
$HOCH_2(CF_2)_2CH_2OH$	85		90	29.6	29.6	3.75	3.7
$HOCH_2(CF_2)_3CH_2OH$	77.5		93	(55.3)[a]	(55.1)[a]	2.82	2.83
$HOCH_2(CF_2)_4CH_2OH$	68		88	27.0	27.4	2.39	2.29
$HOCH_2(CF_2)_3CH_2OEt$		190–191[b,c]	95	35.0	35.0	4.19	4.17
$HOCH_2(CF_2)_4CH_2OMe$		194–195[d,e]	90	30.4	30.5	2.88	2.90

[a] % fluorine. [b] n^{24}_D 1.3630. [c] d^{20}_4 1.43. [d] n^{20}_D below 1.3. [e] d^{20}_4 1.54.

esters of octafluoroadipic, hexafluoroglutaric and tetrafluorosuccinic acids were prepared by azeotropic distillation of the ternary azeotrope of benzene, water and ethanol from a mixture consisting of the acid, ethanol and benzene and were purified by rectification at reduced pressure.

Since 2,2-difluoromalonic acid is difficultly prepared,[6] an alternative route to the preparation of 2,2-difluoro-1,3-propanediol was sought. Prins described the preparation of 2,2-dichloro-3-hydroxypropionic acid by the reaction of formaldehyde with tetrachloroethylene in sulfuric acid.[7] The analogous reaction was conducted with tetrafluoroethylene and paraformaldehyde in concentrated sulfuric acid at autogenous pressures and in the temperature range of 80 to 90°. Esterification of the product with ethanol gave a 15 to 20% yield of ethyl 2,2-difluoro-3-hydroxypropionate. While this work was in progress, a patent was issued to Raasch[8] describing this reaction.

The diethyl esters of perfluorosuccinic, -glutaric and -adipic acids and ethyl 2,2-difluoro-3-hydroxypropionate, were each reduced to the corresponding diols using lithium aluminum hydride. The monoethyl ether of 2,2,3,3,4,4-hexafluoro-1,5-pentanediol and the monomethyl ether of 2,2,3,3,4,4,5,5-octafluoro-1,6-hexanediol were prepared by reaction of the diol with the appropriate dialkyl sulfate in alkaline solution. Physical constants and other data concerning these compounds are described in Table I.

The pK_a values of 2,2,3,3-tetrafluoro-1,4-butanediol were measured and found to be 12.1 ± 0.1 and 13.7 ± 0.2 for the primary and secondary ionization constants while the pK_a values of 2,2,3,3,4,4,5,5-octafluoro-1,6-hexanediol were determined as 12.1 ± 0.1 and 12.8 ± 0.2. 2,2,2-Trifluoroethanol gave a value of 12.3 ± 0.05.

It was found that the results agree within a power of 10 with the values calculated using the equation of Branch and Calvin.[9] From this it is seen that only an inductive effect is operative.

Experimental

Ethyl 2,2-Difluoro-3-hydroxypropionate.—Sixty grams of paraformaldehyde and 1100 g. of 95% sulfuric acid were added to a 2-liter nickel autoclave, which was then closed, flushed with nitrogen and evacuated. About 80 g. of tetrafluoroethylene was added under pressure and the autoclave agitated for 21 hours while being heated to 85°. After cooling, the residual gases were allowed to bleed off, and the contents of the autoclave were poured over 1500 g. of crushed ice. The solution, fuming with hydrofluoric acid, was extracted several times with 100-ml. portions of ether. The combined ether layers were extracted with several portions of 10% sodium hydroxide solution, and the basic water layer was then washed twice with ether. The water layer was acidified with sulfuric acid and extracted several times with ether. The ether was evaporated and the remaining solution of the acid and water was heated at 50° and 40 mm. pressure to yield crude 2,2-difluoro-3-hydroxypropionic acid, a brown sirupy material. Distillation of this material resulted in the formation of a polymeric product. Therefore, the crude acid was treated with a 4 mole excess of ethanol in the presence of anhydrous copper sulfate for 14 hours at reflux temperature. The mixture was filtered, the excess ethanol distilled, and the residue distilled under reduced pressure to yield 24.6 g. of ethyl 2,2-difluoro-3-hydroxypropionate, b.p. 93–95° at 18 mm. pressure.

2,2,3,3,4,4-Hexafluoro-1,5-pentanediol.—Five hundred milliliters of anhydrous diethyl ether was pipetted into a dry, 3-necked flask fitted with a mercury-sealed Hershberg stirrer, a dropping funnel, and a condenser to which was attached a tube filled with soda lime. Lithium aluminum hydride (27.5 g.) was added and stirring begun. After a few minutes the slow addition of 142.7 g. of diethyl hexafluoroglutarate in 300 ml. of anhydrous diethyl ether was started and continued for 6 hours. After the addition was completed, the mixture was stirred for 1 hour and 18 g. of water was added dropwise to destroy the excess lithium aluminum hydride. The semi-solid mixture was poured into 1 liter of 10% sulfuric acid solution, the ether layer separated, the water layer extracted with ether, and the ether extracts combined. The ether was removed by distillation, 200 ml. of benzene was added to the residual liquid, and the distillation continued to remove water. When no more water was evident in the distillate, the hot benzene solution was poured into a beaker and the diol allowed to crystallize. The white solid was recrystallized from benzene, producing 95.4 g. (93% yield) of 2,2,3,3,4,4-hexafluoro-1,5-pentanediol. The other diols listed in Table I were prepared in a similar manner.

2,2-Difluoro-1,3-propanediol was recrystallized from a mixture of benzene and ethyl acetate rather than from benzene alone.

5-Ethoxy-2,2,3,3,4,4-hexafluoro-1-pentanol.—Forty grams (0.2 mole) of 2,2,3,3,4,4-hexafluoro-1,5-pentanediol and 8.0 g. (0.2 mole) of sodium hydroxide pellets were dissolved in 200 ml. of water in a 1-liter flask fitted with a reflux condenser. Fifteen grams (0.1 mole) of diethyl sulfate was added and the mixture heated at 100° for 24 hours. The reaction mixture was then steam distilled, and the lower layer of the distillate separated. The upper aqueous layer was extracted with ether. The ether extracts were combined with the distillate, dried with Drierite and distilled at atmospheric pressure to yield 19 g. (0.08 mole) of 5-ethoxy-2,2,3,3,4,4-hexafluoro-1-pentanol. The conversion was 48% and the yield was 95%. The aqueous residue from the steam distillation was extracted with ether to recover the unreacted diol.

The other ether in Table I was prepared in a similar manner.

Measurement of Ionization Constants.—Twenty-five milliliters of a solution of the alcohol or diol of known concentration was measured into a clean, dry 50-ml. beaker and measured amounts of CO_2-free 0.100 *N* sodium hydroxide, were added from a buret. After each addition of base, the *p*H of the solution was determined using a Leeds and

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[6] A. L. Henne and E. G. Dewitt, THIS JOURNAL, **70**, 1348 (1948).

[7] H. J. Prins, *Rec. trav. chim.*, **51**, 469 (1932).

[8] M. S. Raasch, U. S. Patent 2,452,791 (Nov. 2, 1948).

[9] Branch and Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, p. 223.

Northrup Model 7662 *p*H meter equipped with a special glass electrode for high *p*H range. The *p*H meter was calibrated with a standard buffer solution, 0.05 *M* sodium tetraborate decahydrate *p*H 9.18 ± 0.01 at 25°.[10]

The results are summarized in Tables II and III. The calculations were based on methods discussed by Glasstone.[11,12]

TABLE II

CF_3CH_2OH, 25.00 ml. of a 0.0323 *M* Solution

Run	0.100 *N* NaOH, ml.	*p*H	μ	$K \times 10^{-13}$ mole/liter
I	1.00	11.20	0.00385	4.6
	3.00	11.71	.0107	4.1
	5.00	11.94	.0167	3.9
	7.00	12.10	.0219	3.6
II	2.00	11.54	.0080	4.4
	4.00	11.84	.0138	4.0
	6.10	12.03	.0196	3.8
	8.10	12.17	.0245	3.3

The ionization constant of 2,2,2-trifluoroethanol was obtained by plotting the ionic strength, μ, *versus* K and extrapolating to $\mu = 0$. In the case of the diols, the ionization constants were calculated by means of an equation of the form $K_1K_2 + AK_1 - B$, where A and B are calculated from the experimental data.[11] B was plotted against A and the slope of the straight line obtained was K_1 while the intercept was K_1K_2.

TABLE III

$HOCH_2(CF_2)_2CH_2OH$, 25.00 ml. of a 0.123 *M* Solution

0.100 *N* NaOH, ml.	*p*H, measured	$A \times 10^{12}$[a]	$B \times 10^{24}$[a]
1.00	10.52	4.6	3.95
2.00	10.78	2.5	2.3
3.00	10.99	1.5	1.3
4.00	11.11	2.2	1.8
5.00	11.21	0.88	0.81
6.00	11.31	0.68	0.61

$HOCH_2(CF_2)_4CH_2OH$, 25.00 ml. of a 0.253 *M* Solution

0.100 *N* NaOH, ml.	*p*H, measured	$A \times 10^{11}$	$B \times 10^{25}$
1.00	11.12	11	8.8
2.00	11.45	4.5	4.2
3.00	11.62	3.1	2.7
4.00	11.74	2.2	2.1
5.00	11.84	1.6	1.7

[a] $A = \dfrac{1 - R}{2 - R} a_{H^+}$; $B = \dfrac{R}{2 - R} (a_{H^+})^2$; $R = \dfrac{a_{OR^-} - a_{OH^-}}{C_{HOR} + a_{OR^-}}$

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[10] S. Glasstone, "Introduction to Electrochemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1942, p. 327.

[11] S. Glasstone, *ibid.*, p. 350.

[12] S. Glasstone, "Textbook of Physical Chemistry," 2nd Ed., D. Van Nostrand Co., Inc., New York, N. Y., 1946, p. 980.

LAFAYETTE, INDIANA RECEIVED JULY 19, 1951

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF SOUTHERN CALIFORNIA]

The Self-diffusion Coefficients of the Ions in Aqueous Sodium Chloride and Sodium Sulfate at 25°

BY JULIAN M. NIELSEN,[1] ARTHUR W. ADAMSON AND JAMES W. COBBLE

Procedures are reported whereby the diaphragm cell technique may adequately be adapted to the measurement of ion self-diffusion coefficients in aqueous solution through the use of isotopic labelling of an ion. The problems of stirring and of calibration are discussed: two methods of mechanical stirring are shown to give values of the cell constant that are the same for mean diffusion and for self-diffusion experiments, and two calibration methods, by mean diffusion and by conductance, are shown to give accurate self-diffusion constants. Enhancement of the apparent self-diffusion coefficient at low concentrations is reported and discussed as a surface transport process. The presence of the effect limits the range of concentrations over which accurate solution diffusion coefficients can be determined. Values for the self-diffusion coefficients of Na^+ and Cl^- ions in aqueous sodium chloride and of Na^+ and $SO_4^=$ ions in aqueous sodium sulfate at 25 ± 0.01° are reported for concentrations up to 3 *N*. The results are compared with existing limiting laws and with mean diffusion coefficient data.

The study of ion self-diffusion in electrolyte solutions has received increasing attention during recent years. By means of the convenient diaphragm cell technique, values have been obtained for Na^+ ion in aqueous sodium chloride[2] and sodium iodide,[3] and for Ag^+ ion in aqueous silver nitrate,[4] at 25°, while by the more elaborate, but absolute, free diffusion method, early values are available for Na^+ and Cl^- ions in aqueous sodium chloride at 35°[5] and, recently, for Na^+ and I^- ions in aqueous sodium iodide at 25°.[6] The work presented here comprises results for Na^+ and Cl^- ions in sodium chloride solutions which, being more accurate, supplant those briefly reported previously,[2] results for Na^+ and $SO_4^=$ ions in sodium sulfate solutions, and a detailed experimental analysis of the sources of systematic error involved in the diaphragm method for the determination of self-diffusion coefficients.

Experimental

Apparatus and General Procedure.—The diaphragm cells used were of the type shown in Fig. 1 and described earlier by McBain and Dawson[7]; they consisted of a Pyrex glass cylinder divided into two 25-ml. compartments by means of a medium to fine Corning sintered glass disk. The volumes were determined by filling each compartment in turn with mercury and weighing. Each compartment had two small attached stopcocks, thus permitting filling or emptying without disturbing the liquid in the diaphragm. The general procedure was as follows. One compartment was filled with labeled solution by means of a pipet, after rinsing with four small portions, each of which was drawn through the sintered disk. The stopcocks were closed, and the other compartment filled with unlabeled solution, again after several rinsings. Two to four hours of preliminary

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[1] This paper is based in part on a portion of a dissertation submitted by Julian M. Nielsen, a Frederick Gardner Cottrell Fellow, in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the University of Southern California. Present address: Michelson Laboratory, Naval Ordnance Test Station, Inyokern, California. Send inquiries to the second author.

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[3] A. W. Adamson, *ibid.*, **15**, 762 (1947).

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[5] L. P. Jehle, Ph.D. Dissertation, University of Calif., Berkeley, 1938.

[6] J. H. Wang and J. W. Kennedy, THIS JOURNAL, **72**, 2080 (1950).

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