1750 cc. of the crude acids on alkaline steam distillation gave 200 cc. of neutral oil (11%) and 5–10 cc. of ethyl mercaptan (0.6%) as the distillate. The residue of 1500 cc. (86%) was esterified with methyl alcohol and extracted with ether from alkaline solution, 250 cc. of esters (15%) was separated from 1050 cc. of phenols (71%). The phenols on distillation gave 500 cc., b. p. 190–230° (34%), 75 cc., b. p. 230–265° (4%) and 400 cc. of tar (23%). The first phenolic fraction on subsequent distillation yielded 145 cc. of *o*-cresol (8%), 135 cc. of a mixture of *m*- and *p*-cresols (8%), 60 cc. of undetermined (3%) and 180 cc. of xylenols (10%).

Summary

1. Commercial naphthenic acids from a West Texas pressure distillate were shown to consist for the most part of phenolic constituents.
2. The following compounds have been isolated and identified from the sample: ethyl mercaptan, phenol, *o*-cresol, *m*-cresol, *p*-cresol, 1,3,5-xylenol, 1,4,2-xylenol, isovaleric acid, *n*-heptylic acid, *n*-octylic acid and *n*-nonylic acid.
3. The finding of aliphatic acids and of no cyclic acids tends to throw doubt on the claims of earlier investigators who reported the cyclic compounds exclusively.

HOUSTON, TEXAS RECEIVED JUNE 22. 1935

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

Electron-Sharing Ability of Organic Radicals. IX. Dissociation Constants of Amines and Acids in Ethanol

BY LYLE D. GOODHUE AND R. M. HIXON

The dissociation constants of a series of organic acids and amines in methanol, as measured by the hydrogen electrode, were reported in a previous paper.[1] The constants measured in methanol by the hydrogen electrode were found to agree favorably with the values obtained by Goldschmidt[2] using conductimetric methods. Similar measurements for ethanol solutions are reported in this publication.

Experimental

The resistance of the ethanol solutions was so great that it was necessary to use a vacuum tube null-instrument in the place of the vacuum tube potentiometer[3] used with methanol solutions. An apparatus constructed similar to the one described by Ellis and Kiehl[4] gave convenient measurements with a precision of 0.1 millivolt. All measurements were made in an air-bath maintained at 25 ± 0.1°. A wire screen inside of the cabinet was necessary to prevent electrical disturbances from being transmitted to the vacuum tube measuring instrument.

The standard electrode potential of the silver–silver chloride electrode in ethanol has been reported by MacFarlane and Hartley.[5] The activity of hydrogen chloride in alcohol has been determined by Danner,[6] by Harned and Fleyscher,[7] and by Woolcock and Hartley.[8] With these values known the hydrogen-ion activity of an unknown solution can be measured by using either the silver–silver chloride or the hydrogen half-cell as a reference electrode.

Although the silver–silver chloride electrodes are reproducible, they are inconvenient to use as reference cells due to the great care required in their preparation and the fact that a freshly prepared electrode must be used for each measurement. Mercury–mercuric iodide half cells in alcoholic potassium iodide have been used by Johns and Hixon[9] with flowing junctions to eliminate polarization. Using a static junction through a glass stopcock, the voltage of the concentration cell

$$\mathrm{Hg/HgI_2}\ (0.005\ m)\ \mathrm{KI}\ (0.05\ m)//\mathrm{KI}\ (0.05\ m)\ \mathrm{HgI_2}\ (0.01\ m)/\mathrm{Hg}$$

was found to be 0.0146 volt as compared with the value 0.01455 volt reported by the former investigators using flowing junctions. These half-cells remained constant almost six months during the period of observation. The voltage of these half cells referred to the normal hydrogen electrode in alcohol was determined by measurement against the silver–silver chloride electrode

---

[1] Goodhue and Hixon, THIS JOURNAL, **56**, 1329 (1934).

[2] Goldschmidt, *Z. physik. Chem.*, **99**, 116 (1921); Goldschmidt and Aas, *ibid.*, **112**, 423 (1924); Goldschmidt and Mathiesen, *ibid.*, **119**, 439 (1926).

[3] Goodhue, Schwarte and Fulmer, *Iowa State College J. Sci.*, **7**, 111 (1933).

[4] Ellis and Kiehl, *Rev. Sci. Inst.*, **4**, 131 (1933).

[5] MacFarlane and Hartley, *Phil. Mag.* [7] **13**, 425 (1932).

[6] Danner, THIS JOURNAL, **44**, 2832 (1922).

[7] Harned and Fleyscher, *ibid.*, **47**, 82 (1925).

[8] Woolcock and Hartley, *Phil. Mag.*, [7] **5**, 1133 (1928).

[9] Johns and Hixon, *J. Phys. Chem.*, **34**, 2226 (1930).

in 0.01 *m* lithium chloride and by measurement against an alcoholic solution of hydrogen chloride. The experience in this Laboratory would indicate that the mercury–mercuric iodide half-cells are the most satisfactory reference electrodes for both methyl and ethyl alcohol solutions.

The average of ten closely agreeing values for the cell

Hg/HgI_2 (0.005 *m*) KI (0.05 *m*)//LiCl (0.01 *m*) AgCl/Ag

was found to be 0.3098 volt. Using the same calculations[10] as in water solutions and the mobilities of the ions in ethanol,[11] the liquid junction potential was calculated to be −0.0049 volt. The value of the silver–silver chloride electrode in 0.01 *m* lithium chloride is given by MacFarlane and Hartley[5] as 0.0594 volt positive to hydrogen. The value of the alcoholic mercury–mercuric iodide half-cells can be calculated from these values as

$$-0.3098 - 0.0049 + 0.0594 = -0.2553 \text{ volt}$$

referred to the normal hydrogen electrode in ethanol.

The e. m. f. was found to be −0.1431 volt for the cell

Pt/H_2 (1 atm.) HCl (0.169 *m*)//KI (0.05 *m*) HgI_2 (0.005 *m*)/Hg

The value for the hydrogen half-cell can be calculated as −0.0853 from the activity data of Woolcock and Hartley.[8] The value for the liquid junction can be calculated as −0.0262 by the method described above. Combining these values gives

$$-0.1431 - 0.0262 - 0.0853 = -0.2546 \text{ volt}$$

as the value for the alcoholic mercury–mercuric iodide half cells referred to the normal hydrogen electrode in ethanol. The average of the values obtained by the two independent methods, 0.2550 volt, was used in calculating the hydrogen-ion activities of the ethanol solutions of the acids and amines reported in this paper.

The mercuric iodide half-cells were found to be equally satisfactory when methanol was used as a solvent. The cell

Hg/HgI_2 (0.005 *m*) KI (0.05 *m*)//KI (0.05 *m*) HgI_2 (0.01 *m*)/Hg

gave a value of 0.0137 volt in methanol which remained constant more than one month. New half-cells made up at the end of one month and checked against the old cells showed voltages of less than 0.2 millivolt. The value referred to the normal hydrogen electrode in methanol was obtained by measuring the cell

Hg/HgI_2 (0.005 *m*) KI (0.05 *m*)//NaCl (0.1 *m*) AgCl/Ag

which gave a voltage of −0.2737. Applying the correction of 0.0026 volt for liquid junction potentials and adding 0.0711 volt which is the value of the silver–silver chloride electrode in 0.1 *m*

TABLE I

E. M. F. OF CELLS FOR A SERIES OF HALF NEUTRALIZED ORGANIC ACIDS AND PRIMARY AMINES IN ETHANOL

Pt/H_2 (1 atm.) acid (amine)//KI (0.05) HgI_2 (0.005 *m*)/Hg
salt (salt)

Total acid or amine concn.	E. m. f. corr. to 760 mm.	−log *H*	−log K_{EtOH}
	Acetic acid		
0.0106	0.3589	10.39	
.0212	.3563	10.35	
	p-Toluic acid		
0.0200	0.3600	10.41	
.0200	.3597	10.40	
	Benzoic acid		
0.0200	0.3460	10.17	
.0200	.3478	10.20	
	p-Bromobenzoic acid		
0.0200	0.3149	9.64	
.0200	.3154	9.65	
	m-Chlorobenzoic acid		
0.0200	0.3106	9.57	
.0200	.3089	9.54	
	n-Butylamine		
0.0322	0.4391	11.74	7.40
.0325	.4409	11.77	7.37
	o-Chlorobenzylamine		
0.0210	0.3341	9.97	9.17
.0206	.3338	9.96	9.18
	p-Toluidine		
0.0209	.1436	6.75	12.39
.0163	.1412	6.70	12.44
	Aniline		
0.0482	.1108	6.19	12.95
.0323	.1115	6.20	12.94
.0329	.1104	6.18	12.96
	m-Chloroaniline		
0.0393	0.002[a]	4.35	14.79
.0422	.001[a]	4.33	14.81

[a] These values are probably slightly low due to the reduction by the hydrogen electrode.

---

(10) The following equations were used to calculate the value of this and other liquid junctions in this paper.

$$E_L = \frac{\Lambda_c - \Lambda_a}{\Lambda_c + \Lambda_a}\frac{RT}{F}\log\frac{c_1}{c_2}$$
$$E_L = \frac{RT}{F}\log\frac{\Lambda_c + \Lambda_a}{\Lambda_c' + \Lambda_a}$$
$$E_L = -\frac{RT}{F}\log\frac{\Lambda_c + \Lambda_a}{\Lambda_c + \Lambda_a'}$$

(11) Barak and Hartley, *Z. physik. Chem.*. **A165**, 272 (1933).

sodium chloride[12] the value −0.2032 v. is obtained for the mercuric iodide half-cell in methanol.

The absolute ethyl alcohol was prepared by fractionating large quantities of commercially available absolute alcohol through a 91-cm. Hempel column, discarding the first and last thirds. The specific gravity before treatment indicated the purity to be between 99.8 and 99.9%. After the treatment the specific gravity of a typical sample was found to be 0.78743 compared to 0.78736 as reported for pure ethanol *in vacuo* at 25°.

The acids and amines were prepared and measured in half neutralized solution according to the technique reported in the preceding paper.[1] The values recorded in the tables are the average for two electrodes checking to less than 1 millivolt. Total concentrations are reported in molalities.

Discussion of Results

In the preceding publication the effect of the solvent upon the dissociation constant of the organic acids and primary amines was shown to be a constant and additive factor which is to be expected from Brönsted's[13] generalization. Original data were presented using methanol as the solvent and the generalization based on some scattered values reported by Goldschmidt[2] was extended to ethanol and the following equations were proposed for the acids and amines.

$$K_{aC_2H_5OH} = y = 20e^{0.5x-5.6} - 10.64 \qquad (1)$$
$$K_{bC_2H_5OH} = y = 20e^{0.05x} + 11.02 \qquad (2)$$

The dissociation constants reported in this paper were determined in order to further check these equations.

The experimental procedure used in this investigation is directly analogous to that used for the determination of ionization constants for weak organic acids and amines in water solution. The calculation of the constants has therefore been made in the same manner as for water solutions. The values obtained in this way are considered sufficiently accurate for this purpose but are subject to further refinement as more extensive data concerning ion activities in ethanol are made available.

The hydrogen-ion activities were calculated by the equation

$$-\log \alpha_H = (E + 0.2550)/0.0591$$

The value 0.2550 in the above equation is the voltage determined for the mercuric iodide half-cell which was used as a reference electrode. The ionization constants for the acids were considered equal to the hydrogen-ion activity of the half neutralized solutions. The constants for the amines were calculated by the equation

$$K_{BC_2H_5OH} = (7.28 \times 10^{-20})/\alpha_H$$

using the value 7.28×10^{-20} given by Danner for the dissociation constant of ethyl alcohol. A comparison is made in Table II of the values obtained by the above method, the values obtained by Goldschmidt[2] from conductimetric methods and the values calculated from equations (1) and (2). The values determined by the hydrogen electrode as calculated above are slightly lower than the values reported by Goldschmidt, which is probably due to an error introduced by the liquid junction potential. Methods developed by Harned and others to eliminate this error are not generally applicable in alcoholic solutions due to the very limited range of solubility of these compounds.

TABLE II

A COMPARISON OF THE MEASURED AND CALCULATED DISSOCIATION CONSTANTS FOR A SERIES OF AMINES AND ACIDS IN ETHANOL

		log *K* in ethanol		
Substance	Value of *X*	Conductimetric[a]	Hydrogen electrode[b]	Calcd.[c]
Acetic acid	−1.65	...	10.39	10.61
p-Toluic acid	3.40	...	10.40	10.24
Benzoic acid	3.95	10.43	10.20	10.09
p-Bromobenzoic acid	4.90	...	9.65	9.78
m-Chlorobenzoic acid	5.10	...	9.57	9.68
n-Butylamine	−1.65	...	7.40	7.38
o-Chlorobenzylamine	0.15	...	9.18	9.12
p-Toluidine	3.40	12.91	12.42	12.68
Aniline	3.95	13.44	12.95	13.34
m-Chloroaniline	5.10	14.94	14.80	14.78

[a] Reported by Goldschmidt.[2] [b] Determined as reported in this manuscript. [c] Calculated from equations 1 and 2 in this publication.

Compounds containing the benzene ring were measured with palladium black as the catalyst on the hydrogen electrode. No reduction occurred and very good readings were obtained. Compounds not capable of being reduced such as *n*-butylamine gave identical readings with either platinum or palladium black. The dissociation constants of halogen substituted compounds are difficult to measure with either electrode in ethyl alcohol. The more active halogen compounds cannot be measured satisfactorily under any of the conditions so far attempted. With the more

---

[12] Buckley and Hartley, *Phil. Mag.*, [7] **8**, 320 (1929).

[13] Brönsted, *Chem. Rev.*, **5**, 291 (1928).

inactive halogen compounds, a better reading can usually be obtained with the platinum black electrode as would be expected from the use of palladium for the specific purpose of the catalytic reduction of halogen compounds. Numerous attempts to use the glass electrode have failed. Dole[14] also points out that the glass electrode cannot be used in non-aqueous solutions where the activity of the water is very low.

In using the hydrogen electrode in alcoholic solutions, difficulties of the type indicated are readily recognized by the behavior of the electrode during measurements. If reduction takes place, duplicate electrodes will not agree to 0.5 millivolt and interruption of the hydrogen stream will cause a rapid change in voltage. Also, a change in the rate at which hydrogen is being bubbled into the solution will cause a fluctuation in the voltage. With these criteria as a guide, it seems probable that all of the measurements reported are accurate to within 0.1 *pK* unit with the possible exception of the value for *m*-chloroaniline in ethyl alcohol. The value for this compound is close to the value obtained by Goldschmidt but it is doubtful if the maximum voltage was ever reached.

Summary

1. The dissociation constants have been measured by means of the hydrogen electrode for a series of acids and amines in ethanol.

2. The mercury–mercuric iodide half cell was found to be easily reproducible and stable as a reference electrode for both methyl and ethyl alcohols.

3. The behavior of the platinum black and the palladium black electrodes as well as the glass electrode in alcoholic solutions has been discussed.

AMES, IOWA RECEIVED JANUARY 22, 1935

---

[14] Dole, THIS JOURNAL, **54**, 3095 (1932).

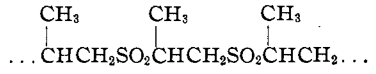
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Reaction between Sulfur Dioxide and Olefins. II. Propylene

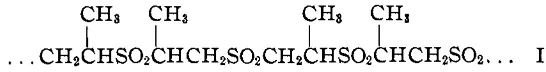
BY MADISON HUNT AND C. S. MARVEL

Sulfur dioxide and propylene combine to give a product $(C_3H_6SO_2)_n$ which differs markedly in physical and chemical properties from the polysulfone which has been obtained from cyclohexene and sulfur dioxide.[1] The propylene derivative is unusual in that it is quite insoluble in all organic solvents and is soluble in dilute aqueous alkalies; but it is very easily decomposed by the alkalies to yield fairly simple products. Staudinger and Ritzenthaler[2] have recently described polypropylenesulfone, but apparently have not noticed that it differs considerably from the other olefin sulfur dioxide addition compounds that have been described.

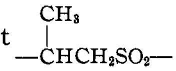
The addition of sulfur dioxide to propylene might lead to either of two polymeric sulfones, I or II. It is also possible that the polymeric sulfone might contain both of these type structures mixed together in a single molecule. Such a mixed structure would not be expected, nor is it supported by the work described in this communication.



$$\ldots\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}\mathrm{HCH_2SO_2}\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}\mathrm{HCH_2SO_2}\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}\mathrm{HCH_2}\ldots$$

 II

$$\ldots\mathrm{CH_2}\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}\mathrm{HSO_2}\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}\mathrm{HCH_2SO_2CH_2}\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}\mathrm{HSO_2}\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}\mathrm{HCH_2SO_2}\ldots$$

A molecule of type I would be expected on the basis of the structures which have been assigned to other polymers formed by addition reactions. Each sulfone linkage in this type is like every other sulfone linkage and alkaline degradation of a molecule of this structure should yield multiples of the building unit  $-\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}\mathrm{HCH_2SO_2}-$ or simple derivatives of it. On the other hand, the second type of structure (II) contains two types of sulfone linkages, one between secondary alkyl groups, the next between primary alkyl groups, and so on alternately throughout the chain. Fenton and Ingold[3] have shown that a sulfone linkage between two secondary alkyl groups is more easily cleaved by alkali than is such a linkage between two primary alkyl groups, hence a polymeric sulfone of type II should be degraded by alkalies to produce

---

[1] Frederick, Cogan and Marvel, THIS JOURNAL, **56**, 1815 (1934).

[2] Staudinger and Ritzenthaler, *Ber.*, **68**, 455 (1935).

[3] Fenton and Ingold, *J. Chem. Soc.*, 2338 (1929).