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

Electron-Sharing Ability of Organic Radicals. VII. Dissociation Constants of a Series of Organic Acids and Amines in Water, Methanol and Ethanol

BY LYLE D. GOODHUE AND R. M. HIXON

A recent discussion of the role of the solvent in acid–base equilibria was given by Hall[1] at the Cincinnati symposium on non-aqueous solutions. Opinion regarding the solvent influence on the physical properties of the solute may be divided into two divergent schools. The summary of Brönsted[2] would indicate that the solvent influence is a constant and additive factor at least for acids and bases in alcoholic solution. Conant,[3] however, considers that the simplest relationships between the structures of compounds and the free energy changes of their reactions will be found in the gaseous state.

It is apparent that an attempt to compare the relative affinities of organic radicals by measuring the electrical properties of polar groupings attached to these radicals cannot be successful if the solvent influence on the free energies of the polar groupings is erratic. As previously stated,[4] it would be expected that the variations in the electrical properties of any polar grouping could be expressed as a function of the electron-sharing ability of the organic radical attached to it. If the polar grouping formed a complex with the solvent, this complex would be expected to be of a characteristic structural type for that particular polar grouping and solvent. The free energy of the polar grouping with its solvent complex would still be a function of the electron-sharing ability of the organic radical, since this is the only variable factor affecting the polar grouping. Erratic or irregular influences due to the solvent would be expected only if the radical contained atoms other than the polar grouping which united with the solvent. If these latter complexes did not themselves dissociate to form electrically charged bodies which would interfere with the measurements for the polar grouping, disturbing influences would be expected only if the second union were located with but four[5] or less atoms between it and the polar grouping.

Goldschmidt's[6] data for the comparative basic strengths of the acids and amines were obtained by the measurement of the degree of alcoholysis of the salts using conductimetric methods. For comparative purposes in extending the measurements to other compounds, it seemed advisable to make duplicate measurements on some of Goldschmidt's compounds using a hydrogen electrode in methanol solutions. A series of four α-substituted pyrrolidines was also measured to demonstrate that the constant influence of the solvent was not limited to the structures characterized by the primary amines and acids. The measurements reported in this paper are limited to methanol solutions.

Experimental Part

The high internal resistance of alcoholic solutions causes considerable difficulty in the measurement of the e. m. f. of cells by ordinary methods. The vacuum tube potentiometer arrangement designed for eliminating this difficulty with the glass electrode in water solutions was equally satisfactory with the alcoholic solutions. The instrument in use in this Laboratory[7] gave a precision of ±0.1 millivolt on cells of the type reported below. All measurements were made in an air-bath at 25° with a control constant to ±0.1°. The Weston standard cell was checked against two cells certified by the Bureau of Standards.

The calomel half cells in methyl alcohol are not constant in voltage and, although convenient to use as reference cells, they must be standardized. The silver–silver chloride electrode was used for this purpose as recommended by Buckley and Hartley.[8] The electrodes were prepared by the electrolytic method of MacInnes and Beattie[9] but were electrolyzed with a current of five milliamperes per electrode for twenty minutes in 0.1 *f* methyl alcohol solution of sodium chloride. The

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(1) Hall, *Chem. Rev.*, **8**, 191 (1932).

(2) Brönsted, *ibid.*, **5**, 291 (1928).

(3) Conant, *Ind. Eng. Chem.*, **24**, 466 (1932).

(4) Hixon and Johns, THIS JOURNAL, **49**, 1786 (1927).

(5) This statement is based on the fact that the influence of the most negative radicals seems to be absorbed completely before transmission through four carbon atoms.

(6) Goldschmidt, *Z. physik. Chem.*, **99**, 116 (1921); Goldschmidt and Aas, *ibid.*, **112**, 423 (1924); Goldschmidt and Mathieson, *ibid.*, **119**, 439 (1926).

(7) Goodhue, Schwarte and Fulmer, *Iowa State Coll. J. Sci.*, **7**, 111 (1933).

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

(9) MacInnes and Beattie, THIS JOURNAL, **42**, 1117 (1920).

electrodes were prepared in duplicate and were reproducible to ±0.2 millivolt.

The calomel half-cells with 0.1 *f* sodium chloride in methyl alcohol used as reference electrodes were always maintained at least in duplicate. The e. m. f. of the cells measured against the silver–silver chloride electrode dropped during the first month from about 0.0475 to 0.0437 volt. Two of these cells after being used by a number of individuals without special precautions over a twelve-month period had an e. m. f. of 0.0458 and 0.0465 volt. Buckley and Hartley report the value of the silver–silver chloride electrode as 0.0711 volt when referred to the normal hydrogen electrode in methanol as zero. This value should be added to the above values of the calomel half cells to give their voltages in reference to the normal hydrogen electrode in methanol.

Both palladium and platinum black were used as catalysts for the hydrogen electrodes. Identical potentials were obtained with these electrodes with compounds not capable of being reduced. The palladium black coating gave more satisfactory measurements with compounds containing the benzene ring. Both electrodes were too active to give satisfactory measurements with the nitro compounds or with the chloroacetic acids, reduction being extremely rapid. Platinum flags were used for both catalysts, the platinum black was deposited from a 3% platinic chloride solution with a current of one-half ampere for three or four minutes; the palladium black was deposited in the same way from a 1% palladium chloride solution. The electrodes were electrolyzed in dilute aqueous sulfuric acid for five minutes, washed several times in 99% alcohol, then in absolute methanol several times to remove traces of moisture.

The cells containing the hydrogen electrodes were constructed so that the hydrogen gas bubbled from the bottom of the cells over the flags. The gas was saturated by bubbling through methanol before entering the cells. Each cell contained two electrodes which generally came to equilibrium within fifteen minutes and gave identical and constant readings (±0.0002 volt) for five hours. The results were rejected if the results varied more than 0.5 millivolt between the two electrodes. The electrodes did not poison easily and could be used repeatedly but to eliminate any uncertainty the electrodes were freshly prepared for each measurement.

The junction between the hydrogen half-cell and the calomel half-cell was made through a glass stopcock kept closed all of the time. Partington and Simpson[10] have shown that liquid junction potentials in concentration cells of sodium iodide in ethyl alcohol can be eliminated by a bridge of saturated potassium thiocyanate. Buckley and Hartley[8] have used a saturated solution of sodium iodide in methyl alcohol but without completely eliminating the liquid junction potential. In a number of cases during this investigation, a saturated potassium thiocyanate or sodium iodide bridge was introduced after the cell had come to equilibrium. In no case was the voltage changed by more than one millivolt by these changes in type of junction.

The absolute methyl alcohol was prepared by the method of Hartley and Raikes.[11] The purity was checked by density and by the calcium carbide–cuprous chloride test recommended by these authors.

In the primary amine series, the *o*-chlorobenzylamine was prepared from *o*-chlorobenzaldehyde by the method of Franzen.[12] The other amines and the acids were purified by fractional distillation or fractional crystallization from purchased stocks. The α-substituted pyrrolidines were furnished by Starr and Bulbrook[13] of this Laboratory.

In the amine series the half neutralized solutions were prepared by weighing equivalent molal quantities of the free base (in ampules) and the hydrochloride salt. In those cases where the salt was not sufficiently stable to purify, the half neutralized solutions were obtained by adding the calculated amount of alcoholic hydrogen chloride to weighed amounts of the free base. The alcoholic hydrogen chloride solution was freshly prepared and never used more than three hours after preparation. The content of hydrogen chloride was determined in each case by titration against standard aqueous solutions.

In the acid series, benzoic, *p*-bromobenzoic and *p*-toluic acids form stable half-neutralized salts which can be recrystallized from alcohol. These were prepared, dried over phosphorus pentoxide and checked for purity by titration. In the other cases, the half-neutralized solutions were prepared by weighing equivalent molal quantities of the free acid and sodium or potassium salt.

All solutions were made by weight and the concentrations are expressed in terms of molality. The solutions were measured within three hours after preparation. Repeated tests showed no detectable difference in hydrogen-ion activity of the half neutralized solutions after five hours, indicating that esterification is not appreciable under these conditions.

The data for the series of organic acids are reported in Table I. The e. m. f. recorded for each concentration is the average of two hydrogen electrodes agreeing to 0.5 millivolt or less. Similar values are recorded in Table II for a

TABLE I

E. M. F. OF CELLS FOR A SERIES OF ORGANIC ACIDS IN METHANOL

Pt/H_2 (1 atm.) Acid // NaCl (0.1 *f*) Hg_2Cl_2/Hg
salt

Substance	Total acid concn.	E. m. f. corr. to 760 mm.	$-\log a_H$
Acetic acid	0.0382	0.6688	9.33
	.0346	.6702	9.36
p-Toluic acid	.0411	.6683	9.33
	.0428	.6683	9.33
Benzoic acid	.0400	.6554	9.11
	.0545	.6558	9.12
p-Bromobenzoic acid	.0340	.6630	8.73
	.0346	.6635	8.74
m-Chlorobenzoic acid	.0447	.6237	8.55
	.0531	.6225	8.58

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(10) Partington and Simpson, *Trans. Faraday Soc.*, **26**, 625 1930).

(11) Hartley and Raikes, *J. Chem. Soc.*, 524 (1925).

(12) Franzen, *Ber.*, **38**, 1417 (1905).

(13) Starr, Bulbrook and Hixon, THIS JOURNAL, **54**, 3971 (1932); Craig and Hixon, *ibid.*, **53**, 4367 (1931).

series of primary amines and for four α-substituted pyrrolidines. An attempt was made to measure the corresponding pyrrolines but the reduction of these compounds by the hydrogen electrode was so rapid that constant readings could not be obtained. Similar difficulties were encountered with nitro substituted compounds and with dichloroacetic acid.

TABLE II

E. M. F. OF CELLS FOR A SERIES OF PRIMARY AMINES AND α-SUBSTITUTED PYRROLIDINES IN METHANOL

Pt/H_2 (1 atm.) Amine // NaCl (0.1 *f*) Hg_2Cl_2/Hg
salt

Substance	Total amine concn.	E. m. f.	$-\log a_H$	$-\log K_{MeOH}$
n-Butylamine	0.0972	0.8113	11.78	4.92
	.0606	.8120	11.79	4.92
o-Chlorobenzylamine	.0751	.7152	10.16	6.61
	.0524	.7154	10.16	6.61
p-Toluidine	.1001	.5132	6.74	9.97
	.0600	.5123	6.73	9.98
	.0536	.5100[a]	6.68	10.02
	.0217	.5106[a]	6.69	10.00
Aniline	.0635	.4792	6.17	10.54
	.0644	.4803	6.19	10.52
m-Chloroaniline	.0361	.3839	4.55	12.15
	.0589	.3854	4.58	12.13
α-Cyclohexylpyrrolidine[b]	.0359	.8123	11.81	4.90
	.0334	.8140	11.84	4.87
α-Benzylpyrrolidine	.0413	.7820	11.29	5.42
	.0317	.7823	11.29	5.42
α-(*p*-Tolyl)-pyrrolidine	.0239	.7682	11.05	5.66
	.0310	.7662	11.02	5.69
α-Phenylpyrrolidine	.0396	.7576	10.87	5.83
	.0381	.7572	10.87	5.83

[a] These values were determined independently by C. L. Mehltretter. The solutions and the remaining ones below were made by half neutralizing the amine with hydrochloric acid in methyl alcohol. The solutions above this point were made from equal molal quantities of the amine and its hydrochloride salt.

[b] The α-substituted pyrrolidines were prepared in this Laboratory by Helen Bulbrook and D. F. Starr.

Discussion of Results

The experimental procedure reported above is directly analogous to the procedure for determining the ionization constants for weak organic acids and primary amines in water solutions. The calculations of the ionization constants for the methanol solutions have likewise been made directly parallel to the corresponding calculations for water solutions. The values obtained in this way are subject to further precision as a more refined technique is developed and a more extensive knowledge of ion activities in methanol is made available.

The hydrogen-ion activities were calculated by the equation

$$-\log A_H = \frac{E - E_{\text{calomel}}}{0.0591}$$

which is analogous to the equation for water solutions. The value of the calomel half-cell was 0.1148 volt during the time the amines were measured and 0.1169 volt during the time that the acids were measured.

The ionization constants for the acids in methanol were taken as identical numerically with the measured hydrogen-ion activities in analogy with the procedure for water solutions at half neutralization.

The ionization constants for the amines were calculated from the hydrogen-ion activities of the half neutralized solutions by the equation

$$K_{BCH_3OH} = 1.95 \times 10^{-17}/\text{H ion activity}$$

The value 1.95×10^{-17} given by Buckley and Hartley[8] for the dissociation constant of methanol was taken since the standard electrode potentials were also from the work of the same authors. The values given by Bjerrum, Unmack and Zechmeister,[14] 1.07×10^{-17} and 0.9×10^{-17}, are in good agreement with this value. For the ethanol solutions, the value 7.28×10^{-20} given by Danner[15] was used to calculate the dissociation constants from the data of Goldschmidt.

A comparison of the values for *p*-toluidine, aniline and *m*-chloroaniline in Table IV and for acetic acid in Table III indicates that the values obtained and calculated by the above procedure

TABLE III

A COMPARISON OF THE MEASURED AND CALCULATED IONIZATION CONSTANTS FOR A SERIES OF ORGANIC ACIDS IN WATER, METHANOL AND ETHANOL

		Log K_A in					
	Value	Water		Methanol		Ethanol	
Acid	of *x*	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.
Acetic	−1.65	4.77	4.73	9.61	9.65[b] 9.34[a]		
Formic	−0.40	4.74	3.68			10.58	11.15
Phenylacetic	− .20	4.73	4.26			10.57	10.34
p-Toluic	3.40	4.40	4.29	9.24	9.33[a]		
Benzoic	3.95	4.25	4.18	9.09	9.12[a]	10.09	10.43
p-Bromobenzoic	4.90	3.94		8.78	8.74[a]		
m-Chlorobenzoic	5.10	3.84	3.82	8.68	8.57[a]		
m-Nitrobenzoic	5.74	3.47	3.50			9.31	9.17
p-Nitrobenzoic	5.90	3.36	3.40			9.20	9.13
Salicylic	6.30	3.02	2.99	7.86	7.88		
3,5-Dinitrobenzoic	6.65	2.74	2.82	7.58	7.44	8.58	8.09
o-Nitrobenzoic	7.20	2.10	2.19			7.94	8.63
2,4-Dinitrobenzoic	7.60	1.50	1.40	6.34	6.47	7.34	7.33
Dichloroacetic	7.65	1.39	1.28	6.23	6.33	7.23	7.28

The values indicated by (*a*) have been determined in this laboratory; the value indicated by (*b*) is reported by Bjerrum;[14] all other values are from the work of Goldschmidt.[6] The value of *x* for the electron sharing ability of the radical was determined graphically.

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(14) Bjerrum, Unmack and Zechmeister, *Kgl. Danske Videnskab. Selskab Math. fys. Medd.*, **6**, No. 11, 34 (1925).

(15) Danner, THIS JOURNAL, **44**, 2832 (1922).

TABLE IV

A COMPARISON OF THE MEASURED AND CALCULATED IONIZATION CONSTANTS OF A SERIES OF PRIMARY AMINES IN WATER, METHANOL AND ETHANOL

Base	Value of x	—Log K_B in— Water Calcd.	Water Obs.	Methanol Calcd.	Methanol Obs.	Ethanol Calcd.	Ethanol Obs.
n-Butylamine	−1.65	3.40	3.39	4.88	4.92[a]		
Ammonia	−0.40	4.60	4.74	6.08	5.92[b]	8.58	8.66
o-Chlorobenzylamine	0.15	5.15	5.20[c]	6.62	6.61[a]		
p-Toluidine	3.40	8.70	8.76	10.18	10.00[a] 10.02	12.68	12.91
m-Toluidine	3.85	9.24	9.20	10.72	10.80	13.22	13.24
Aniline	3.95	9.36	9.30	10.84	10,53[a] 10.70	13,34	13.44
o-Toluidine	4.05	9.48	9.50	10.96	10.80	13.46	13.54
α-Naphthylamine	4.25	9.74	9.72	11.22	11.20	13.72	14.84
β-Naphthylamine	4.45	9.98	10.03	11.46	11.40	13.96	14.04
p-Chloroaniline	4.65	10.24	10.00	11.72	11.80	14.12	14.44
p-Bromoaniline	4.90	10.54	10.06	12.02	11.90	14.42	14.64
m-Chloroaniline	5.10	10.80	10.40	12.28	12.14[a] 12.30	14.78	14,94
m-Bromoaniline	5.10	10.80	10.42	12.28	12.30	14.78	14.94
o-Chloroaniline	5.90	11.86	12.05	13.34	13.15	15.84	15,84
o-Bromoaniline	5.95	11.92		13.40	13.30	15.90	16.04

The values indicated by (*a*) have been determined in this Laboratory; the value indicated by (*b*) has been reported both by Bjerrum[14] and Goldschmidt;[6] the value indicated by (*c*) has been determined by Ware (unpublished); all other values have been calculated from the work of Goldschmidt.[6]

are in approximate agreement with the values obtained by Goldschmidt by conductimetric measurement of the degree of alcoholysis of the salts. The values calculated from the concentration cell measurements are consistently lower than the values obtained by Goldschmidt.

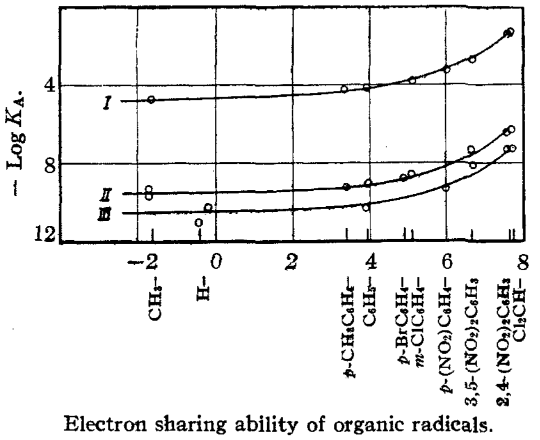


Fig. 1.—The ionization constants of various acids in water (I), in methanol (II) and in ethanol (III) plotted as functions of the electron sharing ability of the organic radicals.

A graphical presentation of the data of Tables III and IV is given in Figs. 1 and 2, respectively. The curves have been drawn by the equations

$$\log K_{\mathrm{BH_2O}} = y = -20e^{0.95x} + 15 \quad (1)$$
$$\log K_{\mathrm{BCH_3OH}} = y = -20e^{0.95x} + 13.52 \quad (2)$$
$$\log K_{\mathrm{BC_2H_5OH}} = y = 20e^{0.95x} + 11.02 \quad (3)$$
$$\log K_{\mathrm{a}}\ \mathrm{H_2O} = y = 20e^{0.5x-5.6} - 4.8 \quad (4)$$
$$\log K_{\mathrm{a}}\ \mathrm{CH_3OH} = y = 20e^{0.5x-5.6} - 9.64 \quad (5)$$
$$\log K_{\mathrm{a}}\ \mathrm{C_2H_5OH} = y = 20e^{0.5x-5.6} - 10.64 \quad (6)$$

Equations 1 and 4 for water solutions are those previously proposed. It will be noted that the equations 1, 2 and 3 for the amines and 4, 5 and 6 for the acids vary only in the value of the constants, as would be expected from Brönsted's[2] generalization.

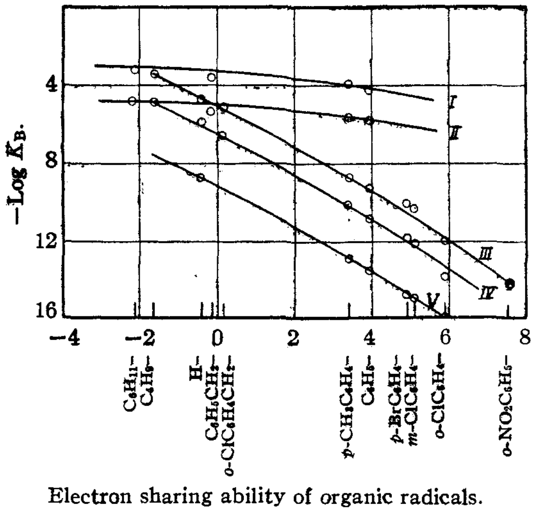


Fig. 2.—The ionization constants of various primary amines in water (III), in methanol (IV) and in ethanol (V) plotted as functions of the electron sharing ability of the organic radicals. Values for corresponding α-substituted pyrrolidines are shown in water (I) and in methanol (II).

The agreement between the measured values and the values calculated by the above equations can be seen in Tables III and IV. The irregularity in the case of formic acid was noted in the first paper[4] and attention should be called to the fact that this irregularity is less in the case of the ethanol measurement than in the case of the water measurement. The greatest deviations are to be found in the values reported by Goldschmidt for the acids in ethanol solution. It should be noted that this irregularity for the ethanol solutions does not hold for his measurements of the amines in the same solvent, all of the amine values being in substantial agreement with the calculated values. With the exception of formic acid, these deviations would appear to be associated with the less soluble compounds and are probably due to the deviations characteristic of saturated solutions. This point can be checked only as additional data are made available.

The ionization constants in methanol of the α-substituted pyrrolidines have been plotted in Fig. 2 to show that they also have a similar relationship to the corresponding values in water.[13] Attention should also be called to the fact that the equilibrium constants for the reaction

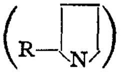
$$R_2Hg + HgI_2 \rightleftharpoons RHgI$$

previously reported[16] were for ethanol solutions and that these values can be expressed as a mathematical function of this same order of the organic radicals.

Summary

1. The ionization constants of acetic, *p*-toluic, benzoic, *p*-bromobenzoic and *m*-chlorobenzoic acids; of *n*-butylamine, *o*-chlorobenzylamine, *p*-toluidine, aniline, and *m*-chloroaniline; of the α-cyclohexyl-, α-benzyl-, α-(*p*-tolyl)-, and α-phenyl-pyrrolidines have been measured in methanol solutions using concentration cell methods analogous to the common procedure for water solutions.

2. The experimental difficulties in the measurement of the e. m. f. of alcoholic solutions due to the high internal resistance of the cells can be eliminated by the use of the vacuum tube potentiometer arrangement devised for measurements with the glass electrode in water solutions.

3. The ionization constants of the organic acids (R—COOH), of the primary amines (R—NH_2), and of the α-substituted pyrrolidines  can be expressed as a mathematical function of the electron sharing ability of the variable organic radicals (R) in the three solvents water, methanol and ethanol.

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

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF IOWA STATE COLLEGE]

Electron-Sharing Ability of Organic Radicals. VIII. The Condensation of Mercaptans with Chloral

BY I. B. JOHNS AND R. M. HIXON

Earlier papers of this series have shown the relationship between an empirically determined property of organic radicals, the electron-sharing ability, and the polar properties of a number of series of compounds. The reactions studied can be grouped in the following classes: (A) ionizations in ionizing solvents—(1) in water, the ionization of the carboxylic acids,[1] the primary amines,[1] the organomercury nitrates,[2] the α-substituted pyrrolidines,[3,4] the α-substituted pyrrolines,[4] and the N-substituted pyrrolidines;[3] (2) in methanol, the ionization of the carboxylic acids,[5] the primary amines,[5] and the substituted pyrrolidines;[5] (3) in ethanol, the ionization of the carboxylic acids,[5] and the primary amines.[5] (B) Metathesis in ethanol: (1) The reversible change of the organomercury iodides into mercuric iodide and di-organo mercury.[6]

These investigations have proved beyond doubt the hypothesis made in the first paper, that "The polar properties of any series of compounds such as ROH, RCOOH, ..., RNH_2, ..., etc., must be a function of the electron-sharing ability of R if we exclude from consideration under R all groupings which themselves have polar linkages."

The organic chemist is often more interested in nonionic reactions which may or may not be reversible. As yet, the only recognized measure of chemical affinity in a reaction is the diminution

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[1] Hixon and Johns, THIS JOURNAL, **49**, 1786 (1927).

[2] Johns and Hixon, *J. Phys. Chem.*, **34**, 2218 (1930).

[3] Craig and Hixon, THIS JOURNAL, **53**, 4367 (1931).

[4] Starr, Bulbrook and Hixon, *ibid.*, **54**, 3971 (1932).

[5] See accompanying paper.

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