[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF BROOKHAVEN NATIONAL LABORATORY]

The Ionization Constants at 50° of *m*- and *p*-Iodoxybenzoic Acids[1]

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The ionization constants of benzoic, *m*-iodobenzoic, *p*-nitrobenzoic, *m*-iodoxybenzoic and *p*-iodoxybenzoic acids in aqueous solutions at 50° have been determined from *p*H–titration curves. The Hammett ρ-function was calculated from the pK_a's of the first three acids and their accepted σ values as 1.09 ± 0.03. The σ-function values for the *m*- and *p*-iodoxy groups were calculated to be 0.63 ± 0.03 and 0.69 ± 0.03, respectively.

Introduction

The bulk of the work on the chemistry of iodoxy-substituted aromatic compounds which has appeared in the chemical literature has been of a preparative nature.[2] The study of structure and reactions has been hindered by the relative insolubility of most compounds of this class, their extreme ease of reduction to the corresponding iodo compounds, and their explosiveness. Such studies as have been made indicate that the iodoxy group is a strongly electron-withdrawing group, and that this effect is largely an inductive one.[3]

In order to obtain information bearing on this point, we have made a study of the ionization constants of *m*- and *p*-iodoxybenzoic acids with a view to determining the Hammett σ-constants[4] for the iodoxy group. The ionization constants were calculated from *p*H–titration curves. Because of the limited solubility of the acids in water at room temperature, it was necessary to operate at 50°. Even at this temperature, the solubility of the iodoxy acids amounted to only about 0.8 mg./ml. The ρ-constant for the ionization of benzoic acids at 50° was found from a plot of the pK_a's of benzoic, *m*-iodobenzoic and *p*-nitrobenzoic acids *versus* the corresponding σ-constants given in Hammett's table,[5] and the σ-values for the *m*- and *p*-iodoxy groups are obtained from this linear plot and the experimentally found ionization constants of the corresponding acids.

Experimental[6]

Materials. Benzoic Acid.—National Bureau of Standards sample No. 140 benzoic acid was stored in a desiccator and used as needed.

***m*-Iodobenzoic Acid.**—Eastman Kodak Co. white label *m*-iodobenzoic acid was recrystallized twice from distilled water (1 g./l.) and dried in a vacuum desiccator for 3 days. The melting range was 186.5–187.0°; reported in the literature[7]: 186.6–186.8°; the neut. equiv. calcd., 248; determined during the titrations, 254.

***p*-Nitrobenzoic Acid.**—Eastman Kodak Co. white label *p*-nitrobenzoyl chloride was hydrolyzed by allowing it to stand with an excess of 5% sodium hydroxide overnight. The solution was filtered, and the acid precipitated by addition of excess 3 *N* hydrochloric acid. The acid was recrystallized twice from distilled water (1 g./l.), and air-dried for two weeks. It then melted in the range 240.0–240.8°; literature: 240°,[8] 241°.[9] The neut. equiv. calcd.: 167; found: 168.5.

***m*-Iodoxybenzoic Acid.**—Eastman Kodak Co. white label *m*-iodobenzoic acid was converted through the dichloride, to the iodoso acid following the directions of Willgerodt.[10] A 2-g. portion of the acid was boiled with 500 ml. of water for 6 hours. The resulting suspension of mixed *m*-iodobenzoic acid and *m*-iodoxybenzoic acid was chilled and filtered. *m*-Iodobenzoic acid was largely removed from the product by washing repeatedly with hot acetic acid. The residue was recrystallized twice from distilled water (0.6 mg./ml.). Small transparent prisms, decomposing close to 265° were obtained. Willgerodt[10] gives the explosion point as 243°.

For analysis, a 5–10 mg. weighed sample was dissolved in 15 ml. of *N* potassium iodide solution, two drops of glacial acetic acid was added, and the liberated iodine was titrated with 0.01 *N* standardized thiosulfate. The calculated equivalent/wt. (mol. wt./14) is 70.0; found, 69.0; neut. equiv. calcd., 280; found, 283.

The precipitated solid acid from the iodometric titration was filtered off and recrystallized once from water. After drying overnight in a vacuum desiccator, it melted 185.5–186.5°; mixed with pure *m*-iodobenzoic acid, it melted 185.6–186.5°.

***p*-Iodoxybenzoic Acid.**—*p*-Iodosobenzoic acid was prepared from Eastman Kodak Co. white label *p*-iodobenzoic acid as described by Willgerodt.[10] The disproportionation reaction to *p*-iodobenzoic acid and *p*-iodoxybenzoic acid, reported by Willgerodt to proceed in very poor or no yield at 100°, can be made to give satisfactory yields by heating an aqueous suspension of the iodosobenzoic acid to 160° for one hour in a rocking hydrogenation bomb.

Two grams of *p*-iodosobenzoic acid suspended in 20 ml. of distilled water gave in this way 1.9 g. of solid acid mixture. The *p*-iodobenzoic acid was removed by digesting the mixture three times with boiling acetic acid. The crude *p*-iodoxybenzoic acid was recrystallized twice from distilled water (0.6 mg./ml.) yielding fine transparent plates, which after drying, decomposed close to 245°; reported in the literature,[11] 227°. Iodometric equiv. wt., calcd., 70.0; found, 68.9; neut. equiv. wt., calcd. 280; found, 280.

The precipitated reduced acid from the iodometric titration, after recrystallization from ethanol, and drying, melted in the range 265.0–266.5°. Mixed with a sample of *p*-iodobenzoic acid melting at 265.5–266.5°, it melted at 265.1–266.5°.

Titrations.—The samples, generally of 3 to 10 mg., were weighed on an Oertling semi-micro balance to 0.01 mg. accuracy. They were placed in 150-ml. lipless beakers and to each sample was added 25 ml. of water (redistilled from sodium hydroxide, to remove carbon dioxide). Solution was effected by heating and stirring. While benzoic and *p*-nitrobenzoic acids dissolved in a few minutes at 50°, the other three acids studied required gentle boiling for 15–20 minutes. Water lost in boiling was replaced before titration. The solution was allowed to reach temperature equilibrium (15–20 minutes) with a water-bath held constant to ±0.01° at a temperature of 50.1° (checked with NBS thermometer); however, it was found that, presumably due to loss of heat by evaporation, the temperature of

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[1] Research carried out under the auspices of the U. S. Atomic Energy Commission.

[2] For a review of the work prior to 1914, see Willgerodt "Die Organischen Verbindungen mit Mehrwertigen Jod," Verlag von Ferdinand Enke, Stuttgart, 1914. Later work has been reviewed by R. B. Sandin, *Chem. Revs.*, **32**, 249 (1943).

[3] A. A. Bothner-By and C. W. Vaughan, Jr., THIS JOURNAL, **74**, 4400 (1952), and leading references.

[4] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, p. 184 ff.

[5] *Ibid.*, p. 188.

[6] All melting ranges determined on a Koefler hot-stage microscope.

[7] H. P. Klug, E. Mack, Jr., and F. C. Blake, THIS JOURNAL, **51**, 288 (1929).

[8] E. Fischer, *Ann.*, **127**, 137 (1863).

[9] J. F. J. Dippy and R. H. Lewis, *J. Chem. Soc.*, 644 (1936).

[10] C. Willgerodt, *Ber.*, **27**, 2328 (1894).

[11] F. Fichter and P. Lotter, *Helv. Chim. Acta*, **8**, 442 (1925).

the solution was 0.2–0.3° below the temperature of the bath.

The *p*H of the solution was measured with a Beckman glass electrode (No. 1190-T, designed for elevated temperatures) and a Beckman calomel electrode, both inserted through a rubber stopper and then immersed in the solution to a depth sufficient to cover the bulb of the glass electrode. Between measurements the two electrodes were kept in a Cenco buffer of *p*H 6.96 at 50°, which was used as a standard. The electrodes were connected to a Beckman Model G *p*H meter, with which a sensitivity of 0.01 *p*H unit could be attained. In accordance with the instructions accompanying the glass electrode, the *p*H meter was standardized (using the buffer of *p*H 6.96) at a setting of (6.96) (323)/(298) or 7.54, and the *p*H values read from the instrument were multiplied by a factor of 298/323 to obtain the true *p*H values at 50°. Two different glass electrodes were used in this work, data for each compound being obtained with both electrodes; no systematic difference could be noticed between the results obtained with the two electrodes.

Increments of sodium hydroxide (carbonate-free, 0.0972 *N*, standardized against potassium biphthalate) were added from a syringe microburet (Micro-Metric Instrument Co., No. SB-1), using a calibrated syringe which delivered 1.01 ml./inch, and a micrometer graduated in 0.001 inch units. After each addition the solution was stirred mechanically for 15 seconds, then the stirrer was stopped and the *p*H was measured. Typical titration curves, up to within 10% of the end-point, are shown in Fig. 1; the *p*H values shown are those read from the instrument, not corrected for temperature. Near the end-point the sodium hydroxide was added in 0.002-ml. increments, and the exact end-point was taken as the point of maximum change in *p*H.

At the conclusion of the titration, the electrode was checked against the standard buffer at 50°, and was always found to be within 0.03 *p*H unit of nominal value. The beaker and contents were weighed to the nearest 0.1 g. and from this the volume of the solution was calculated. The initial concentration of the acid was calculated from this volume and the amount of sodium hydroxide used.

Discussion

Calculation.—The *p*H values at 25, 50 and 75% neutralization were read off from the titration curves and were then corrected for temperature by multiplying by the factor given above.

From each *p*H value, a value of pK_a was calculated, using the following equation which takes into account the change in concentration of the acid and anion due to dissociation of acid[12]

$$pK_a = pH - \log(b + [H^+]) + \log(a - [H^+])$$

where pK_a is the negative logarithm of the dissociation constant, and *a* and *b* are the nominal concentrations of acid and salt calculated from the per cent. neutralization. In these very dilute solutions the concentration of hydrogen ion was frequently as much as one-third the value of *a* and in some cases (25% neutralization of the stronger acids) greater than the value of *b*.

The results of the titrations are given in Table I. The deviations accompanying the individual pK_a values are the average deviations of the three values (at 25, 50 and 75% neutralization) from the mean; no trend could be noted in these deviations. The deviations accompanying the average pK_a values for each compound are the average deviations of the individual titration results, as given in Table I, from their mean.

Conclusions.—Figure 2 shows a graph of the data obtained by plotting the average pK_a values for benzoic, *m*-iodobenzoic and *p*-nitrobenzoic acids against the σ-values for the corresponding substituents listed in Hammett's table, and drawing the best straight line through these points. The slope is −1.09 corresponding to a ρ-value of +1.09. The estimated precision is ±0.03.

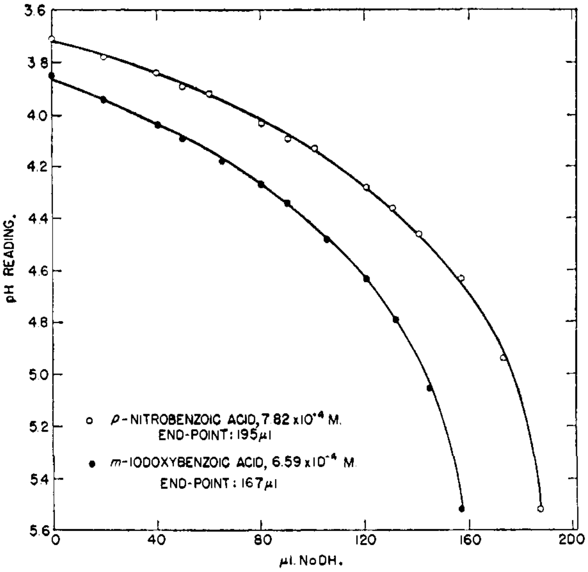

Fig. 1.—Typical *p*H–titration curves.

TABLE I

VALUES OF pK_a AS DETERMINED FROM NEUTRALIZATION CURVES

Compound, acid	Concentration ($M \times 10^4$)	pK_a	Average deviation	Electrode
Benzoic	7.80	4.31	0.01	2
	11.6	4.28	.03	1
	Av.	4.30	.02	
m-Iodobenzoic	7.50	3.88	.01	1
	8.02	3.93	.01	2
	15.4	3.88	.02	1
	Av.	3.90	.02	
m-Iodoxybenzoic	6.59	3.68	.01	2
	7.62	3.53	.02	2
	7.68	3.61	.01	1
	14.2	3.62	.02	2
	14.2	3.57	.01	2
	Av.	3.60	.04	
p-Iodoxybenzoic	6.64	3.60	.00	2
	6.94	3.56	.02	1
	7.00	3.54	.00	1
	15.6	3.48	.01	1
	16.9	3.53	.01	1
	Av.	3.54	.03	
p-Nitrobenzoic	6.92	3.50	.03	1
	7.82	3.43	.03	2
	7.96	3.46	.01	2
	16.4	3.41	.01	1
	17.8	3.44	.01	2
	Av.	3.45	.03	

The pK_a's for *m*-iodoxybenzoic acid and *p*-iodoxybenzoic acid were found to be 3.60 ± 0.04 and 3.54 ± 0.03, respectively. Reading from the plot, we find the corresponding σ-value for the *m*-iodoxy substituent to be 0.63 ± 0.03. Similarly for the *p*-iodoxy group we find the value 0.69 ± 0.03.

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[12] I. M. Kolthoff and V. A. Stenger, "Volumetric Analysis," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1942, p. 26.

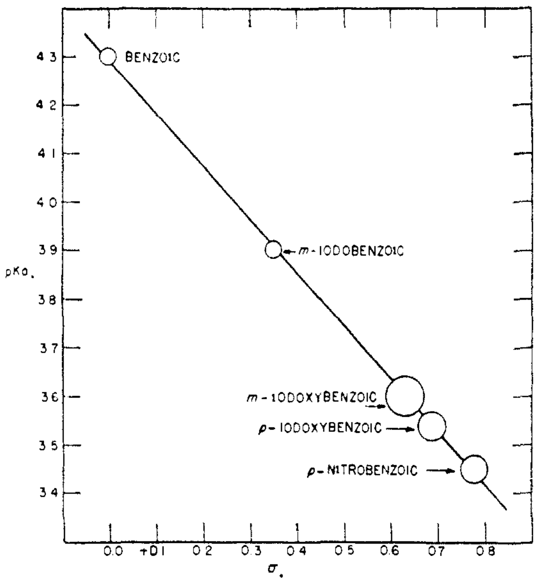

Fig. 2.—Hammett plot of ionization constants of substituted benzoic acids.

These large positive values of the σ constant indicate that the iodoxy group is a strongly electron-withdrawing substituent in either the meta or para position of the benzene nucleus and is comparable in this respect with the nitro-, cyano- and benzeneazo-groups. It is of interest to compare the values of σ for the iodoxy substituent with those for the nitro substituent. The nitro substituent has a slightly greater electron withdrawing power in the meta position ($\sigma = +0.71$), and in the case of the para substituents when compared for derivatives other than anilines and phenols ($\sigma = +0.78$). In nitroaniline and *p*-nitrophenol reactions, it is presumably the involvement of the reacting center in the resonance of the molecule which is the cause of the anomalous higher σ value ($\sigma = +1.27$). The fact that the iodoxy group directs electrophilic substitution in the benzene ring more exclusively meta than does the nitro group[13] may be rationalized on the following basis. The competitive rates of substitution in the meta position are expected to be roughly the same, the rate with iodoxybenzene perhaps being slightly faster. The rate of para-substitution in iodoxybenzene is expected to be considerably slower than in nitrobenzene because of the large electrostatic repulsion between the center of positive charge located at the iodine in the iodoxy group and at the adjacent ring carbon of the activated complex for para-substitution, and the consequent high energy of the latter. Thus the *ratio* of meta to para-substitution in iodoxybenzene would be larger than the corresponding ratio in nitrobenzene. An explanation of the meta-directing influence of the $-N(CH_3)_3^+$ group based on the same considerations has been suggested by Roberts, *et al.*[14]

The working hypothesis of a large positive charge on iodine in the iodoxy group is thus supported by the properties of the material (high-melting, low solubility in water, but less in non-polar solvents, indicating a large internal dipole), previous observations of the chemical reactions,[3] and is supported by the results here reported.

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(13) J. Masson, E. Race and F. Pounder, *J. Chem. Soc.*, 1669 (1935).

(14) J. D. Roberts, P. A. Clement and J. J. Drysdale, This Journal, **73**, 2181 (1951).

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Rearrangement Peaks in the Mass Spectra of Certain Aliphatic Acids

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Purified samples of formic, acetic, propionic, *n*-butyric, isobutyric, *n*-valeric, isovaleric, acrylic, vinylacetic and isocrotonic acids have been examined in a sector-type mass spectrometer, and normalized spectra tabulated. C^{13}-Carboxyl labeled *n*-butyric acid has also been examined in view of the rearrangement peak at mass 60, which is the principal peak in *n*-butyric, *n*-valeric and isovaleric acids. Results in *n*-butyric acid show that the carboxyl group is quantitatively retained in this rearranged ion, suggesting a simple hydrogen transfer as the most probable mechanism of formation. Other rearrangement peaks are noted.

The mass spectrum of formic acid has been studied in detail by Mariner and Bleakney,[1] and spectra of formic, acetic, propionic and *n*-butyric acids have been recorded in the American Petroleum Institute (A.P.I.) series of reference spectra.[2] In the present work, purified samples of these and six other aliphatic acids have been examined in a mass spectrometer, with particular attention to those peaks which can be due only to molecular rearrangement, and not to any combination of bond cleavages, during the ionization and dissociation process.

As might be expected, the published spectra for formic acid do not agree with each other, nor with our results, since ionizing conditions and method of scanning were presumably quite different in the three instruments. Our values for masses 44 and 28 are especially high for this compound. A similar comparison of our spectra of acetic, propionic and *n*-butyric acids with the A.P.I. data also shows expected variations. Agreement is best in the case of *n*-butyric acid, especially in the mass range from 88 down to 60. Such comparisons of mass spectra obtained on instruments of different design can seldom be made directly, but this does not lessen the validity of comparisons between the spectra of related compounds obtained with a single instrument under constant operating conditions, as in the present work.

In the usual picture of ionization by electron im-

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(1) T. Mariner and W. Bleakney, *Phys. Rev.*, **72**, 792 (1947).

(2) *Catalog of Mass Spectral Data*, Amer. Pet. Inst. Res. Proj. 44, Nat. Bur. Stds., Washington, D. C., Series Nos. 300, 301, 302, 303.