through a centered rod column to yield a sample of b.p. 193° (32 mm.), $n^{22}\text{D}$ 1.6015. For analysis a weighed sample of this product (about one gram) was dissolved in warm 95% ethanol and titrated with 0.5 *N* aqueous sodium hydroxide to the phenolphthalein end-point. Hydrolysis to yield two moles of hydrogen chloride per mole of organic dichloride is very rapid under these conditions. Eq. wt. based on Cl, calcd., 118.5; found, 120.0. As a check the resultant solution was made neutral and titrated with standard silver nitrate solution. Eq. wt. based on Cl, found, 120.0.

Diphenyldiethoxymethane.—The ketal of benzophenone was prepared from diphenyldichloromethane and sodium ethoxide by the method of Mackenzie[2]; m.p. 51-51.5°.

Absorption Spectra.—These were measured using a Beckman model DU spectrophotometer equipped with a water-jacketed cell housing for maintenance of constant temperature. In all cases the material in the blank cell was of the same composition as the solvent used for the substance the absorption of which was being measured. The spectra of the ketone and ketal showed no marked deviations with changes in the alcohol-water content or variations in hydrogen chloride concentration of the solvents in which they were investigated.

Absolute Ethanol.—Commercial Solvents absolute ethanol which analyzed as 99.7% ethanol by the paraffin oil test[19] was used in most of these studies. For use in the rate runs on dichloride ethanolysis in the presence of sodium ethoxide it was further dried by the sodium–ethyl formate procedure.[20] The ethanolysis rate constant for the dichloride in the "dried" ethanol without sodium ethoxide was not appreciably different from that obtained using the Commercial Solvents ethanol directly.

For the spectrophotometric rate studies the Commercial Solvents ethanol was used without drying since the experimental procedures were of such a nature that rigidly anhydrous conditions could not be maintained during the course of the runs.

Kinetics of Ethanolysis of Diphenyldichloromethane (A) Volumetric Method.—Samples of the dichloride were weighed into volumetric flasks, and ethanol or standard ethanol solutions of sodium ethoxide at the desired temperature were added to the mark. The flasks were placed in the constant temperature bath (25 ± 0.050°), and aliquots were withdrawn from time to time and added to ice-cold absolute ethanol. The samples were titrated rapidly with alcoholic sodium hydroxide or hydrogen chloride using methyl red indicator.

(B) Spectrophotometric Method.—A solution of approximately 1 mg. of dichloride per 100 ml. of ethanol (previously adjusted to 25°) was prepared using a capillary tip eye dropper, calibrated in terms of the weight of a drop of dichloride, to deliver the dichloride to the solvent. A sample of this solution was placed in an absorption cell in the spectrophotometer cell housing which was maintained at 25°. The sample was allowed to equilibrate to the cell housing temperature for a few minutes before optical density measurements were begun. The exact initial concentration of the solution was calculated from the $d_{230\ \text{m}\mu}$ reading at the completion of reaction and the extinction coefficient of the ketal at this wave length. Absolute ethanol was used as a solvent blank in making optical density readings.

Kinetics of Conversion of Ketal to Ketone.—A stock stolution of diphenyldiethoxymethane in absolute alcohol was prepared. Known volumes of this solution were mixed with measured volumes of solutions of hydrogen chloride in absolute or aqueous ethanol. All solutions were adjusted to 25° before mixing. Samples of the solutions were transferred to absorption cells for measurement of $d_{252\ \text{m}\mu}$ values at 25°. The solvent blank cells contained alcohol and water in the same ratio as was used in the solution investigated. The ketal solutions in aqueous or absolute ethanol were stable in the absence of hydrogen chloride as evidenced by the fact that their spectra did not alter with time.

DAVIS, CALIFORNIA RECEIVED AUGUST 11, 1950

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[19] Robertson, "Laboratory Practice of Organic Chemistry," The Macmillan Company, New York, N. Y., 1937, p. 178.

[20] Reference 19, p. 296.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Reactivities of 4- and 5-Substituted 2-Methylbenzoic Acids

BY JOHN D. ROBERTS AND JOEL A. YANCEY

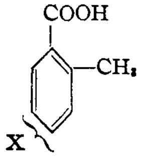
The Hammett equation has been shown to be applicable to the reactivities of a series of 4- and 5-substituted 2-methylbenzoic acids. The results may be interpreted as indicating that the steric effect of an ortho-group on the reactivity of the carboxyl group of benzoic acid can be independent of other substituent groups which might be present.

Hammett[1] has shown that the equilibrium and rate constants *k* of a large number of side-chain reactions of benzene derivatives carrying meta- or para-substituents are related to the corresponding constants k^0 for the unsubstituted compounds by the equation

$$\log k - \log k^0 = \sigma\rho$$

The constant σ is, by definition, dependent only on the nature and position of the substituent while ρ is a reaction constant determined by the experimental conditions and the type of side-chain reaction. The equation is not generally valid for ortho-substituents which suggests the operation of a steric hindrance or proximity effect for such groups.[1]

In the present investigation, the reactivities of some 4- and 5-substituted 2-methylbenzoic acids (I) were measured and compared with those of the corresponding benzoic acids (II) to determine whether the steric influence of a methyl ortho to the reactive carboxyl group is constant when 4- or 5-substituents are introduced. The reactions employed were the ionizations of the acids in 50% water–50% ethanol (by volume) at 25.0° and the relative reactivities toward diphenyldiazomethane in absolute ethanol at 30.0°. The procedures have been described earlier in detail.[2] The experimental data are given in Table I along with the physical constants for the compounds used. The values of the logarithms of the apparent ionization constants (pK_A) of the 4- and 5-substituted 2-methylbenzoic acids are plotted against the Hammett σ-constants in Fig. 1. Here, the σ-values



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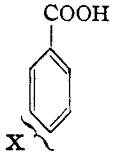

II

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[1] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Company, Inc., New York, N. Y., 1940, Chap. VII.

[2] J. D. Roberts, R. Armstrong and E. A. McElhill, THIS JOURNAL, 71, 2923 (1949).

TABLE I

PHYSICAL CONSTANTS, APPARENT IONIZATION CONSTANTS (25°) AND DIPHENYLDIAZOMETHANE REACTION RATE CONSTANTS (30°) OF 4- AND 5-SUBSTITUTED 2-METHYLBENZOIC ACIDS

Substituent	M. p., °C.	M. p., lit.	Half-point[a]	$K \times 10^{6}$ [b]	Concn. of acid,[c] moles/l.	Half-life,[c] min.	Av. k_2,[c] l./mole-min.
4-NH_2–	150.8–151.5	153[d]	6.83	0.148	0.1240	28.8	0.198
					.0930	37.1	
4-CH_3O–	178.4–178.8	176[e]	6.30	0.500	.0435	36.4	.439
					.0326	48.3	
4-CH_3–	123.4–124.4	125–126[f]	6.09	0.812	.0608	18.0	.631
					.0456	24.2	
5-NH_2–	190.4–192.0	191[g]	5.85	1.41	.0578	15.2	.797
					.0433	19.9	
5-CH_3–	133.5–134.5	132[h]	5.92	1.20	.0495	16.0	
					.0495	16.4	.856
					.0371	22.1	
None	104.8–105.4	102–103[i]	5.76	1.74	.0669	10.9	
					.0669	11.0	.939
					.0502	14.9	
5-CH_3O–	143.2–144.2	146[j]	5.64	2.29	.0448	12.2	1.26
					.0336	16.5	
4-Br–	183.0–183.8	187[k]	5.38	4.16	.0378	11.1	1.65
					.0252	16.8	
5-Br–	169.0–169.2	168.5[l]	5.31	4.90	.0408	8.30	2.12
					.0272	11.7	
5-NO_2–	177.8–179.4	179[m]	4.48	33.1	.0171	10.1	4.01
					.0343	5.03	
4-NO_2–	154.5–155.4	152–153[n]	4.42	38.0	.0130	11.3	4.82
					.0261	5.38	

[a] Reading on *p*H scale of *p*H meter calibrated for aqueous buffer solutions at half-neutralization point using glass and saturated calomel electrodes without correction for liquid junction potentials in 50% water–50% ethanol (by volume) solutions. [b] Calculated assuming unit activities and readings of *p*H meter scale equal to logarithm of reciprocal of hydrogen ion concentrations. [c] For reaction of benzoic acids with diphenyldiazomethane in absolute alcohol solution. [d] M. Hoenig, *Ber.*, **18**, 3449 (1885). [e] C. Schall, *ibid.*, **12**, 825 (1879). [f] O. Jacobsen, *ibid.*, **11**, 18 (1878). [g] O. Jacobsen and F. Wierss, *ibid.*, **16**, 1959 (1883). [h] O. Jacobsen, *ibid.*, **14**, 2111 (1881). [i] "Organic Syntheses," Coll. Vol. II, p. 588. [j] O. Jacobsen, *Ber.*, **16**, 1962 (1883). [k] C. Nourrisson, *ibid.*, **20**, 1016 (1887). [l] K. v. Auwers and L. Harres, *Z. physik. Chem.*, **143A**, 17 (1929). [m] B. B. Dey and P. L. Kantam, *J. Indian Chem. Soc.*, **14**, 144 (1937). [n] M. Mayer, *J. prakt. Chem.*, [2] **92**, 145 (1915).

were used as though the 2-methyl group were *absent* and 2-methylbenzoic acid, itself, was given a σ-value of 0.000. The corresponding plot for meta- and para-substituted benzoic acids obtained previously[2] is also included in Fig. 1. Similar data for the diphenyldiazomethane reactions are shown in Fig. 2.

It is clear that the Hammett equation applies to reactions of 4- and 5-substituted 2-methylbenzoic acids with essentially the same degree of accuracy as with the benzoic acids themselves. The median deviation *r* for the ionization constants is 0.045 as compared with 0.025 for 2-unsubstituted acids[2] and 0.060 for the mean of 52 reactions cited by Hammett.[1] For the diphenyl-diazomethane reaction, *r* was 0.035 as compared with 0.010 for benzoic acids.[2] From these results, it may be concluded that the steric influence of a single ortho-methyl on reactivity of the carboxyl group of ben-

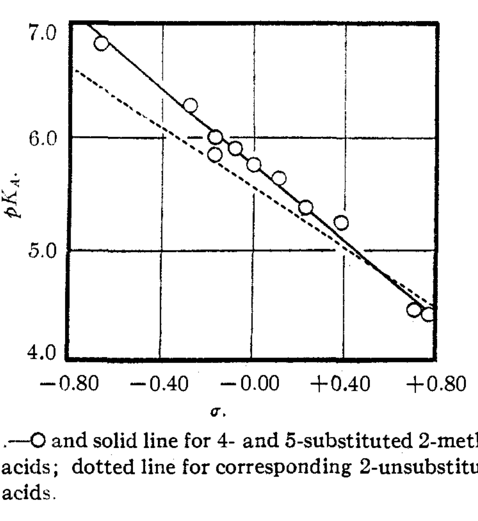

Fig. 1.—○ and solid line for 4- and 5-substituted 2-methylbenzoic acids; dotted line for corresponding 2-unsubstituted benzoic acids.

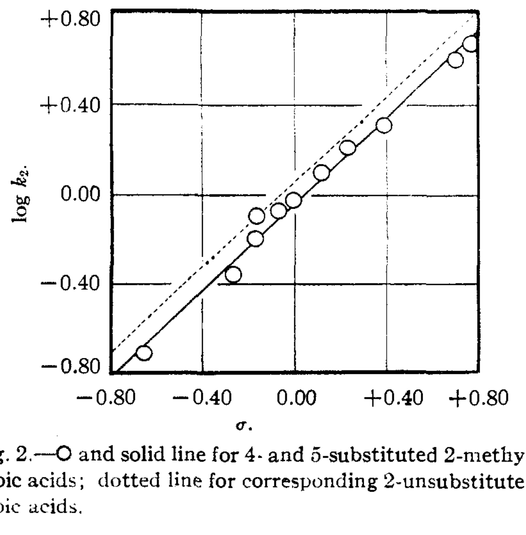

Fig. 2.—○ and solid line for 4- and 5-substituted 2-methylbenzoic acids; dotted line for corresponding 2-unsubstituted benzoic acids.

zoic acid is essentially constant and not altered by substituents in the 4- or 5-position.

Comparison of the σ-constants for the reactions of the 2-methyl- with 2-unsubstituted benzoic acids is particularly interesting. In the diphenyldiazomethane reaction the 2-methyl lowers the reaction rate for each member of the 2-methyl over the 2-unsubstituted series but does not alter the relative influence of a 4- or 5-substituent. In the ionization reaction, ρ for the 2-unsubstituted acids (+1.46) is significantly smaller than for the 2-methyl acids (+1.67). A simple explanation for the apparent anomaly is possible. The influence of a given substituent on the rate of the diphenyldiazomethane reaction is exerted in the slow step which involves proton transfer from the undissociated acid to the diazo compound.[3] In the transition state, the O–H bond of the benzoic acid is at most only partially ionized. Consequently, ionic solvation effects on the reaction are expected to be of relatively minor importance. In the acid ionizations, where equilibria between carboxylate ions and undissociated acids are involved, the effect of the ionic solvating power of the solvent is particularly important and it seems reasonable that ρ for the stabilization of 4- and 5-substituted 2-methylbenzoate ions by solvent molecules could be different than for the corresponding 2-unsubstituted acids.

[3] J. D. Roberts, W. Watanabe and R. E. McMahon, THIS JOURNAL, 73, 760 (1951).

CAMBRIDGE 39, MASSACHUSETTS RECEIVED AUGUST 11, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW MEXICO SCHOOL OF MINES]

A Study of Indium(III) Chloride Complexes by Polarographic Methods

BY JOSEPH A. SCHUFLE, MORRIS F. STUBBS AND RICHARD E. WITMAN

The polarographic reduction of the indium(III) ion has been studied by Lingane[1] and the shift in the half-wave potential of the indium ion with different chloride ion concentrations has been noted by Kolthoff and Lingane.[2] It was believed that the shift in half-wave potential with change in chloride ion concentration was due to formation of an indium chloride complex ion in solution. Aiken, Haley and Terrey[3] have proposed that indium dichloride is derived from $HInCl_4$ and that $InCl_2$ is probably better written In_2Cl_4, or $In^+(InCl_4^-)$, thus suggesting the existence of the chloro-indium complex, $InCl_4^-$.

Theoretical treatment of this subject by Heyrovsky,[4] by Stackelberg and Freyhold[5] and by Lingane,[6] has shown that the shift in half-wave potential with change in concentration of the complex-forming substance may be used to determine the formula of the complex ion and, in some cases, the value of the dissociation constant for the metal complex. Stackelberg and Freyhold,[5] for example, found the formula for the zinc hydroxide complex ion to be $Zn(OH)_4^=$ by determining half-wave potential ($E_{1/2}$) values for zinc solutions at varying hydroxide ion concentrations.

In the case of the indium reduction studied in the present work the trivalent indium ion is reduced in one reversible step to metallic indium at the surface of the mercury electrode

$$In^{+++} + 3e \rightleftarrows In \qquad (1)$$

It is proposed that in the presence of chloride ion in solution, however, the indium(III) ion is partly combined in the form of an indium chloride complex which must also dissociate reversibly if indium(III) is to be present to take part in the reduction indicated in equation (1).

$$InCl_x^{(x-3)-} \rightleftarrows In^{+++} + xCl^- \qquad (2)$$

Combining equations (1) and (2)

$$InCl_x^{(x-3)-} + 3e \rightleftarrows In + xCl^- \qquad (3)$$

The value of $E_{1/2}$ for this reaction, as shown by Stackelberg and Freyhold,[5] is given by the equation

$$E_{1/2} = E_s - \frac{0.0591}{n} \log (a_{InCl_x^{(x-3)-}})/(a_{In}) \qquad (4)$$

where E_s is closely related to the normal reduction potential of the simple metal ion, but is more appropriately represented in this case by the half-wave potential for the reduction of the simple indium(III) ion in a non-complex-forming medium.

The dissociation constant (K_d) for the indium chloride complex ion, obtained from equation (2), is given as

$$K_d = \frac{(a_{In^{+++}})(a_{Cl^-})^x}{(a_{InCl_x^{(x-3)-}})} \qquad (5)$$

Substituting the value of $a_{InCl_x^{(x-3)-}}$ obtained from equation (5) into equation (4)

$$E_{1/2} = E_s - \frac{0.0591}{n} \log \frac{(a_{In^{+++}})(a_{Cl^-})^x}{(a_{In})(K_d)} \qquad (6)$$

Since the value of $E_{1/2}$ for a metal ion is practically independent of the concentration of the metal ion, $a_{In^{+++}}$ may be taken equal to unity. The activity of indium in the metallic state also may be assumed equal to unity ($a_{In} = 1$). Thus equation (6) becomes

$$E_{1/2} = E_s - \frac{0.0591x}{n} \log (a_{Cl^-}) + \frac{0.0591}{n} \log K_d \qquad (7)$$

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[1] Lingane, THIS JOURNAL, 61, 2099 (1939).

[2] Kolthoff and Lingane, *Chem. Revs.*, 24, 1–94 (1939).

[3] Aiken, Haley and Terrey, *Trans. Faraday Soc.*, 32, 1617 (1936).

[4] Heyrovsky, "Physikalische Methoden der analytischen Chemie," Bd. II, W. Böttger, Leipzig, 1936.

[5] Stackelberg and Freyhold, *Z. Elektrochem.*, 46, 120 (1940).

[6] Lingane, *Chem. Revs.*, 29, 1 (1941).