31°, and 500[19] at 16.5° for the surface tension of mercury *in vacuo*, however, have also been obtained recently with the sessile drop method. It would seem, however, that Burdon has taken the most precautions, testing his experimental set-up by measurements of the surface tension of water in paraffin dishes. Nevertheless, the recent results that have been reported with the maximum bubble pressure method, a method which, unlike the sessile drop method, has given consistent results in the hands of different investigators as well as the same investigator, indicate values between 470 and 480 for the surface tension of mercury in dry gases. R. C. Brown[20] obtained 472 at 18° using glass jets and 477 using platinum jets, with nitrogen; Sauerwald and Drath[21] obtained 473 at 19° using silica jets with carbon dioxide; and Bircumshaw[22] obtained 480 as his highest value at 20°, using hydrogen.

I wish to express my thanks to Professor F. E. Bartell and Professor L. O. Case for encouragement and advice.

Summary

A new modification of sessile drop apparatus has been used for the determination of the surface and interfacial tension values of mercury. The results obtained with large flat drops and with small ones were found to be in good agreement with those also obtained by the drop weight method. The following are the main results: (1) for the interfacial tension against water, 374.3 dynes/cm. at 25°; (2) for the surface tension of mercury in dry air and *in vacuo*, the same value within experimental error of about 0.3%, 473 at 25°. (3) It was shown thermodynamically that the surface tension of mercury *in vacuo* has to be at least as high as 447 at 25°. This eliminates some of the values obtained by previous workers. (4) On the basis that the surface oxidation of mercury in air takes place only in the presence of water vapor, some of the perplexing phenomena often observed with mercury can be explained, such as irreversible adsorption effects, and the difference in results sometimes obtained with a static and a dynamic method.

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[19] Bradley, *J. Phys. Chem.*, **38**, 231 (1934).

[20] Brown, *Phil. Mag.*, [7] **6**, 1044 (1928).

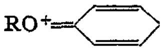
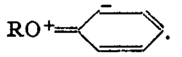
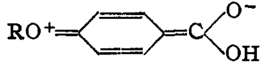
[21] Sauerwald and Drath, *Z. anorg. allgem. Chem.*, **154**, 79 (1926).

[22] Bircumshaw, *Phil. Mag.*, [7] **12**, 596 (1931).

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

The Anomalous Strength of Salicylic Acid

BY G. E. K. BRANCH AND DAVID L. YABROFF

The hydroxyl and alkoxyl groups are negative since they increase the strength of a saturated aliphatic acid when substituted on the α-carbon atom. The negativity factor thus tends to make the hydroxy- and alkoxybenzoic acids stronger than benzoic acid, and to have the ortho, meta, para order of decreasing strengths. Because of the unshared electron pairs on the oxygen atom, there is a resonance that tends to decrease the strengths of the hydroxy and alkoxy aromatic acids, especially the ortho and para compounds. The resonating forms that decrease the strength are  and . This acid-weakening resonance is still further enhanced when an ortho or para acidic group can combine with the negatively charged atoms of a quinoidal form. This theory has been used by Ingold[1] to explain the weakness of *p*-methoxybenzoic acid, and by Branch, Yabroff and Bettman[2] to explain the weakness of *o*- and *p*-phenetylboric acids. In the benzoic acid derivative the quinoidal form involving the carboxyl group is , and a similar form is possible in an ortho compound.

That *p*-hydroxybenzoic and *p*-methoxybenzoic acids are definitely weaker than benzoic acid shows that the resonance is an important factor. Since the negativity of the hydroxyl group is not great, this theory would lead one to suppose that *o*-hydroxybenzoic (salicylic) and *o*-methoxybenzoic acids should be weaker or, at most, only slightly stronger than their meta isomers. This deduction is entirely erroneous, however, in the case of salicylic acid and other *o*-hydroxybenzoic acid derivatives. In water salicylic acid (*Ka* =

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[1] Ingold, *J. Chem. Soc.*, 1120 (1933).

[2] Branch, Yabroff and Bettman, THIS JOURNAL, **56**, 937 (1934).

1×10^{-3}) is more than ten times as strong as *m*-hydroxybenzoic acid ($Ka = 8 \times 10^{-5}$).

It is important to know whether this same anomalously great strength is also shown by *o*-alkoxybenzoic acids. There are some old conductivity measurements[3] which show that the strength of *o*-methoxybenzoic acid does not exhibit this anomaly, but is, as the theory would lead us to expect, slightly weaker than *m*-methoxybenzoic acid. We have confirmed this by measuring the dissociation constants of the hydroxy- and methoxybenzoic acids in an aqueous alcoholic solution containing 25% alcohol by volume (mole fraction of alcohol = 0.091). The dissociation constants previously obtained in water and our values in 25% alcohol are shown in Table I.

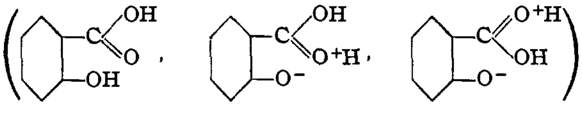
TABLE I

$Ka \times 10^5$ AT 25°

Acid	In 25% EtOH	In water	K_{H_2O}/K_{EtOH}
o-Hydroxybenzoic	63.8[4]	105	1.65
m-Hydroxybenzoic	2.43	8.3	3.3
p-Hydroxybenzoic	0.750	2.9	3.9
o-Methoxybenzoic	2.09	8.2	3.9
m-Methoxybenzoic	2.87	9.0	3.1
p-Methoxybenzoic	1.16	3.6	3.1
Benzoic	2.29[5]	6.6	2.9

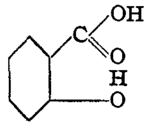
Both sets of measurements show the great strength of salicylic acid, while all the other hydroxybenzoic and methoxybenzoic acids show the competition between the negativity of the substituent group and the acid-weakening resonance. In the last column of the table the ratios of the dissociation constants in water to those in the alcohol solution are given. These ratios present another peculiarity of salicylic acid. The ratio for salicylic acid is markedly lower than that for benzoic acid, while those for the other hydroxybenzoic and methoxybenzoic acids are greater than that for benzoic acid. The ratio for *o*-methoxybenzoic acid is greater than those for its isomers.

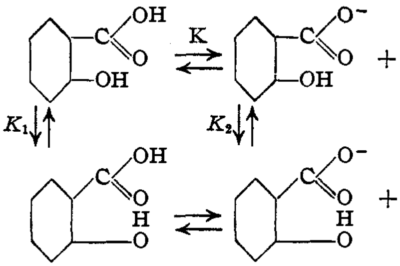
The anomalous strength of salicylic acid indicates that there is another factor governing the strength besides the negativity of the hydroxyl group and the acid-weakening resonance arising from the unshared electron pairs of the phenolic oxygen atom. This factor can only be effective in ortho compounds, and it exists in the hydroxyl compound but not in its ether. It is evidently not a steric interference of the ortho group with the addition of hydrogen ion to the salicylate ion,[6] for then it would be at least as important in *o*-methoxybenzoic acid as in salicylic acid. Nor can it reasonably be supposed that it is due to a dissociation of the phenolic hydrogen atom. It seems likely that this factor is the resonance



which can be seen to be acid-strengthening from the position of the electric charges in the inner-ion forms.

At first sight a resonance of this type seems to be impossible, because it apparently involves a motion of so heavy a particle as a proton. The forms HOC_6H_4COOH and $^-OC_6H_4CO_2{}^+H_2$ can resonate only if (with little or no strain) the phenolic and carboxylic oxygen atoms can be so close to each other that a proton may be within easy bonding distance of both. Then the change of the classical to the inner-ion form requires no motion of the proton but only a rearrangement of bonds. This is only possible in the ortho compound. This resonance cannot exist when an alkyl group is substituted for the phenolic hydrogen atom.

This type of resonance results in the formation of a chelate ring in which a divalent hydrogen atom is a link. The formula of the resonating molecule may be written as  . These cyclic formulas have been suggested by Sidgwick[7] for salicylic acid derivatives, and for the enolic forms of 1,3 diketones. A solution of salicylic



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(3) Ostwald, *Z. physik. Chem.*, **3**, 241 (1889); Euler, *ibid.*, **21**, 257 (1896); Schaller, *ibid.*, **25**, 497 (1898); White and Jones, *Am. Chem. J.*, **44**, 197 (1910); W. Pip, Dissertation, Heidelberg, 1898; Scudder, "Conductivity and Ionization Constants of Organic Compounds," D. Van Nostrand Co., New York, 1914, pp. 180, 181, 199.

(4) This result at mole fraction of alcohol = 0.091 agrees fairly well with that of Halford, 61.6×10^5 at mole fraction of alcohol = 0.084, THIS JOURNAL, **55**, 2272 (1933).

(5) Bettman, Branch and Yabroff, *ibid.*, **56**, 1867 (1934).

(6) Flürscheim, *J. Chem. Soc.*, **95**, 718 (1909).

(7) Sidgwick, "The Electronic Theory of Valency," Oxford University Press, London, 1929, p. 242.

acid may be considered as a tautomeric equilibrium between the classical[7] and the chelate structures. A similar equilibrium exists for the ion. The dissociation constant is then given by the equation $Ka = K\,\frac{(1 + K_2)}{(1 + K_1)}$. K is approximately equal to the dissociation constant of *m*-hydroxybenzoic acid, and Ka is more than ten times as great. Hence, however small K_1 may be, K_2 is a fairly large number, and the ion must exist chiefly as the chelate molecule. As a consequence the second dissociation constant of salicylic acid should be anomalously small. This is found to be the case, $Ka = 1 \times 10^{-13}$.[8]

The above theory also explains the low value of the ratio of the dissociation constant of salicylic acid in water to that in 25% alcohol. The strength of salicylic acid depends on the interaction of the carboxyl group with the phenolic hydroxyl group. The presence of other hydroxyl groups in the solvent tends to weaken the acid since these may also interact with the carboxyl group. As the solvent (water) is diluted with alcohol, the relative effect of the interaction of the phenolic hydroxyl group and the carboxyl group (chelate formation) is increased, and the strength of the acid decreases less rapidly than that of other hydroxybenzoic acids as the alcohol content is increased.

Experimental Section

Materials.—*m*-Cresol was methylated with dimethyl sulfate in the usual manner,[9] giving rise to an 83% yield of *m*-methoxytoluene. This was then oxidized in 63% yield to *m*-methoxybenzoic acid according to the method of Ullmann and Uzbachian.[10] The other methoxybenzoic and hydroxybenzoic acids were available commercially. They were purified by recrystallization from water–alcohol mixtures.

Results.—The measurements were made with a hydrogen electrode. The dissociation constants used are the hydrogen-ion activities at equal concentrations of undissociated acid and negative ion. Measurements were made over a range of concentrations and at 40, 50 and 60% neutralization. The constants were calculated by the equation

$$Ka = \frac{[\mathrm{H^+}][\mathrm{Na^+} + \mathrm{H^+} - Kw/\mathrm{H^+}]}{M - [\mathrm{Na^+} + \mathrm{H^+} - Kw/\mathrm{H^+}]}$$

M represents the total concentration of the acid and its salt. Kw for 25% alcohol was taken as 5×10^{-15}. Details of the method have already been published.[2,11] A summary of the results is given in Table II.

TABLE II

SUMMARY OF DISSOCIATION CONSTANTS AT 25° IN 25% EtOH (NINE MEASUREMENTS OF EACH)

Acid, benzoic	Molality range	Range of Ka	Mean Ka $\times 10^5$	Av. dev. from mean, Ka, %
o-Hydroxy	0.06–0.02	63.0–64.9	63.8	0.7
m-Hydroxy	.06–0.02	2.37–2.47	2.43	1.1
p-Hydroxy	.06–0.02	0.734–0.771	0.750	1.6
o-Methoxy	.06–0.02	2.03–2.12	2.09	1.1
m-Methoxy	.06–0.02	2.82–2.92	2.87	0.8
p-Methoxy	.005–0.002	1.10–1.18	1.16	1.2

Summary

The dissociation constants of the hydroxybenzoic and methoxybenzoic acids have been determined in 25% alcohol.

It is pointed out that the strength of salicylic acid appears anomalously great. An explanation is given based on hydrogen bond formation giving rise to a chelate ring. The theory also explains the low second dissociation constant of salicylic acid, and the observed low value of $K_{\mathrm{H_2O}}/K_{\mathrm{EtOH}}$ for salicylic acid.

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[8] Senter and Bulle, *J. Chem. Soc.*, **101**, 2533 (1912).

[9] Fisher, "Laboratory Manual of Organic Chemistry," 2d ed., John Wiley and Sons, New York, 1924, pp. 180–181.

[10] Ullmann and Uzbachian, *Ber.*, **36**, 1805 (1903).

[11] Yabroff, Branch and Bettman, THIS JOURNAL, **56**, 1856 (1934).