[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF BRITISH COLUMBIA, VANCOUVER 8, CANADA]

The Position of Protonation of the Carboxyl Group[1]

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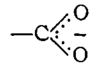
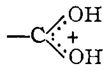
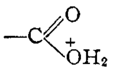
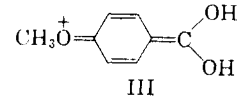
Support for the carbonyl protonated, resonance stabilized form I rather than the hydroxyl protonated form II for the protonated carboxyl group has been obtained. The basicities of 22 *m*- and *p*-substituted benzoic acids have been determined. The close correlation between the basicities of the benzoic acids and those of the corresponding acetophenones indicates that direct conjugation occurs between substituents and the protonated carboxyl group. The effect of substituents on the ultraviolet and infrared spectra of benzoic acid is discussed.

The carboxyl group can undergo protonation at either the carbonyl oxygen to give structure I or at the hydroxyl oxygen to give structure II. The latter formula appears for the most part in the older literature, whereas the former has been favored by most authors in recent years. The fact that structure I is resonance stabilized whereas structure II is not has undoubtedly caused this reversal in general favor. The symmetry of structure I is also a factor in its favor for if one considers the manner in which two protons would be added to the symmetrical carboxylate ion  $-C\langle^{O}_{O}\,-$ to produce the cation $-CO_2H_2^+$, it seems only reasonable that the added protons would not occupy the same site as in II but rather separate, equivalent, sites as in I.[2] However, no clear-cut evidence appears to exist on the question of the structure of the protonated carboxyl group, a species which is an important intermediate in many organic reactions. This research, therefore, was undertaken to establish, if possible, the structure of the ion $-CO_2H_2^+$.


$-C\langle^{OH}_{OH}\,+$ I


$-C\langle^{O}_{OH_2}\,+$ II

The method of approach in this work is based on the fact that the positive charge is localized in structure II, but can be spread by resonance to the attached group in structure I. Thus the following resonance structure will contribute to the stability of the conjugate acid of anisic acid only if carbonyl oxygen protonation occurs. Recent work by several groups of investigators[4] has shown that when direct resonance interaction occurs such as that shown in III the compound's reactivity cannot be correlated by the well known Hammett equation, $\log k/k_0 = \rho\sigma$. The use of a set of modified substituent constants,[4c,d] σ^+, however, has enabled those reaction series in which a positive charge is developed in conjugation with the ring to be successfully treated by a linear free energy relation of the Hammett type, *viz.*, $\log k/k_0 = \rho\sigma^+$. We have previously studied the protonation of acetophenones[5] and benzaldehydes,[6] molecules in which only carbonyl protonation is possible. In both cases the basicities are correlated better by σ^+ than by σ.


III

Experimental

Benzoic Acids.—Commercially available benzoic acids were purified by several recrystallizations. *p*-Ethylbenzoic acid and *p*-phenylbenzoic acid were prepared by the hypochlorite oxidation of the corresponding acetophenones essentially by the method of Newman and Holmes.[7] *m*-Ethoxybenzoic acid was prepared by the etherification of the corresponding hydroxy compound using ethyl iodide and sodium. All melting points checked closely with those in the literature.

Measurement of pK_{BH^+}.—These were determined by the graphical method as previously described[8] and were checked in some cases by other means.[9]

Infrared Spectra.—Solutions of the acids were made up in reagent grade chloroform which had been dried over P_2O_5 and redistilled. To minimize dimerization concentrations of acid in the range 0.01 to 0.05 *M* were used. The spectra of the solutions were recorded on a Perkin-Elmer model 21 double beam recording spectrometer fitted with CaF_2 optics with a solvent blank being employed in all cases. The position of each peak was determined six times and an average value taken. Only *p*-iodo-, *m*-hydroxy- and *p*-hydroxybenzoic acids were not sufficiently soluble to give reproducible spectra. Attempts to observe the changes in OH and C=O stretching frequencies on protonation in strongly acid solutions met with failure owing to the strong absorption of such species as H_2SO_4, H_2O and H_3O^+[10] even when solvent blanks were used.

Results and Discussion

The pK_{BH^+} values for the benzoic acids are listed in Table I together with spectral data for the ionized and neutral forms. In Fig. 1a the pK_{BH^+} values are plotted as a function of the corresponding pK_a values with the straight line drawn with respect to non-deviating points,[5] *i.e.*, *meta* derivatives excluding hydroxyl and alkoxyl. (This is equivalent to a conventional Hammett plot

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[1] (a) Taken in part from a thesis submitted by K. Yates in partial fulfillment of the requirements for the Ph.D. degree, 1959. (b) Presented in part at the San Francisco Meeting of the American Chemical Society, April, 1958.

[2] These arguments do not apply with equal weight to the question of amide protonation. Some evidence exists, in fact, to indicate that N-protonation of amides is favored; see M. Davies and L. Hopkins, *Trans. Faraday Soc.*, **53**, 1563 (1957); E. Spinner, *Spectrochim. Acta*, **2**, 95 (1959) (see, however, ref. 3).

[3] (a) A. Burger, A. Loewenstein and S. Meiboom, THIS JOURNAL, **81**, 62 (1959); (b) G. Fraenkel and C. Niemann, *Proc. Natl. Acad. Sci. U. S. A.*, **44**, 688 (1958).

[4] (a) J. K. Kochi and G. S. Hammond, THIS JOURNAL, **75**, 3445 (1953); (b) J. J. Jaruzelski, N. C. Deno and A. Schriesheim, *J. Org. Chem.*, **19**, 155 (1954); (c) H. C. Brown and Y. Okamoto, THIS JOURNAL, **79**, 1913 (1957); (d) N. C. Deno and W. L. Evans, *ibid.*, **79**, 5804 (1957).

[5] R. Stewart and K. Yates, *ibid.*, **80**, 6355 (1958).

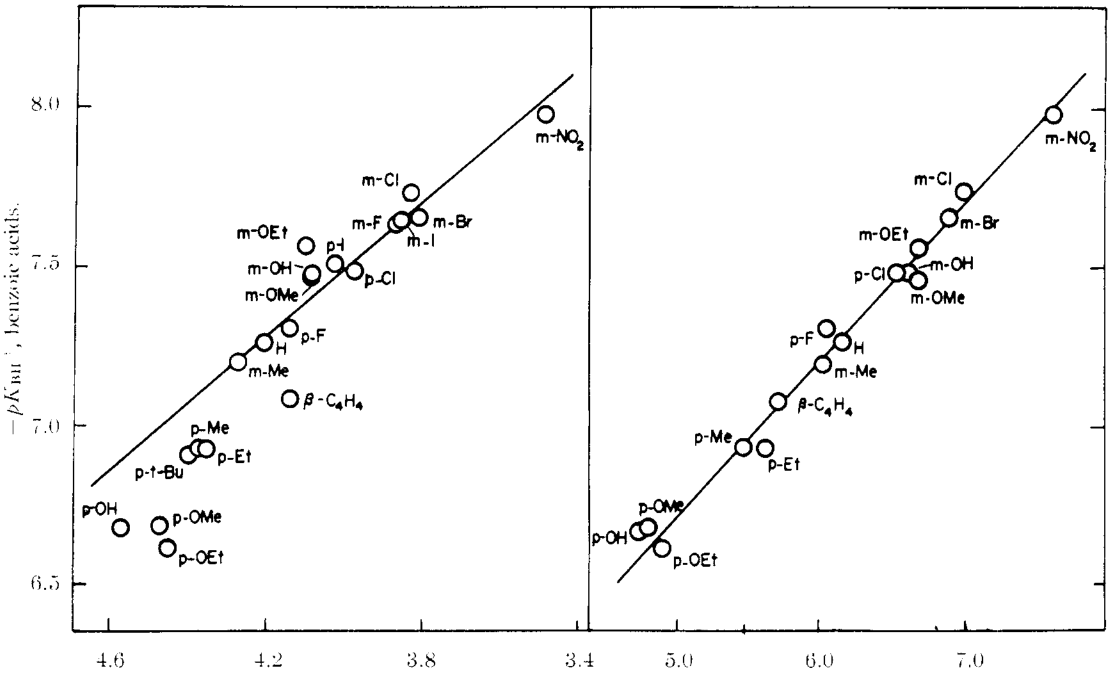
[6] K. Yates and R. Stewart, *Can. J. Chem.*, **37**, 664 (1959).

[7] M. S. Newman and H. L. Holmes, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 428.

[8] C. J. Davis and T. Geissman, THIS JOURNAL, **76**, 3507 (1954).

[9] For a critical evaluation of methods of determining *pK* values of very weak bases see K. Yates, Ph.D. thesis, University of British Columbia, 1959.

[10] M. Falk and P. A. Giguere, *Can. J. Chem.*, **35**, 1195 (1957).



(a) pK_a, benzoic acids. (b) $-pK_{BH^+}$, acetophenones.

Fig. 1.—The pK_{BH^+} values of benzoic acids as functions of (a) the corresponding pK_a values, and (b) the pK_{BH^+} values of the corresponding acetophenones.

since σ is defined in terms of pK_a.[11]) The deviations are similar in both type and magnitude to those previously observed in the acetophenone series.[5] Again those points falling above the line are of the *m*-alkoxy type which can interact with the acidic solvent by hydrogen bonding as previously discussed.[5] Those points falling considerably below the line in Fig. 1a again represent those *p*-substituents which are able to donate electrons by resonance.

Figure 1b shows the pK_{BH^+} values of the benzoic acids plotted against those of the corresponding acetophenones. An excellent linear relation is obtained (correlation coefficient, $r = 0.992$; standard deviation, $s = 0.053$) showing the great similarity between the protonation reactions in the two series. In view of the known mode of basic ionization of acetophenone and acidic ionization of benzoic acid, the results of the pK_{BH^+} measurements provide strong evidence for the existence of structure V as the conjugate acid of benzoic acid rather than structure V. The latter will, of course, be present in equilibrium with IV but will exist, we believe in much lower concentration.[12] It is conceivable that the above equilibrium might actually favor V, for benzoic acid and its derivatives with electron

TABLE I

BASICITY CONSTANTS AND ADSORPTION MAXIMA FOR SUBSTITUTED BENZOIC ACIDS

Substituent	$-pK_{BH^+}$	In 56–63% H_2SO_4 λ_{max}, mμ	In 56–63% H_2SO_4 log ϵ_{max}	In 95–98% H_2SO_4 λ_{max}, mμ	In 95–98% H_2SO_4 log ϵ_{max}
Hydrogen	7.26[a]	235	4.04	260	4.26
m-Methyl	7.19	240	3.88	270	4.11
p-Methyl	6.92	246	4.16	277	4.28
p-Ethyl	6.92	247	4.08	280	4.28
m-Methoxy	7.45	240	3.92	260	4.08
p-Methoxy	6.68	263	4.18	300	4.29
m-Ethoxy	7.56	240	3.96	260	4.12
p-Ethoxy	6.61	260	4.15	300	4.31
m-Hydroxy	7.47	239	3.96	258	4.09
p-Hydroxy	6.67	256	4.08	295	4.30
m-Fluoro	7.62	232	3.94	258	4.07
p-Fluoro	7.30	237	4.09	267	4.27
m-Chloro	7.73	238	4.07	262	4.20
p-Chloro	7.48	249	4.28	279	4.47
m-Bromo	7.65	240	4.00	263	4.17
m-Iodo	7.64	220	4.38	235	4.35
p-Iodo	7.50	261	4.10	313	4.22
m-Nitro	7.97	222	4.35	234	4.38
p-Nitro	. .	265	4.16	269	4.23
β-C_4H_4[b]	7.08	240	4.70	260	4.61
p-*t*-Butyl	6.90	250	4.16	280	4.38
p-Phenyl[c]	6.9	283	3.91	308	4.50
o-Methyl	7.4	238	4.16	266	4.43

[a] M. A. Paul and F. A. Long, *Chem. Revs.*, **57**, 1 (1957), list the corrected value −7.38 for benzoic acid. [b] 3,4-Benzo group as in β-naphthyl. [c] Determined approximately using method of L. A. Flexser, L. P. Hammett and A. Dingwall, THIS JOURNAL, **57**, 2103 (1935), because of insufficient solubility in dilute aqueous acids.

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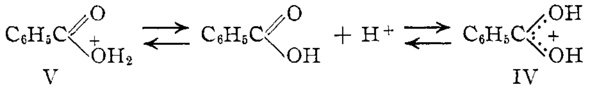
(11) The pK_a values refer to the acid ionization of benzoic acids and were all taken from the σ-constants of D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958). Most of the values correspond closely to the σ-values of H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

(12) A referee has suggested that the present results might be explained in terms of hydroxyl protonation and resonance of the kind

We feel that the structure on the right should have a negligible effect in stabilizing this ion.



$$C_6H_5C(=O)\overset{+}{O}H_2 \rightleftharpoons C_6H_5C(=O)OH + H^+ \rightleftharpoons C_6H_5C(OH)_2^+$$

V IV

withdrawing groups and be simply shifted over toward IV by the substitution of electron-withdrawing groups in the ring. This would be in approximate accord with the results shown in Fig. 1a. The very close correspondence between the effect of substituents on the benzoic acid and acetophenone series, however, indicates that the protonation processes are the same in both.

Further support for the resonance-stabilized form IV can be found by examining the linear inductive free energy relation derived by Taft.

$$\frac{1}{1-\alpha}\left[\log\frac{K_m}{K_H} - \alpha\log\frac{K_p}{K_H}\right] = \rho_I\sigma_I$$

K_m and K_p are rate or equilibrium constants for similarly substituted *m*- and *p*- derivatives and K_H for the unsubstituted compound. The quantities ρ_I and σ_I are the inductive contributions to the usual Hammett parameters.[13] The constant α has a "normal" value of $^1/_2$ to $^1/_3$[14] and apparently represents the ratio of *meta* to *para* resonance effects which result from resonance of the substituent with the aromatic system alone, *i.e.*, resonance polar effect. In his treatment Taft found it necessary to use a smaller value of α, $^1/_{10}$, when a change of conjugation of the *p*-substituent with the side chain reaction center occurs during the process. We find that use of the "normal" value of α gives a wide scatter of points for the basicities of both benzoic acids and acetophenones. Use of the smaller value of α, $^1/_{10}$, for all points (except *p*-nitro which cannot conjugate in any case) in the benzoic acid and acetophenone series gives good linear relations. For example, in the benzoic acid series where enough data for seven points are available, use of $\alpha = {}^1/_{10}$ gave $r = 0.954$ whereas $\alpha = {}^1/_3$ gave only $r = 0.832$. This indicates that there is direct conjugation between the *p*- substituents and the positively charged group of the conjugate acid.

Rho Value.—The ρ-values found for the non-deviating points are 2.17, 1.85 and 1.09 for the acetophenone, benzaldehyde and benzoic acid series. The much lower ρ for benzoic acid reveals the greater importance of resonance within the protonated carboxyl group.

Correlation with Ultraviolet Spectra.—The red shifts in the ultraviolet spectra of benzoic acids produced by protonation can be seen in Table I. The effects of substitution on the wave length maxima is similar in both the neutral benzoic acid series and their conjugate acids. In fact an excellent linear relation exists ($r = 0.979$) when the wave length displacements produced by substitution in the two series are plotted against each other. The slope is 1.71 (conjugate acids on ordinate) indicating the greater stabilizing effect of electron-supplying groups on the excited state of the conjugate acids than on the excited state of the neutral molecules.

Correlation with Infrared Spectra.—We have previously shown that a close relation exists between the carbonyl stretching frequencies and the basicities of acetophenones.[5] Table II lists values of the carbonyl stretching frequency for benzoic acids determined in the present study in chloroform. A correlation exists for these compounds also, but the agreement is less satisfactory ($r = 0.945$) than in the previous case. The slopes in both cases are negative since those substituents which are able to supply electrons tend to lower both the bond order of the carbonyl group and stabilize the conjugate acid.

TABLE II

CARBONYL STRETCHING FREQUENCIES OF SUBSTITUTED BENZOIC ACIDS

Substituent	C=O (monomer), cm.$^{-1}$	Substituent	C=O (monomer), cm.$^{-1}$
Hydrogen	1711 ± 1	*m*-Chloro	1719 ± 1
m-Methyl	1709 ± 1	*p*-Chloro	1714 ± 2
p-Methyl	1708 ± 1	*m*-Bromo	1720 ± 2
m-Methoxy	1712	*m*-Iodo	1716 ± 1
p-Methoxy	1703	*m*-Nitro	1727 ± 1
m-Ethoxy	1712 ± 2	*p*-*t*-Butyl	1708
p-Ethoxy	1702	*p*-Phenyl	1708 ± 1
m-Fluoro	1719 ± 1	β-C_4H_4	1709
p-Fluoro	1714 ± 2	*p*-Ethyl	1707 ± 1

Acknowledgment.—The financial support of the National Research Council of Canada is gratefully acknowledged.

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[13] R. W. Taft, Jr., and I. C. Lewis, THIS JOURNAL, **80**, 2436 (1958).

[14] Reference 13 and personal communication from Professor Taft.