Hydrogen-Bond Relations between Homoconjugates and Heteroconjugates of Substituted Benzoic Acids and Benzoates in Acetonitrile. Dissociation Constants of Substituted Benzoic Acids[1]

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Abstract: Values of $K^f_{HA \cdot Cl^-}$, $K^f_{(HA)_2Cl^-}$ (HA = substituted benzoic acid), $K^f_{HR \cdot A^-}$, $K^f_{(HR)_2A^-}$ (HR = p-bromophenol), $K^f_{HA_2^-}$, and $K^f_{(HA)_2A^-}$ in acetonitrile (AN) are reported in Table I. The negative logarithms of the solubility products of lithium benzoate and sodium m-bromo-, p-nitro-, m-nitro-, 3-nitro-4-chloro-, and o-nitrobenzoates were found to be 10.5, 8.0, 8.2₄, 7.8₈, 7.4₄, and 5.8₈, respectively. They have been calculated from the conductance of their saturated solutions in the presence of various concentrations of HA, knowing $K^f_{HA_2^-}$. With the exception of p-methoxy and p-hydroxy substituents plots of log $K^f_{HA_2^-}$, log $K^f_{HA \cdot Cl^-}$, and $K^f_{HR \cdot A^-}$ *vs.* Hammett σ values are linear. From a comparison of the ratio of ρ values from the Hammett plots of log $K^f_{HA \cdot Cl^-}$ and of log $K^f_{HR \cdot A^-}$, it is concluded that the hydrogen-bond donating properties of phenols as compared to those of benzoic acids are affected by substituents in the same way as the hydrogen-bond accepting properties of the corresponding anions. In AN the ratio of the ρ values for phenols and benzoic acids from the Hammett plots of pK^d_{HA} is 2.0, while the ratio of ρ values from Hammett plots of log $K^f_{HA \cdot Cl^-}$ for phenols and benzoic acids and also of log $K^f_{HR \cdot A^-}$ is equal to 2.1. For o-nitro substituents a value of $\sigma_{o-NO_2} = 1.10$ fits the Hammett plots of pK^d_{HA}, log $K^f_{HA \cdot Cl^-}$, and log $K^f_{HR \cdot A^-}$, while for o-chloro substituents a value of $\sigma_{o-Cl} = 0.60$ fits the Hammett plot of log $K^f_{HA \cdot Cl^-}$. The rotation of the carboxyl group in the above ortho-substituted benzoic acids and benzoates accounts for minimal steric interference in formation of *inter*molecular hydrogen bonds. *Intra*molecular hydrogen bonding in these benzoic acids is practically absent. The Hammett plot of log K ($K = K^f_{HA \cdot Cl^-} K^f_{HR \cdot A^-}/K^f_{HA_2^-} K^f_{HR \cdot Cl^-}$) has a slope of -0.50, identical with the expected sum ($\rho_{HR \cdot A^-} + \rho_{HA \cdot Cl^-} - \rho_{HA_2^-}$). The value of K is independent of the meta- and para-substituted phenol, HR, used.

In a previous study[2] the hydrogen-bond donating capacity of meta- and para-substituted phenols (HA) with reference to chloride, as indicated by the heteroconjugation constant

$$K^f_{HA \cdot Cl^-} = [HA \cdot Cl^-]/[HA][Cl^-]$$
$$f_{HA \cdot Cl^-} = f_{Cl^-} \tag{1}$$

was found to increase with increasing acid strength of HA in acetonitrile (AN). The hydrogen-bond accepting capacity of A⁻ with reference to p-bromophenol (HR), as indicated by

$$K^f_{HR \cdot A^-} = [HR \cdot A^-]/[HR][A^-]$$
$$f_{HR \cdot A^-} = f_{A^-} \tag{2}$$

was found to increase with increasing basic strength of A⁻. The equilibrium constant of the reaction

$$HA_2^- + HR \cdot Cl^- \rightleftharpoons HA \cdot Cl^- + HR \cdot A^- \tag{3}$$
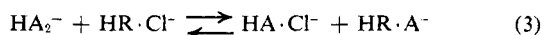
was found close to 1 except for 2,6-dinitro-4-chlorophenol. In the present paper the equilibrium constants (*cf.* eq 1–3) have been determined in AN for substituted benzoic acids, the anions of which have a much more localized charge than the corresponding phenolates.

Included in the present paper are dissociation constants of some meta- and para-substituted chloro-, bromo- and methylbenzoic acids in AN. This was done to ascertain whether the pK^d_{HA} values of m- and p-nitro-substituted benzoic acids lie on the same Hammett plot as those with other meta and para substituents.

In the literature no pK^d_{HA} *vs.* σ plots are to be found in aprotic solvents for nitro-substituted benzoic acids. Recently such a plot has been reported for nitrophenols in AN.[2]

In the present paper a comparison of the ρ values from the Hammett plots of log $K^f_{HA \cdot Cl^-}$ for benzoic acids and phenols (also of similar log $K^f_{HR \cdot A^-}$ plots) is made. These ρ values basically reflect the sensitivity of the two different aromatic systems to substitution with regard to hydrogen-bond formation. Minor effects due to polarization of the phenolate and benzoate ions may arise, due to hydrogen bonding of these anions to the aprotic solvent,[3] although these solvents are generally poor hydrogen-bond donors.

Only recently reliable σ values of o-nitro, chloro, and iodo substituents have become available, as found from the hydroxyl proton nmr chemical shifts in ortho-substituted phenols in hexamethylphosphoramide.[4] In the present paper σ values of these substituents are found by introducing (pK^d_{HA})$_{AN}$, log $K^f_{HR \cdot A^-}$, or log $K^f_{HA \cdot Cl^-}$ values of ortho-substituted benzoic acids or benzoates on the corresponding Hammett plots constructed from data obtained for meta- and para-substituted benzoic acids or benzoates. The resulting ortho σ values yield information concerning the role of steric inhibition of resonance in dissociation and heteroconjugation of ortho-substituted benzoic acids in aprotic media. This will be compared in a future paper to the situation in several aprotic solvents and in water.[5]

(2) I. M. Kolthoff and M. K. Chantooni, Jr., *J. Amer. Chem. Soc.*, **91**, 4621 (1969).

(3) R. Kerber and A. Porter, *ibid.*, **91**, 366 (1969).

(4) M. W. Dietrich, J. Nash, and R. Keller, *Anal. Chem.*, **38**, 1479 (1966).

(5) See, *e.g.*, E. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1959, p 236.
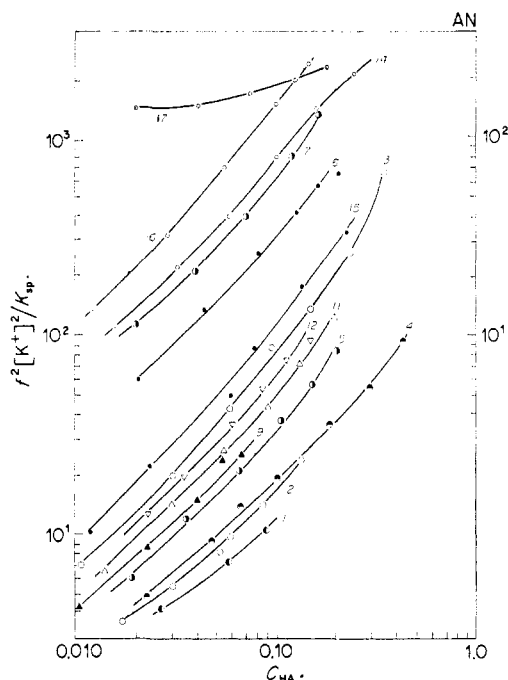
Figure 1. Plots of $f^2[K^+]^2/K_{sp}$ vs. C_{HA} of potassium chloride for various benzoic acids. Numbers are same as those in Table I: right-hand ordinate, curves 6, 7, 14, 16, 17; others, left-hand ordinate.

Values of $K^f_{HA \cdot Cl^-}$ and $K^f_{(HA)_2Cl^-}$ were estimated from the effect of HA on the ionic solubility of potassium chloride, as was done previously with phenols,[2] while values of $K^f_{HR \cdot A^-}$ and $K^f_{(HR)_2A^-}$ were determined from the increase in ionic solubility of the lithium or sodium benzoates in presence of HR or from the effect of HR upon the potentiometrically determined pa_H of a mixture of the substituted benzoic acid and its tetraethylammonium salt.[6] All pK^d_{HA} values[6] and some values of $K^f_{HR \cdot A^-}$ and $K^f_{(HR)_2A^-}$ were determined potentiometrically with the glass electrode.

Experimental Section

Chemicals. Acetonitrile was purified and dispensed as previously described.[7]

Phenols. The following phenols were used previously: p-bromo-,[8] p-methoxy-,[2] o-nitro-,[2] and m-nitrophenol.[9]

Benzoic Acids. The following benzoic acids were used previously: benzoic (unsubstituted), m-bromo-,[10] p-hydroxy-,[10] p-nitro-,[10] and 3,5-dinitrobenzoic.[11] p-Methoxybenzoic, mp 183° (lit. 184°[12]), o-iodobenzoic, mp 162° (lit. 162°[12]), and o-chlorobenzoic acid, mp 141° (lit. 142°[12]), were Eastman Kodak White Label products. 2,6-Dichlorobenzoic, mp 147° (lit. 139°[12]), 3,5-dichlorobenzoic, mp 188° (lit. 182°[12]), 2-nitro-5-chlorobenzoic, mp 141°, and 2,4-dinitrobenzoic acid, mp 181° (lit. 182°[12]), were from Aldrich Co. m-Nitrobenzoic, mp 142° (lit 141°[12]), 3-nitro-4-chlorobenzoic, mp 183°, and o-nitrobenzoic acid, mp 148°, (lit. 148°[12]), were Baker Co. products, while 3,4-dimethylbenzoic acid was from K and K Co., mp

(6) I. M. Kolthoff and M. K. Chantooni, Jr., Anal. Chem., 39, 1080 (1967).
(7) I. M. Kolthoff, S. Bruckenstein, and M. K. Chantooni, Jr., J. Amer. Chem. Soc., 83, 3927 (1961).
(8) I. M. Kolthoff and M. K. Chantooni, Jr., ibid., 85, 2195 (1963).
(9) I. M. Kolthoff, M. K. Chantooni, Jr., and S. Bhowmik, ibid., 88, 5430 (1966).
(10) I. M. Kolthoff and M. K. Chantooni, Jr., J. Phys. Chem., 70, 856 (1966).
(11) I. M. Kolthoff and M. K. Chantooni, Jr., J. Amer. Chem. Soc., 85, 426 (1963).
(12) "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., Cleveland, Ohio, 1967.

167° (lit. 166°[12]). 3,4-Dichlorobenzoic acid was prepared by oxidation of the aldehyde (Aldrich) with hydrogen peroxide in dilute aqueous sodium hydroxide solution.[13] All the benzoic acids were recrystallized from water or water–ethanol mixtures and dried in vacuo at 60°.

Salts. Tetraethylammonium m-nitro-, 3-nitro-4-chloro-, o-nitro-, o-chloro-, 2,6-dichloro-, 3,4-dimethyl-, 3,5-dichloro-, 3,4-dichloro-, 2-nitro-5-chloro-, and 2,4-dinitrobenzoates were prepared by neutralizing potentiometrically the corresponding acid in ethanol with 1 M aqueous tetraethylammonium hydroxide. The latter was prepared as described previously.[7] The ethanolic solutions of the salts were taken to dryness and washed with anhydrous ether and the salts recrystallized from ethyl acetate–ethanol mixtures. They were dried at 60° in vacuo. Assays of the m-nitro- and 2,4-dinitrobenzoates by visual titration in acetonitrile with perchloric acid (in acetic acid) using p-naphtholbenzein as indicator were 99.5, 99.7%, respectively.[14] Tetraethylammonium benzoate, m-bromo-, p-nitro-, and 3,5-dinitrobenzoates, lithium benzoate, and sodium p-nitrobenzoate were products used previously.[10]

Sodium m-bromo-, m-nitro-, 3-nitro-4-chloro-, and o-nitrobenzoates were prepared in the same way as the tetraethylammonium salts and were recrystallized from ethanol. Assay by the above titration procedure in 1:5 acetic acid:AN mixture was 99.0, 99.2, 98.9, and 99.0%, respectively. Prior to the titration, the salts were dissolved in anhydrous acetic acid.[10] Potassium chloride was used previously.[2]

Instrumentation. The experimental techniques employed in the conductometric determination of the ionic solubility of potassium chloride in the presence of the various substituted benzoic acids and of the ionic solubilities of lithium benzoate and sodium benzoates in the presence of both the parent acid and p-bromophenol have previously been described.[2] Potentiometric pa_H measurements were made as described previously.[9]

Results

Ionic Mobilities. The following ionic mobilities at infinite dilution at 25° have been reported: K^+, 76;[10] Na^+, 70;[15] Li^+, 59.5;[15] Cl^-, 89;[16] benzoate, 62;[15] 3,5-dinitrobenzoate, 100;[11] and salicylate, 78.[10] The mobility of the o-nitrobenzoate ion has been assumed equal to that of salicylate. The mobilities of the homoconjugate and heterconjugate (with p-bromophenol) anion of p-nitro-, m-bromo-, m-nitro-, and 3-nitro-4-chlorobenzoate at infinite dilution all have been assumed to be equal to $\lambda_{0,HBz \cdot Bz^-} = 45$;[10] $\lambda_{0,HR \cdot o-nitrobenzoate}$ has been taken equal to $\lambda_{0,HSal \cdot Sal^-} = 56.5$.[10] The mobilities of $(HR)_2A^-$ ions have been assumed equal to those of $HR \cdot A^-$ and of $HA \cdot Cl^-$ and $(HA)_2Cl^-$ to those of $HR \cdot Cl^-$ ($HR = p$-bromophenol).

Determination of $K^f_{HA \cdot Cl^-}$ and $K^f_{(HA)_2Cl^-}$. Conductance of Saturated Potassium Chloride Solutions in the Presence of Various Benzoic Acids. As observed with the phenols,[2] an increase in ionic solubility of potassium chloride was found conductometrically in presence of all the benzoic acids studied. It has been assumed that the potassium ion is not complexed by the benzoic acids. The ionic solubility data of potassium chloride in presence of the various benzoic acids are represented as plots of $f^2[K^+]^2/K_{sp}$ vs. C_{HA} on logarithmic scales in Figure 1, where C_{HA} denotes the analytical acid concentration.[2] In all systems the analytical and equilibrium concentrations of HA can be taken equal. The constants log $K^f_{HA \cdot Cl^-}$ and log $K^f_{(HA)_2Cl^-}$ entered in Table I were evaluated from the data in Figure 1 as described previously,[2] using the value of 1.1×10^{-8} for

(13) R. Shriner and R. Fuson, "Systematic Identification of Organic Compounds," Wiley, New York, N. Y., 1948, p 170.
(14) I. M. Kolthoff, M. K. Chantooni, Jr., and S. Bhowmik, Anal. Chem., 39, 1627 (1967).
(15) S. Minc and L. Werblan, Rocz. Chem., 40, 1537 (1966).
(16) P. Walden and E. Birr, Z. Phys. Chem., 144, 269 (1929).

Table I. Homoconjugation of Substituted Benzoic Acids (HA) and Their Heteroconjugates with Chloride and of Corresponding Benzoates with p-Bromophenol

Substituent on benzoic acid	p$K^d{}_{HA}$	Log $K^f{}_{HA \cdot Cl^-}$	Log $\beta_{HA \cdot Cl^-}{}^a$	Log $K^f{}_{HR \cdot A^-}$	Log $\beta_{HR \cdot A^-}$	Log $K^f{}_{HA_2^-}$	Log $\beta_{HA_2^-}$
1. p-Methoxy		2.09	d				
2. 3,4-Dimethyl	21.25[b]	2.18	d				
3. p-Hydroxy	20.8[c]					3.05[c,f]	d
4. Benzoic (unsubst)	20.7[c]	2.22	−0.13	3.55[e]	0.68[e]	3.60[c,f]	d
5. m-Bromo	19.5[c]	2.41	0.46	3.26[e]	1.08[e]	3.75[c,f]	d
6. o-Iodo		2.42	0.28				
7. o-Chloro		2.56	0.90				
8. 3,4-Dichloro	19.04[b]						
9. m-Nitro	19.29[b]	2.59	0.49	3.06[e]	1.09[e]	4.03[f]	1.57[f]
10. 3,5-Dichloro	18.75[b]						
11. p-Nitro	18.7[c]	2.51	0.33	3.04[e]	1.12[e]	3.85[c,f]	d
12. 3-Nitro-4-chloro	18.55[b]	2.69	0.51	2.98[e]	0.81[e]	3.97[f]	1.14[f]
13. o-Nitro	18.24[b]	2.75	0.65	2.86[e]	d	3.98[f]	1.21[f]
				2.90[f]	0.80[f]		
14. 2,6-Dichloro		2.80	0.24				
15. 3,5-Dinitro	16.9[c]	2.90	0.65	2.56[e]	1.04[e]	4.0[f]	d
						4.22[c,e]	d
16. 2-Nitro-5-chloro		2.99	0.67				
17. 2,4-Dinitro	16.19[b]	3.12	0.57	2.38[f]	0.43[f]	4.29[f]	0.87[f]
				1.90[g]	0.55[g]		
				2.78[h]	0.54[h]		
				1.62[i]	d		

^{a} $\beta_{HA \cdot Cl^-} = K^f{}_{(HA)_2Cl^-}/K^f{}_{HA \cdot Cl^-}$, $\beta_{HR \cdot A^-} = K^f{}_{(HR)_2A^-}/K^f{}_{HR \cdot A^-}$, $\beta_{HA_2^-} = K^f{}_{(HA)_2A^-}/K^f{}_{HA_2^-}$. ^{b} This work. ^{c} I. M. Kolthoff and M. K. Chantooni, Jr., *J. Phys. Chem.*, **70**, 856 (1966). ^{d} No detectable (HA)$_2$Cl$^-$, (HR)$_2$A$^-$, or (HA)$_2$A$^-$ found. ^{e} Solubility value. ^{f} Potentiometric value. ^{g} HR = p-methoxyphenol. ^{h} HR = m-nitrophenol. ^{i} HR = o-nitrophenol.

K_{sp} of potassium chloride[2] and considering the salts KHACl and K(HA)$_2$Cl as completely dissociated.

Determination of $K^f{}_{HR \cdot A^-}$ and $K^f{}_{(HR)_2A^-}$. Conductance of Saturated Solutions of Lithium Benzoate or Sodium Benzoate in the Presence of p-Bromophenol. A marked increase in ionic solubility of lithium benzoate or sodium-substituted benzoates was observed in presence of p-bromophenol. It has been assumed that lithium and sodium ions are not complexed by p-bromophenol. Sodium o-nitrobenzoate has a sufficiently high ionic solubility to allow the direct conductometric determination of K_{sp}; this is not true for sodium m-bromo-, m-nitro-, p-nitro-, 3-nitro-4-chlorobenzoate, or lithium benzoate. For these salts K_{sp} is estimated from the conductometrically determined ionic solubility in presence of a known amount (0.7–2 × 10^{-2} M) of the parent acid. Under these conditions, the predominant anion species is HA$_2^-$; hence, [HA] = C_{HA} − [M$^+$]. The potentiometric value of $K^f{}_{HA_2^-}$ (*vide infra*) was used in eq 7 to evaluate K_{sp}, taking [HR] = 0.

In saturated solutions of the salt, MA, containing *both* the parent acid, HA, and p-bromophenol, HR, the following electroneutrality relation holds.

$$[M^+] = [A^-] + [HA_2^-] + [HR \cdot A^-] + [(HR)_2A^-] \quad (4)$$

Also

$$K^f{}_{HA_2^-} = [HA_2^-]/[HA][A^-] \quad (5)$$

$$K^f{}_{(HR)_2A^-} = [(HR)_2A^-]/[HR]^2[A^-] \quad (6)$$

Substituting eq 2, 5, and 6 and the expression for K_{sp} into eq 4, eq 7 results. Knowing K_{sp} and $K^f{}_{HA_2^-}$ and

$$f^2[M^+]^2 = K_{sp}\{1 + K^f{}_{HA_2^-}[HA] + K^f{}_{HR \cdot A^-}[HR] + K^f{}_{(HR)_2A^-}[HR]^2\} \quad (7)$$

using eq 7, $K^f{}_{HR \cdot A^-}$ and $K^f{}_{(HR)_2A^-}$ were estimated from the ionic solubility, [M$^+$], measured conductometrically, the solutions containing the same analytical concentra-

tion of HA as above and relatively high concentrations of HR (0.02–0.5 M).

It was assumed that [HR] = C_{HR} − [M$^+$]. Under the experimental conditions, [(HA)$_2$A$^-$] can be neglected. When $C_{HR} \geq 0.1$ M, the analytical and equilibrium concentrations, respectively, of HA and of HR become practically equal. Plots of $\{f^2[M^+]^2 - K_{sp} \cdot [1 + K^f{}_{HA_2^-}C_{HA}]\}/K_{sp}$ vs. C_{HR} according to eq 7 are presented in Figure 2. The following analytical concentrations of the benzoic acid, C_{HA}, were taken and the values of $K^f{}_{HA_2^-}$ reported previously[10] are: benzoic acid (unsubstituted), 5.1 × 10^{-2}, 4 × 10^4; m-bromobenzoic acid, 1.1 × 10^{-2}, 6.0 × 10^3; m-nitrobenzoic acid, 1.3 × 10^{-2}, 1.1 × 10^4 (this work); p-nitrobenzoic acid, 1.9 × 10^{-2}, 6.2 × 10^3; and 3-nitro-4-chlorobenzoic acid, 8.0 × 10^{-3}, 9.4 × 10^3 (this work).

The following values of K_{sp} were found: lithium benzoate, 3.2 × 10^{-11}; sodium m-bromobenzoate, 1.0 × 10^{-8}; m-nitrobenzoate, 1.3 × 10^{-8}; p-nitrobenzoate, 5.7 × 10^{-9}; 3-nitro-4-chlorobenzoate, 3.6 × 10^{-8}; and o-nitrobenzoate, 1.3 × 10^6. Values of log $K^f{}_{HR \cdot A^-}$ and log $K^f{}_{(HR)_2A^-}$ are tabulated in Table I.

Viscosity and Ion Atmosphere Corrections. The viscosities of solutions of the benzoic acids were assumed the same as those in 0.062 and 0.35 M 3,5-dinitrobenzoic acid, *i.e.*, 0.365 and 0.412 cP, respectively, while the viscosities of the p-bromophenol solutions were assumed the same as those of resorcinol,[8] *i.e.*, 0.373, 0.400, and 0.428 cP in 0.286, 0.532, and 0.750 M resorcinol. Ion atmosphere corrections were applied to all conductivity data.

Homoconjugation and Heteroconjugation Constants of Benzoic Acids and Benzoates from Potentiometric pa_H Data. Dissociation Constants of Benzoic Acids. Plots of pa_H vs. log C_{HA}/C_{Et_4NA} are presented in Figure 3 of mixtures of m-nitro-, 3-nitro-4-chloro-, o-nitro-, and 2,4-dinitrobenzoic acids and their tetraethylammonium salts. When large excesses of acid over salt are present, the slopes of all the plots in Figure 3 ap-
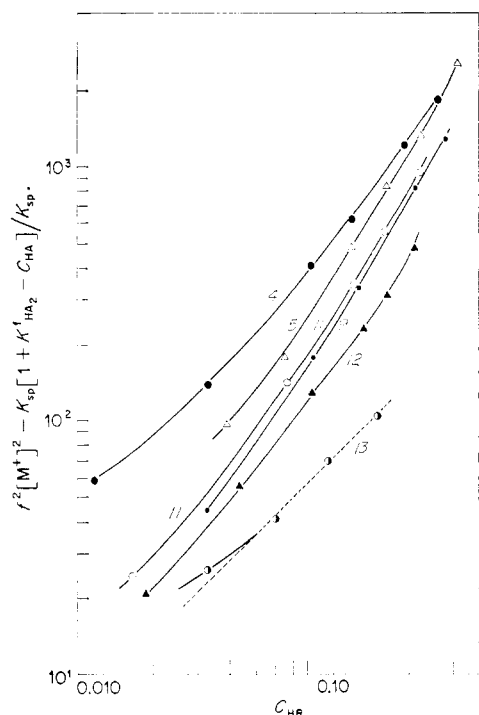
Figure 2. Plots of $[f^2[M^+]^2 - K_{sp}\{1 + K^f_{HA_2}-C_{HA}\}]/K_{sp}$ vs. C_{HR} of lithium benzoate and of sodium-substituted benzoates. Numbers are same as those in Table I. Dashed line in curve 13 has slope of 1.0.
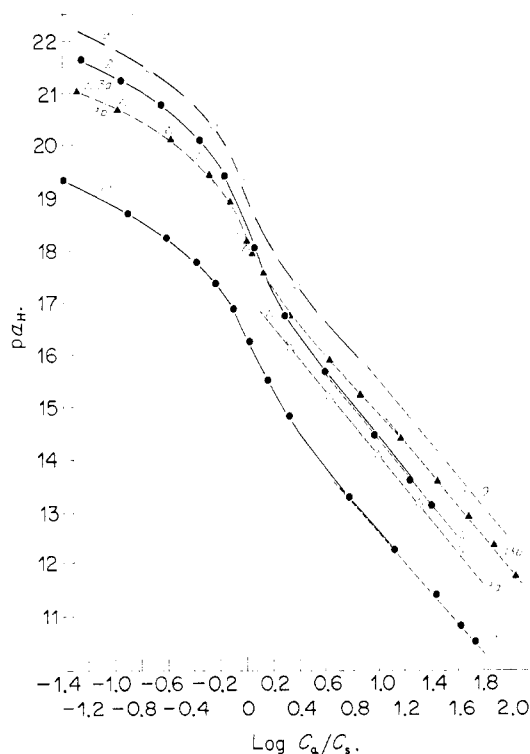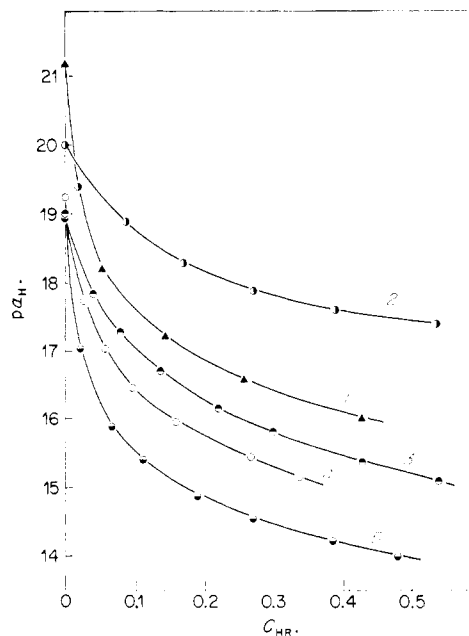

Figure 4. Plots of pa_H vs. C_{HR} in mixtures of nitrobenzoic acids and their tetraethylammonium salts containing HR. HR = p-bromophenol: curve 1, o-nitrobenzoic acid, C_{HA} = 7.00 × 10⁻⁴, C_S = 9.27 × 10⁻³ M; 2,2,4-dinitrobenzoic acid, C_{HA} = 8.55 × 10⁻⁴, C_S = 2.33 × 10⁻² M, HR = o-nitrophenol; 3, C_{HA} = 7.80 × 10⁻⁴, C_S = 7.90 × 10⁻³ M, HR = p-methoxyphenol; 4, C_{HA} = 1.00 × 10⁻³; C_S = 1.03 × 10⁻² M, HR = p-bromophenol; and 5, C_{HA} = 7.80 × 10⁻⁴, C_S = 7.90 × 10⁻³, HR = m-nitrophenol.

Figure 3. Plots of pa_H vs. log C_{HA}/C_S in mixtures of substituted benzoic acids and their tetraethylammonium salts: 9, 4.06 × 10⁻³ M m-nitrobenzoate; 12, 1.01 × 10⁻² M 3-nitro-4-chlorobenzoate; 13a, 8.05 × 10⁻³ M o-nitrobenzoate; 13b, 3.26 × 10⁻³ M o-nitrobenzoate; and 17, 3.44 × 10⁻³ M 2,4-dinitrobenzoate. Dashed lines have a slope of −3.0.

is negligible when $C_{HA} = C_{Et_4NA}$; values of pK^d_{HA} and $K^f_{HA_2}$- were calculated from potentiometric data[17] in solutions where $C_{Et_4NA} \geq C_{HA}$, assuming complete dissociation of Et_4NA and Et_4NHA_2. The assumption that $[(HA)_2A^-]_{1/2} \ll [HA_2^-]_{1/2}$, the subscript denoting half neutralization, i.e., $C = C_{HA} = C_{Et_4NA}$, is justified under our experimental conditions. For o-nitrobenzoic acid, for example, $K^f_{HA_2}$- = 1.0 × 10⁴ (Table I). In a solution 2.81 × 10⁻³ M in both this acid and its tetraethylammonium salt, $K^f_{HA_2}$- = 1.0 × 10⁴ = (2.81 × 10⁻³ − x)/x² or x = $[HA]_{1/2}$ = $[A^-]_{1/2}$ = 4.8 × 10⁻⁴ M; C − x = $[HA_2^-]_{1/2}$ = 2.3 × 10⁻³M. The ratio $\{[(HA)_2A^-]/[HA_2^-]\}_{1/2}$ = β_{HA_2}-$[HA]_{1/2}$ = (1.6 × 10) (2.3 × 10⁻³) = 3.7 × 10⁻², the value of β_{HA_2}- being equal to 1.6 × 10 (see Table I).

In solutions where $C_{HA} \gg C_{Et_4NA}$, on the other hand, it was assumed, as a first approximation, that $[HA_2^-]$, $[A^-] \ll [(HA)_2A^-]$, i.e., $[(HA)_2A^-] = C_{Et_4NA}$ and $[HA] = C_{HA} - 2C_{Et_4NA}$ in the expression $K_{3HA} = K^d_{HA} \cdot K^f_{(HA)_2A^-} = a_H \cdot [(HA)_2A^-]f/[HA]^3$. Knowing K^d_{HA}, K^d_{3HA}, and the pa_H, an approximate value of $K^f_{(HA)_2A^-}$ is found. Therefore, the ratio $[(HA)_2A^-]/[HA_2^-]$ (equal to $K^f_{(HA)_2A^-}\cdot[HA]/K^f_{HA_2}$-) can be estimated. Finally, $[(HA)_2A^-]$ is found from the ratio $[(HA)_2A^-]/[HA_2^-]$ and the conservation relation $C_{Et_4NA} = [A^-] + [HA_2^-] + [(HA)_2A^-]$, neglecting $[A^-]$, and K^d_{3HA} recalculated. Usually, three cycles are required for a constant value of K^d_{3HA}. For example, for o-nitrobenzoic acid: C_{HA} = 0.214, C_{Et_4NA} = 2.8 × 10⁻³ M, a_{H^+} = 4 × 10⁻¹³, K^d_{HA} = 5.8 × 10⁻¹⁹, K^d_{3HA} = 1 × 10⁻¹³ (first approximation). $K^f_{(HA)_2A^-}$ = 1 × 10⁻³/5.8 × 10⁻¹⁹ = 1.7 × 10⁵. Therefore, $[(HA)_2A^-]/[HA_2^-]$ = $K^f_{(HA)_2A^-}\cdot[HA]/K^f_{HA_2}$- = (1.7 × 10⁵)(2.1 × 10⁻¹)/1.0 × 10⁴ = 3.7.

(17) I. M. Kolthoff and M. K. Chantooni, Jr., J. Amer. Chem. Soc., 87, 4428 (1965).

proach −3.0, indicative of (HA)₂A⁻ formation. As a good approximation it was assumed that [(HA)₂A⁻]

Hence, $[(HA)_2A^-] = 2.2 \times 10^{-3}$, yielding $K^d_{3HA} = 0.8 \times 10^{-13}$. Another cycle yields the same value.

Values of log $K^f_{HA_2^-}$, log $\beta_{HA_2^-}$ ($\beta_{HA_2^-} = K^f_{(HA)_2A^-}/K^f_{HA_2^-}$), and p$K^d_{HA}$ of the various benzoic acids are tabulated in Table I.

As the ionic solubility of sodium 2,4-dinitrobenzoate was >0.01 M, the heteroconjugation constants with p-bromo-, p-methoxy-, m-nitro-, and o-nitrophenol, HR, were estimated from potentiometric pa_H data of 2,4-dinitrobenzoic acid, HA, with a large excess of its tetraethylammonium salt.[6] To check the values of $K^f_{HR \cdot A^-}$ and $K^f_{(HR)_2A^-}$ of o-nitrobenzoate derived from solubility data, the potentiometric method was used. It was shown that benzoic acid is not complexed by p-bromophenol.[6] From the potentiometric pa_H data plotted in Figure 4, it is concluded that both o-nitrobenzoates form mono- and diheteroconjugates with p-bromophenol, while 2,4-dinitrobenzoate also forms such conjugates with p-methoxy- and m-nitrophenol, but only the monoconjugate with o-nitrophenol. The potentiometrically determined heteroconjugation constants of o-nitro- and 2,4-dinitrobenzoates with the various phenols are entered in Table I. Acid–base interaction is negligible between 2,4-dinitrobenzoate ion and m-nitrophenol, which has the largest value of K_{2HA} of the four phenols taken ($K^d_{HA} = 1.4 \times 10^{-24}$,[2] $K^f_{HA_2^-} = 1 \times 10^{42}$). The p$a_H$ of a solution 7.80 $\times$ 10^{-4} and 7.90 $\times$ 10^{-3} M in 2,4-dinitrobenzoic acid and its tetraethylammonium salt, respectively, containing 0.482 M m-nitrophenol (HR), was measured to be 14.0. Therefore, $[R^-] = K^d_{HR}[HR]/a_{H^+} = 6.7 \times 10^{-11}$ and $[HR_2^-] = K^d_{HR}K^f_{HR_2^-}[HR]^2/a_{H^+} = 3.2 \times 10^{-7}$, assuming $f = 1$. The sum $[HR_2^-] + [R^-] \ll C_{Et_4NA}$.

Discussion

It is reasonable to suppose that the hydrogen-bond donating property of benzoic acids with respect to chloride ion and the accepting property of benzoates with respect to p-bromophenol should follow linear free energy relationships with substituents on the aromatic nucleus, as was observed with phenols.[2] Using the compilation by Brown[18] of σ values for meta and para substituents, linear relations are found for log $K^f_{HA \cdot Cl^-}$ or log $K^f_{HR \cdot A^-}$ vs. σ, as illustrated in Figure 5. Hence we may write

$$\log K^f_{HA \cdot Cl^-} = \log K_0{}^f_{HA \cdot Cl^-} + \rho_{HA \cdot Cl^-}\sigma$$

$$\rho_{HACl^-} = 0.47 \tag{8}$$

$$\log K^f_{HR \cdot A^-} = \log K_0{}^f_{HR \cdot A^-} + \rho_{HR \cdot A^-}\sigma$$

$$\rho_{HRA^-} = -0.62 \tag{9}$$

The subscript 0 denotes unsubstituted entities. Additivity of σ values is assumed. p-Methoxy- and p-hydroxybenzoic acids deviate from the straight lines, A and C in Figure 5. The σ values of these substituents are known to be dependent on solvent polarity.[19] It is of interest to note that the ratios $\rho_{HA' \cdot Cl^-}/\rho_{HA \cdot Cl^-}$ and $\rho_{HR \cdot A'^-}/\rho_{HR \cdot A^-}$ are equal, being $0.99^2/0.47 = 2.1$, and $1.28^2/0.62 = 2.07$, respectively. Primed superscripts designate phenols; unprimed, benzoic acids. This agreement indicates that the hydrogen-bond donating properties of phenols as compared to those of benzoic
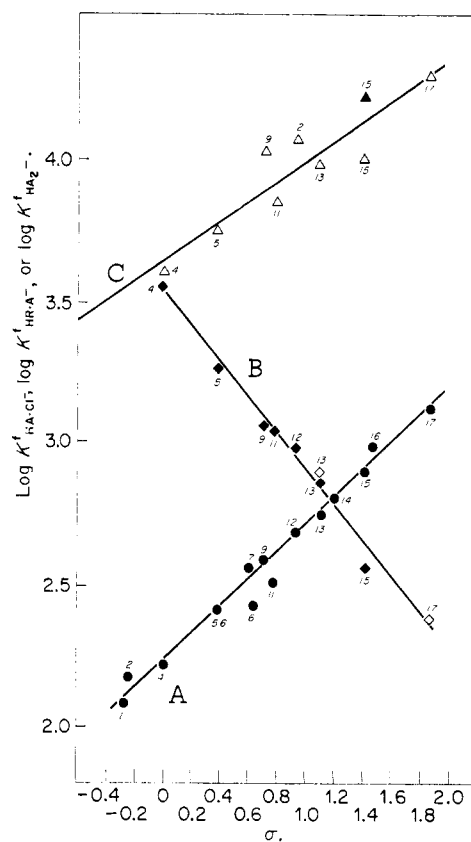
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Figure 5. Hammett plots of log $K^f_{HA \cdot Cl^-}$, log $K^f_{HR \cdot A^-}$, or log $K^f_{HA_2^-}$: (A) ordinate, log $K^f_{HA \cdot Cl^-}$; (B) log $K^f_{HR \cdot A^-}$; and (C) log $K^f_{HA_2^-}$. Numbers are the same as those in Table I. Open symbols, potentiometric values; filled symbols, solubility values. Least-squares straight lines drawn through points in A, B, and C, excluding o-chloro, o-iodo, p-hydroxy, and p-methoxy substituents. Slopes 0.47, −0.62, and 0.35, respectively. Intercepts 2.23, 3.53, and 3.63, respectively.

acids (toward chloride) are affected by aromatic substitution in the same way as the hydrogen-bond accepting properties of the corresponding anions toward p-bromophenol.

A simple relation can be derived for the dependence of the logarithm of the equilibrium constant of reaction 3, log K, upon σ in terms of the effect of the substituents upon the stability of the benzoic acid–benzoate homoconjugates, $K^f_{HA_2^-}$, the benzoic acid heteroconjugates with chloride, $K^f_{HA \cdot Cl^-}$, and the benzoate heteroconjugate with p-bromophenol, $K^f_{HR \cdot A^-}$. In this study it was found experimentally that for benzoic acids

$$\log K^f_{HA_2^-} = \log K_0{}^f_{HA_2^-} + \rho_{HA_2^-}\sigma$$

$$\rho_{HA_2^-} = 0.35 \tag{10}$$

Equation 11 follows immediately from eq 8, 9, and 10.

$$\log K = \log K_0 + (\rho_{HR \cdot A^-} + \rho_{HA \cdot Cl^-} - \rho_{HA_2^-})\sigma \tag{11}$$

A plot of log K vs. σ was found to have a slope of −0.5 (Figure 6, line C), identical with the value calculated according to eq 11. It is expected that the value of K of a given benzoate be independent of the meta- or para-substituted phenol (HR) used. This has been tested and confirmed with 2,4-dinitrobenzoate. From the data in Table I the following values of log K are found: p-bromophenol, −1.17; p-methoxyphenol, −1.37; m-nitrophenol, −1.32; and o-nitrophenol, −0.97.
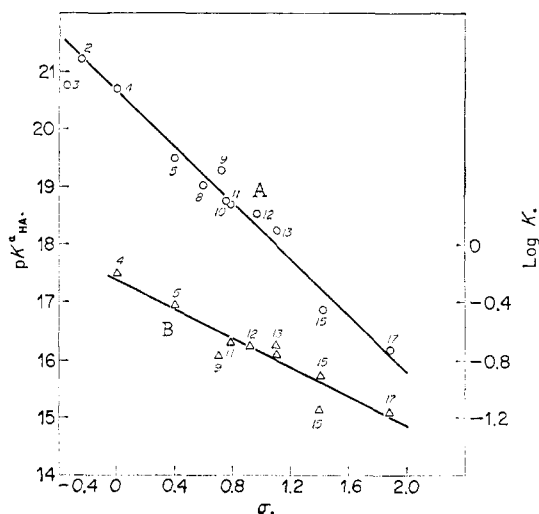
Figure 6. (A) Hammett plot of pK^d_{HA} in acetonitrile of benzoic acids. Least-squares slope, -2.4; intercept, 20.65. (B) Plot of log K ($K = K^f_{HA\cdot Cl^-}K^f_{HR\cdot A^-}/K^f_{HA_2^-}K^f_{HR\cdot Cl^-}$) vs. σ. Slope = -0.50, intercept -0.28. Numbers are the same as in Table I. Left-hand ordinate, line A; right-hand ordinate, line B.

The following values of log $K^f_{HA\cdot Cl^-}$ were reported previously:[2] p-bromophenol, 2.38; p-methoxyphenol, 2.10; m-nitrophenol, 2.93; and o-nitrophenol, 1.42. The steric effects of the o-nitro group in 2,4-dinitrobenzoate ion do not influence its hydrogen-bond accepting capacity (vide infra).

In the benzoic acid homoconjugates the positive value of $\rho_{HA_2^-}$ (0.35) may be associated with possible highly asymmetrical hydrogen bonding in HA_2^- in AN. In fact, clearly defined ν_{OH} bands at 2425 and 1910 cm^{-1} in the infrared spectrum of solid potassium hydrogen di(4-nitrobenzoate)[20] have been ascribed to asymmetrical hydrogen bonding. On the other hand, the hydrogen bonding in some phenol–phenolate conjugates (e.g., in cesium di(3-nitrophenolate) is symmetrical in the crystal, but becomes asymmetrical in dimethyl sulfoxide solution.[21]

We consider now ortho substituents. A value of $\sigma = 1.10$ for the o-nitro group was used in the Hammett plots of log $K^f_{HA_2^-}$, log $K^f_{HA\cdot Cl^-}$, and log $K^f_{HR\cdot A^-}$, this value being equal to the σ value in the Hammett plot of $K^f_{HA\cdot A^-}$ of phenolates.[2] However, in the Hammett plot of $K^f_{HA'\cdot Cl^-}$ of the phenols the o-nitrophenols deviate much from the straight line when $\sigma = 1.10$ is used, as a result of intramolecular hydrogen bonding. In this respect, the behavior of the o-nitrobenzoic acids differs considerably from that of the o-nitrophenols. Apparently, the carboxyl group is rotated out of the plane of the ring in o-nitro- and 2,4-dinitrobenzoate homo- and heteroconjugates $HR\cdot A^-$ and $HA\cdot Cl^-$. The rotation of the carboxyl group[5] accounts for mini-

mal steric interference in formation of intermolecular hydrogen bonds. At the same time, intramolecular hydrogen bonding in the o-nitrobenzoic acids is suppressed by twisting of the $O—H\cdots O$ bond. This accounts for the fact that σ_{o-NO_2} is practically the same in the benzoic acids as in the corresponding benzoates. Recently, a value of $\sigma_{o-NO_2} = 1.20$, in fair agreement with the value of 1.10 found in the present work, was derived by Dietrich, et al.,[4] from the chemical shift of the hydroxyl proton of o-nitrophenols in hexamethylphosphoramide. This solvent is sufficiently basic so as to obviate intramolecular hydrogen bonding. In phenols, steric effects of an o-nitro or o-chloro group (below) are negligible. Hence, the value of σ_{o-NO_2} is indicative of the electrical (resonance and field) effects of the substituent.

In the present study o-chloro- and 2,6-dichlorobenzoic acids are found to lie on the Hammett plot of log $K^f_{HA\cdot Cl^-}$ (Figure 5, line A) when σ_{o-Cl} is taken as 0.60, in fair agreement with the value of 0.50 reported by Traynham.[22] Similar comments for o-chlorobenzoic acids with regard to rotation of the carboxyl group and electrical and steric effects of the o-chloro group, can be made as for the corresponding nitro compounds. For o-iodobenzoic acid, a value of $\sigma_{o-I} = 0.40$ fits the Hammett plot of log $K^f_{HA\cdot Cl^-}$, differing markedly from $\sigma_{o-I} = 0.64$,[22] probably as a consequence of steric effects of the large iodo substituent which could hinder hydrogen bonding between the carboxyl group and chloride ion.

The Hammett plot of the dissociation constant, pK^d_{HA}, in AN of benzoic acids in Figure 6 is linear, with the intercept p$K_0^d_{HA} = 20.65$ and slope $\rho_{HA} = -2.4$. For phenols in AN $\rho_{HA'}$ has been reported previously as -4.76.[2] The ratio $\rho_{HA'}/\rho_{HA}$ is 2.0 as compared to 2.1 for the ratios $\rho_{HA'\cdot Cl^-}/\rho_{HA\cdot Cl^-}$ and $\rho_{HR\cdot A'^-}/\rho_{HR\cdot A^-}$. Of interest is the comparison of the value of the ratio $\rho_{HA}/\rho_{HR\cdot A^-}$ for benzoic acids and phenols, which are 3.87 and 3.73, respectively, in AN. Apparently, the hydrogen-bond accepting property of the two types of anions with respect to p-bromophenol varies with substitution in the same way with basicity of the anion, expressed in terms of the dissociation constant of the parent acid.

o-Nitro- and 2,4-dinitrobenzoic acids are found to lie on the Hammett plot of (pK^d_{HA})$_{AN}$ when σ_{o-NO_2} is again taken equal to 1.10. As in the corresponding conjugates it is concluded that electrical, rather than steric, effects are operative in dissociation of these ortho-substituted benzoic acids in AN. A similar conclusion was drawn by Charton[23] from the acid and alkaline hydrolysis or esterification of ortho-substituted benzoates in aqueous acetone, dimethyl sulfoxide, or ethanol solutions, considering the van der Waals radius of the nitro group as $r_{v_{max}} = 2.59$ Å (perpendicular value).

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