states) is clearly related to the lesser degree of promotion (at R_e of the ion) of the precursor MO 2pσ, but is also attributable in part to greater penetration, although probably not as much as the calculated δ_{pen} of Table IV indicates.

Of considerable interest are the ndσ, ndπ, and ndδ states of H_2 and He_2. The MO's are nonpenetrating and without core precursors, but small δ's do occur, decreasing in the order from ndσ to ndπ just as predicted by the demi-H_2^+ core-splitting model and in accordance with the fact that ndσ and ndπ are promoted MO's but ndδ is unpromoted. The smallness of the δ's for ndσ and ndπ at R_e of the positive ion shows that, in sharp contrast to the npσ cases, promotion is nearly but definitely not quite complete; this is understandable in terms of considerations advanced in section 5 of part VI.[3] The small negative δ's for ndδ are just as expected from the core-splitting model for an unpromoted nonpenetrating MO. The appearance of a small δ_{pen} for the 3dσ and 3dπ MO's deserves comment. It is probably a reflection of the crudeness of the model together with the lack of complete promotion in those MO's, rather than of any real penetration effect.

The calculated δ_{cs} values, hence the derived δ_{pen} values, in Tables III and IV were based on an *assumed* value of 0.5 for the factor ρ of eq 9 and 15, which measures the extent to which the core-splitting perturbation potential (eq 5) is weaker than in H_2^+. Although slightly larger values might have been anticipated, the assumed value of 0.5 gives a distinctly more reasonable set of values for δ_{pen} than a larger value, such as, for example, 0.6.

The agreements between observed δ and dδ/dR values and those expected from the demi-H_2^+ model for H_2 and for He_2 are so good as to lead to the conclusion that this model probably represents the actual situation rather well for the Rydberg MO's of those molecules near the R_e values of their Rydberg states.

Some Hydrogen-Bond Relations between Homoconjugates and Heteroconjugates of Phenols and Phenolates in Acetonitrile[1]

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Abstract: With the exception of *ortho*-substituted phenols, the hydrogen-bond donating capacity with reference to chloride ion of substituted phenols (HA) as indicated by the heteroconjugation constant $K^f_{HA\cdot Cl^-} = [HA\cdot Cl^-]/[HA][Cl^-]$ increases with increasing acid strength of HA. The hydrogen-bond accepting capacity of A^-, as indicated by $K^f_{HR\cdot A^-}$, HR being *p*-bromophenol, increases with increasing basic strength of A^-. This is also true for *ortho*-substituted phenolate ions. A plot of log $K^f_{HA\cdot Cl^-}$ *vs.* the Hammett substituent constants σ yields a straight line with slope of 1.0 except for *ortho*-substituted phenols, while the plot of log $K^f_{HR\cdot A^-}$ *vs.* σ is linear for all phenols tested and has a slope of -1.28. A value of $\sigma = 1.10$ for the *o*-nitro group was used. The equilibrium constant of the reaction $HA_2^- + HR\cdot Cl^- \rightleftharpoons HA\cdot Cl^- + HR\cdot A^-$ was expected and found to be equal to 1, except for 2,6-dinitro-4-chlorophenol. *ortho*-Substituted phenols form only a monoconjugate $HA\cdot Cl^-$, whereas *meta*- and *para*-substituted phenols also form a diconjugate $(HA)_2Cl^-$. A plot of pK^d_{HA} *vs.* α yields a straight line, but the plot of $(pK^d_{HA})_{AN}$ *vs.* $(pK^d_{HA})_{water}$ exhibits considerable scatter.

In an aprotic protophobic solvent like acetonitrile (AN), anions with a localized charge have a large medium activity coefficient with reference to that in water. Such anions can be stabilized in AN either by homoconjugation

$$A^- + HA \rightleftharpoons AH\cdots A^-$$

$$K^f_{HA_2^-} = \frac{[HA_2^-]f_{HA_2^-}}{[HA][A^-]f_{A^-}} \qquad (1)$$

$$f_{HA_2^-} = f_{A^-}$$

or by heteroconjugation

$$A^- + HR \rightleftharpoons RH\cdots A^-$$

$$K^f_{HR\cdot A^-} = \frac{[HR\cdot A^-]f_{HR\cdot A^-}}{[HR][A^-]} \qquad (2)$$

$$f_{HR\cdot A^-} = f_{A^-}$$

in which HR is a reference hydrogen bonder which is such a weak acid that it does not undergo proton exchange with A^-. In the present work we have used *p*-bromophenol as HR. The value of $K^f_{HA_2^-}$ depends on the hydrogen-bond donating capacity of HA and the hydrogen-bond accepting capacity of A^-.[2] Thus the ratio $K^f_{HA_2^-}/K^f_{HR\cdot A^-}$ gives the ratio of the hydrogen-bond donating capacities of HA and HR relative to the anion A^-. The relative hydrogen-bonding capacity of a series of phenols, denoted by HA, with reference to a given hydrogen-bond accepting anion, for which we have used the chloride ion, is given by

$$Cl^- + HA \rightleftharpoons AH\cdots Cl^-$$

$$K^f_{HA\cdot Cl^-} = \frac{[HA\cdot Cl^-]f_{HA\cdot Cl^-}}{[HA][Cl^-]f_{Cl^-}} \qquad (3)$$

$$f_{HA\cdot Cl^-} = f_{Cl^-}$$

We have also determined the hydrogen-bond donating

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(2) See also J. Gordon, *J. Org. Chem.*, **26**, 738 (1961).

capacity of HR (*p*-bromophenol) with reference to the chloride ion

$$\mathrm{Cl^-} + \mathrm{HR} \rightleftharpoons \mathrm{RH \cdots Cl^-}$$

$$K^{\mathrm{f}}_{\mathrm{HR \cdot Cl^-}} = \frac{[\mathrm{HR \cdot Cl^-}]f_{\mathrm{HR \cdot Cl^-}}}{[\mathrm{HR}][\mathrm{Cl^-}]f_{\mathrm{Cl^-}}} \qquad (4)$$

$$f_{\mathrm{HR \cdot Cl^-}} = f_{\mathrm{Cl^-}}$$

The chloride ion was chosen because its basicity is sufficiently weak so as to preclude proton transfer with HA or HR and because its 1:1 conjugate with HR is considerably more stable than those of nitrate and methanesulfonate[3] due to the localized charge on the chloride ion.

The ratio $K^{\mathrm{f}}_{\mathrm{HR \cdot Cl^-}}/K^{\mathrm{f}}_{\mathrm{HA \cdot Cl^-}}$ represents the ratio of the hydrogen-bond donating capacities of HR and HA with reference to the hydrogen-bond accepting property of the chloride ion. In the absence of interfering steric effects the logarithm of the equilibrium constant of the reaction $\mathrm{HA_2^-} + \mathrm{HR \cdot Cl^-} \rightleftharpoons \mathrm{HA \cdot Cl^-} + \mathrm{HR \cdot A^-}$ then should be equal to zero, *i.e.*

$$\log\,[K^{\mathrm{f}}_{\mathrm{HA \cdot Cl^-}}K^{\mathrm{f}}_{\mathrm{HR \cdot A^-}}/K^{\mathrm{f}}_{\mathrm{HA_2^-}}K^{\mathrm{f}}_{\mathrm{HR \cdot Cl^-}}] = 0 \qquad (5)$$

Using some mono- and dinitrophenols we have compared in the present work the experimental value of $K^{\mathrm{f}}_{\mathrm{HA_2^-}}$ with that calculated from the experimentally determined constants $K^{\mathrm{f}}_{\mathrm{HA \cdot Cl^-}}$, $K^{\mathrm{f}}_{\mathrm{HR \cdot A^-}}$, and $K^{\mathrm{f}}_{\mathrm{HR \cdot Cl^-}}$ using eq 5.

All activity coefficients were calculated from the limiting Debye–Hückel relation.

Experimental Section

Chemicals. Acetonitrile was purified and dispensed as previously described.[4]

Phenols. The following phenols have been used previously: *o*-nitro-,[5] *p*-nitro-,[5] *m*-nitro-,[5] 2,4-dinitro-,[5] 2,6-dinitro-4-chloro-,[6] 3,5-dinitro-,[5] and *p*-bromophenol.[7] *p*-Methoxyphenol was Eastman Kodak White Label product recrystallized from water and dried *in vacuo* at 45°: mp 54°, lit. 53°.[8] *α,α,α*-Trifluoro-*m*-cresol was Baker Grade from Baker Chemicals and used without further purification, bp 178–179°. 4-Nitro-3-chlorophenol was a student preparation, recrystallized twice from water: mp 122°, lit. 121°.[9]

Salts. Potassium 2,4-dinitrophenolate was used previously.[5] Potassium 2,6-dinitro-4-chlorophenolate was prepared by adding an excess of the phenol to a methanolic solution of potassium hydroxide, filtering off the potassium salt, washing it with Merck reagent grade anhydrous ether to remove excess phenol, and recrystallizing from methanol. Tetraethylammonium *m*-nitro- and 4-nitro-3-chlorophenolates were prepared as described elsewhere for tetraethylammonium 2,6-dinitrophenolate.[5] They were recrystallized from a mixture of ethyl acetate-ethanol and dried at 60° *in vacuo*. Assay of the 2,6-dinitro-4-chloro-, *m*-nitro-, and 4-nitro-3-chlorophenolate salts by visual titration in AN with 0.5 *M* perchloric acid in acetic acid using *α*-naphtholbenzein as indicator[10] yielded 99.5, 99.0, and 99.1%, respectively. Potassium chloride and periodate were products used previously.[11] Tetraethylammonium chloride was prepared previously in this laboratory by Thomas.[12]

The experimental techniques used in the conductometric determination of the ionic solubility of potassium chloride in the presence of the various phenols are the same as those employed in the study of the effect of water on the solubility of various salts,[11] while the total solubility of the potassium nitrophenolate salts in presence of the parent nitrophenol or *p*-bromophenol was found as described previously.[5] Potentiometric pa_{H} measurements of mixtures of *m*-nitro- or 4-nitro-3-chlorophenol and their tetraethylammonium salts were carried out as previously described.[5] Spectra were recorded on a Cary Model 15 recording spectrophotometer using 1-cm stoppered silica cells. All experiments were performed at 25 ± 1°.

Results

Ionic Mobilities. Dissociation Constants of Potassium 2,6-Dinitro-4-chlorophenolate and 4-Nitro-3-chlorophenolate. The following ionic mobilities at infinite dilution at 25° have been reported: $\mathrm{K^+}$, 76;[13] $\mathrm{Et_4N^+}$, 86;[14] $\mathrm{Cl^-}$, 89.[14] The equivalent conductance of 2.12×10^{-3} *M* tetraethylammonium chloride in the presence of 0.18 *M p*-bromophenol (corrected for viscosity) was 125, yielding $\lambda_{0\,\mathrm{HR \cdot Cl^-}} = 55$. At the low ion concentrations in saturated solutions of potassium chloride containing phenols (HA or HR) the salts KHACl and $\mathrm{K(HA)_2Cl}$ could be considered completely dissociated. In these solutions chloride was present entirely as the conjugates $\mathrm{HA \cdot Cl^-}$ and $\mathrm{(HA)_2Cl^-}$, λ_0 of the two heteroconjugate ions being taken equal to 55.

The following equivalent conductances upon dilution of solutions of potassium 2,6-dinitro-4-chlorophenolate were found: 5.10×10^{-4} *M*, 146; 8.73×10^{-4} *M*, 142; 1.52×10^{-3} *M*, 130; 1.83×10^{-3} *M*, 126; and 3.06×10^{-3} *M* (saturated solution), 112. A Fuoss and Kraus treatment of the above data yields $\Lambda_0 = 182$ ($\lambda_{0\mathrm{A^-}} = 96$) and $K^{\mathrm{d}}_{\mathrm{KA}} = 3.1 \times 10^{-3}$.

Viscosity and Ion Atmosphere Corrections. The viscosity of solutions of all the phenols were assumed the same as those of resorcinol,[15] *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.

Determination of $K^{\mathrm{f}}_{\mathrm{HA \cdot Cl^-}}$ and $K^{\mathrm{f}}_{\mathrm{(HA)_2Cl^-}}$. Conductance of Saturated Potassium Chloride Solutions in the Presence of Various Phenols. A marked increase in ionic solubility of potassium chloride was measured conductometrically in the presence of all the phenols (HA). That this increase cannot be attributed to complexation of potassium ion with the phenols is concluded from the fact that the specific conductance of solutions saturated with potassium periodate (1.7×10^{-4} ohm^{-1} cm^{-1})[11] did not change even upon making such a solution 0.5 *M* in *p*-bromophenol. Therefore the relation between the ionic solubility, $[\mathrm{K^+}]$, and the equilibrium concentration of phenol, [HA], is that as previously derived for potassium 3,5-dinitrobenzoate in the presence of *p*-bromophenol.[15]

$$f^2[\mathrm{K^+}]^2 = K_{\mathrm{sp}}\{1 + K^{\mathrm{f}}_{\mathrm{HA \cdot Cl^-}}[\mathrm{HA}] + K^{\mathrm{f}}_{\mathrm{(HA)_2Cl^-}}[\mathrm{HA}]^2\} \qquad (6)$$

Taking the average value of repeated measurements of the conductivity of saturated solutions of potassium

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[3] Unpublished work.

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Table I. Heteroconjugation of Chloride with Substituted Phenols (HA) and of *p*-Bromophenol (HR) with Corresponding Phenolates (A^-)

Substituent on phenol	$(pK^d_{HA})_{AN}$		Log $K^f_{HA\cdot Cl^-}$	β[a]	Log $K^f_{HR\cdot A^-}$	Log $K^f_{HA_2^-}$ Calcd (eq 5)	Log $K^f_{HA_2^-}$ Found
o-Nitro-	22.1	21.2[b]	1.42	0	3.32[c]	2.36	2.20[c] 2.00[e]
2,4-Dinitro-	16.0	15.34[b]	2.74	0	1.78	2.14	2.08[c]
2,6-Dinitro-4-chloro-	15.0		1.28	0	1.43	0.33	1.00
p-Methoxy-	...		2.10	4.2	...	...	...
Phenol (unsubstituted)	(27.2)		2.18	4.0	...	...	(4.04)
p-Bromo-	...		2.38	7.5	...	...	...
m-CF_3-	...		2.63	9.5	...	...	...
m-Nitro-	23.85		2.93	8.6	3.68	4.23	4.00
p-Nitro-	20.9	20.02[b]	3.02	10.7	2.85[c]	3.49	3.48[c] 3.67[e]
4-Nitro-3-chloro-	19.95		3.33	8.3	2.49	3.44	3.62
3,5-Dinitro-	20.5		3.63	12.3	3.12[d]	4.37	4.64
2,4,6-Trinitro-	11.0		...	...	0.22[c]	...	0.30[c]

[a] $\beta = K^f_{(HA)_2Cl^-}/K^f_{HA\cdot Cl^-}$. [b] Values of J. Juillard, Ph.D. Thesis, University of Clermont Ferrand, 1965. pK^d_{HPi} taken as 11.00. [c] Solubility method (ref 3), for picric acid; see I. M. Kolthoff and M. K. Chantooni, Jr., *J. Am. Chem. Soc.*, 87, 4428 (1965). [d] Spectrophotometric method (ref 3). [e] Values of J. F. Coetzee and G. Padmanabhan, *J. Phys. Chem.*, **69**, 1393 (1965); G. Padmanabhan, Ph.D. Thesis, University of Pittsburgh, Pittsburgh, Pa., 1963.

Table II. Conjugation Constants, $K^f_{HA_2^-}$ and $K^f_{HR\cdot A^-}$, of Nitrophenols from Solubility Data[a]

C_{HA} or C_{HR}, $M \times 10^2$	s_t, $M \times 10^3$	$[M^+] = s_t - [MA]$, $M \times 10^3$	f^2	[HA] or [HR] = $C_{HA} - s_t + [MA]_2$, $M \times 10^2$	$K^f_{HA_2^-}$ or $K^f_{HR\cdot A^-}$ $\times 10^{-1}$
Potassium 2,4-dinitrophenolate, $K_{sp} = 9.5 \times 10^{-6}$, $K^d_{KA} = 2.9 \times 10^{-3}$, $[KA] = 3.3 \times 10^{-3}$. Determination of $K^f_{HR\cdot A^-}$					
0	7.1	3.8	0.66	0	...
1.93	8.70	5.4	0.60	1.35	4.8
3.12	10.4	7.1	0.54	2.89	6.4
5.42	12.2	8.9	0.50	5.38	5.9
11.7	15.3	12.0	0.47	10.5	6.7
				Av	6×10^1
Potassium 2,6-dinitro-4-chlorophenolate, $K_{sp} = 3.1 \times 10^{-6}$, $K^d_{KA} = 3.2 \times 10^{-3}$, $[KA] = 1.0 \times 10^{-3}$. Determination of $K^f_{HA_2^-}$					
0	3.05	2.05	0.73	0	...
14.8	4.41	3.41	0.67	14.5	1.0
28.3	5.36	4.36	0.63	27.9	1.0
				Av	1.0×10^1
Determination of $K^f_{HR\cdot A^-}$					
18.5	6.55	5.55	0.60	18	2.7
33.1	8.45	7.45	0.55	33	2.7
				Av	2.7×10^1

[a] HR = *p*-bromophenol; s_t = total analytical solubility.

chloride (1.80×10^{-5} ohm^{-1} cm^{-1}), $K_{sp} = 1.05 \pm 0.05 \times 10^{-8}$, as compared to the previously reported value of 0.86×10^{-8}.[9] The new value was taken in all calculations of $K^f_{HR\cdot Cl^-}$ and $K^f_{(HR)_2Cl^-}$ using eq 6.

For the sake of brevity ionic solubility data of saturated solutions of potassium chloride in the presence of the various phenols are presented as plots of $f^2[K^+]^2/K_{sp}$ *vs.* C_{HA} on logarithmic scales in Figure 1. In this figure C_{HA} denotes the analytical concentration of phenol taken. From the data in Figure 1, plots of $\{f^2[K^+]^2 - K_{sp}\}/K_{sp}[HA]$ *vs.* [HA] were constructed according to eq 6 from which $K^f_{HA\cdot Cl^-}$ was found from the intercept and $K^f_{(HA)_2Cl^-}$ from the slope. Only in a few instances involving 3,5-dinitrophenol were the equilibrium concentrations of HA appreciably smaller than the analytical ones. Under such conditions virtually only $HA\cdot Cl^-$ was present and the equilibrium concentration of HA equal to $[HA] = C_{HA} - [K^+]$. Values of log $K^f_{HA\cdot Cl^-}$ and of $\beta = K^f_{(HA)_2Cl^-}/K^f_{HA\cdot Cl^-}$ are tabulated for the various phenols in Table I.

Homoconjugation and Heteroconjugation Constants of Nitrophenols from Solubility Data of Their Potassium Salts. The homoconjugation constant of 2,6-dinitro-4-chlorophenol was estimated from the total solubility of its potassium salt in the presence of the parent acid. Likewise, the heteroconjugation constants of this phenolate and of 2,4-dinitrophenolate with *p*-bromophenol (HR) were found. Solubility data are summarized in Table II.

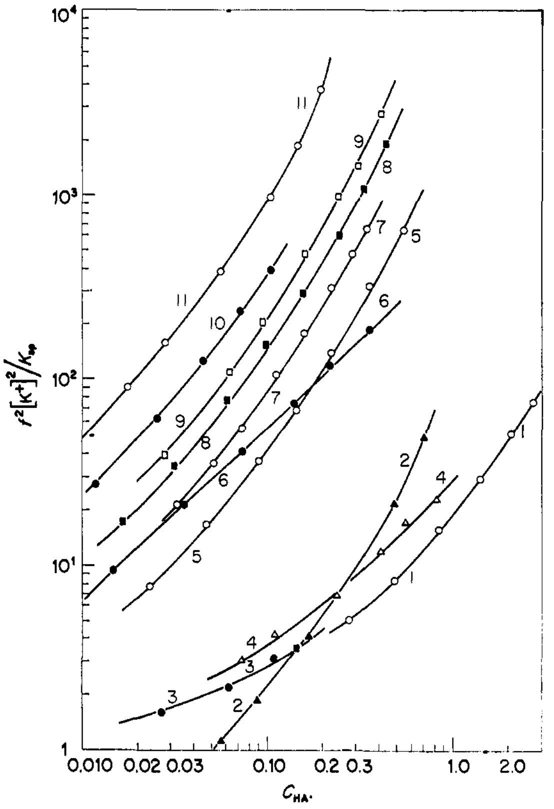

Figure 1. Plots of $f^2[K^+]^2/K_{sp}$ *vs.* C_{HA} for potassium chloride with phenols: (1) *p*-methoxyphenol, (2) phenol, (3) 2,6-dinitro-4-chlorophenol, (4) *o*-nitrophenol, (5) *p*-bromophenol, (6) 2,4-dinitrophenol, (7) *m*-trifluoromethylphenol, (8) *m*-nitrophenol, (9) *p*-nitrophenol, (10) 4-nitro-3-chlorophenol, and (11) 3,5-dinitrophenol.

Homoconjugation and Heteroconjugation Constants of *m*-Nitro- and 4-Nitro-3-chlorophenol from Potentio-

metric Data (HR = *p*-Bromophenol). Since the ionic solubilities of potassium *m*-nitro- and 4-nitro-3-chlorophenolates were found to be fairly large, of the order of 0.01 *M*, the homo- and heteroconjugation constants of the phenols were estimated from potentiometric pa_H data in mixtures of the phenol and its tetraethylammonium salt in the absence or presence of HR,[16] respectively. From the data in Tables III and IV, average values of $K^f_{HA_2^-}$ equal to 1×10^4 and 4×10^3 and of $K^f_{HR \cdot A^-}$ of 4.8×10^3 and 3.2×10^2 were found for *m*-nitro- and 4-nitro-3-chlorophenol, respectively. In addition a triconjugate, $(HR)_3A^-$, of *m*-nitrophenolate apparently is formed with an over-all formation constant of 1.6×10^7.

Table III. Glass Electrode pa_H Measurements in *m*-Nitrophenol Solutions Containing Its Tetraethylammonium Salt in the Absence or Presence of *p*-Bromophenol

C_{HA}, $M \times 10^2$	C_{Et_4NA}, $M \times 10^3$	C_{HR},	[HR], *M*	pa_H Obsd	pa_H Calcd	$K^f_{HA_2^-} \times 10^{-4}$
$pK^d_{HA} = 23.8_5, f^2 = 0.74$. Determination of $K^f_{HA_2^-}$						
0.15	2.00	0	0	23.97		...
0.31	1.95	0	0	22.67		(1.7)
0.46_4	1.90	0	0	22.14		1.1
0.61	1.86	0	0	21.78		1.0
0.88_4	1.77	0	0	21.40		0.9
1.72	1.77	0	0	20.80		0.8
3.11	1.77	0	0	20.16		0.9
4.76	1.77	0	0	19.67		1.1_5
					Av	$0.9_7 \times 10^4$
$pK^d_{HA} = 23.8_5, f^2 = 0.81, K^f_{HR \cdot A^-} = 4.8 \times 10^3, K^f_{(HR)_3A^-} = 1.6 \times 10^7$. Determination of $K^f_{HR \cdot A^-}$						
0.10	0.10	0	0	23.80	23.80	
0.10	0.10	0.0140	0.012	22.00	21.92	
0.10	0.10	0.0175	0.015_5	21.71	21.67	
0.10	0.10	0.020	0.017	21.57	21.59	
0.10	0.10	0.029	0.025_6	21.18	21.33	
0.10	0.10	0.051	0.048	20.50	20.51	
0.10	0.10	0.086	0.084_5	19.80	19.78	

Table IV. Glass Electrode pa_H Measurements in 4-Nitro-3-chlorophenol Solutions Containing Its Tetraethylammonium Salt in the Absence or Presence of *p*-Bromophenol

C_{HA}, $M \times 10^3$	C_{Et_4NA}, $M \times 10^3$	C_{HR}	$[Et_4NA]$, $M \times 10^3$	pa_H	$K^f_{HA_2^-}$ or $K^f_{HR \cdot A^-}$
$pK^d_{HA} = 19.9_5, f^2 = 0.74$. Determination of $K^f_{HA_2^-}$					
0.52_7	1.79	0	0.05	21.13	4.0
1.04	1.76	0	0.05	20.64	4.8
2.27	1.72	0	0.02	19.66	...
4.54	1.62	0	~0	18.63	3.2
23.2	1.62	0	~0	16.92	3.7
43.0	1.62	0	~0	16.16	5.5
				Av	$4._2 \times 10^3$
$pK^d_{HA} = 19.9_5, f^2 = 0.79$. Determination of $K^f_{HR \cdot A^-}$					
1.21	1.21	0	0.03	19.94	...
1.21	1.21	0.019_6	0.01	19.18	0.25
1.21	1.21	0.039_2	~0	18.90	0.25
1.21	1.21	0.056_4	~0	18.70	0.29
1.21	1.21	0.073	~0	18.57	0.31
1.21	1.21	0.118	~0	18.30	0.36
1.21	1.21	0.147	~0	18.23	0.34
				Av	$3._2 \times 10^2$

Values of pK^d_{HA} in AN from Potentiometric Data. Values of pK^d_{HA} in the first column in Table I were taken from a previous publication.[5] In this work values of $(pK^d_{HA})_{AN}$ of 23.8_5 and 19.9_5 were found for *m*-nitro- and 4-nitro-3-chlorophenol, respectively.

Discussion

In the last column of Table I the observed values of $K^f_{HA_2^-}$ are compared with those calculated from eq 5. In the introduction reasons were given why these two values should be equal. Considering the uncertainty in the reported formation constants of the individual 1:1 conjugates the agreement is good, with the exception of 2,6-dinitro-4-chlorophenol, where the deviation is greater than can be accounted for by the uncertainty in the individual constants. This deviation is apparently due to a large extent to substantial steric and intramolecular hydrogen-bonding effects of the two *o*-nitro groups on $K^f_{HA \cdot Cl^-}$. It is interesting to note that eq 5 does hold for the two mono-*ortho*-substituted phenols as well as for *m*-nitro-, *p*-nitro-, 4-nitro-3-chloro-, and 3,5-dinitrophenol. In addition, for 3,5-dinitrophenol as HA, the value of the equilibrium constant corresponding to the reaction

$$HA_2^- + (HR)_2Cl^- \rightleftharpoons HA \cdot Cl^- + (HR)_2A^-$$

(HR = *p*-bromophenol) was found equal to 0.9_2, taking $K^f_{(HR)_2Cl^-}$ and the previously reported value of $K^f_{(HR)_2A^-}$[17] equal to 1.1×10^3 and 1.8×10^4, respectively.

The *ortho*-substituted phenols, *o*-nitro-, 2,4-dinitro-, and 2,6-dinitro-4-chlorophenol, which are poor hydrogen-bond donors as a result of intramolecular hydrogen bonding, form only a monoconjugate $HA \cdot Cl^-$ with chloride, while the other phenols form mono- and diheteroconjugates.

It is interesting to note that, with the exception of the *ortho*-substituted phenols, the stability of the homoconjugate $HA \cdot Cl^-$ increases with acid strength of the phenol (Table I). On the other hand, the ability of $HA \cdot Cl^-$ to add another HA is almost the same (see β values in Table I) for the various *meta*- and *para*-substituted phenols and is roughly independent of acid strength and nature of the substituent. Figure 2, line A, is a plot of log $K^f_{HA \cdot Cl^-}$ of various phenols *vs.* the Hammett substituent constant, σ.[18,19] In this figure (and also in Figure 3) additivity of σ values for disubstituted phenols was assumed. A linear relation between log $K^f_{HA \cdot Cl^-}$ and σ is found, the least-squares slope and intercept being equal to 0.99 and 2.24, respectively, with a standard deviation of 0.05. It is found that *p*-nitro- and 4-nitro-3-chlorophenol lie on the straight line A only when the σ value of the *p*-nitro- group of benzoic acids rather than phenols is used. This is expected, as resonance through the ring in the *p*-nitrophenol–chloride conjugate cannot occur in the absence of proton transfer. Absence of proton transfer in this complex is evident from the small shift in AN in the maximum of the absorption spectrum of $5.6 \times 10^{-5} M$ *p*-nitrophenol from 306 to 322 mμ in the presence of 0.03 *M* tetraethylammonium chloride, when virtually all the nitrophenol is complexed. Absorbance indices for HA and $HA \cdot Cl^-$ of 1.1×10^4[5] and $1.2_2 \times$

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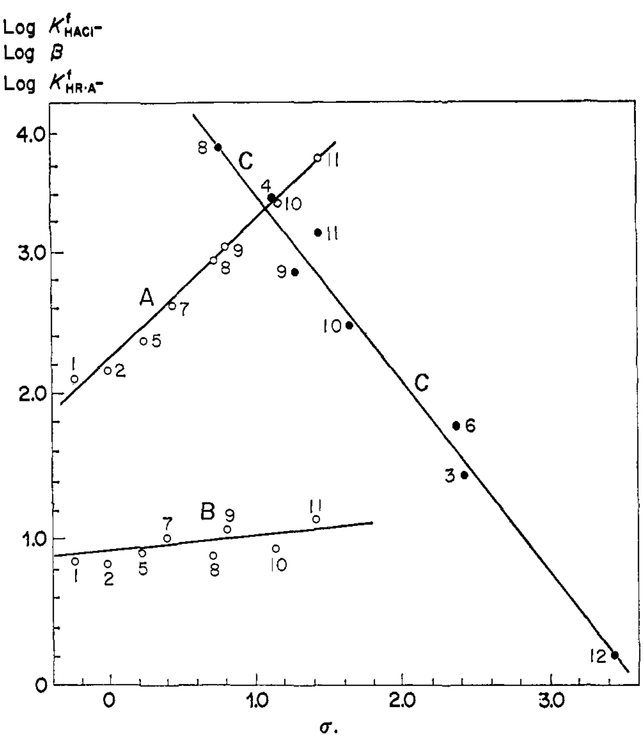

Figure 2. Plots of log $K^f_{HA\cdot Cl^-}$, log β, or log $K^f_{HR\cdot A^-}$ vs. Hammett σ values. $\beta = K^f_{(HA)_2Cl^-}/K^f_{HA\cdot Cl^-}$. Curve A, ordinate log $K^f_{HA\cdot Cl^-}$; curve B, ordinate log β; and curve C, ordinate log $K^f_{HR\cdot A^-}$. Numbers are the same as those in Figure 1: (12) picric acid. Least-squares straight lines drawn through A and C, slopes = 0.99 and −1.28; intercepts = 2.23 and 4.66, respectively.

10^4, respectively, were found. Not plotted in Figure 2, curve A, are data for *ortho*-substituted phenols because, as expected, no simple relation with σ is found.

From the data in Table I it follows that the hydrogen-bond accepting capacity of the anions A^- of the substituted phenols, as indicated by $K^f_{HR\cdot A^-}$, increases with basic strength of A^-. This relation also holds for *o*-nitro-substituted phenols. Curve C in Figure 2 shows a linear relation between log $K^f_{HR\cdot A^-}$ and σ with a least-squares slope and intercept of -1.28 and 4.6_6, respectively, with a standard deviation of 0.15. In this plot the values of the *p*-nitro group in *p*-nitro- and 4-nitro-3-chlorophenol of substituted phenols and not of benzoates have been used. This is accounted for by resonance through the ring in the HR·A⁻ conjugate of the *p*-nitrophenolate ion. It is found that when σ of the *o*-nitro group is taken as 1.10, the three mono- and dinitrophenols and picric acid lie on the straight line of the log $K^f_{HR\cdot A^-}$ *vs.* σ plot (Figure 2, curve C) and on the $(pK^d_{HA})_{AN}$ *vs.* σ plot of Figure 3. It appears that the inductive, resonance, and steric characteristics of the *o*-nitro group are additive in both expressions, intramolecular hydrogen bonding being absent in A^- and $HR\cdot A^-$.

From Figure 3 it appears there exists a linear relation between $(pK^d_{HA})_{AN}$ which involves a proton transfer,

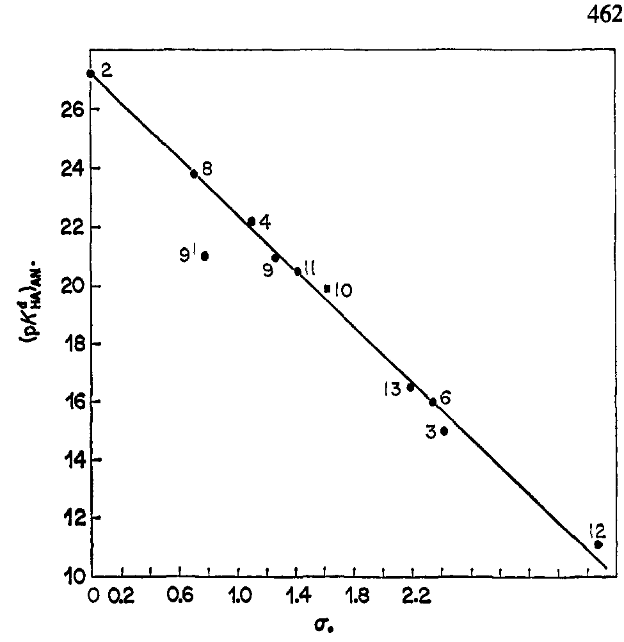

Figure 3. Plot of pK^d_{HA} in acetonitrile *vs.* Hammett σ values. Numbers are the same as those in Figure 1: (12) picric acid, (13) 2,6-dinitrophenol; (9′) benzoic acid value of σ of *p*-nitro group taken. Least-squares slope and intercept are -4.7_6 and 27.2, respectively.

and σ, the value of ρ being 4.7_6 as compared to 2.1, in water.[20] The standard deviation in Figure 3 is 0.3.

Reasons have been given by Parker[21] that in general there is no simple relation between pK^d_{HA} in an amphiprotic and in an aprotic solvent. For similar reasons no close correlation can be expected between pK^d_{HA} in AN and water for a large group of substituted phenols. As a matter of fact, we find the deviation from a straight line in a plot of $(pK^d_{HA})_{AN}$ *vs.* $(pK^d_{HA})_{water}$ of the phenols used considerably greater than the experimental error.

The ionic dissociation of an ammonium phenolate BH^+A^- should decrease with increasing hydrogen-bond accepting capacity of A^- as does K^d_{HA}. In a previous paper[5] we have made a rough estimate of the ionic dissociation constant of some triethylammonium phenolates. The constants were derived from the characteristics of conductometric titration curves. With the exceptions of the picrate, salt formation was quite incomplete and the reported pK^d_{BHA} data involve a considerable uncertainty. However, it is fair to conclude that these data are of the correct order of magnitude. The following pK^d_{BHA} data were reported: *o*-nitro-, 5.2; 3,5-dinitro-, 4.3; 2,4-dinitro-, 3.3; picrate, 2.4, as compared to pK^d_{HA} of 21.2, 20.5, 16, and 11, respectively (Table I). Qualitatively, therefore, the expected relation is found between pK^d_{BHA} and pK^d_{HA}.

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