(2) A. M. O'Connell and E. N. Maslen, *ibid.*, **22**, 134 (1967).
(3) T. Wadanabé, C. H. Koo, J. S. Suh and Y. H. Yeon, To be published (1981).
(4) C. H. Koo and Y. H. Yoen, To be published (1981).
(5) P. L. Dupont, J. Lamotte, H. Campsteyn and M. Vermeire, *Acta Cryst.*, **B34**, 1304–1301 (1978).
(6) P. Main, L. Lessinger, M. M. Woolfson, G. Germain and J. P. Declercq, MULTAN, A System of Computer Programs for the Automatic Solution for X-ray Diffraction Data, Univ. of York, England and Louvain, Belgium (1977).
(7) G. M. Sheldrick, SHELX 76, Program for Crystal Structure Determination, Univ. of Cambridge, England (1976).
(8) E. G. Cox, D. W. J. Cruickshank and J. A. S. Smith, *Proc. Roy. Soc.*, A**247**, 1(1958).
(9) D. W. J. Cruickshank, *J. Chem. Soc.*, 5486–5504 (1961).
(10) H. P. Klug, *Acta Cryst.*, B**26**, 1268 (1970).
(11) L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornnell Univ. Press, Ithaca, N.Y. 1960.

The New Substituent Constants in the Excited States

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The new substituent constants (σ^*) are calculated from the acidity constants (pK^*) of phenol derivatives in the excited state (^1L_b). These substituent constants are applied to the Hammett equations and found good correlation with pK^* of 2,6-di-*tert*-butyl phenol, benzamide, nitroaniline, thiophenol, azobenzene, and benzoic acid derivatives. The correlation was much bettre than that of ground state substituent constants such as σ, σ^+, and σ^-. From these results, the new substituent constants (σ^*) are proposed to be used for the linear free energy relationship in the $^1(\pi,\pi^*)$ excited states of phenyl compounds.

Introduction

The acidity constants in the excited states can be determined by several methods[1]. The two of the most widely used methods are Förster cycle[2] and fluorometric titration[3,4]. The former makes use of O-O electronic transition energy of the aci dand its conjugate base obtained from the UV-VIS spectra as shown in equation 1 and the latter determines the fluorescence quantum yields varying the pH. The 0-0 electronic transition energy in cm^{-1} can be obtained from equation 2. Therefore, the accurate λ^{abs}_{max} from UV-VIS spectra and/or λ^{fl}_{max} from the fluorescence spectra should be determined.

$$\mathrm{p}K-\mathrm{p}K^*=\frac{Nh}{2.303RT}(\bar{\nu}_{AH}-\bar{\nu}_{A^-}) \qquad (1)$$

$$=2.10\times10^{-3}(\bar{\nu}_{AH}-\bar{\nu}_{A^-}) \text{ at } 25^\circ\text{C}$$

$$\bar{\nu}=\frac{1}{\lambda^{abs}_{max}} \text{ or } \frac{1}{\lambda^{fl}_{max}} \text{ or } \frac{1}{2}\left(\frac{1}{\lambda^{abs}_{max}}+\frac{1}{\lambda^{fl}_{max}}\right) \qquad (2)$$

$$\mathrm{p}K=-\log_{10}K \qquad (3)$$

$$\mathrm{p}K^*=-\log_{10}K^* \qquad (4)$$

Where N is the Avogadro number, R is the gas constant, T is the absolute temperature, h is the Planck constant, $\bar{\nu}_{AH}$ and $\bar{\nu}_{A^-}$ are the absorption maximum wavenumber (cm^{-1}) of the acid and its conjugate base respectively, K and K^* are the acidity constants in the ground and excited states respectively.

When the pK^* is determined by Förster cycle, the following precautions should be taken: i) It should be checked whether the protonation entropies are equal in the ground and excited states or not. ii) The correct 0-0 electronic transition energy should be used. The correct 0-0 electronic transition energy can ideally be determined by averaging λ^{abs}_{max} and λ^{fl}_{max} if absorption and fluorescence spectra are mirror images of each other. But the fluorescence spectra are not always available and in many cases, they are not mirror images of absorption spectra. In these cases, λ^{abs}_{max} alone is used in the calculation of the 0-0 transition energy. The error can be minimized even in these cases if λ^{abs}_{max} of the acid and its conjugate base deviates about the same degree and to the same direction from the true 0-0 electronic transition energy. iii) Förster cycle must be applied to the same kind of protolytic equilibrium and electronic band (state).

When the pK^* is determined by the use of fluorometric titration, the attention must be paid to the proton exchange reaction rate constants in the excited states which are smaller than or similar to the fluorescence rate constants ($\overrightarrow{k} \ll kf$, $\overleftarrow{k}[\mathrm{SH_2^+}] \ll kf$, $\overrightarrow{k} \approx kf$, $k[\mathrm{SH_2^+}] \approx kf$) in equation 5. In these cases, incorrect pK^* values are obtained[3,4].

$$\begin{tikzcd}
{[\mathrm{AH}]^* + \mathrm{SH}} \arrow[r, shift left, "\overrightarrow{k}"] \arrow[d, "kf"] & {[\mathrm{A^-}]^* + \mathrm{SH_2^+}} \arrow[l, shift left, "\overleftarrow{k}"] \arrow[d, "kf'"] \\
\mathrm{AH} + h\nu_{AH} & \mathrm{A^-} + h\nu_{A^-}
\end{tikzcd}$$

where SH is the protic solvent.

These difficulties can be overcome by the use of buffer solution, but the usefulness of this method is restricted because fluorescence intensity of some molecules are too weak to determine the fluorescence quantum yields. There are other methods to determine pK^*, for example, pho-

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topotentiometry,[6] but these methods are seldom used.

Jaff é *et al.*[5] and many other workers[6,7] have tried to apply the pK^* to the well-known Hammett equation (eq. 6) utilizing the substituent constants in the ground state (σ, σ^+, σ^-).

$$\log\left(\frac{K_x}{K_0}\right)=\rho\sigma \qquad (6)$$

It was found that pK^* values are better correlated with σ^+ or σ^- than with σ. They attributed the results to the increase of electron donating and releasing effects of the substituents due to the larger resonance contribution in the excited states. However, the correlationship they obtained lacked the sound theoretical background and the best correlationship was established with substituent constants found by trial and error.

The electronic configuration of the excited states is generally different from that of the ground state. Consequently, many physical and chemical properties of the excited states are expected to be different from those of the ground state. For example, there are many evidences which support the larger charge-transfer character in the excited states than in the ground state. One of them is the dipole moment[8]. The dipole moment of *p*-nitroaniline is 6D and 14D in the ground and the first excited state respectively.

The dipole moment of dipolar structure of the compound as shown in Figure 1 is 25D by calculation, and the excited state is expected to have large contribution of this dipolar structure. The charge distribution of benzyl cation in the (π, π^*) excited state is illustrated in Figure 2.[9]

From these charge distribution data, the canonical structure of the resonance forms of benzyl cation in the (π, π^*) excited state can be written as shown in Figure 3 and these structures are confirmed by the solvolysis experiments[9]. The contribution of these resonance structures in ^1L_b and ^1L_a[10] state may not be same but both states will have some contribution of these resonance structures in contrast to the ground state. Therefore, the correlation of pK^* with the substituent constants in the ground state ($\sigma, \sigma^+, \sigma^-, etc$)seems very unreasonable.

In 1977, Lahiri *et al.*[11] calculated the new substituent constants from the pK^* of benzoic acid derivatives and applied them to the pK^* of aniline derivatives without good results. The phenol system had been studied extensively by many workers[12,13] and the pK^* of many phenol derivatives had been determined. In this paper, the new substituent constants (σ^*) are calculated from these pK^* values of phenol derivatives and applied them to other systems.

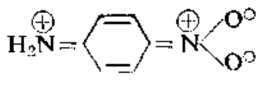


Figure 1. The dipolar structure of *p*-nitroaniline..

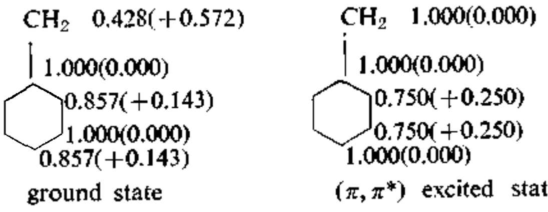


Figure 2. The charge distribution of benzyl cation in the ground and (π, π^*) excited state. Numbers are π-electron densitities and numbers in parentheses are formal charges.

Calculation and Results

The new substituent constants (σ^*) in the excited states of phenol derivatives are calculated by the Hammett equation (eq. 7).

$$\log\left(\frac{K_x^*}{K_0^*}\right)=\rho^*\sigma^* \qquad (7)$$

where K denotes acidity constants, *represents the excited states.

The pK^* of phenol derivatives was determined by many workers[12,13] either by Förster cycle or fluorometric titration method. These pK^* values for phenol derivatives in the excited state (^1L_b in water) are used in the calculation and the values are averaged if more than one pK^* values are reported for one compound. The ρ^* value is arbitrarily taken

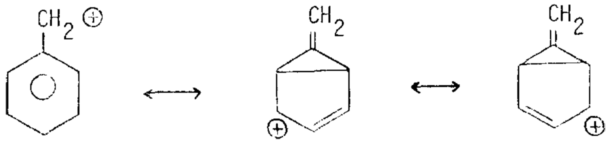
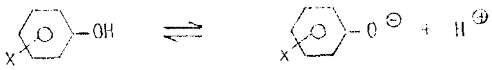


Figure 3. The resonance forms of benzyl cation in the (π, π^*) excited state.

TABLE 1: pK^* of Phenol Derivatives in the Excited State (^1L_b)*. (Solvent: Water)



No.	Substituent	p$K(S_0)$	pK^*	σ^{*a}	σ^b	σ^c	σ^-
1	H	10.0	3.8	0	0	0	0
2	3–F	9.2	3.8	0	0.337	0.352	
3	4–F	9.9	4.0	0.2	0.062	0.073	0.02
4	3–Cl	9.1	3.5	0.3	0.373	0.114	
5	4–Cl	9.4	3.4	0.4	0.227	0.405	
6	3–Br	9.0	2.8	1.0	0.391	0.150	
7	4–Br	9.3	3.0	0.8	0.232	−0.066	0.26
8	3–CH_3	10.1	4.1	−0.3	−0.069	−0.311	
9	4–CH_3	10.2	3.9	−0.1	−0.170	−0.064	
10	3–Et	10.0	4.3	−0.5	−0.07	−0.295	
11	4–Et	10.1	4.3	−0.5	0.151	0.047	
12	3–OCH_3	9.7	3.6	0.2	0.115	−0.778	−0.2
13	4–OCH_3	10.2	4.8	−1.0	0.268		
14	3–OEt	9.5	4.4	−0.6	0.1		
15	4–OEt	10.1	5.3	−1.5	−0.24		
16	3–CH_2OH	9.3	3.2	0.6			
17	3–OH	9.4	3.6	0.2	0.121		
18	4–OH	10.0	3.1	0.7	−0.37	−0.92	
19	4–SO_3^-	9.0	2.4	1.4	0.09		
20	4–$N(CH_3)_3^+$	8.4	1.7	2.1	0.82	0.408	
21	3–NO_2	10.5	0.0	3.8	0.710	0.674	
22	4–NO_2	9.0	−4.0	7.8	0.778	0.790	1.25

*λ_{max}^{abs} of acid and base form of phenol are 270 nm and 286 nm respectively; $^a\sigma^*$=(pK^* of phenol)–(pK of phenol derivatives); ^{b}from ref. 19; ^{c}from ref. 20.

as 1. The results are shown in Table 1.

These new substituent constants (σ^*) and the pK^* of phenol in 50% ethanol[14] are used to calculate the pK^* values of phenol derivatives in the excited states in 50% ethanol and are tabulated in Table 2 (^1L_b state) and Table 3 (^1L_a state). The same method is used for 2,6-di-*tert*-butyl phenol[14] (Table 4, 5) benzamide[15] (Table 6), 2-nitroaniline[16] (Table 7), thiophenol[17] (Table 8), azobenzene[18] (Table 9), and benzoic acid[11] (Table 10).

The correlation coefficients between the pK^* of the compounds and the new substituent constants (σ^*) are calculated and compared with those between the pK^* and σ or σ^+ as shown below.

pK^* *vs.* Substituent constants in the case of phenol (^1L_b, 50% EtOH).

$pK^*=6.73-2.17\sigma$	$r=-0.90$
$pK^*=6.19-1.95\sigma^+$	$r=-0.89$
$pK^*=6.59-0.79\sigma^*$	$r=-0.98$

pK^* *vs.* Substituent constants in the case of phenol (^1L_a, 50% EtOH).

$pK^*=1.87-7.01\sigma$	$r=-0.80$
$pK^*=1.45-6.58\sigma^+$	$r=-0.92$
$pK^*=3.16-1.24\sigma^*$	$r=-0.98$

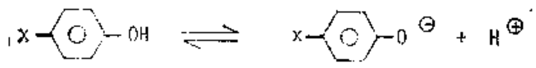
pK^* *vs.* Substituent constants in the case of 2,6-di-*tert*-butyl phenol (^1L_b, 50% EtOH).

$pK^*=7.24-3.99\sigma$	$r=-0.86$
$pK^*=7.00-5.28\sigma^+$	$r=-0.87$
$pK^*=8.25-2.01\sigma^*$	$r=-0.99$

pK^* *vs.* Substituent constants in the case of 2,6-di-*tert*-butyl phenol (^1L_a, 50% EtOH).

$pK^*=0.50-9.75\sigma$	$r=-0.75$
$pK^*=1.17-11.74\sigma^+$	$r=-0.93$
$pK^*=2.82-1.74\sigma^*$	$r=-0.99$

TABLE 2: pK^* of Phenol Derivatives in the Excited State (^1L_b). (Slovent: 50% EtOH)



No.	Substituent	p$K(S_0)$	pK^*	σ^{*a}	σ	σ^+	σ^-
1	H	11.16	6.58	0	0	0	0
2	CH_3	11.60	7.00	−0.1	−0.170	−0.311	
3	*t*-Bu	11.55	7.12		−0.197	−0.256	
4	OCH_3	11.50	7.22	−1.0	−0.268	−0.778	−0.2
5	$Me_3N^{\oplus}$	9.20	4.92	2.1	0.82	0.408	
6	Br	10.57	5.82	0.8	0.232	0.150	0.26
7	$SO_3^{\ominus}$	10.10	7.37^b	1.4	0.09		

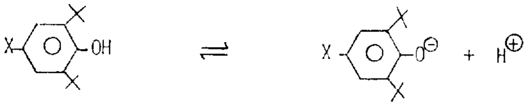
λ_{max}^{abs} of acid and base form of phenol are 271 nm and 288 nm respectively. ^{a}Obtained from Table 1. These values are used in the following Tables. ^{b}This data is omitted in the calculation.

TABLE 3: pK^* of Phenol Derivatives in the Excited State (^1L_a). (Solvent: 50% EtOH)

No.	Substituent	p$K(S_0)$	pK^*	σ^*	σ	σ^+	σ^-
1	H	11.16	2.15	0	0	0	0
2	CH_3	11.60	3.58	−0.1	−0.170	−0.311	
3	*t*-Bu	11.55	3.91		−0.197	−0.256	
4	OCH_3	11.50	5.35	−1.0	−0.268	−0.778	
5	$Me_3N^{\oplus}$	9.20	0.17	2.1	0.82	0.408	
6	Br	10.57	2.46	0.8	0.232	0.159	0.26
7	$SO_3^{\ominus}$	10.10	1.01	1.4	0.09		
8	$CO_2^{\ominus}$	10.61	0.09		0.0	-0.023	
9	COOH						
10	$CONH_2$	0.65	−1.75		0.36		0.62
11	CO_2Et	0.65	−1.86		0.45	0.482	0.68
12	CN	8.80	−1.76		0.66	0.659	0.89
13	$COCH_3$	0.06	−2.53		0.502	0.489	0.85
14	CHO	8.40	−2.79		0.22		1.13
15	NO_2	7.89	−6.20	7.8	0.778	0.790	1.25
16	NO	6.80	−10.29				

λ_{max}^{abs} of acid and base form of phenol are 211 nm and 232 nm respectively

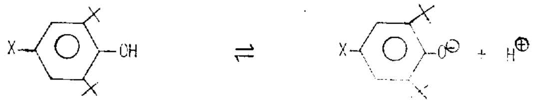
TABLE 4: pK^* of 2,6-Di-*tert*-butyl Phenol Derivatives in the Excited State (^1L_b). (Solvent: 50% EtOH)



No.	Substituent	p$K(S_0)$	pK^*	σ^*	σ	σ^+	σ^-
1	H	14.22	7.92	0	0	0	0
2	CH_3	14.77	8.53	−0.1	−0.170	−0.311	
3	*t*-Bu	14.75	7.55		−0.197	−0.256	
4	OCH_3	14.82		−1.0	−0.268	−0.778	−0.2
5	$Me_3N^{\oplus}$	11.24	3.93	2.1	0.82	0.408	
6	Br	13.23	7.10	0.8	0.232	0.150	0.26
7	$SO_3^{\ominus}$	12.53	5.33	0.4	0.09		

λ_{max}^{abs} of acid and base form of 2,6-di-*tert*-butyl phenol are 271 nm and 295 nm respectively.

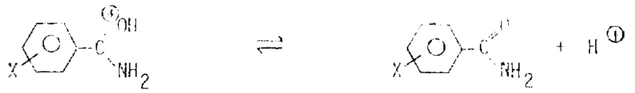
TABLE 5: pK^* of 2,6-Di-*tert*-butyl Phenol Derivatives in the Excited State (^1L_a). (Solvent: 50% Ethanol)



No.	Substituent	p$K(S_0)$	pK^*	σ^*	σ	σ^+	σ^-
1	H	14.22	2.15	0	0	0	0
2	CH_3	14.77	4.17	−0.1	−0.170	−0.311	
3	*t*-Bu	14.75	4.25		−0.197	−0.256	
4	OCH_3	14.82		−1.0	−0.268	−0.778	
5	$Me_3N^{\oplus}$	11.25	−2.05	2.1	0.82	0.408	
6	Br	13.23	2.02	0.8	0.232	0.150	0.26
7	$SO_3^{\ominus}$	12.53	0.18	1.4	0.09		
8	$CO_2^{\ominus}$	13.10	−1.37		0.0	0.023	
9	COOH						
10	$CONH_2$	11.52	0.36		0.36		0.62
11	CO_2Et	11.20	0.45		0.45	0.482	0.68
12	CN	10.15	0.66		0.66	0.659	$0.89
13	$COCH_3$	10.27	0.502		0.502	0.489	0.85
14	CHO	9.33	0.22		0.22		1.13
15	NO_2	7.49	0.778	7.8	0.778	0.790	1.25
16	NO	9.41					

λ_{max}^{abs} of acid and base form of 2,6-di-*tert*-butyl phenol are 214 nm and 244 nm respectively.

TABLE 6: pK^* of Benzamide Derivatives in the Excited State (^1L_a). (Solvent: Water)



No.	Substituent	p$K(S_0)$	pK^*	σ^*	σ	σ^+	σ^-
1	H	−2.16	5.44	0	0	0	0
2	3-CH_3	−2.15	4.76	−0.3	−0.069	−0.066	
3	4-CH_3	−2.01	4.84	−0.1	−0.170	−0.311	
4	3-OCH_3	−2.35	4.90	0.2	0.115	0.047	
5	4-OCH_3	−1.80	6.57	−1.0	−0.268	−0.778	−0.2
6	3-Cl	−2.59	3.40	0.3	0.373	0.399	
7	4-Cl	−2.47	4.10	0.4	0.227	0.114	
8	3-Br	−2.75	2.73	1.0	0.3911	0.405	
9	4-Br	−2.47	3.85	0.8	0.232	0.150	0.26
10	4-F	−2.24	4.80	−0.2	0.062	−0.073	0.02
11	3-NO_2	−3.07	2.89	3.8	0.710	0.674	
12	4-NO_2	−3.23	−3.84	7.8	0.778	0.790	1.25

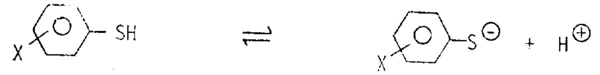
λ^{abs}_{max} of acid and base form of benzamide are 245 nm and 225 nm respectively

TABLE 7: pK^* of 2-Nitroaniline in the Excited State (^1L_a). (Solvent: Water)

No.	Substituent	p$K(S_0)$	pK^*	σ^*	σ	σ^+	σ^-
1	H	−0.29	−4.86	0	0	0	0
2	4-F	−0.44	−5.08	−0.2	0.062	−0.073	0.02
3	4-Br	−1.05	−3.75	0.8	0.232	0.150	0.26
4	4-CF_3	−2.25	−7.39		0.54	0.612	
5	4-NO_2	−4.33	13(28	7.8	0.778	0.790	1.25
6	4-CH_3	0.43	2.96	−0.1	−0.170	−0.311	
7	4-OCH_3	0.77	−2.05	−1.0	−0.268	−0.778	−0.2
8	4-OC_4H_9	0.74	−1.40				
9	−Cl	−1.48	−3.15	0.3	0.373	0.399	
10	−Br	−1.48	−3.38	1.0	0.391	0.405	
11	−NO_2	−2.49	−7.86	3.8	0.710	0.674	
12	−CH_3	−0.09	−2.56	−0.3	−0.069	−0.066	

λ^{abs}_{max} acid and base form of nitroaniline are 266 nm and 413 nm respectively.

TABLE 8: pK^* of Thiophenol Derivatives in the Excited State (^1L_a). (Solvent: Absolute Ethanol)



No.	Substituent	p$K(S_0)^†$	pK^*	σ^*	σ	σ^+	σ^-
1	4-t-Bu				−0.197	−0.256	
2	4-CH_3	6.52	−4.30	−0.1	−0.170	−0.311	
3	3-CH_3	6.58	−3.61	−0.3	−0.069	−0.066	
4	H	6.50	−4.32	0	0	0	0
5	4-Cl	5.90	−3.68	0.4	0.227	0.114	
6	4-NO	4.50	−12.07	7.8	0.778	0.790	1.25

σ^{abs}_{max} of acid and base form of thiophenol are 237 nm and 270 nm respectively. †from ref. 21.

pK^* *vs.* Substituent constants in the case of benzamide.
$pK^*=5.04-6.68\sigma$ $r=-0.82$
$pK^*=4.27-4.90\sigma^+$ $r=-0.79$
$pK^*=4.80-1.02\sigma^*$ $r=-0.94$

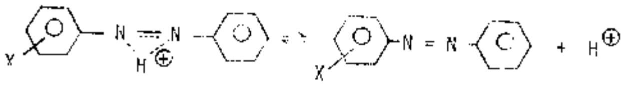
pK^* *vs.* Substituent constants in the case of 2-nitroaniline.
$pK^*=-3.41-7.31\sigma$ $r=-0.78$
$pK^*=-4.29-5.06\sigma^+$ $r=-0.72$
$pK^*=-3.42-1.22\sigma^*$ $r=-0.96$

pK^* *vs.* Substituent constants in the case of thiophenol.
$pK^*=-4.27-8.65\sigma$ $r=-0.90$
$pK^*=-4.76-7.95\sigma^+$ $r=-0.90$
$pK^*=-3.99-10.3\sigma^*$ $r=-0.99$

pK^* *vs.* Substituent constants in the case of azobenzene.
$pK^*=12.76-4.22\sigma$ $r=-0.92$
$pK^*=12.06-3.02\sigma^+$ $r=-0.88$
$pK^*=13.10-0.65\sigma^*$ $r=-0.93$

pK^* *vs.* Substituent constants in the case of benzoic acid.
$pK^*=7.60-7.30\sigma$ $r=-0.85$
$pK^*=7.14-6.81\sigma^+$ $r=-0.86$
$pK^*=5.96-0.75\sigma^*$ $r=-0.96$

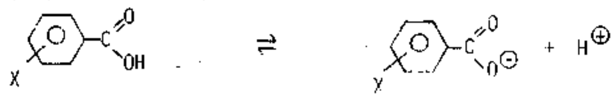
TABLE 9: pK^* of Azobenzene Derivatives in the Excited State (^1B). (Solvent: Aqueous Ethanol)



No.	Substituent	p$K(S_0)$	pK^*	σ^*	σ	σ^+	σ^-
1	H	−2.9	13.7	0	0	0	0
2	4-OEt	−1.28	13.9	−1.5	−0.24		
3	4-OCH_3	−1.36	14.0	−1.0	−0.268	−0.778	−0.2
4	4-CH_3	−2.35	x2.8	−0.1	−0.170	−0.311	
5	3-CH_3	−2.70	x2.5	−0.3	−0.069	−0.066	
6	4-Br	−3.47	x2.8	0.8	0.232	0.150	0.26
7	3-Br	−3.83	11.4	1.0	0.3911	0.405	
8	4-$COCH_3$	−3.98	10.0		0.502	0.489	0.85
9	4-CN	−4.52	9.6		0.660	0.659	0.89
10	3-NO_2	−4.63	10.6	3.8	0.710	0.674	
11	4-NO_2	−4.70	8.0	7.8	0.778	0.790	1.25
12	4-$NOH(CH_3)_2$	−4.65	10.1		0.795		
13	4-OH	−1.02	14.0	0.7	−0.37	−0.92	

λ^{abs}_{max} of acid and base form of azobenzene are 418 nm and 313 nm respectively.

TABLE 10: pK^* of Benzoic Acid Derivatives in the Excited State (^1L_b). (Solvent: Water)



No.	Substituent	p$K(S_0)$	pK^*	σ^*	σ	σ^+	σ^-
1	H	4(20	5.63	0	0	0	0
2	3-I	3.85	5.95		0.352	0.359	
3	3-Br	3.81	5.93	1.0	0.391	0.150	
4	3-Cl	3.83	5.97	0.3	0.373	0.114	
5	3-F	3.86	5.81	0	0.337	0.352	
6	4-Cl	3.99	5.86	0.4	0.227	0.405	
7	4-I	4.00	6.31		0.18	0.135	
8	4-NO_2	3.43	0.53	7.8	0.778	0.790	1.25
9	3-NO_2	3.46	1.95	3.8	0.710	0.674	

λ^{abs}_{max} of acid and base form of benzoic acid are 273 nm and 268 nm respectively.

As an example, the correlation in 2-nitroaniline is shown in Figures 4–6

Since σ^- contants are available only for the limited number (2–4) of *para* substituents, no calculation is attempted to correlate them with pK^*.

Discussion

Acidity constants of phenol, 2,6-di-*tert*-butyl phenol, thiophenol and 2-nitroaniline in the excited state are greater than those in the ground state (p$K^*<$pK), but the reverse is observed for benzamide, azobenzene and benzoic acid derivatives (p$K^*>$pK). From the correlation between pK^* and various substituent constants such as σ, σ^+, and σ^*, the best correlation is observed with σ^* in spite of the approximations involved and the experimental inaccuracy in obtaining the pK^* values.

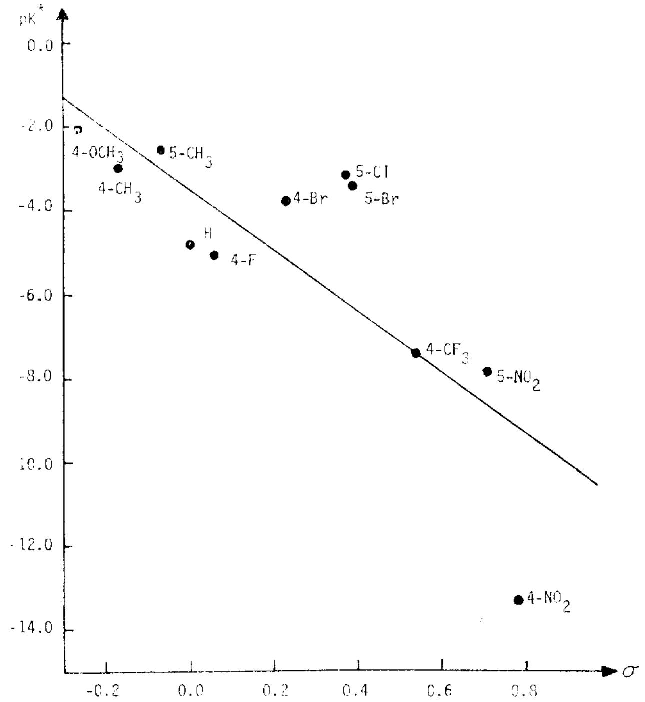


Figure 4. pK^* versus σ in the case of 2-nitroaniline (r= −0.78).

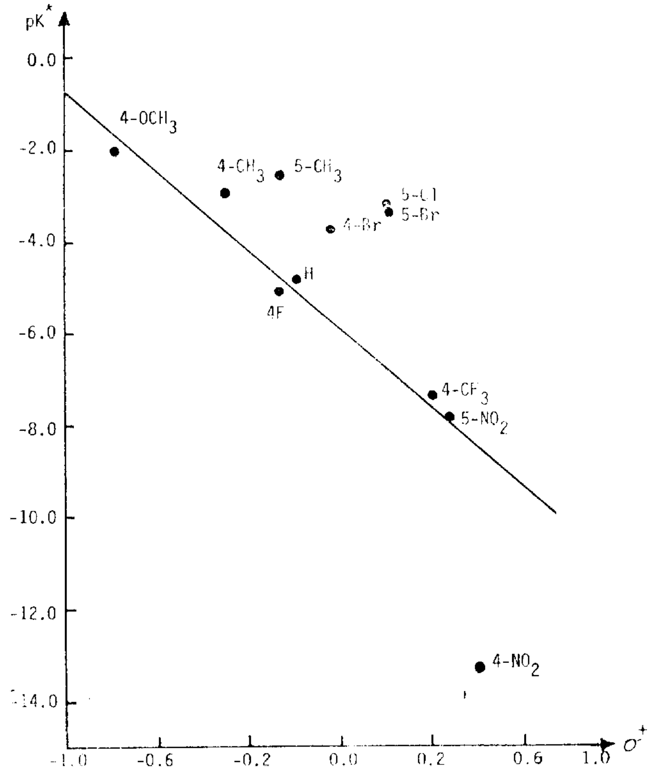


Figure 5. pK^* versus σ^+ in the case of 2-nitroaniline (r= −0.72).

Even though the pK^* values were correlated quite well with σ^- in phenol derivatives,[5] the σ^- values are available only for the limited number of *para* substituents alone and the correlation can be fortuitous. Furthermore, it is not relevant to correlate pK^* with σ^- constants since the electronic configuration of the excited state is generally very different from that of the ground state.

The fact that the best correlationship obtained between pK^* and σ^* constants can be explained by the change of the electronic configuration in the excited states. The mode of resonance contribution is changed in the phenyl derivatives in the excited states compared to the ground state. For example, photosubstitution in nitrophenyl esters and ethers by various nucleophiles is preferred at the *meta*-position over the *ortho*-and *para*- positions in contrast to the nucleophilic substitution in the ground state. The extent of resonance contribution of substituents is also changed in the excited states. Since the excitation energy of the ^1L_b states can be different from one system to other, the resonance and contribution of substituents may be slightly different from inductive system to system. However, the difference is negligible if compared to the differences between those of the ground state and the excited state.

Therefore, the new substituent constants, σ^*, are proposed for the linear free energy relationship in the excited states of

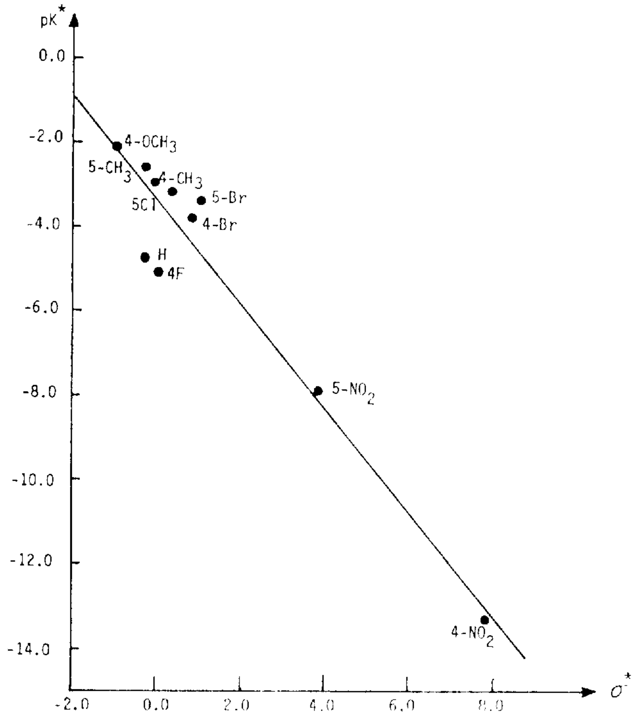


Figure 6. pK^* versus σ^* in the case of 2-nitroaniline (r= −0.96).

phenyl compounds. Other than acidity constants, the fluorescence quenching rate constants can be studied utilizing these σ^* constants.

These new σ^* constants will be applied to the benzoic acid system to test and also to improve their generality. The work is in progress.

References

(1) S. C. Shim and J. W. Park, *Prog. Chem. Chem. Ind.*, **20**(2), 81 (1980).

(2) T. Förster, *Z. Elektrochem.*, **54**, 42 (1950).

(3) N. Lasser and J. Feitelson, *J. Phys. Chem.*, **77**, 1011 (1973).

(4) N. Lasser and J. Feitelson, *J. Phys. Chem.*, **79**, 1344 (1975).

(5) H. H. Jaffé and H. L. Jones, *J. Org. Chem.*, **30**, 964 (1965).

(6) D. D. Rosebrook and W. W. Brandt, *J. Phys. Chem.*, **70**, 3857 (1966).

(7) E. L. Wehry and L. B. Logers, *J. Amer. Chem. Soc.*, **87**, 4234 (1965).

(8) J. A. Barltrop and J. D. Coyle, "Principles of Photochemistry," p. 52, John Wiley & Sons, New York, 1978.

(9) H. E. Zimmerman and V. R. Sandel, *J. Amer. Chem. Soc.*, **85**, 915 (1963).

(10) J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules," p. 91, Chapman and Hall, London, 1963.

(11) D. Sengupta and S. C. Lahiri, *Z. Phys. Chemie (Leipzig)*, **258**, 1097 (1977).

(12) J. F. Ireland and P. A. H. Wyatt., *Adv. Phys. Org. Chem.*, **12**, 131 (1976).

(13) (a) W. Bartock and P. J. Lucchesi, *Photochem. Photobiol.*, **4**, 499 (1965); (b) ref. 7. (c) I. Avigal, J. Feitelson and M. Ottolenghi, *J. Chem. Phys.*, **50**, 2614 (1969); (d) J. D. Winefordner, S. G. Schulman and L. B. Sanders, *Photochem. Photobiol.*, **13**, 381 (1971).

(14) L. A. Cohen and W. M. Jones, *J. Amer. Chem. Soc.*, **85**, 3397 (1963).

(15) J. T. Edward, H. S. Chang, K. Yates and R. Stewart, *Can. J. Chem.*, **38**, 1518 (1960).

(16) J. D. Idoux and C. K. Hancock, *J. Org. Chem.*, **33**, 3489 (1968).

(17) S. I. Miller and G. S. Krishnamurthy, *J. Org. Chem.*, **27**, 645 (1962).

(18) R. H. Ellerhorst and H. H. Jaffé, *J. Org. Chem.*, **33**, 4115 (1968).

(19) A. J. Gordon and R. A. Ford Ed., "The Chemist's Companion," p. 144, New York, John Wiley & Sons, 1972.

(20) H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **80**, 4979 (1958).

(21) S. Patai ed., "The Chemistry of the Thiol Group," Part 1, p. 402, John Wiley & Sons, London, 1974.

The Vacancies-in-Solid Model Applied to Solid Argon

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The molar volumes, the molar heat capacities and the molar entropies of solid argon are calculated from O K to the triple point using the vacancies-in-solid model. In the partition function, the central pairwise additive (Mie–Lennard–Jones 12,6) potential is used by introducing numbers, which is obtained by summing powers over all lattice points of a face-centred cubic in terms of the distance between nearest neighbours. A method of iteration is employed to evaluate the potential parameter, The results are compared with experimental values and other theoretical values. The results show a fair agreement with the experimental results.

Introduction

The rare gas solids have long been used as model substances for testing theoretical studies of thermodynamic properties since the atomic interactions involve predominantly short ranged central forces which can be relatively accurately described for these substances. The representative theoretical studies are those of Herzfeld and Mayer[1], Rice[2], Henkel[3], Zucker[4] and Gupta *et al.*[5] Rice used Debye approximation to determine the thermodynamic properties of solid argon, assuming Grüneisen law be true. This gave best fit to the experimental specific heat data of Clusius[6]. But his cohesive energy expression showed large contributions from anharmonic terms even at low temperatures, which do not seem to be logical. Henkel used Einstein approximation and the effect of anharmonicity to calculate specific heats and