

The New Substituent Constants in the Excited States (II)

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In order to standardize the σ^* , ρ^* is taken as unity for the benzoic acids by analogy with the fact that ρ of benzoic acids in the ground state is taken as unity. The pK_a^* of many benzoic acid derivatives are determined by UV spectroscopy and fluorescence spectral analysis whenever possible. The σ^* constants are derived from the Hammett equation utilizing these pK_a^* values and the pK_a^* of the benzoic acid derivatives showed better correlation with σ^* than σ , σ^+ and σ^- as expected. From these σ^* values, ρ^* of the phenol derivatives was calculated to be 1.28. The new standardized σ^* values are calculated from the pK_a^* values of phenols since more accurate and abundant data are available for phenols than the benzoic acid derivatives.

Introduction

The acidity constants in the excited states can be determined by several methods. These methods are studied by many workers and the acidity constants of many compounds in the excited state have been determined.¹ From these pK_a^* values, there have been some attempts to test whether the Hammett equations are applicable to the excited states or not, and whether the substituent constants in the ground state (σ , σ^+ , σ^- , etc) can be applied to the excited states also or not.

Jaffé *et al.*² and many other workers^{3,4} have tried to apply the pK_a^* to the well-known Hammett equation (eq. 1)⁵ utilizing the substituent constants in the ground state.

$$\log \left(\frac{K_x}{K_0} \right) = \rho\sigma \quad (1)$$

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

In 1977, Lahiri *et al.*⁶ suggested that the Hammett equation is applicable in the excited state as in equation (2), and calculated ρ^* of benzoic acid derivatives with thermodynamic relationships with several assumptions.

$$\log \left(\frac{K_x^*}{K_0^*} \right) = \rho^*\sigma^* \quad (2)$$

They determined the pK_a^* of benzoic acid derivatives and aniline derivatives and tried to correlate pK_a^* of two types of compounds. But their result was poor.

We previously reported that the substituent constant (σ^*) calculated from the acidity constants (pK_a^*) of phenol derivatives in the excited state (1L_b) gave better relationship

with pK_a^* of other aromatic systems⁷ and showed that equation (2) can be used in the excited states as in the ground state.

However, the σ^* constants we used were not standardized since we arbitrarily assumed ρ^* to be unity for phenols. In order to standardize the σ^* , ρ^* is taken as unity for the benzoic acids by analogy with the fact that ρ of benzoic acids in the ground state is taken as unity. Thus we determined pK_a^* of many benzoic acid derivatives by UV spectroscopy and fluorescence spectroscopy whenever possible, and compared the pK_a^* of benzoic acid derivatives and that of phenol derivatives.

Experimental and Calculation

1. Materials

a. solvents. Distilled water was used as the solvent throughout the work. Methanol (Wako E. P. reagent grade) was used after distillation. Sulfuric acid and potassium hydroxide (Wako and Kanto E. P. reagent grade) were used without further purification.

b. benzoic acid derivatives. Benzoic acid derivatives were recrystallized from water or from the water/methanol mixture. Melting points of these compounds after recrystallization and drying were measured with Thomas Hoover capillary melting point apparatus and compared with the literature values.^{8,9}

2. Measurement of λ_{max}^{ab} and λ_{max}^n

Ultraviolet absorption was measured on a Cary 17 spectrophotometer and fluorescence spectra were obtained with an Aminco Bowman spectrophotometer. An 1 cm quartz cell used for absorption and fluorescence measurements was capped with a plastic stopper and purged of air by bubbling nitrogen into the cell by means of a hypodermic needle. The pH of these solutions were measured on a Corning Model 12-Research pH meter. The concentration of these solutions were adjusted to $1 \times 10^{-4} M$ for spectroscopic measurements. The absorption spectra of these compounds were recorded with varying the pH from 1 to 11, and they were measured in 1 N sulfuric acid solutions and in 0.1 N potassium hydroxide solutions as the most probable acid and conjugate base form. Most of all, the λ_{max}^{ab} values for 1L_b transition agree

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TABLE 1: λ_{max}^{ab} and λ_{max}^{fl} of Benzoic Acid Derivatives of the Acid and Base Form in Water and 95 % MeOH

| Substituent | $\lambda_{max}^{ab} (\lambda_{max}^{fl})^a$ | | | |
|----------------------------------|---|----------------|-----------|----------------|
| | Water | | 95 % MeOH | |
| | acid | conjugate base | acid | conjugate base |
| H | 272 (348) | 271 | 271 | 267 |
| 3-Br | 284 | 276 | 281 | 275 |
| 4-Br | 245 | 239 | 241 | 235 |
| 3-Cl | 283 (343) | 275 | 282 | 284 |
| 4-Cl | 282 (330) | 275 | 280 | 267 |
| 3-F | 276 (345) | 271 (420) | 275 | 270 |
| 4-F | 230 | 222 | 228 | 222 |
| 3-CN | 280 (325) | 277 | 287 | 285 |
| 4-CN | 283 (335) | 277 | 291 | 286 |
| 3-NO ₂ | 260 (410) | 265 | 256 | 260 |
| 4-NO ₂ | 262 | 271 | 259 | 264 |
| 4-OC ₂ H ₅ | 254 (336) | 245 | 254 | 246 |

a : in nm

TABLE 2: pK_a^* of Benzoic Acid Derivatives in the Excited States. (L_1) (solvent : water)

| Substituent | $pK_a(S_0)$ | $pK_a(S_1)$ | σ^* | σ | σ^+ |
|----------------------------------|-------------|-------------|------------|----------|------------|
| H | 4.20 | 5.36 | 0 | 0 | 0 |
| 3-Br | 3.81 | 5.95 | 1.0 | 0.391 | 0.150 |
| 4-Br | 3.97 | 6.11 | 0.8 | 0.232 | -0.066 |
| 3-Cl | 3.83 | 5.99 | 0.3 | 0.373 | 0.114 |
| 4-Cl | 3.99 | 5.89 | 0.4 | 0.227 | 0.405 |
| 3-F | 3.90 | 5.31 | 0 | 0.337 | 0.352 |
| 4-F | 4.14 | 7.35 | -0.2 | 0.062 | -0.073 |
| 3-CN | 3.60 | 4.15 | | 0.560 | 0.562 |
| 4-CN | 3.55 | 5.17 | | 0.660 | 0.674 |
| 3-NO ₂ | 3.46 | 1.94 | 3.8 | 0.710 | 0.674 |
| 4-NO ₂ | 3.43 | 0.76 | 7.8 | 0.778 | 0.790 |
| 4-OC ₂ H ₅ | 4.80 | 7.84 | -1.5 | -0.240 | |

with the values in the literature. In addition to water as the solvent, 95 % methanol was used to record the UV absorption and fluorescence spectra at room temperature. The results are shown in Table 1.

3. Calculation of pK_a^* of benzoic acid derivatives in the excited state (L_1).

By making use of acidity constants in the ground state from the literature¹⁰ and the Förster cycle (eq. 3), we could calculate the acidity constants of the benzoic acid derivatives in the excited states.

$$pK_a - pK_a^* = \frac{Nh}{2.303 RT} (\bar{\nu}_{AH} - \bar{\nu}_{A^-}) \quad (\text{eq. 3})$$

$$= 2.10 \times 10^{-3} (\bar{\nu}_{AH} - \bar{\nu}_{A^-}) \text{ at } 25^\circ \text{C}$$

In many cases, fluorescence intensity was too weak to determine $\bar{\nu}_{max}^{fl}$ and we used the λ_{max}^{ab} only in the calculation of the pK_a^* in those cases. The results are shown in Table 2.

All data fitting were obtained by the least square method.

Results and Discussion

There are always some uncertainty in pK_a^* values induced by the error of λ_{max}^{ab} measurements. The extent of uncertainty

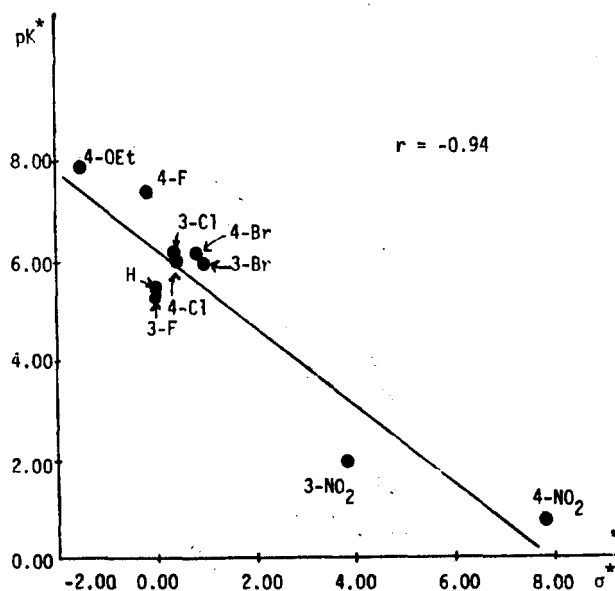


Figure 1. pK_a^* versus σ^* in the benzoic acid derivatives ($r = -0.94$).

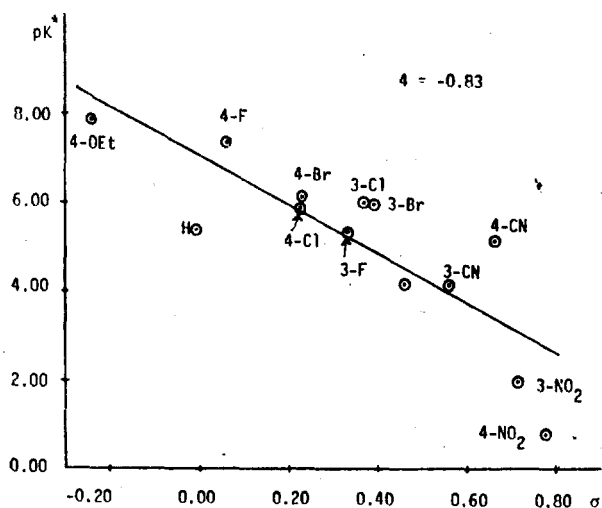


Figure 2. pK_a versus σ in the benzoic acid derivatives ($r = -0.83$).

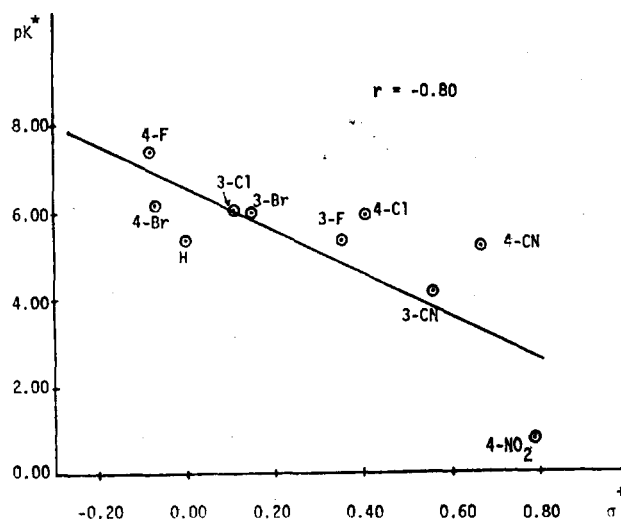


Figure 3. pK_a^* versus σ^+ in the benzoic acid derivatives ($r = -0.80$).

in pK_a^* originated from the experimental error is obvious from the equations shown below.

$$\begin{aligned} pK - pK^* &= 2.10 \times 10^{-3} (\bar{\nu}_{AH} - \bar{\nu}_{A^-}) \\ \Delta pK^* &= 2.10 \times 10^{-3} \left(\frac{\Delta \lambda_{AH}}{\lambda_{AH}^2} - \frac{\Delta \lambda_{A^-}}{\lambda_{A^-}^2} \right) \\ &\approx 2.10 \times 10^{-3} \left(\frac{\Delta \lambda_{AH} - \Delta \lambda_{A^-}}{\lambda_{AH}^2} \right) \\ &\approx 2.10 \times 10^{-3} \left(\frac{\Delta \lambda_{AH} - \Delta \lambda_{A^-}}{\lambda_{A^-}^2} \right) \end{aligned}$$

Thus an error of 0.1 nm at a wavelength of 250 nm deviates 0.34 pK_a units from the true value. Moreover the smaller the λ_{AH} or λ_{A^-} , the larger ΔpK_a^* values are obtained when $\Delta \lambda$ is same. So the λ_{max} must be measured accurately.

There are some difficulties in the determination of pK_a^* when substituent group interferes the acid-base equilibrium. For example, aminobenzoic acid forms the zwitter ion in the excited and ground states and we could not obtain the exact pK_a^* value of carboxylic group of the compound. It could be said that the amino substituent group is the typical type of groups which inhibit the determination of pK_a^* of aromatic carboxylic acids.

When the pK_a^* of benzoic acid derivatives is correlated with the substituent constants σ^* , σ , σ^+ , the following results are obtained.

$$\begin{aligned} pK^* &= 6.22 - 0.78 \sigma^* \quad r = -0.94 \text{ (Figure 1)} \\ pK^* &= 6.50 - 4.89 \sigma \quad r = -0.08 \text{ (Figure 2)} \\ pK^* &= 7.02 - 5.84 \sigma^+ \quad r = -0.83 \text{ (Figure 3)} \end{aligned}$$

As expected, σ^* from phenol derivatives gave the best correlation with the pK_a^* of the benzoic acid derivatives. Moreover we could calculate ρ^* of the phenol derivatives to be 1.28 (1/0.78) if we take ρ^* of the benzoic acid derivatives as unity. So we could standardize the substituent constants in the excited state simply by dividing σ^* obtained from the phenol derivatives by 1.28 (because more accurate and abundant pK_a^* values are available in the phenol derivatives, we made use of the σ^* obtained from phenol derivatives rather than σ^* obtained from the benzoic acid derivatives) and the results are shown in Table 3.

As a result, we could verify the equation (2) again, and the standardized substituent constants (σ^*) which is applicable to study the substituent effects in the phenyl compounds in the excited state are obtained. These new substituent constants are proposed to be used in the study of linear free energy relationship in the excited states of phenyl compounds.

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TABLE 3: The New Standardized Substituent Constants (σ^*)

| No | Substituent | σ^{*a} | σ^{*b} | σ^c | σ^{*d} |
|----|--|---------------|---------------|------------|---------------|
| 1 | H | 0 | 0 | 0 | 0 |
| 2 | 3-F | 0 | 0 | 0.337 | 0.352 |
| 3 | 4-F | -0.2 | -0.16 | 0.62 | -0.073 |
| 4 | 3-Cl | 0.3 | 0.23 | 0.373 | 0.114 |
| 5 | 4-Cl | 0.4 | 0.31 | 0.227 | 0.405 |
| 6 | 3-Br | 1.0 | 0.78 | 0.391 | 0.150 |
| 7 | 4-Br | 0.8 | 0.62 | 0.232 | -0.066 |
| 8 | 3-CH ₃ | -0.3 | -0.23 | -0.069 | -0.311 |
| 9 | 4-CH ₃ | -0.1 | -0.08 | -0.017 | -0.064 |
| 10 | 3-Et | -0.5 | -0.39 | -0.070 | -0.295 |
| 11 | 4-Et | -0.5 | -0.39 | -0.151 | 0.047 |
| 12 | 3-OCH ₃ | 0.2 | 0.16 | 0.115 | -0.778 |
| 13 | 4-OCH ₃ | -0.1 | -0.78 | -0.268 | |
| 14 | 3-OEt | -0.6 | -0.47 | 0.100 | |
| 15 | 4-OEt | -1.5 | -1.20 | -0.240 | |
| 16 | 3-CH ₂ OH | 0.6 | 0.47 | | |
| 17 | 3-OH | 0.2 | 0.16 | 0.121 | |
| 18 | 4-OH | 0.7 | 0.55 | -0.370 | -0.920 |
| 19 | 4-SO | 1.4 | 1.10 | 0.090 | |
| 20 | 4-N ⁺ (CH ₃) ₃ | 2.1 | 1.60 | 0.820 | 0.408 |
| 21 | 3-NO ₂ | 3.8 | 3.00 | 0.710 | 0.674 |
| 22 | 4-NO ₂ | 7.8 | 6.10 | 0.778 | 0.790 |

^a ref. 7 ^b standardized one ^c ref. 11 ^d ref. 12

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