The Substituent Effect. III. The Basicities of Polynuclear Aryl Methyl Ketones

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The basicities of nine polynuclear aryl methyl ketones have been determined spectrophotometrically in various aqueous sulfuric acid solutions. The electronic effects of unhindered polynuclear aryls on pK_{BH^+} can be successfully correlated with our LArSR equation,

$$\log k/k_0 = \rho(\sigma^0 + r\Delta\bar{\sigma}_R^+),$$

using ρ and r values established from *meta*- and *para*-substituted acetophenones. The applicability of this equation to polynuclear aryls is also shown for some other electrophilic reactivities. The $\Delta\bar{\sigma}_R^+$ parameters for polynuclear aryls are derived empirically from the solvolysis of α-arylethyl chlorides; these show a good linearity with the theoretical reactivity indices of the localization energies.

In our continuing studies of the substituent effect on chemical reactivities, it has been established that the linear aromatic substituent reactivity (LArSR) relationship (1)[1-3] is generally applicable with an excellent precision to electrophilic reactions of substituted benzene derivatives;

$$\log k/k_0 = \rho(\sigma^0 + r\Delta\bar{\sigma}_R^+) \quad (1)$$

where r is the variable characteristic of the reaction system describing the degree of the resonance exaltation and where $\Delta\bar{\sigma}_R^+$ is the substituent constant to donate electron by resonance. This equation is a bisecting description of the substituent effect in terms of the unexalted polar effect of substituted phenyl groups and the aryl resonance exaltation effect. Eq. (1) is immediately followed by Eq. (2):

$$1/\rho \log k/k_0 = \sigma^0 + r\Delta\bar{\sigma}_R^+ \quad (2)$$

As has been shown in previous papers,[1,3] the apparent substituent constants of a given *para* substituent generally exhibit a linear correlation, with a substantial slope, against r values for varying reactions. 4-Biphenylyl derivatives satisfy the above equation over a wide range of r. For 2-fluorenyl derivatives we obtained a similar plot with a slope of −0.49 and an intercept of 0.00, as is shown in Fig. 1. These findings mean that the apparent substituent constants for both derivatives can be successfully described in terms of the unexalted aryl polar effect, σ^0, and the exalted resonance effect, $r\Delta\bar{\sigma}_R^+$.

Even for condensed polynuclear aromatic hydrocarbons, such as naphthalene and phenanthrene, the above treatment can be also applicable as is shown in Fig. 2. The changes in the apparent substituent constants of 2-naphthyl are found to be a linear function of r, while those of 1-naphthyl do not satisfy the linear dependence on r. The random scatterings of the latter suggest that the steric interaction of peri-hydrogen with the reaction site depends on the nature of reactions. The linearity of the former is an evidence for the constancy of the resonance substituent constant for the 2-naphthyl group. Therefore, it might be expected that Eq. (1) can be extended so as to correlate the reactivity changes of polynuclear aromatic hydrocarbons, besides those with peri-hydrogen interaction, using ρ and r values established from a series of substituted benzene reactivities.

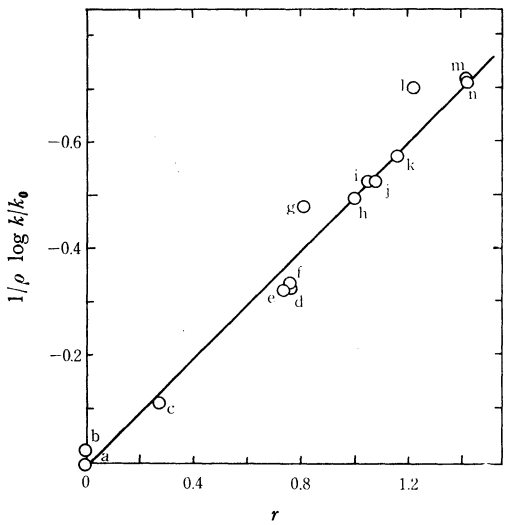

Fig. 1. Relation between apparent substituent constants for 2-fluorenyl group and r values.
Most ρ and r values are quoted from the previous paper, Ref. 1. a) Alkaline hydrolysis, arylcarbinyl benzoates, Ref. 31. b) Alkaline hydrolysis, methyl arylacetates, N, Acton and E. Berliner, *J. Amer. Chem. Soc.*, **86**, 3312 (1964). c) Alkaline hydrolysis, ethyl benzoates, Ref. 34. d) Basicity, aryl methyl ketones, present study. e) Protodesilylation in MeOH-aq. $HClO_4$, C. Eaborn, *J. Chem. Soc.*, **1956**, 4858. f) Protodesilylation in AcOH-aq. H_2SO_4, F. B. Deans and C. Eaborn, *ibid.*, **1959**, 2299. g) Acetylation, H. C. Brown, and G. Marino, *J. Amer. Chem. Soc.*, **84**, 1658 (1962). h) Solvolysis, Brown and Okamoto's σ^+, H. C. Brown and Y. Okamoto, *ibid.*, **80**, 4979 (1958). i) Mercuration, H. C. Brown, and G. Goldman, *ibid.*, **84**, 1650 (1962). j) Acetolysis, α-arylethyl chlorides, Y. Yukawa, Y. Tsuno, Y. Kusuyama, and N. Shimizu, unpublished. ($\rho = -4.70$ and $r = 1.08$). k) Solvolysis, α-arylethyl chlorides, Ref. 29. l) Molecular chlorination, L. M. Stock and H. C. Brown, *J. Amer. Chem. Soc.*, **84**, 1661 (1962). m) Molecular bromination, L. M. Stock and H. C. Brown, *ibid* **84**, 1661 (1962). n) Molecular bromination, L. Altschuler and E. Berliner, *ibid.*, **88**, 5837 (1966). From the linearity with the above bromination, ρ and r in this bromination are calculated to be −9.87 and 1.42, respectively.

As a more simplified treatment, Streitwieser has proposed a Hammett-type equation (3) for polynuclear aryl reactivities, in which the reference reaction in the solvolysis of polynuclear arylcarbinyl chlorides in 80% aq. ethanol.[4]

$$\log k/k_0 = \rho\sigma_{Ar} \quad (3)$$

1) Y. Yukawa, Y. Tsuno, and M. Sawada, This Bulletin, **39**, 2274 (1966).

2) Y. Tsuno, T. Ibata, and Y. Yukawa, *ibid.*, **32**, 960 (1959); Y. Yukawa and Y. Tsuno, *ibid.*, **32**, 965 (1959); **32**, 971 (1959).

3) Y. Yukawa and Y. Tsuno, *Nippon Kagaku Zasshi*, **86**, 873 (1965).

4) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists", John Wiley & Sons, (1964), Chap. 12.

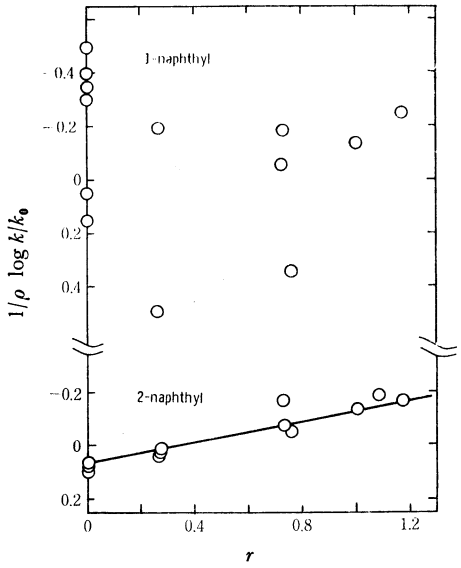

Fig. 2. Relation between apparent substituent constants for 1-naphthyl or 2-naphthyl group and r values.

He has shown a good applicability of Eq. (3) for some solvolysis reactions through a carbonium-ion intermediate. Several authors have utilized this equation and have derived revised or secondary σ values for polynuclear aryls.[5,6] However, the application of this equation is limited to the reaction system analogous to the reference system. This limitation probably arises from the neglect of the varying contribution of the resonance component to the electronic effect of polynuclear aryls.

In a previous paper, a set of σ^0 values for polynuclear aryl moieties was determined by the hydrolysis of arylcarbinyl benzoates and a set of $\Delta\bar{\sigma}_R^+$ values (in Brown Okamoto's σ^+ scale), from the solvolysis of α-arylethyl chlorides, the r value of which was 1.16. According to the LArSR approach, the solvolysis of the polynuclear $ArCH_2X$ system is treated with an extremely high r value of *ca.* 1.6 (see Discussion).

In order to verify this treatment, it is necessary and of interest to study the polynuclear reactivity changes which give the r of an intermediate value. From this point of view, the basicities of aryl methyl ketones was chosen because the r had been established to be 0.76 from that of substituted acetophenones. We have determined the dissociation constants for the conjugate acids of some polynuclear aryl methyl ketones, and have examined whether the electronic effects of polynuclear aryls on pK_{BH^+} could be treated by means of Eq. (1).

Experimental

Materials. The 1-naphthyl and 2-naphthyl methyl ketones were obtained commercially. The former was purified by recrystallization of the picrate, followed by fractional distillation of the regenerated ketone. No impurity was detected by vapor-phase chromatography. The other ketones were prepared by the method described in the literature. The 4-biphenylyl,[7] 2-fluorenyl,[8] 3-phenanthryl,[9] and 1-anthryl[10] methyl ketones were prepared by the Friedel-Crafts acetylation of the corresponding hydrocarbons. The 2-phenanthryl methyl ketone was obtained by the dehydrogenation of (9,10-dihydro) phenanthryl methyl ketone with sulfur.[11]

The 9-phenanthryl isomer was prepared from 9-carbomethoxyphenanthrene by the method of Mosettig and Kamp.[12] The 2-anthryl compound was derived from 9-anthryl ketone by isomerization with $AlCl_3$.[13]

Each isomer of the phenanthryl or anthryl methyl ketone was purified by column chromatography with Al_2O_3, followed by repeated recrystallizations from the appropriate solvents. The absorption spectra (λ_{max} and $\log \varepsilon$) in 95% EtOH were identical with those given in the organic electronic spectral data. The physical properties and analytical data are listed in Table 1.

Sulfuric Acid. Twenty stock solutions of different concentrations of sulfuric acid, ranging from 41.9% to 93.7 % by weight, were prepared by dilution with freshly-distilled water of sulfuric acid which had been purified by three re-solidifications on cooling. In these solutions no optical impurities were observed in the range of wavelengths measured.

The concentrations of the solutions were determined by titrating weighed samples with a satndard NaOH aqueous solution of about 1 N. The H_0 values of the above solutions were obtained by interpolation from a standard curve constructed using the revised values evaluated by Jorgenson and Hartter.[14]

Spectrophotometric Measurements. The method adopted for preparing the appropriate concentration of a ketone in aq. sulfuric acid was essentially the same as that described by Stewart and Yates.[15] A sample weighed on a microbalance was dissolved in 250 m*l* of anhydrous acetone, from which 0.5 m*l* aliquots were pipetted into a 10 m*l* volumetric flask. After the acetone had been carefully evaporated under a moderately reduced pressure, the flask was made up to volume with appropriate acid solutions. The concentration of the sample solution was about 10^{-5} mol/*l*. In the cases of 2- and 9-phenanthryl and 2-anthryl ketones, the solubilities into diluted acids were not so sufficient enough that the step-by-step dilution method was employed in these diluted acids.

The extinction coefficients were measured at room temperature with covered quartz cells of a 1 cm path length using a Hitachi Perkin-Elemr UV-VIS spectrophotometer. A solvent blank of the same concentration of acid as that containing a ketone was employed.

The pK_{BH^+} values were determined by the isosbestic-point method.[16] The isosbestic point was selected as an

5) A. Streitwieser, Jr., H. A. Hammond, R. H. Jagow, R. M. Williams, R. G. Jesaitis, C. J. Chang, and R. Wolf, *J. Amer. Chem. Soc.*, **92**, 5141 (1970).

6) B. G. von Leuwen and R. J. Ouellette, *ibid.*, **90**, 7056 (1968).

7) The method is the same as "Organic Syntheses," Coll. Vol. 1, p. 109.

8) "Organic Syntheses," Coll. Vol. 3, p. 23.

9) E. Mosettig and J. van de Kamp, *J. Amer. Chem. Soc.*, **52**, 3704 (1930).

10) P. H. Gore, *J. Org. Chem.*, **22**, 135 (1957).

11) A. Burger and E. Mosettig, *J. Amer. Chem. Soc.*, **58**, 1857 (1936); B. Riegel, M. H. Gold, and M. A. Kubico, *ibid.*, **64**, 2221 (1942).

12) E. Mosettig and J. van de Kamp, *ibid.*, **55**, 3442 (1933)

13) E. G. E. Hawkins, *J. Chem. Soc.*, **1957**, 3858.

14) M. J. Jorgenson and D. R. Hartter, *J. Amer. Chem. Soc.*, **85**, 878 (1963).

15) R. Stewart and K. Yates, *ibid.*, **80**, 6355 (1958).

16) L. A. Flexser, L. P. Hammett, and A. Dingwall, *ibid.*, **57**, 2103 (1935).

TABLE 1. PHYSICAL CONSTANTS AND ANALYTICAL DATA OF POLYNUCLEAR ARYL METHYL KETONES

Aryl	Mp or Bp(mmHg)	Carbon		Hydrogen	
		Found	Calcd	Found	Calcd
4-Biphenylyl	122[a,b]	85.50	85.64	5.94	6.04
2-Fluorenyl	130.5—131[a]	87.00	86.52	5.49	5.81
1-Naphthyl	127(1)[c]	84.88	84.64	5.85	5.92
2-Phenanthryl	146.5—147[a,d]	87.30	87.25	5.11	5.49
3-Phenanthryl	75.8—76[a,d,e]	87.53	87.25	5.21	5.49
9-Phenanthryl	74—74.8[a,d,f]	87.33	87.25	5.29	5.49
2-Anthryl	194[a,g,h]	87.20	87.25	5.50	5.49
1-Anthryl	109.5—110[a,g,i]	87.52	87.25	5.33	5.49

a) Ref. 30. b) W. F. Huber, M. Renoll, A. G. Rossow, and D. T. Mowry, *J. Amer. Chem. Soc.*, **68**, 1109 (1946); L. M. Long and H. R. Henze, *ibid.*, **63**, 1939 (1941); H. C. Brown, Y. Okamoto, and T. Inukai, *ibid.*, **80**, 4964 (1958). c) Y. Okamoto and H. C. Brown, *ibid.*, **79**, 1903 (1957). d) Ref. 12. e) Ref. 9. f) H. Lund, *Ber.*, **70**, 1520 (1937). g) Ref. 10; E. G. E. Hawkins, *J. Chem. Soc.*, **1957**, 385β; M. Martynoff, M. Chauvin, M. Grumez, and N. Lefevre, *Bull. Soc. Chim. Fr.*, **1958**, 164. h) Ng. Ph. Buu-Hoi and P. Cagniant, *Rec. Trav. Chim.*, **62**, 713 (1943). i) H. F. Bassilios, M. Shawky, and A. Y. Salem, *ibid.*, **81**, 679 (1962); *ibid*, **82**, 298 (1963); S. Akiyama and M. Nakagawa, This Bulletin, **33**, 1291 (1960); E. D. Bergmann and D. Katy, *J. Chem. Soc.*, **1958**, 3216.

intersecting point of two absorption curves for the sulfuric acid of the appropriate concentration, at which a ketone was protonated by approximately 50% (see Table 3). After one series of absorption curves had been shifted laterally to its point, the wavelength for the maximum peak of the fully protonated ketone in the visible wavelength region was taken as a reading wavelength. The extinction coefficients in various acids were measured at the above wavelength, chosen on the basis of the shifted curves, and were used to determine pK_{BH^+}.

Results

In the spectrum of each ketone at a higher concentration of acid, we observed a strong absorption band in the visible wavelength region (around 350—600 mμ); it seemed that this might possibly be a *P*-band characteristic of the π-π* transition of polynuclear aromatic compound. This resulted in a large red shift and a change in the intensity of the *P*-band in going from the neutral ketone to the conjugated acid. We took note of the behavior of this terminal *P*-band and determined the pK_{BH^+} values by means of the isosbestic-point method. Stewart and Yates[15] had employed the method of Davis and Geissman[17] to obtain the pK_{BH^+} values of *m*- and *p*-substituted acetophenones. As a preliminary experiment, we chose the 2-naphthyl ketone and followed their procedure to determine the pK_{BH^+} value from their reported wavelength pair. The derived value agreed with theirs. However, the different choice of wavelength pair gave rather different pK_{BH^+} value. As would be anticipated, the spectra of polynuclear aryl ketones in aq. sulfuric acid had some characteristic bands in the UV and visible regions, which were not sufficiently separated. In such spectra the pK_{BH^+} value based on the Davis approach appeared to be less reliable because of the inclusion of a different kind of band.

To take the highest concentration of acid utilized, as a reference of the 100% protonation, would be at best unappropriate in determining the pK_{BH^+} by the isosbestic-point method, because it seems possible that aromatic hydrocarbon is subject to sulfonation and/or deacylation with higher concentrations of acid.[18] A typical example is shown in Fig. 3, which represents the spectra of the 2-fluorenyl methyl ketone. In the range from 47.2 to 89.0% acid, regular lateral changes were observed, while in 93.7% acid the absorption peak moved suddenly toward the lower wavelength. At concentrations higher than 89.0%, the initial yellow solutions were appreciably decolorized as time went on, and the higher the concentration of sulfuric acid, the faster the rate of change. These findings might be ascribed to certain reactions of the aromatic ketone with sulfuric acid, but not to a simple medium effect on the spectra. Similar features were

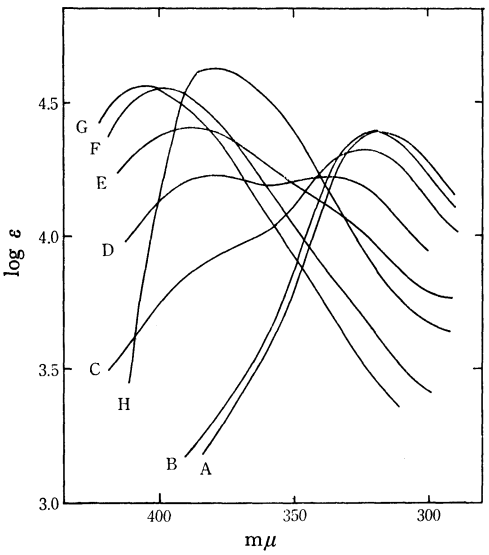

Fig. 3. UV spectra of 2-fluorenyl methyl ketone in various aq. sulfuric acid.
A; 47.2%, B; 52.7%, C; 61.1%, D; 66.8%, E; 71.6% F; 81.1%; G; 89.0%, H; 93.7% aq. H_2SO_4

17) C. T. Davis and T. A. Geissman, *J. Amer. Chem. Soc.*, **76**, 350 7(1954).

18) W. M. Schubert and H. K. Labourette, *ibid.*, **74**, 1829 (1952).

TABLE 2. MEAN pK_{BH^+} VALUES AND SPECTROPHOTOMETRIC DATA IN AQUEOUS H_2SO_4 FOR POLYNUCLEAR ARYL METHYL KETONES

Aryl	H_2SO_4 % for 100% protonation	Isosbestic point			Reading wavelength mμ	Slope	Mean pK_{BH^+}
		mμ	$\varepsilon \times 10^{-3}$	H_2SO_4 % inspection			
4-Biphenylyl	93.7	320	15.3	69.3—71.6	355	0.70	−6·03
2-Fluorenyl	89.0	343	15.3	66.8—69.3	380	0.72	−5.51
2-Naphthyl	93.7	309	9.18	71.6—74.2	333	0.65	−6.25
1-Naphthyl	93.7	352	4.60	71.6—77.7	406.5	0.75	−6.45
2-Phenanthryl	89.0	338.5	11.6	71.6—74.2	373	0.71	−6.22
3-Phenanthryl	89.0	373	6.97	71.6—74.2	420	0.60	−6.08
9-Phenanthryl	93.7	356.5	6.55	71.6—74.2	400	0.76	−6.56
2-Anthryl	89.0	305	31.8	69.3—74.2	320	0.70	−5.92
1-Anthryl	84.8	450	2.80	71.6—74.2	530	0.87	−6.02
Phenyl						(0.73[a])	(−6.36[b])

a) K. Yates and H. Wai *Can. J. Chem.*, **43**, 2131 (1965). b) Ref. 33.

also obtained for several of the other ketones studied. The reference concentrations chosen, at which a ketone would be completely protonated free from unfavorable reactions, are listed in Table 2. Stewart *et al.* were unable to determine the pK_{BH^+} values of 2-fluorenyl and 4-biphenylyl ketones because of their odd-shaped plots.[15] Their failure might be due to the unappropriate choice of 95% acid as the reference of complete protonation.

The plot of the extinction coefficient chosen *vs.* H_0 showed a good sigmoid titration curve, with flat arms in each ketone (see Fig. 4). Although, in the case of some other weak bases, vertical shifts on spectra due to the medium effect of higher concentrations of acid had been observed,[19] such shifts appeared to be small at the higher concentrations of sulfuric acid

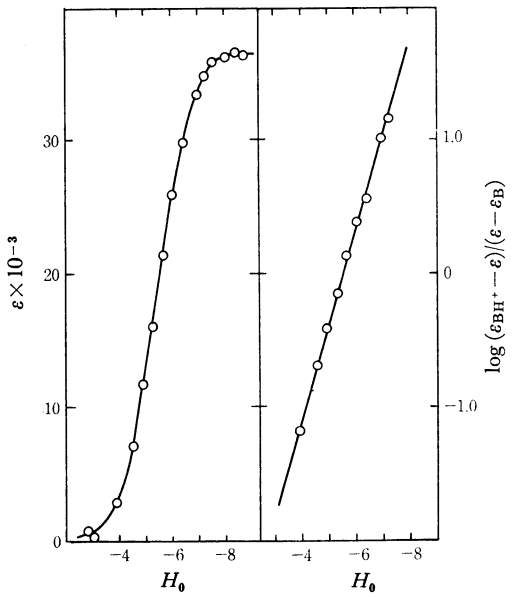

Fig. 4. Extinction coefficient ($\varepsilon \times 10^{-3}$) and $\log(\varepsilon_{BH^+}-\varepsilon)/(\varepsilon-\varepsilon_B)$ plotted against H_0 for 2-fluorenyl methyl ketone.

19) D. C. Noyce and M. J. Jorgenson, *ibid.*, **84**, 4132 (1962); C. C. Greig and C. D. Johnson, *ibid.*, **90**, 6453 (1968).

studied. The pK_{BH^+} value was determined graphically to read the H_0 value, giving $1/2(\varepsilon_{BH^+}+\varepsilon_B)$ on the basis of the sigmoid curve, where ε_{BH^+} and ε_B were the averaged extinction coefficients of completely protonated and unprotonated ketones respectively at the wavelength chosen. The H_0 value of the sulfuric acid, in which the ε value was taken as ε_{BH^+} or ε_B, was at least 2 H_0 units below or above the H_0 corresponding to 50% protonation.

As required by the Hammett-base equation,[20] the logarithms of the ionization ratios must be linear functions of H_0 with intercept equal an to pK_{BH^+}:

$$pK_{BH^+} = H_0 + \log [BH^+]/[B]$$

The other method to determine pK_{BH^+} is to find the intercept by least-square calculations. The ionization ratio, $[B]/[BH^+]$, was calculated by $(\varepsilon_{BH^+}-\varepsilon)/(\varepsilon-\varepsilon_B)$. The extinction coefficients used were the same as those in the former method. The plot thus obtained showed a good linearity in the region corresponding to $\log [B]/[BH^+]=\pm 1.0$ (see Fig. 4). The two methods gave identical pK_{BH^+} values within the limits of experimental uncertainty of 0.02 pK unit. The mean values are listed in Table 2. The values of 1-naphthyl and 1-anthryl ketones were slightly different from the previously-reported data.[21] This is probably due to a different choice of the acid concentration for complete protonation.

However, the values of the obtained slopes were equivalent to 0.72. If polynuclear aryl methyl ketones are to follow precisely the Hammett-base postulate, the slope should be equal to unity. This discrepancy might be mostly caused by the failure of the assumption on activity coefficients.[20] Similar findings have been reported for other non-charged weak bases,

20) M. A. Paul and F. A. Long, *Chem. Rev.*, **57**, 1 (1957); E. M. Arnett, "Progress in Physical Organic Chemistry," Vol. 1, John Wiley & Sons, (1963), p. 223.

21) G. Culbertson and R. Pettit, *J. Amer. Chem. Soc.*, **85**, 741 (1963); A. C. Hopkinson and P. A. H. Wyatt, *J. Chem. Soc., B*, **1967**, 1333.

such as substituted dimethylanilines,[22] benzamides,[23] benzophenones,[24] and diphenyl sulfoxides.[25,26] In view of the fact that the acidity function of the H_0 type depends strongly on the functional base, this result may indicate the possibility that a new acidity function applied to the protonation equilibria of aryl methyl ketones can be constructed.

Discussion

To examine the applicability of our LArSR Eq. (1), it is necessary first of all to evaluate the $\Delta\bar{\sigma}_R^+$ values for polynuclear aryls using the same scale as those for substituted benzenes. The numercial values of $\Delta\bar{\sigma}_R^+$ for substituted benzenes were defined by the subtraction of σ^0 from Brown and Okamoto's σ^+.[1] Since rate data are not available for polynuclear aryls in Brown's σ^+ series,[27] we have chosen the solvolysis of α-arylethyl chlorides in 80% aq. acetone as the secondary reference reaction. From our rate data[29] and Berliner's,[30] the $\Delta\bar{\sigma}_R^+$ values can be derived, using the precise ρ and r values established and, in addition, the σ^0 for polynuclear aryls already reported.[31] The resulting $\Delta\bar{\sigma}_R^+$ parameters, which are measures of the electron-releasing ability of polynuclear aryls by resonance relative to the parent benzene nucleus, are listed in Table 3 together with σ^0.

TABLE 3. σ^0 AND $\Delta\sigma_R^+$ PARAMETERS FOR POLYNUCLEAR ARYLS

Aryl	σ^0 a)	$\Delta\bar{\sigma}_R^+$
Phenyl	0.000	0.000
4-Biphenylyl	0.039	−0.218[d]
2-Fluorenyl	0.001	−0.484[e]
1-Naphthyl	0.048	
2-Naphthyl	0.062	−0.197[d]
2-Phenanthryl	0.131	−0.243[f]
3-Phenanthryl	0.109	−0.301[f]
9-Phenanthryl	0.113	
2-Anthryl	(0.12)[b]	(−0.42)[f]
9-Anthryl	0.004	
2-(9,10-Dihydro)-phenanthryl	(0.06)[c]	(−0.37)[c]

a) Refs. 1 and 31.
b) Data taken from N. Acton and E. Berliner, *J. Amer. Chem. Soc.*, **86**, 3313 (1964).
c) See text.
d) Already reported value in Ref. 1.
e) Data taken from Ref. 29.
f) Data taken from Ref. 30.

In a previous paper,[1] we have mentioned that the literature data on the pK_{BH^+} of *m*- and *p*-substituted acetophenones, which were obtained using Paul's H_0 scale,[20] can be correlated rather excellently by means of Eq. (1). Since the present data are based upon Jorgenson's recent H_0 scale,[14] correction of the published pK_{BH^+} values is required to compare the two series of ketones on the same recent scale.[32] The corrected pK_{BH^+} values for twelve *m*- and *p*-substituted acetophenones can be also correlated satisfactorily by Eq. (1). Using the method of least squares, ρ and r are calculated to be 2.58 and 0.76 respectively. Even when the present polynuclear aryl methyl ketones are included in the least-square calculations, no significant change is observed in ρ, r, and the correlation coefficient (2.57, 0.74, and 0.997 respectively). The total correlation is illustrated in Fig. 5. In order to visualized the degree of the contribution of the resonance component in this protonation, the quantities, $1/\rho \log k/k_0 - \sigma^0$, are plotted against $\Delta\bar{\sigma}_R^+$ in Fig. 6. The correlation line determined by the points of polynuclear aryls is in complete agreement with that of

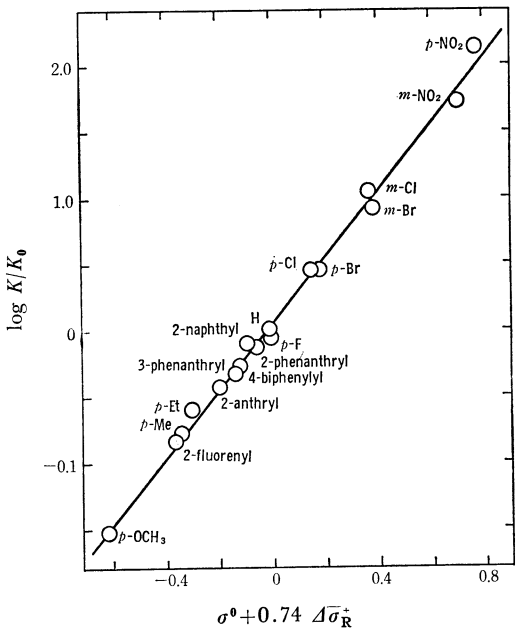

Fig. 5. The LArSR plot for dissociation of conjugate acids of aryl methyl ketones.

22) E. M. Arnett and G. W. Mach, *J. Amer. Chem. Soc.*, **86**, 2671 (1964).
23) K. Yates, J. B. Stevens, and A. R. Katritzky, *Can. J. Chem.*, **42**, 1957 (1964); A. R. Katritzky, A. J. Waring, and K. Yates, *Tetrahedron*, **19**, 465 (1963).
24) T. G. Bonner and J. Phillip, *J. Chem. Soc., B*, **1966**, 650. 1957 (1964).
25) S. Oae, K. Sakai, and N. Kunieda, This Bulletin, **42**, 1964 (1969).
26) K. Yates and H. Wai, *Can. J. Chem.*, **43**, 2131 (1965); P. Haake, R. D. Cook, and G. H. Hurst, *J. Amer. Chem. Soc.*, **89**, 2650 (1967).
27) Brown *et al.* have evaluated σ^+ values for some polynuclear aryls on the basis of the linearity between the solvolysis of aryldimethylcarbinyl chlorides and that of arylmethylcarbinyl chlorides.[28] However, according to our calculations, r of the latter is 1.16 and is slightly different from that of the former being 1.00 by definition. So, their values are not so adequate.
28) H. C. Brown and T. Inukai, *J. Amer. Chem. Soc.*, **83**, 4825 (1961).
29) Y. Yukawa, Y. Tsuno, Y. Kusuyama, and T. Fujii, To be published in this Bulletin.
30) E. Berliner and N. Shieh, *J. Amer. Chem. Soc.*, **79**, 3849 (1957).
31) M. Sawada, Y. Tsuno, and Y. Yukawa, This Bulletin, **45**, 1206 (1972).
32) A convenient method of converting previous pK_{BH^+} to the one in recent scale was described in the literature. On the basis of plotted curve of recent H_0 *vs.* previous H_0, the previous pK_{BH^+} could be directly converted to the recent one. In order to check the applicability of this procedure, pK_{BH^+} for the present ketones with previous scale was converted in the above method. The converted pK_{BH^+} agreed closely with the pK_{BH^+} based on the recent scale within 0.02 pK unit.

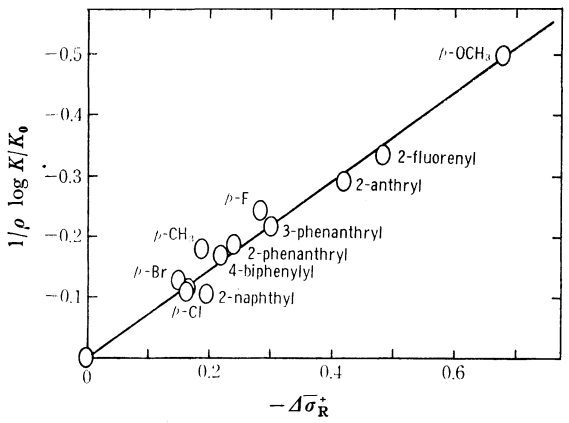

Fig. 6. Resonance contribution in the dissociation of the conjugate acids of aryl methyl ketones.

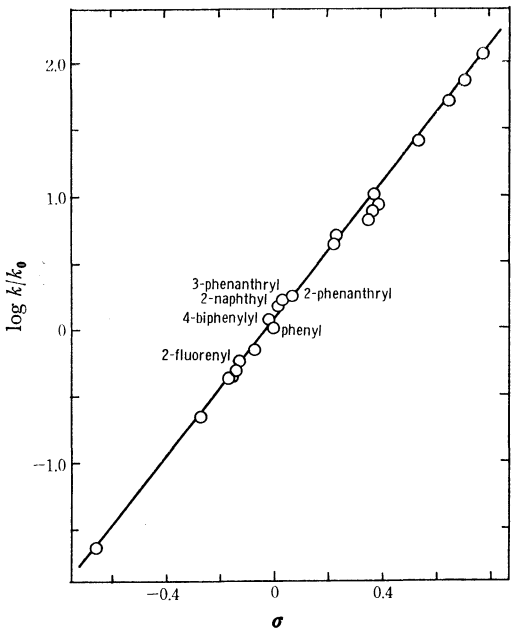

Fig. 7. Hammett plot for the alkaline hydrolysis of ethyl arylcarboxylates in 85% aq. ethanol.

p-substituted benzenes. The identical correlations indicate that the relative basicities of polynuclear aryl methyl ketones can be described by Eq. (1).

Such a treatment of polynuclear aryls has been also applied successfully to our recent data on the alkaline hydrolysis of ethyl arylcarboxylates in 85% aq. EtOH.[34] Since the apparent substituent constants of *para* electron-releasing groups for the above hydrolysis have been analyzed to have a r value of 0.25. The resulting points for polynuclear aryls fall on the line given by the *m*- and *p*-substituents, as is clear in Fig. 7.

It might be expected that the present treatment could be naturally applied to the correlation of reactivity changes for the solvolysis of the $ArCH_2X$ system.[4,5,35] Unfortunately, the definite ρ value and, in consequence, the definite r value can not be estimated for this reaction system.[1,5] However, the relative reactivities for polynuclear aryls in this system can be correlated using the approximate r value of 1.6.

Reactivity data for 2-naphthalene-like polynuclear aryls measured under the same experimental conditions (solvent, temperature, etc.) as those used for *m*- and *p*-substituted benzenes are very scarce in the literature; only the reactions the correlational data of which are summarized in Table 4 are available. The ρ and r values listed are mostly quoted from the results in our previous report.[1] The values of $1/\rho \log k/k_0$ for the 2-, 3-phenanthryl, and 2-anthryl[36] reactivities are plotted against r, as Fig. 8 shows. Satisfactory linear correlations are obtained for the respective unhindered polynuclear aryls. The most important features are that the three straight lines cover a wide variation in r values (0.0—1.6) and that, consequently, the $\Delta\bar{\sigma}_R^+$ values for the respective aryls remain constant in spite of the considerable variations in ρ and r. These facts indicate that Eq. (1) can be generally applicable to correlate polynuclear aryl reactivities as well as substituted benzene reactivities.

A similar linearity appears to be obtained for the 2-(9,10-dihydro)phenanthryl group. There are few reported data other than those for the protodesilylation of aryltrimethylsilane[37] and the solvolysis of α-arylethyl

Table 4. Summary of electrophilic reactivities for unhindered polynuclear aryls measured under the same experimental conditions as those for substituted benzenes

Reaction	ρ	r
Alkaline hydrolysis, $ArCH_2OCOPh$, 70% aq. acetone, 25°C[a]	0.978	0.000
Alkaline hydrolysis, ArCOOEt, 85% aq. EtOH, 25°C[b]	2.59	0.25
pK_{BH^+}, $ArCOCH_3$[c]	2.58	0.76
Protodesilylation, $ArSiMe_3$, aq.-MeOH, $HClO_4$, 50°C[d]	−5.32	0.73
Solvolysis, ArCHClMe, 80% aq. acetone, 45°C[e]	−4.96	1.16
Solvolysis, $ArCH_2OTs$, acetic acid, 40°C[f]	(−3.71)[g]	(1.65)[g]

a) Ref. 31. b) Ref. 34. c) Present study and Ref. 15. d) R. O. C. Norman and R. Taylor, "Electrophilic Substitution in Benzenoid Compounds," Vol. 3, Elsevier (1965), Chap. 9. e) Refs. 29 and 30. f) Ref. 5. g) These values are the total correlational parameters of substituted benzenes and polynuclear aryls. *p*-F derivative is not included in this calculation ($n=11$).

33) K. Yates and B. F. Scott, *Can. J. Chem.*, **41**, 2320 (1963).
34) Y. Yukawa, Y. Tsuno, and M. Sawada, unpublished.
35) B. G. von Leuwen and R. J. Ouellette, *J. Amer. Chem. Soc.*, **90**, 7056 (1968).
36) Data for 2-anthryl reactivities are not so adequate because of experimental difficulties due to low solubilities.
37) Data taken from R. O. C. Norman and R. Taylor, "Electrophilic Substitution in Benzenoid Compounds", Vol. 3, Elsevier, (1965), Chap. 9.

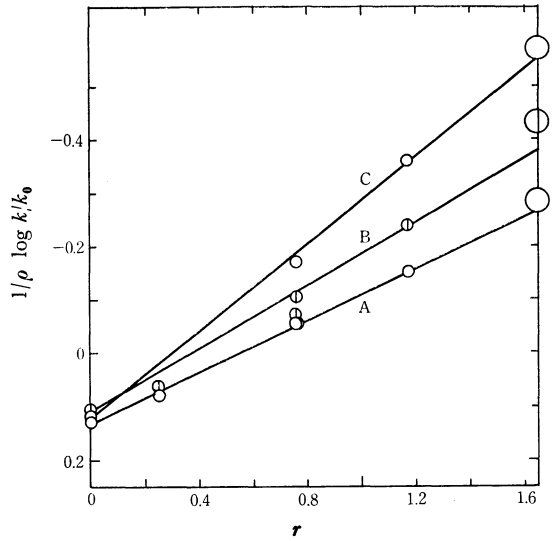

Fig. 8. Linear relationship between apparent substituent constants and r values.
A; 2-phenanthryl, B; 3-phenanthryl, C; 2-anthryl group.

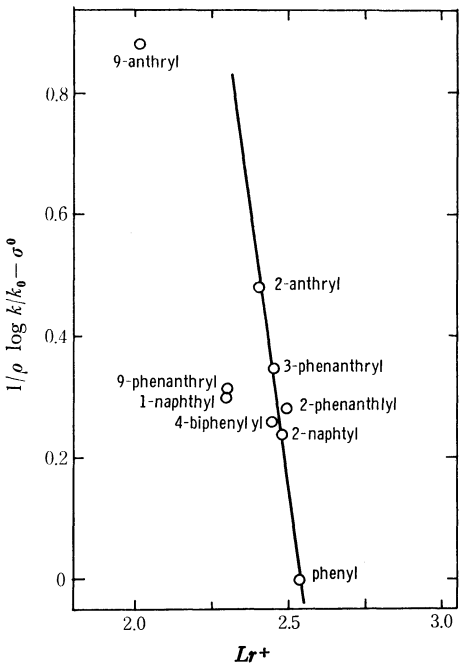

Fig. 9. Linear relationship between $1/\rho \log k/k_0 - \sigma^0$ and Lr^+ for solvolysis of arylmethylcarbinyl chlorides in 80% aqueous acetone at 45°.

chloride.[29] Although additional data should be necessary to examine the numerical value, the $\Delta\bar{\sigma}_R^+$ value for this group can be estimated to be approximately −0.37 on the basis of the above treatment. It is worth noting that the capabilities of biphenyl-type compounds for electron-donation by resonance, $\Delta\bar{\sigma}_R^+$, increase in the order: 4-biphenylyl<2-(9-10-dihydro)phenanthryl<2-fluorenyl. This order can be clearly explained on the basis of the increasing coplanarity between both benzene rings of the biphenyl component.

In the treatment of the reactivity data with theoretical reactivity indices derived from molecular orbital calculations, various authors have directly compared the logarithmus of the relative rates for polynuclear aryl derivatives with various simple MO indices.[4,5,10,38] We consider their approachs to be based on a neglect of the changes in the electronic energy due to the σ-framework effect for the respective polynuclear aryls. We have ourselves successfully separated the substituent effects of substituted benzene reactivities into two terms, the reaction-independent σ-inductive effect and the reaction-variable π-electronic effect.[3,39] On the basis of the same sort of consideration, it may be reasonable to say that the electronic effect on polynuclear aryls also contains the contribution of the σ-inductive effect as well as that of the π-electronic effect. The former may be referable to the electronegativities of the sp^2-carbon σ-framework; it should be characteristic of the reacting position, and also of the size of the polynuclear aromatic ring. On the other hand, the simple MO reactivity index depends on the nature of only the π-electron framework. Therefore, it would be more reasonable to compare a MO index with the quantity that the σ-inductive effect is removed from the observed electronic effect. Such quantities would correspond to $1/\rho \log k/k_0 - \sigma^0$ or residual $r\Delta\bar{\sigma}_R^+$ in our treatment, if the contribution of the σ-inductive effect of polynuclear aryls is independent of the reactions and remain constant.

For the solvolysis of α-arylethyl chlorides,[29,30] a plot of $1/\rho \log k/k_0 - \sigma^0$ against the localization energy, Lr^+,[4] derived from the simple HMO method, is shown in Fig. 9 as a typical example. In practise, 2-naphthalene-like groups show a remarkable linear correlation, and 1-naphthalene-like groups, large deviations. The latter feature is naturally due to peri-hydrogen steric effects. More precisely, the points of 4-biphenylyl and 2-phenanthryl deviate slightly from the correlation line. The minor deviation of the former can presumably be ascribed to the unpreferable Lr^+ value itself, because the different bond order or bond length on the pivot bond in biphenyl is not reflected in the HMO calculations. On the other hand, there is no plausible explanation of the minor deviation of the latter.[40] Of course, the same sorts of features are obtained in such a plot of the present basicity data and other reactivity data on the reactions listed in Table 4. The obtained linear correlation, which indicates a linearity between $\Delta\bar{\sigma}_R^+$ and Lr^+, may be sufficient to indicate a theoretical justification of our analysis of the electronic effect on polynuclear electrophilic reactivities.

38) L. Verbit and E. Berliner, *J. Amer. Chem. Soc.*, **86**, 3307 (1964); N. Acton and E. Berliner, *ibid.*, **86**, 3312 (1964); L. Altschuler and E. Berliner, *ibid.*, **88**, 5937 (1966); M. K. Hoffman and E. Berliner, *J. Org. Chem.*, **35**, 745 (1970).

39) Y. Yukawa and Y. Tsuno, *Mem. Ins. Sci. and Ind. Res., Osaka Univ.*, **23**, 71 (1966).

40) When the localization energy derived from advanced MO method which has been recently proposed by Dewar[41] is adopted for comparison, 2-phenanthryl falls on the correlational line, but 2-anthryl deviates in this plot.

41) M. J. S. Dewar and C. C. Thompson, Jr., *J. Amer. Chem. Soc.*, **87**, 4414 (1965).