# The Substituent Effect. II. Normal Substituent Constants for Polynuclear Aryls from the Hydrolysis of Arylcarbinyl Benzoates

Masami SAWADA, Yuho TSUNO, and Yasuhide YUKAWA

*The Institute of Scientific and Industrial Research, Osaka University, Suita, Osaka*

(Received October 28, 1971)

The rates of the alkaline hydrolysis of 9 polynuclear arylcarbinyl benzoates were measured in 70% (v/v) aqueous acetone at 25°C. The new set of $\sigma^0$ values for polynuclear aryls was obtained, using the $\rho_m$ value established by the hydrolysis of *m*- and *p*-substituted-benzyl benzoates. In the present reaction, it is possible to assume that the peri-hydrogen steric effect is practically absent, bacause *o*-tolyl derivative gives a $\sigma^0$ value comparable with that of *p*-tolyl, and 1-naphthyl with that of 2-naphthyl. The set thus obtained can be successfully described in terms of two components; self-atom polarizability and Streitwieser's inductive index, $\sum r_{ij}^{-1}$.

The correlation of the reactivities of polynuclear aromatic hydrocarbon systems with various molecular orbital reactivity indices is very significant as a connection of the empirical results with the theory.[1] Almost all of the previous comparisons have been based on a neglect of the contribution of substantial inductive effects of polynuclear aryls.[2] In a more exact approach, a consideration of this effect is required. In order to obtain empirically information about the inductive effect, it is useful to introduce the concept of a normal substituent constant,[3] $\sigma^0$, for polynuclear aryls, an insulated aryl polar effect relative to the parent phenyl group.

In our previous papers,[4,5] it has been shown that the LArSR relationship is generally applicable to the electrophilic reactivities of the substituted benzene system:

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

Therefore, it can naturally be expected that the above treatment can be extended without any modification to a correlation of the polynuclear aryl reactivities.[6] In view of the importance of the $\sigma^0$ constants as a standard for the above treatment, it is necessary first of all to examine the normal substituent constants for polynuclear aryls. Thus, we have studied the alkaline hydrolysis of polynuclear arylcarbinyl benzoates in 70% aqueous acetone, $ArCH_2OCOPh$. As has been described in the foregoing paper, it has been established that the hydrolysis of *m*- and *p*-substituted-benzyl benzoates under the same conditions[5] can be correlated by $\sigma^0$, giving a comparatively large $\rho_m$ of 0.981.

The rate constants obtained for polynuclear aryl derivatives are given in Table 1. The $\sigma^0$ constant represents the total electronic effect of substituted phenyl groups arising in response to the perturbation due to the change in the reaction site within the aryl pi-framework; this effect is in turn transmitted to the site without any additional pi-delocalization. This concept of $\sigma^0$ definition may be extended without modification to polynuclear aryl residues as well as to substituted phenyl groups. It is, then, quite reasonable to derive a set of $\sigma^0$ constants for polynuclear aryl moieties from the present insulated system. The apparent substituent constants for polynuclear aryl groups are calculated in the same way as for *m*- and *p*- substituted phenyl groups, using the $\rho_m$ value of 0.981 and $\log k_0 = -2.169$ for the unsubstituted phenyl group. They are given in Table 1. From the uncertainty involved in the $\sigma^0$ values for substituted phenyl groups, the value may be estimated to be reliable to the order of $\pm 0.01$.

TABLE 1. RATE CONSTANTS OF HYDROLYSIS OF ARYLCARBINYL BENZOATES AND $\sigma^0$ VALUES FOR POLYNUCLEAR ARYLS

| Aryl | $10^3 \times k_2$[a] | $\sigma^0$ |
|---|---|---|
| Phenyl | 6.74 | 0.000 |
| *p*-Tolyl | 5.13 | −0.124[b] |
| *o*-Tolyl | 4.97 | |
| 4-Biphenylyl | 7.35 | 0.039[b] |
| 3-Biphenylyl | 6.85 | 0.005 |
| 2-Fluorenyl | 6.78 | 0.001 |
| 1-Naphthyl | 7.54 | 0.048 |
| 2-Naphthyl | 7.74 | 0.062[b] |
| 2-Phenanthryl | 9.12 | 0.131 |
| 3-Phenanthryl | 8.67 | 0.109 |
| 9-Phenanthryl | 8.74 | 0.113 |
| 9-Anthryl | 6.84 | 0.004 |

a) $l \cdot mol^{-1} \cdot sec^{-1}$. b) Ref. 4.

The $\sigma^0$ values obtained are positive for all the polynuclear aryls, that is, all electron-attracting as compared with the reference, the unsubstituted phenyl group. It is worthy of note that the value of $\sigma^0$ appears to change mainly dependent upon the number of rings. Naphthyls give nearly the same values of $\sigma^0$ around 0.05; this is in clear contrast with the results obtained in the other typical insulated reactivities, such as the alkaline hydrolysis of ethyl arylacetates.[7] Similarly, phenanthryl indicates $\sigma^0$ values of the same order of magnitude for three positions.

1) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, New York, (1964).

2) 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); B. G. von Leuwen and R. J. Ouellette, *ibid.*, **90**, 7056 (1968); E. Berliner and N. Shieh, *ibid.*, **79**, 3849 (1957); L. Verbit and E. Berliner, *ibid.*, **86**, 3307 (1964); L. Altschuler and E. Berliner, *ibid.*, **88**, 5937 (1966).

3) R. W. Taft, Jr., *J. Phys. Chem.*, **64**, 1805 (1960).

4) Y. Yukawa, Y. Tsuno, and M. Sawada, This Bulletin, **39**, 2274 (1966); Y. Yukawa and Y. Tsuno, *ibid.*, **32**, 971 (1959).

5) Y. Yukawa, Y. Tsuno, and M. Sawada, This Bulletin, **45**, 1198 (1972).

6) Y. Yukawa, Y. Tsuno, and M. Sawada, *ibid.*, **45**, 1210 (1972).

A very interesting feature in the hydrolysis of arylcarbinyl benzoates is that the 1-naphthyl derivative gives a rate comparable with that of the 2-naphthyl derivative and the *o*-tolyl one comparable with that of the *p*-tolyl one. In the case of the hydrolysis of ethyl arylacetates in aqueous ethanol,[7] the 2-naphthyl group gives an identical apparent $\sigma^0$, while the 1-naphthyl group gives a completely different value (−0.35) from the value in the present reaction. These seems to be a clear difference between the present data and those of the hydrolysis of arylacetic esters. The 1-/2-naphthyl and *o*-/*p*-tolyl rate ratios of insulated reactivities and also the other relevant reactivities are listed in Table 2. The dependency of the ratio on the reaction appears to be nearly the same for both naphthyl and tolyl derivatives, as is to be expected from the geometrical similarity. The different dependency can be reasonably attributed to the structural feature of the present system. As compared with arylacetic esters, the reaction site carbonyl of the arylcarbinyl benzoate is located one oxygen atom far from the aryl moiety.

Berliner *et al.* have recently reported the rates of the alkaline hydrolysis of methyl arylacetates.[8] Figure 1 shows the plots of log $k/k_{(Ph)}$ in aqueous methanol at 25°C against the $\sigma^0$ values. Unhindered aryls apparently fall on or close to a line, whereas the deviations are significant for hindered 1-naphthyl and 9-phenanthryl, and twice as much remarkable for 9-anthryl, which possesses two peri-hydrogens. The disposition can be, of course, attributable to the difference in the locations of the reaction site carbonyls of the two systems. The steric hindrance with peri-hydrogen to the attacking hydroxide ion is significantly operative in the arylacetates, but it should be far less effective in the present system. This is evident from the comparison shown in Table 2.

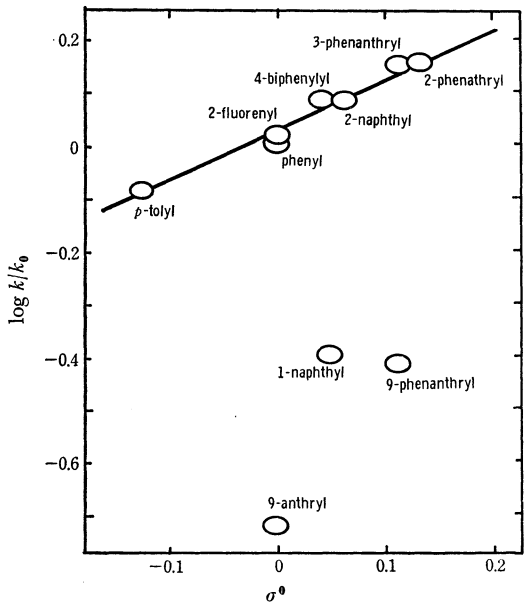


Fig. 1. Plots of the rates of hydrolysis of methyl arylacetates against $\sigma^0$.

It is perhaps not unreasonable to presume that the steric hindrance with peri-hydrogen is effectively absent in the present system. The present set of $\sigma^0$ values for polynuclear aryl groups might be regarded as parameters measuring only electronic effects and practically including no steric effect. As has been mentioned before, the steric effect does not appear to be practically effective in the dissociation of arylacetic or arylpropionic acids; the reactivity ratio of α-/β-naphthyl, 1.05, is comparable with that in the present reaction.[9] Unfortunately, no data for further comparison are available; indeed, even if they will be, the experimental uncertainty would outweigh the minor variation in $\sigma^0$ due to the structural changes of

TABLE 2. RATE RATIOS ($k^1/k^2$ FOR NAPHTHYL AND $k^o/k^p$ FOR TOLYL) OF INSULATED AND OTHER RELEVANT REACTIVITIES

| Reaction | $k^1/k^2$ | $k^o/k^p$ |
|---|---|---|
| Benzyl benzoates+$OH^-$ in 70% aq. acetone | 0.97[a] | 0.97[a] |
| Ethyl phenylacetates+$OH^-$ in 85.4% aq. EtOH | 0.35[b], 0.38[c] | 0.40[d] |
| Ethyl phenylacetates+$OH^-$ in 60% aq. acetone | 0.28[e,f] | 0.34[d,e] |
| Phenylacetic acids, p$K_a$ in water | 1.05[g] | 1.05[h] |
| Benzoic acids, p$K_a$ in water | 2.93[i] | 2.91[j] |
| Ethyl benzoates+$OH^-$ in 85% aq. EtOH | 0.32[k] | 0.27[l] |
| Ethyl benzoates+$OH^-$ in 60% aq. acetone | 0.28[c,m] | 0.29[n] |

a) Present study. b) Y. Ohtsuji, T. Kubo, and E. Imoto, *Nippon Kagaku Zasshi* **80** 1300 (1959). c) J. Fischer, J. Packer, J. Vaughan, A. F. Wilson, and E. Wong, *J. Org. Chem.*, **24**, 155 (1959). d) J. G. Watkinson, W. Watson, and B. L. Yates, *J. Chem. Soc.*, **1963**, 5437. e) Ref. 4. f) Y. Yukawa, Y. Tsuno, and M. Sawada, unpublished results. g) J. F. J. Dippy, S. R. C. Hughes, and J. W. Laxton, *J. Chem. Soc.*, **1954**, 4102. h) J. Frederick, J. F. J. Dippy, and R. H. Lewis, *ibid.*, **1937**, 1008. i) J. F. J. Dippy, S. R. C. Hughes, and J. W. Laxton, *ibid.*, **1954**, 1470. j) J. F. J. Dippy and R. H. Lewis, *ibid.*, **1937**, 1426; J. Frederick, J. F. J. Dippy, and R. H. Lewis, *ibid.*, **1936**, 644. k) M. Adam-Briers, P. J. C. Fierens, and R. H. Martin, *Helv. Chim. Acta*, **38**, 2021 (1955). l) D. P. Evans, J. J. Gordon, and H. B. Watson, *ibid.*, **1937**, 1430. m) J. Packer, J. Vaughan, and E. Wong, *J. Org. Chem.*, **23**, 1373 (1958). n) E. Tommila and C. N. Hinshelwood, *J. Chem. Soc.*, **1938**, 1801; E. Tommila, *Ann. Acad. Sci. Fennicae*, Ser. A57, No. 13, 3 (1941); *Chem. Abstr.*, **38**, 6171[9] (1944).

7) A. Fischer, J. Packer, J. Vaughan, A. F. Wilson, and E. Wong, *J. Org. Chem.*, **24**, 155 (1959); K. Kindler, *Ann.*, **452**, 90 (1927).

8) N. Acton and E. Berliner, *J. Amer. Chem. Soc.*, **86**, 3312 (1964).

9) See Table 2.

polynuclear aromatic hydrocarbons, for the extremely small $\rho$ value of the dissociation.

The noticeable features of the present system, the structurally insulated reactivity with a relatively large $\rho$ value and practically no steric effect with peri-hydrogen, may sufficiently justify our attempt to determine an extended set of $\sigma^0$ values for polynuclear aryl groups on the basis of the present data. The derivative set of $\sigma^0$ values probably consists of idealized substituent constants, especially for hindered aryl moieties. Since the steric effect with peri-hydrogen is generally severe in the existing reactivity data, as may be seen in the hydrolysis of arylacetic esters, the present set of $\sigma^0$ values is not expected to serve widely as a reference for the simple linear free energy relationship, even for $\sigma^0$ reactivity data,

$$\log k/k_{(\mathrm{Ph})} = \rho\sigma^0$$

but instead the set will serve as a reference in estimating the importance of the peri interaction of given systems from the deviations of the hindered derivatives from the $\rho\sigma^0$ correlations.

It appears certain that the set has another important advantage in comparing the empirically derived electronic effects with theory at the various sites in the polynuclear aryl pi-system. As the theory predicts, the electronically most active site in the aryl pi-system being in common the hindered position, a reliable comparison of the electronic effects covering a significant extent of the variation in the theoretical index is possible with the present data, which include the reactivities of hindered sites.

Attempts have been made in vain by various investigators to ascertain the linear free energy relationship for the reactivities of polynuclear aromatic hydrocarbon derivatives, and further attempts have been also made to correlate them with the numerical index from simple MO theory.

As has been described in a previous paper on the analysis of substituent effects in *m*- and *p*-substituted phenyl derivatives, the standard substituent constant can be given by the combination of two intrinsic terms, inductive and pi-electronic effects.[10]

$$\sigma^0 = \sigma_i + \sigma_\pi$$

The $\sigma^0$ constant for polynuclear aryls might be similarly separable into the corresponding two terms. The inductive effect ($\sigma_i$) for polynuclear aryls might be referable to the electronegativities of additional $sp^2$-carbon atoms and might, then, have an electron-attracting character. Therefore, this might depend not only on the size, but also on the position of the site, of the respective aryls. The pi-electronic effect ($\sigma_\pi$) is the effect of only pi-electrons; it should be compared with the reactivity indices obtained by the simple MO theory.

As a theoretical scale measuring the $\sigma_\pi$ effect involved in $\sigma^0$, self-atom polarizability, $\pi_{rr}$, (or free valence) would appear to be the most suitable,[1] for this theoretical index corresponds to the perturbation within the pi-electron framework of the aromatic system without reflecting the exo-conjugation interaction with the reaction site.

On the other hand, there seems to exist no appropriate theoretical indices of the inductive strength of polynuclear aryl groups. Streitwieser and Lawler recently proposed, as the inductive index, the relative quantity, $\Sigma r_{ij}^{-1}$, in which $r_{ij}$ denotes the distance of every carbon atom in the aromatic system from the carbon carrying the reaction site or from the side chain to which the reaction site is attached.[11] The plots of $\sigma^0$ against this set of inductive indices, as is shown in Fig. 2, resulted in a scattered pattern. Un-

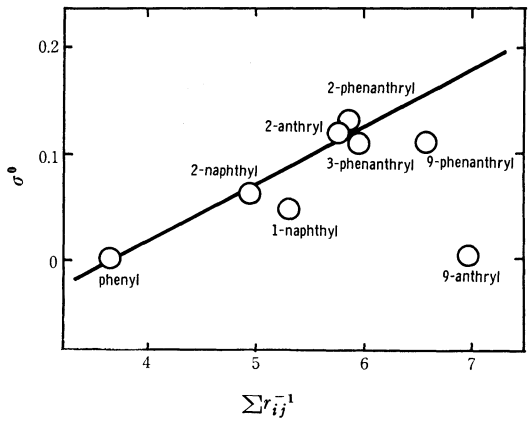


Fig. 2. $\sigma^0$ plotted against Streitwieser's inductive indices.

hindered aryls apparently lie close to a line, whereas a serious deviation is observed here also for hindered 9-anthryl and less significant deviations are noted for 1-naphthyl and 9-phenanthryl groups. Since no steric hindrance with peri-hydrogen is assumed, as has been mentioned above, the disposition of these groups may be attributable mainly to the substantial change in their pi-electronic effect. It is apparent that the groups which fall along the correlation line have $\pi_{rr}$ values of the same magnitude, while, on the other hand, 1-naphthyl and 9-phenanthryl groups have relatively large $\pi_{rr}$ values and fall below the line. The 9-anthryl group, which possesses an extremely high $\pi_{rr}$ value, exhibits a serious deviation. The deviations from the line are apparently proportional to the differences in the corresponding $\pi_{rr}$ values. On least-squares fitting, the $\sigma^0$ values can be correlated with both indices by the equation:

$$\sigma^0 = 0.06\Delta(\Sigma r_{ii}^{-1}) + 1.51\pi_{rr} + 0.06$$

The correlation[12] is rather surprisingly significant; standard deviation=±0.011, and correlation coefficient=0.984.

While this treatment is actually no more than a crude approximation, it suggests the possibility of the empirical separation of the $\sigma^0$ values for polynuclear aryls into inductive polar and pi-electronic effects. Polynuclear aryl groups in $\sigma^0$ reactivities apparently

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

11) A. Streitwieser, Jr., and R. G. Lawler, *J. Amer. Chem. Soc.*, **87**, 5388 (1964); *ibid.*, **85**, 2854 (1963).

12) In this calculation, $\sigma^0$ for 2-anthryl group is included (n=8). The $\sigma^0$ value is estimated to be approximately 0.12 from Ref. 8.

exert an electron-attracting inductive contribution by their intrinsic electronegativity of additional rings, but instead they exert the electron-donative pi-electronic contribution by additional pi-system to a considerable extent. These groups could be treated practically in the range from $\sigma^0$- to $\sigma^+$-type reactivities, as has been done successfully with the +I, −R-type substituents, such as the *p*-phenyl substituent. The treatment of the effect of the polynuclear aryl derivatives on the electrophilic reactivities will be discussed in another paper.[6]

## Experimental

*Materials.* All the polynuclear arylcarbinyl benzoates were prepared by the esterification of benzoyl chloride with the corresponding carbinols in pyridine. The carbinols were obtained from the appropriate ethyl or methyl carboxylates by $LiAlH_4$[13] or $NaBH_4$[14] reduction, except for the 9-anthryl derivative, which was derived from the corresponding aldehyde. All of the esters were purified by fractionation or recrystallization. The physical constants and the elemental analysis data are listed in Table 3.

*Kinetic Measurements.* The rates of the alkaline hydrolyses of all the arylcarbinyl benzoates were determined in a 70% (v/v) aqueous acetone solution at 25°C. The procedure employed for these measurements was generally the same as that described in the previous paper.[5] For less soluble esters, such as 2-fluorenyl, 2- and 3-phenanthryl, and 9-anthryl derivatives, a low initial concentration, 0.01 mol/*l*, was employed, and a 15 m*l* aliquot was utilized in each titration. Since the 9-phenanthryl ester was hardly soluble under these conditions, a more diluted initial concentration, 0.005 mol/*l*, and a larger aliquot, 20 m*l*, was utilized. When the rate determination was carried out for *m*-nitro derivative under these conditions, no concentration effect was observed. As the 1- and 2-anthryl esters were insufficiently soluble even under more diluted conditions, the rate constants of these compounds could not be determined practically.

All runs which involved more than 12 measurements followed the second-order kinetic law, covering reactions up to an extent of 80%. The experimental uncertainty of a run was estimated to be much less than 2%, and the bimolecular rate constants from repeated runs agreed within ±2% or better.

Table 3. Physical constants and analytical data of arylcarbinyl benzoates

| Aryl | Mp or Bp (mmHg) | Carbon | | Hydrogen | |
|---|---|---|---|---|---|
| | | Found | Calcd | Found | Calcd |
| *o*-Tolyl | 144.5(2) | 79.81 | 79.62 | 6.16 | 6.24 |
| 3-Biphenylyl | 58—58.5 | 83.48 | 83.31 | 5.48 | 5.59 |
| 4-Biphenylyl | 61.5—62 | 83.22 | 83.31 | 5.60 | 5.59 |
| 2-Fluorenyl | 98—98.3 | 84.28 | 83.98 | 5.33 | 5.37 |
| 1-Naphthyl | 183.5—184.5(0.15)[a] | 82.24 | 82.42 | 5.28 | 5.38 |
| 2-Naphthyl | 63.5—64[b] | 82.47 | 82.42 | 5.29 | 5.38 |
| 2-Phenanthryl | 95.5—96 | 84.50 | 84.59 | 4.98 | 5.16 |
| 3-Phenanthryl | 86.5 | 85.02 | 84.59 | 4.64 | 5.16 |
| 9-Phenanthryl | 125—126 | 84.80 | 84.59 | 4.51 | 5.16 |
| 9-Anthryl | 93.5—94 | 84.37 | 84.59 | 5.27 | 5.16 |

a) C. W. Hyde and L. Young, *Biochem. J.*, **107**, 519 (1968).
b) R. N. Chakravarti and R. N. Adhya, *Bull. Calcutta School Trop. Med.*, **6** No. 4, 161 (1958); *Chem. Abstr.*, **54**, 2282b (1960).

13) W. G. Brown, "Organic Reactions", Vol. 6, John Wiley and Sons, New York, (1942), Chap. 10, p. 469.

14) S. W. Chaikin and W. G. Brown, *J. Amer. Chem. Soc.*, **71**, 122 (1949).