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# PERI EFFECTS I. IONIZATION CONSTANTS OF 8-SUBSTITUTED 1-NAPHTHOIC ACIDS

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In our earlier investigation (1) on the ortho effects it was found that although steric hindrance itself has a big influence on the acidities of aromatic carboxylic acids, Hammett's $\rho$ values are quite insensitive to the steric hindrance at least in the ionizations of these acids and therefore $\rho$ values become a useful means in the study of ortho effects. Actually this view was utilized to show that in the ionizations of substituted benzoic acids direct dipolar field effect of ortho substituents is comparable in direction and magnitude to the electronic effects of the corresponding para substituents (1,2). It was also shown that introduction of a methyl group into either 3- or 6-position of 2-substituted benzoic acids produces another ortho effects which is again as large as the electronic effects of the corresponding para substituents in its magnitude but opposite in its direction, and the results can best be explained by change in direction of the dipole (2-substituent) toward reaction center presumably due to the buttressing effect of the 3- or 6-methyl group (1,2).

The above situation prompted us to investigate ionizations of a series of 8-substituted 1-naphthoic acids because peri substituents would influence the ionization in a more discriminating way than does ortho substituents.

Table I presents apparent pKa values of a series of 8-substituted 1-naphthoic acids in 50 % (vol.) aqueous ethanol together with the O-H and C=O stretching frequencies of these acids in carbon tetrachloride. In Figure 1 are plotted pKa for these acids against $\sigma_p$ values, the $\rho$ value being almost zero (slightly negative) for these compounds (-0.055 by least square method).

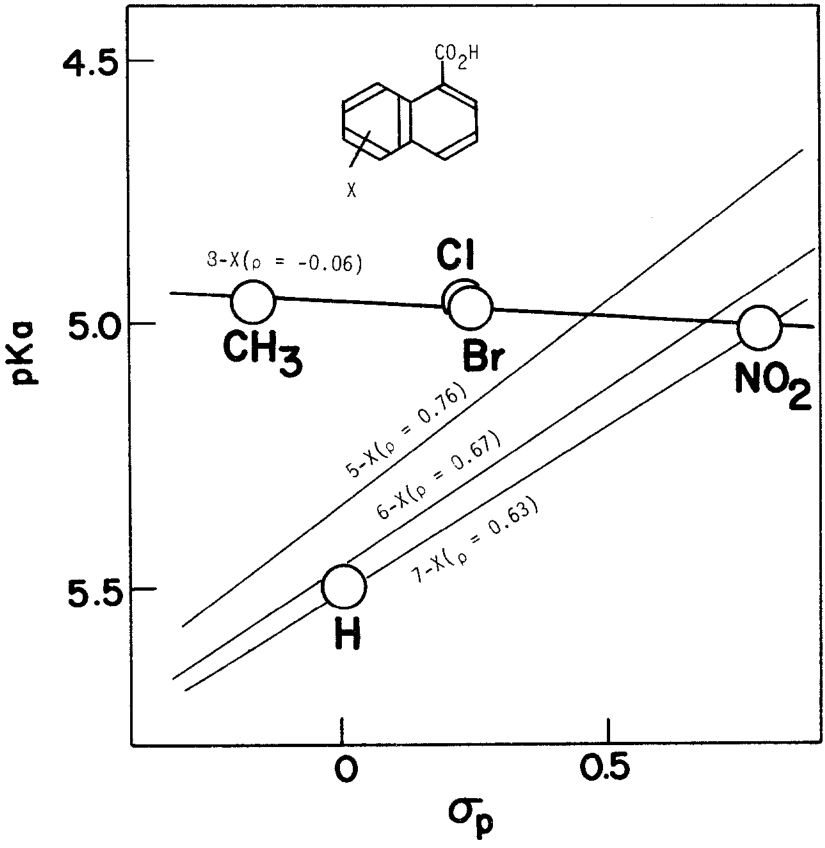

Fig. 1

Plots of pKa for 8-Substituted-1-Naphthoic Acids versus $\sigma_p$. Dotted Lines Show the Results of the Same Plots for 5-, 6- and 7-Substituted-1-Naphthoic Acids.

TABLE I

Ionization Constants and O-H and C=O Stretching

Frequencies of 8-Substituted-1-Naphthoic Acids

| 8-Substituents | Apparent* pKa | $\nu_{O-H}(cm^{-1})$** | $\nu_{C=O}(cm^{-1})$** |
|---|---|---|---|
| H | 5.50*** | 3542 | 1738 |
| $NO_2$ | 5.01 | 3530 | 1751 |
| Br | 4.97 | 3527 | 1752 |
| Cl | 4.96 | 3527 | 1753 |
| $CH_3$ | 4.96 | 3525 | 1750 |

* Potentiometric titration with glass and calomel electrodes without correction for junction potential. Measured in 50 % (vol.) aq. EtOH at 25.0°C. Accurate within $\pm 0.02$.

** 0.002 M in $CCl_4$ at 23°. Accurate within $\pm 2$ $cm^{-1}$.

*** 5.54 by Dewar and Grisdale (3).

The results appear very interesting. Peri substituents behave as if there were no electronic effects on the acidity, while effects of substituents at 5-, 6- or 7- positions are known to be quite normal, their $\rho$ values being estimable from the data of Dewar and Grisdale (3) in the same solvent to be 0.764, 0.670 and 0.634, respectively, by least square method. Another point of interest is that while $\rho$ value for the ionization of benzoic acids increases when one moves substituents from para (1.00 in $H_2O$) to the ortho position (1.91 in $H_2O$), the corresponding approach of the substituents to the reaction center in the present case causes lowering of the $\rho$ values from 0.63-0.76 (in 50 % aq. EtOH) at 5-, 6- or 7- positions to almost zero (in 50 % aq. EtOH) at peri position. This striking and peculiar effects of peri substituents cannot be explained at least in terms of steric strains in the molecules, steric inhibition of resonance or steric inhibition to solvation. Any steric effects would have the influence in the same direction for the two systems, and this is not the case.

Anormaly of peri substituents can also be observed with the IR spectroscopic data. With one exception of unsubstituted acid, all compounds absorb at almost constant frequency in contrast with the large variation in the case of substituted benzoic acids. The situation is very similar to that of ionization.

Probably the present results can be explained by direct dipolar field effect of dipoles of the peri substituents. Direction of the dipoles toward reaction center would be opposite to that in the case of ortho substituted benzoic acids and therefore the field effect would cancel the usual electronic effects of the substituents to result in a much lowering of the $\rho$ values compared to those for 5-, 6- or 7-substituted acids.

The enhanced acidity (about 0.5 pKa unit) of peri substituted acids over the unsubstituted one is certainly due to the steric hindrance. Similar acid strengthening effect of steric origin is observed with ortho substituents.

8-Hydroxy-1-naphthoic acid becomes very strong (pKa = 4.19) owing to the intramolecular hydrogen bonding, and 8-formyl-1-naphthoic acid is very weak (pKa = 8.27) due to the hemiacetal structure of this acid. 8-Methoxy-1-naphthoic acid (pKa = 5.43) also becomes considerably weaker than others presumably because of the unsymmetrical structure of the substituent. All spectroscopic data and discussion on these three acids will be presented elsewhere.

## REFERENCES

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