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A Simple HMO Treatment of the Acidity of Substituted Tropolones

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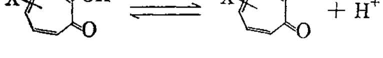
It is known that the dissociation constants of tropolone derivatives which have the phenolic hydroxyl group are linearly correlated with Hammett's substituent constants obtained in benzenoid compounds.[1] In an application of the Hammett equation to tropolone derivatives, we found that the π-electron densities of oxygen atoms and neighboring carbon atoms are correlated with substituent constants.[2]

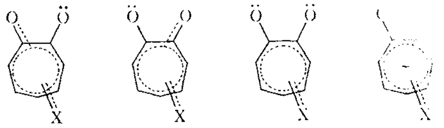
As a molecular orbital treatment, we examined the energy changes in dissociation of some tropolone derivatives in terms of localization energies. This was on the assumption that the dissociation constants of this type of derivatives are directly proportional to the π-electron energy differences between the unionized and the ionized tropolones.

Calculation Method

The simple Hückel molecular orbital method was used for all calculations as in previously reported.[2]

In the molecular orbital treatment of the energy changes in dissociation equilibrium of tropolones (see below), the following localized and delocalized models are assumed. In the dissociation of phenols, the degree of delocalization by the interaction of phenyl group with OH group is smaller than that of phenyl group with O^- group.[3] Similarly, in tropolone derivatives, it is thought that tropolonate anions are more delocalized than tropolones themselves. The localized tropolones can be represented by states [A] or [B] in Fig. 1. However, state [C] was chosen as the model for calculations, since the two oxygen atoms are nearly equivalent in reactivity and the calculation might be simplified. Model [D] was used as the delocalized tropolonate anions. On these assumptions, the energies for the unionized tropolones $(E_\pi)_{AH_i}$ and for the ionized tropolonate anions $(E_\pi)_{A^-_i}$ are calculated, and the energy changes $(\Delta E_\pi)_i$ for dissociation are given by the equation[4]





[A] [B] [C] [D]

Fig. 1. The localized models for tropolones and the delocalized model for tropolonate anions.

$$(\Delta E_\pi)_i = (E_\pi)_{A^-_i} - (E_\pi)_{AH_i}$$
$$= 2\alpha + (\Delta M_i)\beta \qquad (1)$$

As the integral parameters for the oxygen atoms and the adjacent carbon atoms, the parameters we obtained previously are used,[2] and Fueno's parameters[3] are applied to all substituents.

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[1] N. Yui, *Sci. Repts. Tohoku Univ.*, I, **40**, 102 (1956); *Chem. Abstr.*, **51**, 17354^c (1957); *Sci. Repts. Tohoku Univ.*, I, **40**, 114 (1956); *Chem. Abstr.*, **51**, 17354^e (1957).

[2] K. Imafuku and H. Matsumura, This Bulletin, **42**, 1772 (1969).

[3] T. Fueno, T. Okuyama and J. Furukawa, *ibid.*, **39**, 569 (1966).

Results and Discussion

The ΔM_i terms in the energy changes in dissociation of tropolone derivatives are listed in Table 1, together with their dissociation constants. When the values of ΔM_i are plotted against pK_i (Fig. 2), irrespective of many assumptions, an approximately linear relation holds according to the electron-releasing and the electron-attracting forces of substituents. The relationship between pK_i and ΔM_i is represented by the equation

$$pK_i = 7.77 - 2.87\Delta M_i \qquad (2)$$

The calculated pK_i values obtained by this equation are shown with the observed values in Table 1. The correlation coefficient between the observed and the calculated values is 0.98. Thus, the dissociation constants of other tropolone derivatives with substituents in the 4- and 5-positions can be estimated by molecular orbital calculation and equation (2).

TABLE 1. ENERGY CHANGES IN DISSOCIATION AND pK VALUES

No.	Substituent	ΔM_i	pK_i calcd	pK_i obsd
1	5-OCH_3	0.0610	7.59	7.75
2	5-CH_3	0.1550	7.33	7.32
3	4-CH_3	0.1658	7.29	7.26
4	H	0.2530	7.04	6.92
5	5-Cl	0.5232	6.24	—
6	5-Br	0.5486	6.20	6.32
7	5-NO_2	0.8160	5.43	—

No. of substituents are related to those in Fig. 2.

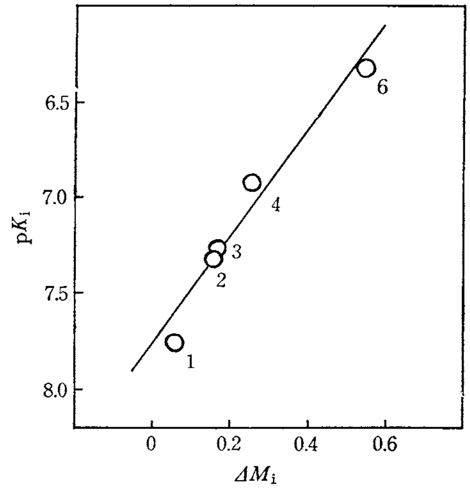

Fig. 2. Correlation of pK_i with ΔM_i.

ΔM_i is correlated with Hammett's substituent constants. This shows that the Hammett relationship is applicable to tropolone derivatives, together with the linearity of the static π-electron densities of oxygen atoms and the neighboring carbon atoms with σ-constants.[2]

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[4] A. Streitwieser, Jr., *Tetrahedron Lett.*, **1960**, 23.