Bond Localization and the Hyperconjugative Effect in the Aromatic Carbonium Ions. II[1]*. Electronic Structures of the Carbonium Ions of Isomeric Xylenes*

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Concerning the basic character of unsaturated hydrocarbons, there are several theoretical investigations[2-7] which have their theoretical standpoints on the localization of the C-H_2 bond of their carbonium ions. There are no reasons, however, for fixing the electronic structure of carbonium ions to only the bond localization one; in general, hyperconjugation of H_2 quasi-atom should also be taken into account. In this paper, the need for introduction of hyperconjugation will be revealed for protonated compounds of isomeric xylenes on the basis of the experimental basicity constants[8].

Dependence of Basicity of Isomeric Hydrocarbons on the π-Electron Energies of their Carbonium Ions

Gold and Tye[2], and also Heilbronner and Simonetta[3] have shown that the equilibrium constant K for carbonium ion formation is expressed as

$$-\boldsymbol{R}T \ln K = E_{BH^+} - E_B + \text{constant} \qquad (1)$$

where E_{BH^+} and E_B are π-electron energies of the aromatic carbonium ion, BH^+, and of the parent base, B, respectively. From Eq. 1, the following equation for the ratio of two K's is obtained:

$$K^I/K^{II} = \exp(-A/\boldsymbol{R}T) \qquad (2)$$

where

$$A = (E^I_{BH^+} - E^{II}_{BH^+}) - (E^I_B - E^{II}_B) \qquad (3)$$

Here superscripts I and II refer to either of the two isomeric types of a particular hydrocarbon.

In the case of xylene isomers, $E^I_B - E^{II}_B$ will be estimated from the empirical hyperconjugation energies obtained by Coulson and Crawford[9]. They have indicated that the empirical hyperconjugation energies per methyl group are 1.48, 1.39 and 1.27 kcal./mol. for *m*-, *p*- and *o*-xylenes, respectively. This shows that *m*-xylene is more stable than *p*-xylene by 0.18 kcal./mol., and *o*-xylene is less stable than *p*-xylene by 0.24 kcal./mol.

Now, from the evaluation of π-electron energies of protonated compounds, the basic strengths of *m*- and *o*-xylenes relative to that of *p*-xylene will be estimated by the use of Eqs. 2 and 3.

Consideration of Basicity of Isomeric Xylenes from the Standpoint of Bond Localization Model of their Carbonium Ions

There are several available points of proton attack in each isomer, and the position of highest proton affininity will be determined as that which makes the π-electron energy of the carbonium ion minimum. Now it will be indicated in the following discussion that only by the bond localization hypothesis the basic behaviors of isomeric xylenes can not be understandable. π-Electron energies of carbonium ions necessary for these considerations are calculated for all possible models with respect to the positions of proton attack on the basis of the bond localization hypothesis, using the semi-empirical LCAO MO method and solving numerically the secular equations constructed by the usual variational method. Several assumptions adopted in these calculations are as follows:

(1) the overlaps between the nearest neighboring atomic orbitals are included; (2) the resonance integral including overlap is proportional to the corresponding

1) Part I, T. Morita, This Bulletin, **31**, 322 (1958).
2) V. Gold and F. L. Tye, *J. Chem. Soc.*, **1952**, 2184.
3) E. Heilbronner and M. Simonetta, *Helv. Chim. Acta*, **35**, 1049 (1952).
4) E. L. Mackor, G. Dallinga, J. H. Kruizinga and A. Hofstra, *Rec. trav. chim.*, **75**, 836 (1956).
5) G. Dallinga, A. A. V. Stuart, P. J. Smit and E. L. Mackor, *Z. Elektrochem.*, **61**, 1019 (1957).
6) E. L. Mackor, A. Hofstra and J. H. van der Waals, *Trans. Faraday Soc.*, **54**, 66 (1958).
7) E. L. Mackor, A. Hofstra and J. H. van der Waals, ibid., **54**, 186 (1958).
8) M. Kilpatrick and F. E. Luborsky, *J. Am. Chem. Soc.*, **75**, 577 (1953).
9) C. A. Coulson and V. A. Crawford, *J. Chem. Soc.*, **1953**, 2052.

overlap integral: $\beta_{C\text{-}H_2}=\beta_{C\text{-}H_3}=2.19\beta$ and $\beta_{C(ring)\text{-}C(methyl)}=0.8\beta$, where $\beta_{C\text{-}H_2}$ is the resonance integral between H_2 quasi-atom and the ring carbon atom connecting with it, $\beta_{C\text{-}H_3}$ is that between H_3 quasi-atom and carbon atom in the methyl group, $\beta_{C(ring)\text{-}C(methyl)}$ is that between the ring- and the methyl- carbon atoms, and β is that between the neighboring atoms in the benzene molecule; the other resonance integrals are taken to be β; (3) the Coulomb integral of H_2 or H_3 quasi-atom is taken as $\alpha_{H_2}=\alpha_{H_3}=\alpha-0.3\beta$, and that of the carbon atom next to H_2- or H_3-group is taken as $\alpha_{C(-H_2)}=\alpha_{C(-H_3)}=\alpha-0.1\beta$, where α is the Coulomb integral of a carbon atom of benzene molecule; the other Coulomb integrals are taken to be α.

Computational results are shown in Table I and in Fig. 1. Charge distributions of parent bases calculated by Crawford[10] are 1.0093, 1.0081 and 0.9995 at the positions 2, 4 and 5 in *m*-xylene (1,3-dimethylbenzene) and 1.0044 and 1.0035 at the positions 3 and 4 in *o*-xylene (1,2-dimethylbenzene), respectively. Inspection of these charge distributions predict the order of proton acceptance. Between this order of proton affinity and stabilities of protonated compounds (Table I), a parallel relation exists. This correlation agrees with experimental reactivity of electrophilic substitution except for the position 2 of *m*-xylene, which may be supposed to have low proton affinity because of the steric effect of two neighboring methyl groups, although it is theoretically the most active toward a proton. From their hydrogen isotope exchange reaction studies, Lauer et al.[11] have indicated that relative reactivity of the position 2 to 4 of *m*-xylene is 0.58 : 1.0. We must take such a fact into account. In *m*-xylene, numbers of position of proton attack will be 2.58 and the energy of its

TABLE I. π-ELECTRON ENERGIES OF THE CARBONIUM IONS OF XYLENE ISOMERS (BOND LOCALIZATION MODELS)

Carbonium ions	Models	π-Electron energies (units of $-\beta$)
m-Xylene-	I	−11.4819
	I′	−11.5342
	I″	−11.4444
p-Xylene-	II	−11.4905
o-Xylene-	III	−11.4914
	III′	−11.4806

10) V. A. Crawford, ibid., **1953**, 2058.
11) W. M. Lauer, G. W. Matson and G. Stedman, *J. Am. Chem. Soc.*, **80**, 6437 (1958); see also, E. L. Mackor, P. J. Smit and J. H. van der Waals, *Trans. Faraday Soc.*, **53**, 1309 (1957).

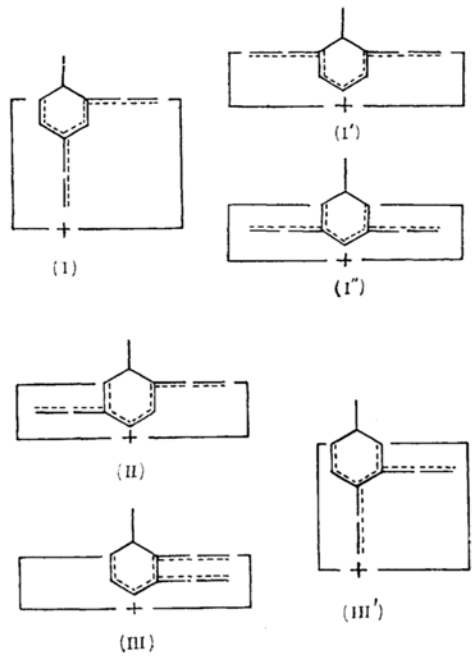

Fig. 1. Models of xylene carbonium ions.
I, I′ and I″: *m*-xylene carbonium ion
II : *p*-xylene carbonium ion
III, III′ : *o*-xylene carbonium ion

probable carbonium ion will be weighted mean of energies of Models I and I′. For *o*-xylene carbonium ion, the stabilities of Models III and III′ are identical, being in agreement with experimental reactivity, halogenation or nitration of *o*-xylene. We assume the energy of protonated *o*-xylene to be the mean of Models III and III′.

The ratio of basicity constants of *m*- and *o*-xylenes to that of *p*-xylene is estimated to be respectively 26 and 1.1 at 20°C from the measurement on the mixtures of these substances with anhydrous hydrogen fluoride[8]. In comparing these values experimentally observed with those theoretically calculated, it must be noticed that the number (Z) of positions of the highest proton affinity of *m*-, *o*- and *p*-xylenes are different from one another. For *m*-xylene, from our treatment mentioned above, $Z=2.58$. For *o*- and *p*-xylenes $Z=4$. Taking these Z values into consideration, the experimentally observed ratio of the reduced basicity constant[6] of *m*-xylene to that of *p*-xylene becomes 40.3 instead of 26, which is in disagreement with the theoretically calculated value, 1.0, using Eqs. 2 and 3. In the case of *o*-xylene, the experimental and theoretical values of K^{III}/K^{II} are 1.1 and 1.0, respectively, so the agreement between these two values

is satisfactory[12]. Thus, basic behavior of isomeric xylenes is not understood by the bond localization hypothesis alone. It is natural to take hyperconjugation further into consideration, as is seen in the following section.

π-Electron Structures of Isomeric Xylene Carbonium Ions

In the following, as an example, the relative basicity of *m*-xylene compared to *p*-xylene will be discussed. From Eq. 3, A can be written as follows:

$$A=\{E^{I}_{BH^+}-(E^{I,0}_{BH^+}+0.18)\}-\{E^{II}_{BH^+}-E^{II,0}_{BH^+}\}-\{E^{I}_{B}-E^{II}_{B}\} \quad (4)$$

where, $E^{I}_{BH^+}$ is the π-electron energy for the actual state of the *m*-xylene carbonium ion, $E^{II}_{BH^+}$ is the similar quantity for the *p*-xylene carbonium ion; $E^{I,0}_{BH^+}$ and $E^{II,0}_{BH^+}$ are the π-electron energies for the bond localization models of protonated *m*- and *p*-xylenes, respectively; E^{I}_{B} and E^{II}_{B} are the π-electron energies of *m*- and *p*-xylenes, respectively; the numerical value 0.18 in the right hand side of Eq. 4 is necessary for making $(E^{I,0}_{BH^+}+0.18)=E^{II,0}_{BH^+}$. This value, which is expressed in the unit of kcal./mol. by the use of $\beta=-60$kcal./mol.[12], estimated by comparing the weighted mean of π-electron energies of types I and I′ for protonated *m*-xylene with the energy of type II for protonated *p*-xylene. Taking $E^{I}_{B}-E^{II}_{B}=0.18$ kcal./mol., Eq. 4 becomes as follows:

$$A=-x+c \quad (5)$$

where

$$-x=E^{I}_{BH^+}-E^{I,0}_{BH^+} \quad (6)$$

and

$$-c=E^{II}_{BH^+}-E^{II,0}_{BH^+} \quad (7)$$

The quantities x and c indicate respectively the stabilization energies through hyperconjugation of H_2 quasi-atom in the actual states of *m*- and *p*-xylene carbonium ions compared with their bond localization models. Experiments show $K^{I}/K^{II}=40.3$[13] at 20°C, consequently from Eqs. 2, 3 and 5, we obtain

$$x=c+8.2 \quad (8)$$

Eq. 8 shows that, if the difference of hyperconjugation energies between protonated *m*- and *p*-xylenes is about eight kcal./mol., the experimentally observed basic behavior of *m*- and *p*-xylenes is understandable. A similar consideration suggests that no change in the hyperconjugation energies exists between *o*- and *p*-xylene carbonium ions. Indeed,

$$x=c+0.09$$

Here it will be noticed that the hyperconjugation energy of protonated *m*-xylene is the weighted mean of hyperconjugation energies by the methylene group for models I and I′, and that of protonated *o*-xylene is the weighted mean for the models III and III′. The value, 8.2 kcal./mol., of change in hyperconjugation energies between protonated *m*- and *p*-xylenes seems too great at first sight. This large difference may not be unreasonable, however, since the substances in question are the so-called "strongly hyperconjugated" systems[14,15].

Discussion

Brown and Brady[16] have shown that change in solvolysis rates between meta- and para-methyl substituted phenyldimethylcarbinyl chloride is explained reasonably, though qualitatively, in terms of valence bond structures. On the stabilities of the protonated isomeric xylenes also, treatment by means of valence bond structures may not be overlooked, and will be tried in the following way.

Model I of protonated *m*-xylene can resonate among three A (AI, AI_1 and AI_2), one B and one C structures (Fig. 2), according to Brown and Brady[16]. However, additional hyperconjugated structures by the two methyl substituents should be taken into account, such as four D, six E, one F, one G and five H structures. The number of resonance structures is altogether twenty-two (Fig. 2). For the models I′, I″, II, III and III′ similar types of resonance structures are considered. Numbers of resonance structures belonging to these types are indicated in Table II. Inspection of Table II suggests that model I is as stable as model I′, model I″ being less stable, and model III will possibly be more stable than model III′. Model I will probably be stable to almost

12) In these calculations, the unit of energy is expressed in kcal./mol. by the use of $\beta=-60$ kcal./mol. See, C. C. J. Roothan and R. S. Mulliken, *J. Chem. Phys.*, **16**, 118 (1948).

13) Here K means the reduced basicity constant.

14) N. Muller and R. S. Mulliken, *J. Am. Chem. Soc.*, **80**, 3489 (1958).

15) N. Muller, L. W. Pickett and R. S. Mulliken, ibid., **76**, 4770 (1954).

16) H. C. Brown and J. D. Brady, ibid., **74**, 3570 (1952).

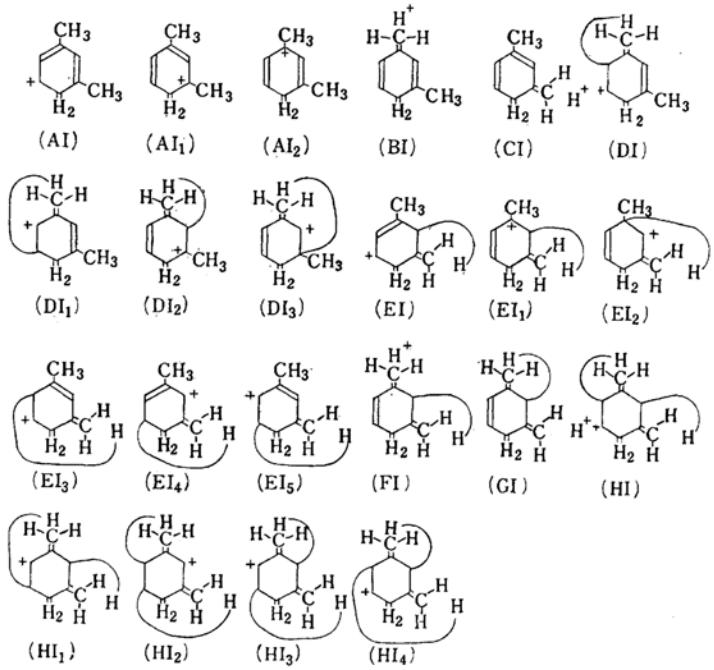

Fig. 2. Valence bond structures of model I of protonated *m*-xylene.

TABLE II. NUMBERS OF THE VALENCE BOND STRUCTURES

Models	A	B	C	D	E	F	G	H	Total
I	3	1	1	4	6	1	1	5	22
I′	3	1	1	5	6	2	2	3	23
I″	3	0	0	0	0	0	0	5	8
II	3	0	1	4	4	1	1	5	19
III	3	0	1	4	7	2	2	3	22
III′	3	1	0	4	4	1	1	2	12

the same extent as model III, which will be more stable than model II. These results are partly in disagreement with experiments. It may be said, however, that the difference of the stability of protonated compounds of xylene isomers will be attributable to that of numbers of hyperconjugation structures by the methyl group, irrespective of hyperconjugation or localization of the methylene.

From their electron spin resonance measurements of isomeric xylene negative ions, Tuttle, Jr. and Weissman[17] have indicated that methyl groups show hyperconjugation in a different manner among these substances and are more hyperconjugated in the *m*-xylene than in the *o*- and *p*-xylene negative ions. As has been hitherto accepted, the hyperconjugation phenomenon seems not so simple but complicated. At all events, it may be likely that the manner in which hyperconjugation occurs depends greatly on the environment of a methyl group.

17) T. R. Tuttle, Jr. and S. I. Weissman, ibid., **80**, 5342 (1958).

Summary

By means of the LCAO MO method, the π-electron energies of xylene carbonium ions are calculated, for all possible models, with respect to the positions of proton attack, on the basis of the bond localization hypothesis. It is indicated that the explanation of the basic behaviors of isomeric xylenes is impossible merely by the bond localization theory of their carbonium ions, and hyperconjugation should be taken into account.

It is indicated that, when the difference of hyperconjugation energies between protonated *m*- and *p*-xylene is about eight kcal./mol., the experimentally observed basic behavior of *m*- and *p*-xylenes is understandable.

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