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An Interpretation of Mass Spectra of Disubstituted Benzenes by Simple LCAO MO Calculation. I

Susumu TAJIMA, Nobuhide WASADA, and Toshikazu TSUCHIYA
Government Chemical Industrial Research Institute, Tokyo, Honmachi, Shibuya-ku, Tokyo

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A part of the mass spectra for derivatives of aniline and anisole was interpreted using the results of MO calculation. Compounds studied were: aniline derivatives: *o*-, *m*-, and *p*-compounds of anisidine, aminophenol, chloroaniline, nitroaniline, aminobenzoic acid, and aminoacetophenone; and anisole derivatives: *o*-, *m*-, and *p*-compounds of anisidine, methoxyphenol, chloroanisole, nitroanisole, methoxybenzoic acid, and methoxybenzaldehyde. The intensities of certain fragment ions in the mass spectra of these compounds were compared with the results of simple LCAO MO calculation for these compounds. A simple relation was found between the intensity and the partial bond order for a frontier electron of the bond ruptured.

Other than the well known quasi-equilibrium theory[1] (Q.E.T.), a method for theoretical interpretation of mass spectra of larger organic compounds has been reported by Hirota *et al.*[2,3] In this method, it is assumed that the scission probability of each of the skeletal bonds of the parent ion is proportional to the positive charge density of the highest occupied molecular orbital localized at the bond. Though the method has been applied successfully to paraffins[2] including cycloparaffins,[3] the basis for the interpretation has not yet been scrutinized as thoroughly as has been done for Q.E.T. The fundamental idea of Q.E.T. is generally accepted now, and the mass spectra of various aliphatic compounds[4-7] have been interpreted by the theory. The calculations involved, however, are rather tedious even for such a simple compound as propane. Nounou[8] has applied Q.E.T. to large aromatic compounds and successfully interpreted the mass spectra of substituted phenanthrenes. Recently, Dougherty[9] reported an interpretation of the decomposition of parent ions caused by electron impact with the perturbation MO method. Difference of mass spectra between aromatic isomers has been elucidated by Tatematsu *et al.*[10] on the basis of the difference of radical electron density, calculated by simple LCAO MO method, on the atoms in the isomers.

The purpose of the present paper is to find an approach to interpret the mass spectra of some aromatic compounds and to clarify the fragmentation mechanism by the results of simple LCAO MO calculation. In the procedure, various factors such as electron density, bond order *etc.* have been calculated by the method on a series of disubstituted benzenes and were compared with the intensity of certain fragment ions in their mass spectra.

Experimental

Mass spectra were obtained with a CEC 21—103C mass spectrometer. Conditions of measurement were: magnetic field, 4100 gauss; ion accelerating voltage, 3500—500 V; electron accelerating voltage, 70 eV; trap current, 10 μA; temperature of ion source, 250°C; temperature of sample manifold, 125—130°C.

The following derivatives of aniline and anisole were investigated: Aniline derivatives—*o*-, *m*-, and *p*-compounds

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[1] H. M. Rosenstock, M. B. Wallenstein, A. L. Wahrhaftig, and H. Eyring, *Proc. Natl. Acad. Sci. U.S.*, **38**. 667 (1952).

[2] K. Fueki and K. Hirota, *Nippon Kagaku Zasshi*, **81**, 212 (1960).

[3] K. Hirota and Y. Niwa, *Tetrahedron Lett.*, **1966**, 5757.

[4] H. M. Rosenstock, Doctorial Dissertation, *Univ. of Utah. Salt Lake City*, 1952.

[5] L. Friedman, F. A. Long, and M. Wolfsberg, *J. Chem. Phys.*, **27**, 613 (1957).

[6] A. B. King and F. A. Long, *ibid.*, **29**, 374 (1958).

[7] F. W. Lampe and F. H. Field, *J. Amer. Chem. Soc.*, **81**, 3238 (1959).

[8] P. Nounou, *Advan. Mass Spectrometry*, No. 4, 551 (1967).

[9] R. C. Dougherty, *J. Amer. Chem. Soc.*, **90**, 5780 (1968).

[10] H. Nakata and A. Tatematsu, *Tetrahedron Lett.*, **1969**, 4303.

of anisidine, aminophenol, chloroaniline, nitroaniline, aminobenzoic acid, and aminoacetophenone; Anisole derivatives—*o*-, *m*-, and *p*-compounds of anisidine, methoxyphenol, chloroanisole, nitroanisole, methoxybenzoic acid, and methoxybenzaldehyde. The compounds were guaranteed reagents. obtained from Tokyo Kasei Co., Ltd., and were used without further purification.

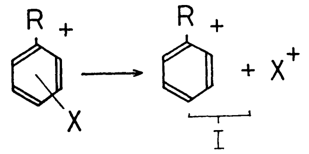

Fig. 1. Fragment ions investigated.

In Fig. 1, R denotes the common substituent, NH_2 or $O\text{-}CH_3$, in the derivatives of aniline or anisole, respectively, and X denotes the other substituent, such as Cl, NO_2 *etc.* The summation of the intensity of ions shown in the right side of Fig. 1, *i.e.*, the ions inferred to be produced directly by a rupture of the bond between the aromatic moiety and the substituent X, was investigated. I desotes the summation of intensity of the ions mentioned above, normalized by the total ion intensity of the compound, *i.e.*, for aniline derivatives, I desotes the normalized ion intensity of $C_6H_4NH_2^+$ (m/e 92) plus X^+, and for anisole derivatives, I denotes that of $C_6H_4OCH_3^+$ (m/e 107) plus X^+. As shall be described, a simple correlation was found to be valid between $\log I$ and the partial bond order P^h for the frontier electron of the bond mentioned above.

TABLE 1. PARTIAL BOND ORDER (P^h) OF FRONTIER ELECTRON

Aniline derivatives X	P^h *o*-	P^h *m*-	P^h *p*-
OCH_3	−0.136	−0.017	−0.134
OH	−0.126	−0.012	−0.126
Cl	−0.043	−0.002	−0.046
COOH	0.020	0.001	0.023
NO_2	0.024	0.001	0.028
$COCH_3$	0.037	0.001	0.046
Anisole derivatives X	**P^h *o*-**	**P^h *m*-**	**P^h *p*-**
NH_2	−0.154	−0.107	−0.151
OH	−0.146	−0.049	−0.143
Cl	−0.049	−0.002	−0.054
COOH	0.017	0.001	0.020
NO_2	0.021	0.001	0.026
CHO	0.035	0.002	0.045

A FACOM 270—30 computer was used for calculation. The parameters used in the calculation were quoted from the accepted values in the literature[11,12]. The results are shown in Table 1, where P^h is the partial bond order for a frontier electron of the bond between the substituent X and the aromatic moiety containing amino or methoxy group.

Results and Discussion

Correlation between the ion intensity I, described above, and various calculated quantities, such as electron density, free valence, and bond order for the molecules, were scrutinized. As a consequence of the investigation, a simple relation was found to be valid between the partial bond order P^h (shown in Table 1) for a frontier electron of the bond ruptured and log I. In Figs. 2, 3, and 4, log I *versus* P^h relation for each of *o*-, *m*-, and *p*-aniline derivatives, respectively, is plotted. The same plot for anisole derivatives is shown

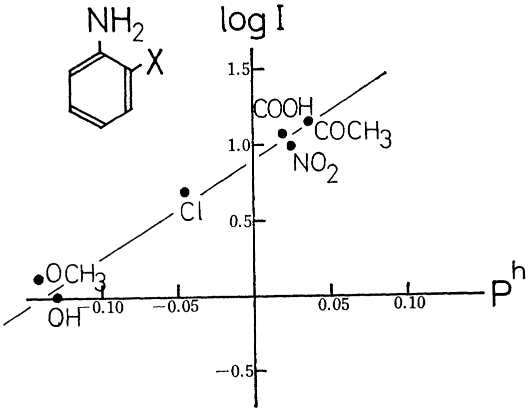

Fig. 2. log I *versus* partial bond order of the frontier electron for *o*-aniline derivatives.

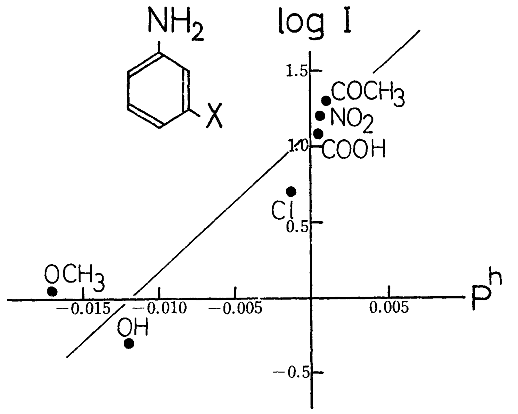

Fig. 3. log I *versus* partial bond order of the frontier electron for *m*-aniline derivatives.

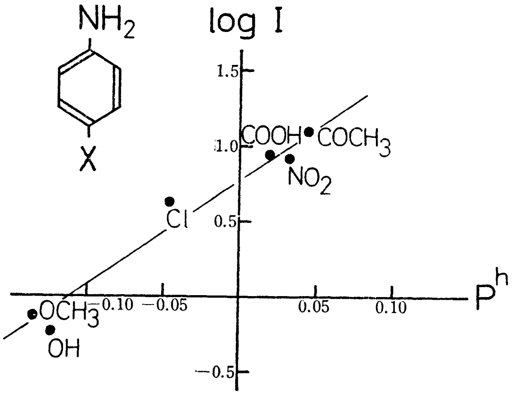

Fig. 4. log I *versus* partial bond order of the frontier electron for *p*-aniline derivatives.

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11) L. E. Orgel, T. L. Cottrel, W. Dick, and L. E. Sutton, *Trans. Faraday Soc.*, **47**, 113 (1951).

12) H. H. Jaffé, *J. Chem. Phys.*, **20**, 279 (1952).

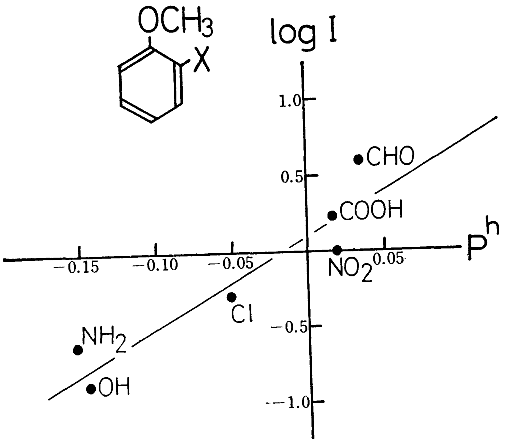

Fig. 5. log *I* *versus* partial bond order of the frontier electron for *o*-anisole derivatives.

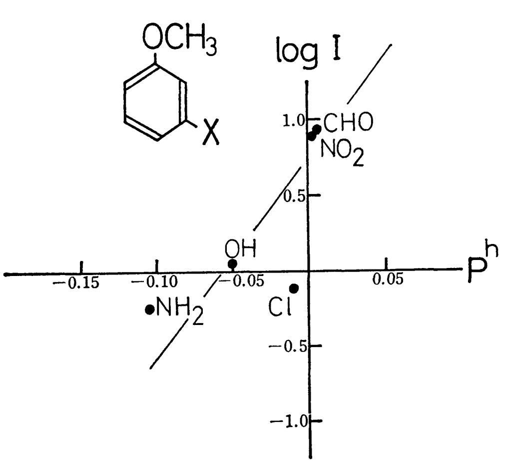

Fig. 6. log *I* *versus* partial bond order of the frontier electron for *m*-anisole derivatives.

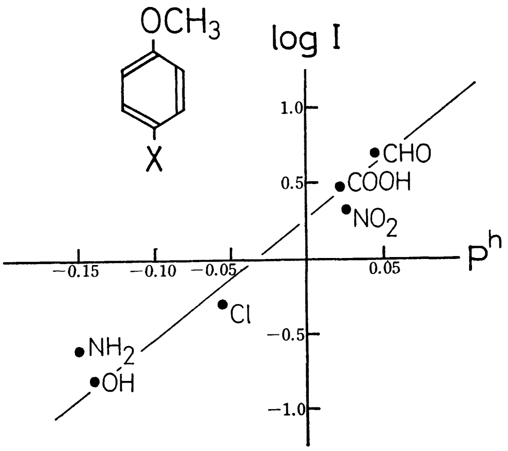

Fig. 7. log *I* *versus* partial bond order of the frontier electron for *p*-anisole derivatives.

in Figs. 5, 6, and 7.

Almost every compound studied exhibited a metastable peak corresponding to decomposition of M^+ into the aromatic moiety of interest, *i.e.*, into $C_6H_4NH_2^+$ for aniline derivatives, and $C_6H_4OCH_3^+$ for anisole derivatives, suggesting that at least a part of the process proceeds according to Q.E.T. mechanism. The implication is that the half life of parent ions is about 10^{-5} sec. The life time of an ion in its excited states is considered to be nearly 10^{-8} sec[13,14]. A molecular ion in its excited states does not decompose immediately after it is produced by electron impact, but rather undergoes many vibrations. During these vibrations there is a high probability of radiationless transitions among the many potential surfaces for the molecular ion, and the ion falls into its ground state or its low lying electronic states before it eventually decomposes.[1]

A linear relation was found between the vertical ionization potential measured by electron impact and H.M.O. coefficient of π-electron obtained by simple LCAO MO calculation for anisidines and chloroanilines. From the results it has been inferred that the first three ionizations of these compounds correspond to removal of a π-electron.[15] Similar conclusion has been obtained for other compounds under consideration in the present study.[16] Thus it is legitimately assumed that the low lying electronic states for the molecular ions in the present investigation are those produced by loss of a π-electron.

In view of the results so far achieved, the experimental results of the present study can be explained by Q.E.T. mechanism as follows. According to the theory, the excited molecular ion produced by electron impact does not decompose immediately into the various fragment ions, but the excited molecular ion falls into its ground or low lying electronic states by radiationless transition in less than 10^{-8} sec. Then the molecular ion decomposes by unimolecular decomposition into fragment ions mentioned above, *i.e.*, $C_6H_4NH_2^+$ and X^+ in the case of aniline derivatives or $C_6H_4OCH_3^+$ and X^+ in the case of anisole derivatives. If these fragment ions are produced from the molecular ion in its electronic ground state, as is assumed in Q.E.T., close correlation would be expected between some of the characteristic quantities of the molecular ion in its electronic ground state and the ion intensity of fragment ions inferred to be produced from the ion. A molecular ion in its electronic ground state is produced when a frontier electron is lost by the molecule. Figures 2—7 illustrate simple relations between the partial bond order for the frontier electron and the summation of the intensity of the fragment ions concerning the bond, normalized by the total ion intensity, and show considerable parts of the fragment ions referred are produced by this mechanism.

In simple LCAO MO calculation, the following expression is derived for the energy E_i of the ith molecular orbital,[17]

$$E_i = \alpha + 2\sum P_j{}^i\beta$$

where $P_j{}^i$ is the partial bond order of an electron in the

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13) H. Sponer, *Radiat. Res.*, *Suppl.* **1**, 558 (1959).

14) M. A. Linotengarten, *Bull. Acad. Sci. USSR*, *Phys. Ser.*, **24**, 1050 (1960).

15) S. Tajima, N. Wasada, and T. Tsuchiya, *Tetrahedron Lett.*, **1970**, 139.

16) S. Tajima, N. Wasada, and T. Tsuchiya, to be published elsewhere.

17) C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.*, **A191**, 39 (1947).

ith MO for the jth bond, α is the Coulomb integral and β is the resonance integral, respectively. One can see that the larger the value of P_j^i for an electron is, the more the electron contributes to the stabilization of the bond. When a molecular ion M^+ in its ground state decomposes into the fragment ions mentioned above by unimolecular decomposition, the larger the partial bond order between the aromatic moiety and the substituent X of the frontier electron removed from the molecule is, the more the strength of the bond decreases by the removal of the electron and the more easily the bond ruptures. The results shown in Figs. 2—7 can be explained qualitatively by the rationalization.

We have not considered on ortho effect in our calculation. If there are appreciable ortho effects, the points in Figs. 2 and 5 will not lie close to a straight line, because the ortho effects may be different as the substituents differ.

For *m*-compounds for aniline derivatives, the partial bond order for the frontier electron in the bond under consideration is very small (Table 1), and the influence of the loss of a frontier electron on the bond strength is considered to be very small, though a trend similar to Figs. 2 and 4 manifests itself as is seen in Fig. 3. For *m*-compounds, when log I is compared with the partial bond order for the second highest occupied molecular orbital P' instead of that for the highest occupied molecular orbital, a relation similar to Fig. 2 and Fig. 4 is obtained as is shown in Fig. 8, except for chloroaniline. From the result, the molecular ions in the state which corresponds to the loss of an electron in the second highest occupied orbital appear to be mainly responsible for the rupture of the bond under consideration in this case. For *o*-, *p*-compounds for aniline derivatives, the partial bond order of the bond for the second highest occupied orbital is very small. For meta anisole derivatives, however, the loss of a frontier electron from the bond under consideration seems to decrease the stability of the bond more effectively than for meta aniline derivatives, since the partial bond order of the frontier electron in the *m*-compounds are larger for anisole derivatives than for aniline derivatives, as is seen in Table 1.

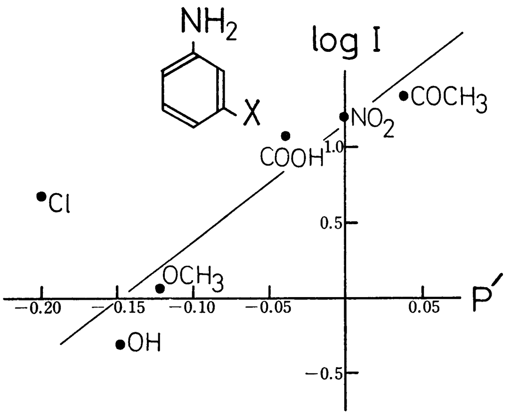

Fig. 8. log I *versus* partial bond order of an electron in the second highest occupied molecular orbital for *m*-aniline derivatives.

Studies on more numerous compounds are desirable, and a quantitative rationalization of the current phenomena and explanation for the abnormal behavior of *m*-chloroaniline, *etc.* deserve further investigation.

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