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An Interpretation of Mass Spectra by Simple LCAO MO Calculation. II. Derivatives of Benzene and Chlorobenzene

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Other than the well-known quasi-equilibrium theory,[1] several methods for the theoretical interpretation of the mass spectra of larger organic compounds have been reported.[2–5] In a previous paper,[6] we described that a simple relation was found between the summation of the intensities of certain peaks and the partial bond order, as calculated by simple LCAO MO method, for a frontier electron of the bond ruptured in the cases of the derivatives of aniline and anisole. The present note will report that the same relation holds for the derivatives of benzene and chlorobenzene.

The mass spectra were obtained with a CEC 21-103C mass spectrometer. The following derivatives of benzene were investigated: phenol, anisole, aniline, benzaldehyde, toluene, benzoic acid, and nitrobenzene; the following *o*-, *m*-, and *p*-derivatives of chlorobenzene were also investigated: hydroxychlorobenzene, methoxychlorobenzene, aminochlorobenzene, chlorobenzaldehyde, methylchlorobenzene, chlorobenzoic acid, and

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[1] H. M. Rosenstock and M. Krauss, "Mass Spectrometry of Organic Ions," ed. by F. W. McLafferty, Academic Press, New York (1963), Chapter 1.

[2] K. Fueki and K. Hirota, *Nippon Kagaku Zasshi*, **81**, 212 (1960); K. Hirota and Y. Niwa, *Tetrahedron Lett.*, **1966**, 5757.

[3] M. V. Gur'ev and M. V. Tikhomirov, *Zh. Fiz. Khim.*, **32**, 2731 (1958); M. V. Gur'ev, *ibid.*, **34**, 475 (1960).

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

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

[6] S. Tajima, N. Wasada, and T. Tsuchiya, This Bulletin, **44**, 884 (1971).

nitrochlorobenzene. All the samples studied were of a research grade, were obtained from the Tokyo Kasei Co., Ltd., and were used without further purification. The experimental conditions have been described previously.[6]

The following daughter ions are produced from the molecular ion, $\text{R-C}_6\text{H}_4\text{-X}^+$, by electron impact:

$$\text{R-C}_6\text{H}_4\text{-X}^+ \longrightarrow \text{R-C}_6\text{H}_4^+ + \text{X}, \text{ and } \text{R-C}_6\text{H}_4 + \text{X}^+ \qquad (1)$$

where R denotes the common substituent, H or Cl, in the derivatives of benzene or chlorobenzene respectively, and where X denotes the other substituent, such as OH or OCH_3.

We examined the correlation between the ion intensity, I, given by Eq. (2), and the partial bond order, P^h, of the bond between the aromatic moiety and the substituent, X, for a frontier electron.

$$I = 100 \times (\text{R-C}_6\text{H}_4^+ + \text{X}^+)/\sum I_i \qquad (2)$$

$\sum I_i$ denotes the summation of the total ion intensities. The parameters used in the calculation of P^h were quoted from the accepted values in the literature.[7,8]

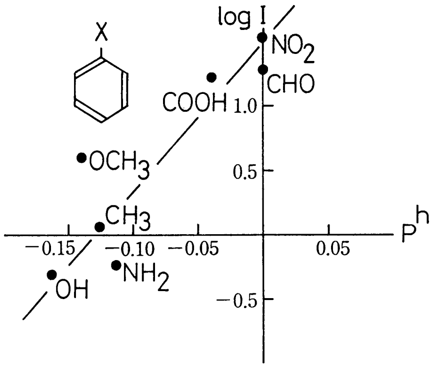

Fig. 1. log *I* *versus* partial bond order, P^h, of the frontier electron for benzene derivatives.

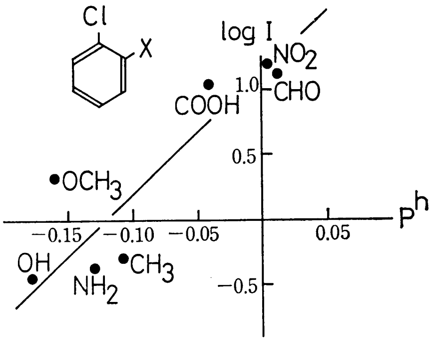

Fig. 2. log *I* *versus* partial bond order, P^h, of the frontier electron for *o*-chlorobenzene derivatives.

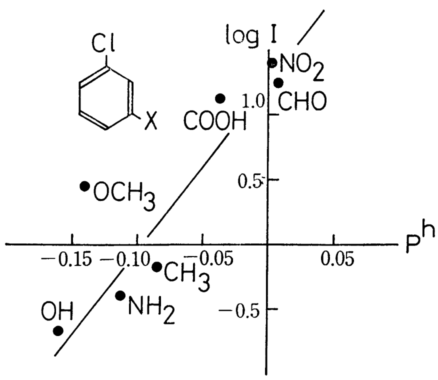

Fig. 3. log *I* *versus* partial bond order, P^h, of the frontier electron for *m*-chlorobenzene derivatives.

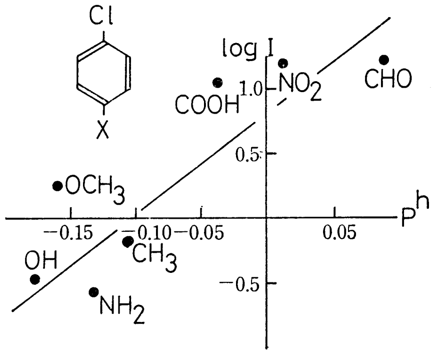

Fig. 4. log *I* *versus* partial bond order, P^h, of the frontier electron for *p*-chlorobenzene derivatives.

In Figures 1—4, plots of log *I* *versus* P^h for the derivatives of benzene and for the *o*-, *m*-, and *p*-derivatives of chlorobenzene are plotted. From each figure, we can see a simple relation: the larger the value of P^h, the larger the log *I*, just as in a previous paper.[6]

Almost every compound studied here exhibited a metastable peak corresponding to the decomposition $\text{M}^+ \rightarrow \text{R-C}_6\text{H}_4^+ + \text{X}$. This means that the half-life of the molecular ions of these compounds is about 10^{-5}—10^{-6} sec.[1] The life time of an ion in its excited states is considered to be less than 10^{-8} sec.[9,10] Therefore, at least a part of the ions shown in Eq. (1) may be considered to be produced by the following mechanism: a molecular ion in its excited state is not decomposed immediately after its production by electron impact, but the ion falls into its ground state by radiationless transitions; then it decomposes eventually to the daughter ions. The correlations indicated in Figs. 1—4 can be explained in the same way as in the previous report.[6]

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

[8] H. H. Jaffé, *J. Chem. Phys.*, **20**, 279 (1952).

[9] H. Sponer, *Radiat. Res. Suppl.*, **1**, 558 (1959).

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