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Mass Spectrometry of Dyes. IV.[1] Electron Impact Reaction of Nitrophenyl Phenyl Ethers and Their Charge Migration

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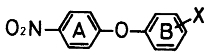
By the electron impact reaction of substituted 4-nitrodiphenyl ethers (1), the substituents on ring B of (1) cause a reasonable change in the intensity of fragment ions which result from the nitro→nitrite ester rearrangement. There is a linear correlation of the M^+–NO fragment ion intensity of (1) with the ionization potential of the molecules, and with Hammett σ constants. These evidences suggest that the charge of ring B will be free to migrate to ring A in the ion state, even if they are separated by O-atom.

In elucidating the mass spectral fragmentation mechanism, two concepts about the mobility of charge, that is, localization and migration, have been reported. The first concept of localized charge as a driving force for unimolecular decomposition reactions induced by electron impact has been used by a number of authors to explain and correlate a large variety of reactions observed in mass spectra.[2] As an extention of this concept, it has been proposed that most decomposition reactions which yield abundant ions can be interpreted as being initiated by the positive charge or the unpaired electron at a particular site.[2c,3]

Biemann and Mandelbaum, however, have documented the mobility of a charge in the mass spectral fragment ions of a series of substituted 1-(valerylphenyl)-3-phenylcyclopentanes,[4] of which two aromatic rings are separated by a cyclopentane ring. On the other hand, Kinstle and Oliver have reported a charge localization by the fact that substituents on ring B of 4-nitrodiphenyl ethers (1) cause a considerable change in the intensity of fragment ions which result from the nitro→nitrite ester rearrangement.[5] However, their examination seemed to indicate some dissatisfaction.



(1)

We will now attempt to re-examine their results. This is based on the fact that there is a linear correlation of the M^+–NO fragment ion intensity in the electron impact reactions of (1) with the ionization potential I_M of the molecules, which are calculated by simple LCAO MO method, and with Hammett σ constants, and that the M^+–NO (or M^+–NO_2) ions, fragment further by the action of substituents X on the other ring B. These evidences suggest that the charge will be free to migrate to the other ring in the ion state.

Experimental

Materials. 4,4′-Dinitrodiphenyl ether was obtained commercially, while 4-nitrodiphenyl ether, 4-chloro-4′-nitrodiphenyl ether, and 4-methoxy-4′-nitrodiphenyl ether were prepared by a known method.[6] Mp and the spectral propeties (UV and mass spectra) confirm the structure.

Electron Impact Reactions. The reactions were carried out using a Hitachi RMU-6E double-focusing mass spectrometer and operating under the following conditions for the

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[1] Previous papers, Part III: K. Yamada, A. Noguchi, T. Konakahara, and H. Iida, *J. Fac. Eng. Chiba Univ.*, **21**, 47 (1970); Part V: K. Yamada, K. Hayashida, and H. Iida, *Kogyo Kagaku Zasshi.* **74**, 952 (1971); Part VI: K. Yamada, A. Noguchi, and H. Iida, *J. Fac. Eng. Chiba Univ.*, **21**, 149 (1970).

[2] See, for example: a) T. Wachs and F. W. McLafferty, *J. Amer. Chem. Soc.*, **89**, 5044 (1967) and references cited therein. b) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, Inc., San Francisco, Calf., (1967), and references cited therein. c) F. W. McLafferty, "Interpretation of Mass Spectra," W. A. Benjamin, Inc., New York, N. Y., (1966).

[3] F. W. McLafferty and T. Wachs, *J. Amer. Chem. Soc.*, **89**, 5043 (1967).

[4] A. Mandelbaum and K. Biemann, *ibid.*, **90**, 2979 (1968).

[5] T. H. Kinstle and W. R. Oliver, *ibid.*, **91**, 1864 (1969).

[6] R. Q. Brewster and T. Groening, "Organic Syntheses," Coll. Vol. II, p. 445 (1966).

above materials: ionizing voltage 80, 70, and 20 eV, heated inlet system at 130—150°C except for 4,4′-dinitrodiphenyl ether (direct inlet system at 180°C), total emission current 80 and 10μA. Other electron impact reaction data were quoted from Ref. 5.

Calculation. The ionization potential I_M values were calculated by simple LCAO MO method,[7] according to the following equation

$$I_M = -\varepsilon_{H.O.}$$

where $\varepsilon_{H.O.}$ is the energy of the highest occupied orbital for the molecule.

The least-squares value of the plot (M^+–NO ion intensity *vs.* Hammett σ) was computed by the usual program.

Results and Discussion

Electron impact reactions are considered as a set of competing consecutive unimolecular decompoiton reactions under highly reduced pressure. The quasi-equilibrium theory (QET) of the electron impact reactions[8] in its simplest form predicts that the rate constant k varies with internal energy E, according to the following equation

$$k = \nu\left(\frac{E-E_0}{E}\right)^{s-1}$$

where ν is a frequency facter, E_0 is the activation energy, and s is the effective numbers of oscillators. In our reaction, Bentley's treatment gives the following relationship theoretically[9,10]

$$\log (k_X/k_H) = \log (Z_X/Z_H)$$
$$\cong [(s-1)/E][(I_M{}^X - I_M{}^H) - (I_B{}^X - I_B{}^H)]$$
$$\log (Z_X/Z_H) \cong [(s-1)/E](K_M - K_B)\sigma = K\sigma$$
$$(Z = [A]/[M])$$

where [A] and [M] are the relative abundances of the peaks due to the M^+–NO fragment and the molecular ion respectively, I_M and I_B are the ionization potentials, K, K_M, and K_B are constants. The subscripts and/or the superscripts, X and H, refer to substituted and parent compound, and the subscripts M and B to the molecule and the M^+–NO ion. The log (Z_X/Z_H) *vs.* ($I_M^X - I_M^H$) plot, ignoring the effect of I_B, was shown in Fig. 1. I_M values were calculated by simple LCAO MO method. In Fig. 2, which are the correlation between log(Z_X/Z_H) and Hammett σ, the use of σ constants gave a plot with slightly less scatter than did Brown's σ^+ values and the least-squares value of the slope (ρ) is $+1.24$. This value for our reaction ($M^+ \rightarrow M^+$–NO) represents a larger numerical reaction constant than most of those previously reported for the rate of an electron impact reaction.[11] Thus, it appears that the reaction is enhanced by an increased positive charge at the reaction site, that is, that the nature of

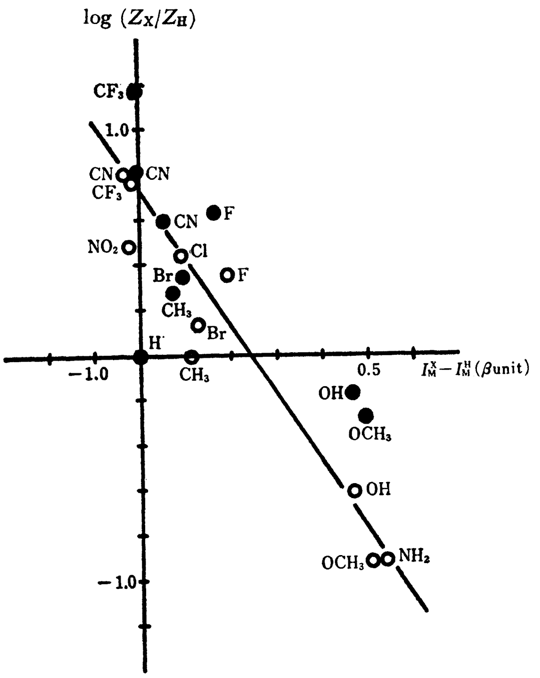

Fig. 1. Correlation of M^+—NO ion intensity with the ionization potential I_M.

$$Z_H = \frac{[OC_6H_4OC_6H_5]^+}{3[O_2NC_6H_4OC_6H_5]^{\dot{+}}};\quad Z_X = \frac{[OC_6H_4OC_6H_4X]^+}{[O_2NC_6H_4OC_6H_4X^+]^{\dot{+}}}$$

$I_M = -\varepsilon_{H.O.}$; Calculated by simple LCAO MO method.
○: *para*; ●: *meta*

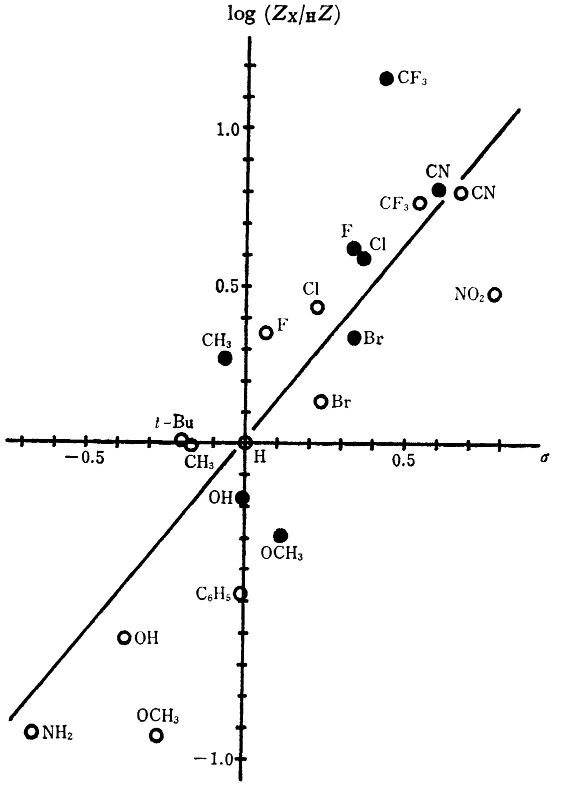

Fig. 2. Correlation of M^+—NO ion intensity with Hammett σ. Least-squares slope (ρ) = +1.24 ($0.85 \leqq \rho \leqq 1.63$), standard deviation=0.29. ○: *para*; ●: *meta*

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[7] Kikuchi's program and usual parameters were used in this paper.

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

[9] T. W. Bentley, R. A. W. Johnstone, and D. W. Payling, *J. Amer. Chem. Soc.*, **91**, 3978 (1969).

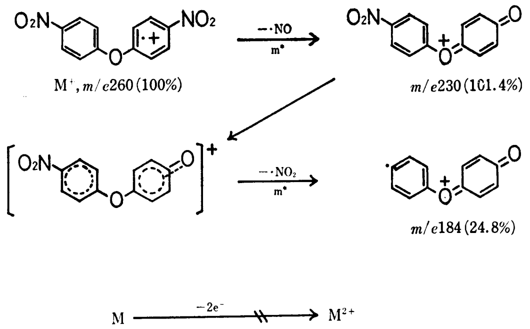
[10] $I_M^X - I_M^H = K_M\sigma$; A. Streitwieser, Jr., *Progr. Phys. Org. Chem.*, **1**, 27 (1963), $I_B^X - I_B^H = K_B\sigma$; A. G. Harrison, P. Kebarle, and F. P. Lossing, *J. Amer. Chem. Soc.*, **83**, 777 (1961).

[11] P. Brown and C. Djerassi, *ibid.*, **89**, 2711 (1967).

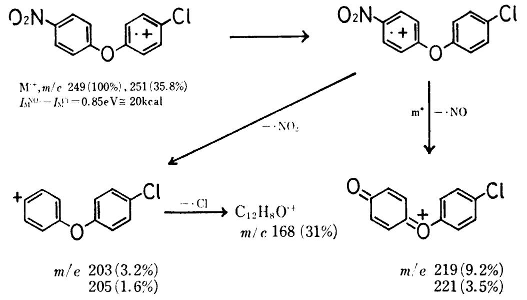
the substituent greatly affects the ionization of the molecule and/or the electronic distribution in the molecular ion. Indeed, the decomposition of the molecular ions seems to depend on the substituents X as described in Ref. 2. It is clear in Fig. 2, that the formation of M^+–NO ion is inhibited by electron-donating substituents X on ring B and facilitated by electron-withdrawing groups X with a large, often "flat-topped" metastable ion, which has been observed in this NO loss from some nitroaromatics.[12]

The ionization potential of the polyfunctional molecule is determined by the functional group with the lowest ionization potential,[13] and the ionization potential of nitrobenzene is the highest in all of the monosubstituted benzenes.[14] Therefore, I_M^X of substituted 4-nitrodiphenyl ethers is determined by the substituent X, and it seems, the initial site of ionization to be localized on substituted ring B. The more electron-withdrawing is the substituent, the more intense is the M^+–NO ion peak. This is undoubtedly the effect of the substituents X. The electron-withdrawing X groups facilitate the charge and/or radical migration to electron-deficient ring A in the odd-electron fragment ions. Initially, this seemed surprising in view of the results of Kinstle *et al.* who documented the localization of a charge in the odd-electron fragment ions.[5] However, unlike their study, in electron impact reaction (both 70 and 20 eV) of 4-nitrodiphenyl ethers with the electron-withdrawing X groups (*e.g.* X=4′-NO_2, 4′-Cl), M^+–NO (or M^+–NO_2) fragment ions displayed, with considerable intensity, further decompositions because of the substituents X on ring B (Scheme I and II). Likewise, in the case of the electron-donating groups X, it seemed that the initial fragment ions due to the substituents X further decomposed by nitro group on ring A (Scheme III).

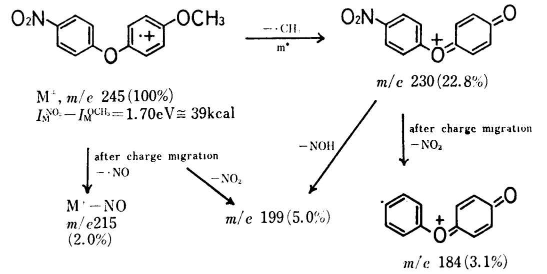
The remainder of the ionization potentials between nitro- and chloro- or methoxybenzene (20 and 30 kcal) shows the ease of ionization on ring B. This process is the same as that of Biemann's report.[4]



Scheme I



Scheme II



Scheme III

These results suggest that the substituent X on ring B of substituted 4-nitrodiphenyl ethers (1) has an important effect on the electronic state of ring A, and that the charge and/or radical migration to electron-deficient ring A in the odd-electron fragment ion is possible by through-conjugation of oxygen *p*-orbital.

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[12] J. H. Beynon, R. A. Saunders, and A. E. Williams, *Z. Naturforsch.*, **20a**, 180 (1965); M. M. Bursey and F. W. McLafferty, *J. Amer. Chem. Soc.*, **88**, 5023 (1966).

[13] G. A. Junk and H. J. Svec, *ibid.*, **89**, 790 (1967).

[14] I. Howe and D. H. Williams, *ibid.*, **91**, 7137 (1969).