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Hammett Correlation in Mass Spectra. Substituent Effects for the Migratory Aptitude of the Aryl Group in the Unimolecular Ion Decomposition of Diaryl Sulfones

Toshikazu Nagai, Tetsuo Maeno and Niichiro Tokura

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka

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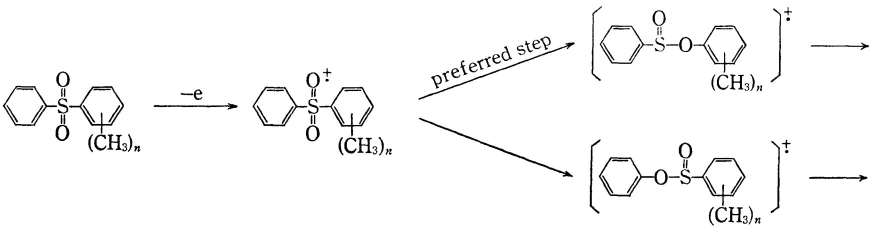
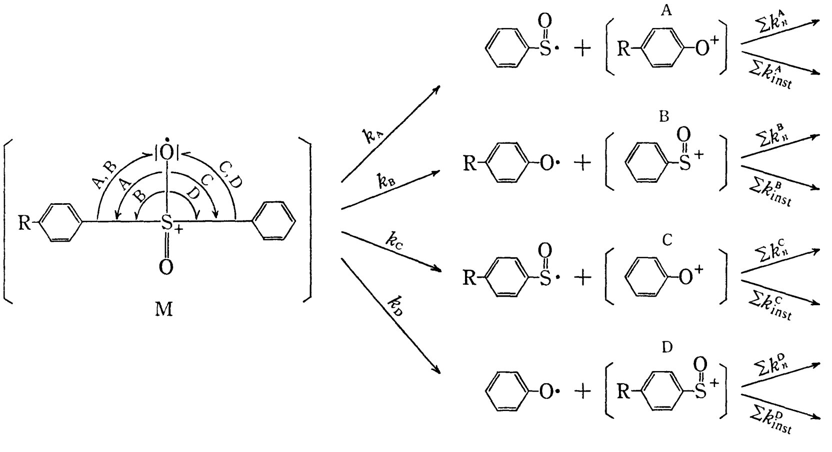
The migratory aptitude of the aryl group in the unimolecular ion decomposition reaction of *p*-substituted diaryl sulfones has been examined. Both electron-donating and -withdrawing substituents showed to be capable of increasing the migratory aptitude. On the other hand, a kinetic treatment allowed a satisfactory Hammett correlation ($\rho=0.3$) on the total abundances of the fragment ions. The energy of the cleaved bond and the production stability were shown to be important factors in the effect of the substituent on the ion decomposition.

In the mass spectra of methyl-substituted diaryl sulfones, the aryl S→O migration has been observed by Meyerson and his co-workers.[1] They have demonstrated that the migratory aptitude apparently increases with an increase in the substitution of the phenyl group by the electron-donating methyl group, and suggested that the electron deficiency is largely localized in a non-bonding oxygen orbital and that, hence, an aryl group better able to function as an electron donor should preferentially migrate (Scheme 1).

In order to obtain further information about substituent effects in the migratory aptitude on diaryl sulfones, we have now dealt with a variety of the *p*-substituted compounds, applying a kinetic method. The results we obtained on the driving



Scheme 1



Scheme 2

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[1] S. Meyerson, H. Drews and E. K. Fields, *Anal. Chem.*, **36**, 1294 (1964).

force of the aryl migration were somewhat different from those obtained by Meyerson and his coworkers.

Results and Discussion

By increasing the electron energy, a variety of fragment ions were formed, along with the A, B, C, and D ions (Scheme 2), as is shown in Fig. 1a. Thus, the voltage of the ionizing electrons used was chosen to be 20 eV in order to keep the products from further decomposition (Fig. 1b).

The ratios of the fragment ions (C+D) due to the migration of the unsubstituted aryl group to those (A+B) of the *p*-substituted aryl group were examined; they are shown in Table 1.

These ratios indicate, interestingly, that both electron-donating and -attracting substituents are capable of increasing their migratory aptitude, indicating a further factor in the migratory aptitude in addition to that proposed by Meyerson *et al.*,[1] that an aryl group better able to function as an electron donor should preferentially migrate.

Thus, we carried out a kinetic study in order to examine the relative rate of bond cleavage. The method by Bursey and McLafferty.[2-4] was modified which was applicable to substituted benzophenone systems involving no phenyl migration.

The concentratioons of ions (A, B, C, and D) in the source of the mass spectrometer were assumed to be dependent on their rates of formation and depletion (whether by further decomposition, $\sum k_n^{\mathrm{A-D}}$ or by instrumental removals, $\sum_{\mathrm{inst}}^{\mathrm{A-D}}$,) according to Scheme 2; the rate of the appearance of A+B+C+D in the source is shown as Eq. 1:

$$\frac{\mathrm{d}\{[\mathrm{A}]+[\mathrm{B}]+[\mathrm{C}]+[\mathrm{D}]\}}{\mathrm{d}t}=(k_{\mathrm{A}}+k_{\mathrm{B}}+k_{\mathrm{C}}+k_{\mathrm{D}})[\mathrm{M}]$$
$$-\{(\sum k_n^{\mathrm{A}}+\sum k_{\mathrm{inst}}^{\mathrm{A}})[\mathrm{A}]+(\sum k_n^{\mathrm{B}}+\sum k_{\mathrm{inst}}^{\mathrm{B}})[\mathrm{B}]$$
$$+(\sum k_n^{\mathrm{C}}+\sum k_{\mathrm{inst}}^{\mathrm{C}})[\mathrm{C}]+(\sum k_n^{\mathrm{D}}+\sum k_{\mathrm{inst}}^{\mathrm{D}})[\mathrm{D}]\} \qquad (1)$$

By the steady-state approximation, Eq. (2) is obtained:

$$(\sum k_n^{\mathrm{A}}+\sum k_{\mathrm{inst}}^{\mathrm{A}})[\mathrm{A}]+(\sum k_n^{\mathrm{B}}+\sum k_{\mathrm{inst}}^{\mathrm{B}})[\mathrm{B}]$$
$$+(\sum k_n^{\mathrm{C}}+\sum k_{\mathrm{inst}}^{\mathrm{C}})[\mathrm{C}]+(\sum k_n^{\mathrm{D}}+\sum k_{\mathrm{inst}}^{\mathrm{D}})[\mathrm{D}]$$
$$=(k_{\mathrm{A}}+k_{\mathrm{B}}+k_{\mathrm{C}}+k_{\mathrm{D}})[\mathrm{M}] \qquad (2)$$

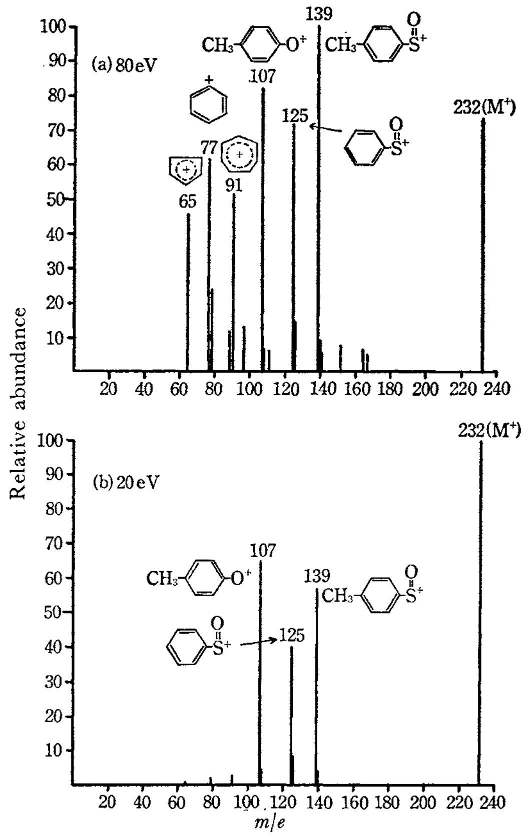

Fig. 1. Relative abundance of the fragment ions of *p*-methyldiphenyl sulfone recorded at 80 eV (a) and 20 eV (b). The peaks below *m/e* 65 are omitted here.

In the present case, if the voltage of the ionizing electrons is so low (20 eV) that no further decomposition products of the A, B, C, and D ions appear in the mass spectrum, then $\sum_n^{\mathrm{A-D}}$ vanishes and Eq. (2) is reduced to Eq. (3), since the instrumental parameters do not vary greatly from compound to compound; *i.e.*, $\sum k_{\mathrm{inst}}^{\mathrm{A}}=\sum k_{\mathrm{inst}}^{\mathrm{B}}=\sum k_{\mathrm{inst}}^{\mathrm{C}}=\sum k_{\mathrm{inst}}^{\mathrm{D}}\equiv\sum k_{\mathrm{inst}}$.

$$\frac{[\mathrm{A}]+[\mathrm{B}]+[\mathrm{C}]+[\mathrm{D}]}{[\mathrm{M}]}=\frac{k_{\mathrm{A}}+k_{\mathrm{B}}+k_{\mathrm{C}}+k_{\mathrm{D}}}{\sum k_{\mathrm{inst}}} \qquad (3)$$

Z/Z_0 values defined as in Eq. (4) are given in Table 2, where the suffix zero refers to an unsubstituted compound:

Table 1. The relative abundances of the fragment ions formed by aryl migration

R	NH_2	OCH_3	CH_3	H	Cl	COOH	CN	NO_2
(C+D)/(A+B)	0.132	0.260	0.533	1.000	0.318	0.534	0.375	0.986

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[2] M. M. Bursey and F. W. McLafferty, *J. Amer. Chem. Soc.*, **88**, 529 (1966).

[3] M. M. Bursey and F. W. McLafferty, *ibid.*, **88**, 4484 (1966).

[4] M. M. Bursey and F. W. McLafferty, *ibid.*, **89**, 1 (1967).

TABLE 2. RELATIVE INTENSITIES OF THE FRAGMENT IONS IN THE MASS SPECTRA OF *p*-SUBSTITUTED DIPHENYL SULFONE RECORDED AT 20 eV

R	$\frac{[A]}{[M]}$	$\frac{[B]}{[M]}$	$\frac{[C]}{[M]}$	$\frac{[D]}{[M]}$	Z	$\log\frac{Z}{Z_0}$
NH_2	0.700	0.028	0	0.096	0.824	−0.477
OCH_3	1.075	0.021	0	0.285	1.381	−0.253
CH_3	0.660	0.409	0	0.570	1.639	−0.178
H	0	1.235	0	1.235	2.470	0
Cl	0	2.190	0	0.695	2.885	0.068
COOH	0	2.420	0	1.292	3.712	0.177
CN	0	2.068	0.291	0.485	2.844	0.061
NO_2	0	1.655	0.974	0.658	3.287	0.124

$$\frac{Z}{Z_0} \equiv \frac{[A]+[B]+[C]+[D]/[M]}{[A_0]+[B_0]+[C_0]+[D_0]/[M_0]} = \frac{k_A+k_B+k_C+k_D}{k_A^0+k_B^0+k_C^0+k_D^0} \equiv \frac{k}{k^0} \quad (4)$$

The correlation of these data with the Hammett σ^+ constants[5] indicates a small positive ρ value (+0.37), as is shown in Fig. 2.

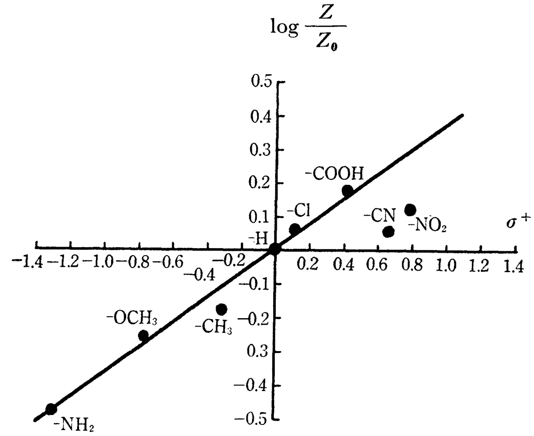

Fig. 2. Relative intensities of the total fragment ions in the mass spectra of *p*-substituted diphenyl sulfones recorded at 20 eV (derived from Eq. (3)) *vs.* σ^+ values.

For this reaction, σ values were less appropriate, indicating the presence of a full positive charge on the substituted molecular ion. Although the total abundances of fragment ions allowed a satisfactory Hammett correlation to be obtained, the effect of a substituent on the abundance of the individual fragment ions was not satisfactorily correlated by the Hammett equation.

In addition to the above-mentioned Z/Z_0 values, we found that Y/Y_0 values as defined in Eq. (5)

$$\frac{Y}{Y_0} \equiv \frac{\ln(1+Z)}{\ln(1+Z_0)} = \frac{k_A+k_B+k_C+k_D}{k_A^0+k_B^0+k_C^0+k_D^0} \equiv \frac{k}{k^0} \quad (5)$$

were applicable to the Hammett correlation, since the proposed values resulted in nearly the same Hammett correlation as in the case of the Z/Z_0 values, as may be seen in Fig. 3.

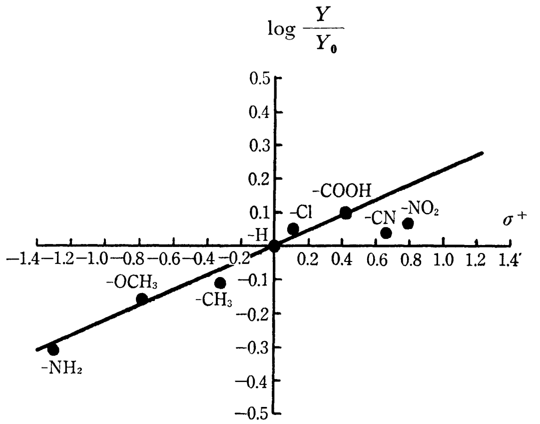

Fig. 3. Relative intensities of the total fragment ions in the mass spectra of *p*-substituted diphenyl sulfones recorded at 20 eV (derived from Eq. (6)) *vs.* σ^+ values.

The coincidence of the two values can be explained by the following considerations.

Applying the general solution of the rate equation of two successive first-order reactions[6] to the present unimolecular competitive reaction shown by Scheme 2 under conditions of negligible $\sum k_n^{A-D}$ rates, Eq. (6) can be obtained by using the equation of $[M]_0 = [M] + \sum_{N=A}^{D}[N]$, where $[M]_0$ is the concentration of [M] at $t=0$:

$$\sum_{N=A}^{D}[N] = \frac{\sum_{N=A}^{D} k_N}{\sum k_{\mathrm{inst}} - \sum_{N=A}^{D} k_N}([M] + \sum_{N=A}^{D}[N])e^{-\sum_{N=A}^{D} k_N t} - \frac{\sum_{N=A}^{D} k_N}{\sum k_{\mathrm{inst}} - \sum_{N=A}^{D} k_N}([M] + \sum_{N=A}^{D}[N])e^{-\sum k_{\mathrm{inst}} t} \quad (6)$$

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[5] H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.* **80**, 4979 (1958).

[6] A. Frost and R. G. Pearson "Kinetics and Mechanism," 2nd Ed., John Wiley & Sons, New York (1961), p. 166.

Assuming $\sum k_{\text{inst}} \gg \sum_{N=A}^{D} k_N$, there results:

$$\frac{\sum_{N=A}^{D}[N]}{[M]} = \frac{\sum_{N=A}^{D} k_N([M] + \sum_{N=A}^{D}[N])}{\sum k_{\text{inst}}[M]} e^{-\sum_{N=A}^{D} k_N t} \tag{7}$$

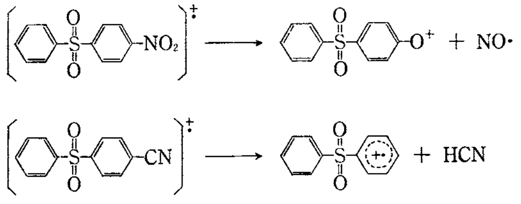
$$\ln \frac{[M] + \sum_{N=A}^{D}[N]}{[M]} = \sum_{N=A}^{D} k_N t - \ln \frac{\sum_{N=A}^{D} k_N}{\sum k_{\text{inst}}} + \ln \frac{\sum_{N=A}^{D}[N]}{[M]} \tag{8}$$

Equation (9) will be obtained if Eq. (3) is substituted for Eq. (8):

$$\ln \frac{[M] + \sum_{N=A}^{D}[N]}{[M]} = \sum_{N=A}^{D} k_N t \tag{9}$$

This situation yields Eq. (5).

As for the greater deviation from the Hammett correlation in the cases of nitro- and cyano-substituents, as Figs. 2 and 3 show, there is a very large destabilization factor of the substituents, since a large abundance of an ion, M^+–NO or M^+–HCN, was formed.



Now, we can explain the findings on the migratory aptitude shown in Table 1.

The ionization potential of sulfur is much lower than that of oxygen, and the ionization of ArSO is much easier than that of ArO; hence, ArO^+ is more sensitive to the substituent effect than $ArSO^+$, as may be seen in Table 2. Namely, the electron-donating group stabilizes ArO^+ more (preferential formation of A) than $ArSO^+$.

Thus, the increase in the migratory aptitude by the electron-donating group is attributable to the product-ion stability, though the over-all rate of bond cleavage is rather slow in the case of the electron-donating substituents, as the Hammett correlation indicates.

On the other hand, it is evident that the electron-withdrawing substituents cause a more rapid cleavage of the bond. In this case, the substituted phenyl carbon-sulfur bond will undergo a readier cleavage than the unsubstituted phenyl carbon-sulfur bond because of the effect of the substituent on the energy of the cleaved bond, for electron-withdrawing substituents destabilize the positive charge.

This may be the reason why the migratory aptitude increases with the substitution of the phenyl ring even by the electron-attracting group, because the effect of the energy of the cleaved bond overcomes the effect of the product-ion stability.

These two effects, the product-ion stability and the energy of cleaved bond, should make an important contribution to the driving force in the ion-decomposition reaction.

Experimental

The compounds used in this study were synthesized by the methods in the literature: diphenyl sulfone,[7] mp 128°C; *p*-aminodiphenyl sulfone,[8] mp 176°C; *p*-methoxydiphenyl sulfone,[9] mp 89—90.5°C; *p*-methyldiphenyl sulfone,[10] mp 124.5°C; *p*-chlorodiphenyl sulfone,[11] mp 91°C; *p*-cyanodiphenyl sulfone,[12] mp 117—118°C; *p*-nitrodiphenyl sulfone,[13] mp 140—141°C, and *p*-phenylsulfonylbenzoic acid,[14] mp 267—268°C. They contained no impurities detectable by mass spectrometry.

The spectra were recorded on a Hitachi RMU-6E single-focusing instrument with both inlet and source temperatures of 250°C.

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[7] Beilsteins "Handbuch," **EII 6**, 290 (1944).

[8] W. R. Waldron and E. E. Reid, *J. Amer. Chem. Soc.*, **45**, 2406 (1923).

[9] H. H. Szmant and G. Suld, *ibid.*, **78**, 3400 (1956).

[10] Beilsteins "Handbuch," **6**, 418 (1923).

[11] *Ibid.*, **EII 6**, 297 (1944).

[12] A. T. Fuller, I. M. Tonkin and J. Walker, *J. Chem. Soc.*, **1945**, 637.

[13] F. Ullmann and G. Pasdermadjian, *Ber.*, **34**, 1154 (1901).

[14] A. Michael and A. Adair, *ibid.*, **11**, 119 (1878).