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Mass Spectra of Phenyl *p*-Toluenesulfonates. Substituent Effect in Fragmentation

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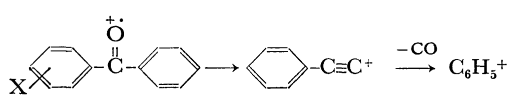
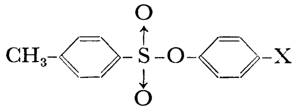
Mass spectra of substituted phenyl *p*-toluenesulfonates were analyzed with the aid of metastable peaks. Three steps in fragmentation were suggested as the main processes for these compounds *i.e.*, the initial S–O bond cleavage giving sulfonylcation, the second desulfonylation and the final loss of acetylene. Effect of substituent on the rate of the decomposition was observed in these three steps. The results are discussed in terms of various internal energies of the initial fragment ions. Apparently, the rates of the initial decomposition depend on the nature of the substituents.

Examination of mass-peak shifts by substituents is the usual method for clarifying the nature of electron impact decomposition. However, the effect of substituent on the rate of fragmentation has not been paid much attention till recently.[1] The substituent effects on the mass spectra hitherto being examined are those of acetophenones, benzophenones,[2–5] phenyl carbonates,[6,8] azobenzenes,[7] benzyl phenyl ethers,[9] dibenzyls,[10] methyl-4-phenyl butylate[11] and butyrophenones.[12] With most of these compounds, the relative peak heights (*Z*-values) of the first step of fragmentation, *i.e.*, the processes leading to the first fragment ions from the molecular ions, were nicely correlated with Hammett σ-values. In the case of substituted benzophenones, the effect of substituents was observed not only in the first step of fragmentation, *i.e.*, the formation of the benzoyl ions from the molecular ions, but also in the subsequent step, namely the decarboxylation of the benzoyl ions.[2]



Recently we have reported the mass spectra of aromatic sulfur compounds having three different S–S bonds *i. e.*, disulfides, thiol sulfinates and thiol sulfonates.[13] As an extention of our previous work, we have examined the mass spectra of the following five diaryl sulfonates (I)



(I)

(X: NO_2, Cl, H, CH_3, OCH_3)

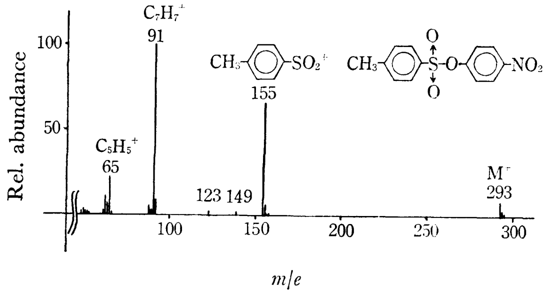
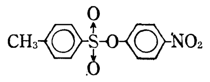


Fig. 1. The mass spectra of  in 80 eV.

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[1] M. M. Bursey, *J. Org. Mass Spectrometry*, **1**, 31 (1968).

[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).

[5] M. L. Gross and F. W. McLafferty, *Chem. Commun.*, **1968**, 254.

[6] P. Brown and C. Djerassi, *J. Amer. Chem. Soc.*, **89**, 2711 (1967).

[7] J. H. Bowie, G. E. Lewis and R. G. Cooks, *J. Chem. Soc.*, *B*, **1967**, 621.

[8] P. Brown and C. Djerassi, *Angew Chem. Intern. Ed. Engl.*, **6**, 477 (1967).

[9] P. Brown, *J. Amer. Chem. Soc.*, **90**, 2694 (1968).

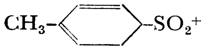
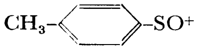
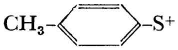
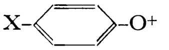
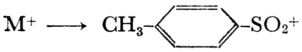
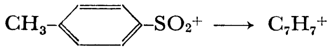
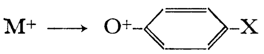
[10] F. W. McLafferty and M. M. Bursey, *ibid.*, **90**, 5299 (1968).

[11] D. G. I. Kingston and H. P. Tannenbaum, *Chem. Commun.* **1968**, 444.

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

[13] S. Kozuka, H. Takahashi and S. Oae, This Bulletin, **43**, 129 (1970).

TABLE 1. RELATIVE INTENSITIES (80 eV)

Ion	Compd.				
	NO_2	Cl	H	CH_3	OCH_3
M^+	8.5	13.5	25.0	27	15.5
	66	37.8	53.5	52	1.8
	1.7	1.2	1.7	1.5	0.4
	1.9	—	1.1	—	—
$C_7H_7^+$	100	100	100	100	11.5
$C_5H_5^+$	21.5	22	28	16.6	8.7
	—	2.5	—	19.0	100
metastableble peak					
	○*	○	○	○	○
	○	○	○	○	○
$C_7H_7^+ \longrightarrow C_5H_5^+$	○	○	○	○	○
	—	—	—	—	○

* ○: metastable peak present

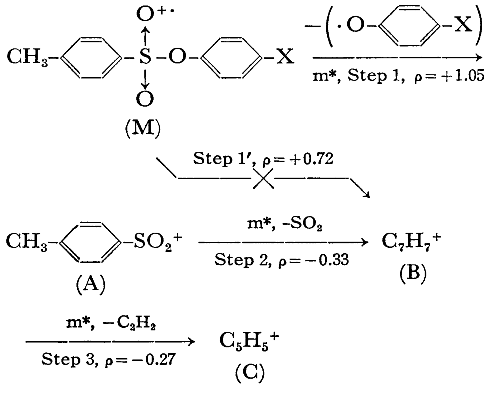
and found that the effects of substituents are clearly observed not only in the first step of the decomposition of the molecular ion but also in the second and third steps of fragmentation. In this paper, we wish to report the fragmentation scheme of diaryl sulfonates, the correlation of the decomposition rate with substituents and the energy states of the particular fragment ions.

Fragmentation. Five *p*-substituted phenyl *p*-toluenesulfonates were analyzed. An example of the mass spectrum is shown in Fig. 1. The intense peaks and metastable peaks of these compounds observed in their mass spectra are listed in Table 1.

All the compounds gave distinct molecular ions, and the subsequent fragment ions were formed by the loss of the phenoxy radicals from the molecular ions. Base peaks of most of these compounds appeared at the mass number of 91 which corresponds to tropylium ion.[9,10,14-17] However, in the case of *p*-methoxyphenyl toluenesulfonate, phenoxy cation was the base peak. This difference may be ascribed to the strong electron-releasing nature of the substituent, *i. e.*, methoxy group. Thus, the cleavage of the S-O bond of the molecular ion leaving a cationic center on the sulfur atom is less favored in the methoxy substituted compound and the heterolytic decomposition giving phenoxy cation would become the predominant process. This observation is in good accord with the previous observation of the mass fragmentation patterns of mono-substituted benzophenones in which similar two competing processes were suggested.[5]

All the patterns shown in Table 1 are similar to those of the thiol sulfonates.[13] A noticeable but minor difference may be the absence of oxygen migration which was presumed to occur from the sulfonyl sulfur to the sulfenyl sulfur atom at the initial stage of fragmentation of the thiol analogues.[13] The major fragmentation scheme suggested for the thiol sulfonates is applicable to the present compounds.

Substituent Effect. The relative peak heights



Scheme 1

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[14] F. W. McLafferty "Mass Spectrometry of Organic Ions," Academic Press, New York and London (1963), p. 488—506.

[15] J. M. S. Tait, T. W. Shannon and A. G. Harrison, *J. Amer. Chem. Soc.*, **84**, 5 (1962).

[16] S. Meyerson, H. Hart and L. C. Leitch, *ibid.*, **90**, 3419 (1968).

[17] P. Brown, *ibid.*, **90**, 4461 (1968).

in mass spectra seem to be related to the rate of the decomposition.[1-5,18,19] The Hammett plots of the relative intensities of the peak heights corresponding to steps 1, 2 and 3 against σ^+ values are shown in Fig. 2. The ρ value of the individual steps calculated by the least square method is also given in Scheme 1.

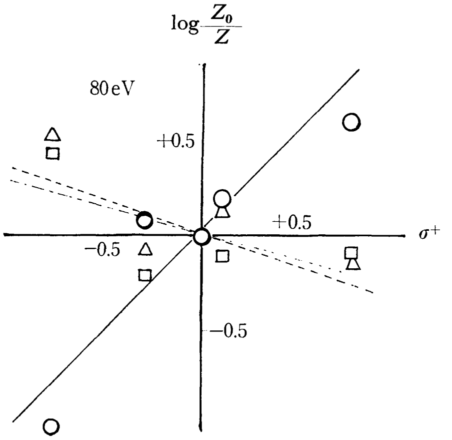

Fig. 2. Correlation of the relative intensities of the ions M^+, A^+, B^+ and C^+ with Hammett σ^+ constant (80 eV).

—○—○—: $Z=\frac{A}{M}$ (step 1)

--△--△--: $Z=\frac{B}{A}$ (step 2)

-·□-·□-·: $Z=\frac{C}{B}$ (step 3)

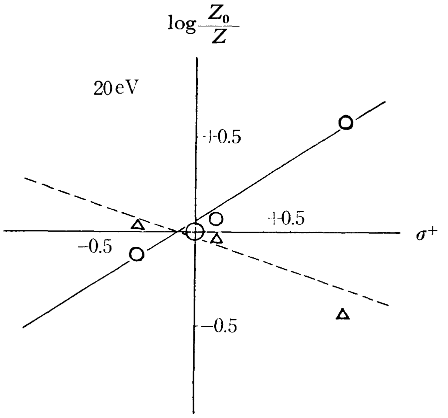

Fig. 3. Correlation of the relative intensities of the ions M^+, A^+ and B^+ with Hammett σ^+ constant (20 eV).

—○—○—: $Z=\frac{A}{M}$ --△--△--: $Z=\frac{B}{A}$

The substituent effects hitherto reported in mass spectra have been correlated with σ values. However, in this particular case, a better correlation was attained with σ^+ values.

The low electron voltage mass spectroscopic determination was usually employed for obtaining a good Hammett plot in order to avoid various decompositions.[4] In this study, we have also examined the mass spectra of the compounds at 20 eV. The results are shown in Fig 3.

In this case, the decomposition of step 3 disappeared completely in all the compounds. The formation of the phenoxy cation in the methoxy compounds was observed more markedly since the formation of ions A and B was too small to be observed. Thus, the data obtained by 80 eV mass spectrometry will be discussed.

The effect of substituents observed at the first step of the decomposition is in good accord with electrostatic consideration. The electron-withdrawing substituent is expected to accelerate step 1 decomposition while the electron-donating substituent such as methoxy group retards the reaction accompanied by the fragmentation through the heterolysis of opposite orientation. The following considerations might help to explain the effect observed at the processes (steps 2 and 3) which do not actually deal with the fragment ions bearing substituents of the precursor ions.

One explanation is to assume the direct process leading to the fragment B from the molecular ion by the C–S bond fission or the concerted two bond fission. The stepwise reaction shown in Scheme 1 could not be neglected because of the existence of the metastable peaks. Thus the two competing processes must be included. The ρ-value obtained from the relative peak heights of the molecular ions and the ion B in the presumed direct process of step 1′ ($\rho=+0.72$) is identical with that of the sum of the ρ-values of steps 1 and 2. (+0.72). The hypothesis involving two competing processes is not in conflict with the additivity of the ρ-values. Therefore, the direct process from M to B is ruled out.

The only plausible explanation is to apply the statistical theory of mass spectra to the present system as was applied to the spectra of substituted benzophenones by Gross and McLafferty.[5] The two competing processes of the decomposition of the molecular ion in the series of substituted phenyl *p*-toluenesulfonates are the formation of *m/e* 155 $R\text{–}SO_2^+$ ion and substituted phenoxy cation. The pathway requiring less activation energy is the formation of the $R\text{–}SO_2^+$ ion when the substituent is electron-withdrawing group. The $R\text{–}SO_2^+$ ion thus formed would be recoiled with a less excess internal energy to accelerate the subsequent decomposition. When the substituent is an electron-donating group, the favored path gives rise to the formation of phenoxy cation. In this case, the

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[18] I. Howe and D. H. Williams, *J. Chem. Soc., B*, **1968**, 1213.

[19] H. Budzikiewicz, C. Djerassi and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, Inc., San Francisco, Cambridge, London, and Amsterdam (1967), pp. 33—37.

$R{-}SO_2^+$ ion formed in the minor path would be endowed with a larger internal energy, and the rate of the subsequent step (step 2) would be more accelerated than that of aryl *p*-toluenesulfonates having electron-withdrawing groups.

The positive and negative ρ-values of the first and the second steps of the decompositions are now rationalized. It is interesting to note that the absolute ρ-values decrease gradually (1.05→0.33→0.27). The deviation of the rate of the second step with the variation of substituents is ascribed to the various rates of the first step of decomposition. The negative ρ-value may result from the consumption of the excess energy of the $R{-}SO_2^+$ ion formed in the first step of fragmentation. If the consumption of the excess energy is enough, the ρ-value of the second step may have a magnitude similar to that of the first step but with opposite sign. If the excess internal energy of the $R{-}SO_2^+$ ion is retained even after the second step, the energy would be consumed by further decomposition processes. The magnitude of the absolute ρ-value of the second step would be smaller than that of the first step, and the ρ-value of the third and forth steps, if any, must have the same sign as that of the second step. The size of the ρ-values of these succeeding steps is considered to decrease to zero until any excess energy formed by the initial step completely disappears. The rates of the decomposition of the fragment ions A and B are influenced by the difference of the activation energies of the first step which depends on the substituent of the molecular ion.

In this connection, the result observed would suggest that the difference of the recoiled energy with the variation of the substituents is retained in the fragment ion even after step 3. The retained energy would be consumed by the succeeding fragmentation. Unfortunately, no clear fragmentation of ion C was observed except for a very small amount of loss of acetylene. However, the peak corresponding to $C_3H_3^+$ was too small to make any sensible plot of the fourth step.

The effect of substituent at the second and third steps of ion-fragmentations in mass spectroscopy is now being tested with other systems.

Experimental

The spectra were recorded with a Hitachi RMU-6E single focus mass spectrometer using 80 eV at the emission current 110 μA. Samples were introduced through an all glass inlet system kept at about 200°C.

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