NOTES

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Mass Spectra of Phenyl *p*-Toluates and Toluanilides Substituent Effect in Fragmentation. II

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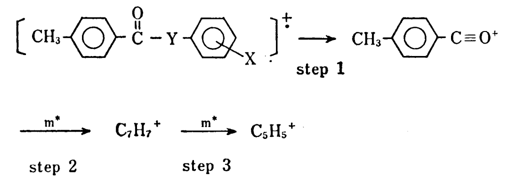
The effect of substituent on mass spectra has been investigated considerably in recent years. In our previous work,[1] the Hammett correlation was observed in the three steps of fragmentation of *p*-substituted phenyl-*p*-toluenesulfonates; a positive ρ-value for the initial step and negative ρ-values for the succeeding two steps. We have extended our study to two classes of compounds, phenyl-*p*-toluates and toluanilides, since the fragmentation is considered to be similar to that of the sulfonates.

As expected, their mass spectra show the following similar three fragmentation steps.



Y=O X: *p*-NO$_2$ *m*-NO$_2$, *p*-Cl, H, *m*-CH$_3$, *p*-CH$_3$, *p*-OCH$_3$, *p*-CN
Y=NH X: *p*-NO$_2$, *m*-NO$_2$, *p*-Cl, H, *m*-CH$_3$, *p*-CH$_3$, *p*-OCH$_3$

The relative peak heights (Z-value) of the fragmentation of these compounds are nicely correlated with the Hammett constants as shown in Figs. 1 and 2.

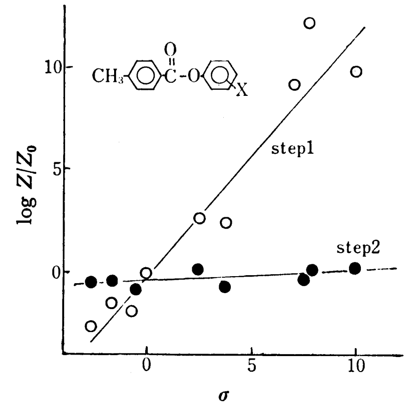


Fig. 1. Hammett plot of the relative peak height obtained in the fragmentation of phenyl *p*-toluates.

The positive ρ-values of the first steps of fragmentation are reasonable. However, no noticeable effect of substituent was found in the second and third steps unlike the case of sulfonates where negative ρ-values were obtained in the suceeding steps.

A possible rationale is that the internal energies resulting from various activation energies of the decompositions of these compounds with different substituents were retained not in the fragment ions but in the leaving groups that depart from the molecular ions, and all acylinium ions resulting from different molecular ions would retain nearly identical internal energies and give rise to no substituent effect in the succeeding steps.

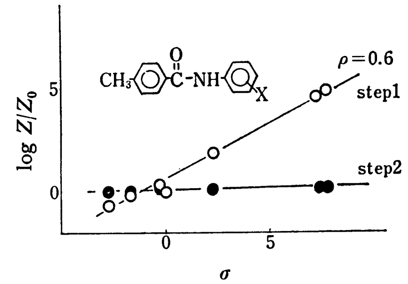


Fig. 2. Hammett plot of the relative peak height obtained in the fragmentation of *p*-toluanilide.

Another possibility is derived from the assumption that the parent and acylinium ions are formed from a common intermediate (super-excited state) as accepted in the usual treatment of fragmentation in terms of molecular orbital theory.[2] If this is the case, the observed substituent effect at the initial step could derived from the two competing reactions, leading to the parent ion and acylinium ion. At present, we have no definite evidence to make a choice between the two possibilities.

It is worthy to note that the acylinium ion formed

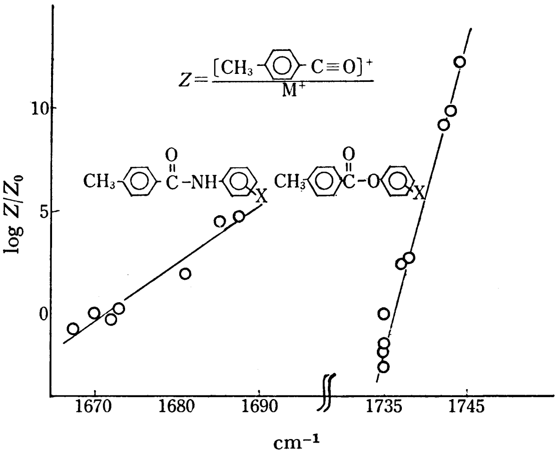


Fig. 3. The plot of the *Z*-values of the initial fragmentations of those compounds against carbonyl streching frequency.

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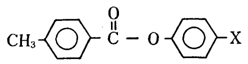
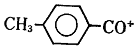
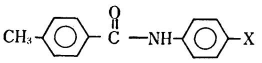
[1] Paper I of this series, S. Kozuka, H. Takahashi, S. Tamagaki, and S. Oae, This Bulletin, **43**, 1408 (1970).

[2] K. Hirota, *Nippon Kagaku Zasshi*, **89**, 327 (1968).

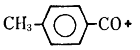
Table 1. Relative abundance of major peaks of phenyl p-toluates and toluanilides



X	M+		$C_7H_7^+$	$C_5H_5^+$
p-No$_2$	0.3	100	36.4	16.7
m-No$_2$	0.5	100	34.6	14.7
m-Cl	2.4	100	35.7	17.4
p-Cl	2.2	100	37.8	19.2
H	4.1	100	36.3	18.1
m-CH$_3$	6.5	100	32.0	15.7
p-CH$_3$	5.8	100	30.4	13.8
p-oCH$_3$	7.5	100	31.5	14.1
p-CN	0.4	100	38.9	19.8



(80eV)

X	M+		$C_7H_7^+$	$C_5H_5^+$
p-No$_2$	8.5	100	30.0	10.0
m-No$_2$	9.2	100	29.0	9.2
p-Cl	16.4	100	29.9	10.4
H	25.6	100	28.5	11.3
m-CH$_3$	24.4	100	28.2	10.3
p-CH$_3$	27.1	100	28.4	9.5
p-oCH$_3$	30.1	100	28.6	8.6

from the ester undergoes more facile decomposition than that derived from the anilide (Table 1). This suggests that the acylinium ions derived from different molecules would retain different internal energies even in the individual fragmentation of those compounds which show no noticeable effect of substituent in the succeeding steps.

The difference of ρ-values observed for the esters and anilides can be ascribed to the difference of bond strengths. As shown in Fig. 3, the deviation of the carboxyl stretching frequency with various substituents is apparently smaller with the esters than with the anilides. This suggests that the effect of substituent is more enhanced in the strength of C–O bond of the ester than that in the C–N bond of the anilide. A similar effect has also been observed in the usual reactions such as alkaline hydrolyses.[3,4]

Experimental

Mass spectra were recorded with a Hitachi RMU-6E single forcus spectrometer. The spectra are shown in Table 1. Infrared spectra were obtained in chloroform solution with 1 mm NaCl cell using JASCO IR-G.

3) M. L. Bender and R. J. Thomas, *J. Amer. Chem. Soc.*, **83**, 4183 (1961).

4) E. Tommila and C. N. Hinihelwood, *J. Chem. Soc.*, **1938,** 1801.