Effect of substituent on the mass spectra of substituted n-phenyl maleimide-multiple linear correlation analysis

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ABSTRACT

Several substituted N-Phenyl maleimide were prepared and their mass spectra in EI mode were recorded. The effects of substituents on the mass spectral fragmentation of compounds under investigation are interpreted by correlating log Z/Z_0 with simple and extended Hammett equations. The log Z/Z_0 values in all the cases were subjected to multiple linear regression analysis using two sets of biparametric equations (Taft and Swain equations). The results of the multiple linear regression analysis are found to be good in the cases.

Introduction

A mass spectrum represents a distribution of products of electron impact ionization of a gaseous molecule; the amount of product is plotted against its mass to charge ratio (m/z); ionic products only being analyzed and detected. The principle fragmentations undergone by the molecular ions are those which give rise to the most stable carbonium ions, radicals or neutral molecules. The introduction of substituents is likely to affect the stabilities of the molecular ion and of the daughter ion or on the fragmentation products. The intensity of a given product ion depends not only in the rate at which it is formed but also on the rate at which it is decomposed (quasi-equilibrium theory). Also, when a molecular ion can undergo a number of parallel fragmentation reactions, the intensities of the ions produced in one of these will be influenced by the rate of all competing processes. Energy quantities associated with mass spectra i.e. ionization potentials; have also been correlated with substituent constants[1-4]. Some relationship of intensities to suitable substituent constants might be hoped for and has been found[4-12].Substituents effects on the abundance of key rearrangement ions were also reported and the data demonstrate quantitatively that the product ion stability governs rates of mass spectral decomposition reactions, as has been suggested before[13], in agreement with the arguments advanced for solution chemistry[14,15].Keeping in view of this we planned to investigate the effect of substituent on mass spectra of N-Phenyl maleimde.

Experimental section

All the reported melting points were taken in open capillaries and are uncorrected (Table.1). In all the cases, the progress of the reaction is monitored by TLC method, which revealed that the reactions were proceeding smoothly in the expected pathway. Mass spectra were recorded on Varian GC/mS# in using methanol as solvent

## General procedure for the preparation of N- Phenyl Maleamide

A mixture m *Maleic anhydride and* substituted *aniline* in 200 ml of *ether* was stirred and the resulting thick suspension was stirred at room temperature for 1 hr and then cooled to 15-20° in an ice bath. The product obtained was a fine, cream-colored powder.

The maleanilic acid obtained as described above was refluxed with acetic anhydride in presence of sodium acetate and the resulting suspension was dissolved by swirling and heating on a steam bath for 30 minutes. The reaction mixture was then poured into ice water. The precipitated product was filtered, and recrystallized from *cyclohexane.*

Results and Discussion

The 70ev mass spectra of the unsubstituted and substituted N-phenylmaleimide were recorded. The fragmentation pattern for the substituted N-phenylmalemide is given in scheme-1 and fragments like [CH=CH-CONPh]+, [CONPh]+, $C_6H_5N^+$, $C_6H_5^+$ and $C_5H_4^+$ are selected for correlation analysis in the present study. From the spectra, it has also been observed that all these compounds gave a stable molecular ion peak. The intensities of the above selected fragment and the molecular ion peak M+ for the substituted N-phenylmaleimide and the intensities of M+, and the fragment ions are given in Table 1.

Scheme 1
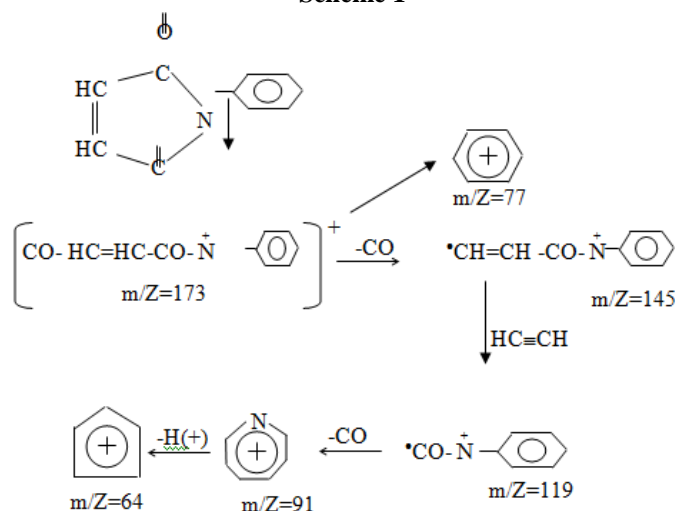
The log Z/Z_0 values of the fragments for the meta and para substituted N-phenylmaleimides (Z_1, Z_2, Z_3, Z_4, Z_5) were calculated using the following expressions and are given in Table 2.

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$$Z_1 = \log \left[\frac{[CH=CH-\overset{\overset{O}{\|}}{C}-N-Ph]_X^+ /[M^+]_X}{[CH=CH-\overset{\overset{O}{\|}}{C}-N-Ph]_H^+ /[M^+]_H} \right] \quad \dots \dots (1)$$

$$Z_2 = \log \left[\frac{[CONPh]_X^+ /[M^+]_X}{[NCOPh]_H^+ /[M^+]_H} \right] \quad \dots \dots (2)$$

$$Z_3 = \log \left[\frac{[C_5H_5N^+]_X /[M^+]_X}{[C_6H_5 \overset{+}{N}]_H /[M^+]_H} \right] \quad \dots \dots (3)$$

$$Z_4 = \log \left[\frac{[C_5H_4]_X^+ /[M^+]_X}{[C_5H_4]_H^+ /[M^+]_H} \right] \quad \dots \dots (4)$$

$$Z_5 = \log \left[\frac{[C_6H_5]_X^+ /[M^+]_X}{[C_6H_5]^+ /[M^+]_H} \right] \quad \dots \dots (5)$$

When log Z/Z_0 values of the fragments –CH=CH CONC$_6$H$_5$ for the substituted N-phenylmaleimide (Z_1) are subjected to linear regression analysis using the equation 6 [Fig.1] a good correlation is obtained.

$$Z_1 = \rho\sigma + h \quad \dots \dots (6)$$

$Z_{1=} 1.4635 \ \sigma + 0.633$

r = 0.06   n = 9   SD = 0.14

The successful correlation of mass spectral data with substituent constant is the result of complex interplay of large number of factors, which can reasonably be expected to correlate with constants for outweigh those for which no correlation can be expected.
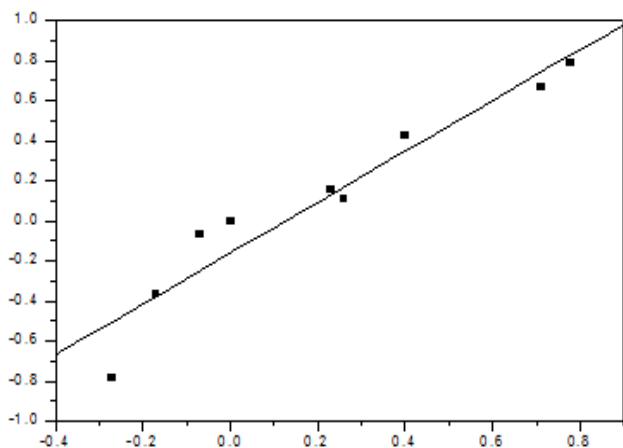
To study quantitatively the extent of operation of inductive, and resonance effects, the multiple regression analysis has also carried out using Taft's σ_I & σ_R and Swain *et al*. F and R equations. The results are given in Table 3 and the results clearly show an excellent correlation for the Taft's σ_I & σ_R parameters.

To get an insight into the extent of operation of localized and delocalized effects in the mass spectral data belonging to the fragment –CH=CH-$\overset{\overset{O}{\|}}{C}$- N-Ph ($Z_1$) of substituted N-phenylmaleimide, multiple regression analysis has been carried out using two sets of independent variables i.e., σ_I, σ_R and F & R and the result are given in Table.4.
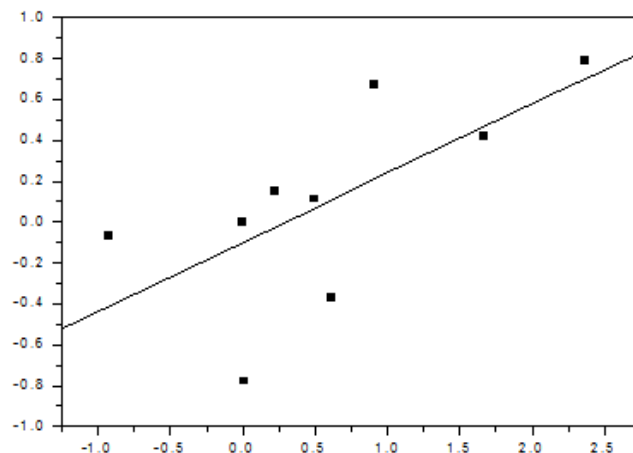

Fig. 3 The plot of Z_3 of N-phenylmaleimide Vs σ

Fig. 1 The plot of Z_1 of N-phenylmaleimide Vs σ

Fig. 4 The plot of Z_4 of N-phenylmaleimide Vs σ

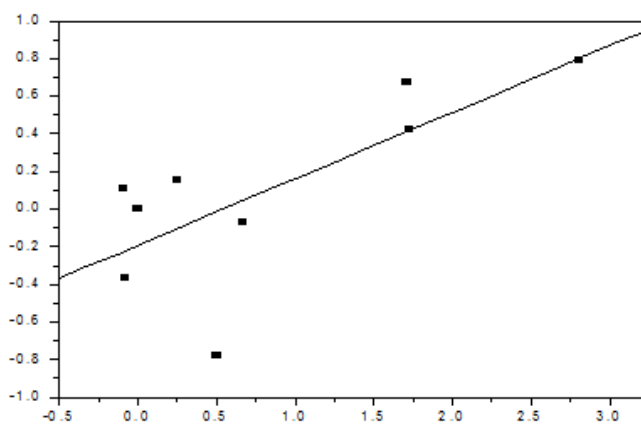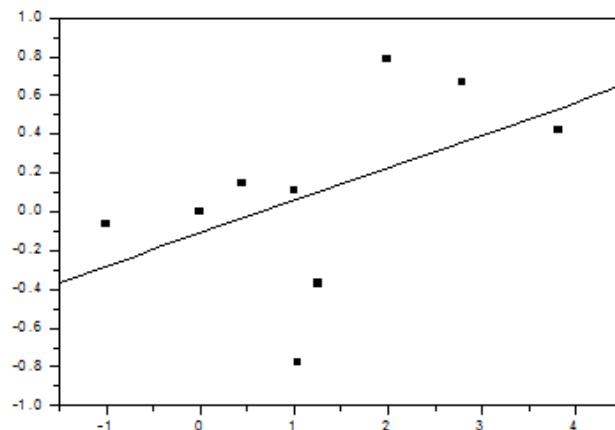**Fig. 2 The plot of Z_2 of N-phenylmaleimide Vs σ**

Fig. 5 The plot of Z_5 of N-phenylmaleimide Vs σ

The results of the analysis also show only fair correlation for σ_I, σ_R parameters. All the coefficients are positive with low standard errors and their magnitude show the predominant spectrum of resonance effect over inductive effects.
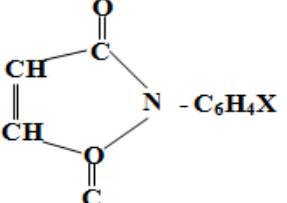
Table 1

S. No.	$N - C_6H_4X$	Melting point (°C)
1.	H	87
2.	P-Br	125
3.	P-CH$_3$	153
4.	M-NO$_2$	124
5.	P- OCH$_3$	152
6.	P-NO$_2$	208
7.	P-COOH	225
8.	m-CH$_3$	122
9.	P-Cl	113

Table 2. Mass spectral relative intensities of M^+ and fragment ions
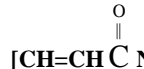
S. No.	Substituents	Relative intensities of					
		M^+	$[CH=CH\overset{O}{\overset{\|}{C}}NPh]^+$	$[\overset{O}{\overset{\|}{C}}NPh]^+$	$C_6H_5N^+$	$C_5H_4^+$	$C_6H_5^+$
1.	H	100	4.86	4.15	9.81	9.96	5.35
2.	P-Br	10.9	1.55	0.75	1.78	7.49	1.65
3.	P-CH$_3$	13.5	1.25	0.55	5.4	1.3	13.47
4.	m-NO$_2$	1.80	11.14	0.14	1.44	9.0	60.66
5.	P-OCH$_3$	12.2	0.38	0.695	1.26	3.8	7.20
6.	P-NO$_2$	0.17	0.085	0.29	4.0	10.7	0.89
7.	P-COOH	0.26	4.19	1.2	1.2	1.35	92.41
8.	m-CH$_3$	14.41	0.065	0.21	4.5	1.14	7.84
9.	P-Cl	13.13	3.99	0.065	0.16	6.0	0.070

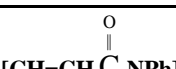**Table 3. The values of log Z/Z_0 of the selected ions for substituted N-phenylmaleimide**

S. No.	Substituents	log Z/Z_0 of				
		$[CH=CH\overset{O}{\overset{\|}{C}}NPh]^+$	$[\overset{O}{\overset{\|}{C}}NPh]^+$	$C_6H_5N^+$	$C_5H_4^+$	$C_6H_5^+$
1.	H	0.	0	0	0	0
2.	ρ-Bs	0.45	0.24	0.22	0.85	0.44
3.	P-CH$_3$	0.27	-0.013	0.61	-0.08	1.26
4.	m-NO$_2$	2.09	0.26	0.91	1.71	2.79
5.	P-OCH$_3$	0.5	0.13	0.013	0.502	1.04
6.	P-NO$_2$	1	1.66	2.37	2.81	1.99
7.	P-COOH	2.56	1.56	1.69	1.73	3.81
8.	m-CH$_3$	-0.045	-0.47	0.5	-0.092	1.00
9.	P-Cl	0.78	-0.93	-0.92	0.668	-1.00

Table 4. Correlation equation with σ_I σ_R and F & R

Fragment	Correlation equation	Substituent
$[CONPh]^+$	$Z_2 = 0.208 +0.682\sigma_I+2.217\sigma_R$ R = 0.651 SE = 0.73 n = 9	X = H, p –Br, *p*-Cl, *p*-OCH$_3$, *m*-CH$_3$, *m*-NO$_2$, *p*-NO$_2$, *p*-CH$_3$ *p*-COOH
	$Z_2 = 0.149 +0.258F+0.495R$ R = 0.566 SE = 0.80 n = 9	

Table 5. Correlation equation with σ_I σ_R and F & R

Fragment	Correlation equation	Substituent
$C_6H_5N^+$	$Z_3 = 0.716 +0.382 \sigma_I+3.304\sigma_R$ R = 0.737 SE = 0.76 n = 9	X = H, p –Br, *p*-Cl, *p*-OCH$_3$, *m*-CH$_3$, *m*-NO$_2$, *p*-NO$_2$, *p*-CH$_3$ *p*-COOH
	$Z_3 = 0.631 -2.59F+0.753R$ R = 0.648 SE = 0.85 n = 9	

Table 6. Correlation equation with σ_I σ_R and F & R

Fragment	Correlation equation	Substituent
$C_5H_4^+$	$Z_4 = 0.231 + 2.571 \sigma_I + 1.858 \sigma_R$ R = 0.926 SE = 0.44 n = 9 $Z_4 = 0.185 + 1.493F + 0.528R$ R = 0.907 SE = 0.49 n = 9	X = H, p –Br, *p*-Cl, *p*-OCH$_3$, *m*-CH$_3$, *m*-NO$_2$, *p*-NO$_2$, *p*-CH$_3$ *p*-COOH

Table 7 . Correlation equation with σ_I σ_R and F & R

Fragment	Correlation equation	Substituent
$C_6H_5^+$	$Z_5 = 1.438 + 0.424 \sigma_I + 4.315 \sigma_R$ R = 0.637 SE = 1.29 n = 9 $Z_5 = 1.303 - 3.729 F + 0.908R$ R = 0.522 SE = 1.43 n = 9	X = H, p –Br, *p*-Cl, *p*-OCH$_3$, *m*-CH$_3$, *m*-NO$_2$, *p*-NO$_2$, *p*-CH$_3$ *p*-COOH

From the above regression analysis it is inferred that as far as the present system is concerted the dependent variable (the intensity of the mass spectral fragments) are correlating well with Taft's σ_I, σ_R parameters, which in two indicate the cleavage of mass spectral fragments are predominantly controlled by resonance and inductive effects.

When the Z_2 values of the fragment (+CO-N-Ph) are correlated against σ constants a linear plot is obtained with fairly good correlation (Fig.2}.

$Z_2 = 1.24\sigma + 0.004$

R = 0.70;   n = 9;   SD = 0.44

The results of the multiple regression analysis for Z_2 along with statistical parameters are given in Table 5. Taft's parameters show only a fair correlation with significant F test value.

The magnitude of ρ_I is less than that of ρ_R. The percentage of resonance character contributing to the polar effect has been found to be 76.47. When the Z_3 values of the fragment $(C_6H_5 \overset{+}{N})$ are correlated against σ constants a fairly good correlation is obtained. But the correlation is well improved when the m-CH$_3$ substituent is excluded (Fig.3).

$Z_3 = (2.13)\ \sigma + (0.45)$

R = 0.90;   n = 8;   SD = 0.39

From the results of the multiple regression analysis it is clear that the resonance effect operates predominantly over the inductive effect.

The linear regression analysis of the log Z/Z_0 values of the fragement $(C_5H_4^+)$ against Hammett σ constant (Fig.4) shows good correlation and the results are given below:

$Z_4 = 2.56\sigma + 0.34$; r = 0.93; n = 9; SD = 0.35

The results of the multiple regression analysis for the Z_4 ion along with statistical parameter are given in Table 6. The results show that the Taft's σ_I σ_R parameter shows an excellent correlation with high F test value. All the co-efficients are positive with low standard error.

From the above regression analysis it is inferred that as far as the present system is concerned the dependent variables are correlating well with Taft's σ_I σ_R parameter which in turn indicates that the cleavage of mass spectral fragments are predominantly controlled by resonance and inductive effect.

When the log Z/Z_0 (Z_5) values of the fragment $(C_6H_5^+)$ are correlated against σ constant a linear plot is obtained with a poor correlation (Fig.5).Table.7.

$Z_5 = 2.61\sigma + 0.61$;   r = 0.60;   n = 9;   SD = 0.45

It is worthwhile to seek the extent of operation of localized and delocalized effects in the mass spectral data belonging ρ

fragment $C_6H_5^+$. So the multiple regression analysis carried out using Taft's σ_I σ_R and Swan's F & R parameters.

In this case also the ρ_I value is less than that of ρ_R the percentage of resonance character constituents has been found to be 91 providing that resonance effect operates exclusively only there is a slight contribution from molecular effect.

Conclusion

The EI mass spectra of the substituted N-phenyl maleimdes were recorded. The log Z/Z_0 values were calculated for specific fragments was correlated against Hammett σ values for substituted N-phenylmaleimide and good correlation is obtained in most of the cases. To quantify the extent of operation of inductive and resonance effects the log Z/Z_0 values in all the cases were subjected to multiple linear regression analysis using two sets of biparametric equations. Except in few cases the results of multiple linear regression analysis in all the cases show good correlation.

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