Correlation Between Polarizability Substituent Effects and Mass Displacements of Gaseous Organic Ions Determined by an Ion Trap

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A linear relationship has been found between mass displacements, representing a direct measure of the polarizability, and the polarizability substituent effects in ion trap experiments.

Primary substituent effects can potentially have four kinds of additive contributions: arising from the field (F), the polarizability (P), the resonance (R) and the electronegativity (χ) effects.[1] For example, the gas-phase substituent acidity effects expressed, as $-\Delta\Delta G°$ values, follow the sum of the product functions for three (F,P,R) of the four kinds of contributions,[2] eqn. (1). Linear regression analysis with eqn. (1) has been utilized

$$-\Delta\Delta G°_{(g)} = \sigma_\alpha\rho_\alpha + \sigma_F\rho_F + \sigma_P\rho_P \qquad (1)$$

and the requirement of non-colinearity between the independent substituent parameters σ_α, σ_F and σ_R, corresponding to P, F and R effects, has been imposed.[2]

Stabilization due to substituent polarizability was first suggested by Brauman *et al.*[3] and these effects are of particular significance when gas-phase ions and highly polarizable alkyl substituents are involved.

The calculated directional electrostatic polarization potentials (PP) provide a definition of a substituent polarizability parameter scale,[1,4] symbolized as σ_α. Excellent linear trends have been obtained for non-conjugated alkyl substituents between the relative gas-phase acidities plotted with respect to the corresponding σ_α values.[4]

When an ion trap is used for mass analysis of gaseous ions, mass displacements with respect to the expected instrumental values are often encountered.[5] It has been observed that these mass shifts increase when the mass of the ion and/or the electron-withdrawing strength of the substituents on the molecule are increased. The phenomenon is not related to instrumental factors, space-charge effects or ion–molecule gas-phase interactions,[6] but it has been interpreted as the result of an interaction between the trapped ions and the radiofrequency electric field present within the ion trap.[5] The result of this interaction leads to a small, but detectable, power consumption of the radiofrequency field, experimentally evidenced as a displacement in the position of the mass peaks. The chemico-physical property directly involved in this interaction is the polarization and, consequently, from mass displacements the polarizability of gaseous ions can be evaluated.[5]

In actual practice, the polarizability refers to the optical frequency range, where only electrons can follow the alternations of the electric field.[7] In the radiofrequency region characteristic of ion traps, however, the total polarizability is the sum of several frequency-dependent contributions: electronic, dipolar and ionic.[7] In the gas-phase the ionic component is negligible and the total polarizability reduces to the electronic component for molecules not possessing permanent dipoles. If this assumption is valid, for analytes like alkylbenzenes or alkylpyridines, a linear dependence should be expected between the mass displacements *i.e.* the polarizability, and the σ_α scale for substituent polarizability, in the form of free energy relationship, eqn. (2), where δ_m represents the experimentally measured mass displacement for an alkyl substituted benzene or pyridine molecular cation and $\delta_m{}^0$ is the mass displacement of benzene or pyridine molecular cations.

$$\log \delta_m/\delta_m{}^0 = \sigma_\alpha\rho_\alpha \qquad (2)$$

Fig. 1 shows the good linear correlation (corr. coeff. 0.99) obtained both with alkylbenzenes and alkylpyridines of increasing linear chain. The pertinent results are collected in Table 1.

The observed variation of the mass displacements with the calculated σ_α scale reflects on several aspects of this problem.

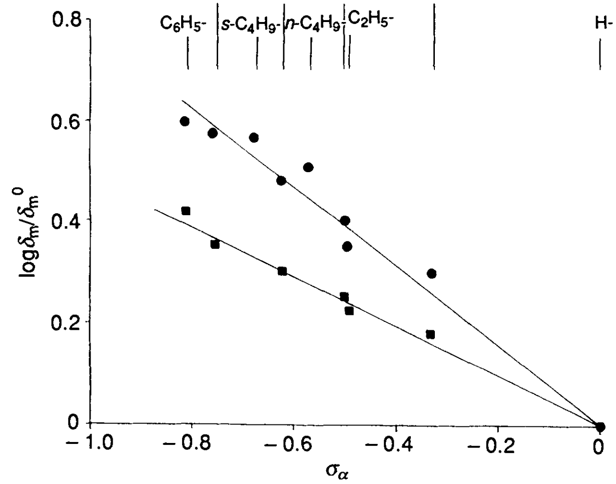

Fig. 1 Mass displacements δ_m plotted with respect to polarizability substituent effects σ_α: (●) $[\text{Y-C}_6\text{H}_5]^{\cdot+}$, (■) $[\textit{para}\text{-Y-C}_5\text{H}_4\text{N}]^{\cdot+}$. The Y substituents are indicated.

Table 1 Mass displacements[a] δ_m and σ_α substituent parameters[b] for a set of alkylbenzene and *para*-alkylpyridine molecular cations

Substituent	σ_α	$[\text{C}_6\text{H}_5\text{-Y}]^{\cdot+}$ δ_m(Da)	$[\textit{para}\text{-Y-C}_5\text{H}_4\text{N}]^{\cdot+}$ δ_m(Da)
H	0	0.04 ± 0.02	0.09 ± 0.02
CH_3	−0.35	0.08	0.14
CH_3CH_2	−0.49	0.09	0.15
$CH_2{=}CH$	−0.50	0.10	0.16
i-C_3H_7	−0.62	0.12	0.18
C_4H_9	−0.57	0.13	—
s-C_4H_9	−0.68	0.15	—
t-C_4H_9	−0.75	0.15	0.20
C_6H_5	−0.81	0.16	0.24

[a] For experimental details see ref. 5. [b] Values from ref. 1.

From one side it is an additional support for the origin of mass displacement as the result of an interaction between the ion and the radiofrequency field and to the involvement of polarizability in this phenomenon. In addition, the linearity shown in Fig. 1 is supportive of the fact that substituent parameter effects may be reasonably employed also in the case of radical cations.[1,8] The final consideration is based on the different slopes (ρ_α values) obtained with alkylbenzenes and alkylpyridines, -0.74 and -0.49, respectively. As pointed out in a previous paragraph, an apparent increase of the mass displacement is usually observed as the mass of the ion is increased. Taking into account that alkylbenzenes and alkylpyridines, bearing the same substituent, differ only by one mass unit and that the ρ_α value represents the susceptibility (or reaction) constant of the process,* these results prove that the proper mass of the ion is not a determining factor in mass displacements.

The extension of this approach to ions possessing field, resonance and electronegativity effects is currently in progress.

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* The ρ_α sign is negative since the neutral substrate is changed to cationic.

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