Linear Correlations Between the Ionization Potentials of Molecules and Changes in Ionization Potentials by Alkyl Groups

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Summary For ionization from a particular type of orbital, the difference between the ionization potential of a molecule, HX, and its homologue, MeX, is linearly related to the ionization potential of HX.

FOR a variety of molecules, RX, plots of ionization potentials *vs.* the Taft inductive (σ_I) or polar (σ^*) substituent constants are linear or nearly so.[1] These observations have led to the suggestion that alkyl groups stabilize radical cations, $RX^{\cdot +}$, by an inductive mechanism,[1b,c] and the effectiveness of transmission of inductive stabilization depends on the proximity of the alkyl substituent to the locus of positive charge in the radical cation.[1c]

However, as shown in the Figure, the difference $[\Delta I_V(Me)]$ between the vertical ionization potential (I_V) of a molecule, HX, and that of its methyl homologue, MeX, appears to be mainly a function of the I_V of the molecule HX, and of the type of orbital involved in ionization. Linear regression analyses of the points in the Figure yield the correlations given in equations (1)—(4) (correlation coefficients are given in parentheses).

All points: $\Delta I_V(Me) = 0{\cdot}28 I_V - 2{\cdot}10 \; (r = 0{\cdot}85)$ (1)

$n(\pi)$ ionizations: $\Delta I_V(Me) = 0{\cdot}34 I_V - 2{\cdot}63 \; (r = 0{\cdot}97)$ (2)

π ionizations: $\Delta I_V(Me) = 0{\cdot}26 I_V - 1{\cdot}94 \; (r = 0{\cdot}98)$ (3)

$n(\sigma)$ ionizations: $\Delta I_V(Me) = 0{\cdot}08 I_V - 0{\cdot}29 \; (r = 0{\cdot}96)$ (4)

When ionization occurs from a lone-pair orbital of π symmetry, such as in halides, ethers, sulphides, and amines,† the change in ionization potential upon methyl substitution is the largest, while for substitution on π systems, lower sensitivity to methyl substitution is observed. For lone pair orbitals of σ symmetry, the change upon methylation is the smallest. The results are in accord with a hyperconjugative effect by the methyl group and by other alkyl groups. In orbital terminology (Koopmans' theorem),[2] a methyl group will raise the energy of the orbital of X from which ionization occurs by mixing an orbital of appropriate symmetry, the π_{Me} group orbital, with the orbital on X.[3] This interaction increases as the difference between the

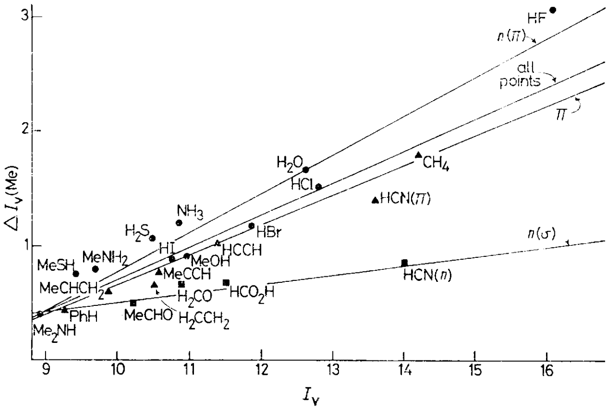

FIGURE. A plot of $\Delta I_V(Me) = I_V(HX) - I_V(MeX)$ *vs.* $I_V(HX)$. ● = $n(\pi)$; ■ = $n(\sigma)$; ▲ = π.

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† The amine lone-pair is not of π symmetry in the neutral molecule, but is a π orbital in the planar radical cation (D. H. Aue, H. M. Webb, and M. T. Bowers, *J. Amer. Chem. Soc.*, 1975, **97**, 4136 and references therein).

energy of the X orbital and that of the π_{Me} orbital (*ca.* $-14{\cdot}2$ eV) decreases [equation (5)], where $H(X - \pi_{Me})$ is the

$$\Delta I_V(\mathrm{Me}) = \frac{H^2(X - \pi_{Me})}{\epsilon(X) - \epsilon(\pi_{Me})} \quad (5)$$

resonance integral for interaction of X with π, and ϵ's are orbital energies before interaction.

The increase in influence of methyl substitution as the I_V of HX increases results from a decrease in the denominator of the perturbation expression; the extent of interaction will also depend roughly on the amount of overlap of π_{Me} and X orbitals.‡ Thus, correlations are observed for delocalized π orbitals [π], lone pair orbitals of π symmetry [$n(\pi)$], and lone pair orbitals of σ symmetry [$n(\sigma)$], with those orbitals expected to overlap best with the π_{Me} orbitals showing the greatest sensitivity to methyl substitution. The fact that the $n(\sigma)$ orbitals show any change at all with methylation (especially in the case of HCN) indicates that indirect effects (σ-inductive and changes in charges at the heteroatom due to hyperconjugative polarization of the π system by methyl group) operate to some extent.

From another point of view, the correlations may be considered to reveal hyperconjugative, rather than inductive, stabilization of the radical cation states. In a valence-bond formalism, the ionized radical cation configuration of HX can be lowered in energy by a resonance interaction with a higher energy radical cation configuration of the methyl group. The extent of interaction, as before, depends on the relative energies of the two configurations; those closest in energy and overlapping best interact most.

Either formalism can explain the alkyl substituent effect in terms of hyperconjugation, rather than induction. This type of correlation also gives quantitative support to the idea that the least stable radical cations (having low-lying half-occupied orbitals) will be stabilized most by hyperconjugative interactions.

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‡ The Mulliken approximation, $H_{ij} = kS_{ij}$, is assumed.

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[2] T. Koopmans, *Physica*, 1933, **1**, 104.

[3] L. Libit and R. Hoffmann, *J. Amer. Chem. Soc.*, 1974, **96**, 1370 and references therein.