

PMO TREATMENT OF STRUCTURE-REACTIVITY RELATIONSHIPS. POLAR EFFECTS IN THE FREE RADICAL ADDITION REACTIONS

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The electronic nature of free radicals in the addition to substituted styrenes was studied by a simple perturbation approach utilising delocalisability D_r as a static index of reactivity. In agreement with experimental results, the calculations reproduce correctly the change in the sign of the Hammett ρ constants in going from electronegative to electropositive radicals.

In contrast to ionic reactions, in which the attacking species can easily be characterised in terms of nucleophilicity or electrophilicity, a substantially more complex situation exists in reactions of free radicals. One of the useful tools allowing us to determine empirically the character of the attacking radical species in a given reaction is the Hammett equation. For instance, negative value of the Hammett ρ constant provides evidence for the electrophilic character of trichloromethyl radicals in the addition to substituted styrenes¹⁻³. On the other hand, Giese and Meister⁴ have shown that tert-butyl and higher *n*-alkyl radicals do add to substituted styrenes as nucleophiles. However, as has been found by Michejda and Campbell⁵, the electronic nature of free radicals can change with complexing. Thus, in the addition to substituted α -methylstyrenes the free dimethylamino radical exhibits nucleophilic behavior ($\rho = 0.69 \pm 0.03$); however, addition of a Lewis acid such as zinc chloride leads to formation of a zinc chloride — dimethylamino radical complex which behaves as an electrophile ($\rho = -0.98 \pm 0.04$). The character of free radicals therefore appears to be affected not only by the structure but also by some secondary effects such as complexation, solvent effect etc.

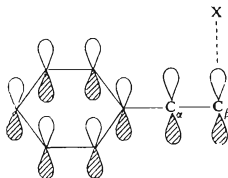
The aim of this communication is to demonstrate that the existing theoretical methods^{6,7} used to study the reactivity of free radicals are capable not only to anticipate, but also to describe and elucidate the observed changes in the nature of radicals attacking C=C bonds. The anti-Markovnikov addition of free radicals to styrene and substituted styrenes was chosen as a model reaction.

CALCULATIONS

The calculations were performed by using the standard CNDO/2 method⁸; in an effort to express more realistically π interactions in the aromatic skeleton, the method was parametrised according to DelBene-Jaffé^{9,10}. The molecules were considered to adopt idealised geometries with standard bond lengths. The prediction of reactivity was based on a perturbation approach using delocalisability D_r (ref.⁶) as the static index of reactivity; D_r can be expressed by Eq. (1),

$$D_r = \sum_i^{\text{occ}} \frac{c_{ri}^2}{\alpha - \varepsilon_i} + \sum_j^{\text{unocc}} \frac{c_{rj}^2}{\varepsilon_j - \alpha}, \quad (1)$$

where c_{ri} and c_{rj} represent expansion coefficients of the r -th atomic orbital (reaction center) in molecular orbitals φ_i and φ_j and where ε_i and ε_j denote the corresponding orbital energies. In our case, the center of the primary attack was presumed to be the p_z orbital at the β -C atom (Scheme I).



SCHEME I

In this approach the radical structure can be characterised only indirectly by the magnitude of α , that expresses the energy of a singly occupied molecular orbital (SOMO) of a radical. By varying the value of α it is thus possible to model to some extent the changes in the nature of attacking free radicals.

RESULTS AND DISCUSSION

Elementary quantum chemical considerations lead to the conclusion that the magnitude of α is in direct relation to the electronegativity of attacking radicals. High negative values of α correspond to the most electronegative radicals (trifluoromethyl, trichloromethyl *etc.*) and the electronegativity of radicals decreases with increasing value of α . It is apparent that such a qualitative description does not allow to assign a definite value of α to any of the radicals under study. However, what is decisive here is rather the general trend of relationships between the value of α and electronegativity and meaningful conclusions can be drawn only on the basis of these trends. In this context we consider the trichloromethyl radical as an electronegative species, characterising it by a model value $\alpha \approx -10$ eV. Another extreme is represented by the tert-butyl radical that we characterise by $\alpha \approx 0$. Other radicals with intermediate values of α lie within both these extremes.

Delocalisabilities D_r calculated in a series of substituted styrenes for several model values of α are summarised in Table I. As these results document, the actual magnitude of α plays a decisive role in defining the transmission of the polar effect in radical addition reactions.

Let us discuss first the addition of the trichloromethyl radical to styrenes which

has been found to follow, taking into account the sign of Hammett ρ constants, an electrophilic mechanism¹⁻³. Fig. 1 (line 1) shows the dependence of theoretical values of delocalisabilities D_r , which are calculated for $\alpha = -10$ eV, upon the Hammett σ constants. It can be seen that the data fit the linear Hammett correlation, with the correlation coefficient r corresponding to 0.942; moreover, the plot reflects correctly the fact that the reactivity decreases with the increasing value of σ constants ($\rho < 0$).

As one passes to the less electronegative radicals (Fig. 1, line 2), there is a decrease in the absolute value of the slope in the plot of D_r vs σ and for $\alpha = -5$ eV the reaction rate is essentially independent of the substituent ($r = 0.993$). This corresponds to reactions for which the Hammett ρ constant is equal approximately to zero.

TABLE I

Delocalisabilities D_r calculated for a series of 4- and 3-substituted styrenes $\text{XC}_6\text{H}_4\text{CH}=\text{CH}_2$ in dependence on the magnitude of parameter α

X	D_r		
	$\alpha = -10$ eV	$\alpha = -5$ eV	$\alpha = 0$ eV
H	-0.3238	-0.1319	-0.2904
4-Cl	-0.2713	-0.1324	-0.3909
4-F	-0.2807	-0.1321	-0.3517
4-Br	-0.2844	-0.1324	-0.3910
3-NO ₂	-0.2146	-0.1334	-0.5314

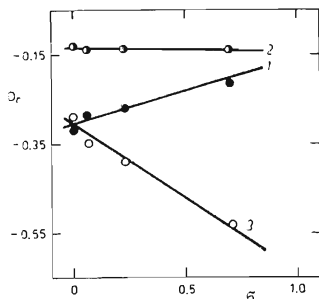


FIG. 1

Delocalisabilities D_r as a function of the Hammett σ constants for $\alpha = -10$ eV (1), $\alpha = -5$ eV (2) and $\alpha = 0$ eV (3)

A further decrease in the electronegativity of the attacking radical modeled by $\alpha \pm 0$ eV makes again the reaction, e.g. that of the tert-butyl radical, sensitive to substituent effect which is characterised, however, by an increase in reactivity as the value of σ increases (Fig. 1, line 3); in other words, one obtains again a linear Hammett correlation ($r = 0.984$), but in this case with a positive sign of the ρ constant.

It is noteworthy that all these results are in complete agreement with experimental observations¹⁻³. The perturbation approach used in this study describes therefore correctly the transmission of polar effects in additions of radicals to the C=C bond of structurally related compounds¹¹ and gives thus a unifying view of the factors influencing the electronic nature of free radical species involved in these reactions.

REFERENCES

1. Sakurai H., Hayasaki S., Hosomi A.: *Bull. Chem. Soc. Jap.* **44**, 1945 (1971).
2. Cadogan G. I. J., Sadler H. I.: *J. Chem. Soc. B* **1966**, 1191.
3. Hájek M., Šilhavý P.: *This Journal*, in press.
4. Giese B., Meister J.: *Angew. Chem.* **89**, 178 (1977).
5. Michejda C. J., Campbell D. H.: *Tetrahedron Lett.* **1977**, 577.
6. Fukui K.: *Fortschr. Chem. Forsch.* **15**, 1 (1970).
7. Ponec R., Hájek M., Málek J.: *This Journal* **46**, 2524 (1981).
8. Pople J. A., Beveridge D.: *Approximate MO Theory*. McGraw-Hill, New York 1970.
9. DelBene J., Jaffé H. H.: *J. Chem. Phys.* **48**, 1807 (1968).
10. DelBene J., Jaffé H. H.: *J. Chem. Phys.* **48**, 4050 (1968).
11. Arnaud R., Subra R., Barone V.: *Nouv. J. Chim.* **6**, 91 (1982).

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