

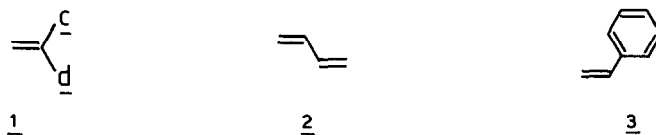
KINETIC EFFECTS IN RADICAL ADDITION REACTIONS TO RADICOPHILES¹⁾

F. Lahousse, R. Merényi, J.R. Desmurs, H. Allaiame,
 A. Borghese and H.G. Viehe

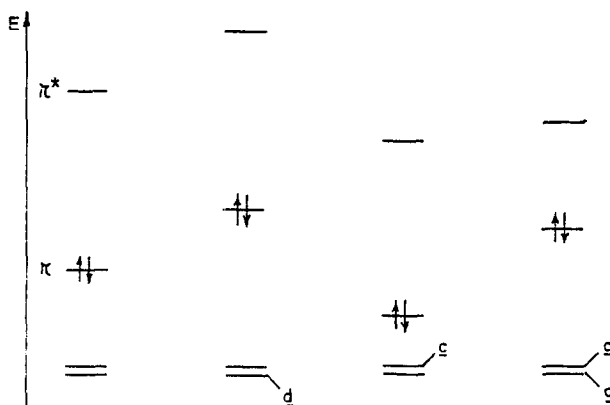
Université de Louvain, Laboratoire de Chimie Organique
 Place L. Pasteur, 1, B-1348 Louvain-la-Neuve (Belgium)

Summary. Beyond expectation from polar effects rate acceleration is observed when captodative (cd) substituted 1,1-diphenylethylenes 6 and styrenes 7 undergo addition of isobutyronitrile radicals. The effect can be rationalised in terms of frontier orbital interactions.

Olefins with captodative (cd) substitution 1 have been defined as radicophiles²⁾. This definition is derived from the character of cd-olefins to give stabilised radical adducts. Systems such as butadiene 2 or styrene 3 behave analogously; in consequence they also are radicophiles.



It has been proposed qualitatively, that relative to the frontier orbitals of ethylene the orbital scheme of cd-olefins 1 should show the simultaneous lowering of the LUMO and rising of the HOMO²⁾ (Scheme 1). This narrowing of the HOMO-LUMO gap characterises also 2 and 3³⁾.

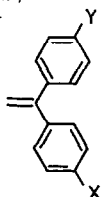
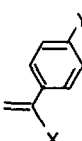



Scheme 1. Frontier orbital energies of donor, acceptor and cd-substituted olefines compared to ethylene.

The SOMO-LUMO or SOMO-HOMO interactions, as one expression of polar effects, are considered as the main factor determining radical addition rates to olefins ^{3,4)} Consequently the overall effect of the frontier orbital energies of radicophiles should lead to acceleration of addition rates because of closing in of olefin frontier orbitals. Indeed conjugated systems such as 2 and 3 behave expectedly and the "resonance effects"⁵⁾ or "phenyl effect"⁶⁾ are the proposed terms to describe this behaviour.

In this communication we show an analogous accelerating effect on the addition rate of the isobutyronitrile radical 5 to diphenylethylene or to styrene derivatives 6 or 7. The method of measurement of the relative rates by monitoring NMR signals and the analysis of the results will be described elsewhere ⁷⁾

TABLE 1. Relative ^{a)} rates of addition of 5 to diphenylethylenes 6 and styrenes 7^{b)}

							
	X	Y	k_{rel}		Y	$k_{rel}^{a)}$	
<u>6a</u>	H	CN	0.87	<u>7a</u>	OMe	0.80	
<u>b</u>	H	H	1	<u>b</u>	OCOMe	0.89	
<u>c</u>	CN	CN	1.11	<u>c</u>	OMe	COOMe	0.90
<u>d</u>	NO ₂	NO ₂	1.13	<u>d</u>	OMe	NO ₂	0.96
<u>e</u>	Br	Br	1.19	<u>e</u>	SPh	H	1.05
<u>f</u>	H	NO ₂	1.28	<u>f</u>		NO ₂	1.20
<u>g</u>	H	OMe	1.31	<u>g</u>	COOMe	OMe	2.99
<u>h</u>	CN	OMe	2.14				
<u>i</u>	OMe	OMe	2.14				
<u>j</u>	NO ₂	NMe ₂	3.04				
<u>k</u>	NMe ₂	NMe ₂	5.99				

a) relative to unsubstituted diphenylethylene (=1)

b) In the NMR-Spectrometer azaisobutyronitrile (AIBN) is heated in benzene solution with two olefins ; vinyl protons are monitored, no polymerisation is observed.

Like in all radical additions to double bonds this reaction is exothermic, and the resonance stabilisation of the radical adduct further increases the exothermicity. Therefore, with a transition state close to reactants, their frontier molecular orbitals can be implied. Generally if polar effects determine the addition rates exclusive SOMO-LUMO or SOMO-HOMO interactions are considered, respectively. In the reaction of radicophiles 6 and 7 with $\text{NC}(\text{CH}_3)_2^\ominus$ 5, a weakly polar radical, relative rates (Table 1) and their Hammett correlation (Figure 1) show the following features :

i) Alteration of the mechanism when inverting from donor to acceptor substituents in 6.

ii) rate acceleration beyond expectation based on polar effects when substituents are captodative

iii) inversion of the sequence expected from polarity only, when the donor is kept constant in 6 or 7.

In Figure 1. relative rates of the addition to diphenylethylenes 6 with two identical para substituents ($X=Y$) and with monosubstitution ($X=H$) are correlated to the $\sigma_x + \sigma_y$ constants. Hammett σ_p -values have been used, which give the best correlation.

For donor substituents the negative value of $\rho = -0.46$ (corr = 0.993) shows the weak electrophilic character of radical 5. These rates appear mostly determined by SOMO-HOMO interactions, whereas for acceptors probably the SOMO-LUMO interactions dominate. To our knowledge this is the first case, when Hammett correlation shows an alteration of mechanism due only to the inversion of electron displacement in the same type a transition state.

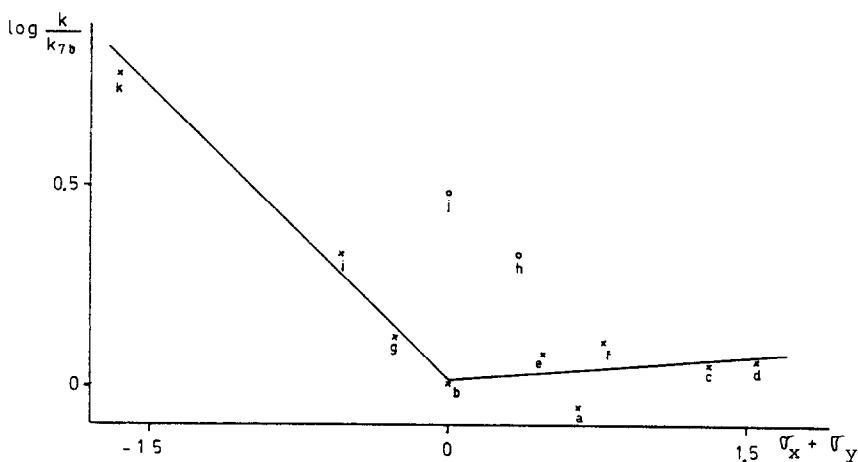


Figure 1. Hammett plot of the addition of the isobutyronitril radical to 6a-g, i, k

Compared to the diphenylethylenes 6a-g, i, k, which correlate, cd-olefins 6h, j show rate acceleration. This cd-effect can be explained by the even more reduced HOMO-LUMO gap; the nucleophilic cyclohexyl radical behaves similarly towards other cd-olefins⁸⁾.

The cd-effect is recognized the easiest within a varying series, keeping either the donor or the captor constant:

1) Captor constant: $\text{NC}(\text{CH}_3)_2\text{C}^\oplus$ being rather electrophilic, the polar and cd effect both lead to acceleration. Thus in 6a, h ($-\text{C}\equiv\text{N}$ is const): $\text{H} < \text{OCH}_3$

in 6d, j (NO_2 ") : $\text{NO}_2 \ll \text{H} < \text{N}(\text{CH}_3)_2$

in 7d, f ($p\text{-NO}_2$ ") : $\text{OCH}_3 < \text{N} \begin{array}{c} \diagup \quad \diagdown \\ \text{---} \quad \text{---} \\ \diagdown \quad \diagup \\ \text{O} \end{array}$

2) Donor constant: polar and cd effect act in opposite sense and a complete inversion of the expected sequence of rates is observed.

in 6g, ih (O-CH_3 const.) : $\text{H} < \text{OCH}_3 = \text{CN}$

in 7a, c, d ($\alpha\text{-OCH}_3$ const) : $\text{OCH}_3 < \text{-COOCH}_3 < \text{NO}_2$

in 7a, b, g ($p\text{-OCH}_3$ const) : $\text{OCH}_3 < \text{OC-CH}_3 < \text{COOCH}_3$

In rate terms this cd effect is not strong, but comparable to the polar effect in addition reactions of weakly polar radicals.

Whereas the thermodynamic cd-radical stabilisation appears to be established, from these results it appears now that cd-substitution leads also to a kinetic accelerating effect in radical additions.

Acknowledgements : We thank for the financial support of SPPS and IRSIA, and for discussions with J. Rouchaud, E. Sonveaux, P. Van Brandt and B. Giese.

References

- 1) Captodative Substituent Effects. Part 18; Part 17 : S. Mignani, Z. Janousek, R. Merényi, H.G. Viehe, J. Riga and J. Verbist, *Tetrahedron Lett.* 1984, **15**, 1571.
- 2) Presented in part at EUCHEM Conference, "Organic Free Radicals" Elmau Oct. 1983.
- 3) H.G. Viehe, R. Merényi, L. Stella, Z. Janousek, *Angew. Chem. Int. Ed. Engl.* **18**, 917 (1979)
- 4) I. Fleming, *Frontier Orbitals and Organic Chemical Reactions*, John Wiley, London 1976
- 5) B. Giese, *Angew. Chem. Int. Ed. Engl.* **22**, 753 (1983)
- 6) J.M. Tedder, *Angew. Chem. Int. Ed. Engl.* **21**, 401 (1982)
- 7) B. Giese, G. Kretzschmar, *Chem. Ber.* **116**, 3267 (1983)
- 8) J.R. Desmurs, F. Lahousse, H. Allaine, A. Borghese, R. Merényi, H.G. Viehe, to be published.
- 9) B. Giese, J. Meixner, *Chem. Ber.* **114**, 2138 (1981)

(Received in France 27 May 1984)