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An ESR Study of Aromatic Olefin Radical Cations

Lydia Bonazzola, Jean-Pierre Michaut, Jacques Roncin, Hiroaki Misawa,†
Hirochika Sakuragi,† and Katsumi Tokumaru*,†
Laboratoire de Physico-chimie des Rayonnements, Université de Paris-sud, Centre d'Orsay, 91405 Orsay Cedex, France
†Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305
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γ-Irradiation of phenyl- and diphenylethenes in $CFCl_3$ matrix at 77 K resulted in the formation of the substrate radical cations. 1,1-Diphenyl-2-methylpropene radical cations exhibit a spin density (ρ=0.45) at the β carbon much higher than those of stilbene and 2-styrylnaphthalene radical cations and comparable to those of styrene and α-methylstyrene radical cations. The spin density at the vinyl carbons appears to play an important role in governing the reactivity of the olefin radical cations with molecular oxygen.

Previously, some of us found that among the free radicals produced from aromatic olefins (aralkenes) like styrenes[1] and 1,1-diphenyl-2-methylpropene,[2] not only the allylic radicals but also the olefin radical cations react with molecular oxygen despite of their low capability as electron donor. These findings led us to investigate the spin density distribution of aralkene radical cations as a basis of understanding their chemical reactivity. The present work reports the spin density distribution in the radical cations of a series of aralkenes like styrenes, stilbenes, and vinylanthracenes.

Experimental

Styrene (**1**), α-methylstyrene (**2**), *cis*- and *trans*-stilbene (**3**) were commercially available and purified by distillation or crystallization before use. *cis*- and *trans*-2-Styrylnaphthalene (**4**) were prepared according to the literature,[3] and separated by SiO_2 column chromatography with hexane as eluent. The cis isomer was purified by distillation and the trans isomer by crystallization from hexane. 9-Vinylanthracene (**5**)[4] was prepared by the Wittig reaction of 9-formylanthracene with the ylide prepared from methyltriphenylphosphonium iodide and potassium *t*-butoxide in THF,[5] and purified by crystallization from hexane–benzene (1 : 1). 1-Vinylanthracene (**6**) was prepared and purified according to the literature.[6] 1,1-Diphenyl-2-methylpropene (**7**)[7] was prepared by reductive coupling of benzophenone and acetone in 1,2-dimethoxyethane in the presence of active titanium metal freshly prepared from titanium trichloride and lithium,[8] and purified by distillation. 3,3-Diphenyl-2-methylpropene (**8**)[9] was prepared by the Wittig reaction of 1,1-diphenyl-2-propanone with the methyl ylide,[5] and purified by distillation.

The aralkenes were dissolved in $CFCl_3$ to a concentration of 2—5$\times$10^{-3} mol dm^{-3}, degassed, and sealed in a suprasil cell. The solutions were γ-irradiated at 77 K to a dose of 1—2 Mrad. The ESR measurements were carried out with a Brucker ER 200D spectrometer at T=140 K. The couplings have been determined from the simulation of experimental spectra and have been assigned to respective hydrogens from INDO calculations and with reference to known results for the corresponding anions. INDO calculations have been performed by using standard bond lengths defined by Pople et al.[10]

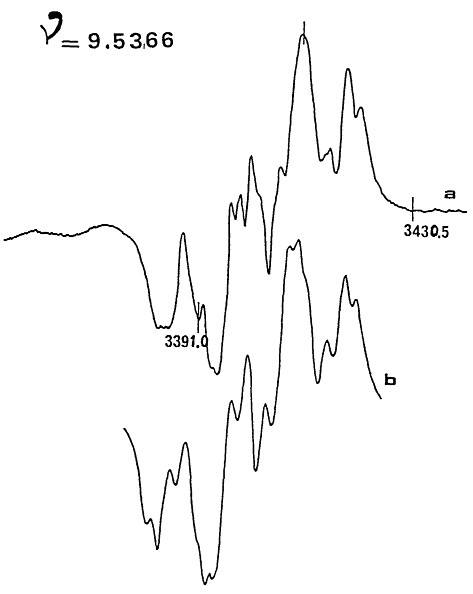


Fig. 1. a) Experimental ESR spectrum of styrene radical cation ($1^{+\cdot}$) in $CFCl_3$ matrix at 140 K.
b) Spectrum of $1^{+\cdot}$ simulated with parameters given in Table 1.

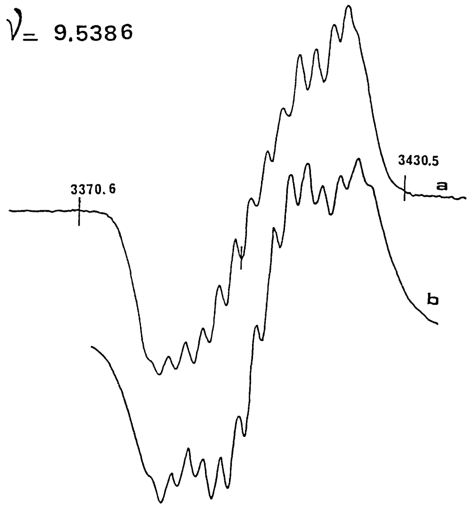


Fig. 2. a) Experimental ESR spectrum of α-methylstyrene radical cation ($2^{+\cdot}$) trapped in $CFCl_3$ matrix at 140 K.
b) Spectrum simulated with parameters in Table 1.

Table 1. Couplings and Spin Densities of Aralkene Radical Cations

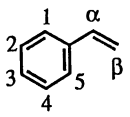
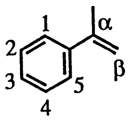
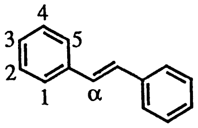
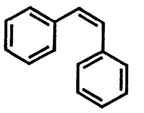
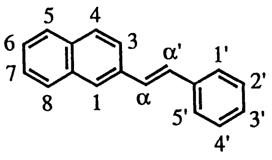
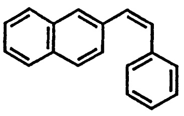
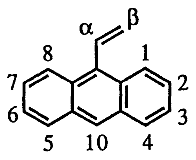
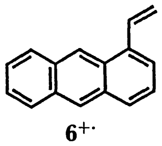
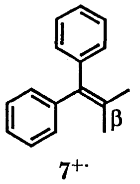
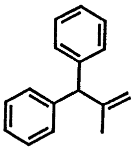
Radical cation (ArH in ArH$^{+\cdot}$)	C	Coupling/G					Spin density		g
		INDO (calc.)	Anion		Cation		ρ_π	$\Sigma\rho_\pi$	
			(experimental)						
 $\mathbf{1}^{+\cdot}$	1	−3.0	−2.0[a]		−2.25		0.09	0.81	2.0028
	2	1.3	0.59						
	3	−5.8	−5.5		−6.75		0.26		
	4	1.6	0.87						
	5	−3.6	−3.82		−3.35		0.13		
	α	0.5	1.51		2.25		−0.08		
	β	−11.1	−7.55		−11.0		0.41		
 $\mathbf{2}^{+\cdot}$	1	−2.5	−2.15[a]		−3.1		0.12	0.82	2.0027
	2	1.2	0.65						
	3	−4.5	−5.07		−6.2		0.23		
	4	1.6	0.29						
	5	−3.2	−3.44		−3.1		0.12		
	α	3.0	1.7		−3.1		−0.09		
	β	−13.3	−4.36		−11.8		0.44		
 *trans*-$\mathbf{3}^{+\cdot}$	1	−3.5	−1.94[b]	−1.90	−2.78[b]	−2.4	0.09	1.08	2.0027
	2	1.9	0.83	0.86	0.72				
	3	−4.3	−4.0	−3.80	−4.35	−4.8	0.18		
	4	2.0	0.70	0.32	0.72				
	5	−3.7	−3.03	−2.96	−2.78	−2.4	0.09		
	α	−4.8	−4.59	−4.3	−4.35	−4.8	0.18		
 *cis*-$\mathbf{3}^{+\cdot}$									2.0028
 *trans*-$\mathbf{4}^{+\cdot}$	1	−6.2			−5.6		0.21	0.97	2.0027
	3	−0.9							
	4	0.5							
	5	1.5							
	6	−3.0			−2.8		0.11		
	7	−2.0							
	8	−3.7			−2.8		0.11		
	α	−2.4							
	1′	−3.4			−2.8		0.11		
	2′	1.9							
	3′	−3.6			−2.8		0.11		
	4′	1.8							
	5′	−3.2			−2.8		0.11		
	α'	−5.3			−5.6		0.21		
 *cis*-$\mathbf{4}^{+\cdot}$									2.0028
 $\mathbf{5}^{+\cdot}$	1	−1.8						0.45	2.0027
	2	−1.4							
	3	0.33							
	4	−3.3			−4.0		0.15		
	5	−3.2			−4.0		0.15		
	6	0.32							
	7	−1.4							
	8	−1.3							
	10	−7.8			−4.0		0.15		
	α	11.2			4.0		−0.15		
	β	−4.3			−4.0		0.15		

Table 1. (Continued)

Radical cation (ArH in ArH$^{+\cdot}$)	C	Coupling/G INDO (calc.)	Anion (experimental)	Cation (experimental)	Spin density ρ_π	$\sum\rho_\pi$	g
 **6**$^{+\cdot}$							2.0027
 **7**$^{+\cdot}$	β			14.7	0.45	0.45	2.0028
 **8**$^{+\cdot}$							2.0027

a) Ref. 12. b) Ref. 13.

Results

γ-Irradiation of aromatic olefins **1**—**8** in $CFCl_3$ matrix at 77 K afforded ESR spectra as shown in Figs. 1—7, 9, and 10. Table 1 summarizes the experimental couplings, which are compared with INDO calculations and couplings for the respective anions. The resonances of powdered samples are distorted by anisotropy and the ESR lines can be represented as a combination of Lorentzian and Gaussian shapes. In all our spectral simulations, the lines have been assumed to be Lorentzian, which overestimates the wings of each line. The anisotropy of the couplings has not been taken into account in simulated spectra. This approximation is rather crude for strong H_α couplings; it is the case for styrene and α-methylstyrene.

Styrene (1) and α-Methylstyrene (2). Experimental and simulated spectra of styrene and α-methylstyrene cations (**1**$^{+\cdot}$ and **2**$^{+\cdot}$, respectively) are shown in Figs. 1 and 2, respectively. The experimentally determined coupling at the α carbon of **1**$^{+\cdot}$ is much larger than that calculated by INDO method (Table 1). The spin density at the β carbons of **1**$^{+\cdot}$ and **2**$^{+\cdot}$ increases on going from the radical anions[11] to the radical cations ($a_\beta{}^H$ is estimated as 10 G for these cations by Symons et al.[12]).

***trans*-Stilbene (*trans*-3) and *cis*-Stilbene (*cis*-3).** The ESR spectrum of *trans*-stilbene in $CFCl_3$ matrix is shown in Fig. 3a. The simulated derivative curve (Fig. 3b) was computed by using four ortho hydrogen

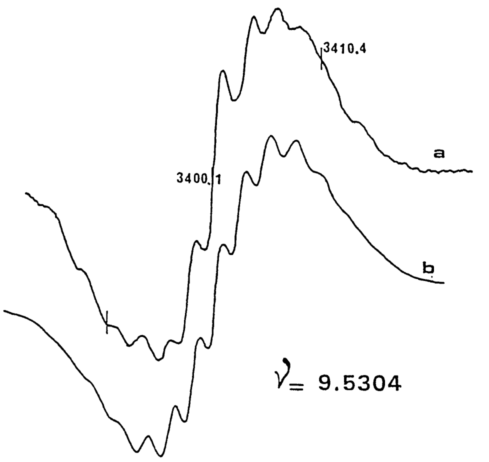


Fig. 3. a) Experimental ESR spectrum of *trans*-stilbene radical cation (*trans*-**3**$^{+\cdot}$) in $CFCl_3$ matrix at 140 K.
b) Simulated spectrum with parameters in Table 1.

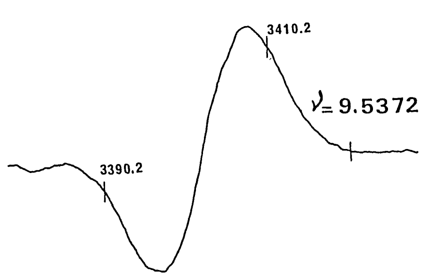


Fig. 4. ESR spectrum of *cis*-stilbene radical cation (*cis*-**3**$^{+\cdot}$) in $CFCl_3$ matrix at 140 K.

coupling constants of 2.4 G and four (two para and two vinyl) hydrogen couplings of 4.8 G. These couplings are assigned to respective hydrogens from INDO calculations and from comparison with *trans*-stilbene anions.[13] Our experimental results are in good agreement with those of Courtneidge et al.[14] for cations of stilbene in solution (Table 1).

Figure 4 shows the ESR spectrum of γ-irradiated *cis*-stilbene in $CFCl_3$. This spectrum consists of a single broad line. Its *g* value corresponds to that of *cis*-stilbene cations. Neither hyperfine couplings nor spin densities could have been determined.

***trans*-2-Styrylnaphthalene (*trans*-4) and *cis*-2-Styrylnaphthalene (*cis*-4).** Figure 5 shows the spectra observed for *trans*-2-styrylnaphthalene in $CFCl_3$. The assignment of the couplings to different hydrogens has been made from comparison of the experimental spectrum with the simulated one (5 couplings of 2.8 G and 2 couplings of 5.6 G) and from INDO calculations. The spin density distribution has been estimated (Table 1).

The spectrum from *cis*-2-styrylnaphthalene (Fig. 6) consists of a broad unresolved singlet which provides no information on the spin density distribution in the cation.

Vinylanthracenes. The only resolved spectrum comes from 9-vinylanthracene (**5**) at 159 K (Fig. 7). A difficulty arises in INDO calculations since strong steric effects (hydrogen bonded to β carbon) in **5** prevent delocalization. INDO calculations varying the dihedral angel α between vinyl and anthracene planes suggest that the conformation of the cation corresponds to α=45° (Fig. 8). The couplings calculated for α=45° are listed in Table 1. The experimental spectrum exhibits an odd number of lines. INDO calculations suggest couplings to 4 equivalent and 2 inequivalent protons. However, this result leads to a spectrum with an even number of lines, which is not

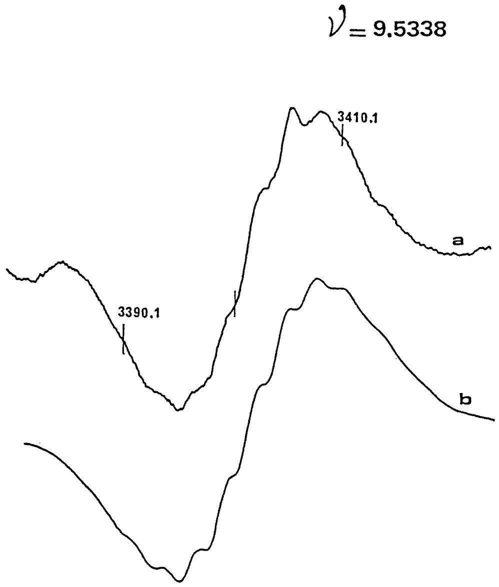


Fig. 5. a) Experimental ESR spectrum of *trans*-2-styrylnaphthalene radical cation (*trans*-$4^{+\cdot}$) in $CFCl_3$ matrix at 140 K.
b) Simulated spectrum with parameters in Table 1.

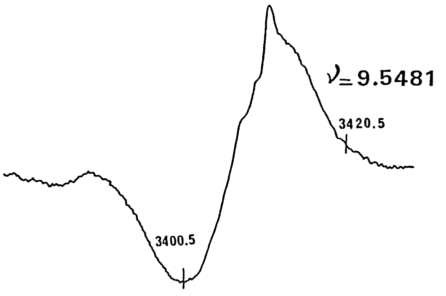


Fig. 6. ESR spectrum of *cis*-2-styrylnaphthalene radical cation (*cis*-$4^{+\cdot}$) in $CFCl_3$ matrix at 140 K.

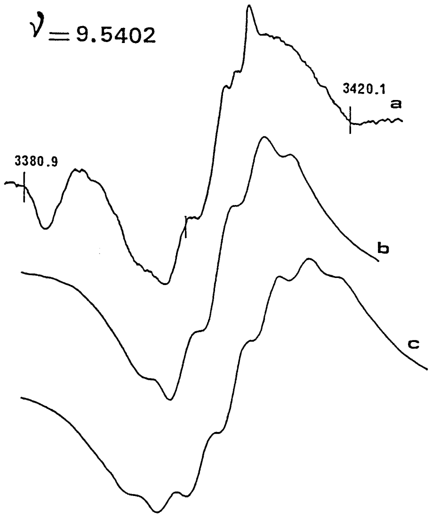


Fig. 7. a) Experimental ESR spectrum of 9-vinylanthracene radical cation ($5^{+\cdot}$) in $CFCl_3$ matrix at 159 K.
b) Spectrum simulated with parameters in Table 1.
c) Spectrum simulated from INDO calculated couplings.

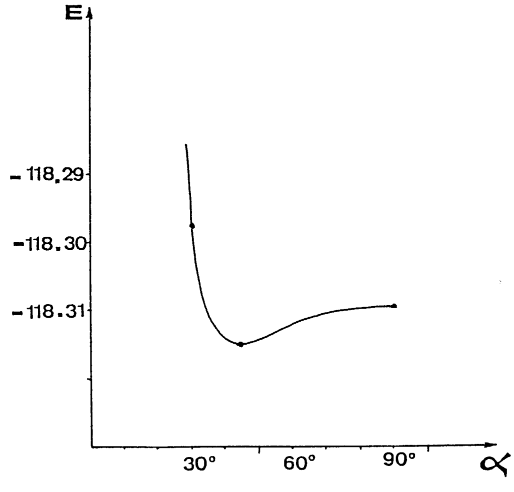


Fig. 8. INDO calculated total energy (Hartrees) of 9-vinylanthracene radical cation ($5^{+\cdot}$) versus α (angle between vinyl and anthracene planes).

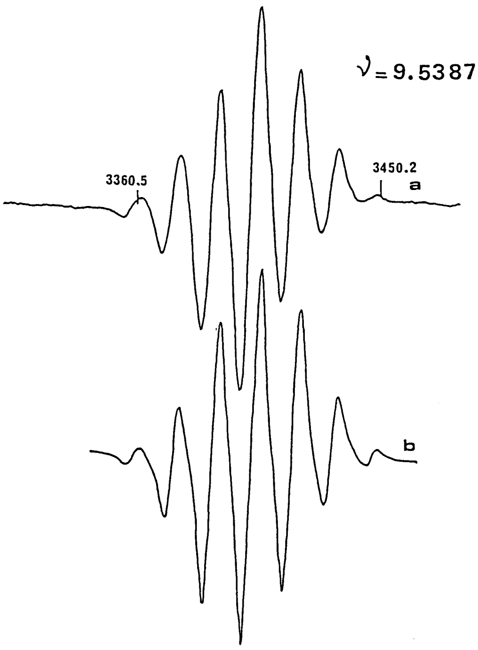


Fig. 9. a) Experimental ESR spectrum of 1,1-diphenyl-2-methylpropene radical cation ($7^{+\cdot}$) in $CFCl_3$ matrix at 140 K.
b) Simulated spectrum (parameters in Table 1).

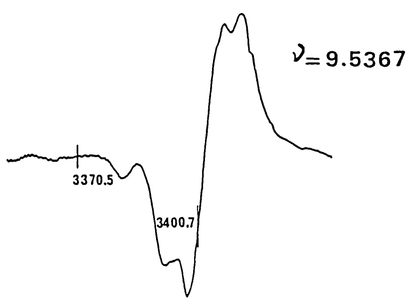


Fig. 10. ESR spectrum of 3,3-diphenyl-2-methylpropene radical cation ($8^{+\cdot}$) in $CFCl_3$ matrix at 140 K.

satisfactory. The spectrum cannot be also analyzed in terms of 4 equivalent protons and 2 other protons with a double coupling since the resulting number of lines is too large (9 instead of 7). The experimental spectrum can be accounted for by assuming a coupling to 6 equivalent protons. This interpretation indicates that INDO calculations overestimate the couplings to hydrogens bonded to C_α atoms.

1,1-Diphenyl-2-methylpropene (7). Figure 9 shows the spectrum of 1,1-diphenyl-2-methylpropene cation. This well defined 7-line spectrum results from hyperfine interaction with 2 sets of 3 methyl equivalent protons. The coupling to other protons does not give resolved structure. The spectrum of an isomer, 3,3-diphenyl-2-methylpropene (**8**) (Fig. 10) is very asymmetric, the value of the couplings to the two methyl groups being appreciably decreased; this change with respect to 1,1-diphenyl-2-methylpropene (**7**) is presumably due to localization of spin density on the phenyl groups.

Discussion

Are the couplings determined from simulations and INDO calculations accurate? We already stressed that neglecting the anisotropy of couplings may be a crude approximation. The anisotropy of H_α coupling is not averaged out by motion even at 140 K in $CFCl_3$ matrix. Fast rotation does not even lead to quasi axial tensors as in naphthalene[15] because of lack of symmetry axes in most studied compounds. Nevertheless, our simulations are reliable for the following reasons: the anisotropic H_α coupling tensors are A; 0; $-A$ and the value of the isotropic constant is $2A$ approximately. Anisotropy vanishes without altering the isotropic coupling when the line width is superior to anisotropy itself, which occurs in the present study; the line widths used for spectral simulations are of 3 to 5 G. Unresolved couplings and non-strictly equivalent couplings contribute to this line width. The couplings given in Table 1 are correct within 20% for small couplings and within 10 to 5% for the large couplings relative to radicals $1^{+\cdot}$, $2^{+\cdot}$, and $7^{+\cdot}$.

ρ_π Density Distribution in Styrene Derivatives Cations. The amount of spin density at different carbon atoms is related to their reactivity. A direct proportionality between the isotropic component of H_α coupling $a_\alpha{}^H$ and the π spin density on C has been theoretically predicted by McConnell;[16]

$$a_\alpha{}^H = \rho_\pi Q \qquad (1)$$

where Q is a proportionality constant, depending on the various types of radicals. We have chosen $Q=-27$ G for carbons of vinyl radicals. The same relation holds for β hydrogens with $Q=33$ G (from the results obtained for butene and isobutene cations),[17] and also for aromatic hydrocarbons with -26.4 G (from the results for benzene cations).[18] Table 1 shows the spin densities calculated by using relation 1. The estimated total spin densities are also included in Table 1. It is noteworthy that most of them are inferior to 100%. This result is due to the facts that small couplings cannot be measured and that the spin densities at carbons which are not bonded to hydrogens are unknown. In Table 1 for radicals $5^{+\cdot}$ and $7^{+\cdot}$ only small numbers of spin densities can be assigned from our experimental spectra.

Trends of Spin Density Variation. There are clear trends for the variation of the spin density distribution with substitution; the magnitude of the spin density at the β carbon increases in going from styrene ($\rho=0.41$) to α-methylstyrene ($\rho=0.44$). In the conjugated stilbene and 2-styrylnaphthalene cations, $3^{+\cdot}$ and $4^{+\cdot}$, delocalization leads to a decrease in spin density at vinyl carbons. Non-planarity of cations $5^{+\cdot}$ and $7^{+\cdot}$

influences their spin density distribution. Cation $\mathbf{7}^{+\cdot}$ exhibits a high spin density (ρ=0.45) at the β carbon, much higher than those of $\mathbf{3}^{+\cdot}$ and $\mathbf{4}^{+\cdot}$ and comparable to those of $\mathbf{1}^{+\cdot}$ and $\mathbf{2}^{+\cdot}$. The fact that cation $\mathbf{7}^{+\cdot}$ reacts with oxygen much more rapidly (rate constant, 5×10^{7} $\mathrm{mol^{-1}\,dm^{3}\,s^{-1}}$)²⁾ than does $\mathbf{3}^{+\cdot}$ (1×10^{6} $\mathrm{mol^{-1}\,dm^{3}\,s^{-1}}$)¹⁾ could be taken to reflect the higher spin density at the β carbon of the former with respect to the latter.

Conclusion

γ-Irradiation of dilute solutions of styrenes and stilbenes in freon $CFCl_3$ matrix at 77 K results in the formation of the substrate radical cations. An analysis was successfully attempted for the rather poorly resolved ESR spectra. Most spectral features were reliably identified by spectral simulations and comparison with ESR spectra of the corresponding anions.

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