Electronic structure of ring and chain substituted styrenes and their reactivities in the reaction with peroxyl radicals

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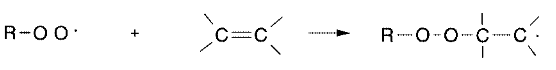
The structure–reactivity relationship in the chain propagation step of radical chain oxidation of styrenes substituted in the ring (*ortho*, *meta* and *para*) and in the vinyl group (position α and β), the addition of a peroxyl radical to the double bond, was investigated. With the PM3 quantum chemical methods the electronic structure of the reactants, transition state (TS) and the enthalpy of reaction (ΔH_R^{add}) were calculated. A linear correlation between ionisation potentials and energies of the HOMO was observed. The calculated bond lengths and charges on atoms at the reaction centre in the TS in comparison to their reactant values and also the negative ΔH_R^{add} show that the TS is early and charge transfer from molecule to radical dominates in the TS. For styrenes a three parameter correlation of the addition rate constants (k) with the reaction enthalpy, E_{HOMO} and coefficient C_1 at the p_z atomic orbital of the HOMO of the attacked carbon atom was obtained.

Introduction

The radical chain mechanism of olefin oxidation proposed by Twigg[1] and Mayo[2] is now generally accepted.[3–6] Considerable effort was devoted to obtain fundamental knowledge of factors which govern the reactivities of radicals and molecules in different steps of chain oxidation reactions. Reactivity in radical additions to alkenes is recognised to derive from a "complex interplay of polar, steric and bond-strength terms".[7–9] The reactivity of an alkene depends on the nature and position of substituents at the double bond. Substituents at the carbon atom which is not attacked exert predominantly polar effects on the rate of addition; substituents at the carbon atom which is attacked exert both polar and steric effects.[8] Furthermore, in the case of ring substituted styrenes, polar (including resonance polar) and spin-delocalisation effects of substituents need to be considered.[10] It has been shown that rates of radical addition to α-methylstyrenes (in the absence of measurable steric effects) can be correlated by a dual-parameter equation with polar and spin delocalisation substituent constants.[10]

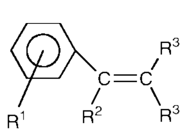
More general considerations of structure–reactivity relationships for radical addition reactions allow the following grouping of all factors:[11–14] thermodynamic factors, connected with the energy of transformation of a reactant to product, *e.g.* reaction enthalpy, energy of bonds being broken or formed; polar and steric effects, which play a key role in stabilisation of the transition state (TS) of the considered reaction, *e.g.* charge transfer, charge and spin distribution, conjugation. It depends on the chemical nature of the substituent as to which of these factors plays the main role in the given reaction. To judge the contribution of the thermodynamic factors usually the Polanyi equation is used and the experimental data on the heat of reaction must be available for that. The polar effects depend on the electronic structure of the TS and in the simplest semiempirical treatments they are connected with donor–acceptor properties of the reacting partners, their ionisation potentials and electron affinities. The necessary experimental data for the estimation of contribution of each factor are not always available for all reactants and the modern quantum chemical methods may be used to calculate them. On the other hand, quantum chemistry gives the relationships between the energy of the interaction in the TS and electronic properties of partners which participate in reaction.

We have focused our investigation on the main chain propagation step of radical chain oxidation of unsaturated compounds, the addition of a peroxyl radical to the double bond, which has been experimentally and theoretically studied,[15–18] eqn. (1).


$$R{-}OO^{\cdot} + {>}C{=}C{<} \longrightarrow R{-}O{-}O{-}\overset{|}{\underset{|}{C}}{-}C^{\cdot} \qquad (1)$$

Experimental and computational methods

A series of styrenes substituted in the ring (*ortho*-, *meta*- and *para*-position) and in the vinyl group (α- and β-position) were investigated. The reactivities of these compounds towards cumylperoxyl radicals and their ionisation potentials were measured and electronic structures calculated using quantum mechanical methods. The rate constants of the reaction of the cumylperoxyl radical with the double bond of these molecules were obtained[15–18] by using the cooxidation method.[19] Ionisation potentials (Ip) were measured by photoelectron spectroscopy (PES).



a) R^1=R^3=H; R^2= H, Me, *t*-Bu, Ph, Cl, Br, CF_3, MeO, cyclo-Pr, $OSiMe_3$
b) R^2= Me; R^3= H; R^1 = *p*-*t*-Bu, *p*-Cl, *p*-Br, *p*-MeO, *p*-CF_3, *o*-Me
c) R^3= H; R^1=R^2= MeO
d) R^2=R^3= Me; R^1 = H, *p*-Cl, *p*-MeO, *m*-CF_3
e) R^3= Me; R^1= H; R^2= EtO, Ph
f) α- and β-Isopropenylnaphthalene, 9-isopropylidenefluorene

The quantum chemical calculations were performed using the PM3 Hamiltonian[20] (MOPAC 6). As has been shown,[21] PM3

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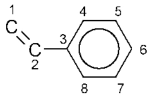
yields better accuracy in heats of formation and geometry of molecules with elements H, C, O, N, F, Cl, Br, Si (present in our molecules) than other semiempirical methods. We have compared the applicability of four Hamiltonians, MINDO/3, MNDO, AM1 and PM3, for the calculation of the ionisation potentials and heats of formation of molecules and radicals in our series. Hamiltonian MINDO/3 gives the closest to the experimental first ionisation potentials, but it fails to predict the optimum geometry. It predicts that the configuration of styrene with a dihedral angle between the benzene ring and ethylenic group of 90° is about 1 kcal mol^{-1} more stable than the planar configuration. The deviation of heats of formation of styrenes calculated by this method from experimental values (about 10 kcal mol^{-1}) is greater than those of the other three methods (2–4 kcal mol^{-1}). The comparison of the distribution of electrons in a molecule of styrene and the energies of its MOs calculated by these methods with those obtained *ab initio* with basis sets 3-21G and 6-31G* shows good linear correlation between the values obtained by the PM3 method, correlation coefficients being 0.998 for charges on atoms and 0.992 for energies of the seven highest occupied MOs. The correlation coefficients for values obtained by MINDO/3 are 0.171 and 0.944, MNDO 0.964 and 0.955, AM1 0.998 and 0.967). Taking into account the results obtained for our series of molecules and the analysis of the accuracy of these methods[21] we have chosen PM3. The calculations of molecules were carried out by the restricted Hartree–Fock (RHF) method, and radicals were calculated by unrestricted Hartree–Fock (UHF). The starting geometric parameters of the molecules (bond length, bond angle, dihedral angle) were taken from ref. 21. All computations were performed with full optimisation of all geometric variables (MOPAC data-files of optimised structures are available).

Results and discussion

The special conformational analysis of styrenes was performed by semiempirical molecular orbital calculation considering the dihedral angle between the vinyl group and benzene ring. All bond lengths and other bond angles were optimised. In the direct optimisation the resulting optimum geometry depends on the starting dihedral angle. A planar starting geometry with symmetric placing of the substituent atoms, using both MINDO/3 and PM3, results in a planar optimum structure with the dihedral angle $\theta^{\mathrm{C1-C2-C3-C4}}$ equal to 0°. However, different results were obtained by using MINDO/3 starting from a structure with the dihedral angle different from 0°. The optimised structure then has a dihedral angle of 90° in all cases, which indicates that it is not planar. The PM3 method yielded different optimised values of this angle for the molecules with different substituents. To obtain the optimised geometry the ethylenic group in styrenes was rotated relative to the benzene ring and the geometry was optimised at each point. We observed that for the molecules where the dihedral angle in the optimised structure was between 0 and 15°, the bottom of the curves that describe the dependence of total energy on dihedral angle is flat, and we have assumed that the structure of the styrenes in this case is planar.



The main theoretical idea of our approach to the interpretation of the structure–reactivity relationship for the addition of a peroxyl radical to the double bond may be described as follows. For the description of the dependence of the reactivity (the activation energy) on the thermodynamic factors (the heat of reaction) we can use the crossing parabola method[22] which has a simple physical basis. The energy change of bonds being broken and formed in the reaction as a function of their length is represented by two crossing parabolas (Fig. 1), where ΔH is the heat, E_a is the observed energy of activation and ΔE is the energy of stabilisation of the transition state by donor–acceptor or interchange interactions. In the case when such interactions are negligible the activation energy (E_{a0}) is equal to the difference between the energy corresponding to the crosspoint of the two parabolas C and the energy of the bond being broken (AC in Fig. 1). The dependence of E_{a0} on ΔH can be described by the parabola crossing eqn. (2),[22] where γ is the

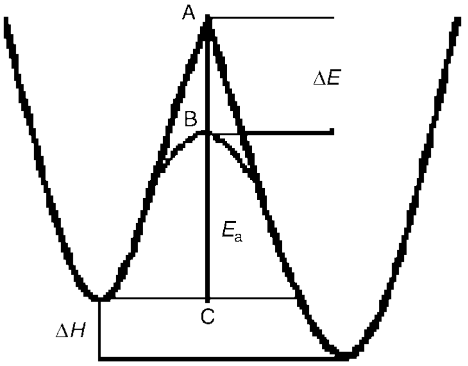


Fig. 1 Two parabola crossing energy profile of addition reaction.

$$E_{a0} = (0.5\beta\gamma + (\Delta H/\gamma\beta))^2 \qquad (2)$$

length of the bond being broken at the crossing point and β is a dynamic characteristic of this bond. This equation is identical with the simplified Marcus equation.[23]

The second very important contribution to the height of the reaction barrier is the energy of the interactions (ΔE) between the partners in the TS. It is equal to AB (Fig. 1) and may be estimated using Klopman's eqn. (3),[24] where s and t refer to atoms

$$\Delta E = -\frac{Q_s Q_t}{R_{st}} + 2\,\Sigma^s \Sigma^t \frac{C_s^m C_t^n \Delta\beta_{st}}{E_m^* - E_n^*} \qquad (3)$$

interacting in the transition state, Q_s, Q_t are the charges on them, R_{st} is the distance between them in the TS, C_s^m is the coefficient at the atomic orbital (AO), E_m^* the energy of the occupied molecular orbital of the first reactant, C_t^n the coefficient at the AO, E_n^* the energy of the unoccupied molecular orbital of the second reactant and $\Delta\beta_{st}$ is the change in the resonance integral. Values of all parameters correspond to the geometry of the reactants in the TS. The observed activation energy (E_a) can be described as in eqn. (4) where E_{a0} and

$$E_a = E_{a0} - \Delta E \qquad (4)$$

ΔE are defined by eqns. (2) and (3). This leads to the dependence of the barrier E_a on the thermodynamic driving force ΔH and the stabilisation resonance energy ΔE in the transition state. If E_m^* and E_n^* may be represented by the ionisation potential (Ip) and electron affinity (EA) of the partners, then E_a is a function of the reaction enthalpy ΔH, ionisation potential (Ip) and electron affinity (EA) of the reactants, charges on the interacting atoms (Q_i) and AO coefficients of these atoms (C_i^{AO}).

In our reaction, where the same electron acceptor radical ROO reacts with different molecules with low ionisation potentials, we may expect that the activation energy E_a should depend only on Q_i, C_i^{AO}, E_{HOMO} of the molecule and the heat of reaction $\Delta H_r^{\mathrm{add}}$.

In the reactions of peroxyl radicals the compensation effect is observed and one can replace the energy of activation with the logarithm of the rate constant in structure–reactivity relationships. Taking into account eqns. (2), (3) and (4) we can see that

Table 1 Experimental (PES) first three ionisation potentials (Ip/eV) and calculated (PM3) dihedral angles (θ/°) of substituted styrenes

N	Substituent	Ip_1	Ip_2	Ip_3	$Ip_2 - Ip_1$	θ
1	None (styrene)	8.50	9.30	10.55	0.80	0.0
2	α-Me	8.50	9.24	10.14	0.74	0.0
3	α-*t*-Bu	8.96	9.17	9.50	0.21	90.0
4	α-Ph	8.23	9.04	9.15	0.81	0.0
5	α-cyclo-Pr	8.40	9.08	9.60	0.68	0.0
6	α-Br	8.78	9.40	9.91	0.62	0.0
7	α-Cl	8.74	9.37	10.14	0.63	0.0
8	α-CF_3	9.40	9.56	10.90	0.16	50.0
9	α-$OSiMe_3$	8.29	9.25	9.69	0.96	70.0
10	*p*-CF_3	8.99	9.45	10.22	0.46	0.0
11	*p*-*t*-Bu, α-Me	8.17	8.92	9.72	0.75	0.0
12	*p*-Br, α-Me	8.68	9.38	9.97	0.70	0.0
13	*p*-Cl, α-Me	8.54	9.39	9.54	0.85	0.0
14	*p*-MeO, α-Me	7.94	9.01	9.15	1.07	0.0
15	*o*-Me, α-Me	8.80	9.00	9.50	0.20	72.7
16	*p*-MeO, α-OMe	7.73	9.00	—	1.27	0.0
17	2,4,6-Me_3	8.30	8.55	9.55	0.25	90.0
18	α,β,β-Me_3	8.28	8.44	9.02	0.16	77.2
19	*p*-Cl, α,β,β-Me_3	8.42	8.50	9.30	0.08	78.8
20	*p*-MeO, α,β,β-Me_3	7.70	8.60	9.00	0.90	68.2
21	*m*-CF_3, α,β,β-Me_3	8.60	10.00	11.70	1.40	51.6
22	α-EtO, β,β-Me_2	7.60	9.20	9.50	1.60	87.1
23	α-Ph, β,β-Me_2	7.90	9.00	10.70	1.10	90.0
24	α-Me,Naphthyl-1	7.90	8.70	9.30	0.80	86.9
25	α-Me,Naphthyl-2	7.88	8.48	8.57	0.60	0.0
26	β,β-Me_2,Fluorenyl	7.77	8.86	9.57	1.09	0.0

E_a is equal to the difference of two non-linear functions of such parameters as C^{AO}, E_{HOMO} (or Ip) and $\Delta H_R{}^{add}$. For similar reactants where the changes in ln k are not large we can expand this non-linear function into a series and take into consideration only the linear part of the expansion as a reasonable approximation, eqn. (5). The approximation in this simplified model is

$$\ln k = a_0 + a_1Q + a_2\mathrm{Ip} + a_3\Delta H_R^{add} + a_4C^{AO} \qquad (5)$$

valid when the second derivatives of ln k with respect to the parameters are negligibly small. We expect that it is so because large changes of measured rate constants do not occur in our reaction series.

Photoelectron spectra and ionisation potentials

The conformation of a molecule is of importance in the electronic properties of substituted styrenes. Conjugation of the benzene ring and the vinyl group is largest in the planar conformation. However, steric hindrance is smaller in the twisted conformation than in the planar one. Owing to these conflicting factors, the most stable conformation of styrenes cannot simply be predicted. Various experimental and theoretical dihedral angles have been reported.[25] Although the most stable conformation of styrene has not been determined exactly yet, the planar structure seems to be most likely judging from the data reported. Moreover, the rotation barrier has been estimated by different methods as between 1.4 and 4.3 kcal mol^{-1}.

Some conclusions about the conformation of substituted styrenes may be drawn from analysis of their PES. The PES for all compounds studied in this work, have been measured. The first group of very distinct bands possessed ionisation energies between 8 and 11 eV. These data are important for the further discussion and therefore they need additional consideration. These bands are associated with the π-orbitals, similar to those of benzene and the ethylene moiety. Furthermore, the changes in PES show significant hindrance to conjugation.[26,27] It is the separation between levels 1 and 3 which seems to be the most characteristic property.[26] It was shown[27] that a linear regression exists between ΔE ($Ip_1 - Ip_4$) and cos θ (dihedral angle C_1–C_2–C_3–C_4) in PES of biphenyls. The energy splitting $\Delta E = 1.8$ eV for biphenyls between levels 1 and 3 suggests an approximately planar conformation, and a splitting of 1.4 eV corresponds to a dihedral angle of 45°. However, the splitting between levels 1 and 2 may be very important as well. The data of Table 1 show that the splittings between experimental Ip_1 and Ip_2 are small for the styrenes with bulky substituents in the α-position (α-*t*-Bu, α-CF_3) and in the *ortho*-position to the vinyl group. Steric hindrance in such molecules does not allow location of the vinyl group in the same plane as the aromatic ring. One rather small Me substituent in the *ortho*- or α-position is not sufficient to induce a large deviation from coplanarity. In the case of *ortho*-substituted styrene the ethylenic group adopts a favourable conformation with the α-hydrogen on the same side as the *ortho*-substituent. At the same time, the PES of styrenes with either two *ortho*- or with *ortho*- and α-substituents reflect significant changes in hindrance. The similar behaviour to that of the benzene ring demonstrates that the α-RO substituent takes up a planar position to the double bond in the optimum geometry; this may be explained by interaction of the lone electron pairs of the O atom with π-electrons of the double bond which leads to a large splitting of the first two levels. A further tendency can be seen from Table 1; the decrease of the splitting with increase of the electron withdrawing properties of substituents. From Table 1 we can see that the first ionisation potentials of substituted styrenes depend on the electronic properties of the substituents and their sizes. The presence of electron donor substituents in any site of the molecule decreases its Ip and the electron acceptor substituents increase it. Bulky substituents in the *ortho*-position or in the ethylenic group also increase Ip.

The calculations of Ip using the PM3 Hamiltonian show a reasonable agreement with these conclusions. Table 2 shows the analogous dependence of E_{HOMO} on the nature and position of substituents. We can compare E_{HOMO} calculated by the PM3 method for molecules having optimised geometry (Table 2) and experimental (measured by PES) ionisation potentials (Table 1). There is a linear correlation ($r = 0.932$, $F(1,24) = 159.25$, $p < 0.00000$) between ionisation potentials and E_{HOMO} (Fig. 2), eqn. (6). To elucidate the influence of a conformation on the

$$\mathrm{Ip} = -(4.38 \pm 1.01) - (1.41 \pm 0.11)E_{HOMO} \qquad (6)$$

ionisation potential of a molecule the energies of the HOMO of some styrenes at different values of bond angle θ were calcu-

Table 2 The experimental rate constants (k/M^{-1} s^{-1}), calculated E_{HOMO} (eV), charges (Q), coefficients C_1, C_2 at the p$_z$ AO of the HOMO on the vinylic carbon atoms, enthalpies of formation of molecules (ΔH_M/kcal mol^{-1}) and of β-peroxy radicals (ΔH_R/kcal mol^{-1}) and enthalpies (ΔH/kcal mol^{-1}) of the reaction of molecules with the MeOO radical. N as in Table 1

N	k	E_{HOMO}	Q_1	Q_2	C_1	C_2	ΔH_M	ΔH_R	ΔH
1	7.0	9.13	−0.158	−0.091	0.468	0.321	39.2	8.5	−33.7
2	12.8	9.04	−0.174	−0.061	0.514	0.357	31.2	0.1	−34.1
3	0.8	9.57	−0.166	−0.066	0.008	0.007	18.4	− 6.8	−28.2
4	15.6	9.05	−0.155	0.022	0.489	0.330	65.9	37.5	−31.4
5	13.6	9.06	−0.175	−0.032	0.593	0.345	59.3	29.9	−32.4
6	33.6	9.36	−0.142	−0.064	0.469	0.303	47.0	18.4	−31.6
7	22.7	9.23	−0.166	−0.096	0.517	0.329	33.1	1.8	−34.3
8	2.8	9.80	−0.064	−0.147	0.306	0.212	−116.9	−145.7	−31.8
9	13.8	8.84	−0.235	0.115	0.651	0.532	−74.5	−96.2	−24.7
10	5.9	9.58	−0.152	−0.077	0.542	0.402	−127.3	−158.2	−33.9
11	14.0	8.90	−0.177	−0.059	0.484	0.323	9.1	−23.2	−35.3
12	9.6	9.19	−0.166	−0.067	0.432	0.280	38.2	7.8	−33.4
13	9.2	8.95	−0.169	−0.064	0.430	0.281	24.4	−7.1	−34.5
14	18.4	8.68	−0.184	−0.053	0.435	0.268	−6.8	−38.7	−34.9
15	3.2	9.36	−0.162	−0.068	0.193	0.144	22.3	0.3	−25.0
16	28.3	8.66	−0.248	0.089	0.534	0.326	−29.6	−63.7	−37.1
17	4.3	9.09	−0.154	−0.086	0.204	0.136	14.9	−11.9	−29.8
18	5.9	9.18	−0.106	−0.100	0.534	0.547	14.6	−2.5	−20.1
19	4.5	9.15	−0.101	−0.096	0.326	0.322	7.7	−9.8	−20.5
20	8.6	8.83	−0.107	−0.092	0.336	0.309	−23.2	−41.0	−20.8
21	3.6	9.29	−0.092	−0.107	0.531	0.521	−143.6	−161.0	−20.4
22	13.0	8.75	−0.171	0.049	0.611	0.529	−17.6	−32.9	−18.4
23	7.3	8.94	−0.083	−0.057	0.458	0.428	49.3	32.5	−19.8
24	4.0	8.77	−0.158	−0.074	0.005	0.001	49.6	19.7	−32.9
25	28.3	8.67	−0.170	−0.063	0.324	0.193	48.7	14.1	−37.6
26	11.4	8.72	−0.048	−0.043	0.492	0.476	57.3	37.6	−22.7

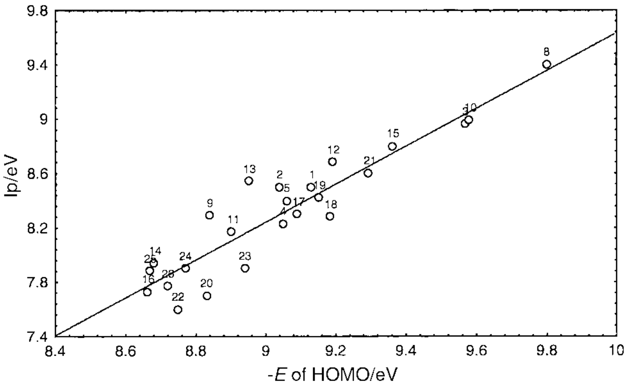


Fig. 2 Correlation between the energy of the HOMO of substituted styrenes and their ionisation potentials. The numbered points correspond to N in Table 1.

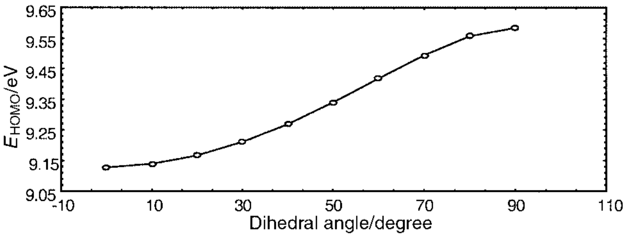


Fig. 3 Plot of calculated energy of the HOMO of styrene against dihedral angle between the benzene ring and vinyl group.

lated. The computation results (Fig. 3) indicate significant dependence of E_{HOMO} on dihedral angle. We can conclude that for the molecules where the barrier to rotation of the ethylenic group is high due to steric hindrance and the θ in the optimum structure is more than 10–15° we can expect higher values of Ip in comparision with planar molecules where $\theta = 0°$. It is interesting that this dependence can be described by a simple function of sin θ, see eqn. (7), where $E_{\text{HOMO}}(0)$ equals the energy of the coplanar conformation and a and b are empirical parameters. For styrene $a = 0.443$, $b = 2.63$ (correlation coefficient $r = 0.998$), for 2-isopropenylnaphthalene $a = 0.129$, $b = 2.10$ ($r = 0.999$), and for α-methylstyrene $a = 0.537$, $b = 3.00$ ($r = 0.996$).

$$E_{\text{HOMO}} - E_{\text{HOMO}}(0) = a \sin \theta^{b} \qquad (7)$$

Calculations of the reaction enthalpy

In order to estimate the role of enthalpy in the reactivity of substituted styrenes in reaction (1), data on the reaction heats become necessary, in other words, we must know the heats of formation of all reagents. Experimentally measured values are available only for a few of them. Semiempirical methods allow one to calculate the enthalpy of formation of molecules with satisfactory accuracy (Table 3). However, the heats of formation of radicals are too low at an average of 12 kcal mol^{-1}, although some exceptions exist (peroxyl radicals). It is a known fact[28] that the use of different spatial orbitals for α- and β-electrons allows for additional correlation. This energy, however, has already been taken into account in the choice of parameters of semiempirical methods. Hence, it is taken account of twice over and leads to the often observed overestimation of radical stability.[28] That shift of the energy scale can be taken into account by comparing the calculated and experimental data for similar radicals. Experimentally available data and values calculated by the PM3 method for the studied molecules and radicals, reactants and products of reaction (1), substituted styrene, benzyl radicals and peroxyl radicals, are presented in Table 3. We can see a constant deviation between calculated and experimental values. The deviation is different for every class of radicals and molecules. It is −3.4 kcal mol^{-1} for molecules, 1.3 kcal mol^{-1} for primary peroxyl radical and 15.0 kcal mol^{-1} for α-substituted benzyl radicals. Taking into account that the empirical parameters in the PM3 method were chosen[20,21] on the basis of the linear dependence between PM3 calculated and experimental values, we may use the obtained deviations to correct the estimated heat of reaction. We can expect that PM3 calculated values will give a linear correlation with experimental ones.

The results discussed above allow us to estimate the reaction enthalpies of two possible reaction paths for the addition

Table 3 Experimental (ΔH_{exp}/kcal mol^{-1}) and calculated (ΔH_{PM3}/kcal mol^{-1}) heats of formation of substituted styrenes, benzyl radicals and peroxyl radicals (298 K)

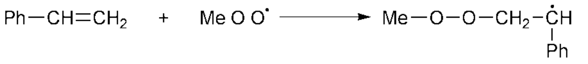
Molecules/radicals	ΔH_{exp}	Ref.	ΔH_{PM3}	$\Delta\Delta H^a$	Mean $\Delta\Delta H^a$
$PhCH{=}CH_2$	35.2	29	39.2	−4.0	
$PhCH{=}CHMe$ *cis*	29.0	29	32.6	−3.6	
$PhCH{=}CHMe$ *trans*	29.0	29	31.6	−2.6	−3.4
p-$MeC_6H_4CH{=}CH_2$	27.4	29	29.8	−2.4	
α $PhCMe{=}CH_2$	27.0	29	31.2	−4.2	
$PhC^{\bullet}Me_2$	33.2	30	19.1	14.1	15.0
$PhC^{\bullet}Me_2$	35.0	31	19.1	15.9	
$CH_2{=}CHCH_2OO^{\bullet}$	23	32	22.6	0.4	
$MeOO^{\bullet}$	6	32	3.0	3.0	1.3
$C_2H_5OO^{\bullet}$	−2	32	−2.4	0.4	

[a] $\Delta\Delta H = \Delta H_{exp} - \Delta H_{PM3}$.

Table 4 The changes in electronic properties, energy and geometric parameters along the reaction path of addition of $MeOO^{\bullet}$ to styrene (St)

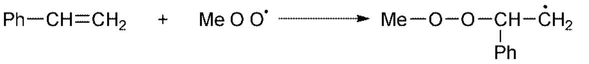
		Reaction coordinate $L_{C1\text{-}O1}$/Å	ΔH/kcal mol^{-1}	Q_{C1}	Q_{C2}	Q_{O1}	L_{CC}/Å	L_{OO}/Å
1	St	∞	39.2	−0.1580	−0.0914		1.3328	
2	$MeOO^{\bullet}$	∞	3.0			−0.1918		1.2639
3		2.1500	51.0	−0.1220	−0.0916	−0.1775	1.3594	1.2878
4	TS	2.0250	52.4	−0.0882	−0.0874	−0.1773	1.3783	1.3118
5		1.9750	52.0	−0.0507	−0.0900	−0.1843	1.3934	1.3365
6	StOOMe	1.3876	8.5	0.0966	−0.1735	−0.1674	1.4853	1.5838
7	Change (%)			28.24	4.87	59.43	29.84	14.97

of peroxyl radicals to styrene (ΔH_R^{add}) at the α- and β-positions. The methylperoxyl radical was chosen as a model radical and the styrene as model olefin. For addition at the β-position, eqn. (8), the reaction enthalpy may be estimated by



$$Ph{-}CH{=}CH_2 + MeOO^{\bullet} \longrightarrow Me{-}O{-}O{-}CH_2{-}\underset{Ph}{\overset{\bullet}{C}H} \qquad (8)$$

using the calculated enthalpies of styrene, 39.2, methylperoxyl radical, 3.0, and β-peroxyalkyl radical, 8.5 kcal mol^{-1} respectively: $\Delta H_a^{add} = 8.5 - 3.0 - 39.2 = -33.7$ kcal mol^{-1}. For addition at the α-position, eqn. (9), the reaction enthalpy is



$$Ph{-}CH{=}CH_2 + MeOO^{\bullet} \longrightarrow Me{-}O{-}O{-}\underset{Ph}{CH}{-}\overset{\bullet}{C}H_2 \qquad (9)$$

$\Delta H_R^{add} = 26.3 - 3.0 - 39.2 = -15.9$ kcal mol^{-1}. The results of this calculation reasonably confirm the formation of the much more stable α-benzylic radical by the addition of a peroxyl radical to the β-C atom of styrene. The difference between the enthalpies of reactions (8) and (9) is more than 17 kcal mol^{-1}. In the case of α,β,β-trimethylstyrene, the difference between the reaction enthalpies for the formation of the β-substituted β-peroxyalkyl radical $MeOOCMe_2C^{\bullet}PhMe$ (−2.5 kcal mol^{-1}) and α-substituted β-peroxyalkyl radical $MeOOCPhMeC^{\bullet}Me_2$ (3.9 kcal mol^{-1}) is 6.4 kcal mol^{-1}. This value is equal to the difference between the heats of the addition reactions. As a result we can conclude that the addition of peroxyl radicals to substituted styrenes of our series occurs at the end β-C atom. The reactions considered are exothermic. According to the Hammond postulate, such reactions should have an early transition state.

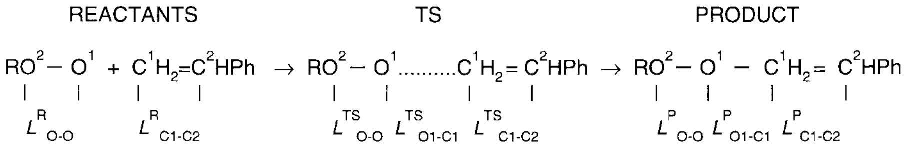
Structure–reactivity analysis

Quantum mechanical methods allow direct calculation of the transition state. The changes in electronic properties and energy with movement along the reaction path and characteristics of the TS for the addition of the MeOO radical to styrene were calculated by use of the PM3 method. As the reaction coordinate, the distance between the terminal C1 atom in styrene and terminal O1 atom in the peroxyl radical ($L^{R}_{C1\text{–}O1}$) was chosen. This distance is equal to infinity in the reactants and to $L^{P}_{C1\text{–}O1}$ in the product. In the first two rows of Table 4 are summarised calculated properties of the reactants (P^R), values (P^P) in row 6 are related to the products, and in row 4 are summarised the properties of the transition state (P^{TS}). The magnitude of change in percent of the bond length and electronic properties in the transition state compared with those in the reactants and products was calculated by eqn. (10). The calculated changes

$$\text{Chg\%} = \frac{(P^{TS} - P^{R}) \times 100\%}{P^{P} - P^{R}} \qquad (10)$$

presented in Table 4 show that the values of bond lengths both being broken and formed are less than 30% in the TS in comparison to the reactants. The changes in charges of C atoms at the reaction centre are similar. Only the change of the characteristics of the end O atom of the peroxyl radical reaches values higher than 50%. These results and the negative reaction enthalpy may be considered as a proof for an early TS.

The fact that the TS is early allows one to use the characteristics of the reactants for discussion of the structure–reactivity relationship. Since the peroxyl radical in our reaction series has always been kept the same, cumyl, only the properties of the olefin molecules are of importance for consideration of the reactivity changes.



$$\underbrace{RO^2{-}O^1}_{L^{R}_{O\text{-}O}} + \underbrace{C^1H_2{=}C^2HPh}_{L^{R}_{C1\text{-}C2}} \rightarrow \underbrace{RO^2{-}O^1}_{L^{TS}_{O\text{-}O}}\underbrace{\ldots\ldots\ldots}_{L^{TS}_{O1\text{-}C1}}\underbrace{C^1H_2{=}C^2HPh}_{L^{TS}_{C1\text{-}C2}} \rightarrow \underbrace{RO^2{-}O^1}_{L^{P}_{O\text{-}O}}\underbrace{{-}}_{L^{P}_{O1\text{-}C1}}\underbrace{C^1H_2{=}C^2HPh}_{L^{P}_{C1\text{-}C2}}$$

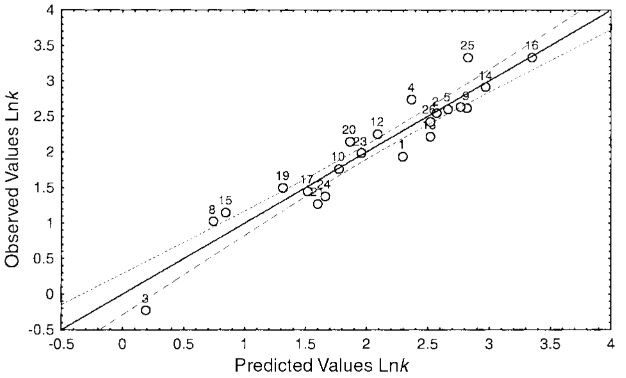


Fig. 4 Predicted (by eqn. (11)) and observed ln *k*. The numbered points correspond to *N* in Table 1.

The eigenvalues calculated for molecules and radicals can be used for qualitative analysis of the frontier MO interaction. The energies of these MOs for styrene are $E_{\mathrm{HOMO}}{}^{\mathrm{styrene}} = -9.116$ and $E_{\mathrm{LUMO}}{}^{\mathrm{styrene}} = -0.135$ eV, and for the MeOO$^{\bullet}$ radical $E_{\mathrm{HOMO}}{}^{\mathrm{MeOO}} = -11.556$ and $E_{\mathrm{LUMO}}{}^{\mathrm{MeOO}} = -0.231$ eV, respectively. The difference between $E_{\mathrm{LUMO}}{}^{\mathrm{styrene}}$ and $E_{\mathrm{HOMO}}{}^{\mathrm{MeOO}}$ is equal to 8.885 eV. It reflects the probability of electron transfer from the olefin molecule to the radical and is less than the difference $E_{\mathrm{LUMO}}{}^{\mathrm{MeOO}} - E_{\mathrm{HOMO}}{}^{\mathrm{styrene}} = 11.421$ eV which reflects the nucleophilicity of the radical in this reaction. In other words, a charge transfer from molecule to radical dominates in the TS. This conclusion is confirmed by direct calculation of the electronic structure of the TS, the results of which show a real charge transfer from styrene to the methylperoxyl radical in the TS, which is about 0.0885*e*. An early transition state, low ionisation potentials of styrenes and the electrophilic character of peroxyl radicals suggest that the HOMO energy of the alkene should gain considerable importance for determination of the rate of radical addition to the alkene. In some series the reactivity of alkenes decreases with increasing ionisation potentials of molecules.[5] Such correlations have been observed recently for addition reactions of other electrophilic species such as dicyanomethyl[33] and perfluoroalkyl[8] radicals.

We have shown recently[34,35] that, for some groups of molecules of our series in which the substituents are changing only at one position (for example *para*), a correlation with one parameter of electronic structure, ionisation potential, is satisfied. However, all 26 studied styrenes do not show such a correlation. Obviously, we have to take into consideration other electronic properties, energy of bond formation and breaking, as well as the enthalpy of the reaction, calculated by the PM3 method (Table 2).

When we take into consideration all 26 studied styrenes, the correlation with any one parameter of those presented in Table 1 is not sufficient (correlation coefficient *r* is less than 0.6). Using three parameters E_{HOMO}, $\Delta H_{\mathrm{R}}{}^{\mathrm{add}}$ and $C_{\mathrm{C1}}^{\mathrm{AO}}$, we have obtained an improved correlation (with all 26 styrenes $r = 0.86$). When we exclude two points (α-chlorostyrene and α-bromostyrene) we obtain for the 24 styrenes a remarkably better correlation with $r = 0.955$ (Fig. 4), eqn. (11). The reliability of

$$\ln k = 14.09 - 0.0442\Delta H_{\mathrm{R}}{}^{\mathrm{add}} + 1.58E_{\mathrm{HOMO}} + 2.52C_{\mathrm{C1}}^{\mathrm{AO}} \quad (11)$$

the relationship between ln *k* and the chosen parameters in our study can be quantitatively estimated and represented using a standard measure, statistical significance level (p-level) and tolerance. From Table 5 we can see that for all variables the tolerances are more than 0.9 and p-levels are less than 5×10^{-5} and regardless of arbitrariness in the decision as to what level of significance will be treated as really "significant", so small p-levels allow us to consider our results as "highly" significant. (Typically, results that yield $p < 0.01$ level are commonly considered statistically significant, and $p < 0.005$ or <0.001 levels are often called "highly" significant.) The data of Table 6 show that there is no correlation between the parameters of eqn. (11). The addition to eqn. (11) of terms $(\Delta H_{\mathrm{R}}{}^{\mathrm{add}})^2$ or $(C_{\mathrm{C1}}^{\mathrm{AO}})^2$ that reflect the non-linearity of the starting function does not increase the correlation coefficient.

Table 5 Regression summary for the relationship (11) (24 styrenes, α-chlorostyrene and α-bromostyrene excluded). $R = 0.954$; $F(3,20) = 67.2$; $p < 0.00000$; standard error of estimate 0.261

	B	Standard error in *B*	*t*(20)	Tolerance	p-level
Intercept	14.09	1.74	8.10		0.000000
$-E_{\mathrm{HOMO}}$	−1.59	0.18	−8.64	0.934	0.000000
C_1	2.52	0.33	7.65	0.928	0.000000
ΔH	−0.0442	0.0086	−5.15	0.985	0.000049

Observed $(\ln k)_{\mathrm{obs}}$, predicted $(\ln k)_{\mathrm{clc}}$ and residual Δln *k* values

N	Substituent	$(\ln k)_{\mathrm{obs}}$	$(\ln k)_{\mathrm{clc}}$	Δln *k*
1	None	1.95	2.29	−0.34
2	α-Me	2.55	2.56	−0.02
3	α-*t*-Bu	−0.22	0.19	−0.41
4	α-Ph	2.75	2.37	0.38
5	α-cyclo-Pr	2.61	2.66	−0.05
8	α-CF_3	1.03	0.73	0.30
9	α-$OSiMe_3$	2.62	2.81	−0.19
10	*p*-CF_3	1.77	1.77	0.01
11	*p*-*t*-Bu, α-Me	2.64	2.76	−0.13
12	*p*-Br, α-Me	2.26	2.09	0.17
13	*p*-Cl, α-Me	2.22	2.51	−0.29
14	*p*-MeO, α-Me	2.91	2.97	−0.06
15	*o*-Me, α-Me	1.16	0.84	0.32
16	*p*-MeO, α-OMe	3.34	3.35	−0.01
17	2,4,6-Me_3	1.46	1.51	−0.05
18	α,β,β-Me_3	1.77	1.77	0.00
19	*p*-Cl, α,β,β-Me_3	1.51	1.31	0.19
20	*p*-MeO, α,β,β-Me_3	2.15	1.86	0.29
21	*m*-CF_3, α,β,β-Me_3	1.28	1.60	−0.32
22	α-EtO, β,β-Me_2	2.56	2.57	−0.01
23	α-Ph, β,β-Me_2	1.99	1.95	0.04
24	α-Me, 1-Naphthyl	1.39	1.65	−0.27
25	α-Me, 2-Naphthyl	3.34	2.83	0.52
26	β,β-Me_2, Fluorenyl	2.43	2.51	−0.08

Table 6 Coefficients of the cross-correlations between parameters of relationship (11)

	$-E_{\mathrm{HOMO}}$	*C*1	Δ*H*
$-E_{\mathrm{HOMO}}$	1.00	−0.25	0.05
*C*1	−0.25	1.00	0.10
Δ*H*	0.05	0.10	1.00

Especially important are the signs of different terms of the obtained correlation equation. The minus at Δ*H* means that the reaction constant increases with increasing reaction exothermicity (as the Polanyi rule predicts). The plus sign at E_{HOMO}, which is itself negative, means that the reactivity of the molecule decreases with decreasing electron donor properties. The plus at coefficient C_1 shows that the overlapping between orbitals of reacting atoms plays some role in the TS. All signs are in accord with the proposed model.

The addition of any new parameter to this correlation equation (except Q_{C1}) does not show any improvement. Introduction of charges on the attacked C_1 atom (Q_{C1}) makes the correlation only slightly ($r = 0.961$) better. It is worthy of notice that the coefficient at Q_{C1} has a minus sign, as in shorter series.[35] It may mean that the repulsion between the attacked C_1 atom

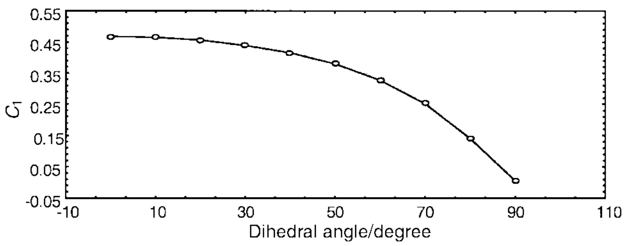


Fig. 5 Plot of calculated coefficient C_1 at the p_z atomic orbital of the terminal C1-atom of the HOMO of styrene against dihedral angle.

and the end O atom of the peroxyl radical, because both have a negative charge, plays some role.

In the case of α-Cl and α-Br substituted styrenes a big deviation from the obtained relationship may be explained by a different reaction mechanism. It was established experimentally that the main products of their oxidation are not epoxides as in all other styrenes but β-halogenoketones, so we can assume the reactions (12) and (13) occur. The calculated heats of formation

$$\mathrm{ROO^{\bullet} + BrPhC{=}CH_2 \longrightarrow RO^{\bullet} + O{=}CPhCH_2Br} \quad (12)$$

$$\mathrm{ROO^{\bullet} + ClPhC{=}CH_2 \longrightarrow RO^{\bullet} + O{=}CPhCH_2Cl} \quad (13)$$

(ΔH°) are: for $\mathrm{PhC(O)CH_2Br}$ -7.5 kcal $\mathrm{mol^{-1}}$, for $\mathrm{PhC(O)CH_2Cl}$ -19.2 kcal $\mathrm{mol^{-1}}$, and MeO -10.3 kcal $\mathrm{mol^{-1}}$, and the heat of reaction (12) is -11.8 kcal $\mathrm{mol^{-1}}$ and for reaction (13) it is -29.5 kcal $\mathrm{mol^{-1}}$. If we take into account these values instead of those presented in rows 6 and 7 of Table 4 we obtain a good correlation for all 26 styrenes ($r = 0.956$, $F(3,22) = 77.34$, $p < 0.00001$).

The comparison of kinetic data with optimum dihedral angles (θ) for substituted styrenes (Table 1) and analysis of the obtained correlation allow us to discuss the nature of steric effects in reaction (1) in more detail. We can see that steric hindrance leads to the decrease of reactivity of molecules. As was shown, steric hindrance is accompanied by an increase of the ionisation potential and it may be the only reason for a decrease of the molecule reactivity. However, as follows from eqn. (11), an additional factor may cause the decrease of reactivity. It is the decrease of coefficient $C_{\mathrm{C1}}^{\mathrm{AO}}$ at the p_z atomic orbital of the HOMO of the attacked carbon atom. The calculation of the dependence of C_1 on dihedral angle θ as depicted in Fig. 5 shows the sharp decrease of the coefficient at the atomic orbital ($C_{\mathrm{C1}}^{\mathrm{AO}}$) of the attacked carbon atom with deviation from planarity. This leads to a decrease of the overlapping of the AO on the O1 atom of the attacking peroxyl radical and the AO on the attacked atom, C1 of the molecule.

Analysis of data of Table 2 indicates that in the series either of styrenes non-substituted in the β-position or of substituted β,β-dimethylstyrenes taken separately the enthalpy factor plays a small role in reactivity changes, and reaction rate can be correlated with ionisation potential. Considering only the enthalpies of reactions we can describe together both series of molecules with steric hindrance (the value of coefficient C^{AO} is important here) using one equation. Thus the β,β-dimethyl substituted styrenes are noticeably less reactive than may be predicted from their ionisation potentials not only for steric reasons but also because of the small reaction enthalpies.

Conclusions

The results of this work show that the above described approach, which is based on the use of thermodynamic characteristics of reaction and electronic properties of reactants, may be successfully applied to the quantitative description of the structure–reactivity relationship in the main step of radical chain oxidation of styrenes, substituted in the ring and in the vinyl group, the addition of a peroxyl radical to the double bond. It provides evidence for the importance of polar factors in the transition state and enthalpy of reaction in the determination of the reaction rate for addition of peroxyl radicals to alkenes. The energy of TS stabilisation may be estimated in terms of Klopman's theory and all necessary parameters may be calculated with semiempirical PM3 methods.

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