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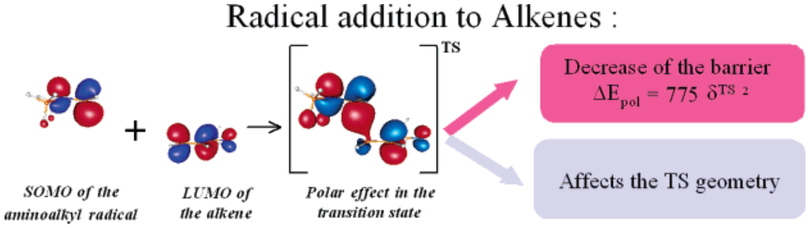
Addition of Carbon-Centered Radicals to Double Bonds: Influence of the Alkene Structure

Jacques Lalevée, Xavier Allonas,* and Jean-Pierre Fouassier

Département de Photochimie Générale, UMR 7525 CNRS,
Ecole Nationale Supérieure de Chimie de Mulhouse, 3 rue Alfred Werner, 68093 Mulhouse Cedex, France

x.allonas@uha.fr

Received September 14, 2004



The radical addition reaction to the double bond is well-recognized in organic chemistry as a powerful tool for C−C bond formation.The reactivity of three selected carbon centered radicals (aminoalkyl, methyl, and cyanomethyl) toward five double bonds, also representative of widespread monomers (vinyl ether, vinyl acetate, acrylonitrile, methyl acrylate, and ethylene), was examined in detail by using molecular orbital calculations. The observed reactivity is strongly influenced by the reaction exothermicity demonstrating that the energy barrier is governed in large part by the enthalpy term. The polar effect, as computed by molecular orbital calculations from the transition state structures, can drastically enhance the reactivity. A clear separation and quantification of the relative role of the polar and enthalpy effects in the different radical/double bond systems are obtained and the observed trend of reactivity is discussed. In addition to the effect of the charge-transfer configurations on the barrier, a large influence on the transition state geometry was evidenced.

Introduction

The factors governing the reactivity of carbon centered radicals (R) toward the addition reaction to a double bond (DB) remain the subject of fascinating discussions in the literature,[1−10] and particularly in the photoinitiation process of radical polymerization.[11] The reaction is depicted according to a State Correlation Diagram (SCD),[1,5−8] which shows the potential energy profiles of the four lowest doublet configurations of the system consisting of the unpaired electron of the radical and the electron pair of the attacked π bond: the reactant ground state, the reactant excited state, and two charge-transfer configurations (CTC) R^+/DB^- and R^-/DB^+. Beyond the fact that the barrier obviously decreases with increasing exothermicity, the involvement of polar effects can also greatly influence the reaction through a decrease of the barrier when decreasing the CTC energies.[1,7−8,12−20] A recent

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* Address correspondence to this author. Phone: 33 (0)389336874. Fax: 33 (0)389336895.

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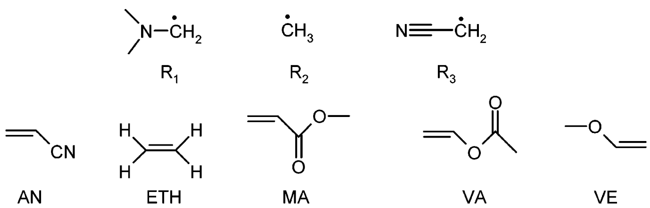
10.1021/jo048381c CCC: $30.25

SCHEME 1



study devoted to the addition of various aminoalkyl radicals to methyl acrylate has clearly demonstrated that the rate constant of addition is governed by both the reaction exothermicity and the participation of polar effects in the transition state (TS):[21] then, a separation of both contributions in the case of a large set of radicals reacting with methyl acrylate has been obtained according to a complete calculation procedure without resorting to any empirical chemical descriptor.[22] We report here the results of molecular orbital calculations carried out on the reactants, the products, and the TSs for the addition of three selected carbon centered radicals to five substituted double bonds. The three radicals were a nucleophilic aminoalkyl radical, an electrophilic cyanomethyl radical, and the methyl radical, which exhibits no marked nucleophilic or electrophilic character. The double bonds, namely vinyl ether (VE), vinyl acetate (VA), methyl acrylate (MA), acrylonitrile (AN), and ethylene (ETH), have different electron acceptor properties: strong effects are thus expected. The separation of both the enthalpy and polar factors as well as their evolution with the double bond will help to investigate in detail the influence of the alkene structure on the addition reaction efficiency. These double bonds being characteristic of very important classes of monomers, this study also allows some light to be shed on the relative reactivity of these compounds toward the initiation process of a polymerization.

Computational Procedure

The radicals and the double bonds studied are shown in Scheme 1.

All the calculation were performed with the hybrid functional B3LYP from the G98 suite of program,[23] this method being shown to be accurate enough for the description of addition reaction.[21,22] This procedure is worthwhile since the same Density Functional Theory (DFT) method can be used on large systems. The regioselectivity of the reaction being governed by the spin density in the alkene triplet state[5,6] (always found more important on the less substituted carbon for the alkenes studied), this study focused on the addition on the less substituted carbon of the double bond. Reactants, products, and transition states were fully optimized at the B3LYP/6-31G* level. The reaction enthalpy (ΔHr) was calculated as the energy difference between product and reactants at this level and corrected for zero point energy (ZPE). The distance d(C−C) between the radical center and the double bond was calculated from the B3LYP/6-31G* transition state structure. The amount of charge transferred δ^{TS} from the radical to the double bond in the transition state was evaluated from the Mulliken charges. The activation energy (Ea^{TS}) was evaluated by performing UB3LYP/6-311++G** single point energies on the corresponding UB3LYP/6-31G* structures (UB3LYP/6-311++G**//UB3LYP/6-31G* level) and ZPE corrected at the UB3LYP/6-31G* level. The spectroscopic triplet energies of the alkenes were computed at the TD/B3LYP/6-311++G** on B3LYP/6-31+G* optimized ground-state structures. Adiabatic ionization potentials (IP) and adiabatic electron affinities (EA) were calculated from the energies of the relaxed neutral molecule and the corresponding relaxed ion at the B3LYP/6-31+G* level and were ZPE corrected at the same level.

TABLE 1. Electronic Properties of the Five Alkenes and the Three Radicals Used

	IP (eV)[a]	EA (eV)[a]	χ (eV)[a]	η (eV)[a]	E_T (eV)[b]
AN	10.5 (10.9)	0.12 (−0.2)	5.3 (5.4)	5.2 (5.5)	3.34
MA	9.64 (9.9)	0.09 (−0.5)	4.9 (4.7)	4.8 (5.2)	3.54 (3.85[c])
ETH	10.21 (10.5)	−1.5 (−1.8)	4.4 (4.4)	5.9 (6.15)	4.06 (3.65[c])
VA	8.91 (9.2)	−0.48 (−1.2)	4.2 (4.0)	4.7 (5.2)	3.86
VE	8.69 (8.8[d])	−1.5 (−2.2[d])	3.6 (3.3[d])	5.1 (5.5[d])	4.13
R_1			2.61[e]	3.01[e]	
R_2			4.95[e]	4.95[e]	
R_3			5.90[e]	4.38[e]	

[a] At UB3LYP/6-31+G* and ZPE corrected. The experimental data from ref 1 are in parentheses. [b] Spectroscopic triplet energy determined at the TD/B3LYP/6-311++G**//B3LYP/6-31+G* level. [c] Experimental data from refs 28 and 29. [d] For ethyl vinyl ether: ref 1. [e] From ref 22.

Results and Discussions

Alkene Properties. The alkenes were characterized in terms of electron donor/acceptor properties. Calculated adiabatic ionization potentials (IP), collected in Table 1, are in good agreement with the experimental values, showing the validity of the method used. The excellent agreement between experimental and calculated adiabatic electron affinities (EA) obtained recently for radicals[22] led us to use the same B3LYP/6-31+G* method for the calculation of alkene EAs. However, in that case, the discrepancy between calculated and experimental values is much larger, as already pointed out in the literature.[24,25]

The electron-deficient or electron-rich character of the different alkenes is represented by their absolute electronegativity (χ_{DB}) and the hardness (η_{DB}) calculated from the general set of eq 1 and eq 2, respectively:[26,27]

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$$\chi = \frac{IP + EA}{2} \tag{1}$$

$$\eta = \frac{IP - EA}{2} \tag{2}$$

The electron acceptor properties of the five alkenes are expected to increase with the absolute electronegativity in the series VE, VA, ETH, MA, AN. The good agreement between the calculated and the experimental values shows that the computational method is accurate enough to describe the electron donor/acceptor properties of the alkene bonds used. The same procedure was used to obtain the absolute electronegativity (χ_R) and the hardness (η_R) of the radicals (Table 1).[22]

Effect of Alkene Structure on the Reaction Enthalpy. Table 2 collects the enthalpy of the reaction ΔHr calculated as the difference between the energies of product and reactant optimized structures. A good agreement between calculated values and experimental ones, when available, can be observed. Electron-withdrawing substituents increase χ_{DB} and stabilize the newly formed radical. Accordingly, ΔHr was found to depend linearly on χ_{DB} for the different radical/alkene systems, as shown in Figure 1a. The reaction exothermicity decreases in the series AN > MA > ETH ≈ VA > VE. A decrease of 1 eV of the alkene absolute electronegativity χ_{DB} is associated with a lowering of about 20−28 kJ/mol of the reaction exothermicity. Therefore, the barrier is expected to decrease with the reaction exothermicity when going from VE to AN for a given radical. This is in line with the fact that the reaction enthalpy and the electronic affinity EA_{DB} of the corresponding alkene already have been shown to correlate,[3,16,30] χ_{DB} and EA_{DB} varying in a similar way for the double bonds studied here.

It should be noted that for some double bonds characterized by both a low IP_{DB} and a high EA_{DB}, such as styrene, EA_{DB} would be a better parameter than χ_{DB} to characterize the reaction exothermicity.

Polar Effects. The importance of the polar effects is reflected by the amount δ^{TS} of the charge-transfer CT from R to DB in the transition state (Table 2).[1,7−8,12,20] The CT extent is strongly influenced by the alkene structure as shown by the quasilinear relationship between χ_{DB} and δ^{TS} (Figure 1b). Electron-deficient alkenes in the presence of nucleophilic radicals, as expected, increase the charge transfer whereas electron-rich alkenes increase the net charge transfer with electrophilic radicals. As a consequence, the $|\delta^{TS}|$ value for the nucleophilic R_1 increases strongly from VE to AN while, for the electrophilic R_3 it increases from AN to VE. For R_2, an ambiphilic character is noted: R_2 behaves as a nucleophilic radical for the addition to MA and AN, the charge-transfer being calculated to occur from R_2 to the double bond, and acts as an electrophilic radical for ETH, VA, and VE, with a charge transfer calculated from the double bond to R_2 in that case.

TABLE 2. Thermodynamical Data and Transition State Properties of the Radical/Alkene Systems

system	$-\Delta Hr^a$ (kJ/mol)	$d(C-C)^a$ Å	$\delta^{TS\ a}$
R_1/AN	90.3	2.544	0.15
R_1/MA	78.3	2.506	0.143
R_1/ETH	51.7	2.289	0.083
R_1/VA	55.8	2.317	0.089
R_1/VE	52.6	2.263	0.042
R_2/AN	135.6 (139)^b	2.497	0.028
R_2/MA	123.6 (117)^b	2.470	0.02
R_2/ETH	98.4 (99)^b	2.364	−0.02
R_2/VA	105.4 (101)^b	2.388	−0.024
R_2/VE	88.4 (100)^{b,c}	2.345	−0.06
R_3/AN	83.4	2.325	−0.032
R_3/MA	75.7	2.301	−0.048
R_3/ETH	56.7	2.248	−0.096
R_3/VA	62.2	2.273	−0.108
R_3/VE	48.4	2.242	−0.154

^{a} At the UB3LYP/6-31G* level, ZPE corrected. ^{b} Experimental data from ref 1. ^{c} For ethyl vinyl ether.

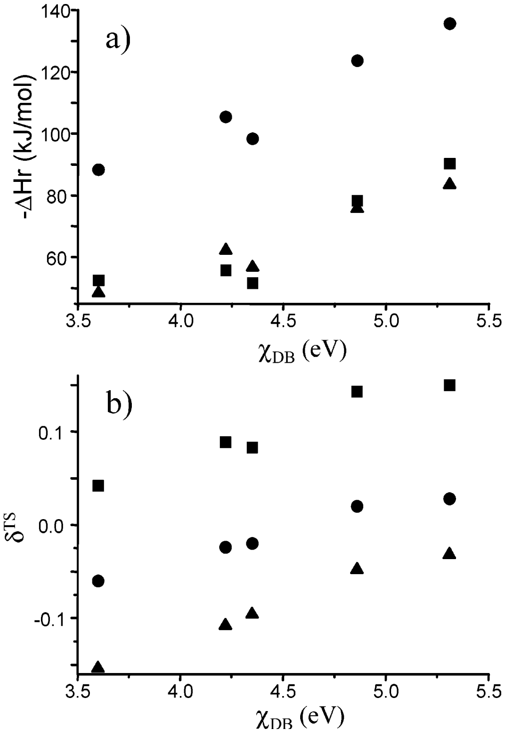

FIGURE 1. Variation of (a) the reaction enthalpy ΔHr and (b) the CT character δ^{TS} vs the absolute electronegativity of the alkene χ_{DB} (R_1: square; R_2: circle; R_3: up triangle).

Effect of Alkene Structure on the TS Geometry. The difference in the bond formation distance d(C−C) between the attacked carbon and the radical center from AN to VE, due to the corresponding variation of the reaction exothermicity, is particularly remarkable for the different radicals studied: 0.281 Å for R_1, 0.152 Å for R_2, down to 0.083 Å for R_3 (Figure 2). In the case of R_1, both polar and enthalpy effects increase from VE to AN, leading to a large increase of d(C−C) (0.281 Å). For R_3, polar and enthalpic effects work in the opposite direction: the reaction enthalpy increases from VE to AN while the polar effect ($|\delta^{TS}|$) decreases in the same time. Therefore the enthalpy factor should lead to an increase of d(C−C) from VE to AN while in the same time the polar effect acts in the other direction. Consequently, the variation of d(C−C) is very small from AN to VE (0.083

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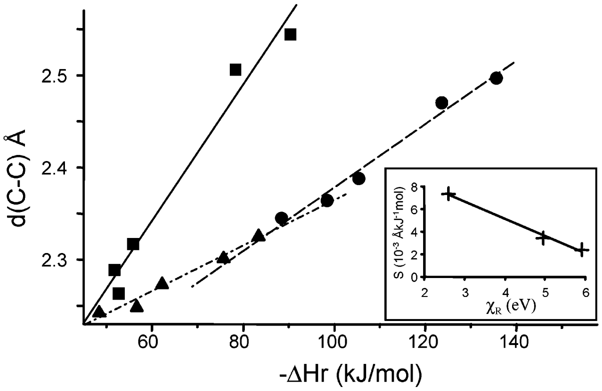

FIGURE 2. Plot of d(C−C) vs the reaction enthalpy ΔHr (R_1: square; R_2: circle; R_3: up triangle). Insert: Variation of the slope S vs the absolute electronegativity χ_R of the radicals.

Å). Finally, for R_2 the polar effect is always weak ($|\delta^{TS}| < 0.06$) and the reaction enthalpy increases from VE to AN, thus leading to an increase of d(C−C) in this series. For this latter radical, the variation of d(C−C) is mainly ascribed to the enthalpy factor and the d(C−C) change exhibits an intermediate value (0.152 Å).

Figure 2 clearly shows that d(C−C) depends linearly on the reaction enthalpy. This is in agreement with the Hammond postulate, which states that the earliness of a transition structure is directly related to the reaction exothermicity.[1,5–8] This is particularly the case for R_2, for which the TS structure is mainly determined by the crossing between the reactant and product configurations and hence by the reaction enthalpy, leading to a slope of 3.47×10^{-3} Å kJ^{-1} mol for the variation of d(C−C) with the enthalpy. In the case of R_1, a different plot is observed with a higher slope of 7.36×10^{-3} Å kJ^{-1}mol: this clearly indicates that the structures of the corresponding TSs are earlier than expected from ΔHr. This is accounted for by a very strong additive polar effect, as suggested from the high calculated charge transfer (Table 2), the participation of charge-transfer configurations to the TS structure influencing the location of the avoided crossing. For R_3, polar and enthalpy effects on d(C−C) are antagonists and a lower slope of 2.45×10^{-3} Å kJ^{-1}mol is obtained.

The linear fits of the correlation obtained between d(C−C) and ΔHr for the different radicals studied show that the enthalpy governs to some extent the TS geometry. More interestingly the corresponding slopes correlate quite well with the electronegativities χ_R of the radicals (Figure 2), unambiguously demonstrating that the polar effect not only affects the energy barrier but also has a large influence on the TS geometry.

Quantitative Separation of Polar and Enthalpy Effects. It has been recently shown[22] that a model due to Parr and Pearson allows the evaluation of the contribution of the polar effect from the electronegativities and the hardnesses of the isolated reactants.[26,27] The charge transfer δ^{PP} is estimated from these parameters by eq 3 and the energy change $\Delta E_{pol}{}^{PP}$ associated with this charge transfer is expressed by eq 4. Results are gathered in Table 3.

TABLE 3. Calculations of δ^{PP} and $\Delta E_{pol}{}^{PP}$ (see text)

	δ^{PP}	$\Delta E_{pol}{}^{PP}$ (kJ/mol)
R_1/AN	0.165	21.5
R_1/MA	0.145	15.7
R_1/ETH	0.098	8.3
R_1/VA	0.104	8.1
R_1/VE	0.061	3.0
R_2/AN	0.018	0.3
R_2/MA	−0.005	0.0
R_2/ETH	−0.028	0.8
R_2/VA	−0.038	1.4
R_2/VE	−0.067	4.3
R_3/AN	−0.031	0.9
R_3/MA	−0.057	2.8
R_3/ETH	−0.075	5.6
R_3/VA	−0.093	7.5
R_3/VE	−0.121	13.4

$$\delta^{PP} \frac{\chi_{DB} - \chi_R}{2(\eta_{DB} + \eta_R)} \qquad (3)$$

$$\Delta E_{pol}{}^{PP} = \frac{(\chi_{DB} - \chi_R)^2}{4(\eta_{DB} + \eta_R)} \qquad (4)$$

From eqs 3 and 4, it is not surprising to observe a good correlation between $\Delta E_{pol}{}^{PP}$ and δ^{PP} for the systems studied, as shown in Figure 3:

$$\Delta E_{pol}{}^{PP} = 775(\delta^{PP})^2 \qquad (5)$$

It can be seen from Table 3 that δ^{PP} values are in very good agreement with those extracted from the optimized TS (δ^{TS}) with the relationship $\delta^{TS} = 0.988\ (\delta^{PP}) - 0.004$ ($R^2 = 0.984$). Therefore in the following discussion, δ^{TS} will be used instead of δ^{PP} in the calculation of ΔE_{pol} (from eq 5) to improve the electronic description of the TS.

Taking into account the expression of ΔE_{pol} and the activation energy Ea^{TS} calculated by molecular orbital calculation, the enthalpy contribution (E_{enth}) can be determined by eq 6. For the different alkenes studied, the variation of E_{enth} with ΔHr is shown in Figure 4. A good correlation is observed (eq 7). Recently, a similar relationship has been found for the addition of 22 radicals to methyl acrylate (eq 8).[22]

$$Ea^{TS} = E_{enth} - \Delta E_{pol} \qquad (6)$$

$$E_{enth} = 65.3 + 0.37\Delta Hr = 65.3 - \Delta E_{enth} \qquad (7)$$

$$E_{enth} = 64.9 + 0.407\Delta Hr \qquad (8)$$

The satisfactory agreement between eqs 7 and 8 assesses that the description of the enthalpy factor as recently proposed in the case of MA can be safely extended to other alkene structures. A value for the energy barrier can be therefore easily calculated from:

$$Ea^{calc} = 65.3 + 0.37\Delta Hr - 775(\delta^{TS})^2 \qquad (9)$$

The barrier is therefore considered as the sum of polar (ΔE_{pol}) and enthalpy (E_{enth}) contributions, the latter being dependent on the reaction enthalpy (eq 7). The decrease of the barrier arising from the reaction enthalpy contribution (ΔE_{enth}) and the polar effect (ΔE_{pol}) is given by

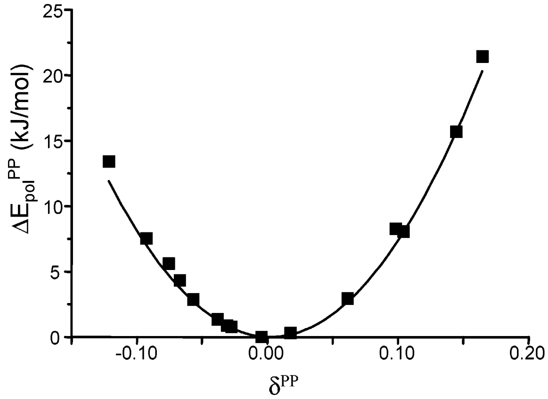

FIGURE 3. Plot of ΔE_{pol}^{PP} vs δ^{PP}.

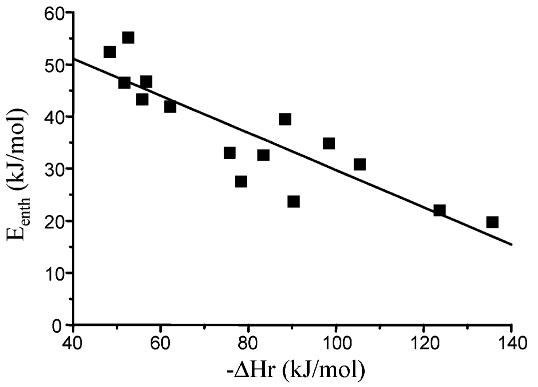

FIGURE 4. Plot of the enthalpy term E_{enth} vs the reaction exothermicity ΔHr.

$-0.37\Delta Hr$ and $775(\delta^{TS})^2$, respectively. The whole set of calculated data as well as some available experimental results are reported in Table 4.

A remarkable agreement is found in the case of R_2/alkene systems between B3LYP and G3(MP2)-RAD levels of calculations.[21,22] This latter method being well accepted for radical reaction studies,[15,31] the good agreement found between G3(MP2)-RAD and B3LYP allows the DFT procedure to be extended to other radical/alkene systems. Concerning the activation energies Ea^{calc} predicted by eq 9, the agreement is quite good with the calculated ones at both B3LYP and G3(MP2)-RAD levels. The discrepancies observed between Ea^{TS} and Ea^{calc}, about 5 kJ/mol, are mostly due to the transfer coefficient of the enthalpic term in the TS structure, which might slightly depend on the double bond unit: a coefficient of 0.407 was found for MA, and slightly different value should be obtained for each different alkene, leading to the average value of 0.37.[32] The possibility of evaluating Ea^{calc} from eq 9 is of great interest since it avoids an experimental determination of the barrier, which is always a hard task or a long calculation of the transition state properties. The experimental and calculated (Ea^{calc} or Ea^{TS}) values for the barrier are in good agreement for R_2/alkene. For R_3/alkene, both values can be considered as constant with the alkene structure, although the Ea^{exp} values are lower than the Ea^{calc} or Ea^{TS} ones when using no temperature correction is used.

Thanks to the separation of ΔE_{enth} and ΔE_{pol}, the evolution of the observed reactivity for the different radicals toward the double bonds can be examined in detail.

In the case of the nucleophilic radical R_1, the barrier is more favorable with alkenes containing a strong acceptor group than with electron-rich alkenes: significant increases of both the reaction exothermicity (19.5 to 33.4 kJ/mol for ΔE_{enth}) and the polar effect (1.4 to 17.4 kJ/mol for ΔE_{pol}) decrease the barrier from VE to AN. This additive effect leads to a large variation of Ea^{calc} throughout the different alkenes: a barrier increase of about 30 kJ/mol was noted between the addition to AN and VE.

For R_2, the polar effect always remained fairly low with a maximum value of ΔE_{pol} of 2.8 kJ/mol for VE. The barrier Ea^{calc} decreases from VE to AN, as a consequence of the increase of ΔE_{enth} from 32.7 to 50.2 kJ/mol in this series. The enthalpy contributing almost alone to the decrease of the barrier, the variation of Ea^{calc} with the different alkenes is lower than that for R_1.

For the electrophilic radical R_3, a worthwhile effect is outlined: the barrier remains almost constant whatever the alkene studied: the increase of the polar effect from AN to VE (0.8 to 18.4 kJ/mol for ΔE_{pol}) is counterbalanced by a decrease of the reaction exothermicity (30.9 to 17.9 kJ/mol for ΔE_{enth}) in this direction.

Influence of the Alkene Spectroscopic Triplet Energy. Computation at the TDB3LYP/6-311++G** (Table 1) level shows that the spectroscopic triplet energy of the alkenes varies from 3.34 eV for AN to 4.06 eV for ETH. When a comparison is possible, a rather good agreement is observed between experimental and calculated values demonstrating the validity of this computational method. All the double bonds studied are characterized by a $\pi\pi^*$ vertical excitation for the lowest excited triplet state, in total agreement with the description of this reaction by the State Correlation Diagram presented above. It should be noted that in the case of $n\pi^*$ triplet states (i.e. for some double bonds with the heteroatom), the use of the corresponding triplet energies might lead to confusing interpretations.

From the SCD it is expected that the triplet energy (E_T) of the double bond could affect the energy barrier:[5,6] a decrease of the spectroscopic triplet energy should decrease the value of the energy barrier. Such behavior has been recently evidenced for the addition of methyl radical to C=C, C=O, and C=S double bonds.[31] For the alkenes studied in this paper, this effect is less pronounced, and the same equation (eq 9) can describe the behavior of the different alkenes, leaving out any term related to the alkene triplet energies. This is mainly due

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[31] Henry, D. J.; Coote, M. L.; Gomez-Balderas, R.; Radom, L. *J. Am. Chem. Soc.* **2004**, *126*, 1732.

[32] Some calculations have been carried out for the addition of R_1 and R_2 to methyl methacrylate (MMA) to confirm the absence of any significant difference between MMA and MA (ref 21). As expected, the close values for the MMA and MA electronegativities (4.6 and 4.86 eV, respectively) lead to similar charge-transfer properties in the TS (δ = 0.135 and 0.01 for the R_1 and R_2 addition to MMA). The enthalpic term is also very close (ΔHr = −84.1 and −128.0 kJ/mol for the addition of R_1 and R_2 to MMA compared to the reaction enthalpies for MA: −78.3 and −123.6 kJ/mol, respectively). The TS structures observed are very similar: for example, d(C−C) = 2.47 and 2.477 Å for the addition of R_2 to MA and MMA. The barriers of 15.1 and 21.3 kJ/mol for the addition of R_1 and R_2 to MMA are obviously found close to those for MA.

TABLE 4. Comparison of Barriers Calculated by the Proposed Model to Experimental Data and Barriers Resulting from Molecular Orbital Calculations

systems	Ea^{calc} (kJ/mol)	ΔE_{enth} (kJ/mol)	ΔE_{pol} (kJ/mol)	$Ea^{TS\ a}$ (kJ/mol)	$Ea^{exp\ b}$ (kJ/mol)	$Ea^{exp(0K)\ c}$ (kJ/mol)	$Ea^{\ G3(MP2)-RAD\ d}$ (kJ/mol)
R_1/AN	14.4	33.4	17.4	6.3			
R_1/MA	20.5	29.0	15.8	11.7			
R_1/ETH	40.8	19.1	5.3	41.2			
R_1/VA	38.5	20.6	6.1	37.2			
R_1/VE	44.5	19.5	1.4	53.8			
R_2/AN	14.5	50.2	0.6	19.1	15.4	16.4	21.1
R_2/MA	19.3	45.7	0.3	21.7	16.9	17.6	21.1
R_2/ETH	28.6	36.4	0.3	34.5	28.2	30.4	36.2
R_2/VA	25.8	39.0	0.4	30.4	24.8	29.9	32.4
R_2/VE	29.8	32.7	2.8	36.7	24.8[e]	28.3[e]	38.3[e]
R_3/AN	33.6	30.9	0.8	31.8	18.4		
R_3/MA	35.5	28.0	1.8	31.3	18.4		
R_3/ETH	37.2	21.0	7.1	39.6	26.5		
R_3/VA	33.2	23.0	9.0	32.9	23.3		
R_3/VE	29.0	17.9	18.4	34.0	20.6		

[a] UB3LYP/6-311++G**//UB3LYP/6-31G* level (ZPE at UB3LYP/6-31G* level); [b] Experimental data from ref 1. [c] Experimental data from ref 1 corrected at 0 K; [d] Barrier determined at the G3(MP2)-RAD level in ref 1. [e] For ethyl vinyl ether.

to the small variation of this parameter (20%) along the alkenes used compared to those studied in ref 31.

Conclusion

In this work, molecular orbital calculations were used to calculate the values of the activation energies and to clearly separate the polar and enthalpy effects invoked in radical addition reactions. For the different double bonds studied, our description appears as powerful to understand the evolution of the radical reactivity with various representative alkenes exhibiting large differences in their nucleophilic/electrophilic characters. While a more systematic study might be of interest to study the evolution of the exothermicity transfer coefficient with the double bond, it appears that the proposed treatment adequately describes the reactivity trends and that the dominant factors giving rise to a high reactivity can be confidently used to predict the efficiency evolution for the addition of a given radical to different alkene structures.

Acknowledgment. We thank CINES (Centre Informatique National de l'Enseignement Supérieur) for the generous allocation of computational time on the IBM Supercomputer.

Supporting Information Available: **Z**-matrixes for reactants, transition states, and products and imaginary frequencies characterizing all the different transition states structures. This material is available free of charge via the Internet at http://pubs.acs.org.

JO048381C