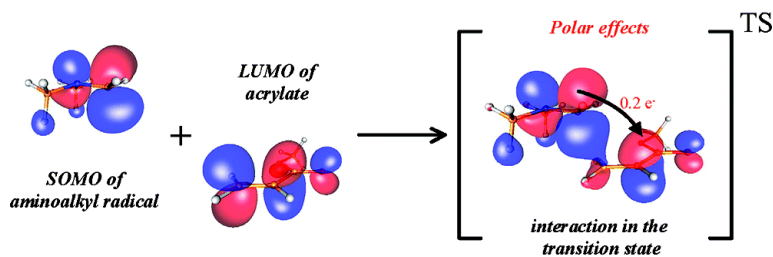Article

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Role of Charge-Transfer Configurations on the Addition Reaction of Aminoalkyl Radicals onto Acrylate Double Bonds

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Abstract: The major factors affecting the reactivity of the important class of aminoalkyl radicals toward the addition reaction onto acrylate double bonds were studied. The rate constants of interaction, directly measured by using laser-induced photoacoustic calorimetry, range from 2.5×10^7 to 4.5×10^7 M^{-1} s^{-1}. The reactivity of these radicals was compared to that of alkyl radicals. Calculations show that the reaction enthalpy is not the driving factor. Molecular orbital calculations of the transition states clearly demonstrated the large participation of charge-transfer configurations relative to nonpolar configurations, leading to a decrease of the barrier height. Moreover a quite good correlation is found when plotting the charge-transfer character in the transition state against the ionization potential. The roles of the different factors governing the reactivity of these species were elucidated.

Introduction

The reactivity of radicals R$^•$ onto double bonds M remains the subject of vigorous discussions and represents a fascinating challenge.[1−3] This addition reaction is usually described by a state correlation diagram[1,4−7] which involves the reactant ground-state configuration R$^•$/M, the excited reactant configuration R$^•$/^{3}M, and two polar charge-transfer configurations (CTC) R$^+$/M$^-$ and R$^-$/M$^+$. In this scheme, the exothermicity of the reaction strongly affects the barrier height. The importance of the polar effects increases as the configuration energy ΔE_{CT} decreases ($\Delta E_{CT} = $ IP(R$^•$) $-$ EA(M) or IP(M) $-$ EA(R$^•$) for the R$^+$/M$^-$ and R$^-$/M$^+$ configurations, respectively, where IP and EA stand for the ionization potential and the electron affinity of the reactants). When the ΔE_{CT} values are low ($<7-8$ eV), an important participation of the CTC in the transition state (TS) structure can contribute to a decrease of the barrier.[1,6−13] For a large set of R$^•$/M couples, enthalpy and polar effects, although undoubtedly observed, are still not easy to separate.[1,6−7,12−13] We report here (i) original measurements using laser-induced photoacoustic calorimetry (PAC)[14−16] of the rate constants (k_q) for the reaction of aminoalkyl radicals onto acrylate or meth-

Chart 1. Experimentally Studied Radicals (R$_1•$−R$_4•$) and Radicals Used for Comparison (R$_0•$, R$_5•$, R$_6•$, R$_7•$)
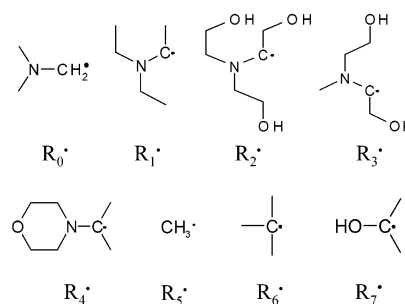
acrylate monomer double bonds (which is one of the most important reactions in free radical photopolymerization[17]), (ii) a comparison with alkyl radical reactivity, and (iii) molecular orbital calculations of the different TSs involved: the occurrence of striking polar effects is clearly demonstrated for aminoalkyl radicals, thus explaining their high reactivity. Finally, aminoalkyl radicals will be compared to dimethyl ketyl radical, which is known to be highly reactive toward acrylate derivatives.[1] The radicals studied are shown in Chart 1.

Experimental Section

R$_1^•$, R$_2^•$, and R$_3^•$ are produced through the well-known reaction between the triplet state of benzophenone and the corresponding amine. Radical R$_4^•$ is formed upon the direct cleavage of Irgacure 907 (Ciba Specialties). The different acrylates used correspond respectively to methylacrylate (MA), methyl methacrylate (MMA), butylacrylate (BA), and butyl methacrylate (BMA).

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A nanosecond Nd:Yag laser (Powerlite 9010, Continuum) operating at 10 Hz with an energy decreased down to 7 mJ/pulse at 355 nm was used for PAC experiment.[15] The attenuated pump beam irradiated a 1 cm cell equipped with a 1 MHz piezoelectric detector (A603S, Panametrics) through a pinhole. The signals corresponding to the measurement of the acoustic waves were amplified 10 times (Ortec 9301) and fed into a transient digitizer (TDS 3052, Tektronix). The time resolution τ_{tr} of the experimental setup is 120 ns. A solution of 2-hydroxybenzophenone was used as calorimetric standard. Optical densities of samples were about 0.2. Oxygen was removed by argon bubbling.

Molecular calculations have been carried out using the Gaussian 98 series of programs.[18] All the geometries, including transition states, were optimized at the B3LYP/6-31G* level. Energetic parameters were obtained on these geometries at the B3LYP/6-311++G** level or after full optimization at this level. Ionization potentials of the radicals were calculated at the B3LYP/6-31+G* level after full optimization of the neutral radical and the corresponding cation. Transition states were frequency checked, and the deduced activation energies E_a were ZPE corrected at the UB3LYP/6-31G* level. The charge transfer δ was calculated on the basis of Mulliken charges, according to the classical procedure.[1,6,7]

Results and Discussion

Aminoalkyl radicals usually exhibit no absorption in the classical spectral window offered by laser flash photolysis with transient UV/visible detection, so that the rate constants of interaction k_q between radicals and monomer remain largely unknown. Therefore, a new methodology based on the measurement by PAC of the heat evolved from the reaction was developed for their determination.[16] For a system producing radicals in solution, the subsequent addition of monomer results in a decrease of the radical lifetime and the release in the media of the corresponding heat of reaction. The acoustic wave resulting from the heat release is recorded for different amounts of monomers. A simple mathematical treatment allows the determination of k_q:

$$g(S_F) = \ln\left(\frac{S_F - h\nu + \phi_{rad}E_{rad} + \Delta H_r'}{\Delta H_r'}\right) = -\tau_{tr}\left(\frac{1}{\tau_0} + k_q[M]\right)$$

(1)

Here S_F corresponds to the fast heat release, $\phi_{rad}E_{rad}$ represents the energy stored in the radicals before addition of the monomer, $\Delta H_r'$ stands for the apparent heat of reaction, and τ_0 is the lifetime of the initiating radical $A^\bullet$.

The validity of this method has been already checked for a set of radicals by comparison with some values available from the literature.[16] A typical evolution of S_F for the interaction of the triethanolamine derived radical with methyl methacrylate is shown in Figure 1. A growth of S_F can be observed when the monomer concentration increases, corresponding to the addition of $A^\bullet$ onto M.

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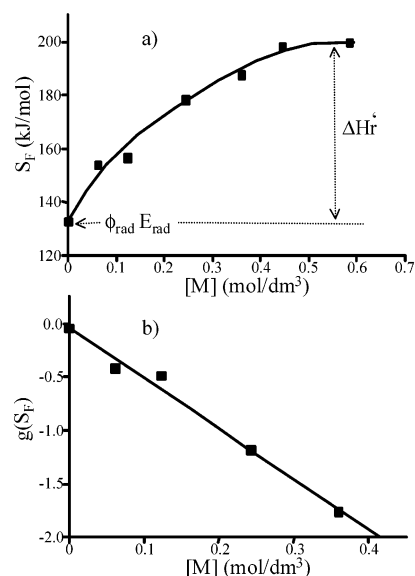
Figure 1. (a) Evolution of the fast signal S_F with increasing monomer concentration and (b) data treatment according to eq 1 for the system benzophenone/triethanolamine/methyl methacrylate in acetonirile.

Table 1. Rate Constants of Interaction k_q between Aminoalkyl Radicals and Various Monomers in Acetonitrile (in 10^7 M^{-1} s^{-1})

	MA	MMA	BA	BMA
$R_1^\bullet$	4.1	3.3	3.0	3.5
$R_2^\bullet$	2.7	3.0	3.5	4.0
$R_3^\bullet$	3	4.0	3.0	2.5
$R_4^\bullet$	4.5		4.0 (2.9[b])	
$R_5^\bullet$	0.034[a]	0.049[a]		
$R_6^\bullet$	0.11[a]	0.066[a]		
$R_7^\bullet$	3.5[a]	1.6[a]	1.3[b]	

[a] Reference 1. [b] Reference 21.

Chart 2
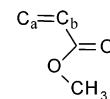
The k_q values (($2.5-4.5 \pm 1.0$) $\times 10^7$ M^{-1} s^{-1}) gathered in Table 1, for the aminoalkyl radical/M reactions, are very close to the maximum value reported for the addition of other kinds of secondary or tertiary carbon centered radicals onto double bond (10^7-10^8 M^{-1} s^{-1})[1,9,19,20] and 30–100 times higher than those obtained in the case of alkyl radicals. For $R_4^\bullet$, k_q is in very good agreement with the value obtained by using an indirect method demonstrating the validity of the approach used.[21]

Prior to any detailed investigation, it should be useful to address the question of the regioselectivity for the radical addition reaction. Different works have been already devoted to this problem. From experimental studies, it has been demonstrated that the addition can proceed through two different pathways: the normal one is the addition on the less substituted carbon C_a, and the abnormal one corresponds to the addition on the more substituted carbon C_b (Chart 2).[22]

Theoretical investigations have been performed on this problem, and it has been demonstrated that the radical attack is favored on the carbon (i) exhibiting the highest spin density in

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**Table 2.** Parameters Characterizing the Regioselectivity of the Addition Reaction

	C_a	C_b
spin density[a]	1.02	0.83
$-\Delta H_r$ ($R_0^\bullet$/t-MA) (kJ/mol)[a]	78.3	38.8
$-\Delta H_r$ ($R_5^\bullet$/t-MA) (kJ/mol)[a]	123.3	84.4

[a] At the UB3LYP/6-31G* level, ZPE included.

the triplet state and (ii) leading to the more favorable enthalpy of reaction ΔH_r.[5,23,24] Molecular calculations were carried out for the reaction of $R_0^\bullet$ and $R_5^\bullet$ toward MA. The results obtained are gathered in Table 2 and confirm that the addition onto the less substituted carbon C_a is largely favored. C_a corresponds both to the more spin rich carbon in the $\pi\pi^*$ triplet state and to the most exothermic reaction. Indeed, the spin density is higher for C_a than for C_b by ca. 0.19. The difference in the enthalpy of the addition reaction onto C_a and C_b is found very close to 39 kJ/mol for both $R_0^\bullet$ and $R_5^\bullet$. This is the result of the important stabilization of the product obtained with the addition onto C_a by a possible delocalization of the unpaired electron (of C_b) onto the carbonyl. These calculations clearly indicated the high regioselectivity of the reaction. In the following, it will be confidently assumed that the reaction occurs on the less substituted carbon atom, whatever the radical/monomer system considered.

From the calculated enthalpies for the addition reactions onto t-MA, listed in Table 3, the expected reactivity should follow the order $R_5^\bullet > R_7^\bullet \sim R_6^\bullet > R_2^\bullet \sim R_3^\bullet > R_1^\bullet > R_4^\bullet$ (alkyl radicals should be more reactive than aminoalkyl ones), which does not correspond to the experimental one $R_1^\bullet \sim R_2^\bullet \sim R_3^\bullet \sim R_4^\bullet \sim R_7^\bullet > R_6^\bullet > R_5^\bullet$. This result clearly demonstrates that the enthalpy is not the driving factor of the overall reactivity. This result is particularly emphasized by the behaviors of $R_4^\bullet$ and $R_5^\bullet$; e.g. despite a 3−5 times higher reaction enthalpy, $R_5^\bullet$ radical is experimentally found 100 times less reactive. The effect observed is particularly important, and the opposite reactivity between aminoalkyl and alkyl radicals can indicate an enhancement of the k_q values for aminoalkyl radicals through an important participation of charge-transfer configurations in the transition state (for a discussion on the results concerning $R_7^\bullet$, vide infra).

The computed ionization potentials of the radicals are reported in Table 3. Aminoalkyl radicals are characterized by very low IPs compared to alkyl ones. This can be ascribed to the existence of a two-orbital−three-electron interaction between the carbon centered unpaired orbital and the nitrogen lone pair: two
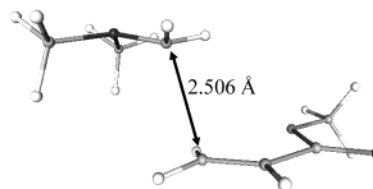
Figure 2. Transition state structure for the $R_0^\bullet$/t-MA reaction optimized at the UB3LYP/6-31G* level.

electrons lie in the bonding orbital while the unpaired electron, located in the upper antibonding orbital, can be easily removed.[15] This stabilization also explains the lower reaction enthalpy for aminoalkyl radicals. Using EA = −0.49 eV for MA,[1] the CTCs R^+/M^- for these radicals are characterized by $\Delta E_{CT} \ll 7$ eV, thereby evidencing an important stabilization of TS through polar effects (the CTCs for R^-/M^+ are not considered because PI(MA) = 9.8 eV[1] and the EA values of aminoalkyl radicals calculated at UB3LYP/6-31+G(d) level lie between −0.5 and 0.5 eV i.e., ΔE_{CT}'s ~10 eV).

More detailed molecular calculations have been carried out on the TSs at the UB3LYP/6-311++G**//UB3LYP/6-31G* level (optimization of geometry at UB3LYP/6-31G* level followed by a single point calculation at UB3LYP/6-311++G** level). The performance of such DFT methods for the calculation of barriers and reaction enthalpies for other radical additions has been already evaluated[25] and found to be reliable.

The energy difference between the cis (c-MA) and trans (t-MA) structures of MA being very low, it can be assumed that the two forms coexist in solution. A similar assumption has been recently made for MMA.[26] The difference of reactivity between the two forms calculated for $R_0^\bullet$ and $R_5^\bullet$ (Table 3) is very weak; i.e., the geometrical and energetic parameters for the corresponding TSs are quite close. Very similar TSs are computed for the addition of $R_0^\bullet$ onto MA and MMA (Table 3), which is in line with the close k_q values found for the addition of the aminoalkyl radicals onto acrylates and methacrylates. Therefore, in the following for a comparison of aminoalkyl vs alkyl radical reactivity, only the results obtained for t-MA will be discussed. A typical TS structure obtained for the addition of $R_0^\bullet$ onto MA is shown in Figure 2.

Calculated E_a values can differ from the experimental ones (16.9, 8.4, and ~0 kJ/mol for $R_5^\bullet$, $R_6^\bullet$, and $R_7^\bullet$, respectively[1]). This problem has been already pointed out in the literature and may arise from both theoretical calculations (~5.6 kJ of differential has been reported for similar calculations[25]) and experimental determinations.

Table 3. Computational Results for the Addition Reactions at the UB3LYP/6-31G* Level: Reaction Enthalpy (ΔH_r), Ionization Potential (IP), and Parameters Characterizing the Transition State

system	$-\Delta H_r$ (kJ/mol)	IP(R)[a] (eV)	d(C-C)[b] (Å)	$E_a{}^c$ (kJ/mol)	δ^d
$R_0^\bullet$/c-MA	80.1; 57[e]	5.62 (5.7)[g]	2.59; 2.443[f]	7;[e] 9.9[f]	0.134; 0.13[e]
$R_0^\bullet$/t-MA	78.3; 54.7;[e] 52.6[f]	5.62 (5.7)[g]	2.506; 2.42[f]	11.7;[e] 12.5[f]	0.143; 0.134[e]
$R_0^\bullet$/MMA	84.1; 61.2;[e] 61[f]	5.62	2.487	15.1[e]	0.135; 0.12[e]
$R_1^\bullet$/t-MA	54; 36.7[e]	4.96	2.416	10[e]	0.199; 0.21[e]
$R_2^\bullet$/t-MA	73.8; 50.6[e]	5.43	2.432	14.5[e]	0.174; 0.244[e]
$R_4^\bullet$/t-MA	39; 21.9[e]	4.9	2.364	5.1[e]	0.194; 0.29[e]
$R_5^\bullet$/c-MA	123.3; 105.4;[e] 106.3[f]	9.9 (9.84)[g]	2.474; 2.431[f]	20.6;[e] 20.7[f]	0.02; 0.005[e]
$R_5^\bullet$/t-MA	123.6; 106;[e] 106.3[f]	9.9 (9.84)[g]	2.470; 2.425[f]	21.7;[e] 21.6[f]	0.02; 0.02[e]
$R_6^\bullet$/t-MA	78.9; 65.9;[e] 65.7[f]	6.78 (6.7)[g]	2.382	20.6[e]	0.096; 0.125[e]
$R_7^\bullet$/t-MA	82; 65.9[e]	6.25 (6.5)[g]	2.411	7.7[e]	0.129; 0.168[e]

[a] Adiabatic ionization potential at UB3LYP/6-31+G* after optimization of the radical and the cation geometries. [b] Distance between the attacked carbon and the C-centered radical. [c] Activation energy. [d] Amount of charge transfer from the radical to the alkene. [e] UB3LYP/6-311++G**//UB3LYP/6-31G* (ZPE at UB3LYP/6-31G* level). [f] UB3LYP/6-311++G**. [g] Experimental values.[1,27] For $R_3^\bullet$, IP of 5.27 eV has been calculated.
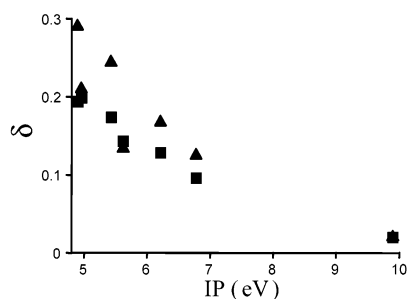
Figure 3. Plot of the charge-transfer δ in the TS between the radicals and *t*-MA vs the ionization potential IP of the radicals (UB3LYP/6-31G*, square; UB3LYP/6-311++G**//UB3LYP/6-31G*, up triangle).

Polar effects can be directly evidenced by the calculations of the charge transfer (δ) from R$^\bullet$ to MA in the TS structure.[6,7] Interestingly, when δ is plotted against IP, a good correlation (Figure 3) is observed: the δ values obtained for the aminoalkyl radicals are about 7−10 times higher than that for the methyl radical, which still underlines the decisive role of the polar effects to enhance the reactivity of these species. For R$_1$$^\bullet$ and R$_4$$^\bullet$, characterized by the lower IPs, a very important charge-transfer character is observed ($>$0.2) compared to R$_5$$^\bullet$ ($\sim$0.02).

The preexponential factors for the C-centered radical addition onto double bonds usually span on a narrow range[1] 7.5 $<$ log-(A) $<$ 8.5: it is assumed in a first approach that the preexponential factor (A) in the Arrhenius's law for the different radicals studied are similar. Thus, the calculated activation energies (E_a) must reflect the reactivity of the different radicals studied. Aminoalkyl radicals exhibit the highest reactivity: this is in agreement with an important decrease of the barrier due to a mixing of the CTCs with nonpolar configurations in the transition state, as shown by their high δ term. The *tert*-butyl radical, characterized by a higher IP (6.78 eV) and a lower δ value (0.096), exhibits a higher E_a and is found experimentally less reactive. The methyl radical, despite a more favorable reaction

enthalpy, presents the highest activation energy and the lowest reactivity. This result is in agreement with its low δ value.

The activation energy slightly changes for the different aminoalkyl radicals studied. It is well-known that tertiary C centered radicals exhibit a slightly lower A value than secondary radicals.[1,13] Slightly lower barriers are calculated for R$_4$$^\bullet$, relative to R$_1$$^\bullet$ and R$_2$$^\bullet$ (Table 3); the similarity in observed rate constants may be explained by small differences in A factors.

The relative behavior of aminoalkyl radicals and dimethyl ketyl radical R$_7$$^\bullet$, two kinds of radicals exhibiting high nucleophilic character and high reactivity toward acrylate derivatives (see Table 1), can be now discussed. The parameters characterizing the reactivity of R$_7$$^\bullet$ onto MA are gathered in Table 3. The enthalpy of reaction is clearly not the main parameter governing the reactivity of this compound. Indeed, similarly to aminoalkyl radicals, R$_7$$^\bullet$ exhibits a less favorable enthalpy of reaction than R$_5$$^\bullet$ but reacts much more efficiently. R$_7$$^\bullet$ being characterized by a low IP (close to R$_0$$^\bullet$), a large enhancement of the reactivity by a participation of charge-transfer configurations into TS can be expected. The computed δ value for R$_7$$^\bullet$/*t*-MA clearly evidences this fact, the charge-transfer being 5−7 times higher than for R$_5$$^\bullet$/*t*-MA. Figure 3 shows that the corresponding data satisfies the above-discussed relationship between δ and IP. The enthalpies of reaction are slightly less favorable for aminoalkyl radicals compared to R$_7$$^\bullet$. However, this fact is counterbalanced by the higher nucleophilic character of aminoalkyl radicals (lower IP and higher δ) that involves a more important polar effect in TS.

Conclusion

Due to their very strong nucleophilic character (very low IP), aminoalkyl radicals appear as useful candidates to give evidence of large polar charge-transfer configurations in the state correlation diagram for radical/double bond reactions. Their reactivity toward (meth)acrylate monomers is mainly controlled by the amount of charge transfer δ in the TSs. More generally, this study opens a new opportunity for the investigation of structure/properties relationships in radical photoinitiators of polymerization.

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