Macromolecules **2005,** *38,* 4521−4524

Prediction of Initiation Efficiency in Radical Photopolymerization: The Case of Benzoyl and Isopropylketyl Radicals

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Received January 31, 2005; Revised Manuscript Received March 14, 2005

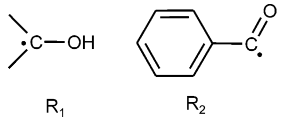
ABSTRACT: The addition of two carbon centered radicals R (benzoyl and isopropylketyl) as initiating radicals to acrylonitrile, methyl acrylate, methyl vinyl ether, and vinyl acetate as monomers M was examined in detail by using molecular orbital calculations. The influence of the radical and monomer structures on the reactivity of the various R/M systems were studied. It was found that both polar and enthalpy effects account for the activation energies for this reaction. The quantitative evaluation of these effects allows to predict quite well the change of the experimental addition rate constants.

Introduction

The photoinitiator (PI) plays a crucial role in radical photopolymerization reactions, yielding after light absorption to the formation of initiating radicals. The use of time-resolved experimental techniques as well as, in the last few years, the development of molecular modeling techniques offers new opportunities for the investigation of the reactivity of PIs. We have been interested for many years in this problem, and very recently, we have studied several aspects concerned with the energy transfer processes in photoinitiating systems,[1] the photodissociation of cleavable PI,[2] the bond dissociation energies of amines usable in type II PIs,[3] the addition of radicals to a double bond,[4] and the evaluation of intersystem crossing quantum yields.[5] The knowledge of the excited states and the understanding of the observed reactivity are fascinating challenges for the improvement of the PI practical efficiency.

The addition reaction of a free radical R onto a monomer double bond M is one of the most important steps in the radical polymerization reaction. However, this reaction generally competes with side reactions such as hydrogen transfer or oxygen reaction with the initiating radical, and these side reactions decrease the whole efficiency of the photoinitiated polymerization process. On the other hand, the large amount of commercial photoinitiators available gives one the possibility to tune easily the chemical structure of the initiating radical and to choose the one that will lead to the best efficiency for the initiation reaction. To improve the initiation reaction, it is of prime importance to understand the factors governing the reactivity of carbon centered radicals toward double bonds. Many works have been devoted to this problem, mainly focusing on the determination of the activation energy (E_a) of the reaction.[6−13] It is now widely accepted that this latter parameter depends on two main factors: (i) the reaction exothermicity (ΔH_r) of the R/M addition and (ii) polar effects ascribed to the participation of the charge-transfer configurations R^+/M^- or R^-/M^+ to the transition state (TS) structure.[4,6,8,9,12,13.]

The aim of this paper is to study how the reactivity of the initiating radical can be predicted on the basis of molecular orbital calculations. Isopropylketyl (R_1) and benzoyl (R_2) radicals, which exhibit very different rate constants for the R/M addition (k_i), were used as prototypical initiating radicals for photopolymerization reactions. These structures correspond to widespread efficient polymerization initiating radicals[14] and can be produced by photocleavage of 2-hydroxy-2-methyl-1-phenyl-1-propanone (Irgacure 1173, Ciba specialties; Esacure KL200, Lamberti) from the lowest triplet state. Benzoyl radical derivatives are also formed by photocleavage from a lot of commercial PIs such as benzyldimethylketal (Irgacure 651 or Esacure KB1), 2-methyl-1-(4-methylthiobenzoyl)-2-morpholinopropan-1-one (Irgacure 907), 2-benzyl-2-(dimethylamino)-1-(4-morpholinophenyl)-1-butanone (Irgacure 369). In this paper, the reactivity of isopropylketyl and benzoyl radicals toward different monomers was investigated, and the results help us to account for the observed k_is. Four well-known structures of monomers are considered: methyl acrylate (MA), methyl vinyl ether (VE), vinyl acetate (VA), and acrylonitrile (AN). Ethylene (ETH) was also studied for sake of comparison.



Background and Computational Procedure

As stated above, the initiation efficiency will strongly depend on the rate constant k_i for the addition reaction of the initiating radical to the first monomeric unit.[14] This rate constant can be expressed through the usual Arrhenius equation:

$$k_i = k_0 \exp\left(-\frac{E_a}{RT}\right) \qquad (1)$$

It is well-known that the preexponential factor k_0 is almost constant for the addition of carbon centered radicals to double bonds ($7 < \log(A) < 8$).[6] Therefore, in a first approach, one can assume that k_i values are mainly dependent on the energy barrier (E_a). Among the huge amount of literature devoted to this problem, it has been found recently that the activation energy

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10.1021/ma050203d CCC: $30.25

Table 1. Reaction Parameters Calculated for the Various R/M Couples (See Text)

system	$-\Delta H_r$ (kJ/mol)[a]	d(C−C) (Å)[a]	δ^{TS} [a]	χ (eV)[b]
R_1/AN	94.8	2.467	0.148	5.31 (5.35[c])
R_1/MA	82	2.411	0.129	4.86 (4.7[c])
R_1/ETH	59.9	2.268	0.083	4.35 (4.35[c])
R_1/VA	68.5	2.298	0.08	4.22 (4[c])
R_1/VE	57.2	2.262	0.052	3.6
R_2/AN	104.6	2.409	0.095	5.31 (5.35[c])
R_2/MA	92.4	2.386	0.088	4.86 (4.7[c])
R_2/ETH	69.2	2.279	0.034	4.35 (4.35[c])
R_2/VA	71.9	2.306	0.026	4.22 (4[c])
R_2/VE	54.2	2.205	−0.064	3.6

[a] At UB3LYP/6-31G* level, ZPE corrected. [b] At UB3LYP/6-31+G* level, ZPE corrected. [c] Experimental values, see ref 6.

can be estimated by an additive model described by the following expression:[12−13]

$$E_a^{calc} = E_a^{0} - \Delta E_{enth} - \Delta E_{pol} \qquad (2)$$

Here $E_a^0 = 65.3$ kJ/mol and $\Delta E_{enth} = -0.37\Delta H_r$ and ΔE_{pol} describes possible polar effects.[12] Equation 2 shows that E_a is partly related to the reaction enthalpy ΔH_r. The contribution of the polar effect (ΔE_{pol}), treated according to the Parr and Pearson model, is calculated from the amount of charge transferred from the radical to the monomer δ^{TS}:[12,13,15]

$$\Delta E_{pol} = 775\ (\delta^{TS})^2 \qquad (3)$$

Quite obviously, it is expected that this term depends on the electron donor/acceptor properties of both monomer and radical moieties.

Structural and energetic factors governing the addition reaction were determined by molecular orbital calculations using density functional theory (DFT), as already described.[12,13] Calculations were carried out on fully optimized structures of reactants and products at UB3LYP/6-31G* level. All these geometries were frequency checked. The transition states (TS) were optimized using the same functional using a lengthened adduct geometry as starting reactant. Only one imaginary frequency was found for each TS. The addition reaction enthalpy (ΔH_r) was calculated as the energy difference between the product and the reactants. From the TS structure, the distance d(C−C) between the radical and the monomer was extracted and the amount of charge transfer (δ^{TS}) between the two moieties was calculated by use of Mulliken charges. Single point energy on optimized structures for the reactants and TSs at UB3LYP/6-311++G** level yielded to the determination of the activation energy to the reaction (E_a^{TS}). All calculations were performed using the Gaussian 98 suite of programs.[16] The electron deficient or electron rich character for the different monomers was described by the absolute electronegativities χ, as estimated by

$$\chi = (\mathrm{IP} + \mathrm{EA})/2 \qquad (4)$$

where the ionization potential IP and the electron affinity EA were calculated at the uB3LYP/6-31+G* level and ZPE corrected.

Results and Discussions

The different parameters characterizing the R/M addition reaction are reported in Table 1. The electron acceptor properties of the monomer unit decreases with the absolute electronegativity χ in the series AN > MA > VA ∼ ETH > VE. A good correlation between ΔH_r and the χ values of the monomer is observed. The substituents that make the monomers more electron deficient both increase χ and stabilize the newly formed radical, thereby decreasing the reaction enthalpy in the series AN > MA > ETH ∼ VA > VE. In the present case, a decrease of χ about 1 eV is associated with a decrease about 20−28 kJ/mol for ΔH_r. Moreover, for any monomer, the reaction enthalpy is rather close for R_1 and R_2: for AN, MA and ETH, ΔH_r is found to be slightly higher for R_2 (by about 10 kJ/mol). This result is also reflected in the rather similar C−H bond dissociation energies of the hydrogenated parent compounds (91 and 86.9 kcal/mol for 2-propanol and benzaldehyde, respectively) roughly indicating a similar stabilization for both radicals.

E_a being dependent on the reaction enthalpy, it is expected that the barrier will increase from AN to VE for a given radical and slightly decrease from R_1 to R_2 for a given monomer. However, in the latter case, the addition rate constants (Table 2) do not follow this expected trend: the reactivity for AN decreases by more than 4 orders of magnitude from R_1 to R_2, and in the case of MA the reactivity decreases by more than 1 order of magnitude from R_1 to R_2. This suggests that the higher reactivity of R_1 toward AN can be ascribed to a significant contribution of the polar effect ΔE_{pol} to the barrier (see eq 2). The electronegativity of R_1 is lower than that of R_2 (3.02 eV vs 3.64 eV for R_1 and R_2, respectively) demonstrating that R_1 will be a better nucleophilic radical than R_2.[12]

This polar term is of prime importance to understand the relative reactivity of these radicals, and is well reflected by the charge transfer (δ^{TS}) between R and M in the transition state.[6,12−13,19−22] Table 1 shows that δ^{TS} increases linearly with increasing χ (Figure 1a). As expected, electron deficient monomers increase the charge transfer of nucleophilic radicals and electron rich monomers increase the net charge transfer of electrophilic radicals: the nucleophilic character of R_1 strongly increases from VE to AN. On the opposite, R_2 behaves as a nucleophilic radical for the addition to MA-VA and an electrophilic radical in the case of VE. In other words, highly nucleophilic radicals should be preferably used for the addition to AN and MA while electrophilic radicals are more appropriate to enhance the reactivity toward VE.[23]

The distance d(C−C) between the carbon centered radical and the attacked carbon in the TS is an important parameter that characterizes the geometry of the TS and gives valuable information on the R/M system reactivity. Table 1 shows that the extent of bond formation well correlates with ΔH_r, in accordance with the Hammond's postulate which states that the earliness of a transition structure is directly related to the reaction enthalpy (Figure 1b). However, the TS structure can be affected by polar effects that lead to earlier TS than expected.[13] In that case, the change of d(C−C) between different monomers is related to the extent of the polar effect for the studied radical. The linear fits obtained for the d(C−C) vs ΔH_r evidence this behavior: the slopes increase from 4.1×10^{-3} Å·kJ^{-1} mol for R_2 to 5.8×10^{-3} Å·kJ^{-1} mol for R_1 in agreement with the variation of the polar effect which increases in a similar way. For comparison, the methyl radical which is

Table 2. Calculated Energy Barriers E_a^{calcd} from Eq 2, Enthalpic ΔE_{enth} and Polar ΔE_{pol} Contributions to the Barrier, Computed Energy Barrier E_a^{TS} from Transition State Optimization, Experimental Data for the Energy Barrier E_a^{expt}, and Addition Rate Constants k_i

systems	E_a^{calcd} (kJ/mol)	ΔE_{enth} (kJ/mol)	ΔE_{pol} (kJ/mol)	$E_a^{TS\ a}$ (kJ/mol)	$E_a^{expt\ b}$ (kJ/mol)	$k_i^{expt\ b}$ ($M^{-1}\ s^{-1}$)
R_1/AN	13.2	35.1	17.0	5.6	0	1.5×10^8
R_1/MA	22.1	30.3	12.9	7.7	0	3.5×10^7
R_1/ETH	37.8	22.2	5.3	31.4		
R_1/VA	35.0	25.3	5.0	29.2	20.6	7500
R_1/VE	42.0	21.2	2.1	39.4		320^d
R_2/AN	19.6	38.7	7.0	19.5		$2 \times 10^{4\ e}$
R_2/MA	25.1	34.2	6.0	23.1		$2.7 \times 10^{5\ c}$
R_2/ETH	38.8	25.6	0.9	40.3		
R_2/VA	38.2	26.6	0.5	34.4		$1.2 \times 10^{5\ e}$
R_2/VE	42.1	20.1	3.2	34.8		

[a] UB3LYP/6-311++G**//UB3LYP/6-31G* level (ZPE corrected at UB3LYP/6-31G* level). [b] Experimental data from ref 6 except otherwise stated. [c] From ref 18 for butyl acrylate. [d] For ethyl vinyl ether. [e] From ref 17.

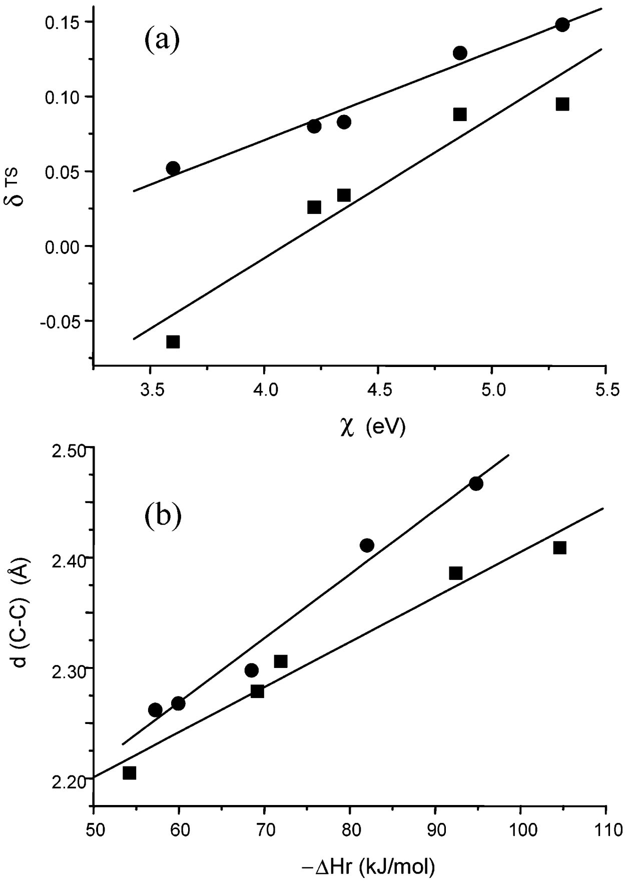

Figure 1. (a) Plot of the amount of charge transfer δ^{TS} vs the absolute electronegativity χ of the monomer for R_1/M systems (circles) and R_2/M systems (squares). (b) Plot of the distance in the transition state d(C−C) vs the reaction enthalpy ΔH_r for R_1/M systems (circles) and R_2/M systems (squares).

characterized by low δ^{TS} values yields a slope that is only 3.47×10^{-3} Å·kJ^{-1} mol.[13] In a recent work, a good correlation between χ of the radical and the slope of the d(C−C) vs ΔH_r plots has been observed. Figure 2 shows that this correlation remains quite good when R_1 and R_2 are taken into account, demonstrating the large polar effect on the TS geometry.

The activation energies E_a^{calc} predicted by eq 2 for the addition reaction are in good agreement with those calculated from transition state optimization (E_a^{TS}), which gives confidence to the model used. As stated above, E_a^{calc} can be therefore directly connected with the addition rate constant. However, a bad agreement between E_a^{calc} or E_a^{TS} and E_a^{exp} is observed for R_1. This could likely arise from the inherent error made in the determination of the experimental barrier which is based on an average value for the preexponential factor. The behavior of R_1 is governed by important enthalpy and polar effects and both effects decrease the barrier from VE to AN: a barrier decrease of more than 30 kJ/mol is observed for the addition reaction in this series, in line with the large increase by 6 orders of magnitude for k_i. For AN and MA, the comparison of R_1 and R_2 reactivity is particularly valuable: in the case of the strong nucleophilic R_1 radical, the enthalpy effect is rather similar to that of R_2 but the polar effect is more important (12.9−17 vs 6−7 kJ/mol). Therefore, the barriers are more favorable for R_1 in agreement with the experimental rate constants which are found higher. For the R_1 and R_2 additions to ETH, VA, and VE, the low polar effects and the almost similar enthalpy effects explain the similar high values of the calculated barriers as well as the low experimental addition rate constants (10^3−10^5 $M^{-1}\ s^{-1}$). For R_2 which leads to lower polar effects, the barrier change for the different monomers is only about 20 kJ/mol, in agreement with the smaller range of the k_i values.

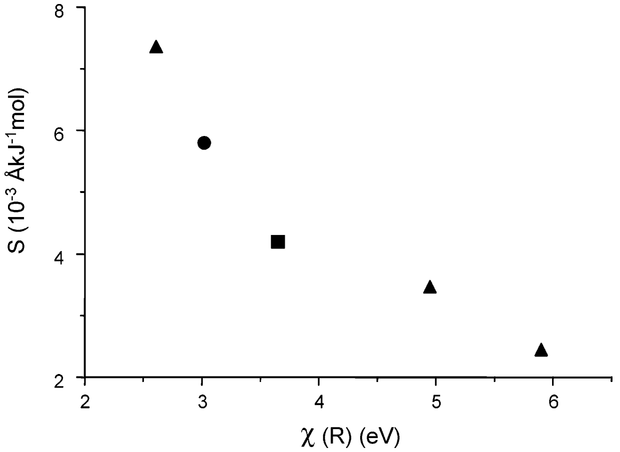

Figure 2. Change of the slope (S) of the d(C−C) vs ΔH_r plots with the absolute electronegativity χ of the radical as obtained for three radicals studied in ref 13 (triangles), for R_1 (circle) and R_2 (square).

Another point of interest could be the comparison of the acrylate/methacrylate reactivity, both monomers being characterized by a widespread use in the field of polymer. Molecular orbital calculations for the R_1/methyl methacrylate (MMA) system were carried out. The geometrical parameters characterizing the TS for the addition reaction to both monomers are very similar with d(C−C) values of 2.406 and 2.411 Å for MMA and MA, respectively. The charge-transfer characters are also very close ($\delta^{TS} = 0.119$ and 0.129 for the addition to MMA and MA) in agreement with the very similar charge-transfer properties of these monomers.[13] Therefore, due to their similar TS structures, the reactivities of these two monomers are very close, the energy barrier being 10.5 and 7.7 kJ/mol for the addition of R_1 to MMA and MA, respectively.

Conclusion

The separation of the relative contributions of the enthalpy and polar effect to the activation energies can explain the reactivity of the benzoyl and isopropyl radicals toward different monomers, allowing to predict the change in addition reaction efficiency. This approach—which should be considered as of prime importance in the field of polymerization—can be extended to many other systems and will be applied, in a forthcoming paper, to the rate constants of propagation and termination of a growing macromolecular chain.

Acknowledgment. The authors thank CINES (Centre Informatique National de l'Enseignement Supérieur) and IDRIS (Institut du Développement et des Ressources en Informatique Scientifique) for the generous allocation of computational time on the IBM SP3 Supercomputer.

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(23) One reviewer has pointed out that there is a good correlation between the calculated values of $-\Delta H_r$ and the Q parameter derived from the $Q-e$ scheme for copolymerization reaction. Interestingly, δ_{TS} also correlates with the published values of e. This can be accounted for by the fact that the properties of the monomers govern both the addition of initiating and propagating radicals.

MA050203D