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Investigation of cleavage processes in photoinitiators: from experiments to molecular modeling

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Abstract

The present paper shows an original approach combining laser induced photoacoustic calorimetry (PAC) and molecular modeling for the investigation of the cleavage process in radical photoinitiating systems. The bond dissociation enthalpies (BDE) and the enthalpies for the photodissociation reaction ΔHr_{diss} of the photoinitiators are calculated and the quantum yields of dissociation ϕ_{diss} from the excited state are determined. It appears that these quantum yields are not unity and do not correlate either with BDEs or ΔHr_{diss}.

Keywords: Photocleavage; Photoinitiator; Bond dissociation energy

1. Introduction

In radiation curing technologies, most of the photochemical reactions are based on radical or cationic polymerization of organic materials (monomers, oligomers or polymers) photoinduced by light in the presence of a photoinitiating system (PIS) [1–5]. The role of PIS, as a driving factor of the polymerization reaction efficiency has been fully emphasized over the past 30 years. The photophysical and photochemical processes involved in the excited states determine the yield of the different primary processes that occur before the initiating step, such as cleavage reactions, energy or electron transfer reactions between the photoinitiator (PI) and a photosensitizer (PS), electron transfer reactions of PI with amines, quenching by monomer, oxygen or light stabilizers, or secondary reactions with hydrogen donors or PS. Therefore, the efficiency of these different reactions governs the overall reactivity of PIS.

Investigation of the mechanisms involved in PIS was generally performed by using time-resolved laser spectroscopies [1,6,7]. In addition to few works based on CIDNP-NMR [8] or CIDEP-ESR [9,10] techniques, most of the studies on the excited state processes of PIs have been carried out through the well-known transient absorption spectroscopy that provides useful information on the excited state processes. More recently, time-resolved photothermal techniques were found to be very helpful to study thermodynamics and kinetics of photochemical processes involved in PIS [11,12]. On the other hand, direct evidence of ions or radical ions generation is easily followed by time-resolved photoconductivity [13]. Finally, a very promising technique is the time-resolved FT-IR vibrational spectroscopy that allows direct investigation of radicals [14].

With the development of quantum mechanical methods, a new approach based on both experiments and molecular modeling techniques start to be used in the field of PIS. Conformational and thermodynamical properties of ground state molecules, excited states or radicals can be calculated: molecular modeling helps to obtain new data and support the involved mechanisms from a theoretical point of view.

The present paper intends to (i) briefly outline, in selected recent works how experiments and molecular modeling can be combined to study photochemical reactivity of PIS and (ii) present such a study on the cleavage process in ketone derivatives. Indeed, a new approach is developed to estimate ϕ_{diss} from the direct measurement of the heat evolved in solution during the photodissociation through PAC measurements and by taking into account the computed bond dissociation enthalpy (BDE) of the PI at ab initio level. This allows the discussion of the connection between ϕ_{diss} and thermodynamical parameters such as the BDE and the enthalpy for the dissociation reaction from the triplet state ΔHr_{diss}.

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2. A short overview of the approach combining experiments and molecular modeling

It is very well known for many years that information such as transient absorption spectra, lifetimes of excited states and rate constants of the various interaction reactions can be easily determined by time-resolved absorption spectroscopy (TRAS) on the nanosecond time scale. Extended to the picosecond time scale, this technique permits the study of ultrafast processes [15,16]. These experiments allow (i) the description, from a kinetic point of view, of the overall diagram of evolution of the excited states and reactive intermediates of PIS and then, (ii) to discuss on the structure/properties relationships of the studied compounds: for example, this has been still recently reported by us on camphorquinones [17], bisimidazoles based systems [18], Rose Bengal/ferrocenium salt [19], sulfonylketones [20]. However, in this technique, the transients must absorb the analyzing light to be optically detected. This problem is crucial when studying the interactions between an initiating radical and a monomer double bond because most of these radicals, especially the amine derived ones, do not absorb at the analysing wavelength or are difficult to observe. Therefore, time-resolved photothermal techniques—thermal lens spectroscopy (TLS) and laser induced photoacoustic calorimetry (PAC)—have been recently introduced in our laboratory [11,12,21] as complementary techniques to TRAS, since the analysis is based on the monitoring of the heat evolved from non-radiative processes originating from the transient states. Moreover, TLS and PAC give the possibility to study the characteristics of the PI triplet states: intersystem crossing quantum yields, triplet state energy levels, lifetimes, enthalpies of formation of the radicals, quantum yields of dissociation of cleavable PIs, bond dissociation energies of amines used as coinitiator. In addition, the interaction between an initiating radical and a monomer double bond can be followed by PAC; the thermal energy evolved from the reaction allows the measurement of both the enthalpy ΔHr and the rate constant for the addition reaction [12]. Molecular modeling calculations on the transition states should help in the understanding of the reactivity of an initiating radical onto a monomer double bond.

A fascinating problem is encountered in sensitization processes which are very often used in PIS. For molecules exhibiting a certain degree of flexibility, the usual plot of the energy transfer rate constants vs. the triplet energy levels of the acceptor departs from the expected behavior; this has been termed as “non-vertical energy transfer” (NVET) and was the subject of controversy for 40 years. The consequence is that the spectroscopic triplet state energy depends on the conformation of the molecule and differs from the relaxed triplet state energy. We have recently investigated this problem on oxime derivatives usable as photobases in photoresist technology [22]. TRAS was used to measure the rate constant of energy transfer reaction and molecular modeling to calculate the potential energy surfaces of ground and triplet states of oximes. It was possible to show how the flexibility of the molecule determines the evolution of the spectroscopic triplet energy, and propose a new model based on thermal activation of the bond torsion that definitively explains in a quantitative way the NVET phenomenon [23,24].

Amines are extensively used in two component PIS based on the photoreduction of an aromatic ketone through an electron/proton transfer. This reaction yields aminoalkyl radicals that are very good initiating species; a better knowledge of their reactivity is useful, and the measurement of the bond dissociation energy of the amine is of prime importance. By using PAC, the heat released during the quenching of the benzophenone triplet state by different amines was measured. From thermodynamical cycle, the BDE can be evaluated and compared with calculated values from molecular modeling. This allows the study of the molecular factors that stabilize the aminoalkyl radicals [25] and govern their reactivity towards double bonds.

3. PAC technique and calculations

Excitation of absorbing species in solution results in the creation of excited states that are doomed to deactivate or react. Photophysical deactivations occurring through non-radiative processes and exothermic photochemical reactions both release heat in solution. Therefore, the measurement of the heat produced in the medium can provide important kinetic and thermodynamic information on the system studied. This temperature jump causes a volume expansion and a variation of pressure, that leads to the generation and propagation of acoustic waves through the media.

In laser induced PAC, the acoustic wave formed after excitation of the sample by the pulsed Nd/YAG laser is detected by a piezoelectric crystal [26]. The heat release can be considered as “fast” or “slow” depending on the experimental setup and the time evolution of the chemical system. In fact, the experimental setup was adapted in order to consider that (i) the heat evolved from internal conversion, intersystem crossing and photoreactions following the excitation is detected to be as fast, and (ii) the energy stored in the long lived photoproducts (i.e. radicals) is too slow to be detected (see Fig. 1) [12,25,26]. If α_{fast} and α_{slow} are the corresponding fractions of the incident energy E_a that is released in the environment as heat, a simple energy balance consideration leads to

$$E_a = \alpha_{\text{fast}} E_a + \alpha_{\text{slow}} E_a \qquad (1)$$

The fluorescence quantum yield was neglected for the compounds studied here. The amplitude of the PAC signal is described by

$$S_f = K \alpha_{\text{fast}} E_a (1 - 10^{-A}) \qquad (2)$$

where K contains the thermoelastic parameters as well as the experimental sensitivity constant, and the quantity

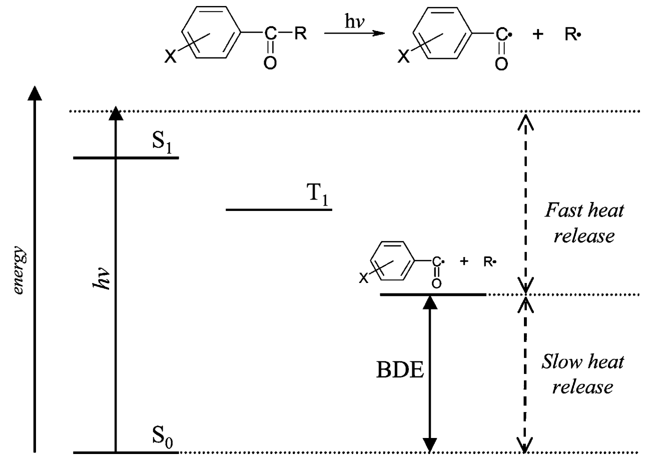


Fig. 1. Energy diagram for the dissociation of a cleavable PI.

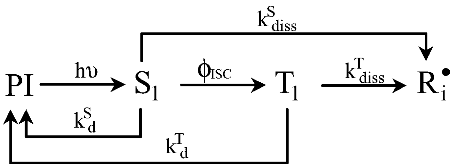
$(1 - 10^{-A})$ the fraction of light absorbed. The S_f value is normalized by using hydroxybenzophenone as a calorimetric reference [25,26]. Therefore α_{fast} can be extracted from the experimental PAC signals, and α_{slow} can be calculated. This yields thermodynamical results that can be combined with quantum mechanical calculations such as BDE.

The calculation of BDEs for organic compounds has attracted many interests in the past. Ab initio theories were usable with severe pitfall that are computationally very expensive [25,27–29]. The most accurate methods, such as CBS, G2 or G3, are based on the combination of different high-level ab initio calculations. This leads to BDE values that are computed with a mean average deviation as low as 1–2 kcal/mol. More recently, density functional theories (DFT) were applied successfully to the BDE calculations [30–32] and the fact that they are less expensive and accurate enough render these methods to be very popular. It has been shown that the error on the BDE can be lower than 2 kcal/mol, depending on the heteroatom present on the molecular structure. Recalling that these methods can deal with larger molecules than ab initio ones, one can found this slightly higher error acceptable.

4. Cleavage processes in acetophenone derivatives

The most reactive photosensitive systems for radical polymerization reactions are usually the cleavable PIs, and particularly those derived from acetophenone [2,33]. Such compounds (PI) are excited into their singlet state and convert, through intersystem crossing, to their triplet state. These excited states can undergo a direct formation of two radicals. Then, one or both of these radicals can initiate the polymerization reaction through an addition reaction onto the monomer double bond leading to the first monomeric radical.

The photochemical reactivity of PI is strongly governed by the overall quantum yield of dissociation ϕ_{diss} which is connected to the different deactivation pathways of the excited states (Scheme 1).



Scheme 1.

ϕ_{diss} depends on the quantum yields of photodissociation ϕ^S_{diss} and ϕ^T_{diss} arising from both the singlet state S_1 and the triplet state T_1, respectively:

$$\phi_{diss} = \phi^S_{diss} + \phi^T_{diss} \tag{3}$$

with

$$\phi^S_{diss} = k^S_{diss}\tau_S \quad \text{and} \quad \phi^T_{diss} = \phi_{ISC}k^T_{diss}\tau_T \tag{4}$$

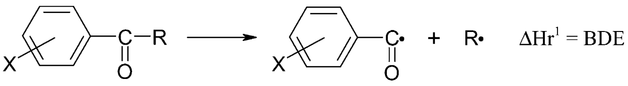
where k^S_{diss} and k^T_{diss} are the rate constants for cleavage of the singlet state and triplet state, respectively, τ_S and τ_T the corresponding lifetimes and ϕ_{ISC} the quantum yield of intersystem crossing. The cleavage process for commercially available PIs occurs from the triplet state [2,33].

The evaluation of ϕ_{diss} is a difficult task, and there was not a great deal of studies in this field. Classical methods to evaluate ϕ_{diss} were only operative in very few examples [6,34,35] and remained difficult to use. More surprisingly, one must outline that the factors controlling the photodissociation in the triplet state of large organic molecules remain unclear. The common idea states that the BDE of the bond being broken should play a crucial role [33], but there is no direct evidence that this factor alone governs the dissociation efficiency. The combined use of photothermal techniques and molecular modeling should lead with a limited number of assumptions to both quantum yields of dissociation and thermodynamical data such as BDE or the enthalpy of the photocleavage reaction ΔHr_{diss}.

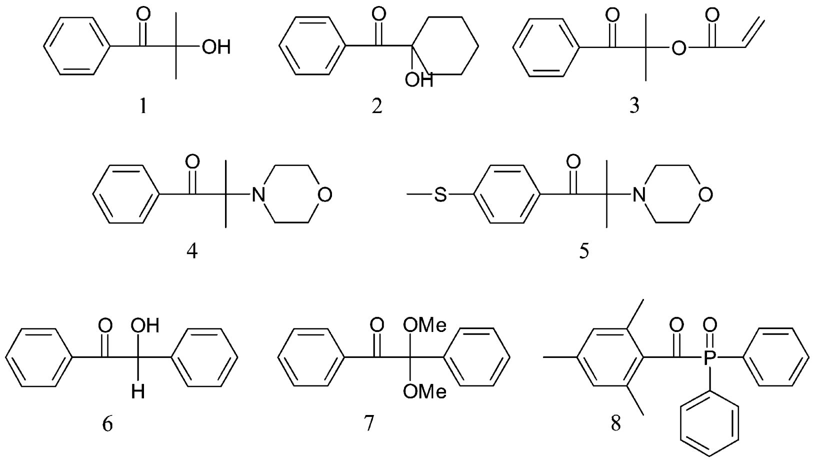
Eight cleavable PIs (obtained from Ciba Specialties) belonging to well-known structures have been selected (Scheme 2): acetophenone derivatives (1, 2, 3), morpholino ketone derivatives (4, 5), benzoïn (6), 2,2-dimethoxy-2-phenyl-acetophenone (7), and a phosphine oxide derivative (8).

4.1. BDE calculations

The BDEs of the compounds studied here were first directly determined from ab initio calculations, as the enthalpy change corresponding to the reaction:



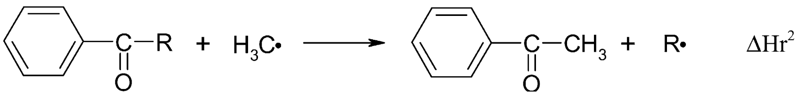
Such a determination can suffer from the choice of the DFT method and the basis set. Indeed, the BDE values



Scheme 2.

calculated for the acetophenone used as a model compound (Table 1) can exhibit some discrepancy comparing to the experimental one (81.9 kcal/mol [36]). The differences between the functionals in the case of BDE of hydrocarbons were very recently discussed in the literature [32] and ascribed to the electron correlation calculation. From Table 1, it appears that the B3LYP hybrid functional leads to the best agreement with the experimental values when associated with an extended basis set such as 6-311++G**. The fact that such a basis set is required for an accurate description of the BDE is merely attributed to a better description of radicals when including diffuse functions. It turns out from these results that accurate BDEs are calculated under the conditions that a large basis set is used.

However such calculations are time consuming and a second approach was applied to the BDE calculations, that consists in the computation of an isodesmic reaction enthalpy change:



With this method, the error made on the BDE of the reference molecule (acetophenone) is used to correct the BDE of the studied PI [25,29]. The BDE value of PI can then be obtained from the enthalpy change ΔHr^2 of the isodesmic reaction according to

$$\mathrm{BDE(PI)} = \mathrm{BDE(acetophenone)} + \Delta Hr^2$$

The BDE values calculated with different functionals are gathered in Table 2 for compound 1. As discussed above for acetophenone, the direct calculation leads to BDE values that are strongly dependent on the method used for the calculations. On the contrary, the calculations performed by use of an isodesmic reaction are very consistent whatever the functional used, even with a medium basis set.

The results of the calculations are collected in Table 3 for the whole set of PIs using the B3LYP functional. The trend observed in the case of compound 1 remains valid for all the compounds; the BDE values calculated directly using an extended basis set or evaluated from an isodesmic reaction are very close. These values range from 50 to 65 kcal/mol depending on the α-carbonyl substituent.

Table 1
Calculated BDEs (kcal/mol) of acetophenone according to the different DFT methods and basis sets used (experimental: 81.9 kcal/mol)

Functional	Basis set		
	6-31G*	6-31+G*[a]	6-311++G**[a]
B3P86	90.5	88.1	87.1
B3PW91	87.5	85.1	84.1
B3LYP	86.0	83.1	81.8

[a] From computed single point energies using the structures optimized with the 6-31G* basis set and the corresponding functional.

4.2. PAC investigation

Under irradiation, the cleavable PIs lead to a direct production of two radicals. The slow heat release corresponds to the energy stored into the radicals (in fact, the BDE) that do not recombine or further react within the time window of

Table 2
BDEs (kcal/mol) of compound 1 directly computed and calculated by using an isodesmic reaction

Functional	Direct	Isodesmic reaction
B3P86/6-31G*	74.5	65.9
B3PW91/6-31G*	70.9	65.3
B3LYP/6-31G*	69.8	65.7

Table 3
Triplet energies E_T (kcal/mol), calculated BDEs (kcal/mol), measured values of $\phi_{diss} \times$ BDE (kcal/mol), experimental quantum yields of dissociation ϕ_{diss} and values from the literature ϕ_{diss}^{lit}, for the different PIs

PI	E_T	BDE				$\phi_{diss} \times$ BDE	ϕ_{diss}[a] (±0.1)	ϕ_{diss}^{lit}
		Direct		Isodesmic				
		B3LYP/6-31G*	B3LYP/6-311++G**//6-31G*	B3LYP/6-31G*	B3LYP/6-311++G**//6-31G*			
1	71.4[b]	69.8	65.0	65.7	65.0	51	0.8	0.38[b]
2	66.8[c]	68.9	63.5	64.8	63.5	53	0.8	1.0[d]
3	73.4[e]	64.9	60.1	60.8	60.2	0	0	0.05[e]
4	62[f]	66.8	61.9	62.7	61.9	17	0.3	–
5	61[f]	61.4	56.8[g]	–	–	18	0.3	0.13[h]
6	72.2[i]	64.8	59.95	60.9	60.0	29	0.5	0.35[i]
7	66.2[c]	56.0	51.0	51.9	50.9	49	0.95	1.0[j]/0.52[d]
8	62.6[k]	62.0	57.0[l]	57.9[l]	57[l]	41	0.7	0.5[m]/0.8[d]

[a] Evaluated with the BDE calculated using the isodesmic reaction method and energies computed at the B3LYP/6-311++G**//6-31G* level.
[b] From Ref. [34].
[c] From Ref. [37].
[d] From Ref. [35].
[e] Value for 2,2-dimethylacetophenone acetate [34].
[f] From Ref. [38].
[g] Value used in the calculation of ϕ_{diss}.
[h] From Ref. [33].
[i] From Ref. [39].
[j] Accepted value because of the very short lived triplet state [33].
[k] From Ref. [40].
[l] Value computed for a parent compound where the three methyl substituents are missing.
[m] From Ref. [6].

the setup (Fig. 2). Therefore, neglecting the volume change during the reaction, one can write

$$\alpha_{slow} E_a = h\nu(1 - \alpha_{fast}) = \phi_{diss}\,\text{BDE} \quad (5)$$

The experimental values of ϕ_{diss} BDE are listed in Table 3. Extremely different reactivities are observed for the compounds, some of them (compounds 1, 2 and 7) being very reactive (with quantum yield reaching unity), and some others (such as compound 3) yielding a full deactivation without formation of any radical.

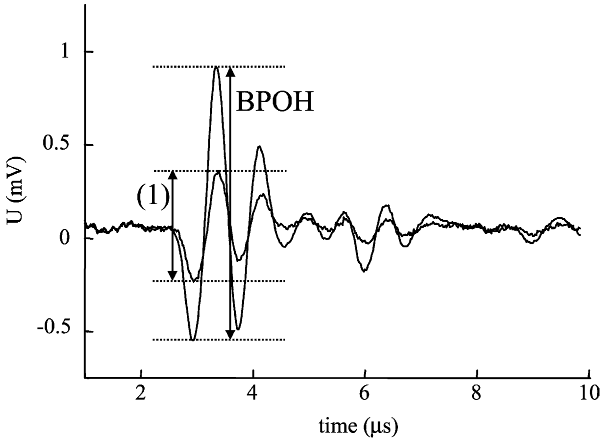


Fig. 2. Typical PAC signal in the case of (1) compared to that of hydroxybenzophenone (BPOH).

4.3. Quantum yields of dissociation

The quantum yields of dissociation determined from Eq. (5) and the calculated BDEs are gathered in Table 3 and compared to those found in the literature. It clearly appears that the quantum yields of dissociation of the highly efficient cleavable PIs studied in this paper are not unity. This is either due to the intersystem crossing quantum yield which is not unity and to the presence of deactivation pathways (other than the cleavage process) that take place in the triplet state.

There is a good agreement between our results and most of the values already published [6,33–35,39]. Looking in more details shows that in the case of compounds 2, 5, 6 and 8, the agreement is quite good, knowing the difficulty to measure ϕ_{diss} by classical techniques. The value for compound 3 is compared to that published for an other ester derivative of hydroxyacetophenone. Both of these compounds do not exhibit significant dissociation under irradiation. There is no data published for compound 4, but our results show that its behavior is very similar to that of compound 5. In the case of compound 1, our value is higher than that published recently [34] but quite similar to that of 2. These two compounds are structurally very close and it is not surprising to find similar values of ϕ_{diss}.

It is known that dimethoxybenzyl radical derived from the photolysis of compound 7 may undergo thermal or photochemical fragmentation. These two processes do not actually affect the PAC measurements since the thermal fragmentation occurs at very low rate and PAC experiments were performed with so low energy pump that the photochemical fragmentation is avoided [41]. Therefore, compound 7 exhibits a high quantum yield of dissociation, as expected [33] (although a lower value was also published [35]). This points out the striking differences that can be obtained using different techniques:

(i) With the classical flash photolysis, one has to assume that the radicals formed during the excitation do not absorb at the analysing wavelength and the quantum yield is measured as the photobleaching of the ground state. Therefore, if the radicals absorb, the quantum yield can be underestimated.

(ii) The quantum yields determined by steady state photolysis reflect the whole mechanisms that can contribute to the disappearance of the PI; working in solution favors the recombination of the radicals leading to a quantum yield of photolysis lower than the quantum yield of dissociation.

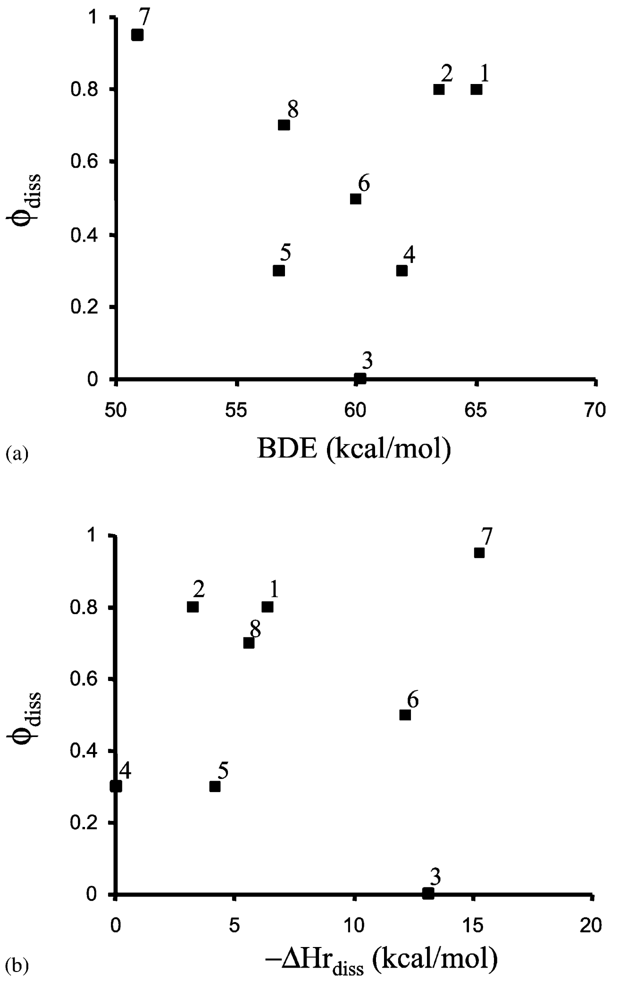


Fig. 3. Plot of the quantum yield of dissociation ϕ_{diss} vs. (a) the BDE and (b) the enthalpy of reaction ΔHr_{diss}.

These two comments explain why the ϕ_{diss} obtained in our work—that correspond to those of the primary photochemical process and without any assumption on the properties of the radical formed—can exhibit higher values than those already measured by other techniques. Consequently, to our opinion, the values measured by the combined approach used here are the most representative for the cleavage efficiency.

Fig. 3a clearly shows that there is no correlation between the BDE values and ϕ_{diss}. The common statement saying that the efficiency of a dissociation reaction becomes higher when the bond energy decreases is presumably not correct. Such an idea can be valid when considering a closely homogeneous class of compounds (such as substituted anilines [42]) but our results demonstrate that the knowledge of the BDEs is not sufficient to estimate the ability of a PI to efficiently dissociate.

Since the photodissociation occurs in the triplet state for the compounds studied here, one can calculate the enthalpy of the dissociation reaction ΔHr_{diss} as the difference between the BDE and the energy of the triplet state E_T of the compound:

$$\Delta Hr_{diss} = BDE - E_T \qquad (6)$$

and it is therefore tempting to relate the quantum yield of dissociation with ΔHr_{diss}. Fig. 3b shows that there is no clear correlation between these parameters, leading to the conclusion that the efficiency of the photodissociation is not clearly governed by the enthalpy of reaction. The knowledge of the key parameter controlling the dissociation remains a fascinating challenge that is out of the scope of the present paper.

5. Conclusion

The PAC technique described above and the use of molecular modeling appear very powerful for the investigation of excited state processes occurring in the PIs of polymerization. In the present case, they allow a direct determination of the quantum yield of dissociation. Forthcoming papers will develop different aspects, in particular the study of the parameters which govern the cleavage process and the reactivity of radicals onto double bonds.

6. Experimental

The quantum calculations were performed using Gaussian 98 suite of programs [43]. Molecule and radical structures were optimized with different functionals (B3P86, B3PW91, B3LYP) using the 6-31G* basis set. Single point energies were then calculated with different basis sets (6-31G*, 6-31+G*, 6-311++G**).

The PAC experimental setup has been fully described elsewhere [25]. Briefly, the attenuated beam of a Nd:YAG laser

(Powerlite 9010, Continuum) irradiated the cell through a calibrated 200 or 500 μm pinhole. The photoacoustic signal was detected at right angle by a piezoelectric detector (A603S Panametrics) and recorded by a transient digitizer (Tektronix 2052). All the experiments were performed in acetonitrile under argon atmosphere.

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