A New Approach of the Photoinitiator Reactivity

Xavier Allonas*, Jacques Lalevée and Jean-Pierre Fouassier

*Département de Photochimie Générale, UMR CNRS 7525,
Ecole Nationale Supérieure de Chimie,
3 rue Alfred Werner, 68093 Mulhouse Cedex – France
x.allonas@uha.fr*

New techniques for the investigation of primary processes involved in photopolymerisation reactions are presented. Besides the well known time resolved laser absorption spectroscopy techniques operating in the nanosecond or picosecond time scale, experimental techniques such as laser induced photoacoustic calorimetry or nanosecond laser induced step scan FTIR, recently introduced in our lab, are discussed with respect to their applications for the investigation of photopolymerization processes, specially the possibility to gain informations on the excited states which were not easily accessible up to now. On the other hand, molecular modeling results obtained at high level of theory are shown to provide unique thermodynamical data on the processes that govern the overall efficiency of the photoinitiating systems. A new approach that combines both aspects is developed and presented on the basis of recent selected examples.

Keywords: photoinitiator, laser spectroscopy, molecular modeling

1. Introduction

Radiation Curing is a very well known technology which develops quite rapidly. The major chemical reaction encountered in the area (e.g.[1,2]) is based on a photoinduced radical polymerization reaction of a monomer (M) in the presence of a photoinitiating system (PIS) under exposure under UV or UV/Visible lights emitted by conventional sources or lasers. The role of PIS was fully emphasized over the past three decades. Apart a practical approach which requires a lot of trials, the increase of the PIS efficiency seems to lie nowadays on a better knowledge of the excited state characteristics and new investigations of the processes involved by using theoretical studies. Combining both an experimental and a theoretical approach should improve the design of new PISs. Such an approach will be exemplified in this paper.

2. Backgrounds

As known, the efficiency of the initiating

step is largely governed by the photophysical and photochemical processes involved in the excited states of PIS. Usual processes involve cleavage reactions, electron transfer reactions between the photoinitiator and amines, hydrogen abstraction reactions with hydrogen donors, quenching of triplet states by monomer, oxygen, light stabilizers or other additives, energy or electron transfer reactions, secondary reactions... The yield of these primary reactions will govern the yield in initiating radicals. This yield is strongly dependent on (i) the kinetics in the excited states (lifetimes of the transient spectroscopic states, rate constants of interaction) and (ii) other characteristics which are generally very difficult to determine such as intersystem crossing quantum yields, triplet state energy levels, quantum yields of dissociation of cleavable photoinitiators, bond dissociation energies of amines, rate constants of

interaction between the initiating radical and the monomer double bond...

In fact, most of the original studies were based on laser spectroscopies: time-resolved laser absorption spectroscopies (e.g.[1-6]), time resolved photoconductivity [7] and more recently time resolved FTIR vibrational spectroscopy [8]. They bring about mechanistic informations on the PIS - such as transient absorption spectra, lifetimes of excited states and rate constants of a lot of interaction reactions - and help to describe, from a kinetic point of view, the overall diagram of evolution of the transient states of PIS.

However, there is an important lack of data about the energetics of the processes involved. In recent years, laser photothermal spectroscopies such as Time-Resolved Thermal Lens Spectroscopy (TRTLS) or Laser Induced Photoacoustic Calorimetry (LIPAC) helped to solve this problem. These techniques allow the measurement of the heat produced in the medium, providing the knowledge of the characteristics mentioned above [9].

Molecular modelling was also recently shown to allow a new approach for the investigation of the PIS reactivity where conformational and thermodynamical data of ground state molecules, properties of excited states or radicals and geometry, charge density and energy of transitions become accessible. This combined approach has been recently used for the investigation of several problems. For example, α -cleavage of ketone derivatives was studied, and it was clearly shown that the enthalpy for the cleavage reaction is not the main parameter governing the efficiency of the reaction [10]. Recently, the sensitization reactions which occur in oxime derivatives usable as photobases in photoresist technology [13] have been definitively explained on the basis of a proposed new model based on a thermal activation of bond torsion [11,12] which related to a nonvertical energy transfer process. Using a similar approach, the bond dissociation energy BDE of amines and the molecular factors that stabilize the aminoalkyl radicals [14] and govern their reactivity towards double bonds [15] have been also investigated.

3. Experimental

3.1. Laser Induced Photoacoustic Calorimetry

The experimental setup of the LIPAC, shown Figure 1, was fully described elsewhere [9,14] : the attenuated beam of a frequency tripled nanosecond Nd:YAG laser (Powerlite 9010, Continuum) irradiated a 1 cm cell equipped with a piezoelectric detector (Panametrics A609S 5MHz or A603S 1 MHz) through a 200 μ m or 500 μ m pinhole; the amplified signal was monitored by a transient digitizer (Tektronix 3052).

Figure 1. LIPAC Experimental setup.

The optical density of the samples was adjusted to 0.2 at the excitation wavelength. 2-hydroxybenzophenone (BPOH) was used as a standard. Oxygen was removed by argon bubbling for 15 minutes.

Excitation of molecules in solution results in the creation of excited states which deactivate or react. As known, both photo-physical deactivations occurring through non-radiative processes and exothermic photochemical reactions release heat in solution. This temperature jump causes a change of pressure that generates propagating acoustic waves through the media which are consequently related to the photochemistry of the studied system. The high frequency component of this acoustic wave (that corresponds to the fast photochemical processes) is directly monitored by LIPAC and therefore, the heat released from states deactivating within the 20-100 ns time window gives a detectable signal. The BPOH reference is known to release the whole excitation energy in solution in less than 1 ns; on the opposite, a given photoinitiator PI sample gives rise to a triplet state that deactivates more slowly in solution, and

therefore the fast heat release results in a lower acoustic wave [9,11] as shown Figure 2.

Figure 2. Experimental LIPAC signal for **BPOH** and **4** in benzene.

The values of the signal corresponding to the reference (S_{BPOH}) and the photoinitiator (S_{PI}) are related to the energy level E_T and the quantum yield ϕ_T of the PI triplet state through the following equation [9]:

$$\phi_T \cdot E_T = h\nu \cdot \left(1 - \frac{S_{PI}}{S_{BPOH}}\right) \quad \text{Eq. 1}$$

where $h\nu$ is the energy of the absorbed photon. If the triplet energy of the photoinitiator is not known, an energy transfer experiment is used. In that case, the excited photoinitiator must be totally quenched by a well characterized energy acceptor A according to:

The amount of acceptor triplet state formed during this process directly depends on the ϕ_T of PI and then, the slow heat release corresponds to the deactivation of A triplet state. Knowing the triplet energy of this acceptor, it is quite easy to retrieve ϕ_T . The latter value can be used in Eq. 1 to deduce E_T .

3.2. Molecular modeling

All quantum calculations were carried out using the Gaussian 98 suite of programs. Calculations have been carried out in part at the IDRIS national computer center (Orsay, CNRS France) and in part on the Origin 2000 of the Laboratory. The computations for the different photoinitiators (**1**) to (**8**) were carried out using the hybrid functional B3LYP and the 6-31G* basis set. Although this medium basis set would not lead to accurate

results, it represents a good compromise between accuracy and computation time.

4. Results and Discussion

4.1. β -cleavage of sulfoketone photoinitiators

A potential class of photoinitiators, described on the following scheme and in Table 1, was investigated in order to study the role of the triplet energy level on the cleavage mechanism [16-18].

Table 1 : Structure of the compounds studied.

Compound	R1	R2
1	H-	-CH ₃
2	CH ₃ O-	-C ₆ H ₄ CH ₃
3	CH ₃ -	-C ₆ H ₄ CH ₃
4	CH ₃ S-	-C ₆ H ₄ CH ₃
5	C ₆ H ₅ S-	-C ₆ H ₄ CH ₃
6	C ₆ H ₅ (C=O)C ₆ H ₅ S-	-C ₆ H ₄ CH ₃
7	CH ₃ S-	-CH ₃
8	C ₆ H ₅ -	-C ₆ H ₄ CH ₃

Ketosulfones have been shown to yield β -cleavage from the triplet state, resulting in the formation of alkyl and sulfonyl radicals.

Among the factors governing the cleavage of a photoinitiator, the excited state energy is expected to play a crucial role. Transient laser absorption spectroscopy allows the measurement of the triplet state lifetime that can be related to the rate constant of cleavage [19]. The measured triplet lifetimes are gathered in Table 2. It can be seen that among the sulfones studied, compounds (**1**) to (**3**) exhibit short triplet lifetimes, due to the fast cleavage that occurs from the triplet state. On the contrary, compounds (**4**) to (**8**) are characterized by long lifetimes, typically in the microsecond time scale, a fact indicating that no efficient bond breaking occurs from the triplet state: these compounds therefore require a coinitiator to yield radicals through hydrogen abstraction.

The reason for this totally different

behaviour has to be cleared up by investigating the energetic requirement for the photodissociation reaction. In order to get both the triplet state energy and quantum yield, we have performed some experiments with the LIPAC setup. LIPAC was used to determine ϕ_T and E_T according to the methodology described above. Figure 3 shows an example of such a measurement using 1-methylnaphthalene as a triplet acceptor for the determination of ϕ_T .

Figure 3: LIPAC experiment for the determination of a) ϕ_T and b) E_T for (4) in benzene.

The results are gathered in Table 2. The quantity $\phi_T \times E_T$ was measured for each compound by LIPAC. In addition, quenching of the triplet states by 1-methylnaphthalene ($E_T = 249$ kcal/mol [20]) afforded the determination of ϕ_T .

The triplet energies vary from 60 kcal/mol to 74 kcal/mol. The R2 substituent has a significant influence on the triplet energy. Indeed, for (4) the p-tolyl substituent increases the triplet energy by 5 kcal/mol compared to the methyl substituted compound (7). The R1 substituent affects more strongly the triplet energy by varying the energy levels of the aromatic ketone moiety. For instance, replacing an hydrogen or a methyl group by a methyl thioether group significantly decreases the triplet energy, as exemplified for compounds (1) and (7), or (3) and (4).

From Table 2, it clearly appears that (1), (2) and (3) lead to fast bond breaking ($\tau_T < 0.3$ μ s) compared to (4) to (8) ($\tau_T > 4$ μ s), the former three compounds being characterized by the highest triplet energy levels. From these results, it ensues that fast bond breaking occurs for compounds which exhibit a triplet energy higher than 67 kcal/mol.

Table 2 : Properties of the compounds studied. a) From LIPAC measurements. b) Calculated at the B3LYP/6-31G(d) level.

	τ (μ s)	ϕ_T^a	E_T^a (kcal/mol)	BDE ^b (kcal/mol)	C _{C=O} ^b spin density
1	0.13	0.81	74	41.8	0.54
2	0.28	0.85	73	39.8	0.48
3	0.075	0.86	73	39.5	0.51
4	4-8	0.93	67	39.6	0.36
5	10	0.84	67	39.8	0.10
6	5	0.78	66	37.7	0.0
7	4-8	1.0	62	42.1	0.30
8	4-8	0.98	60	39.4	0.01

At a first glance, it would be satisfactorily to claim that the bond breaking occurs in the triplet state when the triplet energy is higher than the β C-S bond dissociation energy (BDE). In order to test this hypothesis, it is of great interest to estimate the BDEs for the different photoinitiators studied here.

4.2. Molecular modeling

Use of Density Functional Theory (DFT) made affordable high level calculations even for large molecules as the ones discussed here. All the geometries were optimized for both ground and triplet states. The radicals formed from the β -cleavage were also fully optimized, leading to the calculation of the BDE as the enthalpy of the following reaction:

No zero point energy (ZPE) correction was applied. The calculated BDE are gathered in Table 2. The BDE span within a narrow range of values from 39 kcal/mol to 42 kcal/mol, excepted for (6) for which the BDE is slightly lower (BDE = 37.7 kcal/mol). It is quite surprising that the difference between the E_T values and the BDE values are so important. The R1 substituent has no significant effect on the BDE, indicating that the delocalization of the carbonyl group over the substituted phenyl ring does not affect the C-S bond being broken. This is consistent with the fact that a single C-C bond separates the σ_{C-S} bond from the π system. On the contrary, the R2 substituent has a marked effect, the methyl substituent leading to a value of about 2 kcal/mol higher than the phenyl one. The

bond stabilization in the latter case suggests a small delocalization on the sulfone group and the phenyl ring.

The enthalpy change ΔH_r of the photodissociation reaction from the triplet state can be evaluated from :

$$\Delta H_r = \text{BDE} - E_T \quad \text{Eq. 2}$$

From the experimental E_T and the calculated BDE, one can calculate that ΔH_r varies from -33.2 kcal/mol for (2) to -19.9 kcal/mol for (7). The reaction is therefore strongly exothermic for all the studied compounds. This is in contrast with the fact that the dissociation, if it occurs to some extent, operates at very slow rate for compounds (4) to (8).

It results that the enthalpy of reaction ΔH_r is not the main parameter governing the bond dissociation. This also implies that the triplet state energy does not drastically affect the efficiency of the process.

Apart the fact that the effect of the R1 substituent is to decrease the triplet energy, it also results in an increase of the triplet state delocalization. The spin density being distributed over all the chromophoric groups, this could affect the bond dissociation. It has been proposed that the α -cleavage of some carbonyl compounds could involve a spin polarization along the molecular skeleton [21]. In such a case, the spin density of the $C_{C=O}$ would play a significant role in the process.

This could be tested through the calculated value of the $C_{C=O}$ spin density in the triplet state for each compound. The results, reported in Table 2, show that the $C_{C=O}$ spin density strongly vary depending on the chemical structure. Generally, the $C_{C=O}$ value decreases when the delocalization increases.

For compounds (1) to (3), the spin densities are quite high (~ 0.5) compared to compounds (4) to (8), compound (6) exhibiting a spin density value as low as zero. Therefore, the dissociation will be favored for localized triplet states.

These results suggest that the dissociation favorably occurs for compounds exhibiting $C_{C=O}$ spin density higher than 0.4. Therefore, the relative long lifetime of the triplet states of (4) to (8) are explained on the basis of large delocalization of the

Figure 4: plot of the triplet spin density for a) 1 and b) 8.

chromophoric group that diminishes the spin density near the C-S bond, thereby rendering the dissociation less efficient.

5. Conclusion

In this paper, the main parameters governing the β -cleavage of ketosulfone derivatives were investigated. Laser Induced Photoacoustic Calorimetry was used to determine the intersystem crossing quantum yield and the energy of the triplet state. Molecular modeling at the DFT level was used to evaluate the BDEs of the compounds. It was found that the triplet state energy level and the BDEs do not strongly affect the dissociation from the triplet state, provided that the difference is high enough to ensure that the dissociation reaction could be exothermic. More interestingly the spin density of the carbonyl group plays a crucial role. The dissociation occurs from the triplet state when the spin density is higher than 0.35.

References

1. J.P. Fouassier, "Photoinitiation Photopolymerization and Photocuring", Hanser Publishers, Munich, New York, (1995).
2. K. Dietliker, "A Compilation of Photoinitiators Commercially Available for UV Today", Sita Techn. Ltd, London,

- (2001).
3. W. Schnabel in “*Lasers in Polymer Science and Technology*”, J.P. Fouassier, J.F. Rabek Eds., CRC Press, Boca Raton, vol. II, (2000).
4. S. Jockusch, N.J. Turro, *J. Am. Chem. Soc.*, **120** (1998) 11773
5. X. Allonas, J.P. Fouassier, L. Angiolini, D. Caretti, *Helv. Chim. Acta*, **84** (2001) 2577.
6. U. Kolczak, G. Rist, K. Dietliker, J. Wirz, *J. Am. Chem. Soc.*, **118** (1996) 6477.
7. X. Allonas, C. Ley, R. Gaume, P. Jacques, J.P. Fouassier, *Trends in Photochem. Photobiol.*, **5** (1999) 93.
8. C.S. Colley, D.C. Grills, N.A. Besley, S. Jockusch, P. Matousek, A.W. Parker, M. Towrie, N.J. Turro, P.M.W. Gill, M.W. George, *J. Am. Chem. Soc.*, **124** (2002) 14952.
9. X. Allonas, J. Lalevée, J.P. Fouassier, in “*Photoinitiated Polymerization, ACS Symposium Series*”, K.D. Belfield, J. Crivello Eds, Chap. 12, (2003), 140.
10. J. Lalevée, X. Allonas, J.P. Fouassier, *J. Photochem. Photobiol. A: Chem.*, **159** (2003) 127.
11. X. Allonas, J. Lalevée, J.P. Fouassier, *Chem. Phys.*, **290** (2003) 257.
12. J. Lalevée, X. Allonas, F. Louerat, J.P. Fouassier, *J. Phys. Chem. A.*, **106** (2002) 6702.
13. J. Lalevée, X. Allonas, J.P. Fouassier, H. Tachi, A. Izumitani, M. Shirai, M. Tsunooka, *J. Photochem. Photobiol. A: Chem.*, **151** (2002) 27.
14. J. Lalevée, X. Allonas, J.P. Fouassier, *J. Am. Chem. Soc.*, **124** (2002), 9613.
15. J. Lalevée, X. Allonas, J.P. Fouassier, *J. Am. Chem. Soc.*, **125** (2003) 9377.
16. J.P. Fouassier, X. Allonas, J. Lalevée, M. Visconti, *J. Pol. Sci. Part A : Pol. Chem.*, **38** (2000) 4531.
17. X. Allonas, C. Grotzinger, J. Lalevée, J.P. Fouassier, M. Visconti, *Eur. Pol. J.*, **37** (2001) 897.
18. G. LiBassi, L. Cadona, F. Broggi, *Proc. RadCure 86*, Baltimore, (1986) p.4.27.
19. D. Ruhlmann, J.P. Fouassier, *Eur. Pol. J.*, **29** (1993) 1079.
20. S.L. Murov, “*Handbook of Photochemistry*”, Marcel Dekker, New York, (1973).
21. H.E. Zimmerman, *Adv. Photochem.*, **1** (1963) 183.