4182 *Macromolecules* **1992,** *25,* 4182–4193

Sensitization of α-Aminoketone Photoinitiators: A Time-Resolved CIDNP and Laser Spectroscopy Investigation

G. Rist* and A. Borer

Physics Department, Ciba-Geigy AG, CH-4001 Basle, Switzerland

K. Dietliker* and V. Desobry

Additives Research, Ciba-Geigy AG, CH-1701 Fribourg, Switzerland

J. P. Fouassier* and D. Ruhlmann

Laboratoire de Photochimie Générale, Unité Associée au CNRS, Ecole Nationale Supérieure de Chimie, 8, rue A. Werner, F-68093 Mulhouse Cedex, France

Received February 28, 1992

ABSTRACT: Time-resolved laser spectroscopy and CIDNP experiments have been used to study the excited-state interactions between photoinitiators and thioxanthones used as photosensitizers. The thioxanthones are shown to interact with α-morpholino-substituted acetophenone photoinitiators bearing various substituents on the benzoyl moiety. These interactions are discussed in terms of electron and energy transfer, the balance of which is dependent on the nature of the thioxanthone and the polarity of the medium.

Introduction

Pigmented systems have for a long time been a challenge in the development of UV curing systems. While many photoinitiators are available for the curing of clear coatings, they usually do not have sufficient absorption in the UV/visible part of the spectrum to make efficient use of the restricted amount of light penetrating a pigmented formulation.

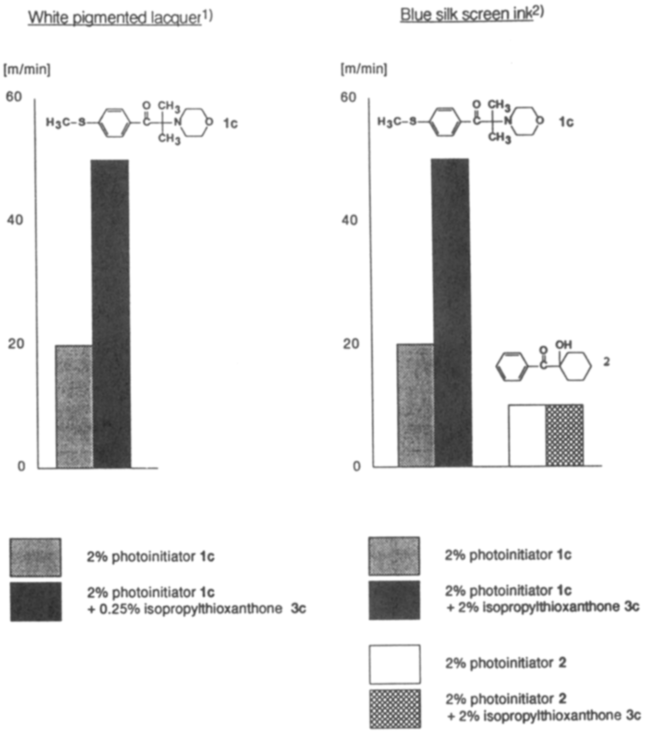
A major improvement in this field was made with the introduction of substituted α-amino ketone photoinitiators.[1,2] These compounds have higher absorption coefficients in the 300–400-nm region than the usual acetophenone type photoinitiators and are, therefore, suitable for the curing of pigmented systems.

The reactivity of these systems is further improved by the addition of sensitizers such as thioxanthones.[1-3] The effect of sensitization is demonstrated in Figure 1 for 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropan-1-one (**1c**)[4] in a white lacquer and a blue printing ink. Isopropylthioxanthone (**3c**) was used as sensitizer. For comparison, another acetophenone type photoinitiator, 1-hydroxycyclohexyl phenyl ketone (**2**)[5] is shown in a silk screen ink application. The highest possible belt speed producing hard surface-cured films is taken as a measure of reactivity.

Depending on the system, an important increase of reactivity can be obtained using the combination of the α-amino ketone **1c** and the thioxanthone **3c**. The improvement is highest at relatively high film thickness or in highly pigmented systems, where the light screening effect of the pigment is most pronounced.[3] Photoinitiator **2**, on the other hand, is less reactive than **1c** in this application, and the reactivity is not improved upon addition of the sensitizer.

The reactivity enhancement is due to the fact that thioxanthones have longer wavelength absorptions (λ_{max} ~380 nm) than the initiators, which allows better use of the light passing the spectral window of the pigment. The photoinitiator is subsequently activated by interacting with the excited state sensitizer.

Though for a technical application the improvement of reactivity is of importance regardless of the mechanism causing the synergistic effect, the understanding of the latter is crucial in view of the continuing effort to improve photoinitiator efficiency in order to meet the requirements of new technologies.



1) Formulation on the basis of urethane acrylate containing 38.5% rutile TiO_2.
Light source: Fusion "D-bulb".

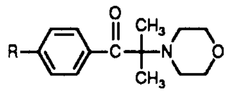
2) Blue silk screen printing ink, layer thickness 10μm.
Light source: Medium pressure mercury bulb, 80 Watt/cm

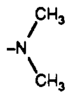
Figure 1. Sensitization effect of the combination 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropan-1-one (**1c**)/isopropylthioxanthone (**3c**) in a white lacquer and a blue silk screen printing ink.

In a continuation of earlier work,[3] the processes occurring upon sensitization of α-morpholino ketone photoinitiators **1a**–**1d** (Table I) have been studied using new experimental techniques.

0024-9297/92/2225-4182$03.00/0

Table I
α-Morpholino Ketone Photoinitiators



compd	R	E_T (kcal/mol)[a]
1a	-H	62
1b	-O-CH$_3$	65
1c	-S-CH$_3$	61
1d		63

[a] Data determined from phosphorescence spectra in 2-methyltetrahydrofuran at 77 K.[3]

Earlier Studies

Direct Photolysis of α-Morpholino Ketone Photoinitiators. ^{1}H NMR CIDNP studies,[2,3] laser spectroscopy investigations[6] as well as trapping experiments using both 2,2,6,6-tetramethylpiperidinyl-1-oxyl[1] and methyl 2-*tert*-butylacrylate[3] have shown that the photoinitiator **1c** undergoes a fast α-cleavage reaction upon direct irradiation, affording a substituted benzoyl and an α-aminoalkyl radical. CIDNP experiments indicated that compounds **1a**, **1b**, and **1d** also follow this photochemical reaction path.

In solution, the α-cleavage of these photoinitiators is partially followed by a disproportionation reaction of the two primary radicals within the solvent cage, affording the corresponding benzaldehyde derivatives. The strong polarization (enhanced absorption) of the signal of the aldehyde protons was attributed to a triplet-state precursor which is in agreement with Kaptein's rules.[7] The detection of this polarized aldehyde signal is an unequivocal proof for a triplet-state reaction.

Sensitization Experiments. Earlier CIDNP and trapping experiments on the sensitized photodecomposition of photoinitiator **1c** demonstrated the formation of the 4-methylthiobenzoyl radical.[3] At the same time, products arising from electron-transfer reactions between sensitizer and initiator were also detected.

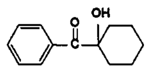
These findings were tentatively interpreted by two parallel reaction pathways: (1) Energy transfer from the excited-state sensitizer to the photoinitiator would produce a triplet-state α-amino ketone, which subsequently undergoes the same Norrish I reaction as upon irradiation without sensitizer. (2) Electron transfer from the α-amino ketone to the excited sensitizer would lead to other reaction products. In fact, electron transfer from simple amines to excited benzophenones or thioxanthones (mostly followed by a proton transfer) is a well-known photochemical reaction.[8]

The benzoyl radicals formed via the energy-transfer route act as initiating species for the polymerization process. These σ-radicals are well-known to add efficiently to vinylic double bonds.[9] Other radicals produced by either of the two reaction pathways are possibly involved either in initiation or termination processes, although no effort to elucidate this point has been undertaken so far.

A recent paper[10] suggested that an electron-transfer mechanism could also be responsible for the sensitized α-cleavage process observed with initiator **1c** (see Figure 11). Further investigations of the processes occurring upon the sensitization of this photoinitiator with thioxanthones using new experimental techniques were therefore undertaken in order to gain a better understanding of this technically important synergism.

Experimental Section

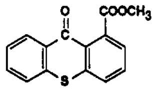
Materials. The α-amino ketones **1a**–**1d** (Table I) were used as photoinitiators. Compounds **1a**, **1b**, and **1d** were synthesized according to the method in ref 11. Compounds **1c**[4] and 1-hydroxycyclohexyl phenyl ketone (**2**)[5] are commercially available photoinitiators.



2

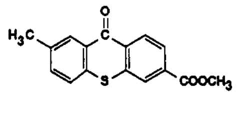
(E_T = 67 kcal/mol)

The following thioxanthones were used in combination with the photoinitiators **1a**–**1d** and **2**:



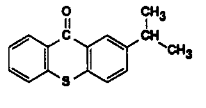
3a

E_T = 63 kcal/mol



3b

E_T = 58.4 kcal/mol



3c1)

E_T = 61.4 kcal/mol

1) Commercially available isopropylthioxanthone is a mixture of the 2- and 4-substituted compounds containing mainly 2-isopropyl thioxanthone.

The thioxanthones **3a** and **3b** were prepared according to the method in ref 12. Isopropylthioxanthone is a commercial photoinitiator.[13]

Experimental Techniques. The CIDNP experiments were performed on a Bruker AM-200, wide bore spectrometer. In these experiments, the light source was a Questek excimer laser in combination with a Lambda Physics dye laser (diphenylstilbene (DPS) solution, 404.5 nm). At this wavelength only the thioxanthones absorb sufficient light to undergo efficient photochemical reactions. The duration of the laser pulse was approximately 20 ns; the duration of the radio-frequency pulse, 1 μs. The irradiation experiments were carried out in perdeuterated benzene or methanol. The NMR absorptions were saturated immediately before the laser pulse, so that the spectra only exhibit polarized resonances of the photoproducts.

The laser spectroscopy apparatus has been described elsewhere in greater detail.[14] The excitation consists of a short pulse of light (~5 ns) at λ = 430 nm delivered by a dye laser pumped by a YAG/Nd laser. The time resolution of the analyzing device is limited by the pulse duration.

Preparative irradiations were performed using a Philips HPK 125 mercury medium-pressure lamp in an immersion vessel. Solutions were degassed by nitrogen purging. Products were isolated and identified by usual preparative and analytical techniques.

Results and Discussion

CIDNP Experiments. CIDNP experiments reported in ref 3 were carried out under continuous irradiation of the sample. The experimental data are averaged over a relatively long time (several seconds). Under these conditions, CIDNP intensities are strongly influenced by nuclear spin relaxation.

In the present investigation a time-resolved CIDNP technique[15] was used. The time resolution is limited by the width of the radio-frequency pulse (~1 μs). Delay times in the order of 1 μs are short enough that nuclear spin relaxation does not influence the CIDNP intensities. For given hyperfine coupling constants and *g* values, the signal intensities are a measure for the relative amount of

Table II
Qualitative Results of Sensitization of Photoinitiators 1a–1d and 2 with Thioxanthone 3a (E_T = 63 kcal/mol) in Benzene and Methanol

solvent[a]	initiator, triplet energy[b] (kcal/mol)	spin-polarized aldehyde signal	energy transfer	spin-polarized sensitizer	electron transfer
benzene	**1a**, 62	no	*c*	*d*	
	1b, 65	no	*c*	*d*	
	1c, 61	strong	yes	*d*	
	1d, 63	no	*c*	*d*	
	2, 67	no	no	*d*	
methanol	**1a**, 62	weak	*c*	yes	yes
	1b, 65	weak	*c*	yes	yes
	1c, 61	medium	yes	yes	yes
	1d, 63	no	*c*	yes (very strong polarization of **1d**)	yes
	2, 67	no	no	no	no

[a] Perdeuterated solvents. [b] Triplet energies determined from phosphorescence spectra in 2-methyltetrahydrofuran at 77 K.[3] [c] No or very little energy transfer. [d] Not detectable in an apolar solvent under the experimental conditions.

spin-polarized species formed and hence for the rate of the reaction affording these compounds.

In order to observe CIDNP-effects from radical pair reactions, the radical pairs should have lifetimes of at least 10^{-8}–10^{-9} s. This time scale allows for recombination reactions following radical reencounter, which give rise to the nuclear spin polarizations observed in the CIDNP experiment.[16]

Radical ion pairs are not stabilized in apolar solvents and hence decay in a very short time. Electron-transfer reactions in these media are in general not expected to lead to significant CIDNP signals under these experimental conditions, although electron transfer may be an important primary reaction.

In polar solvents, radical ion pairs should be sufficiently stabilized, and nuclear spin polarization can therefore be detected and serve as a probe for electron-transfer processes. CIDNP spectroscopy in general is thus a suitable method for studying electron-transfer reactions in polar media, while information on the same processes in apolar solvents usually has to be obtained by other experimental methods.

As it will be discussed in the section on the mechanism of sensitized α-cleavage for the initiator molecules studied in this work, spin-polarized aldehyde formed in the apolar solvent benzene is interpreted as an indication of energy transfer. This interpretation is very likely to hold in methanol solvent as well. Taking into account the rate constants for α-cleavage given in Table IV, the aldehyde polarization is an approximative measure for the efficiency of the energy transfer for experiments in the same solvent. Sensitizer/initiator pairs with a great energy difference allowing exothermic transfer from the sensitizer to the initiator exhibit strong polarized signals.

On the other hand, spin-polarized signals of thioxanthone derivatives are evidence for electron-transfer processes (see section on sensitization experiments in methanol).

Qualitative results of sensitization experiments in an apolar (benzene) and a polar solvent (methanol) are presented in Tables II and III. Only the occurrence of polarized aldehyde and sensitizer signals are reported, indicating energy transfer and/or electron-transfer processes as detected by CIDNP spectroscopy.

Sensitization Experiments in Benzene. A time-resolved CIDNP spectrum of an irradiated sample of a mixture of the α-amino ketone **1c** and the thioxanthone **3c** in benzene is shown in Figure 2. The spectrum was measured approximately 1 μs after the laser pulse. It shows the typical resonances associated with a substituted benzoyl and an α-aminoalkyl primary radical pair.

Table III
Qualitative Results of Sensitization of Photoinitiator 1c (E_T = 61 kcal/mol) with Thioxanthones 3a–3c in Benzene and Methanol

solvent[a]	sensitizer, triplet energy[b] (kcal/mol)	spin-polarized aldehyde signal	energy transfer	spin-polarized sensitizer	electron transfer
benzene	**3a**, 63	strong	yes	*d*	
	3b, 58.4	no	*c*	*d*	
	3c, 61.4	strong	yes	*d*	
methanol	**3a**, 63	medium	yes	yes	yes
	3b, 58.4	weak	*c*	yes	yes
	3c, 61.4	medium	yes	yes	yes

[a] Perdeuterated solvents. [b] Triplet energies determined from phosphorescence spectra in 2-methyltetrahydrofuran at 77 K.[3] [c] No or very little energy transfer. [d] Not detectable in an apolar solvent under the experimental conditions.

The strong signal at 9.64 ppm vs TMS (enhanced absorption) is attributed to the aldehyde proton of 4-(methylthio)benzaldehyde (**4**). Its polarization is the same as in experiments where the initiator **1c** is directly excited by light of shorter wavelengths. The signals of two olefin protons (3.98 and 3.86 ppm) and of the methyl group (1.68 ppm) of 2-morpholinopropene (**5**) also carry enhanced absorption. These polarizations are proof for the triplet spin character of the radical pair affording these products: The formation of the aldehyde and the enamine can be explained by an in-cage disproportionation of the radical pair i, as it was found for the Norrish I reaction occurring upon direct irradiation of this photoinitiator (Figure 3).[1]

The enamine was not detected in the time-averaged CIDNP spectrum reported earlier.[3] Two reasons can account for this behavior: First, the enamine **5** is an unstable product which undergoes facile hydrolysis to give morpholine and acetone. Second, the same product is formed via an escape reaction pathway which leads to opposite polarization of the enamine signals in the CIDNP spectrum: An encounter radical pair of two 2-morpholinopropyl radicals ii can undergo another disproportionation reaction affording the enamine **5** and 2-morpholinopropane (**6**) (Figure 4). These opposite polarizations strongly decrease the signal intensities in the time-averaged CIDNP spectrum. A polarized signal at 0.87 ppm (emission type polarization) for the methyl groups of 2-morpholinopropane (**6**) is further proof for this reaction pathway.

The CIDNP spectrum shown in Figure 2 was obtained upon irradiation of a carefully degassed sample. When the same experiment is repeated using a solution containing molecular oxygen, the spectrum shown in Figure 5 is

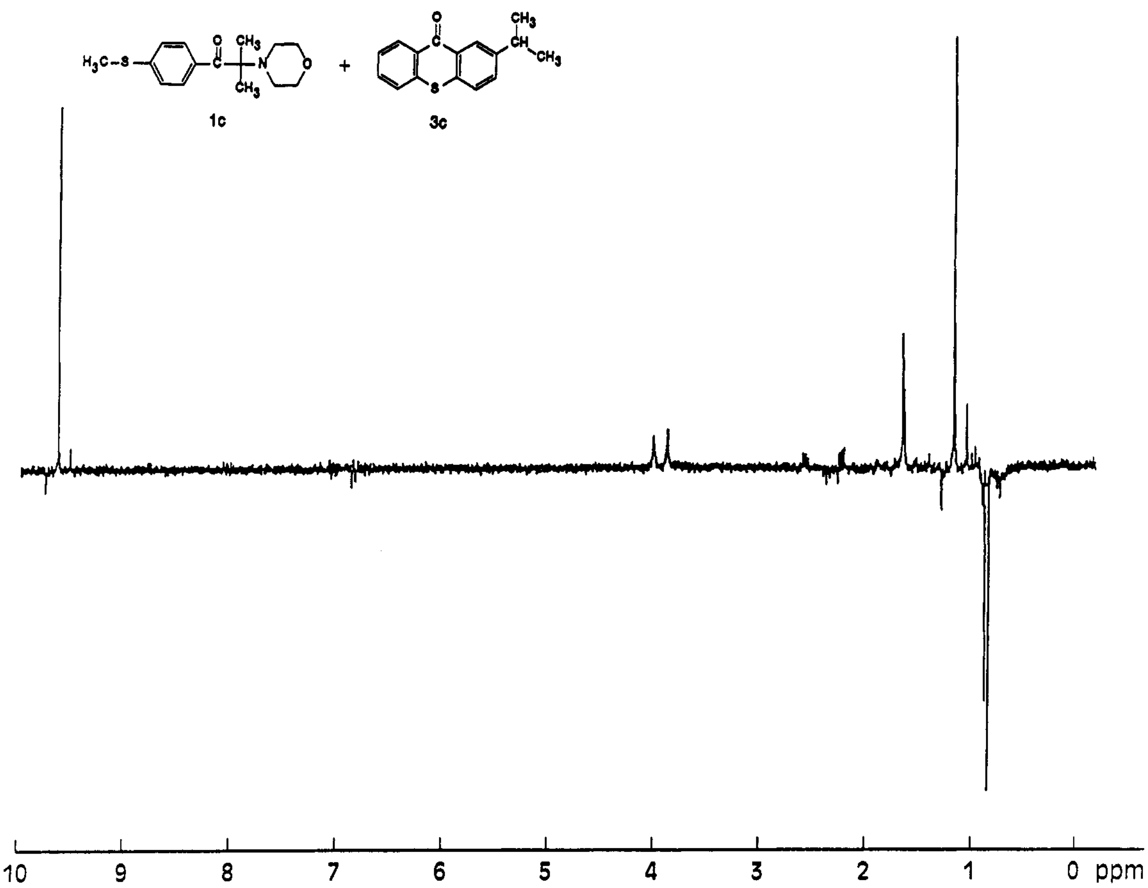


Figure 2. Time-resolved ^{1}H NMR CIDNP spectrum of an irradiated degassed sample of **1c** and **3c** in benzene.

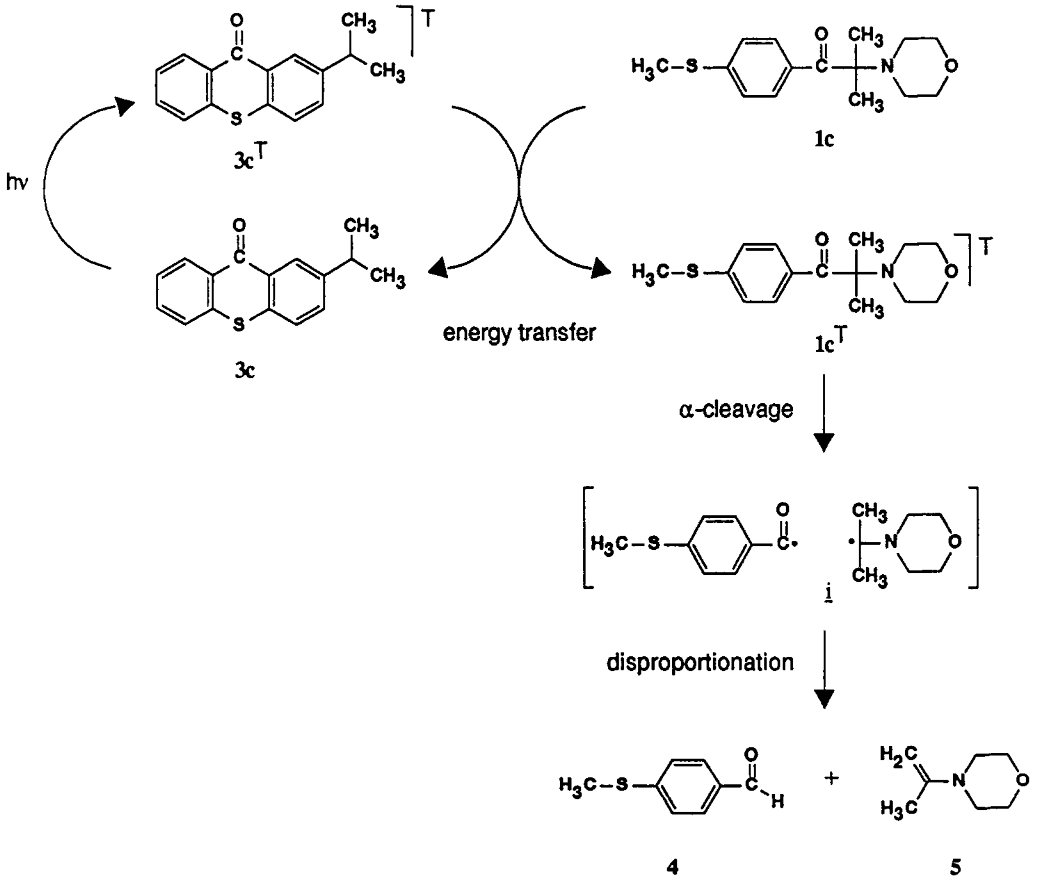


Figure 3. α-Cleavage of photoinitiator **1c** induced by energy transfer.

obtained. Note that this spectrum is reproduced with a higher amplification factor than that in Figure 2.

The spectrum is clearly different from the previous one: The enamine resonances at 3.98, 3.86, and 1.68 ppm are broadened, and the emission line of the methyl group of**6** at 0.87 ppm has become much weaker. Since the signal intensities are independent of nuclear relaxation, these findings indicate the occurrence of another interfering

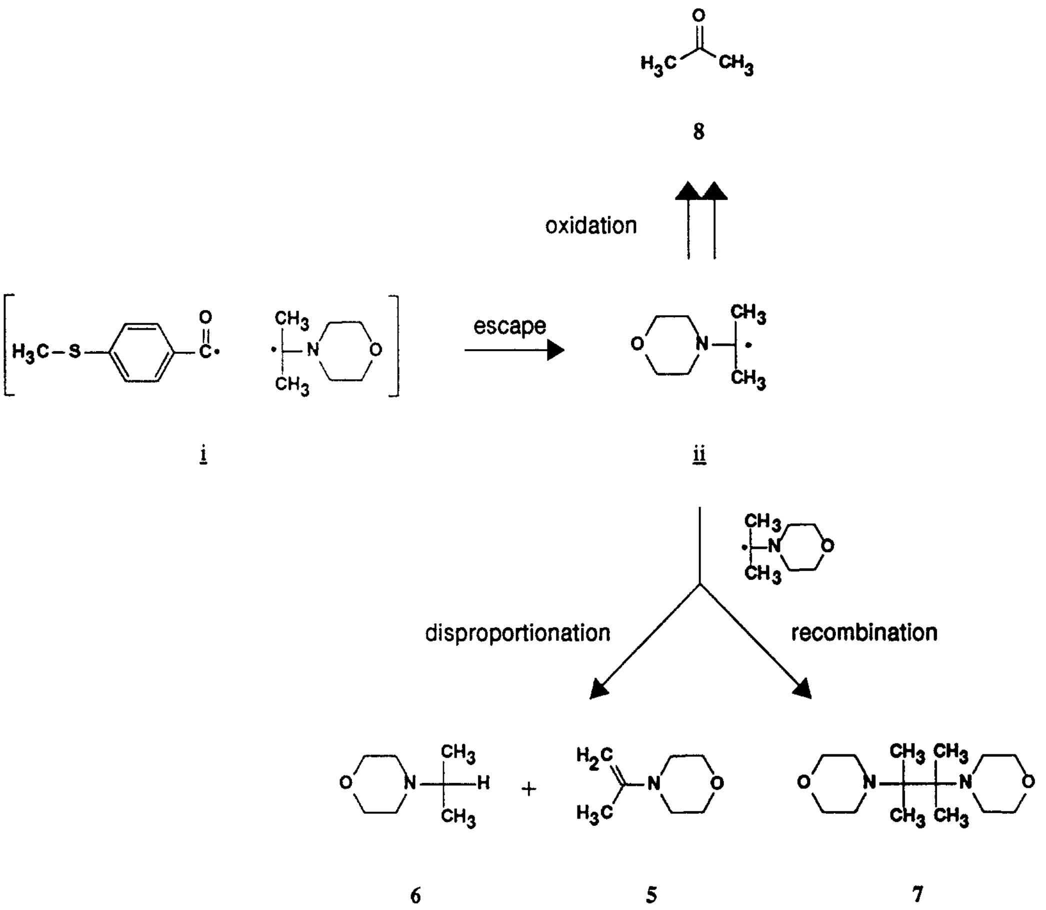


Figure 4. Reactions of escaped 2-morpholinopropyl radicals.

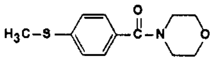
reaction of the 2-morpholinopropyl radical.

A strong resonance of acetone (8) (emission) has emerged at 1.60 ppm. The polarization of this signal is of escape character, and formation of acetone is therefore attributed to oxidation of the escaping 2-morpholinopropyl radical. Fast oxidation of the enamine to acetone as the main reaction path can be ruled out by the fact that the enamine resonances in both experiments (Figures 2 and 5) exhibit recombination-type polarization (Kaptein's rule[7]). It can be concluded from the time scale of the experimental technique that the oxidation must occur in a fast process within less than 1 μs after the α-cleavage reaction. At longer reaction times a small fraction of unpolarized acetone is formed even in degassed solution, presumably via hydrolysis of the enamine 5.

Formation of acetone upon sensitized photodecomposition of 3-morpholino-3-methylbutan-1-one via an electron-transfer process using 9,10-dicyanoanthracene as sensitizer was recently reported.[17] A mechanism involving transfer of the acetyl moiety from the intermediate radical cation to the sensitizer was proposed, which results in formation of a 2-morpholinopropyl radical. A second electron transfer of this radical would then afford the corresponding immonium salt, which is finally hydrolyzed to give acetone and morpholine. A similar mechanism could also explain the observed formation of acetone in the experiments reported here. However, the multistep reaction sequence is hardly in agreement with the fast process detected by CIDNP spectroscopy in this experiment. Further, the reaction mechanism proposed in ref 17 would not lead to aldehyde formation.

The signals at 1.16 ppm (strong enhanced absorption) both in Figures 2 and 5 are due to the recombination of the primary radicals affording the starting material.

Both direct irradiation of initiator **1c** as well as sensitization of **1c** with thioxanthone **3a** yielded 4-[4-(methylthio)benzoyl]morpholine (**9**), which was detected both by product isolation in preparative irradiation experiments and by NMR spectroscopy. The formation of this amide could explain the fate of the morpholino fragment obtained by decomposition of the 2-morpholinopropyl radical or by hydrolysis of 5.



9

The reaction pathway leading to product 9 is not completely understood. Formation of benzamides from benzoyl radicals and α-aminoalkyl radicals (obtained from secondary amines) has been reported in the literature.[18] A similar reaction between the 4-(methylthio)benzoyl radical and a morpholino species obtained by decomposition of the 2-morpholinopropyl radical could account for this product.

In addition to the products detected by time-resolved CIDNP experiments, 4-(methylthio)isobutyrophenone (**10**) was also isolated in minor amounts from preparative irradiation experiments, pointing to β-elimination as a minor photochemical reaction of compound **1c** (Figure 6).

No spin-polarized aldehyde signals were detected when the same experiments using initiator **1a**, **1b**, **1d** were performed in benzene. Clearly, no or only very little sensitizer/initiator interaction, analogous to that found for **1c**, takes place. These findings are in good agreement with the proposed energy-transfer mechanism leading to α-cleavage products (Figure 3). Compound **1c** has the lowest triplet energy and hence is most efficiently sen-

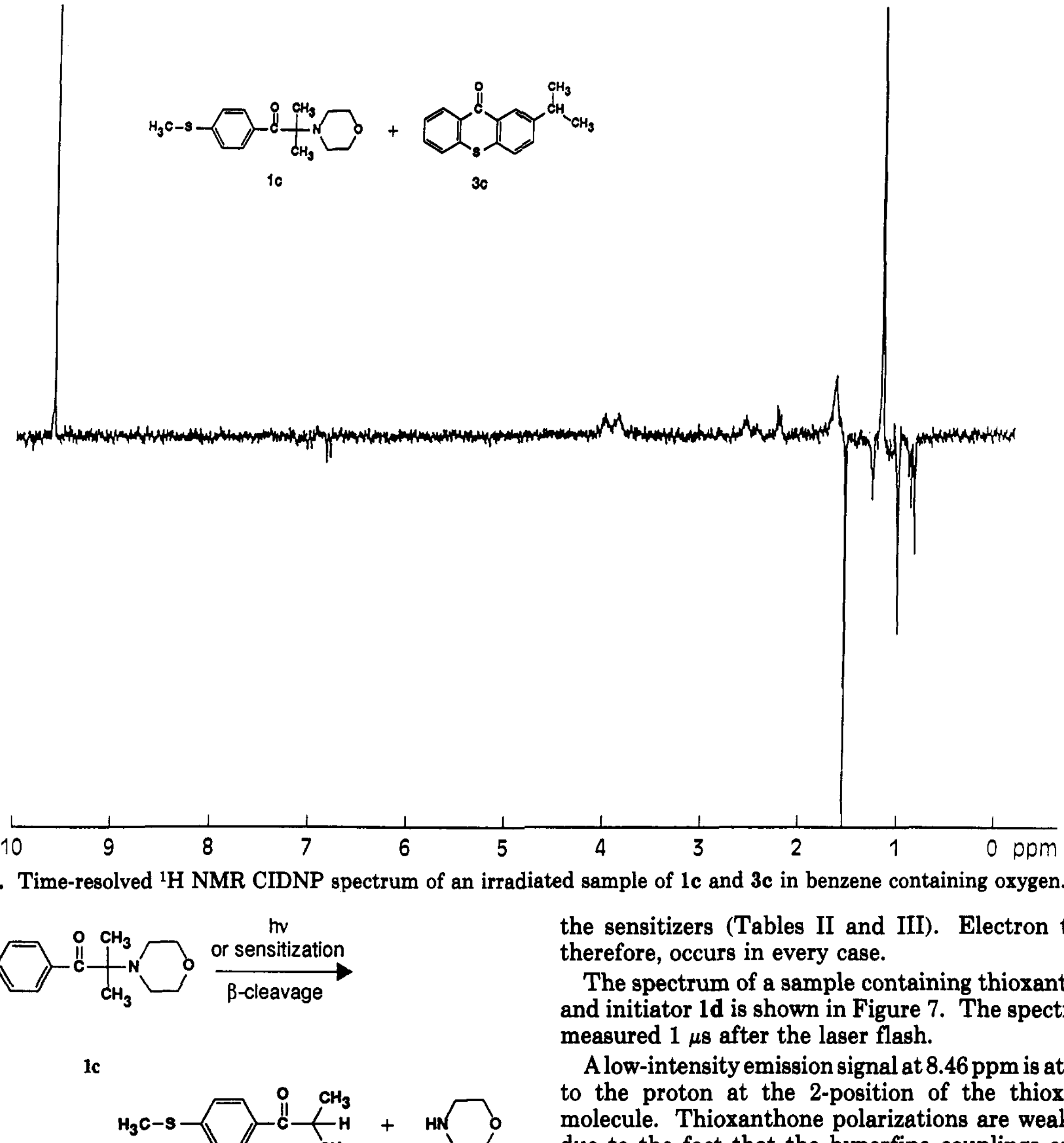


Figure 5. Time-resolved ^{1}H NMR CIDNP spectrum of an irradiated sample of 1c and 3c in benzene containing oxygen.

Figure 6. β-Cleavage of initiator 1c.

sitized, while the energy-transfer process would be endothermic for the other initiator/sensitizer pairs.

As mentioned before, no information on electron-transfer processes in benzene solution could be obtained by CIDNP experiments, although such processes do occur for all sensitizer/initiator pairs (see below).

Sensitization Experiments in Methanol. Electron transfer from the photoinitiator to the excited thioxanthone affords a radical ion pair (radicals i and ii in Figure 8 or 9) which partly undergoes electron back-transfer to the starting compounds. Provided that the lifetime is sufficiently long, spin-polarized signals of both thioxanthone and photoinitiator can be observed in the CIDNP spectrum. In methanol, this requirement is fulfilled due to the good stabilization of the ionic species by the polar solvent. The occurrence of spin-polarized thioxanthone signals is thus strong evidence for electron transfer between sensitizer and initiator.

Time-resolved CIDNP spectra of all α-amino ketone/thioxanthone pairs studied exhibit polarized signals of the sensitizers (Tables II and III). Electron transfer, therefore, occurs in every case.

The spectrum of a sample containing thioxanthone 3a and initiator 1d is shown in Figure 7. The spectrum was measured 1 μs after the laser flash.

A low-intensity emission signal at 8.46 ppm is attributed to the proton at the 2-position of the thioxanthone molecule. Thioxanthone polarizations are weak, partly due to the fact that the hyperfine couplings are much smaller than in the counter radical cation. However, in burst-type experiments, where the NMR spectrum is sampled after 20–40 laser pulses in intervals of 20 ms, the same signal exhibits strong emission-type polarization and is hence easily detected.

The protons of the morpholino ring (3.66 and 2.57 ppm) do not exhibit any pronounced polarization. The morpholino nitrogen in compound 1d is thus not involved in the electron-transfer process to any measurable extent. Hence, electron transfer in this molecule must occur from the aromatic amino group.

Initiator 1d has an emission line at 2.93 ppm attributed to the *N*-methyl protons. This type of polarization is in agreement with Kaptein's rules:[7] The electron g value of the thioxanthone ketyl anion radical (g = 2.0035[19]) is presumably larger than that of the cation radical. Since the radical pair is formed in the triplet state and the hyperfine value of the polarized *N*-methyl protons in the radical state is positive, emission polarization is expected.

The enhanced absorption of the signals at 6.68 ppm (protons at C(3) and C(5) on the benzoyl moiety) proves that the unpaired electron is delocalized into the aromatic ring. These findings also exclude a neutral radical pair, obtained by proton transfer following the oxidation of the amine, as a main source of polarization. The strongest

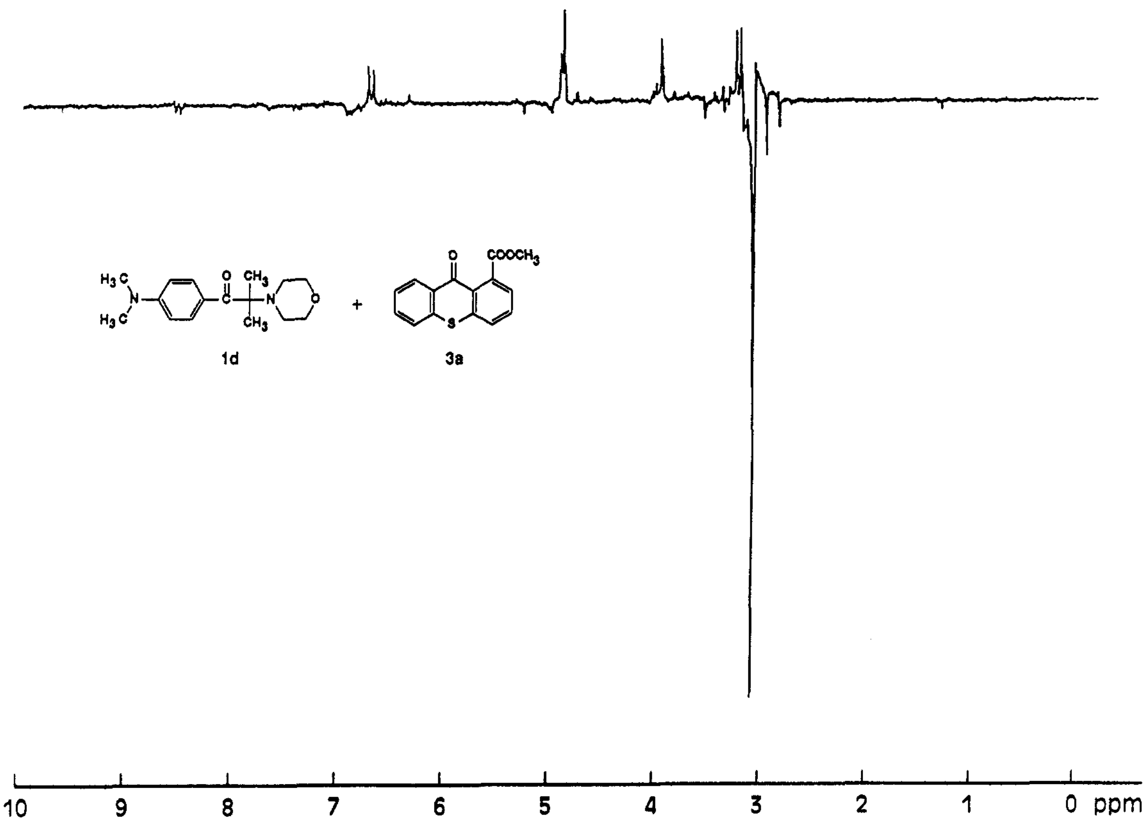


Figure 7. Time-resolved ^{1}H NMR CIDNP spectrum of an irradiated sample of **1d** and **3a** in methanol.

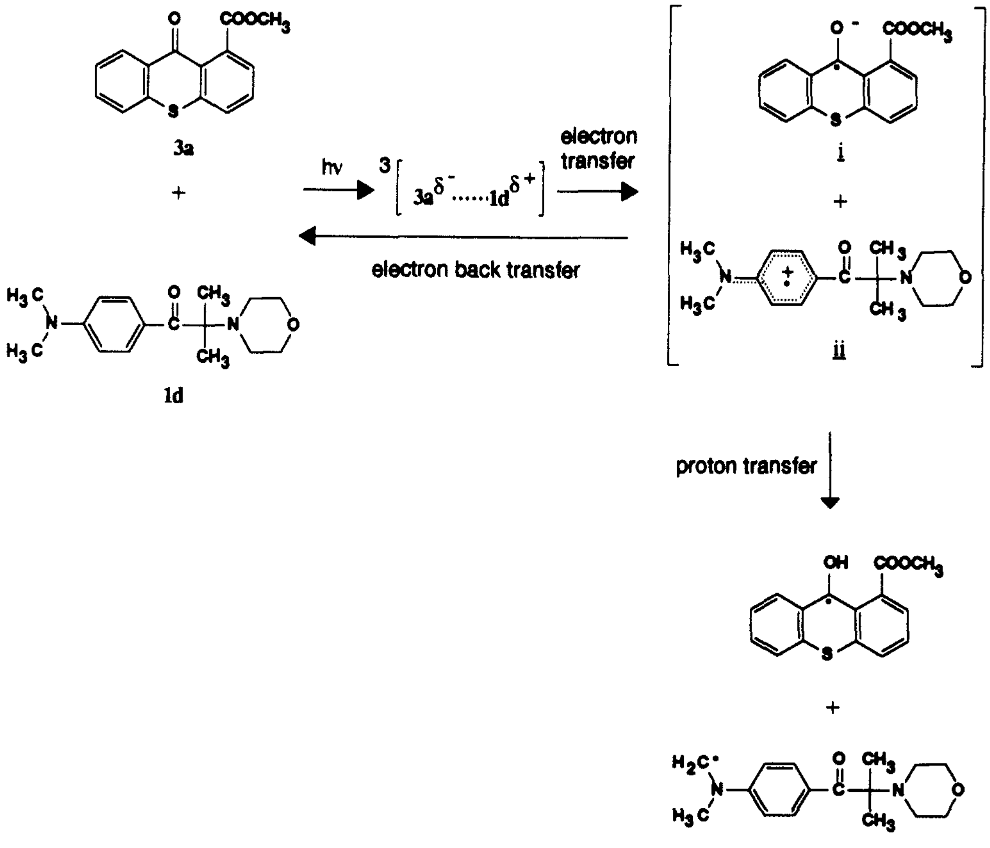


Figure 8. Light-induced electron-transfer processes between **3a** and **1d**.

signals observed in the CIDNP spectrum are due to a fast electron-back-transfer reaction, while polarized signals of other products are much weaker (Figure 8).

The initiators **1a**, **1b**, and **1c** bearing no aromatic amino group, undergo an electron-transfer process from the morpholino nitrogen to the excited thioxanthone, as it is shown for the initiator **1c** in Figure 9. The strongest polarization for all these compounds is the enhanced absorption of the morpholino *N*-methylene group at ca. 2.56 ppm. The polarization has to be linked with the back-transfer of the electron. The polarization of the sensitizer protons indicates that for all pairs the electron *g* value of the thioxanthone ketyl radical anion is smaller than that of the α-amino ketone radical cation. Enhanced absorption of

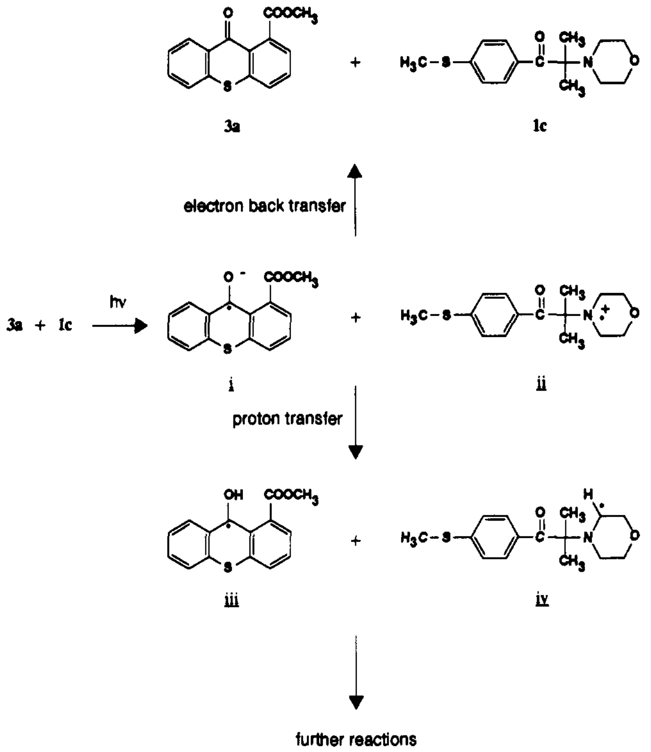


Figure 9. Electron-transfer-induced processes between **3a** and **1c**.

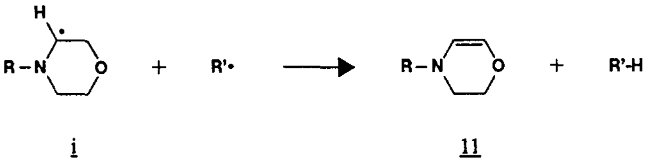


Figure 10. Formation of a dehydrogenated morpholino derivative.

the morpholino methylene group adjacent to nitrogen further points to a positive hyperfine coupling constant of the two protons, which is in agreement with the proposed radical ion pair.

Apart from electron back-transfer, the primary radical pair undergoes a variety of subsequent reactions, as detected by the appearence of a large number of polarized resonances in the aliphatic chemical shift region. Further experiments are needed to establish the different reaction pathways in detail.

The spectra obtained with compounds **1a**, **1b**, and **1c** additionally exhibit signals in the region between 4.9 and 6.0 ppm with a typical olefin vicinal coupling constant of approximetely 5 Hz.[20] These signals are tentatively assigned to a structure **11** possessing a partially dehydrogenated morpholino moiety. Such compounds could for example arise via hydrogen abstraction from an α-aminoalkyl radical (i in Figure 10), either in a disproportionation reaction or by another radical species. α-Aminoalkyl radicals such as i are likely to be formed under the reaction conditions. The structure of the substituent R could not be established with certainty from the spectrum of the product mixture.

Signals of spin-polarized benzaldehyde derivatives are also detected upon irradiation of samples containing initators **1a**–**1c** (Tables II and III). The intensities of these signals are much smaller than those of the polarizations observed from the electron-back-transfer reaction and from other products following electron transfer. They are also weak compared with the aldehyde resonances observed in benzene. This intensity behavior indicates that formation of aldehyde and electron transfer are competitive reactions. Since the initiator **1c** with the lowest triplet energy again shows the strongest aldehyde resonances, at least part of the aldehydes observed in methanol are formed via energy transfer.

Irradiation of thioxanthone **3a** in the presence of photoinitiator **2** afforded no polarized signals of either benzaldehyde nor polarized thioxanthone in benzene or methanol, respectively. Since the triplet energy of this compound is too high for energy transfer and the compound has no functionality which could easily participate in an electron-transfer step, no reaction takes place under these experimental conditions.

Mechanism of Sensitized α-Cleavage. Time-resolved CIDNP spectra obtained upon irradiation of thioxanthones **3a** or **3c** and initiator **1c** at 404.5 nm are strong evidence for the formation of the primary radical pair i (Figure 3) in benzene.

This radical pair can be formed via Norrish type I cleavage of the triplet excited initiator **1c**, as shown in Figure 3. Such a mechanism requires energy transfer from the excited sensitizer to the initiator. The frequency of energy transfer is strongly dependent on the relative triplet energy differences between the two compounds.[21] In order to make a direct triplet energy transfer feasible and efficient, the initiator energy has to be below the sensitizer energy. This is the case for the sensitizer/initiator pairs **3a**/**1c** and **3c**/**1c**, provided that the triplet energies are not strongly solvent dependent.

The results presented in Tables II and III (benzene solvent) for other thioxanthone/initiator pairs are in good agreement with an energy-transfer process. A strong or medium polarized aldehyde signal is observed, if E_{T}(sensitizer) $\geq$ E_{T}(initiator), and the polarized signal is strongest for the pair **3a**/**1c** possessing the largest energy difference. In those cases where the energy difference is presumably reversed, no or only weak aldehyde formation is observed.

There is, however, an ionic reaction pathway which could engender the same radical pair. Electron transfer from the nitrogen atom of the photoinitiator would give an amino radical cation i and the ketyl radical anion ii formed from the sensitizer (Figure 11). The amino radical cation could undergo a subsequent homolytic cleavage of the carbonyl–C(α) bond, affording the substituted benzoyl radical iii and an immonium cation iv. Electron back-transfer from the ketyl radical anion to the immonium cation would finally lead to the α-amino radical v and the ground-state sensitizer **3c**.

Similar scissions of amino radical cations are discussed in the literature.[22-24] 2-Morpholino-1,2-diphenylpropan-1-one was reported to afford the benzoyl and the α-aminoalkyl radical by an analogous route, if ruthenium bipyridyl complexes or 1,2-diketones are used as electron acceptors.[10] Since the α-amino ketone investigated in that study is structurally similar to the photoinitiators **1a**–**1d**, these findings suggested that the sensitized cleavage of the α-bond in the α-amino ketones could also occur via electron transfer instead of energy transfer.

The primary radical ion pairs i and ii (Figure 11) should give rise to strong CIDNP effects. Signals of spin-polarized sensitizers were detected in methanol (see Tables II and III and the discussion in the foregoing section), while the analogous signals could not be detected in benzene, probably because of the short lifetime of the radical ions in this solvent.

However, the mechanism shown in Figure 11 is ruled out for benzene solutions by the following arguments.

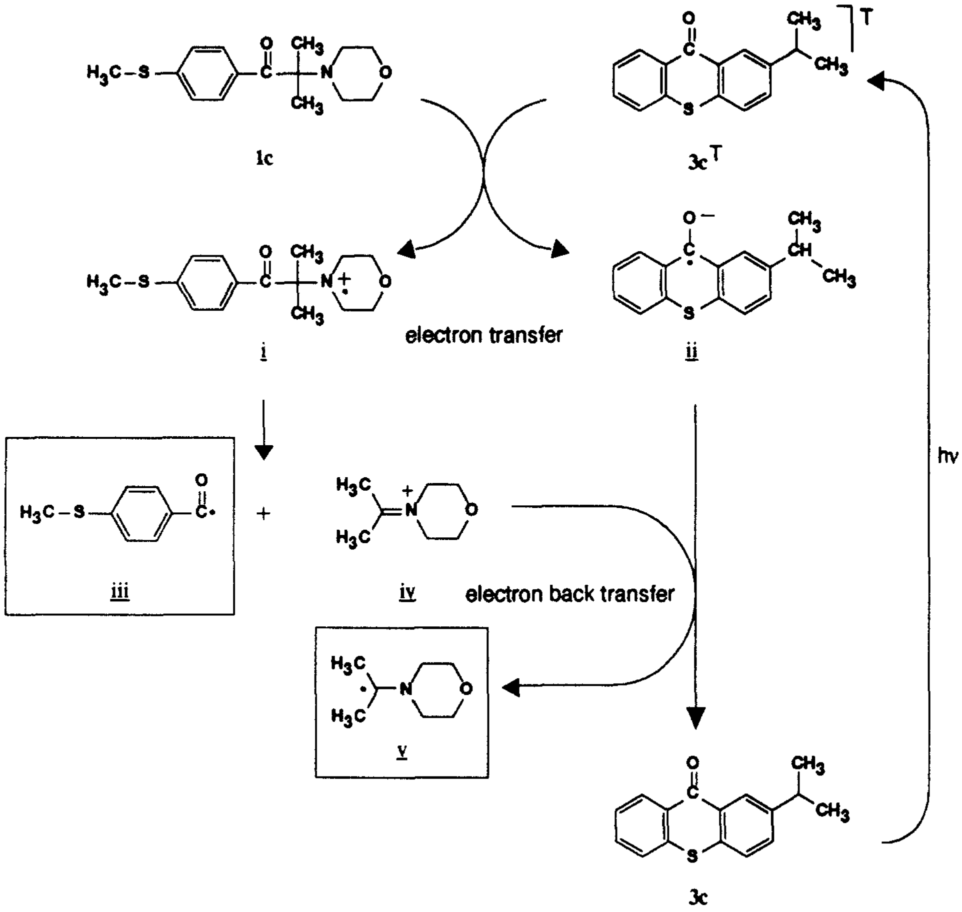


Figure 11. Formation of the 4-(methylthio)benzoyl and the 2-morpholinopropyl radicals via an electron-transfer mechanism.

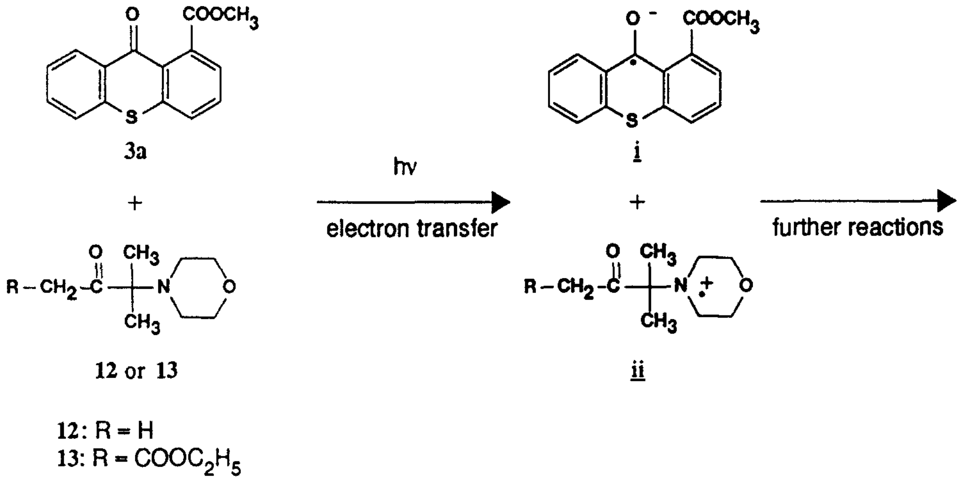


Figure 12. Reaction of model compounds 12 and 13 with thioxanthone 3a.

(1) No energy-transfer step occurs in the course of this mechanism. Hence the efficiency of the formation of radicals such as i and v should not depend on the relative triplet energies of the sensitizer and initiator. For a given thioxanthone, the electron-transfer should only depend on the oxidation potential of the amine moiety of the initiator, and initiators 1a–1c possessing the same α-amino group should fragment with similar efficiency. Compound 1d could react differently, since the electron transfer occurs from the aromatic amine and not from the morpholino moiety. The experimental results (Tables I and II), however, clearly indicate a dependence of the sensitizing efficiency on the relative triplet energies.

(2) The longer lifetime of the radical ion pair in a polar environment should allow this reaction pathway to compete more efficiently with electron back-transfer in methanol than in benzene. Benzaldehyde polarization should therefore be more intense in the polar solvent. This is in contrast to the experimental finding of stronger polarization in benzene than in methanol for initiator 1c.

(3) Two α-amino ketone model compounds 12 and 13 were investigated in combination with thioxanthones (Figure 12). The high triplet energies of aliphatic ketones (>70 kcal/mol) prevent energy transfer from the thioxanthone, while an electron transfer and subsequent fragmentation as shown in Figure 11 should be possible with an efficiency similar to that for the initiators 1a–1c.

No polarized aldehyde signals could be detected in benzene. Strong polarized CIDNP signals assigned to products arising from a primary radical pair (i and ii in Figure 12) by electron back-transfer and other reactions were observed in methanol. However, no signals which

Table IV
α-Cleavage Rate Constants of the Photoinitiators 1a–1d

	compd			
	1a	**1b**	**1c**	**1d**
$10^{-8}k_\alpha$ (s^{-1})	10	25	2	0.005

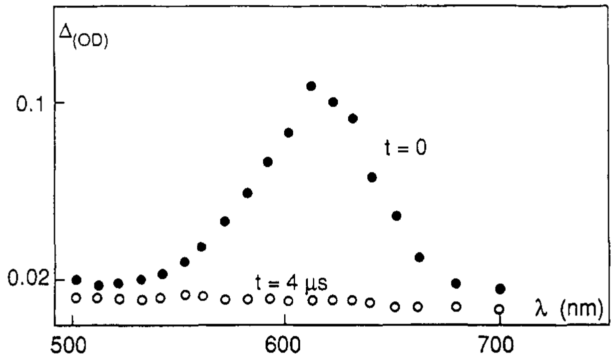
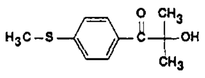


Figure 13. Transient absorption spectra of the triplet state and the residual ketyl species (formed by addition of 10^{-3} M methyldiethanolamine) of thioxanthone **3a** in methanol.

could be attributed to the formation of aldehydes were detected. These results are proof for the occurrence of electron transfer between compounds **12** or **13** and thioxanthones in benzene. Radical ions are formed in methanol; however, the radical cation ii does not undergo homolytic fragmentation of the carbonyl–C(α) bond to produce an alkanoyl radical.

Photofragmentation of **12** in the presence of 9,10-dicyanoanthracene was recently reported.[17] The amino radical cation ii (R = H) formed via electron transfer to the anthracene derivative undergoes a cleavage reaction which is assisted by the radical anion and gives rise to acetylated anthracene derivatives as reaction products. No evidence for unassisted fragmentation of ii was found, which is in agreement with the results presented here.

Initiator **1c** could also undergo an electron transfer from the sulfur lone pair to the thioxanthone. However, no evidence for this process was found in the CIDNP spectra. This is in agreement with the finding that addition of a thioxanthone to the corresponding α-hydroxy ketone **14**



14

(E_T = 63 kcal/mol) does not improve the reactivity in a white pigmented lacquer:[3] Energy transfer being excluded for this compound, electron transfer from the thiomethyl group is apparently not a significant process either.

Time-Resolved Laser Spectroscopy Experiments. Excited States of Photoinitiators 1a–1d. Laser excitation of photoinitiators **1a–1d** in toluene at λ = 355 nm generates the triplet states of these compounds, which subsequently undergo the Norrish type I reaction as demonstrated by CIDNP experiments. Rate constants of the α-cleavage reaction of these photoinitiators determined from time-resolved laser spectroscopy experiments are listed in Table IV.

Excited States of Thioxanthones. It is well-known that long-lived triplet states (lifetime in the microsecond range) are formed through light excitation of thioxanthones. This behavior is also found for thioxanthones **3a–3c**, as is shown by the triplet–triplet absorption spectra of **3a** in methanol (Figure 13).

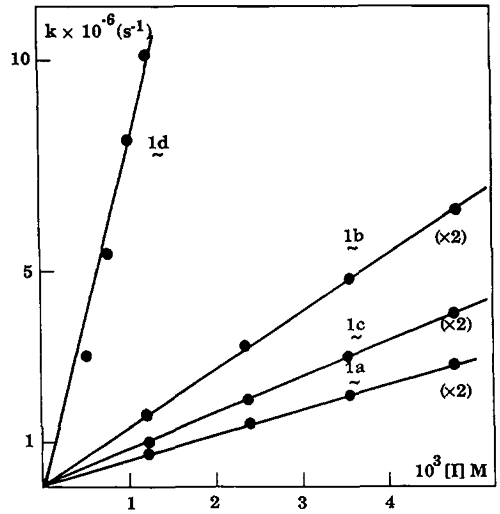


Figure 14. Stern–Volmer plots of the reciprocal value of the triplet-state lifetime of thioxanthone **3a** as a function of the photoinitiator concentration. Conditions: solvent, methanol; wavelength of detection, λ = 620 nm.

These long-lived triplet states are quenched by amines such as methyldiethanolamine (quenching rate constant in methanol: $k_q = 1.3 \times 10^9$ M^{-1} s^{-1}) and monomers such as methyl methacrylate ($k_q \approx 10^6$ M^{-1} s^{-1}). Ketyl species (radical or/and radical anion) are formed under these conditions, as was already observed for a series of thioxanthones in the presence of amines. Both the ketyl radical and the ketyl radical anion exhibit an absorption between 400 and 650 nm,[25,26] which is enhanced for the radical anion in the 600–650-nm range.

In the nonpolar solvent toluene, a ketyl radical is expected to be detectable, whereas in methanol, which stabilizes ionic species better, an ion pair may be preferentially formed. However, the weakness of the absorptions detected in these experiments (Figure 13) makes an unequivocal assignment of the ketyl species difficult.

Excitation-Transfer Experiments. Excitation transfer between thioxanthones and initiators **1a–1d** and **2** was followed by monitoring the decay of the thioxanthone triplet state T_1 (generated by direct excitation of the thioxanthones at λ = 430 nm) as a function of the concentration of unexcited initiators. The bimolecular rate constant k_T for this quenching reaction

$$T_1(\text{thioxanthone}) + S_0(\text{photoinitiator}) \xrightarrow{k_T} \text{excitation transfer} \quad (1)$$

is calculated from the usual Stern–Volmer plot (Figure 14):

$$k = k_0 + k_T[\text{photoinitiator}] \quad (2)$$

where k_0 and k are the decay rate constants of the triplet excited state of the thioxanthone in the absence and presence of the photoinitiator. The calculated k_T values obtained for different thioxanthone/initiator pairs in the solvents toluene and methanol are listed in Table V.

In some cases, the excitation transfer is accompanied by the formation of a ketyl radical on the thioxanthones that likely results from a charge-transfer interaction, as is shown for thioxanthone **3a** and the initiator **1d** in Figure 8.

The formation of an exciplex and the generation of a ketyl species, observed upon addition of an amine to thioxanthones, is solvent dependent (Table VI). With morpholine (IP = 8.91 eV, calculated for the nitrogen lone

Table V
Rate Constants (k_T) of Excitation Transfer between the Thioxanthones 3a–3c and the Photoinitiators 1a–1d and 2

thioxanthone	initiator	solvent[a]	ketyl species[b]	$10^{-6}k_T$ (M^{-1} s^{-1})
3a	**1a**	T	*c*	100
		M	yes, *d*	290
	1b	T	*c*	75
		M	yes, *d*	380
	1c	T	*c*	240
		M	yes, *d*	630
	1d	T	*c*	4700
		M	yes, *d*	7900
	2	T	*c*	<1
		M	*c*	<1
3b	**1c**	T	yes	12
		M	*c*	110
3c	**1c**	T	*c*	60
		M	*c*	55

[a] T = toluene; M = methanol. [b] Ketyl species means ketyl radical or/and ketyl anion radical. The complete recording of the absorption spectrum of these species (formed after excitation of thioxanthones at λ = 430 nm, in the presence of **1a**–**1d**) is difficult in the expected wavelength range of maximum absorption of ketyl species (420–460 nm). [c] "No" or not calculable. [d] Under conditions where only excitation transfer occurs, the yield of ketyl species with **1c** is at least 3 times lower than with **1a** or **1b** and 5 times lower than with **1d**.

Table VI
Rate Constants of Electron Transfer between Thioxanthones 3a–3c and Amines (in 10^8 M^{-1} s^{-1})

thioxanthone	amine[a]	toluene	methanol
3a	MMP	3.6	8.2
3b	MDEA	30	9
	MO	6.3	3.1
	MMP	1.5	4.3
3c	MDEA	6	1.4
	MO	12	1.1
	MMP	1	3.4

[a] MDEA, methyldiethanolamine; MO, morpholine; MMP, 2-methyl-2-morpholinopropane.

pair[27]), the rate constant decreases when toluene is replaced by methanol. An opposite trend is observed for 2-methyl-2-morpholinopropane, whose IP is presumably lower due to the *tert*-butyl substituent on the nitrogen atom, which induces a higher basicity of the lone pair.

A comparison of the ionization potentials of the oxygen and nitrogen lone pairs in morpholino derivatives (e.g. ionization potential of 1-morpholino-2-methylpropane, 9.61 and 8.46 eV, respectively[27]) suggests that in an electron-transfer process an electron is removed from the nitrogen atom. The same behavior can be expected for the initiator **1c**.

Addition of an acrylic monomer to thioxanthones leads also to the formation of an exciplex; however, no ketyl radicals are formed under these conditions.[28] The rate constant of this process decreases as a function of increasing solvent polarity. These findings are rationalized in terms of a solvent effect which renders the nature of the triplet state ($n\pi^*$ or $\pi\pi^*$) solvent dependent. This behavior, which is also observed with amines such as morpholine and methyldiethanolamine, but not with 2-methyl-2-morpholinopropane, has to be investigated in more detail.

Since 2-methyl-2-morpholinopropane is a better model of the morpholino moiety in photoinitiators **1a** and **1b** than morpholine, it is apparent that the increase of k_T with increasing solvent polarity (Table V) for the combination of sensitizer **3a** with initiators **1a** or **1b** can be explained on the basis of an electron-transfer process, which is more efficient in a polar solvent. The same is true for initiator **1d**, with the difference that electron transfer occurs with high efficiency from the aromatic amine and not from the morpholino moiety. Evidence for this process was obtained from CIDNP spectra (see section on sensitization experiments in methanol) and from the rate constant, in Table V, which is higher by 1 order of magnitude than those for compounds **1a**–**1c**.

A more complex situation is found for photoinitiator **1c**. Again electron transfer occurs from the morpholine nitrogen atom, which should show a behavior similar to that in 2-methyl-2-morpholinopropane.

In the pair thioxanthone **3a**/initiator **1c**, energy transfer is present in both solvents. If thioxanthone **3c** is used, the efficiency increase of the electron-transfer process upon replacing toluene by methanol is accompanied by a decrease in the efficiency of the energy-transfer process, which average to an insignificant change in the overall excitation-transfer efficiency. For the combination thioxanthone **3b** and initiator **1c** the situation is reversed. Energy transfer is weak in both solvents and electron transfer is more efficient in the polar solvent. The relative increase in overall efficiency is thus higher than for the other sensitizer/initiator pairs.

Excitation Transfer in Bulk Media. Industrial photopolymerization is carried out in formulations consisting mainly of monomers and oligomers. Under these conditions, the triplet-state lifetimes of the thioxanthones are expected to be shortened because of monomer quenching processes. Further, the rate constant for the bimolecular excitation-transfer process decreases according to the higher viscosity of the medium. Polarity effects may also significantly influence this process. Sensitization processes are thus expected to be less efficient in a photopolymerizable formulation than in solution.

Preliminary experiments using time-resolved laser spectroscopy have been carried out in bulk media. As a example, the triplet-state lifetime τ_0 of the thioxanthone **3a** was found to be still long (1.8 μs) in a 50/50 mixture of 1,6-hexanediol diacrylate (HDDA) and an epoxy acrylate in air. The rate constant k_T for excitation transfer to the photoinitiator **1c** in this medium was determined to be 22×10^6 M^{-1} s^{-1}, i.e. 1 order of magnitude lower than the rate constant for the same process in toluene (Table V). From these values, the efficiency Φ_T of the sensitization process can be calculated as

$$\Phi_T = \frac{k_T[\mathbf{1c}]}{1/\tau_0 + k_T[\mathbf{1c}]} \qquad (3)$$

For a photoinitiator concentration of 5×10^{-2} mol L^{-1}, the efficiency of this process is 0.66 in air. To the best of our knowledge, these data are the first determination of sensitization efficiency in a bulk medium which is similar to that encountered in a practical industrial application. The result confirms the high efficiency of excitation transfer between thioxanthones and the photoinitiator **1c** under these conditions and is in good agreement with the excellent curing efficiency measured for this photoinitiator/sensitizer pair in pigmented systems.

Further results on photochemical processes in highly viscous media will be presented in a forthcoming paper.

Conclusions

The results obtained by time-resolved CIDNP and laser spectroscopy can be summarized as follows.

(1) In an apolar medium such as benzene or toluene, energy transfer is an efficient process for the sensitizer/initiator pairs **3a**/**1c** and **3c**/**1c** but is of very low efficiency for **3b**/**1c**. Other sensitizer/initiator combinations do not

undergo efficient energy transfer, neither in a polar nor in an apolar solvent. The relative energies of the triplets of the thioxanthones **3a**–**3b** and the photoinitiators **1a**–**1d** are in good agreement with the order of magnitude of the rate constants for triplet energy transfer. The values are highest for the pair **3a**/**1c** and **3c**/**1c** where this process is exothermic, while energy transfer is inefficient for the other sensitizer/initiator pairs with unfavorable relative energies.

(2) In all solvents investigated efficient electron transfer occurs in the pairs **3a**/**1a**, **3a**/**1b**, and **3a**/**1d**. For initiator **1d** containing an aromatic amino moiety, the electron is transferred from the dimethylamino group (CIDNP evidence), thus explaining the high value of the rate constants for excitation transfer. The order of magnitude for this process is in good agreement with the rate constants observed for benzophenone/dimethylaniline in benzene ($k_{\mathrm{T}} = 2.7 \times 10^{9}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ [29]). The high ionization potential of anisole and propyl ether[30] and the rather low value of the rate of quenching of benzophenone by these ethers suggest that in compound **1b** the methoxy group is not involved in the electron-transfer step. This is also in agreement with the finding of similar yields of ketyl radical from initiators **1a** and **1b** and the occurrence of polarized signals of the morpholino protons in the CIDNP spectra of these compounds.

(3) The weak signals of spin-polarized aldehydes detected in methanol upon sensitization of initiators **1a**, **1b**, and **1c** (CIDNP evidence) are best explained by the existence of two competitive processes occurring from the excited triplet-state sensitizer. Both electron transfer and energy transfer occur, the latter being of little importance for compounds **1a**, **1b**, and **1d**. These results also rule out significant α-cleavage of these photoinitiators via an electron-transfer process. The energy-transfer channel engenders α-cleavage products, while other products are obtained via electron transfer.

(4) The striking effect on reactivity of thioxanthone addition to pigmented UV-curable formulations containing these initiators stems to a good part from energy transfer,[3] if initiator **1c** is used, and from electron transfer with the other initiators. This interpretation is also in agreement with findings on α-hydroxy ketones of analogous structure:[3] 2-hydroxy-1-(4-methoxyphenyl)-2-methylpropan-1-one and 2-hydroxy-1-[(4-methylthio)phenyl]-2-methylpropan-1-one (14) do not give a significant improvement of curing efficiency by addition of thioxanthones, while 2-hydroxy-1-[(4-dimethylamino)phenyl]-2-methylpropan-1-one does. All three α-hydroxy ketones have triplet energies which are too high to allow energy transfer; the *p*-amino-substituted compound, however, can undergo electron transfer from the nitrogen atom.

Acknowledgment. We acknowledge Dr. G. Wermuth for stimulating discussions on mechanistical aspects of this work. G.R. acknowledges very helpful discussions with Prof. H. Fischer, University of Zurich.

References and Notes

(1) Meier, K.; Rembold, M.; Rutsch, W.; Sitek, F. In *Radiation Curing of Polymers*; Randell, D. R., Ed.; Special Publication No. 64, Royal Society of Chemistry: London 1987; p 196.

(2) Rutsch, W.; Berner, G.; Kirchmayr, R.; Hüsler, R.; Rist, G.; Bühler, N. In *Organic Coatings—Science and Technology*; Parfitt, G. D., Patsis, A. V., Eds.; Marcel Dekker Inc.: New York, 1986; Vol. 8, p 175.

(3) Dietliker, K.; Rembold, M.; Rist, G.; Rutsch, W.; Sitek, F. *Radcure Europe 87*, Proceedings of the 3rd Conference Association of Finishing Processes SME: Dearborn, MI, 1987.

(4) 2-Methyl-1-[4-(methylthio)phenyl]-2-morpholinopropan-1-one is a commercial product of Ciba-Geigy, called Irgacure 907.

(5) 1-Hydroxycyclohexyl phenyl ketone is a commercial product of Ciba-Geigy, called Irgacure 184.

(6) Fouassier, J. P.; Burr, D. *Eur. Polym. J.* **1991**, *27*, 657.

(7) Kaptein, R. *J. Chem. Soc., Chem. Commun.* **1971**, *732*. Kaptein, R. *J. Am. Chem. Soc.* **1972**, *94*, 6251.

(8) Lamola, A. A.; Roth, H. D. *J. Am. Chem. Soc.* **1974**, *96*, 6270.

(9) Hageman, H. J. In *Photopolymerisation and Photoimaging Science and Technology*; Allen, N. S., Ed.; Elsevier Applied Science: London 1989; p 1.

(10) Lee, L. Y. C.; Ci, X.; Giannotti, C.; Whitten, D. G. *J. Am. Chem. Soc.* **1986**, *108*, 175.

(11) Felder, L.; Kirchmayr, R.; Hüsler, R. Eur. Pat. Appl. 3002 (Prior. 22.12.1977) to Ciba-Geigy AG, 1977.

(12) Kvita, V.; Zweifel, H.; Roth, M.; Felder, L. Ger. Offen. DE 3018891 (Prior. 18.5.1979) to Ciba-Geigy AG, 1979.

(13) A mixture of 2- and 4-isopropylthioxanthone is a commercial product of IBIS International Bio-Synthetics, called Quantacure ITX.

(14) Fouassier, J. P.; Lougnot, D. J.; Paverne, A.; Wider, F. *Chem. Phys. Lett.* **1987**, *135* (1), 30.

(15) Closs, G. L.; Miller, R. J. *J. Am. Chem. Soc.* **1981**, *103*, 3586.

(16) Kaptein, R. In *Chemically Induced Magnetic Polarization*; Muus, L. T.; Atkins, P. W., McLauchlan, K. A., Pedersen, K. B., Eds.; Nato Advanced Study Institutes Series; M. Reidel Publishing Co.: Dordrecht, The Netherlands, 1977; p 1.

(17) Bergmark, W. R.; Whitten, D. G. *J. Am. Chem. Soc.* **1990**, *112*, 4042.

(18) Phan, X. T. *J. Radiat. Curing* **1980**, *13* (1), 11.

(19) Janzen, E. G.; Du Bose jun, C. M. *J. Phys. Chem.* **1966**, *70*, 3372.

(20) Colonna, F. P.; Distefano, G.; Pignataro, S.; Pittaco, G.; Valentin, E. *J. Chem. Soc., Farad. Trans. 2* **1975**, *71*, 1572.

(21) Lamola, A. A. *Photochem. Photobiol.* **1968**, *8*, 601.

(22) Hyatt, J. A. *J. Org. Chem.* **1972**, *37*, 1254.

(23) Ci, X.; Lee, L. V. C.; Whitten, D. G. *J. Am. Chem. Soc.* **1987**, *109*, 2536.

(24) Ci, X.; Whitten, D. G. *J. Am. Chem. Soc.* **1987**, *109*, 7215.

(25) Yates, S. F.; Schuster, G. B. *J. Org. Chem.* **1984**, *49*, 3349.

(26) Matteo, J. L.; Allen, N. S. *J. Photochem.* **1989**, *50*, 249.

(27) Colonna, F. P.; Distefano, G.; Pignataro, S.; Pittaco, G.; Valentin, E. *J. Chem. Soc., Farad. Trans. 2* **1975**, *71*, 1572.

(28) Fouassier, J. P.; Jacques, P.; Encinas, M. V. *Chem. Phys. Lett.* **1988**, *148*, 99.

(29) Guttenplan, J. B.; Cohen, S. G. *J. Am. Chem. Soc.* **1972**, *94*, 4040.

(30) Jacques, P. *Chem. Phys. Lett.* **1987**, *142* (1), 96.

Registry No. **1a**, 71867-90-8; **1b**, 93216-90-1; **1c**, 71868-10-5; **1d**, 97459-03-5; **3a**, 77084-33-4; **3b**, 77084-51-6; **3c**, 5495-84-1.