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Photochemistry and Photophysics of α-Hydroxy Ketones

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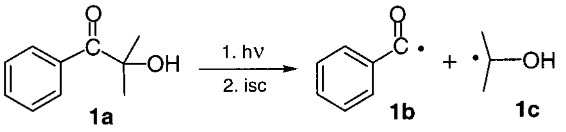
ABSTRACT: Time-resolved laser flash spectroscopy with transient detection by time-resolved UV−vis, IR, and EPR has been employed to investigate the photochemistry and photophysics of a series of derivatives of 2-hydroxy-2-methyl-1-phenyl propanone, a model photoinitiator for free radical polymerization. H, Cl, and F substituents at the para position promote the n,π^* nature of the lowest triplet state and favor fast and efficient α-cleavage from T_1 upon irradiation. In contrast, dimethylamino and thioether substitution in the para position of the benzoyl moiety change the configuration of the lowest triplet states into a π,π^* and are characterized by a lack of α-cleavage from T_1. Alkoxy substitution in the para position represents an intermediate for which α-cleavage occurs efficiently, but at a relatively slow rate. Alkylation of the 2-hydroxy group promotes fast α-cleavage upon irradiation (picosecond time scale), in contrast to the analogous ester derivative for which slow cleavage was observed (microsecond time scale). The conclusions are consistent with phosphorescence characterization of the triplet states and are supported by photopolymerization studies.

Introduction

2-Hydroxy-2-methyl-1-phenyl propanone (**1a**) and its derivatives have been widely used as photoinitiators for free radical polymerization.[1−5] Upon irradiation, **1a** undergoes classical type I cleavage to produce a benzoyl−ketyl radical pair (**1b**, **1c**) with a high rate constant and good efficiency (eq 1).[6,7] The radicals separate and add to monomer to initiate polymerization.



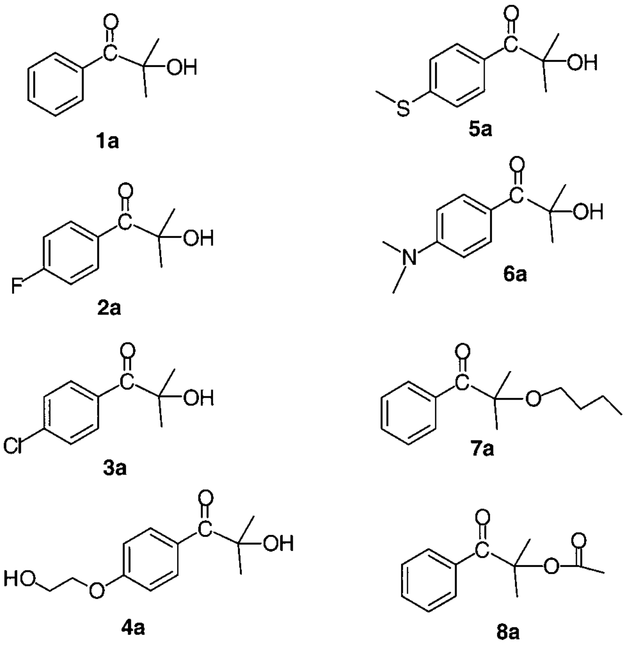
(1)

For photocuring of pigmented coatings, a high molar absorptivity in the 300−400 nm region of the photoinitiator is desired. Unfortunately, **1a** has relatively low absorption above 300 nm ($\epsilon^{300\mathrm{nm}} = 67$ L mol^{-1} cm^{-1}; acetonitrile solution). A bathochromic shifted absorption of **1a** can be achieved through modification of **1a** with different substituents (Scheme 1). However, substituents can also change the photochemistry of α-hydroxy ketones. To be successful as photoinitiators, derivatives of **1a** must undergo rapid and efficient α-cleavage (eq 1). Some of the compounds shown in Scheme 1 have been investigated by laser flash photolysis employing UV−vis.[6−10] In this paper we describe a systematic study of the influence of substituents on the photochemistry and photophysics of derivatives of **1a** employing time-resolved laser spectroscopy with transient detection by UV−vis, IR, EPR spectroscopy, and phosphorescence spectroscopy.

Experimental Section

The α-hydroxy ketones (**1a**−**6a**) (Ciba Specialty Chemicals) were used as received. Their purities were checked by GC-MS (>95%). Acetonitrile, ethanol, and methylcyclohexane (Aldrich spectrophotometric grade) were used as received.

Scheme 1. Structures of α-Hydroxy Ketones (1a−6a), Ether (7a), and Ester Derivative (8a) Investigated in This Report



The butyl ether derivative **7a** was prepared from the parent α-hydroxyl ketone **1a** using the alkylation protocol.[11] The α-hydroxy ketone **1a** (10 g, 61 mmol) and butyl bromide (16.7 g, 121 mmol) were added sequentially to a stirred solution of powdered KOH (13.5 g) in 120 mL of anhydrous DMSO. The reaction was stirred for 25 min and poured into water (250 mL). The organic material was extracted with dichloromethane (3 × 400 mL). The combined organic extracts were dried over $MgSO_4$ and concentrated on a rotary evaporator. The butyl ether was purified via chromatography on silica (9:1 hexanes: ethyl acetate) to yield 3.2 g (14.5 mmol) of a slightly yellow oil (24% yield). The structure and purity (>99%) of the product (**7a**) were determined by ^1H NMR and GC-MS analysis. ^1H NMR (300 MHz, $CDCl_3$): δ 8.29 (2H, m), 7.54 (1H, m), 7.44

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(2H, m), 3.28 (2H, t, $J = 6.7$ Hz), 1.52 (6H, s), 1.46 (2H, m), 1.27 (2H, m), 0.82 (3H, t, $J = 7.3$ Hz).

The ester derivative (**8a**) was synthesized by esterification of **1a** (0.02 mol) with acetyl chloride (0.03 mol) in the presence of pyridine (0.02 mol) in 20 mL of cyclohexane for 3 days at 60 °C. Unreacted acetyl chloride was hydrolyzed in water in the presence of $NaHCO_3$. Derivative **8a** was extracted with CH_2Cl_2, washed with water, dried ($CaCl_2$), and recrystallized from hexane, ethanol, and again hexane (yield: 50%). The structure and purity (>99%) was determined by ^1H NMR and GC-MS. ^1H NMR (300 MHz, $CDCl_3$): δ 8.02 (2H, m), 7.51 (1H, m), 7.42 (2H, m), 1.93 (3H, s), 1.72 (6H, s).

Product studies after laser irradiation (266 nm, 4 mJ/pulse, 5 ns, Spectra Physics GCR-150-30 Nd:YAG laser) in Suprasil quartz cells were carried out using a GC-MS (Hewlett-Packard 5890 system with 5972 mass detector). Products were identified by comparison of retention time and fragmentation pattern with authentic samples.

Low-temperature phosphorescence spectra were recorded on a Fluorolog 1680 0.22 m double spectrometer (SPEX) using a liquid nitrogen dewar for measurements at 77 K. Time-resolved phosphorescence measurements were performed by multichannel scaling on a OB900 fluorometer (Edinburgh Analytical Instruments) using a pulsed xenon lamp (μF 900, Edinburgh Analytical Instruments) as excitation source.

Laser flash photolysis experiments (time-resolved UV spectroscopy) employed the pulses from a Spectra Physics GCR-150-30 Nd:YAG laser (266 or 355 nm, ca. 8 mJ/pulse, 5 ns) or from a Lambda Physik Lextra 50 excimer laser (308 nm, ca. 8 mJ/pulse, 20 ns) and a computer-controlled system that has been described elsewhere.[12] Solutions of the photoinitiators were prepared at concentrations such that the absorbance was ~0.3 at the excitation wavelength employed. Transient absorption spectra were recorded employing a Suprasil quartz flow cell (1 × 1 cm) to ensure that a fresh volume of sample was irradiated by each laser pulse. Quenching rate constants were measured using argon-saturated static samples contained in 1 × 1 cm Suprasil quartz cells. Fresh solutions were prepared at each quencher concentration.

Time-resolved EPR experiments employed the pulses (308 nm, ca. 10 mJ/pulse, 20 ns) from a Lambda Physik Lextra 50 excimer laser, a Bruker ER 100D X-band EPR spectrometer, and a PAR boxcar averager and signal processor (models 4420 and 4402). Argon-saturated solutions were flowed through a quartz flow cell (~0.3 mm thick) in the rectangular cavity of the EPR spectrometer. Further details are described elsewhere.[13,14]

Time-resolved IR experiments employed the pulses (266 nm, ca. 4 mJ/pulse, 5 ns) from a Spectra Physics GCR-150-30 Nd: YAG laser as excitation source. The IR probe consisted of a Mütek MDS 1150/2 diode laser fitted with a Mütek MDS 1400S monochromator and sample chamber with a Kolmar Technologies HgCdTe photodiode (KMPV11-1-J1). The signal from the photodiode was amplified using a SR 560 low noise preamplifier (Stanford Research Systems) and digitized with a TDS 360 storage oscilloscope (Tektronix). Argon-saturated acetonitrile solutions were flowed continuously through a 1 mm path length gastight IR cell fitted with calcium fluoride windows. For each decay trace the IR signals of approximately 1000 laser pulses were averaged.

The photolysis quantum yields of the ketones **1a**−**6a** were determined by observation of the ground-state bleaching in air-saturated acetonitrile solutions employing a SPEX Fluorolog 2 spectrophotometer equipped with internal silicon photodiode reference. Solutions (2 mL) in 1 × 1 cm cells were stirred during irradiation, and the change in ground state absorbance was determined by UV spectroscopy. To determine the absolute photon flux, a spectrally calibrated 2 × 1 cm flat silicon photodiode was placed into the sample chamber.

Results

Phosphorescence Spectroscopy. At low temperatures (77 K) in an ethanol glass, all of the ketones **1a**−**8a** exhibit strong phosphorescence with a degree of vibrational fine structure (Figure 1). A clear vibrational progression of the phosphorescence is observed for ketones **1a**−**4a**, **7a**, and **8a** (1600−1700 cm^{-1}), which is typical for a C=O ground-state vibration. However, in the case of ketones **5a** and **6a** the vibrational fine structure is less pronounced. From the (0,0) emission bands, the triplet energies of the ketones were determined and are summarized in Table 1. The phosphorescence quantum yields at 77 K for ketones **1a**−**8a**, estimated by comparison to the phosphorescence quantum yield of benzophenone, are at least 0.1 or higher. The lifetimes of the phosphorescence in ethanol glass at 77 K were determined by multichannel scaling using a pulsed Xe lamp for excitation and are also summarized in Table 1.

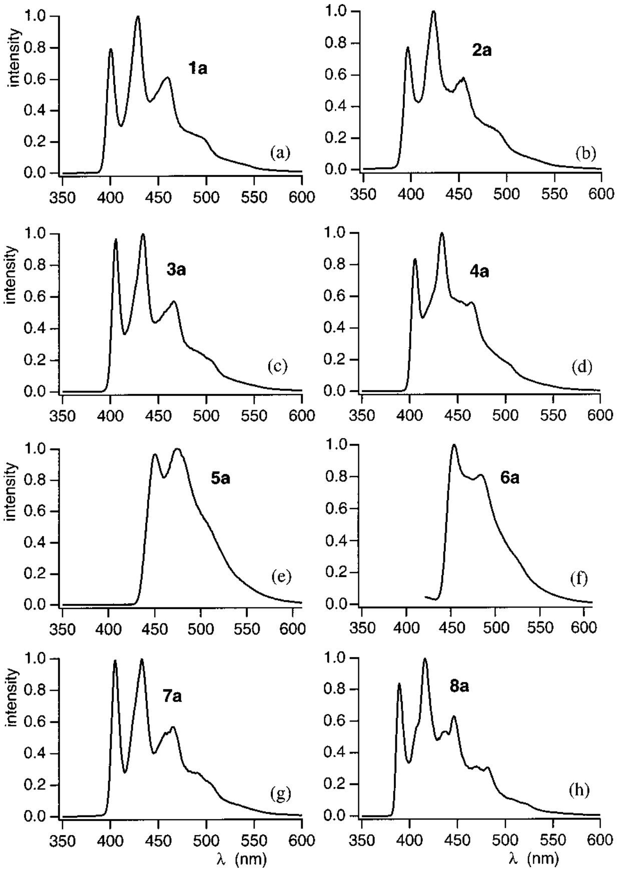
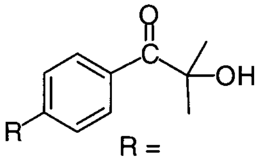
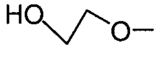
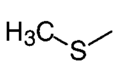
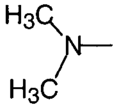
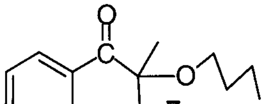
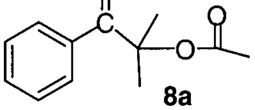


Figure 1. Phosphorescence emission spectra of **1a**−**8a** in ethanol glass at 77 K. $\lambda_{ex} = 320$ nm (**1a**−**4a**, **7a**, **8a**), $\lambda_{ex} = 330$ nm (**5a**); $\lambda_{ex} = 340$ nm (**6a**).

Time-Resolved UV Spectroscopy. Laser flash photolysis (355 nm excitation) of argon-saturated acetonitrile solutions of ketones **4a**−**6a** afford readily detectable transient absorption spectra (Figure 2), which decay by first-order kinetics ($\tau_{4a} = 11$ ns, $\tau_{5a} = 7$ μs, and $\tau_{6a} = 12$ μs). These transients were assigned to the triplet states of **4a**, **5a**, and **6a**, respectively, since signals were efficiently quenched by naphthalene (E_T = 255 kJ/mol[15]), and the grow-in of the naphthalene triplets at 412 nm,[16] produced by energy transfer from the ketone triplets, was observed. These results provide strong evidence for the triplet nature of the observed transients.

In the case of ketones **1a**−**3a** laser flash photolysis did not produce detectable triplet−triplet absorption

Table 1. Photophysical Properties of α-Hydroxy Ketone Derivatives

 R =		λ_{max}^{S-S} (a) (nm)	λ_{max}^{T-T} (b) (nm)	τ_T (c) 23 °C (ns)	τ_P (f) 77 K (ms)	E^T (g) (kJ / mol)	triplet nature	Φ_α (h)
H—	**1a**	243	320(m)	0.37(d)	3.7	299	nπ*	0.38(i)
F—	**2a**	245	—	0.86(d)	4.0	301	nπ*	0.67(i)
Cl—	**3a**	251	—	1.0(d)	7.3	295	nπ*	0.60(i)
	**4a**	273	390	11(e) 13(d)	57	295	nπ*/ ππ*	0.29(i)
	**5a**	302	460	7,000(e)	110	266	ππ*	0.01(i)
	**6a**	335	460	12,000(e)	520	264	ππ*	0.03(i)
	**7a**	245	—	0.31(d)	2.4	295	nπ*	0.33(k)
	**8a**	242	335	3,000(e)	22	307	nπ*	0.05(k)

[a] λ_{max}^{S-S}: optical absorption maximum of the π,π^* transition in acetonitrile. [b] λ_{max}^{T-T}: triplet–triplet absorption maximum in acetonitrile. [c] τ_T: triplet lifetime in acetonitrile at 23 °C. [d] Determined from naphthalene quenching experiments. [e] Determined from transient absorption decay kinetics. [f] τ_T: phosphorescence lifetime in ethanol glass at 77 K. [g] E^T: triplet energy in ethanol glass at 77 K. [h] Φ_α: quantum yield of α-cleavage. [i] Determined by ground-state bleaching (ref 36). [k] Determined from GC analysis (ref 37). [m] From ref 8.

spectra. The rate constant for the cleavage of triplet **1a** in toluene has been reported to be $k_\alpha = 7.14 \times 10^8$ s^{-1}.[8] Thus, the ketones **1a**–**3a** undergo α-cleavage to produce benzoyl (**1b**–**3b**) and dimethylketyl radicals (**1c**–**3c**) (eq 1) within a time scale of the laser pulse. Very weak transient absorption was detectable below 380 nm probably caused by the benzoyl (**1b**–**3b**) and dimethylketyl radicals (**1c**–**3c**), which were formed within the laser pulse by the α-cleavage **1a**–**3a** (eq 1). These radicals possess low extinction coefficients at wavelengths higher than 300 nm.[6,17,18]

Since the triplets of **1a**–**3a** possess shorter lifetimes than our instrument response, we determined the triplet lifetimes by employing an indirect method of triplet quenching. Naphthalene should quench the triplets of **1a**–**3a** efficiently, since its triplet energy is lower than the triplet energies of ketones **1a**–**3a** (see Table 1). Argon-saturated acetonitrile solutions of **1a**, **2a**, and **3a** were irradiated with laser pulses (355 nm) in the presence of different concentrations of naphthalene. The triplet–triplet absorption of naphthalene at 412 nm[16] was formed within the laser pulse. Since naphthalene does not absorb at 355 nm, it was concluded that the ketone triplets are initially generated and then are subsequently quenched by energy transfer to naphthalene in competition with α-cleavage. With increasing concentrations of naphthalene, a corresponding increase in the amount of naphthalene triplets was observed. The Stern–Volmer constant $k_q\tau_T$ was determined by application of the experimental data to a Hammond plot (1/A vs 1/[Q]; eq 2) shown in Figure 3.[19–21] In eq 2, A is the absorbance of naphthalene triplets observed at the end of the laser flash at 412 nm (which is proportional to the quantum yield for its formation), A_L is the limiting absorbance that would be observed if all triplets of **1a**–**3a** were quenched by naphthalene, τ_T are the triplet lifetimes of **1a**–**3a**, k_q is the rate constant for its quenching by naphthalene, and [Q] is the concentration

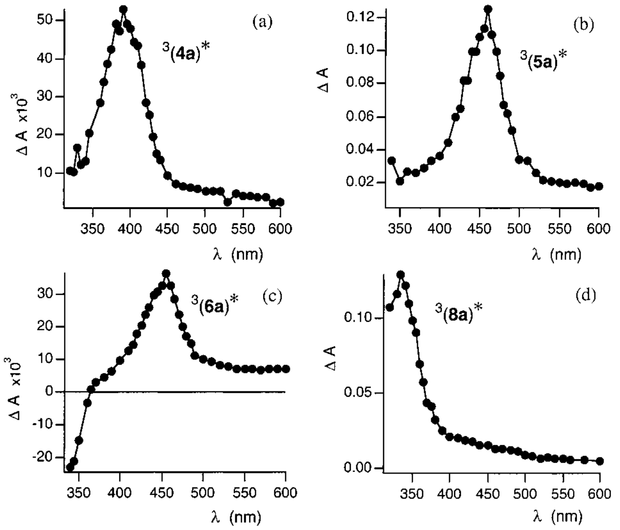


Figure 2. Transient optical absorption spectra recorded 0−8 ns (a), 0.1−1.1 μs (b, d), and 0.1−1.6 μs (c) following laser excitation (355 nm (a−c); 308 nm (d)) of argon-saturated acetonitrile solutions containing **4a**, **5a**, **6a,** or **8a** at 23 °C.

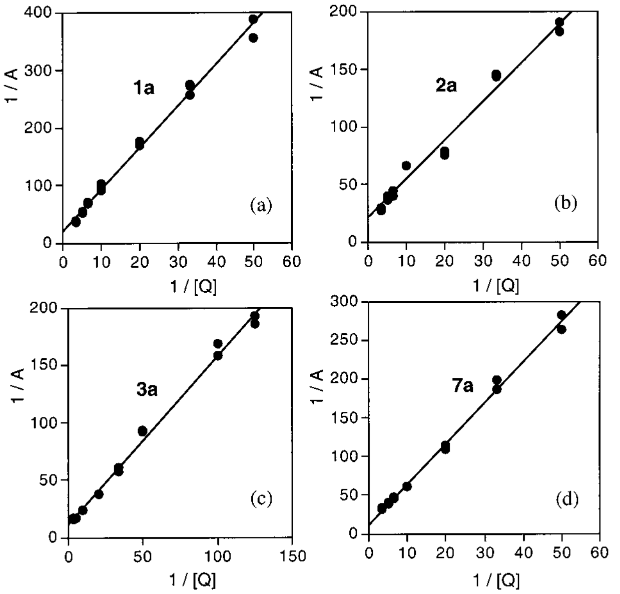


Figure 3. Plots of reciprocal absorbance at 412 nm vs reciprocal naphththalene concentration according to eq 2. Laser flash photolysis of argon-saturated acetonitrile solutions (355 nm excitation) of **1a**−**3a** and **7a** in the presence of different concentrations of naphthalene at 23 °C.

of naphthalene.

$$\frac{1}{A} = \frac{1}{A_L} + \frac{1/\tau_T}{A_L k_q[Q]} \qquad (2)$$

$$k_{obs} = k_0 + k_q[Q] \qquad (3)$$

The value for k_q applied to eq 3 is crucial for the accurate determination of the triplet lifetime. The rate constant for naphthalene quenching was determined for triplets of **5a** by pseudo-first-order treatment of the decay of the triplet absorption at 460 nm according to eq 3, where k_{obs} represents the observed pseudo-first-order rate constant at various concentrations of naphthalene and k_0 the first-order rate constant for the decay of the triplet of **5a** in the absence of added quencher. As is expected for triplet energy transfer, a rate constant k_q for **5a** close to the diffusion limit was observed (k_q = 7.4 × 10^9 M^{-1} s^{-1}). Assuming that the quenching rate constants for the triplets of the ketones **1a**−**4a** by naphthalene are similar, this value for k_q was used to obtain estimates for the lifetimes of the triplet excited states for **1a**−**3a**, which are summarized in Table 1.

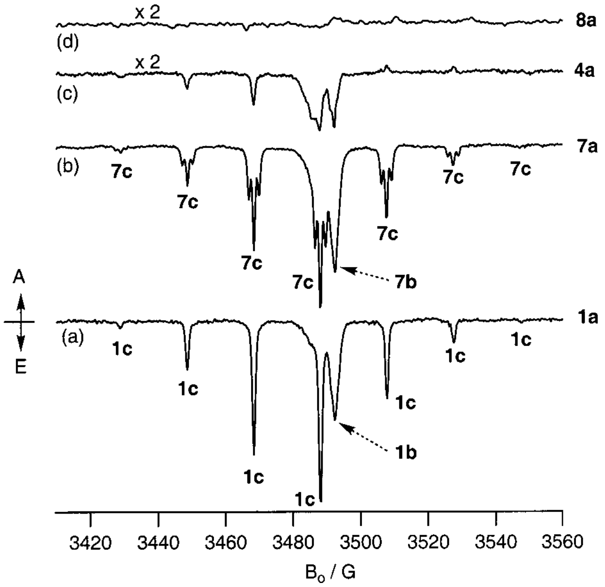


Figure 4. TR-EPR spectra recorded 300−600 ns following laser excitation (308 nm) of **1a**, **4a**, **7a**, and **8a** in argon-saturated acetonitrile solutions at 23 °C. Spectra c and d are amplified by a factor of 2.

To confirm the validity of this indirect method for the determination of short-lived triplet states, the triplet lifetime of **4a** was determined in two ways: directly from the triplet decay kinetic (τ_{4a} = 11 ns) and indirectly by naphthalene quenching (τ_{4a} = 13 ns). Both values are considered to be identical within experimental error.

In the case of the ether derivative **7a**, no triplet−triplet transient absorption was observed after laser flash photolysis of argon-saturated acetonitrile solutions of **7a**. Similar to the hydroxy ketones **1a**−**3a,** α-cleavage from the triplet state occurs within the laser flash. The triplet lifetime was determined by the naphthalene quenching method used for ketones **1a**−**3a** (see above) and is approximately 310 ps (Figure 3d).

Laser flash photolysis (308 nm excitation) of acetonitrile solutions of the ester derivative **8a** affords a readily detectable transient absorption spectrum (see Figure 2d), which decays obeying first-order kinetics (τ_{8a} = 3 μs). This transient was quenched by oxygen (k_{O_2} = 1.3 × 10^9 M^{-1} s^{-1}) and naphthalene (k_q = 7 × 10^9 M^{-1} s^{-1}). In addition, the grow-in of the naphthalene triplet at 412 nm was observed in naphthalene quenching experiments. Therefore, we concluded that this transient corresponds to the triplet state of **8a** and that α-cleavage is slow or negligible for triplets of **8a**.

Time-Resolved EPR Spectroscopy. Time-resolved electron paramagnetic resonance (TR-EPR) provides a direct method to investigate the radicals produced by α-cleavage of a triplet ketone if the radicals are produced with electron spin polarization.[22,23] Laser flash photolysis (308 nm excitation) of argon-saturated acetonitrile solutions of **7a** affords TR-EPR spectra shown in Figure 4b. The spectra display emissive septets of triplets centered near $g = 2$ due to the dimethyl butoxymethyl radical (**7c**) ($a_H(C_\beta H_3)$ = 19.6 G, $a_H(C_\gamma H_2)$ = 1.5 G). The radicals **7b** and **7c** are emissive

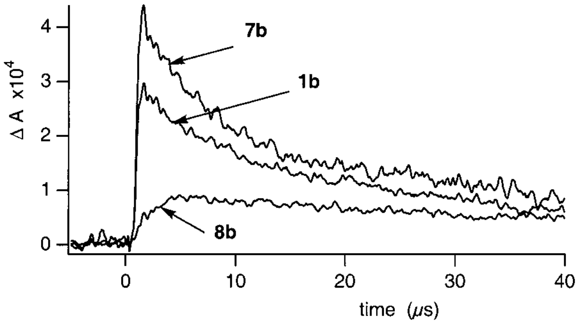


Figure 5. Transient IR absorption kinetics observed at 1826 cm^{-1} following laser excitation (266 nm) of **1a**, **7a**, and **8a** in argon-saturated acetonitrile solutions at 23 °C.

spin-polarized, as expected for spin-polarization by the triplet mechanism of electron polarization,[23] consistent with a rapid α-cleavage from the triplet state of **7a**. The overall emissive signal is distorted by a small emission/absorption radical pair mechanism polarization, which is typical for radicals produced from triplet state precursors. In addition, a broad emissive line near $g = 2$ assigned to the benzoyl radical (**7b**) was observed. In comparison, the TR-EPR spectrum for **1a** is also shown (Figure 4a) and is in good agreement with previously published spectra.[24] The dimethyl ketyl radical (**1c**) showed a typical splitting into a septet of emissive lines ($a_H(C_\beta H_3) = 19.7$ G).

TR-EPR experiments involving **4a** under the same conditions as that for **1a** and **7a** (same absorbance at 308 nm) yielded in a weak polarized EPR spectrum of the radicals **4b** and **4c** (Figure 4c). The low field lines of **4c** are emissive spin polarized and the high field lines are weakly absorptive polarized, indicating that the spectrum has significant contribution from the radical pair mechanism for electron polarization. However, a contribution from the triplet mechanism for spin-polarization is evident due to the increased intensity of the emissive low field lines of **4c** compared to the high field lines. The significant contribution of the radical pair mechanism together with the weaker spin-polarization compared to TR-EPR experiments involving **1a** and **7a** is consistent with a slower α-cleavage of **4a** compared to **1a** and **7a**.

Laser irradiation (308 nm excitation) of the ester derivative **8a** under the same experimental conditions as those for **1a**, **4a**, and **7a** (same absorbance at 308 nm) yielded a very weak TR-EPR spectrum, which is emissive/absorptive polarized probably derived from the radicals **8b** and **8c** (Figure 4d). The hyperfine splitting for **8c** ($a_H(C_\beta H_3) \approx 22$ G) is slightly larger than in the case of the dimethyl ketyl radical **1c**. The weak polarized signal suggests that α-cleavage of **8a** is slow and/or inefficient.

Time-Resolved Infrared Spectroscopy. Laser flash photolysis (266 nm excitation) of argon-saturated acetonitrile solutions of **1a** affords readily detectable transient IR absorption monitored at 1826 cm^{-1}. The signal is formed within the response time of our TR-IR detection system (50 ns) and decayed in the microsecond time scale with mixed first- and second-order kinetics (Figure 5). This transient has been assigned to the benzoyl radical **1b**.[25,26] Consistent with the results from time-resolved UV spectroscopy and time-resolved EPR, benzoyl radicals **7b** were also detected by time-resolved IR spectroscopy after laser flash photolysis of **7a**, which shows decay kinetics similar to **1b** (Figure 5).

The *p*-methoxy benzoyl radical possesses an IR absorption at 1813 cm^{-1}.[25] Laser irradiation ($\lambda_{ex} = 355$ nm) of **4a** in acetonitrile solution produced an IR absorption at 1813 cm^{-1}, which was correlated to the alkoxy-substituted benzoyl radical **4b**. The signal is formed within the response time of our TR–IR detection system (50 ns), which is consistent with the triplet lifetime of ^{3}**4a*** ($\tau = 11$ ns). The transient decayed in the microsecond time scale with mixed first- and second-order kinetics (results not shown).

In contrast to the TR-IR experiments using **1a**, **4a**, and **7a**, where transient formation at 1826 cm^{-1} due to **1b**, **4b**, and **7b** was observed (within our instrument response time), the transient IR absorption at 1826 cm^{-1} rises within 4 μs of observed after laser irradiation of **8a** (Figure 5). The slow rise is consistent with a slow α-cleavage of **8a** from the triplet state to form the benzoyl radical **8b**. Time-resolved UV spectroscopy showed a triplet lifetime of 3 μs (Table 1).

Discussion

Photolysis of α-hydroxy ketone **1a** gives a high yield of reactive radicals upon α-cleavage.[6–8,27,28] Introduction of substituents into the benzoyl moiety (**2a**–**6a**) shifts the optical absorption (π,π* transition) bathochromically into spectral regions that are more attractive for their applications as photoinitiators of radical polymerization (see $\lambda_{max}^{S-S}(\pi,\pi^*)$, Table 1). The biggest bathochromic shift is achieved by the dimethylamino group (**6a**). However, these substituents also change the photochemistry.

In general, α-cleavage is the major photochemical process occurring from the triplet state of the ketones investigated. The lifetime of the triplet state (τ_T) is limited by the sum of processes for its decay, which are shown in eq 4, where k_p is the rate constant of phosphorescence, k_d is the rate constant of thermal deactivation into the singlet ground state, and k_α is the rate constant of α-cleavage.

$$\tau_T = \frac{1}{k_p + k_d + k_\alpha} \tag{4}$$

The triplet lifetimes at room temperature for the hydroxy ketones **1a**–**3a** are between 0.3 and 1.0 ns and are determined by the high rate constant for α-cleavage. For these ketones, the phosphorescence lifetime at 77 K are on the order of several milliseconds (Table 1). These results, together with the relative high phosphorescence quantum yields and the typical vibrational structure of ca. 1700 cm^{-1}, allow assignment of a n,π* nature of the lowest triplet states of **1a**–**3a**.[29,30]

In the case of the thioether (**5a**) and dimethylamino (**6a**) substituted hydroxy ketones, the triplet–triplet absorption maximum is shifted bathochromically by approximately 140 nm compared to the unsubstituted compound **1a**. In addition, the phosphorescence lifetime at 77 K for **5a** and **6a** increased to 110 and 520 ms, respectively. This suggests a dominant π,π* nature of the lowest triplet states of **5a** and **6a**. Furthermore, the vibrational structure of the phosphorescence spectrum of **5a** and **6a** at 77 K in ethanol glass is blurred compared to the phosphorescence of ketones with greater n,π* nature (Figure 1). Broadening and loss of fine structure in phosphorescence spectra are commonly observed for π,π* triplets.[29–31] The triplet lifetimes of **5a** and **6a** at room temperature increased significantly

(7 and 12 μs, respectively) compared to **1a** (0.37 ns). The absence of radicals resulting from α-cleavage from the irradiation of **5a** and **6a** indicates that triplet decay is dominated by k_d (eq 4). In addition, the bleaching quantum yields are low (Table 1). We, therefore, conclude that amino and thioether substituted α-hydroxy ketones possess π,π^* state triplets and do not cleave efficiently.

Our findings were also supported by photopolymerization studies.[5] The initiation efficiency of **1a**, **4a**, **5a**, and **6a** for radical polymerization of acrylate monomers was investigated by photodifferential scanning calorimetry. Irradiation of **1a** and **4a** in the presence of acrylates produced much higher polymerization yields than initiation with **5a** and **6a**.[5]

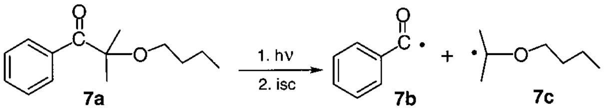
The nature of the lowest triplet state of the alkoxy derivative **4a** appears to be an interesting intermediate case based on the following evidence. A triplet−triplet absorption maximum, which is between that found for the ketones of n,π^* triplet nature (**1a**) and π,π^* triplet nature (**5a** and **6a**), was observed (see Table 1). Also, the phosphorescence lifetime at 77 K is of intermediate value. However, **4a** undergoes efficient α-cleavage with a good quantum yield ($\Phi_\alpha = 0.38$). The triplet lifetime of 11 ns of **4a** suggests that the rate constant for α-cleavage is approximately 1 order of magnitude smaller than for the ketones which possess pure n,π^* nature of the lowest triplet state (**1a**−**3a**) but is still fast enough to compete effectively with other modes of deactivation.

The relatively slow α-cleavage of **4a** is also consistent with its weak TR-EPR spectrum (Figure 4c). In contrast, TR-EPR experiments of **1a** showed strongly emissive spin-polarized radicals **1b** and **1c**, as expected by the triplet mechanism for electron spin polarization.[23] Spin-polarized triplet states, produced by triplet sublevel selective intersystem crossing, can transfer their polarization to the resulting radicals if α-cleavage occurs within the spin−lattice relaxation-lifetime of the triplet states, which is typically of the order of a nanosecond.[32] Since the rate of α-cleavage of **1a** is faster (picosecond time scale) than the rate of spin−lattice relaxation of the triplet states, the triplet mechanism is very effective in generating spin-polarized radicals. In contrast, the triplet lifetime of **4a** (11 ns) is longer than the lifetime of spin-polarized triplets. Therefore, the triplet mechanism for electron spin-polarization is not efficient for generating spin-polarized radicals **4b** and **4c**.

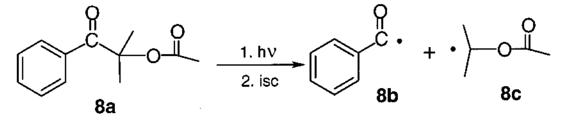
Similar substituent effects on α-cleavage of ketones have been reported.[33] Phenyl *tert*-butyl ketone, which possesses a n,π^* nature of the lowest triplet excited state, showed fast α-cleavage ($k_\alpha = 1.1 \times 10^7$ M^{-1} s^{-1}). In contrast, triplets of 4-phenylphenyl *tert*-butyl ketone (π,π^* nature) showed no evidence for α-cleavage. Slow α-cleavage was observed for 4-methoxyphenyl *tert*-butyl ketone ($k_\alpha = 6.8 \times 10^5$ M^{-1} s^{-1}).[33] This is another example, where methoxy-substituted aryl alkyl ketones are of intermediate effect.

The influence of the nature of the excited triplet state of carbonyl compounds on reactivity has been extensively demonstrated for hydrogen atom abstractions.[34] Wagner et al. studied the influence of ring-substituted valerophenones on type II photoeliminations, which are initiated by intramolecular hydrogen abstraction.[35] The lowest triplet state of a *p*-methoxy-substituted valerophenone is of π,π^* nature.[35] The spectroscopic measurements indicated that *p*-methoxyvalerophenone reacts primarily from equilibrium concentrations of upper n,π^* triplets, with a ΔE^T of 18 kJ/mol in methanol solutions.[35] An equilibrium between a nearby n,π^* triplet and the lowest π,π^* triplet could also explain the intermediate rate of α-cleavage of **4a**.

Conversion of α-hydroxy ketones to the alkyl ether (**7a**) or ester (**8a**) does not appear to change the nature of the lowest triplet state. For these ketones the lowest triplet states are of n,π^* nature, based on their phosphorescence lifetime at 77 K, their structured phosphorescence spectrum at 77 K, their triplet energy, and their triplet−triplet absorption (Table 1). The butyl ether (**7a**) underwent efficient α-cleavage to produce benzoyl and dimethylbutoxymethyl radicals (eq 5) according to TR-IR and TR-EPR studies.



(5)



(6)

The short triplet lifetime ($\tau_{7a} \sim 310$ ps) suggests that the rate constant for α-cleavage is similar to the rate constant for the hydroxy ketone (**1a**), which has a lifetime of 370 ps. The resulting radicals (benzoyl and dimethylbutoxymethyl radicals, eq 5) were observed directly by TR-EPR (Figure 4b). The radicals are strongly emissive spin-polarized, as is expected by the triplet mechanism for electron spin-polarization.[23] The degrees of spin-polarization of the radicals **7b** and **7c** are of the same order as those for radicals **1b** and **1c** generated by photolysis of **7a** and **1a**, respectively, as judged from the intensity of the TR-EPR signal (Figure 4a,b).

Additional evidence for α-cleavage is shown by product studies using GC-MS after photolysis of argon-saturated acetonitrile solutions of **7a** by laser irradiation (266 nm). Benzil, which is formed by combination of two benzoyl radicals (**7b**), is a major photoproduct. Moreover, the decomposition quantum yield (Φ_α) determined by GC analysis after photolysis of **7a** is similar to **1a** (Table 1).

To use alkyl ether derivatives as photoinitiators for free radical polymerization not only must α-cleavage be fast and efficient but also the addition rate constant of the dimethylalkoxy radical to olefinic monomers must be high. The addition rate constant of dimethylbutoxymethyl radicals (**7c**) to *n*-butyl acrylate was determined by competition quenching with crystal violet in laser flash photolysis experiments: $k = 1.3 \times 10^7$ M^{-1} s^{-1}. The same method was employed earlier to determine the addition rate constant of dimethylketyl radicals (**1c**) to *n*-butyl acrylate: $k = 1.3 \times 10^7$ M^{-1} s^{-1}.[28] Both rate constants are the same within experimental error, showing that replacement of a hydroxy to an ether function does not change the addition rate constants of the radicals to acrylate monomers.

Although the lowest triplet of the ester derivative (**8a**) is of n,π^* nature, our results indicate that although α-cleavage occurs to some extent, it is slow and inefficient. The decomposition quantum yield (Φ_α) after photolysis of **8a** is 1 order of magnitude lower than for

1a (Table 1). The triplet–triplet absorption was observed of **8a** by laser flash photolysis (Figure 2d) and is similar to the spectrum reported for triplets of the hydroxy ketone (**1a**).[8] The long triplet lifetime ($\tau_{\mathbf{8a}} = 3$ μs) is consistent with slow α-cleavage (eq 8). The α-cleavage kinetics were directly observed by time-resolved IR (Figure 5). The rise time of the benzoyl radical (**8b**) observed by TR-IR displays kinetics is similar (ca. 2 μs) to the decay of the triplet state (^{3}**8a***) observed by its optical absorption after laser flash photolysis. In addition, the time-resolved EPR of **8a** displayed only weak spin-polarized radicals **8b** and **8c**. The weak spectrum was assigned to the radical pair mechanism, also consistent with a slow α-cleavage, since fast α-cleavage (e.g., **1a**) shows strong triplet polarization of radicals produced from α-cleavage. Spin-polarization by the triplet mechanism was not observed, which would generate an emissive polarized EPR signal as in the case of **1a** and **7a**. Because of the slow α-cleavage rate of **8a**, the spin-polarized triplet states, produced by triplet sublevel selective intersystem crossing, are equilibrated before the cleavage occurs. This eliminates the triplet mechanism polarization, and only weak polarization due to radical pair mechanism is observed (Figure 4d). The slow rate of cleavage of the triplet of **8a** is consistent with the proposed[33] polarity dependence of α-cleavage, for which the buildup of positive character on the alkyl moiety is favored by electron-releasing groups, such as alkoxy functions, and disfavored by electron-withdrawing groups, such as acetate functions.

Additional evidence, that some α-cleavage to form benzoyl radicals **8b** upon irradiation of argon-saturated acetonitrile solutions of **8a**, was found in product studies using GC-MS. After photolysis of **8a** by laser irradiation (266 nm) benzil was identified, which is formed by the combination of two benzoyl radicals (**8b**).

Summary and Conclusion

The photochemistry and photophysics of **1a** and its derivatives **2a**–**8a** were investigated. Substituents at the benzoyl moiety can change the photochemistry and photophysics significantly by changing the nature of the lowest triplet state from n,π* to π,π*. The hydroxy ketones **1a**–**3a**, which possess a n,π* nature of the lowest triplet state, undergo fast ($k_\alpha > 10^9$ s^{-1}) and efficient α-cleavage ($\Phi_\alpha \sim 0.4$–0.6) upon irradiation. In contrast, the hydroxy ketones of π,π* nature of the lowest triplet states (**5a** and **6a**) show no evidence for α-cleavage on the time scale investigated (ca. 100 μs). The alkyl ether derivative (**7a**) exhibits fast α-cleavage upon irradiation, but slow cleavage was observed for the ester derivative (**8a**). Derivative **4a** represents an intermediate case, where α-cleavage occurs efficiently ($\Phi_\alpha \sim 0.3$) but at a slower rate ($k_\alpha = 8 \times 10^7$ s^{-1}) than that observed for **1a**–**3a**. From the basic photochemistry point of view, our investigations show that **1a**–**4a** and **7a** are good photoinitiators for free radical polymerization due to their fast and efficient α-cleavage and high addition rate constant of the dimethylketyl and dimethylbutoxymethyl radicals to acrylates. These ketones share the common feature of possessing rapid intersystem crossing from the S_1 to T_1 state and a relatively pure n,π* character of the T_1 state. An exception to the correlation between n,π* character and photoinitiation efficiency is found in the case of **8a** for which the replacement of the hydroxy function with the acetate function slows the rate of cleavage by a factor of nearly 1000 and removes this ketone from the list of effective photoinitiators.

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References and Notes

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(37) The α-cleavage quantum yield was determined by GC analysis of photolyzed acetonitrile solutions ($\lambda_{irr} = 254$ nm) relative to the ground state bleaching quantum yield of **1a** ($\Phi_\alpha = 0.38$).

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