Two-Photon Cleavage of Benzil in the Laser-Jet: Intermolecular Reactions of Transient Benzoyl and *tert*-Butoxy Radicals in the Photolysis of *tert*-Butyl Peroxide Mixtures

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Abstract: Normal irradiation of benzaldehyde in *tert*-butyl peroxide as solvent afforded benzil and minor amounts of *tert*-butyl benzoate (**1**), whereas in the laser-jet mode exclusively ester **1** was observed. On photolysis of benzaldehyde in a 1:1 mixture of *tert*-butyl peroxide and CCl_4 as solvent, only benzoyl chloride was found on normal irradiation. However, in the laser-jet mode also ester **1**, chlorobenzene, and hexachloroethane were observed. Chlorobenzene arises from decarbonylation of the intermediary benzoyl radicals and subsequent chlorine abstraction from CCl_4 by the resulting phenyl radicals. Benzil was cleaved in the laser-jet through a two-photon process and afforded the same benzoyl radical-derived products as in the photolysis of benzaldehyde, except that also α,α,α-trichloroacetophenone (**2**) was formed by an in-cage reaction.

Introduction

On normal lamp irradiation benzil is photostable in hydrogen-nondonating solvents,[1,2] while in hydrogen-donating solvents it undergoes efficient photoreduction.[3] In view of the strong absorption bands at 370 and 480 nm[4–6] of the benzil triplet and its rather long triplet lifetime of about 4 ms,[7] further excitation under laser conditions is likely and the photochemistry of such photochemically generated transients is feasible. Indeed, excitation of triplet benzil in the visible band results in cleavage into benzoyl radicals.[8,9] The thermal fate of the benzoyl radicals is either dimerization in inert solvents or hydrogen and halogen abstraction from appropriate hydrocarbon and halocarbon solvents.[12] In the gas phase at elevated temperatures also decarbonylation has been observed.[13] The kinetic behavior has been monitored by ESR[2,10,11] or by IR spectroscopy under laser flash photolysis conditions.[12] Although the UV spectrum of the benzoyl radical shows weak absorption at 370 nm,[2] no photochemistry of this transient appears to have been reported.

The laser-jet technique[14] allows to conduct photochemical reactions at high photon densities on concentrated solutions (up to 0.1 M) of the substrate, which generates enough of the two-photon products for identification or characterization. Presently we report the results of our investigations on the photochemistry of the benzoyl radical which have been produced on two-photon cleavage of benzil or hydrogen abstraction from benzaldehyde by *tert*-butoxy radicals under laser-jet conditions.

Results and Discussion

First the photochemistry of the benzoyl radical under laser-jet conditions was investigated. By starting from benzaldehyde, high concentrations of *tert*-butyl peroxide had to be used, because the molar extinction coefficient of the latter at the available laser lines in the UV region (333, 351, and 364 nm) is rather low [ϵ (333 nm) = 0.4 M^{-1} cm^{-1}]. Irradiation of a solution of benzaldehyde in *tert*-butyl peroxide with the widened beam of an argon ion laser yielded mainly benzil (Table I, entry 1), besides small amounts of ester **1**; thus, dimerization to benzil is the normal fate of the benzoyl radicals.[12] The ester **1** is the coupling product between benzoyl and *tert*-butoxy radicals (Scheme I).

A complete change in the product distribution was achieved under laser-jet conditions. The only detectable product was ester **1** (Table I, entry 2). This implies that under laser-jet conditions an extremely high steady-state concentration of *tert*-butoxy radicals is maintained so that cross-coupling between benzoyl and *tert*-butoxy radicals to give ester **1** prevails over dimerization of the benzoyl radicals to benzil.

When the irradiation of benzaldehyde was performed in a 1:1 mixture of CCl_4 and *tert*-butyl peroxide with the widened laser beam, benzoyl chloride and hexachloroethane were obtained as the only products (Table I, entry 3). Benzoyl chloride is the chlorine abstraction product of benzoyl radicals from CCl_4, while hexachloroethane is the dimerization product of $^{\bullet}CCl_3$ radicals. At the high concentration of CCl_4 used in this experiment, the previous reaction pathways of the benzoyl radicals, i.e., dimerization to benzil and coupling to ester **1**, cannot compete with chlorine abstraction, and consequently these products were not observed in the normal photolysis experiments with the widened laser beam.

On the other hand, upon laser-jet photolysis (Table I, entry 4) the amount of ester **1** grew substantially (81%), benzoyl chloride decreased (16%), and also a small amount of the decarbonylated product chlorobenzene (3%) was found. Thus, chlorine abstraction by benzoyl radicals was effectively suppressed in favor of coupling with *tert*-butoxy radicals, which unquestionably arises

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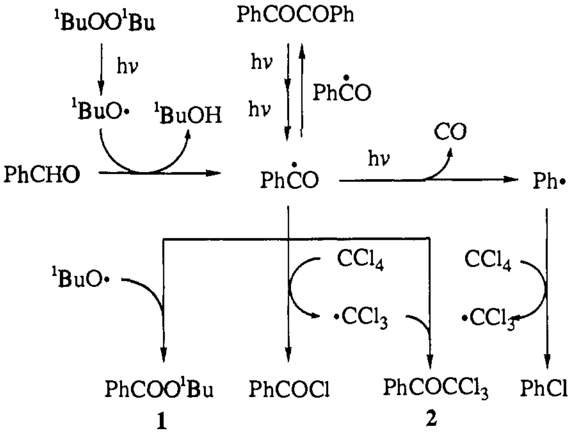
Scheme I. Reactions of the Benzoyl Radical in CCl_4 and $^tBuOO^tBu$ as Solvents



from the high stationary concentration of the latter in the laser-jet photolysis of *tert*-butyl peroxide as cosolvent. In fact, this competition between CCl_4 and *tert*-butoxy radicals for the benzoyl radicals allows to estimate the stationary concentration of $^tBuO^•$ produced in the laser-jet of about millimolar.[15] This result illustrates that the laser-jet technique is a valuable tool for the study of the intermolecular chemistry of radicals in view of the high steady-state concentrations of such transients generated under these conditions.

The low yield (ca. 3–4%) of the side product chlorobenzene (Table I, entries 4 and 8) derives from the decarbonylation of the intermediary benzoyl radical, followed by chlorine abstraction from CCl_4 of the resulting phenyl radicals, a well-established process.[16] The thermal decarbonylation of $PhCO^•$, i.e., from its ground state, has an activation energy of about 29 kcal/mol[13] and even at 80 °C takes place to the extent of only ca. 4%.[17] Thus, at 20 °C, at which the laser-jet photolyses were carried out, such thermal decarbonylation should be negligible. Nevertheless, in the focal region of the laser-jet the thin stream could heat up sufficiently so that significantly higher local compared to bulk temperatures could result and promote thermal decarbonylation. On the other hand, the benzoyl radical has a weak absorption at 370 nm,[2] which is accessible by the strong 364-nm UV line of the argon ion laser (40% of the UV output). Consequently, a competing photochemical decarbonylation through the electronically excited benzoyl radical might comprise an alternative pathway to thermal decarbonylation in the laser-jet.[18] However, as interesting as this postulated two-photon process, i.e., the photodecarbonylation of benzoyl radicals may be, it must occur at best only to a small extent because during the laser-jet irradiation of benzaldehyde in *tert*-butyl peroxide (Table I, entry 2) the phenyl radical derived products benzene (H abstraction) and phenyl *tert*-butyl ether (coupling with $^tBuO^•$ radicals) were not detected.

The laser-jet photolysis of benzil in *tert*-butyl peroxide as solvent yielded ester **1** as the only product (Table I, entry 5). It is of interest to mention that also in the normal photolysis (Table I, entry 6) a small amount of benzil is cleaved to afford exclusively ester **1**. Two reaction pathways may be considered for the latter result: either the benzil cleavage occurred by a two-photon process also in the normal photolysis (low intensity), or in a thermal reaction benzil was attacked by *tert*-butoxy radicals at the carbonyl group and cleaved subsequently into benzoyl radicals and ester **1**. To exclude this alternative thermal pathway, as control experiment *tert*-butoxy radicals were generated by thermolysis of *tert*-butyl peroxide in the presence of benzil in the dark (Table I, entry 9). No cleavage of benzil was observed, although *tert*-butyl peroxide was shown to decompose efficiently under these dark conditions to generate the required $^tBuO^•$. This was confirmed by means of a further control experiment (Table I, entry 10), in which under identical conditions benzaldehyde was converted into benzil on heating in *tert*-butyl peroxide. On the basis of these results, the thermal pathway for the cleavage of benzil by *tert*-butoxy radicals is unlikely.

The two-photon cleavage of benzil was previously[8] observed also in dilute benzene solutions with the help of two pulsed lasers, in which triplet benzil was generated by irradiation at 308 nm with a XeCl excimer laser and excited in the visible region at 517 nm by using a dye laser. Our present results reveal that two-photon cleavage of benzil can also be achieved by UV excitation in the laser-jet mode. The advantage of the latter is that significantly more concentrated solutions (5×10^{-2} M) can be employed compared to the pulsed-laser mode (5×10^{-4} M), which enables complete product studies. Thus, at the high steady-state concentration of $^tBuO^•$ produced in the laser-jet photolysis, the benzoyl radicals derived from the cleavage of benzil are subsequently trapped by *tert*-butoxy radicals to give the ester **1**. However, in view of the long lifetime of triplet benzil (4 ms)[7,19] and the extensive irradiation time (5 min normal irradiation *versus* only 350 μs in the laser jet), the photocleavage of benzil can also be observed to a small extent (2%) under normal irradiation conditions (Table I, entry 6).

No photocleavage of benzil was noted when the normal irradiation was conducted in CCl_4 (Table I, entry 7), although upon laser-jet photolysis benzil was cleaved efficiently in this solvent (Table I, entry 8). Besides benzoyl chloride as a major product (66%), also 30% of α,α,α-trichloroacetophenone (**2**) and 4% chlorobenzene were found. The formation of the acetophenone **2** derives presumably from cross-coupling between $PhCO^•$ and $Cl_3C^•$ directly in the radical cage, because this product was not observed when benzaldehyde was used as benzoyl radical precursor. Thus, the photolysis of benzil generates a pair of benzoyl radicals, of which one abstracts from CCl_4 (the solvent) a chlorine atom to yield benzoyl chloride and a $^•CCl_3$ radical, the latter couples subsequently with the remaining benzoyl radical in the radical cage to give acetophenone **2** (Scheme I).

With the help of the laser-jet technique we have acquired valuable results on the chemistry of the benzoyl radical. The resulting benzoyl radical is trapped quantitatively by the *tert*-butoxy radical, which is produced in a high steady-state concentration during the laser-jet photolysis. With the help of the laser-jet technique, the two-photon cleavage of benzil can be effected by employing concentrated solutions of the substrate. In addition to the products formed in the benzaldehyde irradiations, also the acetophenone **2** was found. It derives from a cage reaction in CCl_4 as solvent. These results underline the value of the laser-jet technique for the investigation of the intermolecular chemistry of photochemically generated transients.

Experimental Section

Materials and General Techniques. The benzaldehyde was distilled prior to use, and benzil and CCl_4 were reagent grade. The *tert*-butyl peroxide was filtered over basic alumina before use. The GC analyses were carried out on a Carlo Erba HRGC, equipped with a SE 54 fused silica column (30 m). NMR spectra were recorded on a Bruker AC 200 or a Bruker AC 250 spectrometer.

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(15) The stationary concentration of *tert*-butoxy radicals was calculated from

$$[\mathbf{1}]/[\mathrm{PhCOCl}] \cong k_{\mathrm{trap}} \times [^t\mathrm{BuO}^\bullet]/(k_{\mathrm{Cl}} \times [\mathrm{CCl_4}])$$

to be $[^tBuO^•] \cong 1.5$ mM, by using the rate constant of chlorine abstraction ($k_{Cl} = 5.6 \times 10^4$ M^{-1} s^{-1}),[12] the concentration of CCl_4 (5.4 M), the rate constant for trapping (k_{trap} ca. 10^9 M^{-1} s^{-1}), and the ratio of ester **1** and benzoyl chloride (81:16).

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(18) A precedent for such thermal versus photolytic competition has been reported in the demethylation of the α,α-dimethoxybenzyl radical under high-intensity photolysis.[2]

Table I. Product Studies of the Reaction of Benzoyl Radicals with CCl_4 and *tert*-Butoxy Radicals

		conc			solvent composition (%)			conv[a]	mb[b]	product distribution[a,c]				
entry	substrate	(10^{-2} M)	mode	time	CCl_4	^{t}BuOO^{t}Bu	$C_6H_4Cl_2$	(%)	(%)	PhCOCOPh	PhCO$_2$^{t}Bu	PhCOCl	PhCOCCl$_3$	PhCl
1	PhCHO	10.0	normal[d]	1 min		100		76	90	96	4			
2	PhCHO	10.0	LJ[e]	ca. 50 μs		100		15	>95	*f*	>99			
3	PhCHO	1.00	normal[d]	10 s	50	50		99	90	*f*	*f*	>99	*f*	*f*
4	PhCHO	1.00	LJ[e]	ca. 50 μs	50	50		34	>95	*f*	81	16	*f*	3
5	PhCOCOPh	5.00	LJ[e]	ca. 350 μs		100		16	>95	*g*	>99			
6	PhCOCOPh	5.00	normal[d]	5 min		100		2	>95	*g*	>99			
7	PhCOCOPh	1.00	normal[d]	5 min	100			<1	>95	*g*		*f*	*f*	*f*
8	PhCOCOPh	1.00	LJ[e]	ca. 350 μs	100			33	90	*g*		66	30	4
9	PhCOCOPh	1.00	Δ[h]	15 min		50	50	<1	>95	*g*	*f*	*f*	*f*	*f*
10	PhCHO	1.00	Δ[h]	15 min		50	50	35	80	>99	*f*			

[a] Detected by GC analysis, error ±5% of the stated value. [b] Mass balance, error ±10% of the stated value. [c] Normalized to 100%. [d] Direct irradiation with the widened beam of the argon ion laser, 3.5 W all UV lines (333, 351, 364 nm). [e] Laser-jet experiment, 3.5 W all UV lines, 100-μm capillary, flow rate of 0.60 mL/min. [f] Not detected, i.e., <1%. [g] Substrate. [h] Thermolysis at 190 °C in the dark.

Normal Laser Photolyses. Irradiations were carried out in Schlenk tubes. The solutions were degassed by purging with a slow stream of dry argon gas for 20 min and irradiated at the 333-, 351-, and 364-nm lines of the Coherent INNOVA 100 argon ion laser (3.5 W over all UV lines), supplied with UV optics. The beam was widened with a quartz lens (*f* = 50 mm) to a size of 1 cm in diameter. The 2-mL samples were irradiated for the time stated in Table I.

High-Intensity Photolyses. The experimental setup is described in detail in two recent publications.[14] The beam of the argon ion laser (3.5 W over all UV lines) was focussed by means of a quartz lens (*f* = 80 mm) onto a free-falling liquid stream of the photolysis solution. The free-falling liquid stream was maintained by means of a Bischoff 2200 HPLC pump and passed through a 100-μm capillary. The samples were degassed by purging with a slow stream of dry argon gas for 20 min. The irradiation chamber was kept under a positive argon gas pressure, and the substrate solutions were either passed once through the focal point (benzaldehyde irradiations, irradiation time ca. 50 μs) or recycled (benzil irradiations, irradiation time ca. 350 μs). A 1-mL aliquot was withdrawn by means of a syringe for GC analysis.

Thermolyses. The solutions were degassed by purging with a slow stream of dry argon gas for 20 min. The thermolyses were carried out in Schlenk tubes, which were equipped with a reflux condenser and kept under argon gas atmosphere. The samples were heated for 15 min at 190 °C, and the solutions were analyzed by GC.

Product Studies. Quantitative product studies were performed by GC with the help of naphthaline as internal standard. *tert*-Butyl ester (**1**)[20] was isolated from an irradiated *tert*-butyl peroxide solution of benzaldehyde by employing the laser-jet mode and characterized on the basis of its ^{1}H and ^{13}C NMR spectra. An authentic sample of α,α,α-trichloroacetophenone (**2**) was synthesized according to the literature.[21] Benzoyl chloride and chlorobenzene were identified by coinjection with authentic materials.

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