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Ultrasound Effects on the Photopinacolization of Benzophenone

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Ultrasonic irradiation is able to modify the course of several photochemical reactions, especially bimolecular, proceeding via triplet states. These effects were illustrated in the study of benzophenone photopinacolization in ethanol. The rates and yields increase when sonication is applied simultaneously to UV irradiation. An explanation is based on a 2-fold effect: (i) light-absorbing transient species undergo sonolytic decomposition, making the photoconversion more efficient, and (ii) sonication induces the triplet state quenching, as shown by Stern–Volmer plots from experiments run in the presence of naphthalene, probably due to the easier collisional deactivation processes favored by the homogeneous distribution of the activated species.

Introduction

The specificities of sonochemistry with respect to photochemistry have been envisaged in a number of papers. The photo- and sonolyses of metal carbonyls,¹ and of bromotrichloromethane in the presence or absence of 1-alkenes,² display significant differences, absent in the decomposition of arenediazonium salts.³ Much less attention has been paid to reactions performed under simultaneous ultrasound and light irradiations. The photolyses of water,⁴ trifluoromethyl phenyl ketone,⁵ and dihalo benzils⁶ were shown to be substantially influenced by sonication. Not only photocleavages, but also photoisomerization and -coupling reactions, can also be affected by ultrasound.⁷ From the data reported, general trends seem to appear: (i) a monomolecular process, e.g., the photoisomerization of 2-phenylindane-1,3-dione to 3-benzylidenephthalide,⁸ is practically unchanged by sonication; (ii) bimolecular reactions undergo significant changes in rates and selectivity as observed in the photodimerization of acenaphthylene,⁸ the addition of cyclohexanone to cyclohexene, and the Paterno–Büchi reaction of acetone to ethyl vinyl ether.⁹ An explanation can be the

homogeneous distribution of the reactive excited states throughout the solution by cavitation microstreaming, known to provide an ideal stirring.^{10,11} A recent study of the photorearrangement of diphenyl ether could support the idea that cavitation enhances the quenching of some excited states or cleaves intermediate excimers or exciplexes.¹² To explore further the effects of the combined actions of light and acoustic waves, the photoreduction of benzophenone was investigated, and the results are described in this paper.

Results and Discussion

The experiments were run in a quartz cuvette (for UV spectroscopy, 1 cm × 1 cm section) sealed with a septum and placed in a HP-8452A array spectrophotometer. Photolyses were effected at 366 nm with an OSRAM xenon lamp (Figure 1), the incident light ("excitation beam") covering the totality of the cuvette surface. Nitrogen bubbling through a capillary placed in the top half of the cuvette was used to ensure agitation in the nonsonicated experiments. This agitation method proved to be efficient enough in the small volume of the cell and did not interfere with the analytic system, whose beam ("analytic beam") propagates in the bottom half of the cell perpendicularly to the excitation beam. The ultrasonic microtip horn (3 mm diameter, fitted to a Branson Sonifier 250, power setting $21.5 \pm 1 \text{ W} \cdot \text{cm}^{-2}$)¹³ was inserted through the septum, at a reproducible position obtained by a three-axes screw device. A solution of benzophenone (Aldrich, recrystallized from methanol) in 96% ethanol (Merck, UV grade) placed in the cuvette was degassed under 10^{-4} Torr by three freeze–thaw cycles

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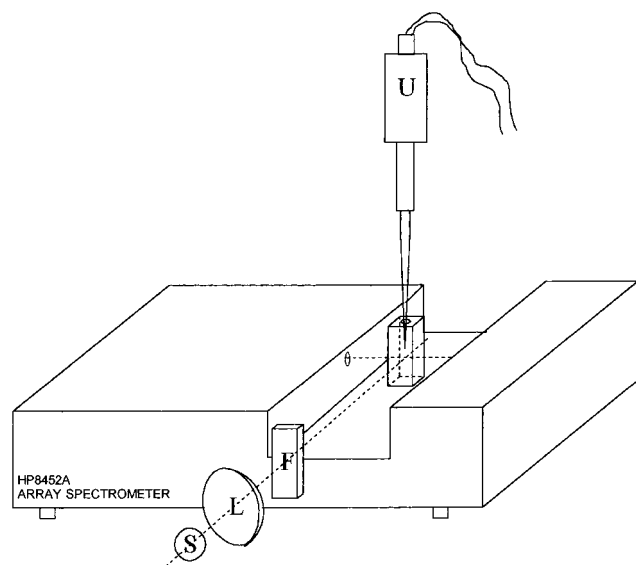
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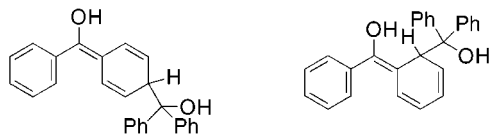
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S - lamp; L - lens; F - filter; U - ultrasound

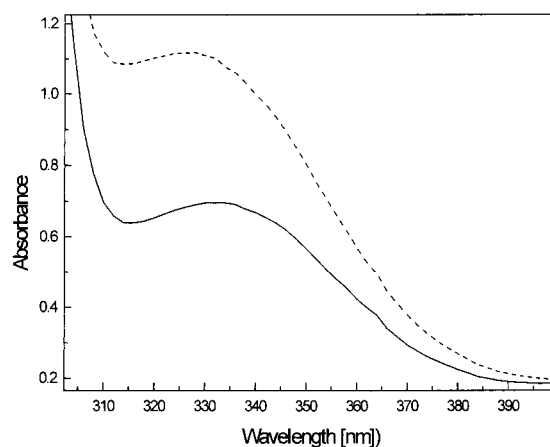
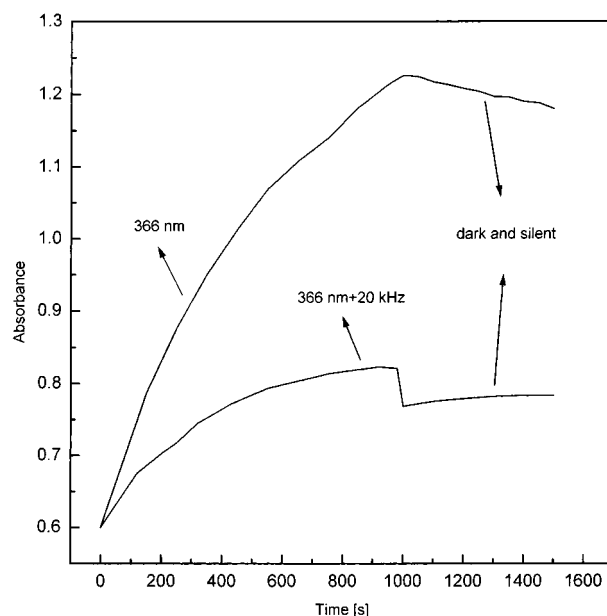
Figure 1. Experimental setup.**Table 1. Photoreduction of Benzophenone 1: Relative Amounts of Residual Benzophenone 1, Benzpinacol 2, and Benzhydrol 3 after Reaction for 1000 s**

1 (C_0) ^a	conditions	1	2	3
7.2	UV	4.34 ± 0.04	1.39 ± 0.01	0.08 ± 0.01
	UV +))))	3.37 ± 0.03	1.85 ± 0.02	0.07 ± 0.01
3.63	UV	1.95 ± 0.02	0.81 ± 0.01	0.07 ± 0.01
	UV +))))	1.80 ± 0.02	0.87 ± 0.01	0.05 ± 0.01
1.76	UV	0.91 ± 0.01	0.39 ± 0.01	0.04 ± 0.01
	UV +))))	0.89 ± 0.01	0.42 ± 0.01	0.02 ± 0.01

^a All the concentrations in mmol·L⁻¹.**Scheme 1**

with repressurization by oxygen-free nitrogen and thermostated to 23 ± 0.3 °C. All the experiments were run for 1000 s. Comparative experiments prolonged for 2000 s provide practically identical results. The course of the reaction was followed by recording simultaneously with irradiation the UV spectra of the mixture every 10 s. The rate constants were calculated from the 100 spectra thus obtained. The composition of the mixture was determined by HPLC with a UV array detector at 230 nm. The results given in Table 1 represent an average of at least two runs. The accuracy of the measurements can be estimated to better than 1%. Table 1 gives the amounts of the photoproducts which can actually be isolated. In the absence of light, sonication does not initiate any detectable reaction.

Previous workers have shown that during the photolysis of benzophenone in the presence of hydrogen donors, light-absorbing transients (LAT, Scheme 1) are formed.^{14,15} These species, characterized by a λ_{\max} at 327 nm, hypsochromically shifted by several nanometers as compared

**Figure 2.** Spectra of oxygen-free ethanolic benzophenone before (solid line) and after (dotted line) UV irradiation.**Figure 3.** Time dependence of LAT formation and decomposition under photolysis (upper curve) and photosynthesis (lower curve), C_0 Ph₂CO = 0.6 mmol·L⁻¹.

to benzophenone (Figure 2), cannot be isolated due to their high sensitivity to oxygen and thermal lability.

Even at low concentrations (ca. 1% of the initial Ph₂CO),¹⁶ they act as internal light filters (LAT ϵ_{333} 5×10^4 M⁻¹·cm⁻¹; Ph₂CO ϵ_{333} 167 M⁻¹·cm⁻¹) and quench the benzophenone triplet.¹⁴ The higher conversion observed under sonication can thus mean that lower amounts of LAT are formed, a hypothesis that was checked by recording the absorbance of the solution as a function of time: the LATs formed when sonication is applied reach only 25% of the amount formed without sonication, independently from the initial concentration (Figure 3).

Photosynthesis of a solution previously photolyzed for an initial 400 s period [Figure 4 (top), curve 1] produces a sharp decrease of the absorbance as soon as ultrasound is switched on. Conversely, sonication inhibits the photochemical formation of the LATs, which appear as soon as ultrasound is switched off [after 500 s, curve 2]. With continuous simultaneous illumination and sonication, the

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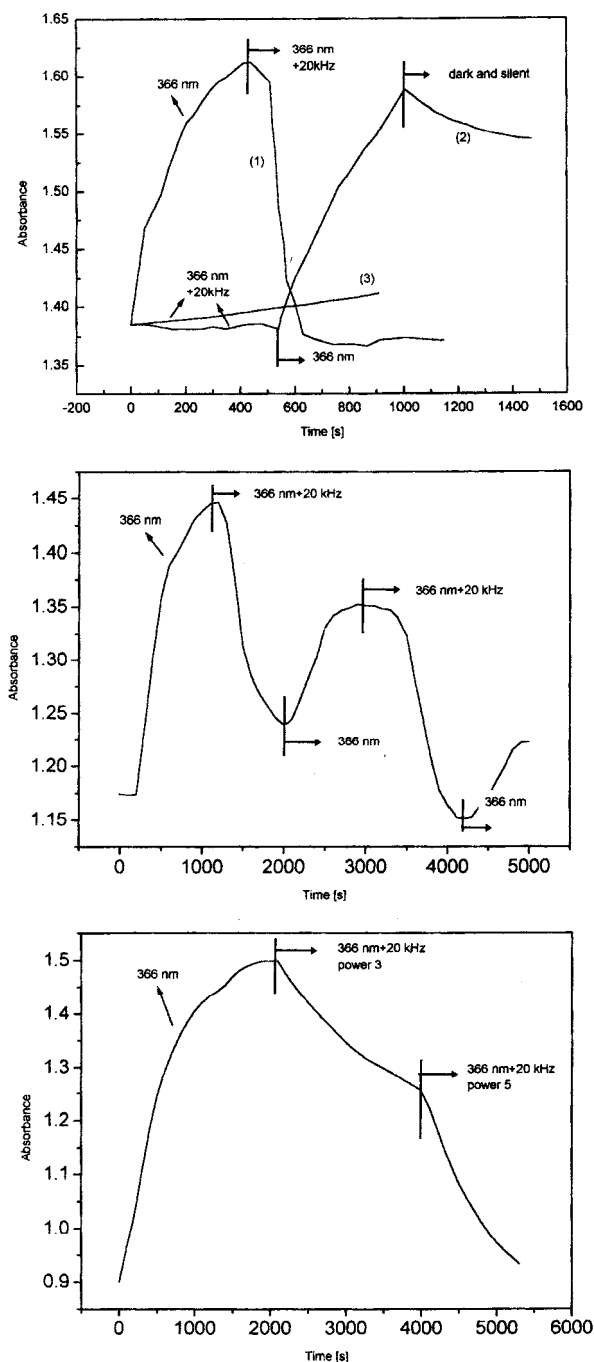


Figure 4. Absorbance of the continuously photolyzed solution vs time. Changes in the sign of the slope coincide with the switching on or off of ultrasound. Top frame: curve 1: initial 366 nm irradiation followed after 400 s by simultaneous (366 nm + 20 kHz) irradiations; curve 2: initial (366 nm + 20 kHz) irradiations followed after 500 s by UV only; curve 3: continuous (366 nm + 20 kHz) irradiations. Middle frame: alternate 366 nm and (366 nm + 20 kHz) irradiations. Bottom frame: same as top, curve 1, with ultrasound power setting 3 ($5.7 \pm 0.5 \text{ W}\cdot\text{cm}^{-2}$) and 5 ($50 \pm 2 \text{ W}\cdot\text{cm}^{-2}$).

level of LAT formed remains very low (curve 3). The absorbance increase/decrease from alternate UV/(UV+ultrasound) irradiations can be repeated [Figure 4 (middle)], illustrating the reversibility of the reactions. That sonication plays a direct role in the LAT concentration lowering is also demonstrated in Figure 4 (bottom): the absorbance decreases faster when the ultrasound intensity is increased from $5.7 \pm 0.5 \text{ W}\cdot\text{cm}^{-2}$ (power

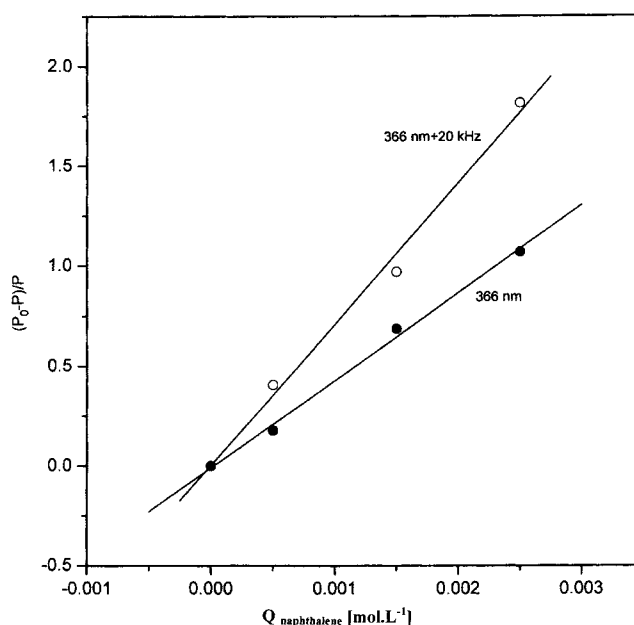


Figure 5. Quenching of benzophenone triplet by naphthalene. [EtOH] = $17.15 \text{ mol}\cdot\text{L}^{-1}$; slope of (366 nm + 20 kHz) line: $710 \text{ mol}^{-1}\cdot\text{L}$; slope of (366 nm) line: $440 \text{ mol}^{-1}\cdot\text{L}$.

setting 3) to $50 \pm 2 \text{ W}\cdot\text{cm}^{-2}$ (power setting 5). Kinetic measurements show that the LAT decomposition is very slow without sonication ($k_{\text{sono}} = 0.128 \pm 0.007 \text{ mol}^{-1}\cdot\text{s}^{-1}$ at $21.5 \pm 1 \text{ W}\cdot\text{cm}^{-2}$; $k_{\text{silent}} = 0.0092 \pm 0.0002 \text{ mol}^{-1}\cdot\text{s}^{-1}$). An explanation was envisaged by considering the known sensitivity of the LATs to oxygen, which can form by sonolysis of the solvent and the water contained in it. However, this hypothesis is invalidated by the results shown in Figure 4 (top), curve 2: if oxygen is generated in the solution by sonolysis (endogenous oxygen), the steep rise in absorbance as soon as sonication is stopped should not occur. In addition, the spontaneous decay of LATs under oxygen without sonication requires 1–2 days.¹⁶ This sonochemical decomposition of LATs remains an experimental observation for which it is premature to propose a reasonable mechanism.

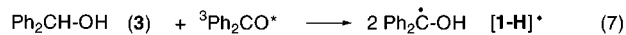
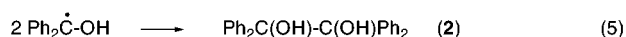
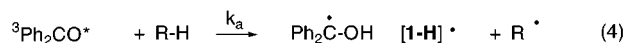
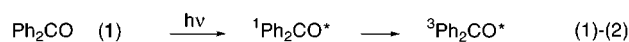
The net result is that in the absence of the LAT internal light filters, the photoconversion increases, to a higher degree for the more concentrated solutions. The higher conversion yields under sonication demonstrate that the effect of the cavitation bubble cloud is minimum. If light scattering by this cloud was important, a lesser amount of excited molecules should be produced, leading to lower yields, in opposition to the experiment. Similarly, if light scattering decreases the intensity received by the detector, the “apparent” absorbance should increase at the ultrasound switch-on, and decrease at the switch-off, again the opposite of what is observed.

It was, however, suspected that lowering the LAT amount was not the sole effect of sonication, and further experimentation was undertaken to determine if ultrasound can actually quench some activated species. The same experiments as above were run in the presence of naphthalene,¹⁷ and the results expressed by Stern–Volmer plots (Figure 5).

Sonication of the mixtures with naphthalene increases the Stern–Volmer constant K_{SV} , with a ratio $K_{\text{SV(sono)}}/$

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Scheme 2



$K_{\text{SV(silent)}} = 1.61$. In the equation $K_{\text{SV}} = k_q/(k_a[\text{RH}])$ applied to the silent reaction, it can be assumed that the diffusion-controlled quenching rate constant is similar to the diffusion rate constant:¹⁵ $k_{q(\text{silent})} = k_{\text{diff}} = 5.4 \times 10^9 \text{ mol}^{-1}\cdot\text{s}^{-1}$.¹⁸ The hydrogen abstraction rate constant $k_{a(\text{silent})}$ (Scheme 2),^{19,20,21} is calculated as $7.19 \times 10^5 \text{ mol}^{-1}\cdot\text{s}^{-1}$.

In a first hypothesis, if the hydrogen abstraction reaction 4 is assumed to be independent of cavitation, then $k_{a(\text{silent})} = k_{a(\text{sono})}$ and the ratio $k_{q(\text{sono})}/k_{q(\text{silent})}$ is equivalent to $K_{\text{SV(sono)}}/K_{\text{SV(silent)}} = 1.61$, giving the sonochemical quenching rate constant $k_{q(\text{sono})} = 8.7 \times 10^9 \text{ mol}^{-1}\cdot\text{s}^{-1}$. On the other hand, if reaction 4 is also accelerated by sonication (in agreement with the general effects of sonication on mass transport dependent processes), the sonochemical quenching rate constant will reach even larger values. The origin of this effect is difficult to

determine. Obviously these reactions should occur in the bulk solution, out of the cavitation bubbles, where the thermal effects vanish rapidly as the distance from the bubble increases. Pressure and/or shock waves effects can propagate at longer distances, and a parallel could be given to the pressure enhancement of the quenching reaction, observed previously.²² Last, it is observed that, whereas sonication increases the conversion and the yield of benzpinacol, the formation of benzhydrol **3** does not follow the same tendency. Benzhydrol acts as an efficient hydrogen donor to triplet Ph_2CO (Scheme 2, reaction 7), a reaction most probably accelerated by sonication according to the perfect stirring effect, contributing to keep the amount of **3** at a low level in all the cases and to accelerate the conversion of **1** and the quenching.

As a conclusion, this work has established experimentally that sonication can play a direct role in photochemical mechanisms. The higher benzophenone conversion and pinacol yields observed under sonication should find their origin in the sonochemical decomposition of the internal light filtering LATs leading to a higher efficiency of the excitation. Other interpretations at this stage are certainly premature, and further experimentation is required. One can just point out that the homogenization of sonicated solutions enhances all the processes, implying the encounter of two species, (i) the triplet benzophenone with naphthalene, (ii) the same triplet with a hydrogen donor (solvent, benzhydrol), (iii) and the dimerization of radical $[\text{1-H}]^*$ to benzpinacol.

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