The Efficiency of Transformation of Electronic Energy to Heat for Derivatives of 2-Hydroxybenzophenone as Studied by Laser-Induced Opto-Acoustic Spectroscopy

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The coefficient of transforming the absorbed light to the heat was determined by laser-induced opto-acoustic spectroscopy (LIOAS) for ten derivatives of 2-hydroxybenzophenone in cyclohexane and acetonitrile. For most derivatives the value of the coefficient is equal to one in both solvents as for the parent 2-hydroxybenzophenone. The largest deviation from one upwards outside the error limit is observed for 5-nitro and 4-propoxy derivatives. It is suggested that there are derivatives in this class of substances which exhibit a more effective transformation of electronic energy to heat than the parent 2-hydroxybenzophenone. Less effective than 2-hydroxybenzophenone are 4-nitro and 5-methoxy derivatives, which indicates that longer living states are involved in the radiationless process. The effect of intramolecular hydrogen bond on the radiationless process is discussed.

Derivatives of 2-hydroxybenzophenone mostly substituted in position 4 by alkoxy group are known as light stabilizers for polyolefins, polystyrene, poly(vinyl chloride), and other polymers [1—3]. Recently, they have been substituted by more efficient hindered amines in most applications [1—3]. In polar polymers as poly(vinyl chloride) or polyamides they are, however, still widely used. Original assumption concerning their efficiency, namely about their being UV screeners, was corrected in a sense that they might act as chain breakers as well [4]. High efficiency in transformation of absorbed energy to heat, for 2-hydroxybenzophenones [1], 2-hydroxybenzotriazoles [5], and other hydroxy aromatics [6], is related to their intramolecular hydrogen bond. The process begins with fast transfer of proton. The details of the following processes are still a matter of discussion.

The development of photoacoustic spectroscopy made it possible to measure the efficiency of the transformation of electronic energy to heat and to compare this process with those for compounds of different structure [7]. The amplitude of photoacoustic signal is given as follows

$$H = K\,\alpha\,E_0(1 - 10^{-A})$$

where H is experimentally determined amplitude of photoacoustic signal in V, E_0 is incident laser pulse energy in μJ, K is instrument constant depending on the geometry of the experiment and thermoelastic properties of medium and detector, A is absorbance of the solution which is adjusted to 0.1 [8], α is the fraction of the absorbed energy transformed to heat within the time of resolution of the set-up. It is set to one by using the compound where the radiationless process proceeds with 100 % efficiency.

Recently it has been demonstrated that unsubstituted 2-hydroxybenzophenone can be used as a standard in the UV region at low energies of excitation [7, 8].

The aim of this communication is to report on the influence of substituents on the radiationless process in derivatives of 2-hydroxybenzophenone.

EXPERIMENTAL

The derivatives of 2-hydroxybenzophenone were of the same kind as described previously [9, 10]. Cyclohexane (Riedel de Haen AG, Selze, Hannover, FRG) and acetonitrile (Janssen Chimica, Geel, Belgium) were for UV spectroscopy.

Experimental set-up for time-resolved photoacoustic spectroscopy was the same as described in the paper [7]. As a detector, a sensitive microphone (Panametrics A 603S 1.0/0.5) was used with time resolution less than 10^{-6} s. It means that all radiationless processes, faster than 10^6 s^{-1} are detected as prompt heat. The height of the first maximum of the photoacoustic signal was measured at different intensities of excitation energy. The least-square method was used to determine the slope of this dependence in the linear part [8]. Unsubstituted 2-hydroxybenzophenone (Aldrich Chemicals) was

used as a standard. The optical density of solutions is adjusted to about 0.1 and the values of slope are corrected for differences in absorbance.

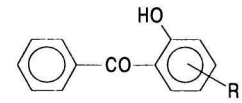
RESULTS AND DISCUSSION

The plots of dependence of photoacoustic signal on the laser energy were linear as it is shown in Figs. 1 and 2 for some 2-hydroxybenzophenone derivatives in cyclohexane and acetonitrile, respectively. The slopes of these dependences after correction on absorbance are the coefficients α which are given in Table 1.

The proton transfer and all other processes involved in the radiationless process, transforming the electronic energy to heat, are fast. Therefore, this heat for 2-hydroxybenzophenone is recorded as prompt one due to time resolution of the set-up. As it is evident from Table 1, most examined derivatives of 2-hydroxybenzophenone under study exhibit coefficient α of transformation of the absorbed radiation to heat about 1 in the limit of experimental error ± 5 % in nonpolar cyclohexane and polar acetonitrile as well. It means that this process is of the same efficiency for unsubstituted 2-hydroxybenzophenone and its derivatives substituted in position 4, 5, and 6. It was found for 2-hydroxybenzophenone, substituted in position 6 by methyl, that the intensity of the longest wavelength band decreases at addition of polar solvent [10]. This is caused by twisting 2-hydroxybenzophenone ring due to formation of intermolecular hydrogen bond to the polar proton accepting solvent [11]. In spite of the fact that the intramolecular hydrogen bond is sensitive to polar solvents for 6-substituted derivatives, acetonitrile does not influence absorption of the longest wavelength band. The efficiency of this transformation is not changed because absorbance of the longest wavelength band is proportional to the fraction of molecules which have preserved intramolecular hydrogen bond.

In the past, we have demonstrated that the influence of substituents in position 4 and 5 of 2-hydroxybenzophenone derivatives is rather complex [12]. Two-parametric Hammett type relationship was needed for proper accounting of inductive and mesomeric effect of substituents on the chemical shift of hydrogen of bonded hydroxy group. Seemingly there is no direct relationship between the strength of intramolecular hydrogen bond and the efficiency of transformation of absorbed energy to heat. On the other hand, its presence secures that this part of the molecule is planar. The proton transfer in the excited state is very fast under these conditions (in picosecond time region [6]).

Table 1. The Coefficients α of Transformation of Absorbed Energy to Heat for Derivatives of 2-Hydroxybenzophenone



Substituent	Solvent	
	Cyclohexane α	Acetonitrile α
Unsubstituted	1.00	1.00
4-Methyl	1.02	–
5-Methyl	1.01	–
4-Nitro	0.87	0.79
5-Nitro	1.21	1.06
4-Propoxy	1.08	1.07
5-Methoxy	0.95	–
4,6-Dimethyl	1.03	1.01
3-*tert*-Butyl-6-methyl	0.95	1.04
2,2′-Dihydroxy	1.00	0.97

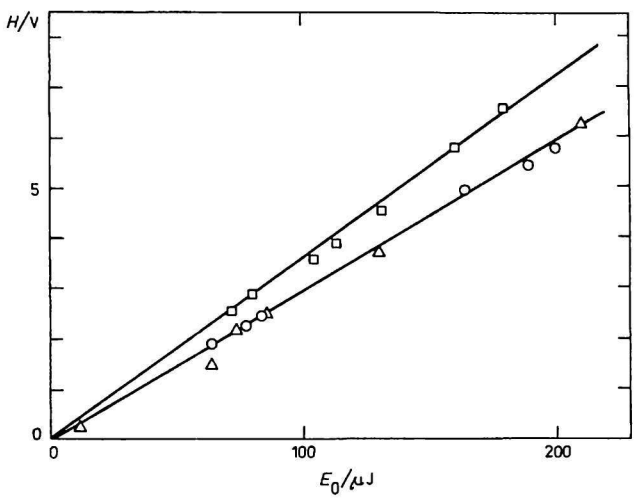


Fig. 1. The amplitude of the opto-acoustic signal as a function of laser energy for 2-hydroxybenzophenone (○), 2-hydroxy-4-propoxybenzophenone (□), and 2-hydroxy-4-nitrobenzophenone (△) in cyclohexane.

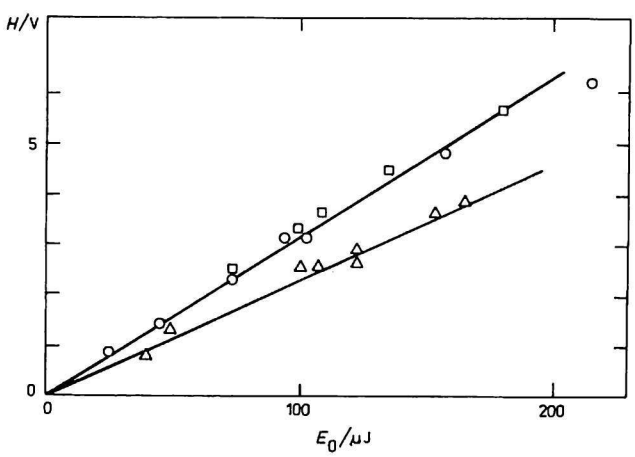


Fig. 2. The amplitude of the opto-acoustic signal as a function of laser energy for 2-hydroxybenzophenone (○), 2-hydroxy-4-propoxybenzophenone (□), and 2-hydroxy-4-nitrobenzophenone (△) in acetonitrile.

It is evident from Table 1 that there are some deviations outside the error limit (± 5 %) of 1 on both sides. It is rather difficult to interpret the value higher than 1 for 5-nitro and 4-propoxy derivatives in both solvents. These two derivatives exhibit more effective transformation of absorbed electronic energy to heat than the unsubstituted 2-hydroxybenzophenone. In the case of 4-propoxy derivative this conclusion is supported by the fact that 4-alkoxy derivatives of 2-hydroxybenzophenone are widely used as light stabilizers [1]. The 4-alkoxy group fulfils several functions:

1. It modifies the absorption spectrum by hypsochromic and hyperchromic effect compared to unsubstituted 2-hydroxybenzophenone.
2. It improves compatibility with the polymers, mainly polyolefins.
3. It acts as chain breaker [1, 4].

Values of α that are lower than 1 are easier to explain. The largest deviation is observed for 4-nitro derivative. It means that at least one quarter of the absorbed energy is transformed slowly and an intermediate (triplet state) living longer than 1 μs is involved in this transformation. The same is valid for 5-methoxy derivative, too. It is worth to note that methoxy and nitro substituents have opposite effect in position 4 and 5.

We can conclude that laser-induced opto-acoustic spectrometry might contribute to better understanding of light stabilizers. This type of measurement, performed in thin films or in bulk polymers, could yield data even more relevant to understanding of the mechanism of the light stabilization of polymers.

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