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Ultrasound effects on photochemical reactions 2. A study of ultrasound effects on some monomolecular and bimolecular photochemical reactions

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Abstract

The ultrasound effect on two well-described photochemical reaction was studied. Ultrasound does not affect the initiated photoisomerization of 2-phenylindan-1,3-dione to 3-benzylidenephthalide in the case when any additive is present, which is a monomolecular process, but enhances the effect of quenchers on its photoisomerization, which is a bimolecular process. The photodimerization of acenaphthylene is considerably affected by simultaneous sonication, which results in different ratios of the stereoisomers in comparison with the silent process. Sonication appears to affect the first reaction by homogeneous distribution of the excited states, or intermediates and possibly by quenching the excited triplet state of the second reaction. Two new reactors were designed allowing simultaneous irradiation of the reaction mixture by UV light and ultrasonic waves.

Keywords: Ultrasound effects; Photochemical reactions; Photoisomerization

1. Introduction

The effect of ultrasound on different chemical reactions is widely studied during the last two decades both in cavitation and pre-cavitation regime [1–4]. It was found that ultrasound affects mostly the velocity of reactions, the yields and in some cases the ratio of formed products. One of the ultrasound effects, especially in heterogeneous reactions, is the mechanical effect responsible for the mass transfer, that is, a thorough stirring of the reaction mixture, the activation of the surface of the solid reagents or catalysts, etc. This is the reason for the application of ultrasound in heterogeneous catalysis and in sonoelectrochemistry [5,6]. The second effect of ultrasound, the most pronounced in homogeneous reactions, is caused by high temperatures (up to 5000 K) and high pressure (up to 400 atm), which are evolved in the collapsing bubbles (cavities) in the ultrasound field. This is known as a hotspot effect. Molecules evolved in the reactions are for a very short time in the extreme conditions. In this sense, the sonochemical reactions could be compared with photochemical reactions, but the energy, which is absorbed by a single molecule, is much higher at photochemical reaction. Some similarity between photochemistry and sonochemistry of norharmane was described very recently [7].

It is well known that transmission of light through a reaction solution produces excited molecules, which are the real reactants in a photochemical reaction. The outcome of the photochemical reaction depends on the concentration of such excited species, and can be modified also by their photophysical extinction (destruction). Photochemical reactions are only apparently homogeneous processes, since the concentration of excited molecules is not equal over the whole reaction volume. The concentration of these species is the highest in close proximity to the walls of the UV lamp immersion unit. The results of photochemical reactions are therefore very dependent on the light intensity, as well as effective stirring of the reaction mixture [8–11]. A solution to this problem would be a design of photochemical reactor with perfect stirring, which has been described in several papers [12–15]. It should be stressed that mechanical stirring is always more or less a local stirring being the most effective near the stirrer, but not so effective in the close proximity of the reactor walls. The sonochemical stirring is even distributed over the whole reaction volume, as cavities are formed, and implode at every place of the reaction mixture. It is even more probable that implosion of cavities is more frequent at

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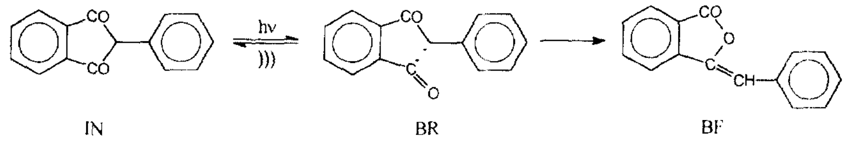


Scheme 1.

the walls of the reactor, which means that this critical place of photochemical reaction should be extremely well 'homogenized'. Another problem of photochemical reactions, especially those yielding high conversions, are connected with large light absorbance changes, and this problem has also been described [16–19]. Ultrasound, therefore, can have significant effect on photochemical reactions, especially at those where there is a high concentration of absorbing reactant and some photolytic reactions. In our previous papers [20,21], we found that simultaneous sonication of photochemical reactions has a beneficial and simplifying effect on the course of reactions.

The main goal of this work was to examine possible ultrasound effects on some monomolecular and bimolecular photochemical reactions. For this reason, only such well described photochemical reactions were chosen for our study, and the reaction were studied at the described conditions. It was proved also that ultrasound alone has no effect on the reactions under study. We were particularly interested to study the ultrasound effect on the homogeneous distribution of the excited states in the reaction medium (the non-homogeneous light absorption and distribution of the excited states is well described by the Lambert–Beer law).

2. Results and discussion

The photochemical reactivity of 2-phenylindan-1,3-dione was described several years ago [22,23]. It was proposed that indan-1,3-dione (IN^{So}) is excited to its singlet (IN^{S1}), and triplet (IN^{T1}) state. The next reaction step is α-cleavage leading to the biradical (BR), which can then either rearrange to 3-benzylidenephthalide (BF), or recombine back to the starting material.

A side reaction is the abstraction of hydrogen from the solvent (Scheme 1). Both excited state of indan-1,3-dione may be quenched by suitable additives, which suppress izomerization. The most important reaction steps of this reaction are depicted in Eqs. (1)–(10).

$$IN^{So}+h\nu\rightarrow IN^{S1} \quad (1)$$

$$IN^{S1}\rightarrow IN^{So}+h\nu_F \quad (2)$$

$$IN^{S1}\rightarrow IN^{T1} \quad (3)$$

$$IN^{T1}\rightarrow IN^{So} \quad (4)$$

$$IN^{T1}\rightarrow IN^{So}+h\nu_P \quad (5)$$

$$IN^{T1}\rightarrow BR \quad (6)$$

$$BR\rightarrow BF \quad (7)$$

$$BR\rightarrow IN^{So} \quad (8)$$

$$IN^{S1}+Q\rightarrow IN^{So}+Q^{S1} \quad (9)$$

$$IN^{T1}+Q\rightarrow IN^{So}+Q^{T1} \quad (10)$$

Processes described by Eqs. (1)–(8) are monomolecular, while Eqs. (9) and (10) are bimolecular processes. We decided to examine the effect of ultrasound on both types of 2-phenylindan-1,3-dione reactions. The reaction mixture was irradiated with UV light with $\lambda > 290$ nm and both silent and ultrasonic reaction were carried out at the conditions given in Refs. [22,23]. The course of the reaction was followed by measuring the concentration of the starting material, 2-phenylindan-1,3-dione at $\lambda_{max} \approx 370$ nm, 3-benzylidenephthalide is $\lambda_{max} \approx 350$ nm. From Fig. 1, it is possible to see that ultrasound produces only a negligible rate reduction on the clean phototransformation of 2-phenylindan-1,3-dione. This is in accord with the fact that it is a pure monomolecular process, which cannot be complicated by a side reaction (hydrogen abstraction by BR), since benzene, used as the solvent, is a poor hydrogen donor. The concentration gradient of the excited states of 2-phenylindan-1,3-dione is also affected by the low extinction of 2-phenylindan-1,3-dione at λ_{irr} ($\varepsilon = 4.85$ l mol^{-1} cm^{-1}), which results in conditions close to homogeneous light absorption.

Our next aim was to modify the 2-phenylindan-1,3-dione to 3-benzylidenephthalide rearrangement from a monomolecular to a bimolecular mode. This can be achieved by the addition of either a sensitizer or a quencher. If the acetone (A), is used as the sensitizer as well as the solvent, then this should lead [22] to suppression of the processes described by Eqs. (1), (2), (3) and (9), i.e., those going via an excited singlet state of indandione. Acetone, after absorption of the

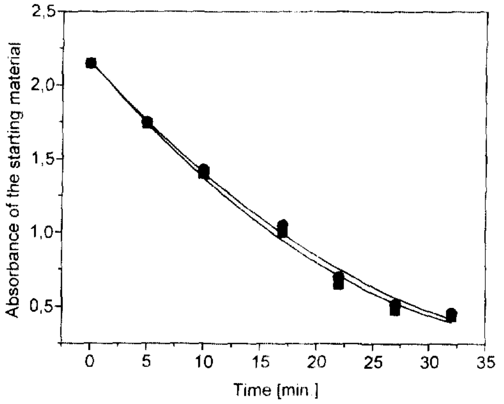


Fig. 1. Photochemical rearrangement of 2-phenylindan-1,3-dione to benzalphthalide in benzene (● with and ■ without ultrasound).

light, undergoes ISC (intersystem crossing), and its triplet state is formed. The excited triplet of acetone transfers energy to 2-phenylindan-1,3-dione, which is a bimolecular process. It could therefore be assumed that ultrasound should affect the reaction under these conditions, because the lifetime of acetone triplets is greater than the time of bubble growing at the frequency of applied ultrasound (20 kHz).) The result shown in (Fig. 2) demonstrates that no effect of ultrasound was observed. This observation can be explained by the fact that the energy of the singlet state of acetone (84 kcal mol^{-1}) is high enough to generate the singlet state of indan-1,3-dione. As the lifetime of singlet states is 10^{-9}–10^{-6} s, ultrasound cannot affect the homogeneity of their distribution. The result is that photolysis of 2-phenylindan-1,3-dione is not affected by sonication. In such a case, ultrasound should affect only such acetone sensibilized reaction, where hydrogen abstraction by BR can play a role as the triplet state of acetone is known to abstract hydrogen from hydrocarbons, alcohols, ethers, etc. [24]. This was proved by acetone sensibilized photoizomerization of indane-1,3-dione in cyclohexane. At a lower concentration of acetone ($5\cdot10^{-2}$ mol l^{-1}) (Fig. 3) light is absorbed by 2-phenylindan-1,3-dione as well as by acetone in the ratio $c_{IN}\varepsilon_{IN}/c_A\varepsilon_A$. The conditions are optimal both for direct, as well as sensitized reaction. Sonication homogenizes the reaction mixture and facilitate the hydrogen abstraction by acetone triplet excited states, which lowers at the same time the probability of energy transfer to indan-1,3-dione and therefore slows the rate of rearrangement.

Addition of an appropriate quencher to the solution of 2-phenylindan-1,3-dione in UV benzene changes the mode of its photochemical rearrangement from monomolecular to bimolecular. As quencher, we used 2,5-dimethyl-2,4-hexadiene (ES = 103 kcal mol^{-1}, ET = 58.7 kcal mol^{-1}) The quencher has the λ_{max} (in methanol) at 210 nm, and its 5×10^{-2} solution in benzene (the reaction condition, λirr > 290 nm) has the $A = 0.1$ a.u.

Quenching of the photochemical reaction is, from the kinetic point of view, the same process as its sensitization. The processes given in Eqs. (9) and (10) can play a role. As the lifetimes of singlet excited states is 10^{-9} to 10^{-6} s, and the lifetime of the triplet excited states is $\geq 10^{-5}$ s [25], ultrasound can quench only the triplet states, as the lifetime of the cavity or destruction of cavity walls is around 5–10 μs [26]. Quenching of the transition states is then diffusion-controlled and ultrasound may control its effectiveness by homogenization of the reaction mixture. If this is correct, then the rate of the reaction should be dependent on the quencher concentration. This is confirmed by comparing the results depicted in Fig. 4 (lower concentration of the quencher) with Fig. 5 (higher concentration of the quencher). The effect of ultrasound is as expected more pronounced at the lower quencher concentration. It is a proof that ultrasound can, by powerful mixing of the reaction mixture, more effectively quench the excited states of indan-1,3-dione molecules.

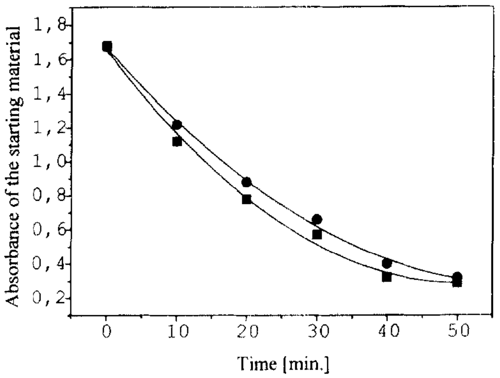


Fig. 3. Photochemical rearrangement of 2-phenylindan-1,3-dione to benzalphthalide in lower concentration of acetone (● with and ■ without ultrasound).

The outcome of the photochemical reactions can be seriously affected also by formation of polymer films, or deposits on the walls of the photochemical immersion unit. In spite of the fact that we proved [21] that application of ultrasound decreases the formation of such polymer deposits, we decided to exclude the possibility that this would be the only effect of ultrasound. For that reason, we carefully cleaned the walls of the immersion unit very frequently, at every occasion when

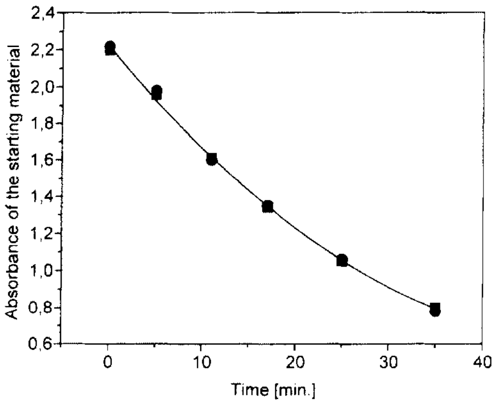


Fig. 2. Photochemical rearrangement of 2-phenylindan-1,3-dione to benzalphthalide in acetone (● with and ■ without ultrasound).

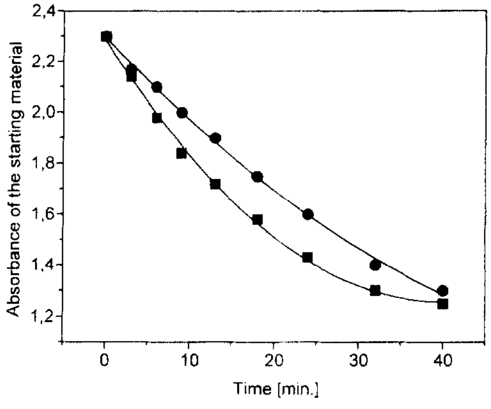


Fig. 4. Photochemical rearrangement of 2-phenylindan-1,3-dione to benzalphthalide in benzene with 2,5-dimethyl-2,4-hexadiene as a quencher ($c = 0.05$ mol l^{-1}) (● with and ■ without ultrasound).

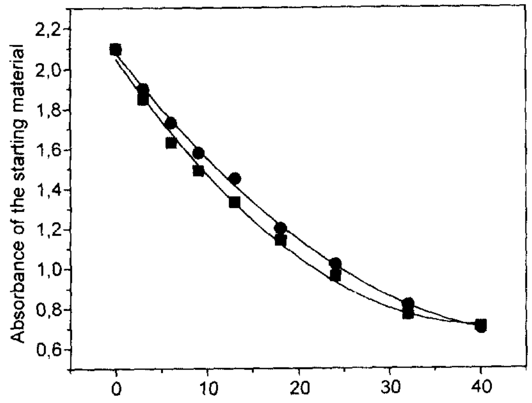


Fig. 5. Photochemical rearrangement of 2-phenylindan-1,3-dione to benzalphthalide in benzene with 2,5-dimethyl-2,4-hexadiene as a quencher [c = 0.005 mol l^{-1}] (● with and ■ without ultrasound).

a sample for analysis was withdrawn from the reactor, both at the silent and ultrasonic reactions.

As true bimolecular photochemical reaction, the photodimerization of acenaphthylene was chosen (Scheme 2). Cowan and Drisco [27] and Haga et al. [28] suggested that photodimerization of acenaphthylene proceeds from both singlet and triplet excited states: *Syn*-dimer is formed from singlet excimer only, while the anti-dimer is formed both from singlet excimer and the collision of excited acenaphthylene triplet with another acenaphthylene molecule in the ground state. They proved that photodimerization of acenaphthylene is quenched by oxygen or addition of ferrocene and just *syn*-dimer was formed under such conditions. To investigate the influence of ultrasound, we performed the photodimerization of acenaphthylene, both with and without sonication, at the condition given in Cowan and Drisco paper [27].

From the results depicted on Fig. 6, it is apparent that sonication of the reaction mixture during photolysis dramatically changes the ratio of *syn*/anti-dimers. It was not possible to continue the reaction until a photostationary state as dimers crystallized out of the solution after 15 h of photolysis. Great attention was paid to cleaning the immersion unit of the UV lamp to exclude that the results that could be affected by precipitation of the product on the walls of photochemical cell (see above). It is reasonable to anticipate that ultrasound cannot affect the photodimerization of acenaphthylene going from the excited singlet state of acenaphthylene, but can affect the photodimerization going from the excited triplet state of acenaphthylene. The question still remains if it is caused by quenching the triplet state, or suppressing the anti-dimer formation by some other means. The identification of a real quencher is not possible on the basis of our dimerisation results and would require the photophysical study of excited acenaphthylene molecules during the sonication. A similar effect of ultrasound was observed also on Paterno–Büchi reaction of acetone with ethyl vinyl ether [29].

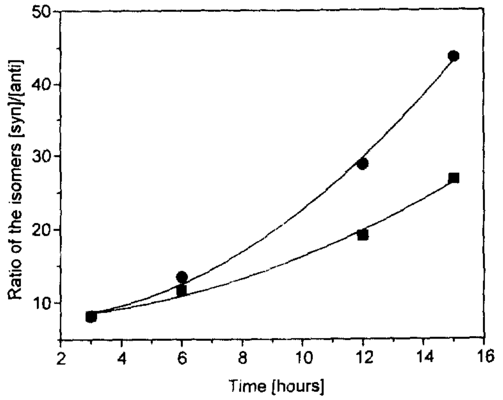


Fig. 6. Photodimerization of acenaphthylene in benzene (● with and ■ without ultrasound).

We assume that application of ultrasound to the photochemical reaction can result, in quenching of the triplet excited states and at least in the bimolecular reactions, in homogenization of the primary light effect inside the whole reaction medium, as well as homogeneous distribution of the intermediates or the reaction products. The effect of this homogenization on the reaction rate and/or the balance of the reaction is demonstrated by following reasoning.

Let us assume a photochemical reaction

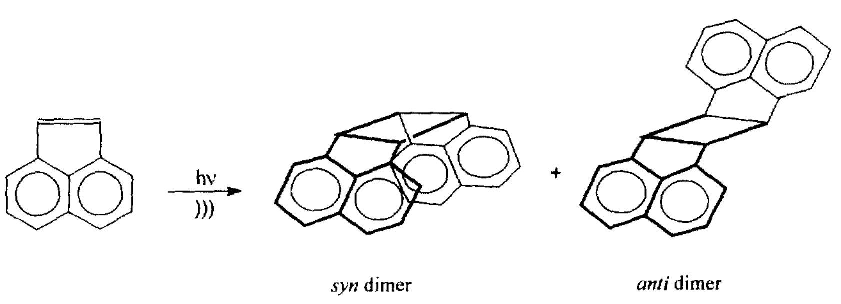
$$A + B \rightarrow \text{product}$$

where B is a light absorbing entity, then the energy absorbed in the cuvette by a unit of volume ($V = SL$), (L equals the thickness of the layer of the reaction mixture exposed to light, and S is the illuminated area) can be defined by equation:

$$I_{abs} = \frac{I_0 - I}{L} = I_0 \varepsilon [B] \qquad \text{(I)}$$

The reaction rate of homogeneous activation can be defined by equation

$$r = k[A]^m I_{abs}^n = k[A]^m (I_0 \varepsilon [B])^n \qquad \text{(II)}$$



Scheme 2.

The light can be nearly completely absorbed just passing the path 1_x, which is very short in comparison with the thickness of the photolyzed solution L. The light intensity is then changed as the factor of the path 1, which was passed by the light. That means, for the case that diffusion, streaming of the liquid, and stirring are not effective, that the energy is not equally absorbed by the medium. The photochemical reaction is then much more intensive near the walls of photochemical cell, than inside the cell. The absorbed light intensity, in the above-mentioned bimolecular photochemical reaction, in any volume unit having the width $d1$ and the thickness can defined as

$$I_1=I_0e^{-\varepsilon[B]_0 1} \tag{III}$$

and the reaction rate as

$$\boldsymbol{r_1=k[A]_1^m(\varepsilon'[B]_1 I_1)^n} \tag{IV}$$

At the very beginning of the reaction, concentrations of A and B are equal in the whole volume of the reaction mixture and the intensity of the light transmitted through the path 1 is expressed by the Lambert–Beer equation

$$I_1=I_0e^{-\varepsilon[B]_0 1} \tag{V}$$

and the reaction rate in the chosen place can be expressed by the equation

$$\boldsymbol{r_1=k[A]_0^m(\varepsilon'[B]_0 I_0)^n e^{-\varepsilon}[B]_0\mathrm{ln}} \tag{VI}$$

The average rate in the path L, through which the light beam passed is expressed as

$$\boldsymbol{\bar{r}=\frac{1}{L}\int_0^L r_1\,dl} \tag{VII}$$

or, after integration, as

$$\bar{r}=\frac{1}{L}k[A]_0^m(\varepsilon[B]_0 I_0)^n\frac{1-e^{-\varepsilon[B]_0 Ln}}{\varepsilon[B]_0 n} \tag{VIII}$$

When $I\doteq 0$ the expression $\epsilon[B]L$ in Eq. (VIII) is large, and the exponent is negligible in comparison with 1. For the average reaction rate, Eq. (IX) is valid.

$$\boldsymbol{\bar{r}=\frac{1}{L}\frac{k}{n}[A]_0^m(\epsilon'[B]_0)^{n-1}I_0^n} \tag{IX}$$

In the case when $n=1$, this equation is identical to the equation for homogeneous activation (II), and the starting reaction rate is not dependent on the concentration of B. When $n\neq 1$, then the rate of homogeneous activation and the average rate of non-homogeneous activation is in the ratio

$$\boldsymbol{\frac{r}{\bar{r}}=\frac{k[A]^m I_0^n n(\varepsilon'[B]_0)^{1-n}L}{L^n k[A]^m I_0^n}}, \text{ resp.} \tag{X}$$

$$\frac{r}{\bar{r}}=n(\varepsilon'[B]_0 L)^{1-n} \tag{XI}$$

If $n<1$, then non-homogeneous activation must be manifested by lowering the amount of transformed material, as $\varepsilon'[B]_0 1>1$. It means that with non-homogeneous light irradiation, ($n\neq 1$), the rate of photochemical reaction is dependent on $[B]$.

This explanation is in good agreement with our experimental results. Changes in reaction rates, as well as higher yields of the products, are caused by very good homogenization of the active species, a situation caused by sonication of the reaction mixture.

3. Conclusion

From the result of this and our previous work, it follows that ultrasound cannot affect monomolecular photochemical reactions. On the other hand, ultrasound can seriously affect bimolecular photochemical reactions predominantly due to the perfect homogenization of the reactants and excited states in the solution. Photochemical reactions proceed more cleaner when they are sonicated simultaneously. In the case when two isomers are formed in the photochemical reaction, then a different ratio of isomers is observed in the 'silent' and 'ultrasonic' photochemical reaction. This could be caused by the quenching of the triplet excited states or disruption of excimers (exciplexes), etc.

4. Experimental

4.1. Photochemical ultrasonic reactors

The first photochemical reactor allowing simultaneous ultrasound irradiation (Fig. 7) was assembled as follows. A sandwich piezoelectric transducer (50 W, 20 kHz, intensity ≈ 16 W cm^{-2}) (A) was attached by an epoxy resin to the bottom of a normal photochemical reactor (45 mm diameter, 125 ml volume) (B). The immersion unit (not depicted) fitted with a medium pressure 125 W mercury lamp is immersed into (B). Both the immersion unit and the ultrasonic reactor are water-cooled.

The second reactor (Fig. 8) does not have an attached transducer but an ultrasonic cleaning bath (Tesson 1, 150 W,

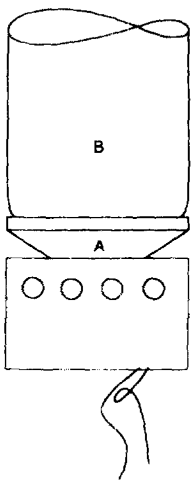


Fig. 7. Photochemical reactor where the ultrasonic cleaning bath was used as a source of ultrasound.

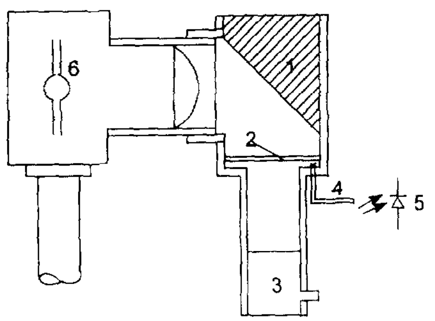


Fig. 8. Photochemical reactor with simultaneous ultrasound irradiation.

35 kHz) is used as the source of ultrasound. The polychromatic light produced by the high pressure mercury lamp HBO50 (6), is reflected by the mirror (1), passing the interference filter (2), and entering the silica cuvette (3). This cuvette is immersed in the ultrasonic cleaning bath cooled by circulating water. The light passes the light transducer (4), and its intensity is monitored by a photon counter (5).

4.2. Materials and experimental procedure

Acenaphthylene (Aldrich) was vacuum sublimed before use. 2-Phenylindan-1,3-dione was prepared as previously described [30]. Acetone, benzene and cyclohexane were of UV purity (Merck).

Irradiations were carried out under nitrogen in internally water-cooled reactors with a 125-W medium pressure mercury lamp. During irradiation, the solution was flushed with nitrogen.

4.3. Irradiation of acenaphthylene

The irradiation was performed in the reactor depicted on the Fig. 8. A solution of acenaphthylene 2 g in 145 ml of benzene (0.09 mol solution) was irradiated by UV light with $\lambda > 290$ nm for 15 h. Products were analyzed by gas chromatography and compared with literature [27].

4.4. Irradiation of 2-phenylindan-1,3-dione

The irradiation was performed on the reactor depicted on the Fig. 7. A solution of 2-phenylindan-1,3-dione 1.1 g ($5 \cdot 10^{-2}$ mol l^{-1}) in benzene or acetone was irradiated by UV light with $\lambda > 290$ nm for 35 min. Products were analyzed by gas chromatography or UV spectroscopy. Gas chromatographic analysis were carried out on a HP 5890 Series II (Hewlett-Packard) instrument fitted with a Model 7673 automatic injector, with a split–splitless injection system, and flame ionization detection. The signal was received and processed at a NEC computer with a HP Chemstation 3365-II. UV spectra were measured on Diode Array Spectrometer HP 8452 A.

4.4.1. Chromatographic conditions

With split–splitless injection, the conditions were as follows: carrier gas, hydrogen; head pressure, 50 kPa, 1:40; purge flow, 1.5 min^{-1}; injection temperature 300°C; detector temperature, 300°C; initial column temperature, 40°C, rising at 20°C min^{-1} to 320°C. With splitless injection, the conditions were as follows: carrier gas, helium; head pressure 50 kPa; split flow-rate 27 ml min^{-1}, splitless time, 3 min; purge flow, 1.5 ml min^{-1}. The injection volume was 1 μl in both instances; a 5-μl Hamilton syringe was used.

Quantification with phenanthrene as an internal standard was based on the peak areas obtained from each analysis by interpolation on a calibration graph.

4.5. Instrumental analysis MS/FID

HRGC analysis of the samples was performed on a Hewlett- Packard (HP) (Palo Alto, CA, USA) 5890a Series II gas chromatograph equipped with split–splitless injector (300°C, splitting ratio 1:30) and flame ionization detector operated at 300°C. Chromatographic data were processed with a HP Chemstation 3365-II. The columns used were a CP-SIL 5 CB (Chrompack) crosslinked fused-silica capillary column (10 m×0.32 mm i.d.) coated with polydimethylsiloxane (0.25 μm phase thickness). The oven temperature was programmed from 40°C to 320°C at 20°C min^{-1}. Helium (Tatragas, 99.995%) was used as the carrier gas (inlet pressure 50 kPa). Air and hydrogen flow rates were maintained at 300 and 30 ml min^{-1}, respectively *n*-tetradecane (0.5 μl) was used as an internal standard. Peak areas from different chromatograms were compared after they had been normalized with an internal standard.

A HP 5890A Series II gas chromatograph interfaced to a HP 5971A mass-selective detector with a HP MS Chemstation data system was used for identification of the GC components. The columns, gas, and temperature program used were as described above. The injection temperature was kept at 300°C, and the volume injected was 0.5 μl. The temperatures of the ionization chamber of the transfer line were 180°C and 280°C. The electron energy was 70 eV. Mass spectra and reconstructed total ion chromatogramss were obtained by automatic scanning in the mass range m/z 30–350 at 2.2 scans s^{-1}.

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