

The Effect of Ultrasound on Diphenyl Ether Photochemistry

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Simultaneous sonication and UV irradiation of diphenyl ether in methanol decreases the rearrangement of diphenyl ether as well as the rate of 4-hydroxybiphenyl formation. Ultrasound did not change the rate of 2-hydroxybiphenyl formation, but enhanced the rate of phenol formation, especially in experiments performed at higher concentrations of diphenyl ether. A new insight into the mechanism of the photochemical rearrangements of diphenyl ether is suggested.

The application of ultrasonic irradiation to the solution results in the formation, growth, and collapse of cavitation bubbles filled with inert gas or vapour of the solvent. Extremely high temperatures (up to 5000 K) and high pressures (up to 40 MPa) arise during the collapse of these cavities [1–4] and the collapse is accompanied by extremely powerful solvent microstreaming. Molecules present during such cavitation are exposed to these extreme conditions for a very short time and can undergo chemical or physical changes (sonochemistry). Therefore it was of interest to study whether ultrasound could also affect photochemical reactions during which the molecules are also subjected to extremely high energy. We have demonstrated [5, 6] that ultrasound cannot influence monomolecular photochemical reactions but it can influence the course of bimolecular types either through the powerful stirring effect of cavitation within the reaction mixture or by destroying some short-lived species. Ultrasonic destruction of short-lived species, intermediates or triplet excited states has been proved in the case of benzophenone pinacol coupling [7]. A similar beneficial effect of ultrasound has been described in the photodegradation of phenyl trifluoromethyl ketone in water [8] as well as in the photodegradation of dihalogenated benzils in 1,4-dioxane [9]. It is of interest to note that ultrasound can substantially accelerate the rate of photochemical decomposition of water mediated by titanium dioxide [10].

There are many papers describing the mechanisms of photochemical rearrangements, *e.g.* by Claisen [11] and Fries [12]. The photorearrangement of diphenyl ether was studied thoroughly [13–15]. The rate-determining step is C—O bond cleavage which occurs

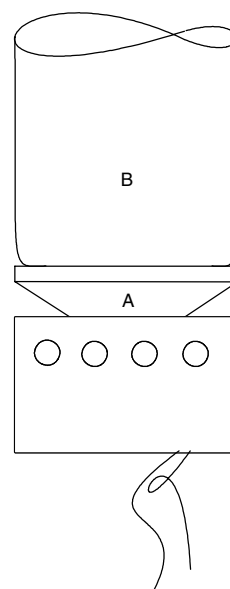


Fig. 1. Photochemical reactor with simultaneous ultrasound irradiation (A – piezoelectric transducer, B – photochemical vessel).

at the excited state of diphenyl ether. The phenyl and phenoxy radicals formed are then transformed to the products.

Ogata et al. [15] suggested that hydroxybiphenyl was formed from the singlet excited state of diphenyl ether. *Haga* [14] proved unambiguously that both 2-hydroxybiphenyl and 4-hydroxybiphenyl are formed *via* an intramolecular process which is going in the solvent cage.

The investigation of the effect of ultrasound on the photolysis of diphenyl ether was of the special inter-

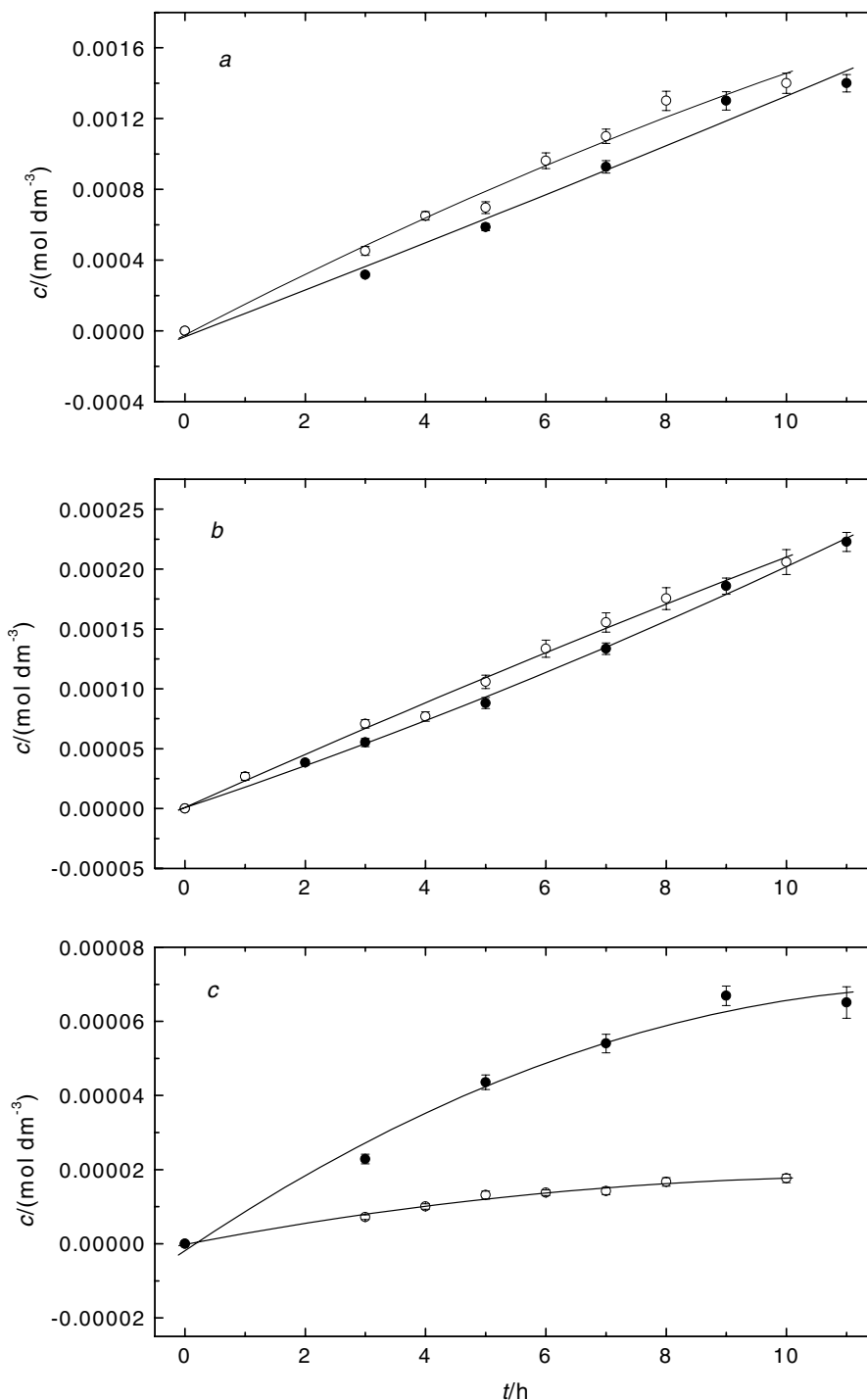


Fig. 2. Product distribution of diphenyl ether ($c = 0.01 \text{ mol dm}^{-3}$) photolysis in methanol. a) Phenol, b) 2-hydroxybiphenyl, c) 4-hydroxybiphenyl (● without SONO, ○ with SONO).

est for us because the photochemical rearrangement of diphenyl ether [14, 15] is a monomolecular process and therefore no ultrasound effect should be observed. On the other hand, the same authors [14] have suggested that the reaction is going in a solvent cage and that there could be some differences in the mechanisms of the formation of 2-hydroxybiphenyl (concerted process) and that of 4-hydroxybiphenyl (radical

pair mechanism), which means that some ultrasound effect could be observed.

EXPERIMENTAL

Diphenyl ether (Aldrich) and spectral grade methanol (Merck) were used without further purification. 4-Hydroxybiphenyl and 2-hydroxybiphenyl were

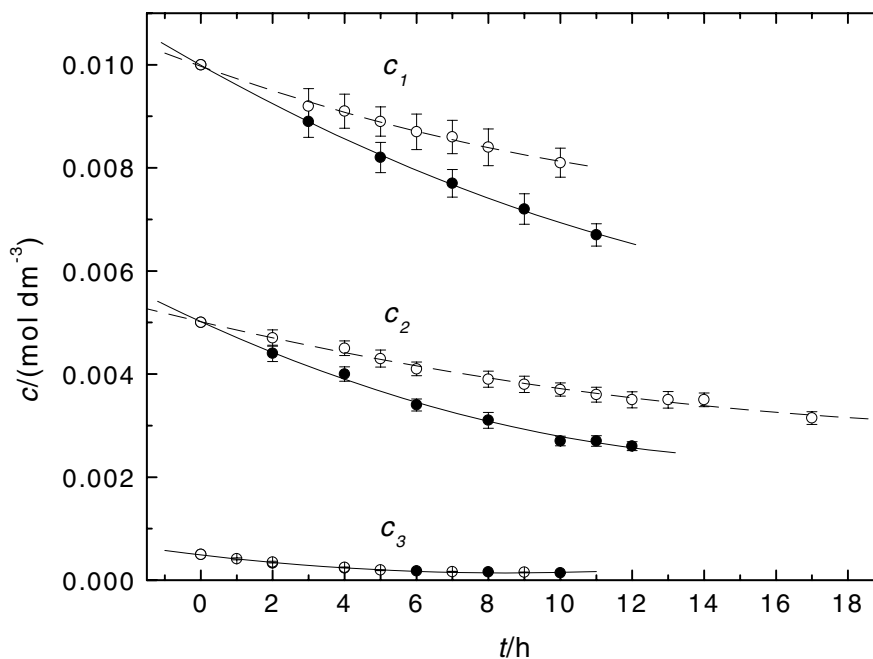


Fig. 3. The effect of initial diphenyl ether concentration on the rate of its conversion. $c_1 = 0.01 \text{ mol dm}^{-3}$, $c_2 = 0.005 \text{ mol dm}^{-3}$, $c_3 = 0.0005 \text{ mol dm}^{-3}$ (● without SONO, ○ with SONO).

prepared from 4-aminobiphenyl and 2-aminobiphenyl (Aldrich), respectively by their diazotation and subsequent acid hydrolysis with sulfuric acid, an analogous method to phenol preparation [17] (2-hydroxybiphenyl, m.p. = 56–58.5 °C, Ref. [18], m.p. = 56–56.5 °C and 4-hydroxybiphenyl, m.p. = 175.5–177 °C (in a seal capillary), Ref. [19] gives m.p. = 161–165 °C).

Diphenyl ether photolysis. All sonophotocatalytic and silent photochemical experiments were carried out in the reactor which has been described [5] (Fig. 1). The only difference between sonophotocatalytic and silent photochemical experiments was that for the sonophotocatalytic experiments the ultrasound was switched on. A diphenyl ether solution (250 cm³, $c = 1 \times 10^{-2} \text{ mol dm}^{-3}$) in methanol was irradiated at room temperature using a 15 W low-pressure mercury lamp and the reaction mixture was continuously flushed with nitrogen. The reaction course was followed by GC/MS (HP 5890 Series II (Hewlett—Packard) with phenanthrene as an internal standard) and UV VIS spectrophotometer HP 8452A.

RESULTS AND DISCUSSION

The photorearrangements of diphenyl ether have been described [13–15] and were performed with a high-pressure Hg lamp and a very long reaction time (25–40 h) was necessary to finish the reaction. We decided to carry out our experiment with a low-pressure Hg lamp the 95 % of emitted irradiation of which has the energy corresponding to 253.7 nm and which is more effective than the high-pressure mercury lamp. The rate of photolysis of diphenyl ether, using UV,

is higher with a low-pressure Hg lamp compared to a high-pressure Hg lamp. Using the higher UV extinction signal of diphenyl ether at 253.7 nm ($\epsilon = 951.0 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) rather than that at 366 nm ($\epsilon = 24.5 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) allowed us to work with a high concentration of radicals. The sonophotocatalytic and photochemical experiments were performed under exactly identical conditions and were repeated several times. The reaction mixture was not stirred, but adequately flushed with nitrogen at silent as well as sonochemical experiments. Concentration higher than 0.01 mol dm^{-3} cannot be used due to the low solubility of diphenyl ether. The product distribution of diphenyl ether sonophotolysis in methanol is shown in Fig. 2. The effect of initial diphenyl ether concentration on the rate of its conversion is shown in Fig. 3 and in Fig. 4 is presented the products distribution of diphenyl ether sonophotolysis in propan-2-ol. The results shown in Figs. 2–4 can be summarized as follows: 1. Decrease of the rate of diphenyl ether conversion due to ultrasonic irradiation. 2. Decrease in the rate of 4-hydroxybiphenyl formation due to ultrasonic irradiation. 3. Minimal effect of ultrasonic irradiation on the rate of 4-hydroxybiphenyl formation. 4. Increased formation of phenol under ultrasonic irradiation at higher concentration of diphenyl ether (0.01 mol dm^{-3}) (Fig. 3).

Effects 1–3 were also observed in experiments at concentrations of $0.005 \text{ mol dm}^{-3}$ of diphenyl ether.

These observed results can be explained as follows. Haga [14] proved that photocleavage of diphenyl ether is going in the solvent cage *via* a singlet excited state. The observed decrease of the diphenyl ether consump-

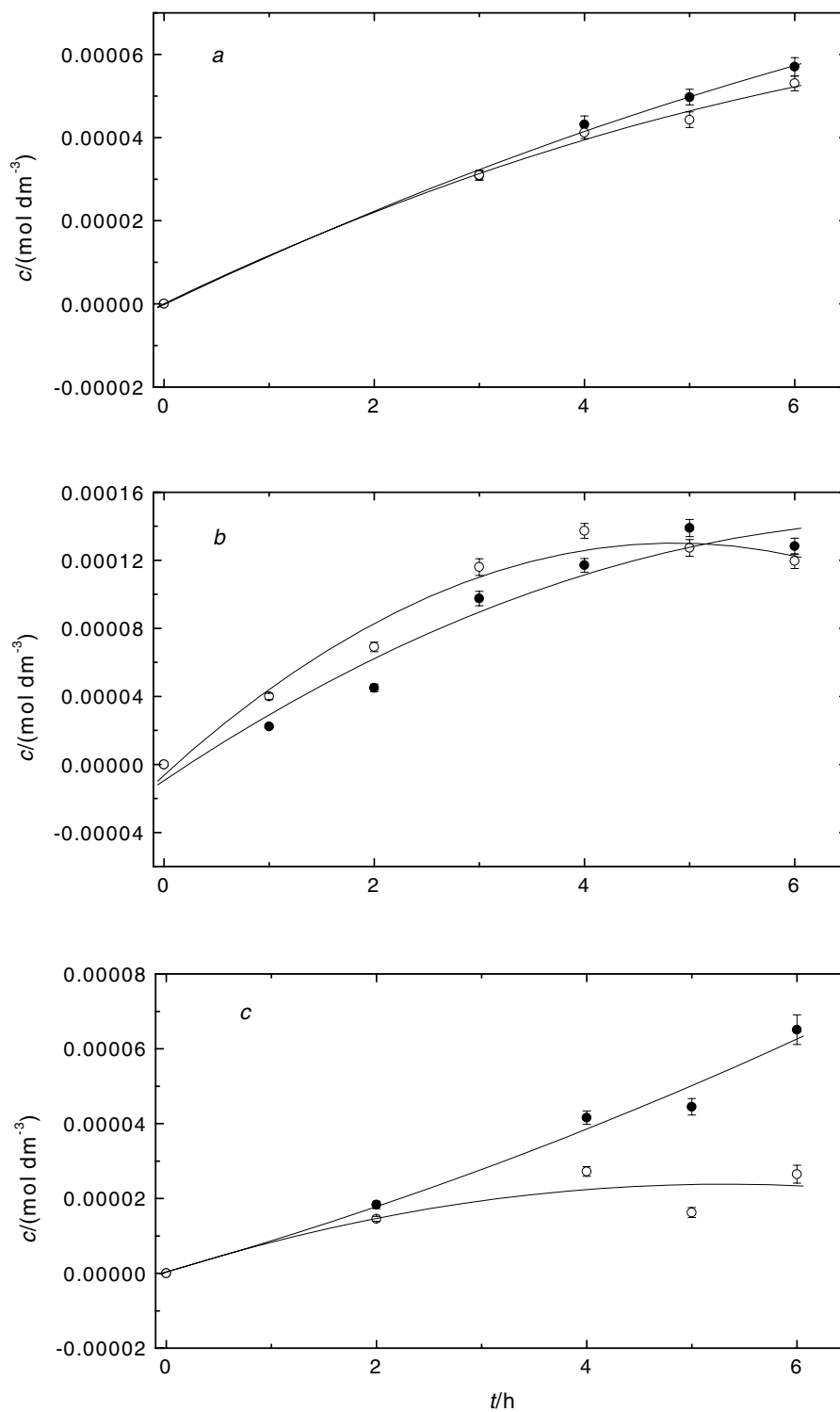
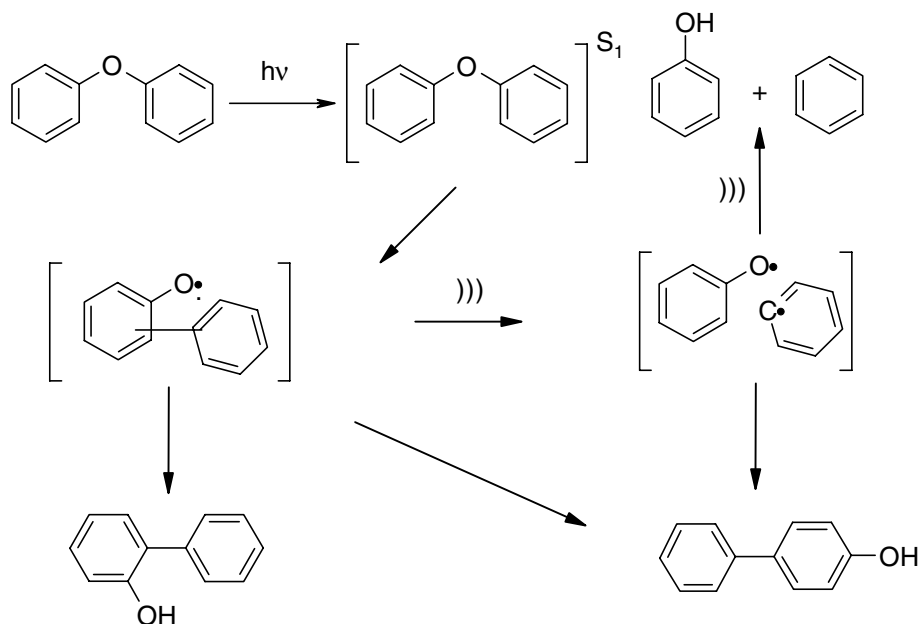


Fig. 4. Product distribution of diphenyl ether ($c = 0.01 \text{ mol dm}^{-3}$) photolysis in propan-2-ol. a) Phenol, b) 2-hydroxybiphenyl, c) 4-hydroxybiphenyl (● without SONO, ○ with SONO).

tion rate by ultrasound can be explained by assuming that some exciplexes are involved in this photocleavage and ultrasound could destroy these exciplexes. Singlet exciplexes as reactive intermediates were detected by *Chiyonobu et al.* [16] at photocycloaddition reactions.

The fact that formation rate of 2-hydroxybiphenyl is not affected by sonication is in accord with the proposed concerted mechanism of its formation [14]. The observed decrease of the rate of 4-hydroxybiphenyl formation can be explained by the fact that it is a radical pair process [14], which is much slower



Scheme 1

than the concerted process, and ultrasound can destroy the solvent cage, the result being the escape of phenyl and phenoxy radicals into the solvent and rise of the phenol and benzene formation (Scheme 1).

It is worth to mention that the rate of the 2-hydroxybiphenyl formation is at least one order of magnitude higher than the rate of 4-hydroxybiphenyl formation (see Figs. 2 and 4).

The fact that ultrasound can enhance the rate of phenol formation at a higher concentration of diphenyl ether is an indirect proof that the solvent cages are destroyed by ultrasound, which results in the enhancement of the reaction of phenoxy radicals with the solvent.

In order to investigate the effect of viscosity on the course of rearrangements of diphenyl ether the photolysis in propan-2-ol and acetonitrile was performed. The results from these experiments are complicated because the ultrasound effect depends on the solvents. However, it can be concluded that ultrasound had a similar effect in all solvents used in this study, which is documented in Fig. 4, when the reaction was carried out in propan-2-ol.

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