

Sono-photolysis of phenylglyoxylic acid and stability studies of D,L-2,3-diphenyltartaric acid

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Abstract

Photodecarboxylation and photoreduction of phenylglyoxylic acid as well as the influence of ultrasound on these reactions were studied. Ultrasound considerably enhanced photodecarboxylation of phenylglyoxylic acid in acetonitrile with low content of water (CH₃CN–H₂O, 0.5%, v/v). No ultrasound effect was observed at higher content of water. Photoreduction of phenylglyoxylic acid resulted in formation of isomers of 2,3-diphenyltartaric acid. We found out that photosonication had no influence on the rate of formation of 2,3-diphenyltartaric acids but affected only the ratio of D,L and *meso* isomers of this acid. The thermal instability of 2,3-diphenyltartaric acids can affect the course of photoreduction of phenylglyoxylic acid. Phenylglyoxylic and benzoic acids were the main products after the thermal decomposition of D,L-2,3-diphenyltartaric acid in 2-propanol. The rate of decomposition of D,L-2,3-diphenyltartaric acid was very sensitive to its concentration, temperature and a presence of oxygen as well as water in the reaction mixture. Sonication caused a large decrease of the rate of decomposition of D,L-2,3-diphenyltartaric acid.

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1. Introduction

The photochemistry of α -keto acids and their esters had been already studied [1–3]. Phenylglyoxylic acid as well as its aliphatic analogue, pyruvic acid, undergo photodecarboxylation and photoreduction [1]. Photodecarboxylation was particularly efficient in aqueous solution and benzaldehyde was the main photoproduct. Thermal decarboxylation of carboxylic acids is frequently used reaction in organic synthesis [4], and in the most cases this process is going through the carboxylate anion. Decarboxylation is also important in a number of biological processes, for instance, the thiamine-mediated decarboxylation of pyruvic acid to acetaldehyde and CO₂ [5]. The earlier studies of photodecarboxylation of aliphatic carboxylic acids and lactones had been summarised by Calvert and Pitts [6].

Phenylglyoxylic acid in the mixture of acetonitrile and water (3:1) had been proposed as a convenient chemical actinometer for the 250–400 nm region [7].

Photoreduction process was observed when phenylglyoxylic acid was irradiated in organic solvents, which are good donor of hydrogen. The main products of this reaction

were D,L- and *meso*-2,3-diphenyltartaric acids [7–10]. It is known that the reaction proceeds via T₁ (λ_{\max} =322 nm) state.

Also, it is known that non-homogeneous absorption of light creates concentration gradient of excited states or reaction intermediates in photochemical reactor (Fig. 1). Concentration of excited molecules or reaction intermediates, respectively, is not constant in all reaction mixture (Fig. 1a). If the reaction order $n \neq 1$, then the rate of the reaction depends on the concentration of the excited molecules or reaction intermediates and is a function of d (distance of concentration gradient from the lamp). Photochemists can change this gradient by stirring of reaction mixture using ultrasound [11–13]. When sonication is applied to this system, significant changes should be produced. Acoustic cavitation and shock waves generate an intense mixing, which has led to consider a sonicated vessel as a perfectly agitated reactor, i.e. a domain where the concentration of the solutes is the same at any point. Thus, when sonication is applied to the photochemical irradiation (for intermediates with long lifetime), Fig. 1a becomes Fig. 1b.

The goal of this work was to study the effect of ultrasound on the photodecarboxylation of phenylglyoxylic acid, photochemical synthesis of D,L- and *meso*-2,3-diphenyltartaric acids, the influences of different factors on the

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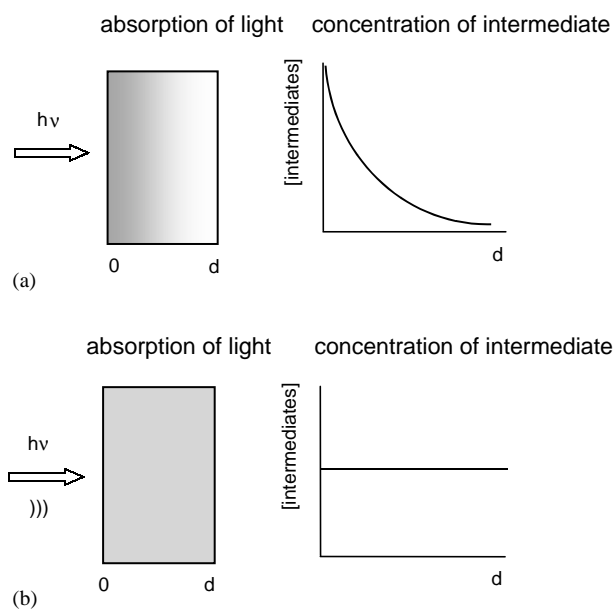


Fig. 1. (a) Non-homogenous absorption of light and (b) homogenous absorption of light in the presence of ultrasound (d is the distance of concentration gradient from the lamp).

stability of D,L-2,3-diphenyltartaric acid, as well as to compare the effect of mechanical stirring (bubbling by nitrogen or oxygen) and ultrasound stirring of the reaction mixture.

2. Experimental details

2.1. Materials

Phenylglyoxylic acid (Merck, >99%) was recrystallised from benzene–petroleum. Acetonitrile and 2-propanol (Lichrosolv grade, Merck) were used without further purification. Redistilled water was used in the study. Purity of products was established by elemental analysis and melting point [7].

2.2. Analytical methods

UV-Vis spectra were measured at room temperature using diode array spectrophotometer HP 8452A.

ESR spectra were recorded using ERS 230 (ZWG Akad. Wiss., Berlin, Germany), working in the X band (~ 9.3 GHz) at modulating amplitude 0.1 mT and microwave power 5 mW. The spin trapping method was used to determine short time living radical species. *N-tert*-Butyl- α -phenylnitron was used as the spin trap.

Elementar analysis was carried out with CHN analyser Carlo Erba 1106.

Isotachophoretic analysis (ITP) of the samples was performed on Analyser ZKI-O2 (Labeco Co., Spišská Nová Ves, Slovakia) using a column-coupling technique. The diameter of the pre-separation column was 0.8 and 0.3 mm for

the analytical column. Both columns were equipped with a conductivity detector.

2.2.1. Photodecarboxylation of phenylglyoxylic acid and decomposition of D,L-diphenyltartaric acid

Determination of ions was accomplished by the following electrolyte system—solvent: H₂O; leading ion: 10 M chloride; counter ion: bis-tris propane, β -alanine; additive: 0.1% (w/v) methyl-hydroxyethyl cellulose (m-HEC); pH = 3.6; terminating ion: 5 M caproic acid; counter ion: histidine; pH = 6.0.

2.2.2. Preparation of D,L- and meso-diphenyltartaric acids by irradiation of phenylglyoxylic in 2-propanol

Determination of ions was accomplished by the following electrolyte system—solvent: H₂O; leading ion: 10 M chloride; counter ion: histidine; additive: 0.1% (w/v) m-HEC; pH = 6.0; terminating ion: 5 M caproic acid; counter ion: histidine; pH = 6.0.

2.3. Experimental set-up

All the experiments were carried out with the set-up described previously [11,12]. The photochemical reactor was equipped with a glass (SIMAX) insertion cell and the ultrasound emitter (25 kHz, 16 W cm⁻²). Temperature was kept constant at 18 °C by circulation of water. The source of UV light was mercury 125 W lamp from Tesla Holešovice, Czech Republic.

Photolysis and sono-photolysis were performed with 180 ml of 0.025 M solutions of phenylglyoxylic acid in the mixture of acetonitrile and water as well as in 2-propanol. For ITP analysis, the mixture of acetonitrile and water was removed by vacuum pump and the residue was dissolved with water. Concentration of solution used for decomposition of photodimer was 1×10^{-3} and 5.7×10^{-3} M. The samples were deaerated (saturated) by bubbling of nitrogen (or oxygen) through the solution, before and during the irradiation. The reaction was monitored by withdrawal of aliquots volume of the solution. Phenylglyoxylic acid, benzoic acid and D,L- and meso-2,3-diphenyltartaric acid were analysed by isotachophoretic method in water. 2-Propanol was removed by stream of nitrogen and then the samples were dissolved in water. Absolute concentrations of reactants and products were determined by ITP. In comparison with ITP, the same results were obtained by UV analysis. All the experiments, with and without sonication, were performed under identical conditions.

3. Results and discussion

3.1. The influence of ultrasound on photodecarboxylation of phenylglyoxylic acid

In this study, we compared the photodecarboxylation of phenylglyoxylic acid with and without ultrasound. In

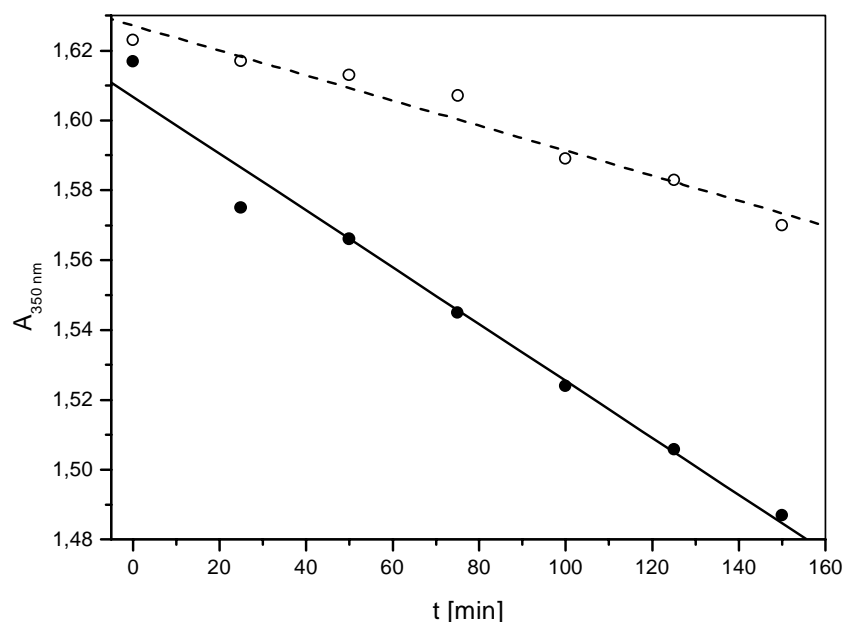


Fig. 2. Photodecarboxylation of phenylglyoxylic acid (0.025 M, 20 °C) in the mixture of CH₃CN–H₂O (0.5%, v/v): (●) with and (○) without ultrasound.

agreement with [12], we did not observe any ultrasound effect on the rate of photodecarboxylation of phenylglyoxylic acid, which is a monomolecular reaction. No effect of ultrasound was observed in water or in the mixture of acetonitrile–water (25%, v/v of water). These results were proved by ITP and UV analyses. On the other hand, we observed effect of ultrasound on this reaction when content of water in acetonitrile was very low (0.5%, v/v). In this case, ultrasound increased the rate of photodecarboxylation of phenylglyoxylic acid (Fig. 2). These results proved that molecules of water had influence on the photodecarboxylation process probably via water-assisted fission of the C–C bond. We supposed limited dissociation of phenylglyoxylic acid in mixture with the low content of water. Higher content of water in the mixture with acetonitrile increased the dissociation of phenylglyoxylic acid.

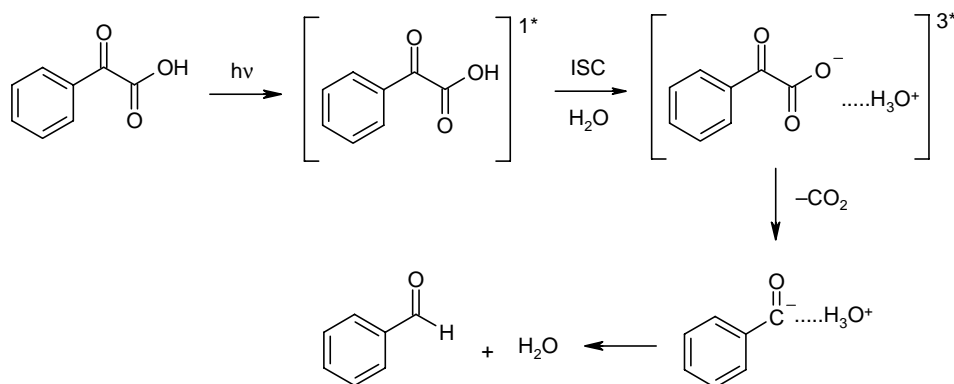
If we accepted the mechanisms [8,14] of photodecarboxylation of phenylglyoxylic acid, then ultrasound can

enhance the reaction rate because reaction become bimolecular when the content of water in the reaction mixture is low (Scheme 1).

Application of ultrasound on this photoreaction enhances the probability of interaction between the molecules of water and excited triplet state of acid. Consequently, excited state of the carboxyl group was deprotonated. If the content of water is high, the course of this reaction can be described by the pseudo-first order equation. Therefore, we did not observe any effect of ultrasound on the course of photoreaction.

3.2. The influence of ultrasound on photoreduction of phenylglyoxylic acid

It is well known that irradiation of phenylglyoxylic acid leads to the formation of a primary radical pair via hydrogen transfer from 2-propanol to the excited triplet



Scheme 1.

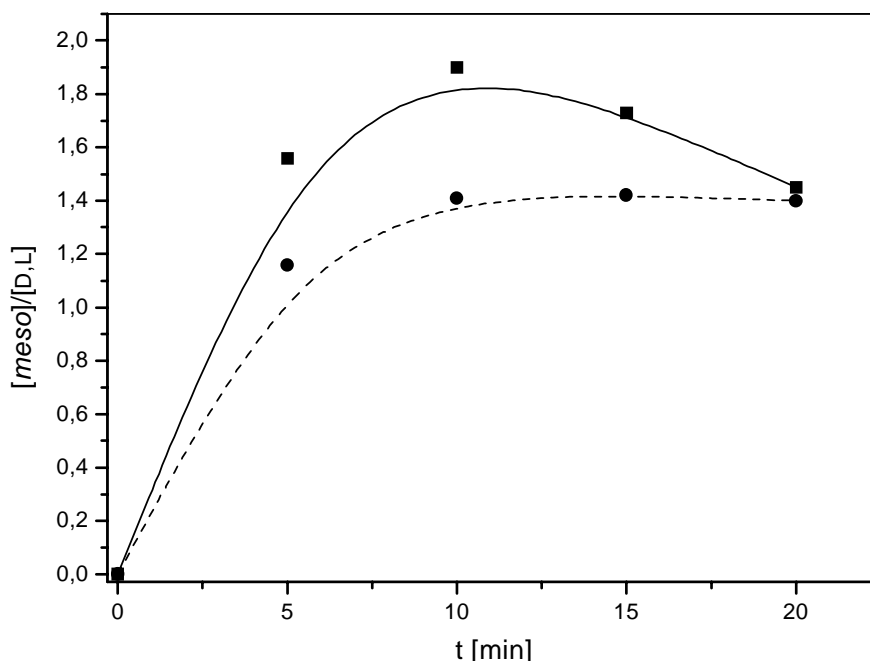
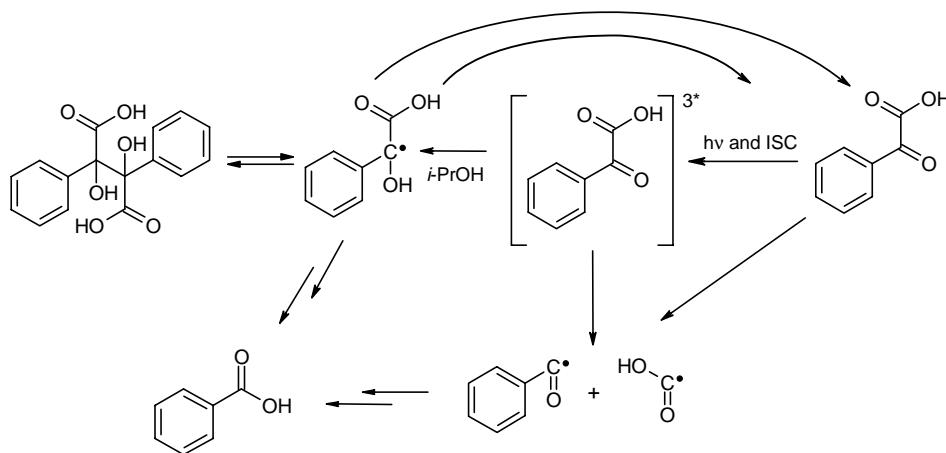


Fig. 3. Irradiation of phenylglyoxylic acid in 2-propanol and effect of ultrasound on ratio $[meso]/[D,L]$ of diphenyltartaric acid: (●) with and (■) without ultrasound.

state of the acid. Escaping α -carboxy- α -hydroxybenzyl (ketyl) radicals were involved in several recombination reactions. Main products of photoreduction were D,L- and *meso*-2,3-diphenyltartaric acids produced by dimerisation of two ketyl radicals [7,10]. The yield of products was dependent on reaction conditions as well as on the stability of the isolated products. We attempted to isolate both diastereomers by crystallisation [7] but we were not able to isolate a pure *meso*-2,3-diphenyltartaric acid. The *meso* form is probably less stable than the D,L form. We assumed that different intramolecular H bonds affected stability of these forms of 2,3-diphenyltartaric acid. For this reason,

the isolation of *meso* form of 2,3-diphenyltartaric acid was complicated.

Defoin et al. [7] have found that quantum yields of photoreduction of phenylglyoxylic acid in 2-propanol gave irreproducible results. They have suggested that the formation of D,L- and *meso*-2,3-diphenyltartaric acids was sensitive to the impurities. This explanation cannot be fully accepted, because quantum yields of photoreduction of many carbonyl compounds are good reproducible. We assumed that the impurities were not the only reason of these difficulties, and the thermal instability of D,L- and *meso*-2,3-diphenyltartaric acids can also be important. The stability of ketyl radicals



Scheme 2.

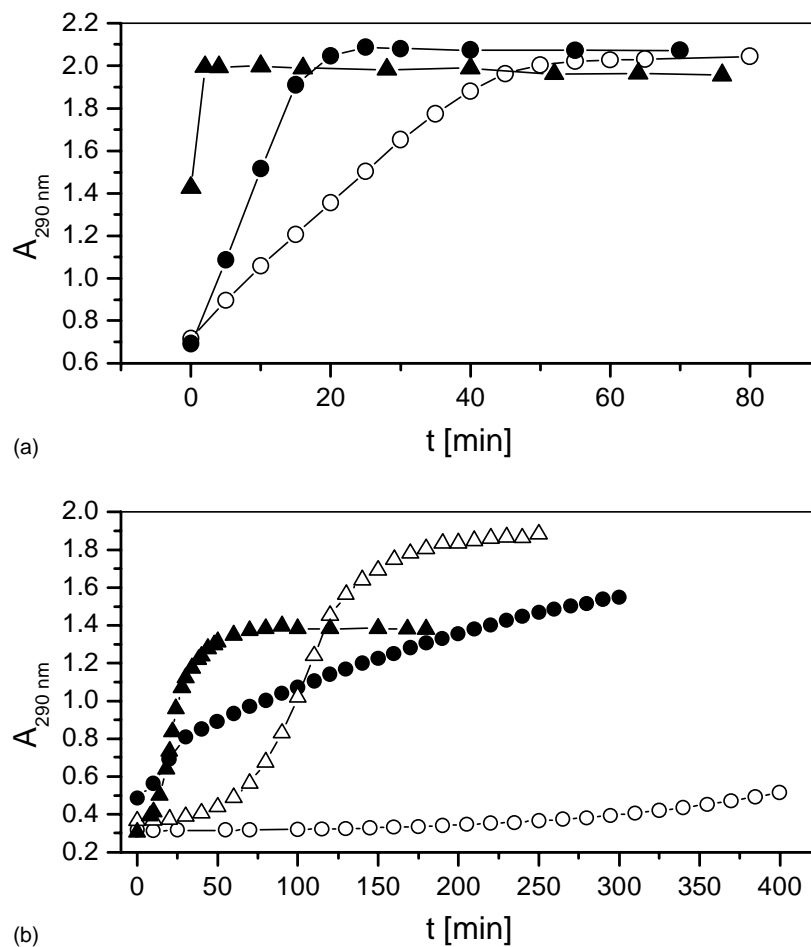


Fig. 4. Effect of temperature and water content on the rate of formation of phenylglyoxylic acid from D,L-2,3-diphenyltartaric acid ($c = 1 \times 10^{-3}$ M) in: (a) 2-propanol and (b) 2-propanol–H₂O (1:1) ((○) 20°C, (●) 30°C, (△) 40°C, and (▲) 50°C).

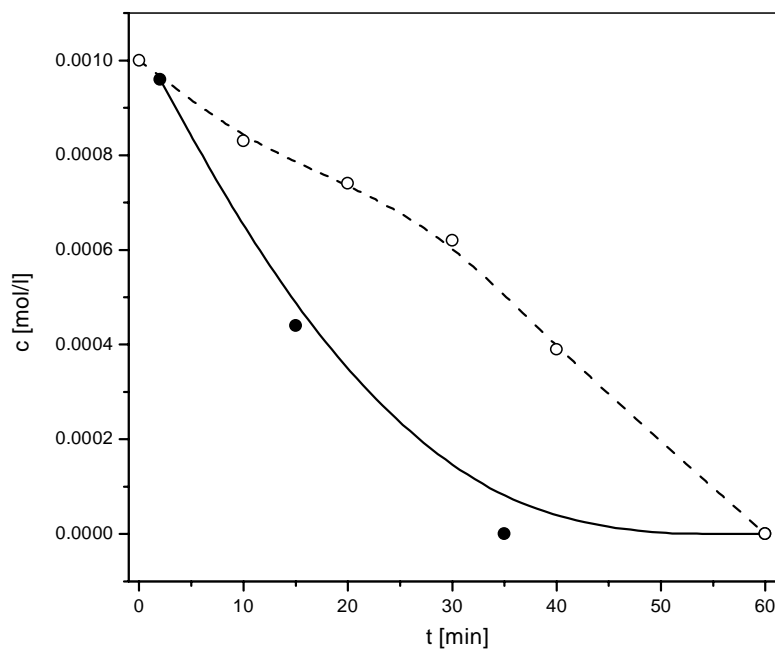
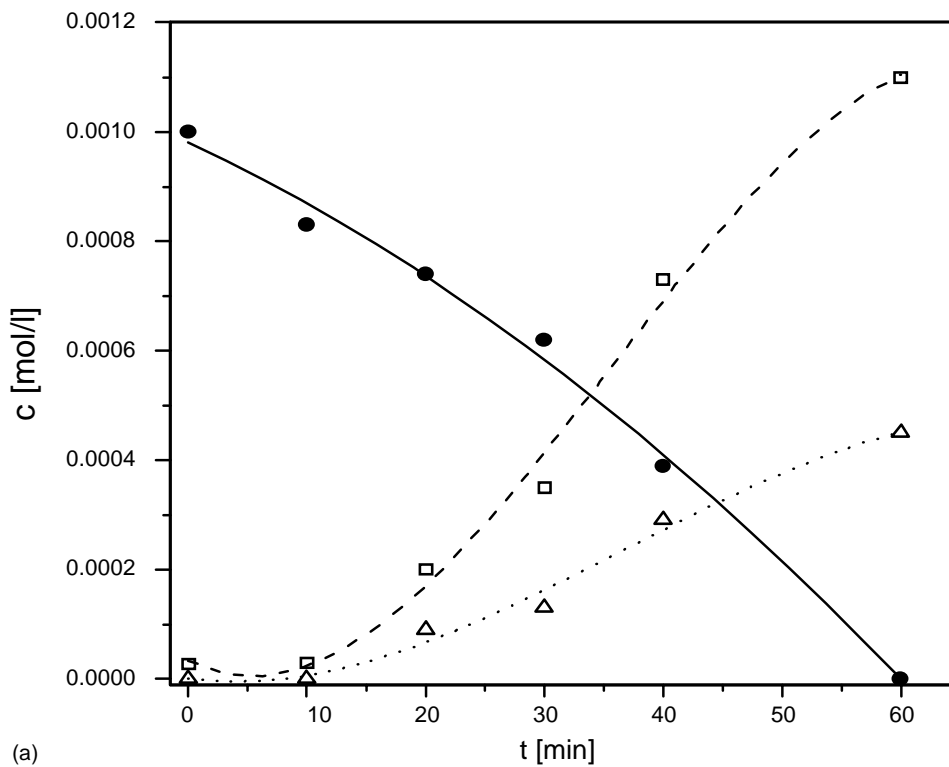
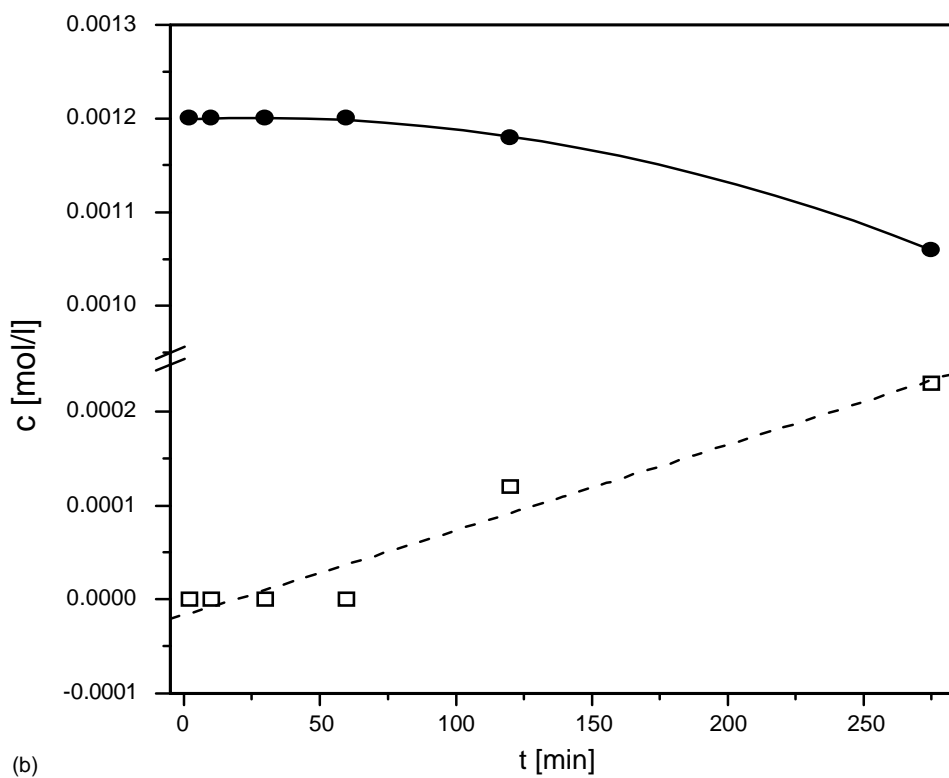


Fig. 5. Rate of decomposition of D,L-2,3-diphenyltartaric acid ($c = 1 \times 10^{-3}$ M, 20°C) in: (○) 2-propanol and (●) solution of phenylglyoxylic acid ($c = 2 \times 10^{-3}$ M) in 2-propanol.



(a)



(b)

Fig. 6. Effect of oxygen on the rate formation of phenylglyoxylic (□) and benzoic (Δ) acids from D,L-2,3-diphenyltartaric acid (●) in 2-propanol (20 °C): (a) with and (b) without oxygen.

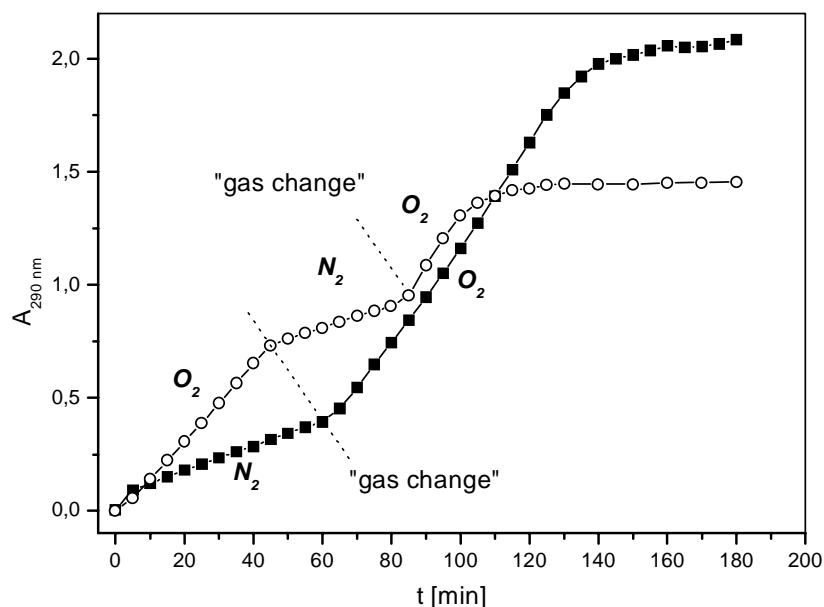


Fig. 7. Effect of oxygen concentration on rate of formation of phenylglyoxylic acid from decomposition of D,L-2,3-diphenyltartaric acid (20 °C, $c = 1 \times 10^{-3}$ M) in 2-propanol.

of 2,3-diphenyltartaric acid can play an important role in the decomposition of this acid. We decided to investigate the thermal instability of both 2,3-diphenyltartaric acids to test our hypothesis. If our assumption about the small thermal stability of 2,3-diphenyltartaric acids was right, then the thermal decomposition of this acid would be the source of ketyl radicals (discussed later in this paper).

Further, we observed no influence of ultrasound on the rate of photoreduction of phenylglyoxylic acid. We found out that ultrasound changed the ratio of D,L and *meso* isomers of 2,3-diphenyltartaric acid after irradiation of phenylglyoxylic acid (Fig. 3).

3.3. Thermal decomposition of D,L-2,3-diphenyltartaric acid

We focused our attention on the thermal decomposition of D,L isomer of diphenyltartaric acid, because we did not isolate the *meso* form in sufficient purity. Decomposition of D,L-form of diphenyltartaric acid gave phenylglyoxylic and benzoic acid (Scheme 2).

Both products were determined by ITP compared with the standards. Presence of two kinds of radicals (Scheme 2) was proved by ESR experiments. One of these radicals was $\text{PhC}^{\bullet}(\text{OH})(\text{COOH})$ [8] and another one was benzoyl. We did not find mandelic acid in the reaction mixture after thermal decomposition of D,L-2,3-diphenyltartaric acid in 2-propanol. Rate of formation of phenylglyoxylic acid from D,L-2,3-diphenyltartaric acid was the function of temperature and content of water in 2-propanol (Fig. 4).

Presence of water decreased the rate of decomposition of D,L-2,3-diphenyltartaric acid. The case depicted in Fig. 4b is typical for catalytic reactions. The course of the reaction was in agreement with the dependence on concentration of phenylglyoxylic or benzoic acid, respectively (Fig. 5). These acids acted as catalysts of decomposition which is an example of autocatalytic reaction.

Water destroyed intramolecular H bonds in the molecule of D,L-2,3-diphenyltartaric acid. Unlike phenylglyoxylic or benzoic acid, water is a weak acid (can act here as the base) and increased relatively the dissociation of D,L-2,3-diphenyltartaric acid. The anion of D,L-2,3-diphenyltartaric acid was not convenient for decomposition. The degree of dissociation was then indirectly related to the rate of molecular ionisation.

Concentration of oxygen in solution also had a significant role in decomposition of D,L-2,3-diphenyltartaric acid (Fig. 6). Presence of oxygen increased the decomposition rate. Initially formed ketyl radical was trapped by oxygen and subsequently peroxy radical was formed. This radical then oxidised another molecule of diphenyltartaric acid and propagated the chain reaction.

The change of decomposition rate was observed when oxygen was replaced by nitrogen (Fig. 7).

Reaction, which took place in oxygen-saturated 2-propanol gave lower concentration of phenylglyoxylic acid compared to nitrogen-saturated solution. In the nitrogen-saturated solution, only phenylglyoxylic acid was formed. When reaction was performed in oxygen-saturated solution, both phenylglyoxylic and benzoic acids were formed and the concentration of diphenyltartaric acid was decreased rapidly.

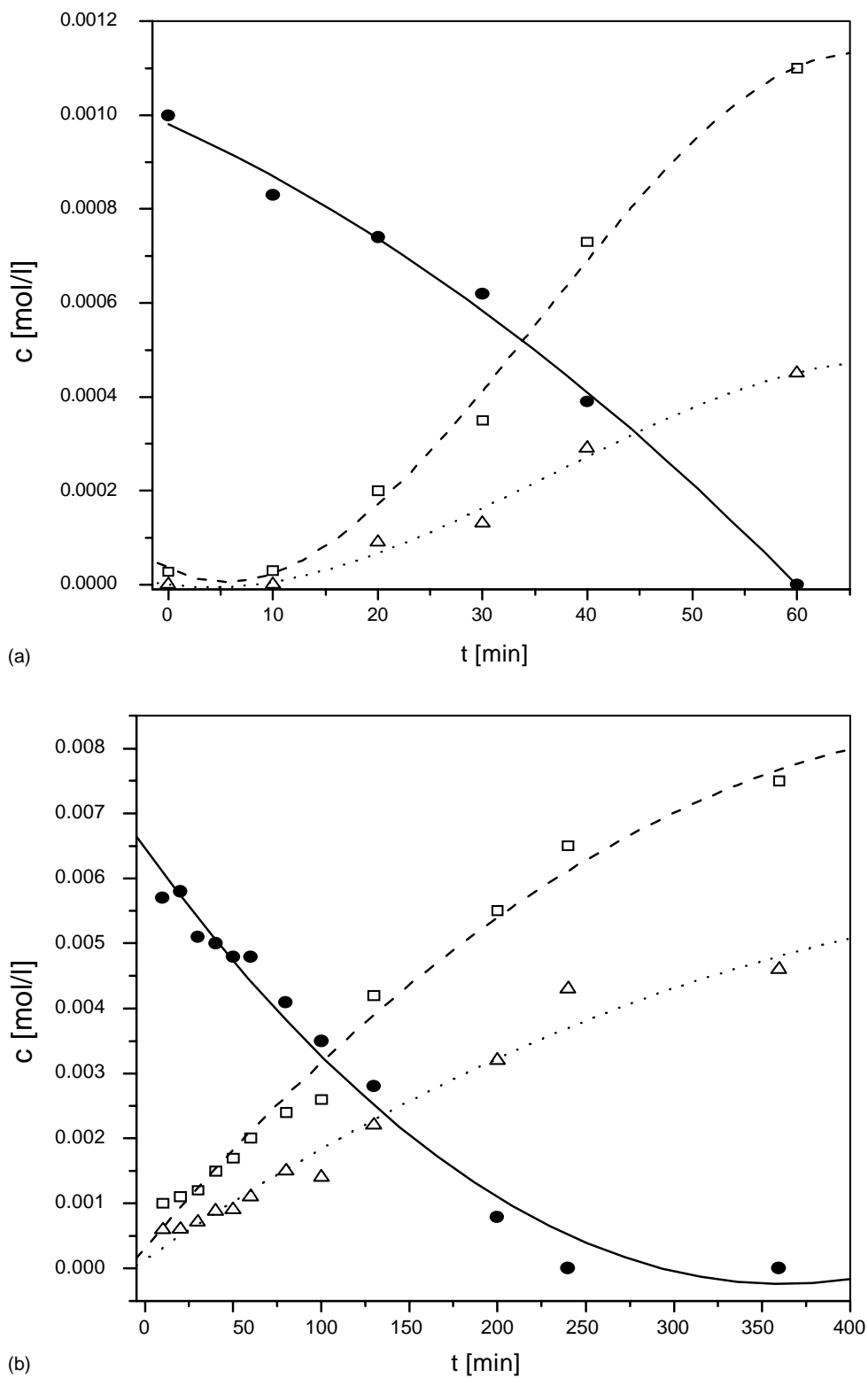


Fig. 8. Decomposition of D,L-2,3-diphenyltartaric acid (●) in 2-propanol as a function of its concentration at 20°C ((a) 1×10^{-3} M and (b) 5.7×10^{-3} M), and formation of phenylglyoxylic (□) and benzoic (Δ) acids.

Concentration of D,L-2,3-diphenyltartaric acid also had an influence on this decomposition. The rate of decomposition was inversely dependent on its concentration (Fig. 8).

3.4. Ultrasound effect on the thermal decomposition of D,L-2,3-diphenyltartaric acid

We observed large effect of ultrasound on thermal decomposition of D,L-2,3-diphenyltartaric acid in 2-propanol. The ultrasound decreased the rate of decomposition of this acid (Fig. 9).

Decomposition of D,L-2,3-diphenyltartaric acid in 2-propanol took place through a primary radical pair formed by fission of C–C bond. The difference between decomposition of diphenyltartaric acid with and without ultrasound can be explained by the fact that the ketyl radical disappeared from the solution by reaction with oxygen. Sonication of the reaction mixture expelled the oxygen from the solution and decreased the rate of decomposition. The effect of oxygen on the course of reaction corresponded with our explanation (Fig. 6).

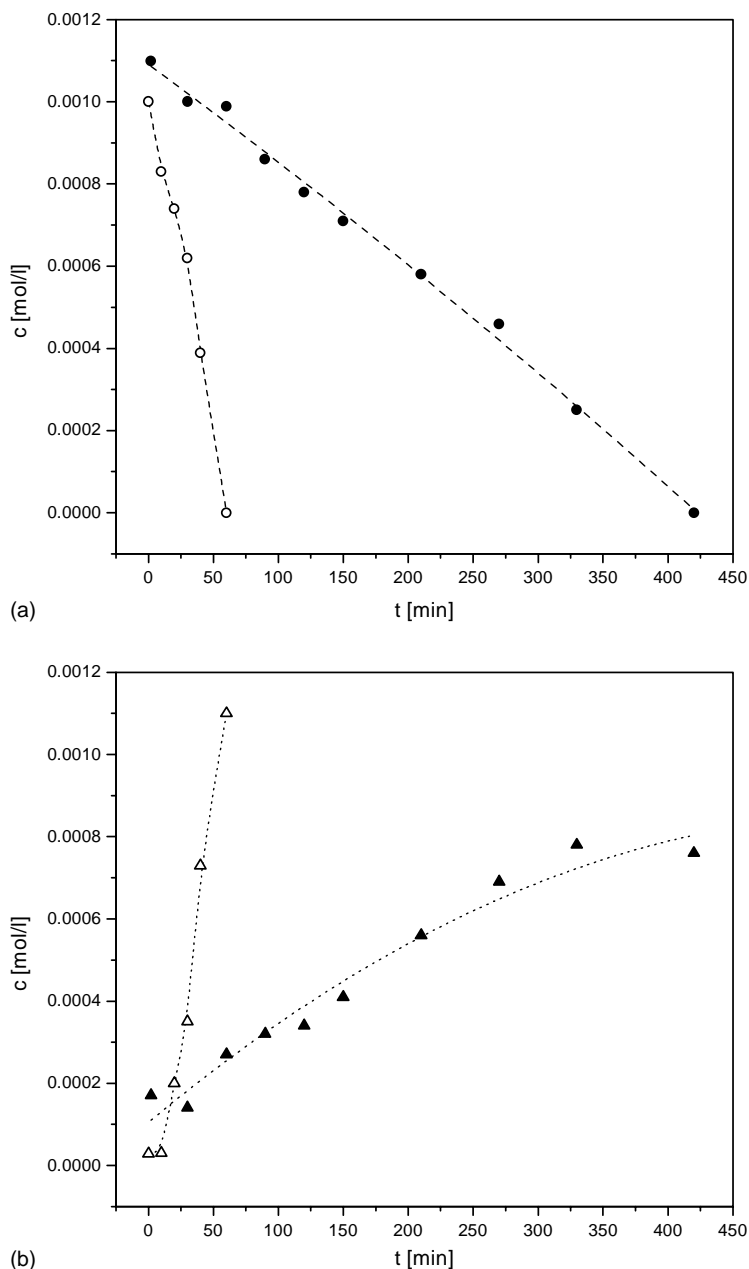


Fig. 9. (a) Rate of decomposition of D,L-2,3-diphenyltartaric acid in 2-propanol: (●) with and (○) without ultrasound. (b) Formation of phenylglyoxylic acid from decomposition: (▲) with and (△) without ultrasound. (c) Formation of benzoic acid from decomposition: (■) with and (□) without ultrasound.

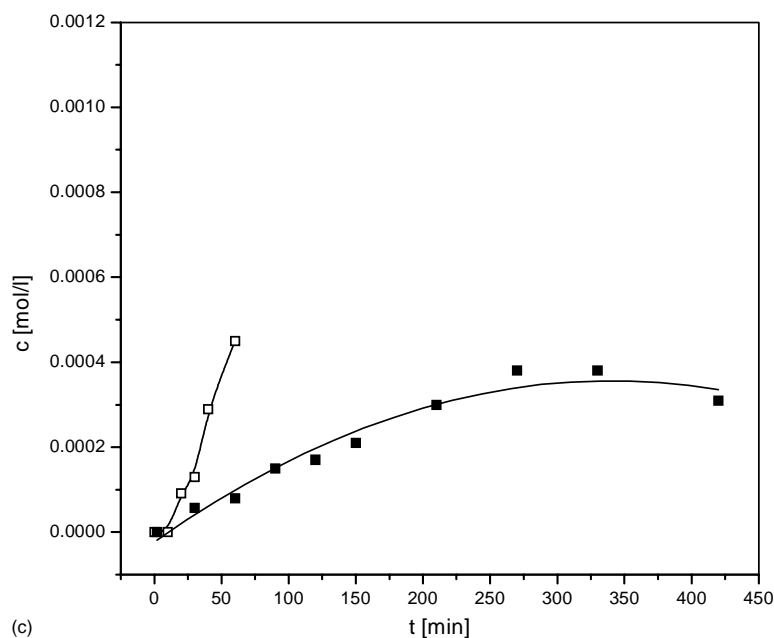


Fig. 9. (Continued).

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References

- [1] P.A. Leermakers, G.F. Vesley, *J. Am. Chem. Soc.* 85 (1963) 3776–3779.
- [2] B.M. Monroe, *Adv. Photochem.* 8 (1971) 97–98.
- [3] S. Hu, D.C. Neckers, *J. Photochem. Photobiol. A: Chem.* 118 (1998) 75–80.
- [4] J. March, *Advanced Organic Chemistry*, third ed., Wiley, New York, 1985.
- [5] A. Fersht, *Enzyme Structure and Mechanism*, Freeman, Reading, UK, 1977.
- [6] J.G. Calvert, J.N. Pitts Jr., *Photochemistry*, Wiley, New York, 1966.
- [7] A. Defoin, R. Defoin-Straatmann, K. Hildenbrand, E. Bittersmann, D. Kreft, H.J. Kuhn, *J. Photochem.* 33 (1986) 237–255.
- [8] H.J. Kuhn, H. Görner, *J. Phys. Chem.* 92 (1988) 6208–6219.
- [9] T. Fujisawa, B.M. Monroe, G.S. Hammond, *J. Am. Chem. Soc.* 92 (1970) 542–544.
- [10] T. Fujisawa, G.S. Hammond, *J. Am. Chem. Soc.* 94 (1972) 4175–4177.
- [11] A. Gáplovský, M. Gáplovský, Š. Toma, J.-L. Luche, *J. Org. Chem.* 65 (2000) 8444–8447.
- [12] A. Gáplovský, J. Donovalová, Š. Toma, R. Kubinec, *J. Photochem. Photobiol. A: Chem.* 115 (1998) 13–19.
- [13] A. Gáplovský, Š. Toma, J.-L. Luche, T. Kimura, B. Jakubíková, K. Gáplovská, *J. Photochem. Photobiol. A: Chem.* 152 (2002) 135–140.
- [14] H. Görner, H.J. Kuhn, *J. Chem. Soc., Perkin Trans. 2* (1999) 2671–2680.