

Ultrasound Effect on the Course of Gif Reactions

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The effect of ultrasound on cyclohexane and cyclooctane oxidation under Gif conditions was studied. Ultrasound considerably enhanced the oxidation when hydrogen peroxide was used as an oxidant. Higher cyclohexanone content was achieved after 30 min sonication than after 24 h of silent reaction. Just a minor ultrasound effect was observed when *tert*-butyl hydroperoxide was used as the oxidant.

The first paper on hydrocarbon oxidation under conditions similar to the physiological conditions was published in 1983 by *Barton* [1], who observed an easy adamantane oxidation by hydrogen peroxide in pyridine, using iron(III) chloride as the catalyst. Since then, great attention has been paid to this process, known as Gif reaction and the progress of work in this field has been the subject of two reviews [2, 3]. A vivid discussion has spread about the mechanism of Gif reaction: While *Barton* [4] favoured the nonradical SET mechanism, *Perkins* [5] preferred the radical mechanism.

The Gif reactions need very long reaction time (up to 24 h) to reach a reasonable conversion at the classical conditions. On the other hand, ultrasound should accelerate both radical and SET processes [6, 7]. Therefore we decided to examine the effect of ultrasound on the reaction rate and the products distribution as well as Gif reactions using hydrogen peroxide promoting nonradical SET mechanism and *tert*-butyl hydroperoxide as the oxidant promoting radical mechanism.

EXPERIMENTAL

tert-Butyl hydroperoxide (TBHP) and hydrogen peroxide were purchased from Fluka. Cyclooctane, cyclohexane, pyridine, and picolinic acid were purchased from Aldrich. FeCl₃ and triphenyl phosphine (PPh₃) were purchased from Avocado.

The sonochemical Gif reactions with hydrogen peroxide [8] and *tert*-butyl hydroperoxide [9, 10] as the oxidants were performed at the same conditions as described for conventional reactions. Ultrasonic horn-type reactor, UUA 001 Ultragen (Nitra, Slovakia) (20 kHz, 300 W) under pulsed conditions (pulse length:

4 s; 50 % duty) was used throughout the study. The conventional experiments were performed at the same conditions. The concentration of the reaction products was determined by GC-MS analysis of the reaction mixture. 0.5 cm³ of crude reaction mixture was taken for GC-MS analysis with 2 mm³ of *p*-xylene as internal standard.

Typical reaction was performed under following conditions:

Silent oxidation: Reaction mixture consisted of 15 cm³ of pyridine, 0.5 mmol of FeCl₃, 1.5 mmol of picolinic acid, and 20 mmol of hydrocarbon (cyclohexane or cyclooctane). Hydrogen peroxide (14 mmol of 30 % H₂O₂) was slowly added to cold mixture and let at room temperature for 24 h.

Sonicated oxidation: Reaction mixture had the same composition as at silent reaction. Hydrogen peroxide (14 mmol of 30 % H₂O₂) was slowly added to the sonicated mixture during first 5 min and sonication was ended after elapsing chosen reaction time. Reaction mixture has to be cooled with ice bath during sonication.

Reaction with PPh₃: Composition of the reaction mixture was the same as above, just instead of picolinic acid, 1.5 cm³ of acetic acid was used and 10 mmol of PPh₃ was added (in accord with [11]).

Reaction with *tert*-butyl hydroperoxide: Conditions are the same as in reaction with H₂O₂ oxidant, just as oxidant 5 mmol of TBHP are used.

DISCUSSION

It is obvious (Table 1) that ultrasound enhanced considerably the cyclohexane oxidation with hydrogen peroxide in pyridine under FeCl₃ catalysis. Especially the application of ultrasound enhanced the formation

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Table 1. Gif Oxidation of Cyclohexane with Hydrogen Peroxide ($n(\text{products})/\text{mmol}$)

Products	Gif		US (Gif)			
	24 h	120 min	30 min	60 min	90 min	120 min
Cyclohexanol	0.042	0.032	0.095	0.08	0.083	0.094
Cyclohexyl chloride	0.012	0.009	0.240	0.143	0.012	0.017
Cyclohexanone	0.870	0.620	0.985	1.010	1.045	1.081

Table 2. Gif Oxidation of Cyclohexane with Hydrogen Peroxide and PPh_3 Addition ($n(\text{products})/\text{mmol}$)

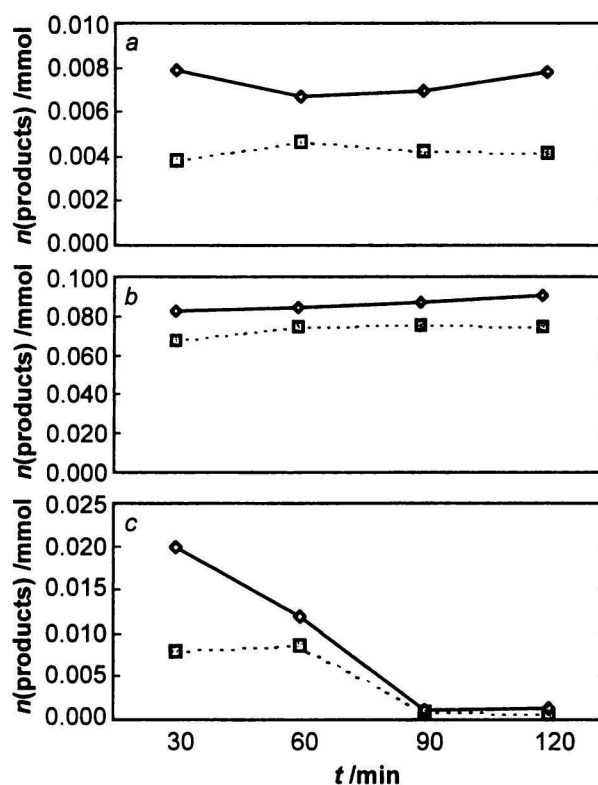
Products	Gif	US (Gif)			
	24 h	30 min	60 min	90 min	120 min
Cyclohexanol	0.016	0.203	0.219	0.222	0.215
Cyclohexyl chloride	0.349	0.277	0.269	0.286	0.271
Cyclohexanone	0.033	0.050	0.072	0.069	0.061

of cyclohexanol and cyclohexanone: higher yields of these products were obtained after 30 min sonication than after 24 h of stirring. The yields can be further increased by prolonged sonication (2 h). Also interesting could be the fact that the amount of cyclohexyl chloride in sonochemical experiments decreases by prolonging reaction time. This can be caused by well-known decomposition of halogenated solvents by ultrasound [12, 13].

It is also well known that hydrogen peroxide is produced by water sonolysis [11]. Therefore we performed the experiment in which water was added instead of hydrogen peroxide into the reaction mixture, but a formation of products was not detected. The most probable reason is that very low concentration of hydrogen peroxide was formed. Very interesting fact results from an experiment without picolinic acid. It is known that adding of picolinic acid to reaction enhances reaction rate $10\,000 \times$ [8]. To our surprise the reasonable amount of cyclohexanone (0.27 mmol) was determined in the reaction mixture after 2 h sonication without addition of picolinic acid. In silent reaction just traces of products were detected.

We tested also the effect of ultrasound on Gif reaction performed with addition of triphenylphosphine. From the results given in Table 2 it follows that even in such experiments ultrasound enhanced considerably the cyclohexanol formation, but not formation of cyclohexyl chloride. Surprisingly the decrease of cyclohexanone concentration was observed, probably due to the fact that cyclohexanone was consumed by some side reaction. It is in contradiction with results of silent process [11] and could indicate some ultrasound switching of the reaction course.

Another point of interest was to examine if ultrasound could change the order of cyclohexane *vs.* cyclooctane reactivity. That reaction was designed as the test for nonradical course of Gif reactions using hydro-

**Fig. 1.** The comparison of cyclohexane and cyclooctane in sonochemical Gif reaction. Products' concentration is normalized per number of hydrogen atoms. a) ■ Cyclooctanone, ♦ cyclohexanone; b) ■ cyclooctanol, ♦ cyclohexanol; c) ■ cyclooctyl chloride, ♦ cyclohexyl chloride.

gen peroxide as the oxidant [10]. Our results given in Fig. 1 proved higher reactivity of cyclohexane, which is in accord with the Barton's nonradical mechanism.

Our experiments on ultrasound effect on Gif oxidation using *tert*-butyl hydroperoxide as an oxidant

Table 3. Gif Oxidation of Cyclohexane with *t*-Butyl Hydroperoxide (*n*(products)/mmol)

Products	TBHP			US (TBHP)
	24 h, 20 °C	5 h, 60 °C	2 h, 20 °C	2h, 20 °C
Cyclohexanol	0.011	0.072	0.0042	0.053
Cyclohexyl chloride	0.004	0.138	0.0025	0.006
Cyclohexanone	0.233	0.945	0.024	0.045

revealed that ultrasound just slightly accelerated this type of reaction (Table 3). This calls the proposed radical mechanism for this oxidation in question, under the assumption that the hypothesis according to which ultrasound accelerates the radical reactions is valid.

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