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Microwave photochemistry. Photoinitiated radical addition of tetrahydrofuran to perfluorohexylethene under microwave irradiation

Vladimír Církva, Milan Hájek*

Institute of Chemical Process Fundamentals, AS CR, Rozvojová 135, 6-Suchdol, 165 02 Prague, Czech Republic

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Abstract

Generation of UV radiation by microwave field has been applied to a photochemical reaction of perfluorohexylethene with tetrahydrofuran. Reactions were carried out under microwave and UV combined irradiation using a new simple photochemical reactor developed for organic synthetic reactions. Comparative experiments with conventional mercury lamps showed the higher efficiency of microwave electrodeless lamps providing high yield of product in shorter reaction time. © 1999 Elsevier Science S.A. All rights reserved.

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In recent years, the activation of chemical reactions by microwave (MW) energy has become a very attractive tool in synthetic organic chemistry because of its great ability to accelerate reactions and to improve yields and selectivity [1,2]. Microwaves are considered as a new method for activation of chemical reactions, in addition to UV irradiation and ultrasound, even though the microwave energy is substantially lower than that of UV irradiation (E_{MW}=1.6×10^{-3} eV, E_{UV}=4.1 eV) and, therefore, is not sufficient to cleave chemical bonds.

Our idea was to apply microwave irradiation to photochemistry, i.e. to examine combination of MW and UV energy for activation of chemical reactions. This approach has not yet been applied. The above combination has so far been exploited only in such processes like sterilization [3], waste [4] and polymer [5] treatment. We have developed a new MW-UV system for the application in organic synthesis. The unique feature of our system is that UV irradiation is generated by microwaves, i.e. by wireless way. It provides very simple, economic and efficient design of results in simultaneous MW and UV radiation of the reagents.

We have used the fact that mercury lamps generate UV radiation when exposed to electromagnetic field [6]. We have found that a relatively low MW energy output (10–20 W) is sufficient to put the UV lamp in operation. This electrodeless mercury lamp was developed and made by TESLAMP company. The intensity of UV radiation has not been measured at this early stage because the necessary equipment was not available. The UV lamp is simply immersed into the reaction mixture placed in a multimode cavity and exposed to MW irradiation under reflux.

In order to test the microwave photoreactor and simultaneous action of microwave and UV irradiation, the addition of tetrahydrofuran (THF) to perfluorohexylethene has been chosen as a model reaction. Neither microwave- nor photoinitiation of this reaction has been reported. It has only been known that this reaction when thermally initiated under reflux proceeds very slowly (reaction time 5–7 days) [7]. The reaction proceeds via a radical chain mechanism according to Scheme 1.

In the photochemical reaction, perfluorohexylethene (**1**) is excited by UV light absorption to a diradical-like triplet state **3** (initiation) that is able to abstract hydrogen atom from THF to generate the radicals **6** and **4**, in the initiation step, as shown in Scheme 1. The radical **6** starts a propagation cycle by addition to alkene **1** giving the adduct-radical **7** which is transformed to the final product **2**. The fluoroalkane **5** and 2,2′-bioxolane **8** may be formed as byproducts, however in very low yields [8]. In our reaction only formation of monoadduct **2** was observed.

In this study we have performed comparative experiments with mercury UV lamps of two types:

1. conventional medium-pressure UV lamps TESLA (RVK 125 W and RVK 400 W),
2. microwave electrodeless UV lamps TESLAMP (MWL_1 and MWL_2).[1]

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*Corresponding author.

[1] Electrodeless MWL_2 lamp corresponded to three times bigger MWL_1 lamp.

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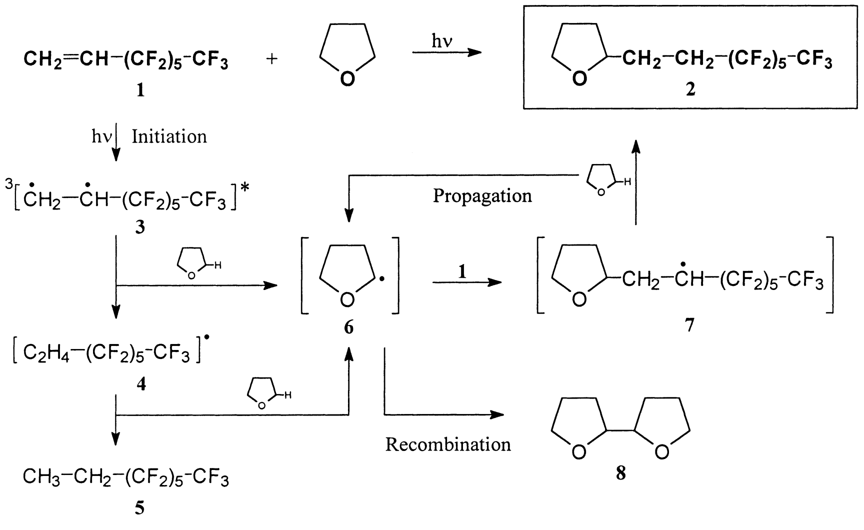

Scheme 1. Reaction path of addition reaction.

Table 1
Radical addition of THF to perfluorohexylethene[a] initiated by UV and/or MW irradiation

Run	Irradiation source[b]	Temperature (°C)	Time (h)	Conversion of **1**[c] (%)	Yield of **2**[d] (%)
	None	64	168	99	76[e]
1	UV (RVK 125W)	20	1	0	0
2		64	1	0	0
3	UV (RVK 400W)	20	1	61	55
4		64	1	63	58
5		64	3	93	88
6	MW	77	1	0	0
7		77	3	0	0
8	MW+UV (MWL_1)	77	1	69	63
9		77	3	96	90
10	MW+UV (MWL_2)	77	1	96	91

[a] THF (72.1 g, 1.00 mol), perfluorohexylethene (6.92 g, 0.02 mol).
[b] RVK (middle-pressure lamp), MWL (microwave electrodeless lamp).
[c] GC analysis.
[d] Isolated yield, b.p.=100–102°C/1.33 kPa. The product **2** was identical with an authentic sample.
[e] Ref. [7].

The first part of experiments was carried out in a commercial immersion-well photoreactor (100 ml) by irradiating the reaction mixture with medium-pressure UV lamps (RVK 125 W or 400 W) at room temperature and under THF reflux (Table 1). On using a low-output lamp RVK 125 W, no reaction has been observed either at room temperature or under reflux (64°C). In the case of the high-output lamp RVK 400 W, the reaction proceeded readily under reflux with the almost complete conversion of fluoroalkene **1** (93%, yield 88%) within 3 h (run 5, Table 1).

The second part of experiments was carried out in the microwave photoreactor placed in a multimode microwave oven.[2] The photoreactor consisted of a round-bottom flask (250 ml) equipped with a reflux condenser (placed out of the oven) and with an electrodeless lamps (MWL_1 or MWL_2) [1] immersed in the reaction mixture. Reactions were carried out under reflux at 77°C under atmospheric pressure (Table 1).[3]

When microwave irradiation was used separately (i.e. without UV irradiation) no reaction occurred (runs 6, 7). This finding comforts with the statement that the energy of microwaves is too low to induce chemical bond cleavage and to initiate radical reactions. On using the MWL_1 lamp, the reaction proceeded readily and provided similar results as with the conventional UV lamp (runs 4, 5 and 8, 9, Table 1).

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[2] All microwave experiments were carried out in MILESTONE Lavis 1000 Basic microwave instrument with 1000 W power output, and equipped with magnetic stirring and PC temperature control via IR thermometer.

[3] The higher boiling point of reaction mixture (77°C instead of 64°C) was caused by superheating of reactants [9] because most of the MW energy was absorbed by the reaction mixture thus brought to boil. From the theory of photochemical reactions it is known that the temperature has a slight effect on photochemical reactions [10].

When the MWL_2 lamp was used, the reaction time was reduced three times, affording the high yield of product **2** (91%, Table 1). Rate enhancement was most likely due to the higher intensity of UV irradiation generated by MWL_2 lamp. An additional effect of microwave irradiation on the reaction rate has not been observed.

In conclusion, the results demonstrate that microwave irradiation can provide UV radiation sufficient for initiation of chemical reactions. A microwave photoreactor with an electrodeless non-contact lamp of simple construction has been found convenient and efficient. Further applications of the microwave irradiation to photochemistry are under study.

Acknowledgements

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