

The electrodeless discharge lamp: a prospective tool for photochemistry Part 6. Photochemistry of valerophenone and 4-nitroanisole in high-temperature water

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Received 21 October 2004; received in revised form 3 December 2004; accepted 7 December 2004

Available online 12 January 2005

Abstract

Two temperature-sensitive model photochemical reactions, the Norrish Type II reaction and photochemical nucleophilic aromatic substitution on 4-nitroanisole by the hydroxide ion, carried out in high-temperature water (100–200 °C) in a pressurized vessel under microwave heating, are reported. The observed chemoselectivity and the ability to increase the solubility of hydrophobic organic compounds in this environmentally friendly solvent are promising results for prospective green (photo)chemical applications.

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Keywords: Photochemistry; Microwave; Electrodeless discharge lamp; High-temperature water; Valerophenone

1. Introduction

Recent experiments have shown that supercritical (above its critical point) but also high-temperature water (HTW) (over 100 °C) has the ability to accelerate organic reactions and enhance their reaction selectivities [1–3]. Such a research is motivated by a great variety of applications: from geochemical production of petroleum to destruction of hazardous waste [4,5] or even environmentally benign organic synthesis [6,7]. The synthetic chemists have been striving to limit the use of dangerous organic solvents and to look for alternatives. The “solvent-free” experiments rarely evade the use of organic solvents at least during the subsequent isolation procedures. The attempts to use water as a solvent for organic reactions did not appear to be predetermined to a success because of the low water-solubility of most organic compounds. Nevertheless, a decrease in relative permittivity in line with increasing temperature enhances solubility even of relatively non-polar organic compounds.

The application of microwave (MW) heating in chemistry often means a significant reduction of reaction times, cleaner reactions, and higher chemical yields [8–10]. Recently, we have successfully utilized electrodeless discharge lamps (EDLs), which are able to generate ultraviolet UV radiation when placed into the microwave field, in the microwave-assisted photochemistry studies [11]. In the field of analytical chemistry, an efficient microwave-assisted photolytical reactor for high-temperature water digestion procedures has been developed by Florian and Knapp [12]. This work is a part of our program, in which simultaneous effects of both UV and MW irradiation on chemical reactions, and new MW/UV techniques are investigated [13–17]. We wish to report on the study of two models photochemical transformations carried out in high-temperature water using EDLs.

2. Experimental

2.1. Chemicals and solvents

Valerophenone (VP) (>99%) and hexadecane (99%) were obtained from Aldrich Chemicals Co. and were used as

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received. Acetophenone (pure), 4-nitrophenol (pure) and dichloromethane (pure) were purchased from Prolabo, NaOH (pure) and 4-methoxyphenol (99%) from Acros Organics. 4-Nitroanisole was prepared from 4-nitrophenol and dimethyl sulfate by a standard synthetic procedure and it was purified by recrystallization from a diethyl ether–methanol mixture [13].

2.2. Equipment

High-pressure irradiation experiments were carried out in a MicroSYNTH microwave labstation (Milestone Microwave Laboratory Systems, Italy). The microwave apparatus contained a high-pressure Teflon reactor with an irradiated solution and an electrodeless discharge lamp UVQ0007 (12 mm × 85 mm, Milestone, Italy) with a quartz envelope (>254 nm).

The irradiation of valerophenone and 4-nitroanisole under atmospheric pressure was accomplished in a modified microwave oven Whirlpool M401 (900 W) with an opening on the side, facilitating the simultaneous MW heating and UV irradiation from an external UV light source [17] (a medium pressure mercury lamp) through a quartz filter (>254 nm).

Gas chromatography (GC) was accomplished on a Shimadzu GC-2010 gas chromatographer and on a Carlo Erba Strumentazione, HRGC 5160 apparatus, connected to a PC by a Perkin-Elmer NCI 900 network chromatography interface.

2.3. Irradiation procedures

2.3.1. Valerophenone (1) photochemistry

A high-pressure Teflon reactor containing the electrodeless discharge lamp, magnetic stirring bar and valerophenone (8.1–81 mg; 5×10^{-5} to 5×10^{-4} mol) in water (50 ml) was sealed, placed in the microwave apparatus containing an APC55 automatic pressure sensor and an ATCFO automatic temperature optical fiber sensor. A stirred mixture was first heated up by microwaves at low MW-output power (125 W); this power was too low to induce a discharge in the lamp but, at the same time, sufficient to heat up the mixture up to 160–170 °C. When the temperature reached the desired level,

the MW output power was increased to 300–400 W, which consequently resulted in the ignition of EDL. The irradiation was interrupted after 3–20 s. The reaction mixture was then cooled down, the starting material (valerophenone) and products (acetophenone and cyclobutanol derivatives) were extracted into dichloromethane and analyzed on GC using hexadecane as an internal standard according to known procedures [18]. No other compounds were detected under the described conditions.

2.3.2. 4-Nitroanisole (4) photochemistry

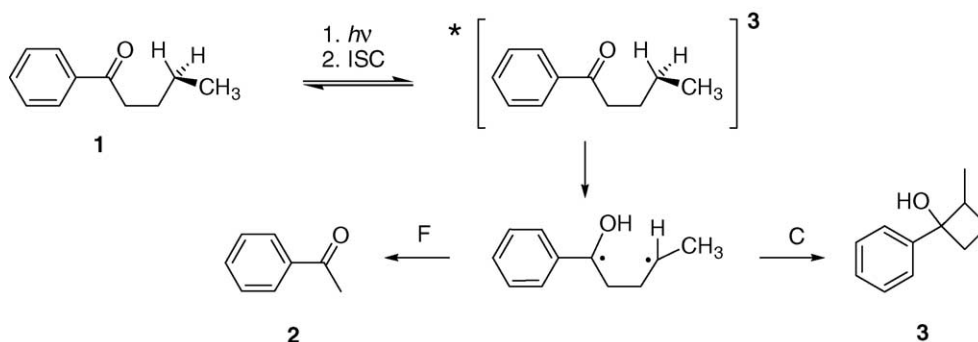
Both the experimental arrangement and the procedures used were similar to those employed in valerophenone photochemical experiments. The irradiated samples contained a solution of 4-nitroanisole (15.3 g; 1×10^{-4} mol) and NaOH (400 mg; 1×10^{-2} mol) in water (50 ml). After the irradiation, the basic solution was neutralized by 1 mol l⁻¹ aqueous HCl, extracted into dichloromethane, and analyzed on GC.

Several atmospheric pressure experiments were also carried out in a modified domestic microwave oven. One series of the 4-nitroanisole samples (30.6 g (2×10^{-4} mol) of 4-nitroanisole in 30 ml of aqueous NaOH (0.01 mol l⁻¹)) was irradiated by an external UV light source under simultaneous MW heating for 20 min. The other series was only heated for the same period of time so that the efficiencies of both photochemical and thermal reaction pathways could be determined and compared. The relative standard deviation for duplicate samples was found below 6% in all analyses.

3. Results and discussion

3.1. Norrish Type II reaction

Excited alkyl phenyl ketones with hydrogen on γ carbon react on their alkyl chains according to the Norrish Type II reaction via the triplet state to produce triplet 1,4-biradicals, which intersystem cross to the short lived singlet biradicals that can fragment (F), cyclize (C) (Yang cyclization), or disproportionate back to the starting ketone (e.g. valerophenone (1) in Scheme 1) [19]. Valerophenone forms two major products, acetophenone (2) upon fragmentation and 2-methyl-1-



Scheme 1.

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