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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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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.

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

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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

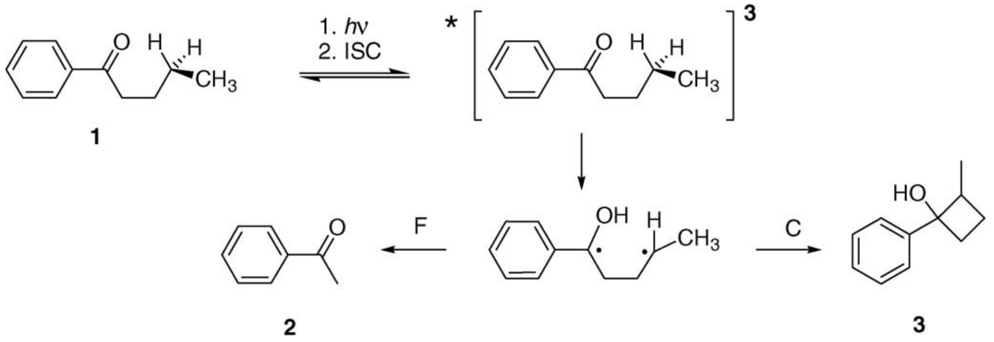
Both the experimental arrangement and the procedures used were similar to those employed in valerophenone photochemical experiments. The irradiated samples contained a solution of 4-nitroanisole (15.3 g; 1×10^{-4} mol) and NaOH (400 mg; 1×10^{-2} mol) in water (50 ml). After the irradiation, the basic 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.

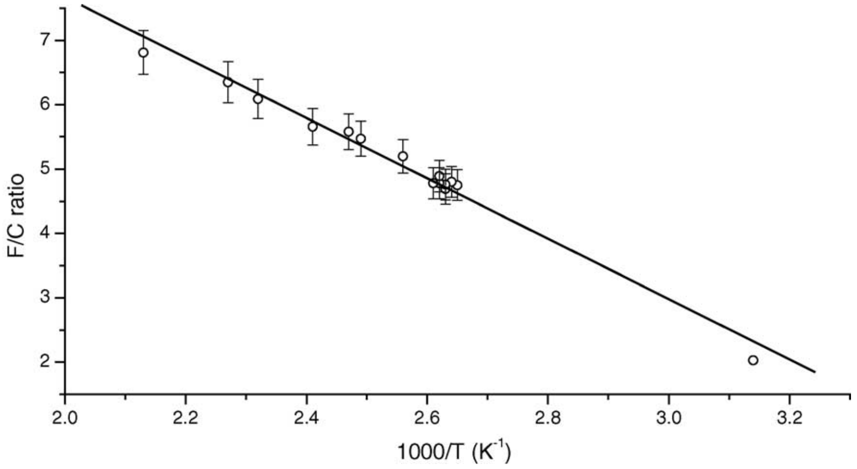


Fig. 1. F/C ratio plotted against the reciprocal temperature values (1000/*T*). The error bars represent the standard deviation.

phenyl-cyclobutan-1-ol (**3**) upon cyclization reactions. Effects of structure and solvation on their photoreactivity have been extensively studied over four decades. Earlier studies showed that the Type II cleavage and cyclization quantum yields reach nearly unity in water or other highly polar solvents, in contrast to much lower quantum yields in non-polar organic solvents [20,21]. The fragmentation/cyclization ratio was found to be also solvent- and temperature-dependent [15,16,18]. The Norrish Type II photoreactions can be used for preparation of compounds, which cannot be easily prepared by traditional synthetic methods [19].

In this work, a set of experiments was carried out in order to investigate the photobehavior of valerophenone in HTW (100–200 °C) in a pressurized vessel under MW irradiation. Due to a low solubility of VP in water ($c_{max} \sim 10^{-3}$ mol l^{-1}) [21], such a hydrophobic compound is not predetermined for the synthetic use in this medium. Heating up to 200 °C, however, enhanced the solubility, thus experiments with the VP concentrations up to 10^{-2} mol l^{-1} were performed in order to find the scope and limitations of such an application. The fragmentation/cyclization (F/C) ratio (i.e. the concentration ratio of the products (**2**)/(**3**)) served as a measure of the reaction chemoselectivity. The acquired F/C ratios in water (Table 1) were strongly temperature-dependent, and are plotted against 1000/*T* in Fig. 1 showing a good linear fit. The F/C ratio proved to be independent on valerophenone concentration, as well as on its conversion. The ignition and operation of the EDL inside the reactor was visually monitored through the Teflon reactor wall, however, its intensity (and subsequently the quantum yields) was not measured due to the technical limitations of the commercial sealed pressurized vessel. Nevertheless, the F/C ratio values equal to the ratio of the corresponding quantum yields since the reaction is unimolecular. Comparatively smaller quantum efficiencies of the VP photolysis of more concentrated samples (e.g. $c = 5 \times 10^{-3}$ mol l^{-1} in Table 1), were affected by the internal filter effect, that is most of the UV radiation emitted by EDL was absorbed by VP molecules in the immediate vicinity of the lamp. No chemistry was observed in the “dark” control experiments.

Table 1
Irradiation of VP ($c = 5 \times 10^{-5}$ mol l^{-1}) in HTW at >254 nm

Temperature (°C)	Time (s)	Pressure range (bar)[c]	Conversion (%)	F/C ratio
20	n.a.[e]	n.a.	n.a.	2.03[d]
101[a]	20	1.0–1.3	16.7	4.52
104[a]	10	1.0–1.3	9.9	4.75
106	3	1.1–1.2	22.4	4.80
107	3	1.2–1.3	14.9	4.69
107	10	1.0–1.3	41.5	4.76
108	15	1.1–1.3	29.8	4.78
109	10	1.2–1.4	38.5	4.89
110	20	1.2–1.3	37.7	4.78
117	15	1.4–2.7	70.2	5.20
128	15	2.0–3.4	66.9	5.47
131[b]	490	1.0–3.0	26.3	5.58
142	15	4.0–6.2	86.5	5.66
157	10	6.0–7.8	79.0	6.09
168	10	7.1–9.1	65.5	6.35
196	6	18.7–22.0	64.6	6.81

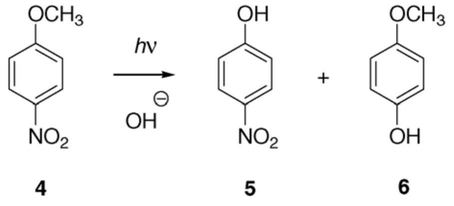
[a] $c = 5 \times 10^{-4}$ mol l^{-1}.
[b] $c = 5 \times 10^{-3}$ mol l^{-1}.
[c] The pressure inside the reactor.
[d] From reference [21].
[e] Not applicable.

Scaiano’s group provided temperature studies of valerophenone and its 4-methoxy derivative in non-polar solvents [22] and Wagner studied temperature effects on photochemistry of molecules, in which two different phenyl ketones are attached to a flexible tether [23]. Zepp et al. showed that going from 20 to 30 °C, the triplet reactivity of VP in water increased and that F/C ratio equals to 2.03 in water at 20 °C [21]. In addition, we have already shown that the temperature dependence of the ratio is highest in polar acetonitrile, lower in ethanol, and negligible in benzene, thus it must be dependent on the polar interactions with the OH group of the biradical [18]. The fact that high temperatures enhanced the fragmentation at the expense of cyclization in this work was presumably caused by lowering the energy barrier hindering the cleavage of Cα–Cβ bond in the biradical, but above all, due to the favoured formation of a thermodynamically more stable product (acetophenone). Basic polar solvents generally slow the disproportionation of biradicals but a higher temperature causes hydrogen bonding weakening. Since both products were found stable under the experimental conditions, the partitioning process must occur when the biradical collapses or before. In addition to the internal filter effect in higher concentrated samples, we should also consider a more efficient self-quenching [24] of the chromophoric compounds that could limit the synthetic applications. The effectiveness of such a photochemical process must be considered. If the chemoselectivity or other advantages of photochemistry in HTW are not substantial, a flow reactor with an atmospheric-pressure vessel or other more conventional photochemical tools are advised. Thus, the main advantage of this technique remains in solubility being increased with temperature and enhanced selectivity, which may not be available under different experimental conditions.

3.2. Photochemistry of 4-nitroanisole

Nucleophilic substitution on aromatic compounds is a typical reaction for the excited species [25]. The relative reactivity of the positions in excited aromatics is usually different from that in the ground state. The main products from the photosubstitution reaction of 4-nitroanisole (**4**) with the hydroxide anion were reported by Letsinger et al. [26] and de Vries and Havinga [27] to be 4-nitrophenol (**5**) and 4-methoxyphenol (**6**) (Scheme 2). The formation of 4-methoxyphenol is in agreement with the orientation rule for an electron donating substituent [27] but the mechanism of the 4-nitrophenol formation is still unclear. We have recently reported on the temperature-sensitive photochemical nucleophilic aromatic substitution on 4-nitroanisole by the hydroxide ion in various aliphatic alcohols under atmospheric pressure [13]. It was found that reaction regioselectivity dramatically changed with temperature in the region of −20 to 196 °C. In this report, the 4-nitroanisole aqueous photochemistry was chosen as an example of the bimolecular reaction, where both starting nitroanisole (a phenolate in the basic solution) and the inorganic hydroxide are relatively well soluble in water.

While the irradiation of 4-nitroanisole in basified solutions of aliphatic alcohols resulted in a formation of two photoproducts [13], only one product – 4-nitrophenol (**5**) – was observed in water at temperatures ranging up to 170 °C. Surprisingly, this product was obtained even in the absence of UV light, though in a lower yield, while no “dark photochemistry” was observed when aliphatic alcohols were used as solvents [13]. Two identical experiments were carried out in a MW reactor – one with EDL present in the reactor and the other “in dark” – to compare the effectivenesses of both synergic processes. The photolysis in a heated solution was found more efficient at least by 25%, which means that the thermal pathway is dominant and producing the same product (Table 2). This difference was not significant but since we could not control the UV flux from EDL, the individual reaction efficiencies in HTW remained undisclosed in this experiment. To proceed further, the photochemical experiments were carried out in the modified domestic MW oven [17] *under atmospheric pressure*. Interestingly, these experiments yielded both 4-nitrophenol (**5**) and 4-methoxyphenol (**6**). In the absence of the UV radiation, when the mixture was heated solely by microwave heating (100 °C), 4-nitrophenol was the only product obtained. No traces of 4-methoxyphenol were found as in the HTW experiments. In addition, the quantum efficiency of 4-nitroanisole degradation was smaller by ∼50% than that in the case of the UV irradiated experiments. The regioselectivity change of this reaction was significant; while the (**5**)/(**6**) ratio in MW heated solutions was over 99, the MW-assisted photochemical experiments provided (**5**)/(**6**) ∼1. It means that the thermal reaction yields practically one product (**5**), in contrast to the photochemical reaction pathway that leads to the formation of both 4-methoxyphenol and 4-nitrophenol (Table 2). This generally corresponds to the observations in the previous work, where the product **5** was largely favoured at higher temperatures in aliphatic alcohols and it justifies the idea that temperature-dependent process occurs after the partitioning between replacement of the nitro group and the methoxy group has taken places. Considering the quantum efficiencies of the both pathways at 100 °C and the temperature-dependent regioselectivity, the results from the HTW experiments are congruent. The advantages of HTW photochemistry were not quite fulfilled because of a limited increase in the reaction efficiency; however, a “dark” HTW application provided a very efficient product formation with an exceptional regioselectivity not observed at lower temperatures.



Scheme 2.

Table 2
Photochemistry of 4-nitroanisole[a]

Conditions	Temperature (°C)	4-Nitrophenol (**5**) formation[b]	4-Methoxyphenol (**6**) formation[b]
MW[c]	170	>99	n.d.[d]
MW + UV	170	>99	n.d.
MW	100	>99	n.d.
MW + UV	100	53 ± 2	47 ± 2

[a] Initial concentration 2×10^{-3} mol l^{-1}; <25% conversions.
[b] Relative amounts in %.
[c] Low reaction efficiency.
[d] Not detected.

In conclusion, this work presents an attempt to carry out a model photochemical transformation in high-temperature water under microwave irradiation. The Norrish Type II reaction of valerophenone was found to provide preferentially the cleavage product (acetophenone) without any unwanted side-products even at 200 °C. The second reaction studied, photochemical nucleophilic aromatic substitution on 4-nitroanisole, proceeded primarily by a thermal pathway. A more environment-friendly substitution of organic solvents by water, an increased chemoselectivity in the temperature-sensitive photochemical reactions, and an increased solubility of hydrophobic organic compounds undoubtedly hold a promise of photochemical synthetic applications in HTW.

Acknowledgments

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