ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 128 (1999) 145–149

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.nl/locate/jphotochem

The electrodeless discharge lamp: a prospective tool for photochemistry

Petr Klán [a,*], Jaromír Literák [a], Milan Hájek [b]

[a] *Department of Organic Chemistry, Masaryk University, Kotlárská 2, 611 37 Brno, Czech Republic*
[b] *Institute of Chemical Process Fundamentals, Academy of Sciences, Rozvojová 135, 165 02 Praha, Czech Republic*

Received 23 June 1999; accepted 29 June 1999

Abstract

A simple photochemical reactor has been developed and tested for photochemical reactions. It consisted of an electrodeless discharge lamp (MWL) placed into the reactor vessel of a commercial microwave oven. The microwave (MW) field generated ultraviolet irradiation by the lamp at the same time as it interacted with a studied sample. This technique brings a unique possibility to study the simultaneous effect of both UV/VIS and MW irradiations on photochemical reactions. The use of MWL in a MW reactor has been studied in terms of (1) an operating MW power and temperature influence on the lamp, (2) solvent polarity influence, (3) MWL heating capabilities, and (4) dependence of the photoreaction efficiency on the MW power output. It was found that the lamp produced enough heat to quickly warm up any liquid to boil even in case of 'transparent' liquids in the MW field. An efficiency of light-induced photofragmentation reaction of valerophenone (Type II reaction) was investigated as a function of the MW input power and solvent polarity. It was found that conversions of acetophenone production showed almost linear dependence on the input MW power. Efficiencies in acetonitrile were higher than those obtained in benzene, only by a factor of 1.2, which was explained by lowering the MWL intensity, thanks to MW absorption by the solvent.
©1999 Elsevier Science S.A. All rights reserved.

Keywords: Microwave photochemistry; Electrodeless discharge lamp; Valerophenone; Type II reaction; Solvent effects

1. Introduction

Researchers all over the world have showed considerable interest in the application of microwave (MW) irradiation to various chemical transformations [1–4]. However, there are virtually no known experimental data about microwave irradiation effect on photochemical reactions. This might be partially because microwave chemistry is still a developing part of chemistry, and also because of experimental difficulties that accompany simultaneous application of ultraviolet and microwave irradiation.

An effect of MW irradiation on the dynamic behavior of photochemically generated radical pairs is one of the rare problems investigated [5–6]. It was found that the lifetime of the radical pair, produced by a photochemical hydrogen abstraction reaction of a naphthoquinone derivative in micelles, was significantly shorter when MW pulse was applied. MW irradiation caused the triplet–singlet interconversion rate to increase, and was comparable to the radical escape rate from the micelle. An effect of MW irradiation on radical pair lifetimes in photosynthetic reaction centers was also described recently [7]. In addition, Chemat and coworkers studied the rearrangement of *o*-aryloxyacetophenone and the degradation of humic acid in an original microwave–ultraviolet combined reactor [8].

The idea of an electrodeless discharge lamp absorbing MW energy is not new. It is covered by numerous patents and papers [9–10]. Some applications of low powered and low-pressure lamps are found in spectroscopy, analytical chemistry, and even in photochemistry four decades ago [11–13]. One of us recently showed that an electrodeless discharge mercury lamp (or microwave electrodeless lamp, MWL) may be a very convenient tool for 'microwave photochemistry' experiments [14]. The lamp was placed into the reactor vessel of a simple MW cavity so that the MW field caused UV irradiation at the same time as it could interact with the reaction mixture.

Microwave photochemistry is definitely a new field of chemistry. This is the reason why we wish to introduce first consistent information about the technique, its scope and limitations. The application of MWL in a MW reactor has been studied in terms of (i) an operating MW power and temperature influence on the lamp, (ii) solvent polarity influence, (iii) MWL heating capabilities, and (iv) a dependence

---

[*] Corresponding author.

1010-6030/99/$ – see front matter ©1999 Elsevier Science S.A. All rights reserved.
PII: S1010-6030(99)00165-3

of the photochemical efficiencies on the MW power output in various solvents.

2. Experimental section

2.1. Equipment

^{1}H and ^{13}C NMR spectra were obtained for solutions in $CDCl_3$ on an Avance Bruker DRX 500. Gas chromatography was accomplished on a Shimadzu GC-17A apparatus and on a GC/mass system TRIO 1000 (FISONS Instruments). Temperature and kinetics studies were conducted in a microwave instrument, Synthewave 402 (Prolabo), equipped with an IR pyrometer (not calibrated), quartz reaction vessel, and a cooling system. Microwave reactor operated with maximum 300 W output power at 2450 MHz frequency. Electrodeless discharge mercury lamps (MWL) were manufactured by Teslamp, Prague, Czech Republic. The lamp was made of 9 mm Simax (Pyrex equivalent) tubing of 20 mm length, filled with mercury and argon, and sealed under 20 Torr vacuum. Simax absorbs most of the UV irradiation below 280 nm.

2.2. Chemicals and solutions

Valerophenone (99+%) was obtained from Aldrich Chemical Co., and was purified by distilling under reduced pressure. Hexadecane (99+%), from Schuchardt, was used as received. All solvents were purified by standard procedures. Valerophenone samples were degassed by bubbling the solutions with argon for 15 min. Parallel high temperature experiments using a conventional medium-pressure mercury lamp (400 W, Conrad-Hanovia) were conducted in 100 mm × 13 mm Simax tubes.

2.3. Microwave experiments

The experimental system consisted of an electrodeless discharge lamp (MWL) placed into 20 ml of solvent or valerophenone solution in a 70 cm^3 quartz reaction vessel. Most of the solution was under direct MW irradiation. The vessel, equipped with a condenser, rotated under argon atmosphere in the Synthewave chamber. The volume of a liquid remained same at the end of every experiment, as was in the beginning. The MW power and temperature was controlled by Prolabo software.

In photochemical experiments, the solution was MW preheated to 40–50°C, and the lamp was quickly inserted into the vessel. Microwave irradiation of the desired power started immediately, causing MWL initiation practically at the same time, and was maintained for a specific time.

Working with superheated flammable and toxic solvents in a microwave reactor needs special attention.

2.4. Photoproduct identification and analysis

Ketone solutions (0.05 M) were irradiated using MWL or a conventional lamp, and the photoproduct concentrations were determined on GC, equipped with a nonpolar column (DB-5), using hexadecane as an internal standard. The conversion of valerophenone fragmentation was kept below 20%. For comparison, a solution of valerophenone in acetone (4×10^{-4} M) was irradiated using Simax-filtered radiation from a conventional 400 W mercury lamp. Valerophenone, acetophenone, and cyclobutanols were analyzed by GC and GC/mass, as described in the literature [15–16]. No other photoproducts were detected. Acetophenone was also isolated by flash chromatography, and its ^{1}H and ^{13}C NMR spectra were compared to those obtained from the authentic sample.

3. Results

3.1. Temperature experiments

We attempted to distinguish heat produced from MWL operation from that caused by solvent MW absorption or by the magnetron performance. Benzene, cyclohexane, acetonitrile, and ethanol were used in those experiments. Temperature was studied as a function of: (1) time, (2) the MW power output, and (3) the solvent polarity.

MWL was placed into the reaction vessel with a liquid and the MW power was adjusted to a desired value. Temperature was detected by an IR pyrometer (not calibrated) and by a conventional thermometer just immediately after MW irradiation was stopped. Lamp initiation was observed through the instrument window.

Fig. 1 shows typical temperature versus time dependencies for benzene and ethanol. Benzene is an example of

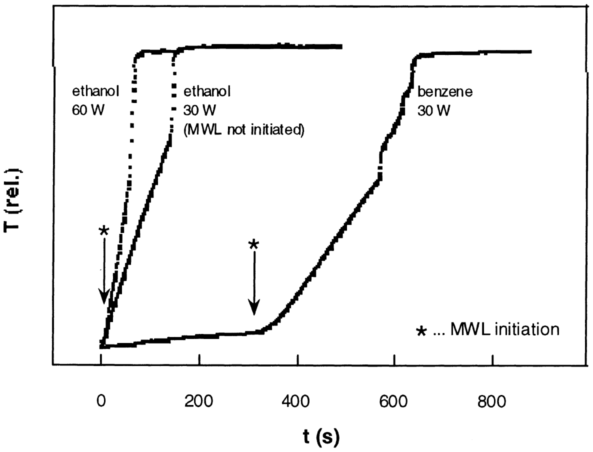


Fig. 1. Effect of MW power and the solvent polarity on temperature (T) and the electrodeless lamp operation in time (t). Temperature detected by an IR pyrometer was not calibrated. The lamp was initiated at time as indicated.

Table 1
Temperature of MW irradiated liquids in the presence of MWL

Solvent/T (°C)[a]	Output power (W)	MWL: Time (s)/T (°C)[b]	Boil: Time (s)[c]
Benzene/20	15	420/33	1000
Benzene/20	30	240/30	300
Cyclohexane/20	30	260/28	600
Cyclohexane/30	30	60/33	450
Acetonitrile/20	30	30/33	60
Acetonitrile/20	15	not initiated	200
Ethanol/20	30	not initiated	100

[a] Initial temperature. All data found for the same lamp; using a different lamp could lead to different values.

[b] Time and temperature (measured by a thermometer) when MWL was initiated.

[c] Time when a liquid started to boil (counted from the beginning of the MW experiment).

a 'transparent solvent' in the MW field (remains virtually unaffected), while polar ethanol efficiently absorbs MW and quickly comes to boil. However, temperature rose dramatically in benzene (or cyclohexane) when MWL was immersed and was initiated. Fig. 1 shows that benzene came to boil in 4 min at 30 W, thanks to the MWL heating. Ethanol boiled without MWL in 3 min at the same power. Temperature of the curve plateau, corresponding to a boiling liquid (or superheated [17–18]), was verified by a standard thermometer immediately after the experiment was finished. Our attempts to maintain temperature below the boiling point when MWL was used remained unsuccessful even for the lowest output power (15 W) used. This value was also found to be a minimal energy for the lamp initiation in the MW field without the presence of any solvent.

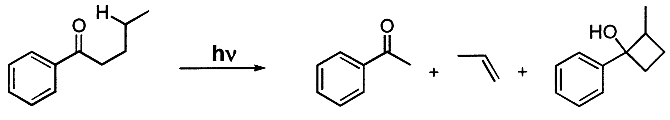
Application of MWL in polar solvents was troublesome. A solvent started to boil too quickly and was difficult to keep it under control even at a lower MW power.

The initial temperature (or warming up) was found to be crucial for lamp initiation. While the lamp initiated in polar solvents almost immediately after MW irradiation started, initiation in benzene or cyclohexane occurred after a much longer time. In addition, MWL initiated in non-polar solvents at every output power, but initiation in polar liquids needed more energy (Table 1).

When the MW power control program was modified to lower energy gradually from 60 to 15 W, the lamp did not cease to operate in all liquids. When MW irradiation was forcefully stopped in a hot liquid and started again, the lamp usually initiated immediately.

3.2. *Type II photoreaction*

Numerous investigations of the photoreactions on aromatic alkyl ketones have provided a detailed information concerning structural and solvent effects on triplet reactivities [19–23]. Valerophenone, a typical representative, with hydrogen on γ-carbon reacts on its alkyl chain via the triplet state to produce a 1,4-biradical that can cleave, cyclize, or disproportionate back to starting ketone (Scheme 1). In our MW experiments, the Type II products — acetophenone, propene and cyclobutanols — were determined by GC. No other products were detected.



Scheme 1.

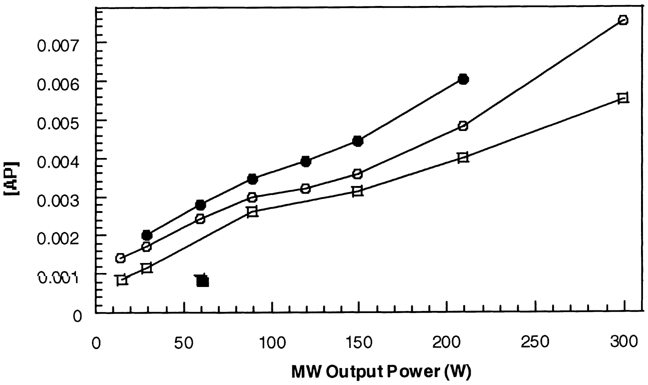


Fig. 2. Effect of changing the MW output power on valerophenone Type II photofragmentation in benzene (○), cyclohexane (□), acetonitrile (●), and ethanol (■) in the presence of the electrodeless discharge lamp (MWL). Values (AP) are molar acetophenone concentrations and are the mean of triplicate measurements with estimated error ±10%.

Wavelength of UV irradiation coming from the MWL was considered to be >280 nm since the lamp was made from Simax glass. We measured conversions of the fragmentation reaction in a constant period of time and at a different MW power output in various solvents. We have not attempted to measure absolute quantum yields because of obvious experimental difficulties. The fragmentation/cyclization ratios were also obtained under those conditions, and were then compared with the experiments in the absence of MW field.

Experiments started by MW heating the solutions. After a temperature of 40–50°C was reached, the lamp was quickly inserted and MW irradiation of the desired power was introduced. The lamp initiated immediately in all presented measurements. Both types of irradiation were maintained for such period of time so that the fragmentation conversion

Table 2
Comparison of yields of valerophenone Type II products in benzene and acetonitrile in microwave photochemical experiments with conventional photochemical experiments[a]

Solvent/T (°C)	MW output power (W)	Yield (%)	
		Acetophenone	Cyclobutanols
Benzene	15	80	20
Benzene	210	82	18
Benzene/78°C[b]	–	81	19
Benzene/20°C	–	81	19
Benzene/20°C[c]	–	82	18
Acetonitrile	15	83	17
Acetonitrile	210	84	16
Acetonitrile/80°C[b]	–	83	17
Acetonitrile/20°C	–	82	18
Acetonitrile/20°C[c]	–	85	15

[a] 0.05 M valerophenone solutions were irradiated by a medium-pressure Hg lamp using Simax filter.

[b] Ref. [24].

[c] 0.1 M valerophenone solution irradiated at 313 nm at 20°C (ref. [25]).

was below 20%. Results from valerophenone irradiation in benzene, acetonitrile, cyclohexane and ethanol are shown in Fig. 2, and the photoproduct distribution (the fragmentation/cyclization ratio) are presented in Table 2.

More or less linear increase in the acetophenone conversion with the output power was observed in all solvents (Fig. 2). Larger differences appeared when a higher MW power was applied. The values in benzene were found to be higher than those observed in cyclohexane and lower than those found in acetonitrile approximately by a factor of 1.2. The conversion in ethanol at 60 W power was significantly lower.

4. Discussion

We mentioned in Section 1 that the idea of an electrodeless discharge lamp and its application in photochemistry is quite rare, although not new. Those few papers, published in 1950s and 1960s, have not presented any systematic research, and were more physics oriented [11–13]. The concept was abandoned for some time until now. One of us recently published the study of photoinitiated radical addition of tetrahydrofuran to perfluorohexylethene under microwave irradiation [14]. The reaction was carried out in the MW field in presence of MWL that generated UV irradiation. Since effects of MW field on photochemical reactions are essentially unknown, and an application of MWL in photochemistry seems to be so simple, we wish to present the first systematic study of its application. In the following discussion, the technique of MWL applications is discussed, taking into account a ‘heating’ effect originating from the lamp operation. Next, conditions necessary for lamp initiation are considered. Finally, we present one photochemical application — a study of a MW power output influence on an efficiency of the Type II photofragmentation of valerophenone.

4.1. MWL spectral output and ‘warming up’

Phillips [9] presented advantages of electrodeless lamp use, instead of a conventional one:

1. The lamp warms up quicker than a conventional lamp and can be extinguished and then re-ignited almost instantaneously when radiation is required.
2. The lack of electrodes eliminates the lamp deterioration processes associated with electrodes.
3. The discharge fills the entire length of the tube.

The spectral characteristics of the electrodeless lamp resemble more those of high-pressure mercury lamps. The spectral output of the electrodeless discharge mercury lamp is known [26]. The lamp gives over three times as much UV radiation as the conventional electrode lamp. Nevertheless, infrared loss is still large.

As we expected, the application of MWL in our experiments was always connected to a temperature increase of the system. Irradiated with the lowest MW power (15 W), which is a minimal energy for lamp operation, all liquids, including non-polar (not absorbing) solvents (benzene, cyclohexane), were heated, thanks to the lamp IR output (Fig. 1, Table 1). Almost similar temperature tendencies were found for polar solvents (acetonitrile and ethanol), no matter if MWL was applied. This means that MW heating of the polar liquids was more efficient than MWL heating effect.

It is well known that photochemical reactions are usually not very sensitive to temperature. However, a heating effect, thanks to either MW or MWL, might be desirable whenever a high temperature has a positive effect on the reaction conversion or selectivity. On the contrary, quenching of an excited state, thus shortening the lifetime, might accompany some MW applications. Gáplovský and his coworkers suggested that ultrasound application on a photochemical reaction, in which solvent cavities are also superheated, enhances the effect of quenchers on photochemical isomerization [27].

The lamps initiated usually when temperature of the liquid reached approx. 30°C. When the lowest MW power was applied, MWL was initiated only in benzene and cyclohexane. The power had to be increased to 30–45 W for a proper functioning in polar solvents. We believe that polar solvents absorb most of MW energy at a low power, so the lamp does not have enough power to operate. This suggestion was supported by photochemical experiments described later. With increasing MW output power, the solvent absorption ability is saturated and the remaining energy serves for lamp operation.

The fact that MWL was initiated after a longer time in non-absorbing solvents (Table 1), was probably connected to the fact that the lamp was cooled by the environment. It is known that the lamp itself usually warms up very quickly from cold, comparing with a conventional lamp [9]. It is quite intriguing that once the lamp was operating in a hot solvent, a lowering of the power did not caused its extinguishing. This fact was then successfully adopted in the following experiments. *In those rare cases when initiation* *failed, internal or external source of visible light was successfully used to begin initiation.*

4.2. Valerophenone photochemistry

The Type II reaction of valerophenone is one of the ‘textbook’ standards in photochemistry, and is commonly used in UV actinometry (Scheme 1). We studied valerophenone photofragmentation dependence on the UV intensity of MWL, which was controlled by the MW output power. As we expected, the acetophenone production increase was basically linear in all solvents (Fig. 2). Since all data were well reproducible, a shift from the ideal linearity (notice a similar tendency in all solvents) was attributed to the performance of the MW instrument. Comparable conversions in nonpolar solvents are not surprising because it is well known that quantum yields of acetophenone formation in benzene and alkanes at 313 nm are in the range of 0.3 to 0.4 [28–29]. On the other hand, quantum yields are known to rise to unity in acetonitrile and ethanol; thus, an increase by a factor of 3. Despite the fact that our experiments were performed in boiling solvents (all solvents used have boiling points around 80°C), we expected significantly higher photoproduct conversions in polar solvents. That was not observed in our experiments. Conversions in acetonitrile were only slightly higher comparing with those found in nonpolar solvents, and the only value obtained in ethanol was quite low [1]. We also analyzed the photoproduct distribution in the Type II reaction in all measurements and the fragmentation/cyclization ratios were found nearly identical to those without MW action (Table 2). Thus, it seems that neither high temperature nor MW field affect conformational behavior of the biradical intermediate.

We suggest two explanations that could explain low conversion values in polar solvents. First, the lower photochemical efficiency may be connected to the fact described in the previous paragraph. Benzene and cyclohexane do not absorb MW; thus, the power was consumed only by lamp operation. However, acetophenone formations in both acetonitrile and ethanol were diminished because a part of MW energy was absorbed by the solvent, so the light intensity produced by the lamp was lower. Since polar acetonitrile ($\mu = 3.44$ D) and ethanol ($\mu = 1.66$ D) absorb more MW energy with respect to a much larger dipole moment, the lower photochemical efficiency is justified.

Our second suggestion is based on a presumption that higher temperature and/or the MW field affect the Type II reaction. Polar solvents are known to increase cleavage quantum yields by suppressing disproportionation reaction, thanks to solvation of a hydroxy biradical intermediate [15,28,29]. A higher temperature and superheating in the MW field could alter those interactions. Hydrogen bonding might weaken with increasing temperature [30], and so the solvent effects on the Type II reaction could be smaller. This would mean a lowering of the acetophenone conversion in polar solvents, which is also in accord with our findings. The hypothesis whether MW induced any other effects except heating the reaction mixture, will be a subject for our future research.

Acknowledgements

We thank Alfred and Isabel Bader for funding through the Foundation for a Civil Society. We thank R. Kareš for his assistance with identification of the photoproducts using GC/mass spectrometry and his help with MW experiments.

References

[1] R. Dagani, Chem. Eng. February (1997) 26.
[2] S. Caddick, Tetrahedron 51 (1995) 10403.
[3] R.A. Abramovitch, Org. Prep. Proc. Intl. 23 (1991) 683.
[4] D.M.P. Mingos, D.R. Baghurst, Chem. Soc. Rev. 20 (1991) 1.
[5] Y. Sakaguchi, A.V. Astashin, B.M. Tadjikov, Chem. Phys. Lett. 280 (1997) 481.
[6] A.V. Astashin, Y.J. Sakaguchi, Chem. Phys. 106 (1997) 9190.
[7] S.A. Dzuba, I.I. Proskuryakov, R.J. Hulsebosch, M.K. Bosch, P. Gast, A. Hoff, J. Chem. Phys. Lett. 253 (1996) 361.
[8] S. Chemat, A. Aouabed, P.V. Bartels, D.C. Esveld, F. Chemat, J. Microwave Power and Electromagnetic Energy 34 (1999) 55.
[9] R. Phillips, in: Sources and Applications of Ultraviolet Radiation. Academic Press, London, 1983, p. 282 and references therein.
[10] W. Lautenschläger, Eur. Pat. Appl. (1991) 0 429 814.
[11] W.S. Gleason, R. Pertel, Rev. Sci. Instr. 42 (1971) 1638 and references therein.
[12] N.L. Ruland, R. Pertel, J. Am. Chem. Soc. 87 (1965) 4213.
[13] K.R. Osborn, C.C. McDonald, H.E. Gunning, J. Chem. Phys. 26 (1957) 1638.
[14] V. Církva, M. Hájek, J. Photochem. Photobiol. A Chem. 123 (1999) 21.
[15] R.B. LaCount, C.E. Griffin, Tetrahedron Lett. 21 (1965) 1549.
[16] R.G. Zepp, M.M. Gumz, W.L. Miller, H. Gao, J. Phys. Chem. A 102 (1998) 5716.
[17] G. Bond, R.B. Moyes, S.D. Polington, D.A. Whan, Chem. Ind. September 16 (1991), p. 686.
[18] K.W. Watkins, J. Chem. Educ. 60 (1983) 1043.
[19] P.J. Wagner, G.S. Hammond, J. Am. Chem. Soc. 88 (1966) 1245.
[20] P.J. Wagner, Acc. Chem. Res. 4 (1971) 168.
[21] P.J. Wagner, Acc. Chem. Res. 16 (1983) 461.
[22] M.B. Zimmt, C.E. Doubleday Jr., N. Turro, J. Chem. Phys. Lett. 134 (1987) 549.
[23] P.J. Wagner, Acc. Chem. Res. 22 (1989) 83.
[24] P. Klán, J. Literák, Collect. Czech. Chem. Commun., submitted for publication.
[25] P.J. Wagner, J. Am. Chem. Soc. 89 (1967) 5898.
[26] D.M. Spero, J.C. Matthews, J. Radiat. Curing. 6 (1979) 6.
[27] A. Gáplovský, J. Donovalová, Š. Toma, R. Kubinec, J. Photochem. Photobiol. A 115 (1998) 13.
[28] P.J. Wagner, A.E. Kemppainen, H.N. Schott, J. Am. Chem. Soc. 95 (1973) 5604.
[29] P.J. Wagner, J. Am. Chem. Soc. 89 (1967) 5898.
[30] H.E. Dorsett, R.O. Watts, S.S. Xantheras, J. Phys. Chem. A 103 (1999) 3351.

---

[1] Experiments with a higher power output than 60 W in ethanol and 210 W in acetonitrile were not accomplished because solvents boiled too vigorously and a cooling system was not quite sufficient.