



MICROWAVE PHOTOCHEMISTRY OF SUBSTITUTED PHENOLS

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INTRODUCTION

The fact that electrodeless discharge lamp (EDL) generates ultraviolet radiation when placed into the microwave field (MW) has been known for long time [1-3]. The low powered and low-pressure electrodeless lamps were utilized in spectroscopy and analytical chemistry four decades ago [4]. However, its application for organic photochemistry has been shown only recently [5-11].

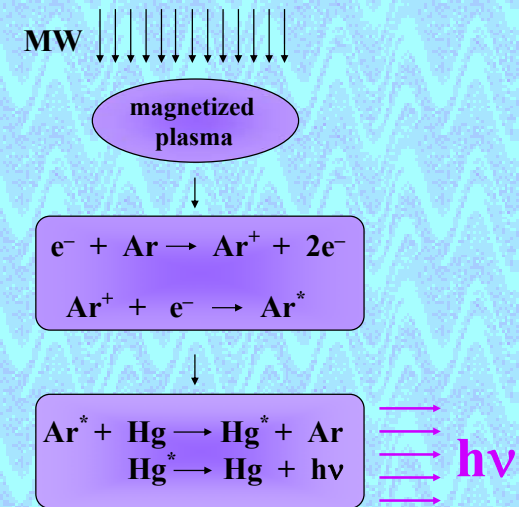
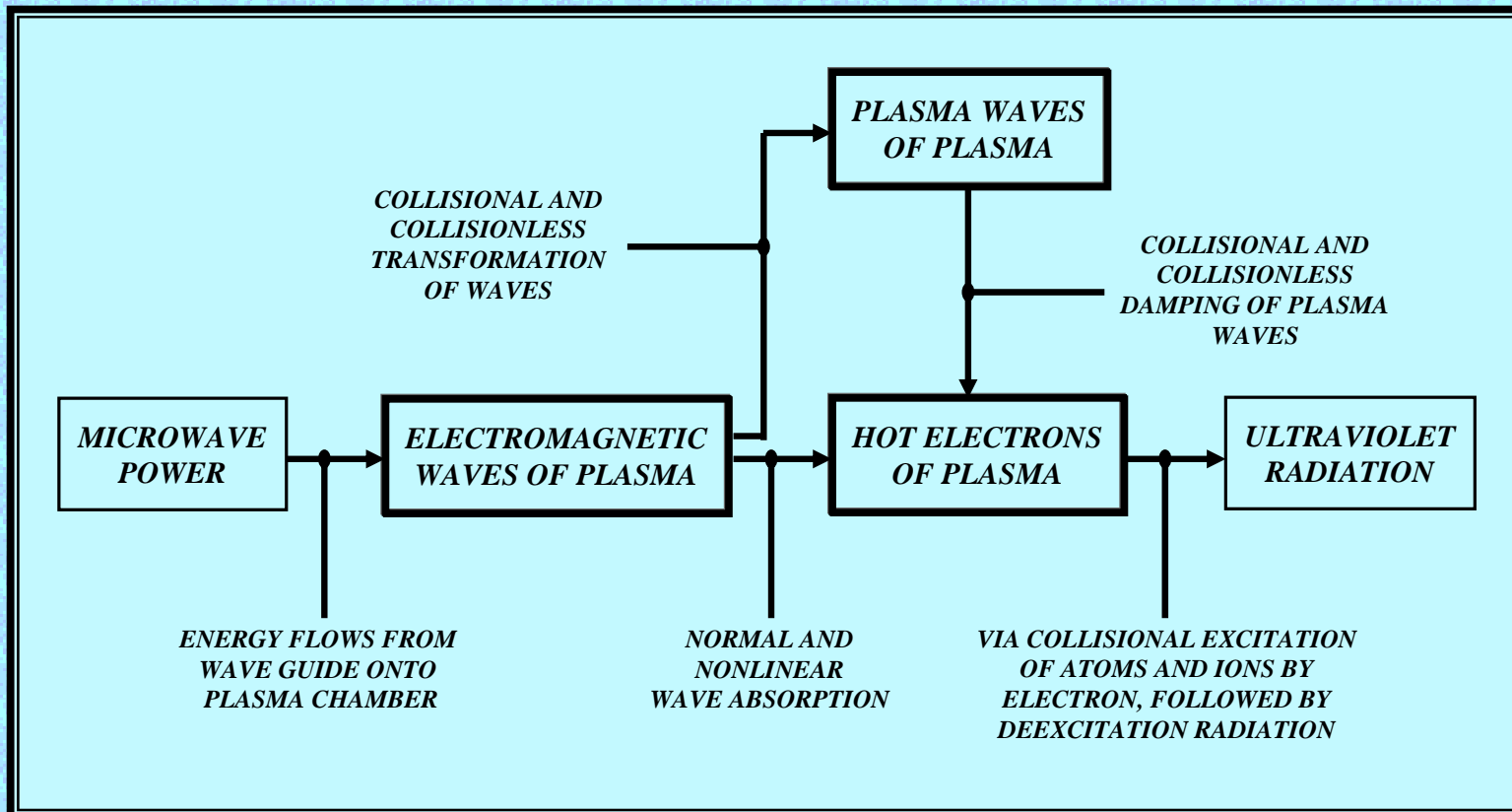
We disclosed the studies of microwave photochemistry of substituted phenols in an original photochemical reactor consisting of EDL placed into the reactor vessel of a commercial microwave oven [7, 12]. The UV discharge in the lamp [1, 13] is generated by microwave field with a consequence of the simultaneous UV and MW irradiation of the sample. Such simple arrangement brings a unique possibility to study photochemical reactions under extreme thermal conditions.

ELECTRODELESS DISCHARGE LAMPS

Electrodeless discharge lamps (EDL) [13] were made of quartz tubings, filled with Hg and Ar, and sealed under 20 Torr vacuum [14]. The size of lamp was from 20x50 mm. The spectral characteristics [1] of the electrodeless lamp resemble more those of high-pressure mercury lamps and are known.

MICROWAVE GENERATION OF THE UV IRRADIATION

The microwave energy which is at a high power density in the medium causes electrons to be generated in densities exceeding the cut-off density. The electrons are generated by processes including the collisionless and collisional transformation of waves and normal and non-linear wave absorption. The energetic electrons collide with the heavy particles of the plasma thereby exciting them and the heavy particles emit the desired radiation upon deexcitation.



- ELECTRODELESS LAMPS**
- quartz cover (l = 4-5 cm, d = 1-2 cm), inert gas (Ar, 20 mm Hg), mercury
 - advantages - high intensity
 - simple construction
 - low price

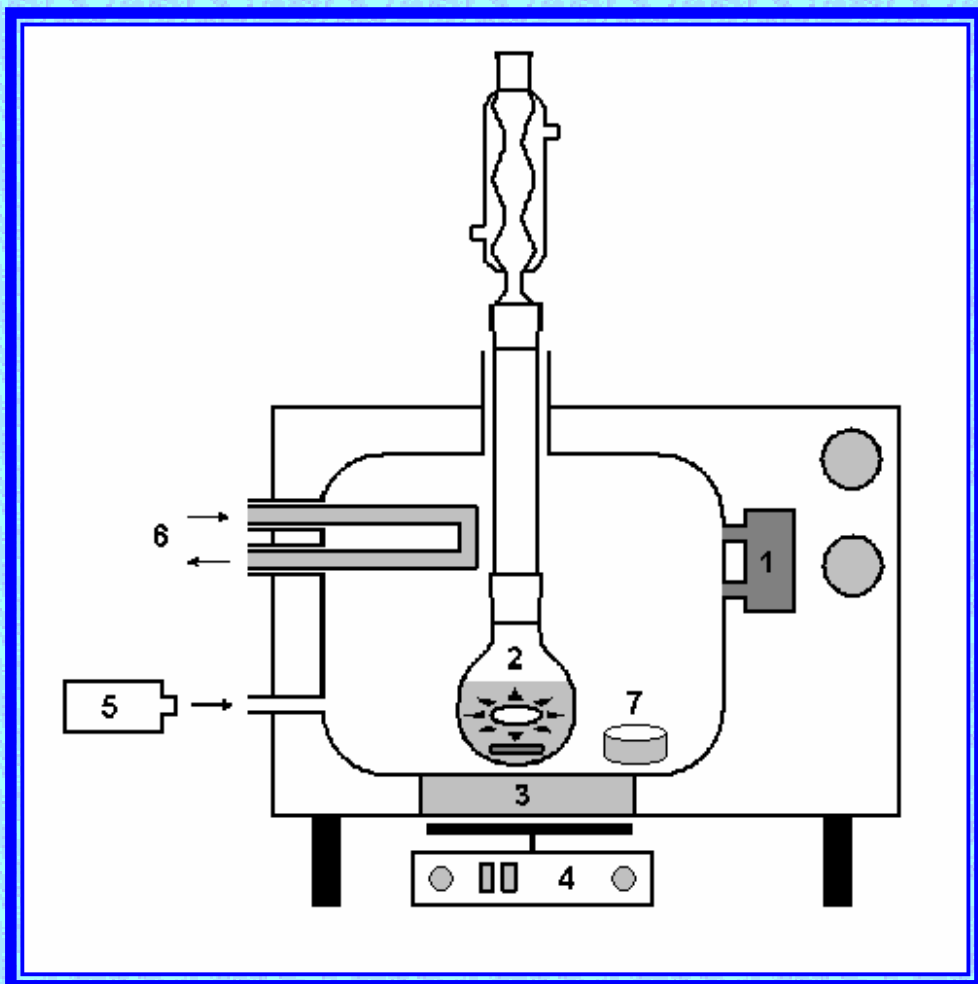
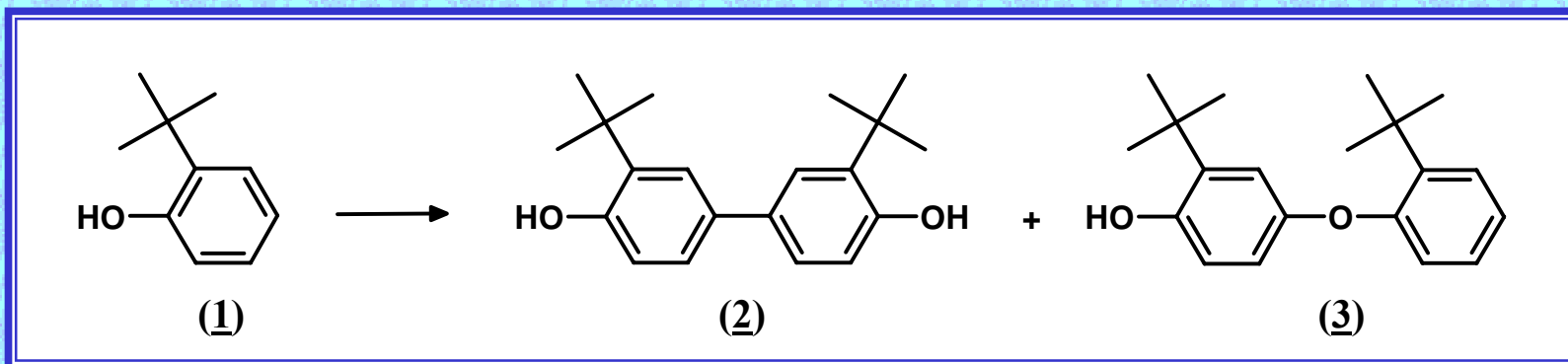


Figure: A modified MW oven for microwave photochemical experiments: (1) magnetron, (2) reaction mixture with EDL and stir bar, (3) aluminum plate, (4) magnetic stirrer, (5) infrared pyrometer, (6) circulating water in a glass tube, (7) a solid absorber (dummy load) inside the oven cavity.



PHOTOCHEMISTRY OF 2-*tert*-BUTYLPHENOL

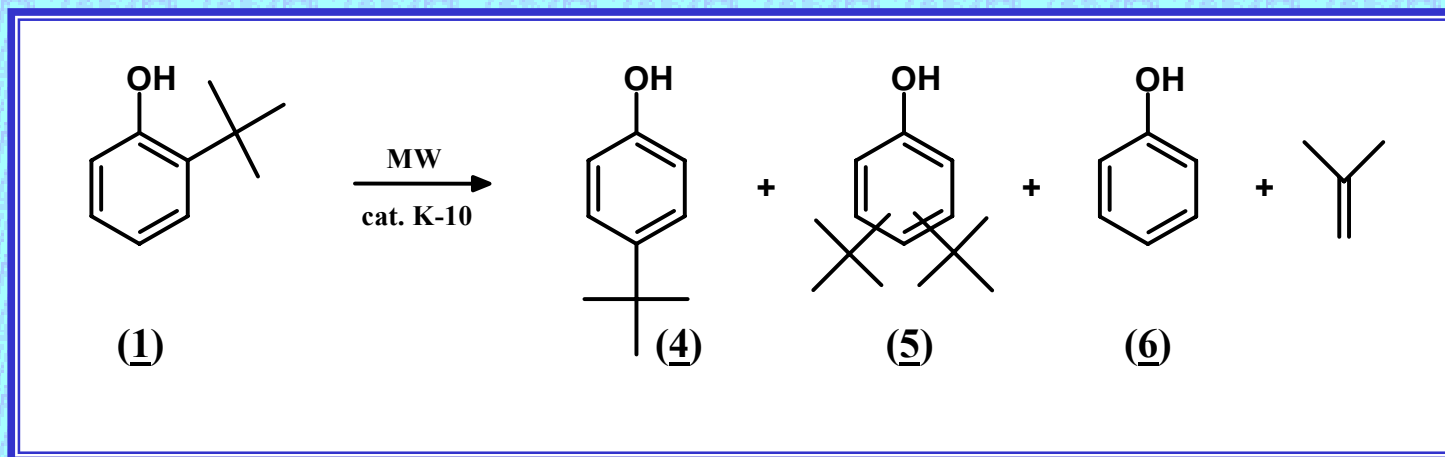
We reported here the photochemical reaction of 2-*tert*-butylphenol in non-polar (hexane, heptane, decane, toluene) and polar (acetonitrile, methanol) solvents under MW irradiation using system with electrodeless or classical UV lamps (RVC-400 W). The study is focused on the temperature products distribution in different types of solvents.



2-*tert*-Butylphenol (1) provide the mixture of products, mainly 3,3'-di-*tert*-butyl-4,4'-dihydroxybiphenyl (2) and 2-*tert*-butyl-4-(2-*tert*-butylphenoxy)phenol (3). The ratio and type of photoproducts were dependent on temperature, type of solvents and MW irradiation.

Solvent	Irradiation	Product (2) [%]	Product (3) [%]	(2)/(3)	Conversion [%]
Hexane	MW-UV	45	55	0.82	34
	UV	40	60	0.66	17
Heptane	MW-UV	44	56	0.79	34
	UV	45	55	0.82	24
Decane	MW-UV	55	45	1.22	41
	UV	31	69	0.45	23
Toluene	MW-UV	44	56	0.79	12
Acetonitrile	MW-UV	0	100		3
	UV	0	100		2
Methanol	MW-UV	0	0		0
	UV	0	0		0

THERMAL TRANSFORMATION OF 2-*tert*-BUTYLPHENOL



The product distribution was completely different, i.e. 2-*tert*-butylphenol provided only isomeric (4) transalkylated (5) and dealkylated (6) products. The MW had a strong effect on both the reaction rate and the selectivity.

Transformation of 2-*tert*-butylphenol in liquid phase catalyzed by montmorillonite KSF catalyst under microwave (MW) and conventional (conv) conditions carried out for 1h at boiling point of the solvents [15]:

Solvent	Heating	Product (4) [%]	Product (5) [%]	Product (6) [%]	Conversion [%]
Hexane ^a	MW	80	12	8	98
	conv	71	19	10	95
Heptane ^b	MW	82	12	6	99
	conv	79	12	9	99
Methanol ^c	MW				0
	conv				0

^a at 75°C, ^b at 105°C, ^c at 65°C

CONCLUSIONS

In the photochemical reaction of 2-*tert*-butylphenol in non-polar solvents the only difference in selectivity was observed in decane. In acetonitrile the only 2-*tert*-butyl-4-(2-*tert*-butylphenoxy)phenol (**3**) was obtained. In methanol under MW-UV and UV radiation transformation of 2-*tert*-butylphenol does't proceed.

Microwave-induced catalytic transformation of 2-*tert*-butylphenol provide quite different products. In non-polar solvents only 4-*tert*-butylphenol (**4**), di-*tert*-butylphenols (**5**) and phenol (**6**) was obtained. In methanol MW-assisted catalytic transformation does't proceed too.

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