MICROWAVE PHOTOCHEMICAL REACTOR FOR SYNTHESIS

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INTRODUCTION

The fact that electrodeless discharge lamp (or microwave lamp, MWL) generates ultraviolet (UV) radiation when placed into the microwave field 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 for the first time by us in three subsequent publications [5-7]. We reported on the studies in an original photochemical reactor consisting of MWL placed into the reactor vessel of a commercial microwave oven. The MW field generated UV discharge in the lamp 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. In addition to our investigations, Chemat and his coworkers [8] recently described a MW-UV reactor in which the UV source was external.

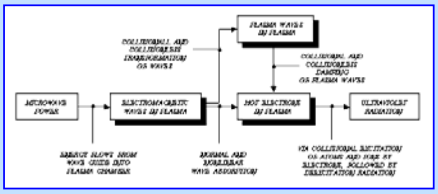
In this work we wish to describe details of working with our MW-UV reactor, necessary modifications to a domestic microwave oven for *microwave photochemistry* experiments [9].

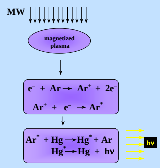
ELECTRODELESS DISCHARGE LAMPS

The electrodeless discharge mercury lamps (MWL) [10] were made of quartz or Simax tubings, filled with mercury and argon, and sealed under 20-Torr vacuum [11]. The size of our lamps varied from 10x20 to 20x50 mm. The spectral characteristics [12] of the electrodeless lamp resemble more those of high-pressure mercury lamps and are known. The lamp gives over three times as much UV radiation as the conventional electrode lamp [1].

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

PHOTOCHEMICAL MICROWAVE REACTOR

Our modifications to a domestic microwave oven are similar to those described for microwave chemistry experiments. Several commercially available ovens were modified according to the Figure. In a typical design, at least four holes were drilled to the oven walls: two 30-mm holes, one for a condenser tube in the oven top and the other from the side for an IR pyrometer, and two 20-mm ports for a glass tube with circulating water (inlet and outlet). External aluminum tubes of the same diameter (~10 cm long) were attached to the holes in order to eliminate possible MW leaking. A special attention was paid to the opening for the pyrometer, which has to aim to the reaction vessel. A part of the oven bottom was replaced by a round aluminum plate (200 mm of diameter), carefully attached to the framework, to allow magnetic stirring.

The typical experiment consisted of a reaction vessel (25-1000 ml) with a reaction mixture, equipped with a Teflon-covered stir bar and MWL. Such arrangement allowed irradiating the whole volume of the solution by UV light. The vessel was connected to a very efficient water-cooled condenser by a 100-300-mm long glass tube. The microwave power was adjusted to a maximal value of the particular oven (800-900 W), which guaranteed a continual MW radiation. The circulating cool water or some amounts of a solid, MW absorbing material (basic Al_2O_3, molecular sieve etc.) were used in those cases when a small quantity (<50 ml) of a polar liquid or non-absorbing (non-polar) liquids for microwave photochemical experiments were used. It removed the excess microwave power and/or prevented the magnetron to be destroyed by overheating.

The temperature of a liquid was monitored an IR pyrometer [13] or by a fiber-optic probe [14]. Each liquid started to boil very quickly because of the lamp heat operation. Polar liquids (e.g., water, ethanol, or acetonitrile), when used in higher amounts, often prevented the lamp initiation because they absorb most of the microwave power [6]. The lamp overheating causes the lamp emission failure [5,6].

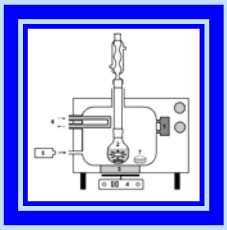
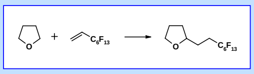


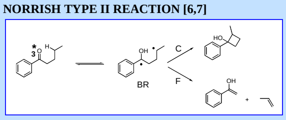
Figure: A modified MW oven for microwave photo-chemistry experiments: (1) *magnetron*, (2) *reaction mixture with MWL and stir bar*, (3) *aluminum plate*, (4) *magnetic stirrer*, (5) *infrared pyrometer*, (6) *circu-lating water in a glass tube*, (7) *a solid absorber inside the oven cavity.*

EXAMPLES OF USED COMMON PHOTOREACTIONS:

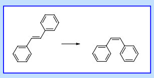
1) PHOTOINICIATED RADICAL ADDITION [5]



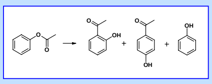
4) NORRISH TYPE II REACTION [6,7]



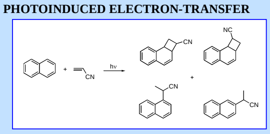
2) PHOTOISOMERIZATION



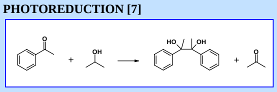
5) PHOTO-FRIES REACTION [7]



3) PHOTOINDUCED ELECTRON-TRANSFER



6) PHOTOREDUCTION [7]



CONCLUSIONS

The MW photoreactor can be characterized as follows:

a) Very simple construction and convenient device for synthetic photochemistry

b) Reaction rates are higher and therefore the reaction time can be significantly reduced

c) Energy consumption for UV generation is substantially lower compared to a conventional lamp

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