

MICROWAVE PHOTOCHEMISTRY IN ORGANIC SYNTHESIS

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It is known that organic reactions can be accelerated by different methods like ultrasound, high pressure, ultraviolet radiation and recently applied microwave radiation. The paper is focused on combination of UV and microwave radiation technique, i.e. on the combination of short- and long-waves to induce chemical reactions.

According to our knowledge this method has not been described in the literature up to now to be used for activation of chemical reactions. This idea is based on the possibility to take advantages of both methods. Some information have been found in patent literature which concern combinations of different methods [1-3] with principal aim of their practical utilization (e.g. for sterilizing various materials, waste water treatment, curing of coatings, synthesis of polymers, generation of electromagnetic radiation, and other applications).

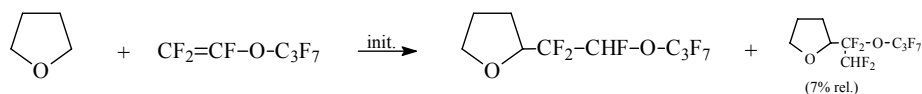
It is known that the energy of microwaves is too low (1.2 J/mol) to be able to split off chemical bond. On the other hand UV radiation is able to do it because its short-wave energy is over several orders higher (300-665 kJ/mol).

Basic and important condition for photochemical transformation of molecules is the excitation of their valence electrons to the higher, so called antibonding orbital [4]. However, the excitation of molecules per time unit should be considered too (i.e. the efficiency of the radiation source) since theoretically, microwave energy ($E = 1.2 \text{ J/mol}$) is not high enough to induce even rotation excitation ($E_{\text{rot}} \approx 400 \text{ J/mol}$). The first condition, leading in practice to generation of energetically much higher excited states has been evidenced by several examples of excitations of atoms or molecules by lamps and by the existence of photochemical reactions from so called "hot" state [4]. This phenomenon indicates that some reactions which can not proceed under conventional conditions could be initiated by this new way of activation.

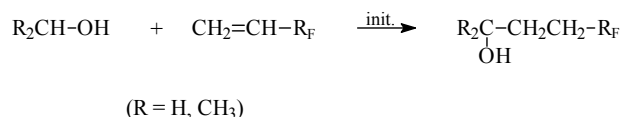
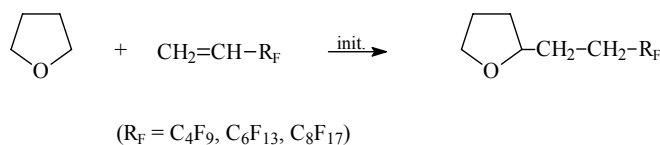
The transfer of electron to the excited state changes also the space structure of molecule [4,5]: interatomic distances increase and molecular symmetry changes. Information concerning geometry of excited particles can be obtained from calculated dipole moments (obtained by analyses of absorption and emission spectra) which undergo significant changes. It is a case of microwave radiation which is absorbed by a molecule, depending on its dielectric polarization. This second condition concerns the potential ability of selective heating-up of different excited states, and invokes the re-evaluation of the theorem of temperature effects on photo-chemical reaction [4].

Our proposed original idea of combination of the microwaves with UV irradiation was tested on the reactions which proceed under photochemical conditions only. We have got sufficiency of experiences with such reactions (cf. our earlier studies of photochemically initiated additions to fluoroalkenes [6,7] and we have tried to examine the scope and limitation of this new method of activation.

Therefore the addition of cyclic ether, such as tetrahydrofuran (THF), to perfluoroalkyl vinyl ether ($C_3F_7O-CF=CF_2$) was used as the model reaction:



The classical method of photochemical initiation was not successful in the case of the radical additions of alcohols or tetrahydrofuran to perfluoroalkyl ethylenes ($R_F-CH=CH_2$, $R_F = C_4F_9, C_6F_{13}, C_8F_{17}$). Therefore, acetone has to be used as an excellent triplet sensitizer [7]. However, the microwave-photochemical initiation of addition was successful without any sensitizers:



The following initiation systems were examined: the combined microwave and UV irradiation and the microwave radiation combined with a radical initiator, like dibenzoyl peroxide and *tert*-butyl peroxide. Their effect on the course of the reaction was evaluated with regard to final product(s) from the following aspects:

- the regioselectivity of addition of THF, i.e. the cleavage of the α - CH_2 bond and/or formation of α,ω -dialkyl THF,
- the regioselectivity of addition on fluorinated alkene, i.e. the addition to terminal or internal carbon of the alkene $C=C$ double bond (comparison of regioisomers ratio).

All experiments were carried out in MILESTONE Lavis 1000 Basic microwave instrument with 1000 W power output and equipped with PC temperature control via IR thermometer and specially made UV lamp (low pressure).

Acknowledgements

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