UV-induced generation of free radicals from aromatic and heteroaromatic molecules isolated in cryogenic matrices

Igor Reva

University of Coimbra, CIEPQPF, Department of Chemical Engineering, Coimbra, Portugal reva@eq.uc.pt

Here we present an overview of our selected experimental works, carried out within the last decade, ¹⁻⁸ and dedicated to studies of photochemistry of aromatic and heteroaromatic molecules. Monomers of phenol, indole, and of their several derivatives were isolated in cryogenic argon matrices and characterized by infrared spectroscopy. The samples were irradiated *in situ*, using either broadband or narrowband UV light. The structures of both the starting compounds and of the photoproducts were identified by comparing their observed infrared spectra with vibrational spectra computed theoretically. A common feature of all the selected studies is generation and experimental identification of free radicals resulting from the cleavage of OH, NH, or SH bonds. The mechanistic analysis of the observed photochemistry will be presented.

Acknowledgement

I acknowledge L. Lapinski, M. J. Nowak, H. Rostkowska, B. M. Giuliano, C. M. Nunes, A. J. Lopes Jesus, J. P. L. Roque, M. T. S. Rosado, and R. Fausto, who contributed to these works. The Chemical Process Engineering and Forest Products Research Centre (CIEPQPF) is supported by the Portuguese "Fundação para a Ciência e a Tecnologia" (FCT) through projects UIDB/EQU/00102/2020 and UIDP/EQU/00102/2020.

¹ Giuliano, B.M.; Reva, I.; Lapinski, L.; Fausto, R. Infrared spectra and ultraviolet-tunable laser induced photochemistry of matrix-isolated phenol and phenol-*d*₅. *J. Chem. Phys.* **2012**, *136*, 024505.

² Reva, I.; Nowak, M. J.; Lapinski, L.; Fausto, R. Hydrogen Atom Transfer Reactions in Thiophenol: Photogeneration of Two New Thione Isomers. *Phys. Chem. Chem. Phys.*, **2015**, *17*, 4888-4898.

³ Reva, I.; Lapinski, L.; Lopes Jesus, A. J.; Nowak, M. J. Photoinduced Transformations of Indole and 3-Formylindole Monomers Isolated in Low-Temperature Matrices. *J. Chem. Phys.*, **2017**, *147*, 194304.

⁴ Nowak, M. J.; Reva, I.; Rostkowska, H.; Lapinski, L. UV-Induced Hydrogen-Atom Transfer and Hydrogen-Atom Detachment in Monomeric 7-Azaindole Isolated in Ar and n-H₂ Matrices. *Phys. Chem. Chem. Phys.*, 2017, 19, 11447-11454.

⁵ Lopes Jesus, A. J.; Reva, I.; Fausto, R. UV-Induced Transformations in Matrix-Isolated 6-Methoxyindole. J. Photochem. Photobiol. A: Chem., 2017, 336, 123-130.

⁶ Nowak, M. J.; Reva, I.; Lopes Jesus, A. J.; Lapinski, L.; Fausto, R. UV-promoted radical formation, and near-IR-induced and spontaneous conformational isomerization in monomeric 9-methylguanine isolated in low-temperature Ar matrices. *Phys. Chem. Chem. Phys.*, **2019**, *21*, 22857-22868.

⁷ Lopes Jesus, A. J.; Rosado, M. T. S.; Fausto, R.; Reva, I. UV-induced radical formation and isomerization of 4-methoxyindole and 5-methoxyindole. *Phys. Chem. Chem. Phys.*, **2020**, 22, 22943-22955.

⁸ Reva, I.; Lopes Jesus, A. J.; Nunes, C. M.; Roque, J. P. L.; Fausto, R. UV-Induced Photochemistry of 1,3-Benzoxazole, 2-Isocyanophenol, and 2-Cyanophenol Isolated in Low-Temperature Ar Matrixes. *J. Org. Chem.*, **2021**, *86*, 6126-6137.