



TGA/DTA–FTIR–MS coupling as analytical tool for confirming inclusion complexes occurrence in supramolecular host–guest architectures



Cristian-Dragos Varganici^a, Narcisa Marangoci^a, Liliana Rosu^a, Cristian Barbu-Mic^{b,c}, Dan Rosu^{a,*}, Mariana Pinteala^a, Bogdan C. Simionescu^{a,b,c}

^a Centre of Advanced Research in Bionanoconjugates and Biopolymers, “Petru Poni” Institute of Macromolecular Chemistry, 41A Gigore Ghica-Voda Alley, 700487 Iasi, Romania

^b “Petru Poni” Institute of Macromolecular Chemistry, 41A Gigore Ghica-Voda Alley, 700487 Iasi, Romania

^c Department of Natural and Synthetic Polymers, “Gh. Asachi” Technical University of Iasi, 73 Dimitrie Mangeron Boulevard, 700050 Iasi, Romania

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ABSTRACT

The paper deals with the insights on the thermal decomposition of a viologen included in a [2]rotaxane structure alongside β -cyclodextrin. Thermal stability studies were conducted by dynamic thermogravimetry in inert atmosphere. Complexation phenomena occurrence led to an increase in inclusion complex thermal stability. Simultaneous TGA–DTA analysis indicated lower intensity of the complexed guest molecule melting profile. Kinetics of the thermal decomposition process was conducted by applying the isoconversional methods of Friedman and Flynn–Wall–Ozawa. Global kinetic parameters values exhibited an increase with the conversion degree, indicating a complex thermal degradation process. The form of the kinetic model which best described the thermal decomposition process and the kinetic parameters values corresponding to each degradation stage were determined with a multivariate non-linear regression method. A two dimensional diffusion (D2) kinetic model best fitted the thermogravimetric data. A correlation between kinetic data and structural changes during thermal decomposition was established. The evolved gas analysis was conducted on a coupling of simultaneous thermal analysis device to a quadrupole mass spectrometer and a Fourier transform infrared spectrophotometer. The complex gaseous mixture evolved during thermal decomposition of the structure was comprised of: water, carbon monoxide, carbon dioxide, hydrogen cyanide, methanol and ethanol, acetic acid, hydrogen bromide and amine and furan derivatives.

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1. Introduction

One main feature of 4,4-bipyridine resides in its property to form diquaternary salts regarded to as viologens. Their name was attributed on the basis of their color changing when exposed to a series of physical factors (e.g. light). The scientific interest of such salts grew due to some specific applications including electron carriers, pro-oxidants for oxidative stress testing, cardiovascular agents, herbicides, neuromuscular and hypotensive agents, molecular wires in electronic devices, electrochromic display devices [1,2]. Viologens also exhibit antibacterial efficiency against some microorganism species [3], such as *Escherichia coli*, due to their DNA strand scission ability [4]. Michaelis first exploited viologens' electrochemical properties in 1933 [5]. Due to their low redox

potential and the toxic effect on mammals [6], viologens aroused suspicions regarding their toxicity on the human organism and thus many works were reported on evaluating their action, for example those undertaken for methyl viologen (Paraquat) herbicide [7,8]. In a work by Hatcher and co-authors [9] there is even reported an increase in Parkinson's disease because of some viologen herbicides. After ingestion, 4,4'-bipyridyl viologens (Bpy^{2+}) undergo an enzymatic reduction mechanism during which there is generated a radical cation ($\text{Bpy}^{\bullet+}$). This cation, in the presence of O_2 and/or H_2O_2 , further produces extremely reactive radicals, such as HO^\bullet . This leads to the oxidation of biochemical important entities, such as lipid membranes, proteins and nucleic acids [2,10]. In this sense, current research in the domain is focused on the reduction of viologens toxicity and thus to exploit their redox potential for pharmacological interest. One such method, already published by our group, consists in incorporating viologens, through different procedures, in β -cyclodextrin (βCD), forming host–guest inclusion complexes [2].

* Corresponding author. Tel.: +40 232 217 454; fax: +40 232 211 299.
E-mail addresses: drosu@icmpp.ro, dan.rosu50@yahoo.com (D. Rosu).