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Time-resolved ESR studies on transient radicals photogenerated in solutions of melamine in ethylene glycol

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Abstract

Chemically Induced Dynamic Electron Polarization (CIDEP) spectra of transient radicals generated by laser pulse with $\lambda = 248$ nm in solutions of melamine in ethylene glycol have been studied by means of time-resolved (TR) ESR at room temperature. The main products are radicals of the solvent molecules formed through abstraction of hydrogen from ethylene glycol by excited melamine molecules and a melamine radical with attached hydrogen atom on melamine. Parameters obtained from well resolved TR ESR spectra coincide with parameters of radical of ethylene glycol $HOC^{\cdot}HCH_2OH$ and methylol $^{\cdot}CH_2OH$, and an unresolved ESR spectrum was attributed to the melamine radical. The electron spin polarization results from the radical pair mechanism (RPM) involving S–T_0 mixing (ST_0M) and additionally from a small part of triplet mechanism (TM). In order to establish the possible structure and nature of melamine radical quantum-chemical calculations by the DFT B3LYP method using several different basis sets have been done. The reaction pathway and mechanisms of alcohol and melamine radicals formation are proposed and supported by DFT calculations within B3LYP and CIS(D) methods. Melamine and ethylene glycol free radicals relaxation time T_2 was estimated as 1.5 and 0.5 μs, respectively.

Keywords: Time-resolved ESR; Melamin; Radical; Flash photolysis

1. Introduction

Wide industrial and medical applications of melamine (2,4,6-triamino-s-triazine) and melamine derivatives stimulate their investigations by different physical methods, including NMR, IR, UV, X-ray, and quantum-chemical calculations, but most of them dealt with the neutral molecules of triazines [1–6]. Theoretical studies of the structure of the melamine molecule using force field, semiempirical and ab initio Hartree–Fock methods [1,4,5] indicate that the geometry of melamine is nearly planar with the amino-hydrogens deviating slightly from the plane of the triazine ring. The calculations seem to agree with experimental crystallographic data for the melamine molecule [1]. To our knowledge no observation of the short-time photochemical radical reactions with melamine in solutions and in solid state have been reported up to now. To study these reactions we have started our investigations with melamine in ethylene glycol solution by flash photolysis and have registered the

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