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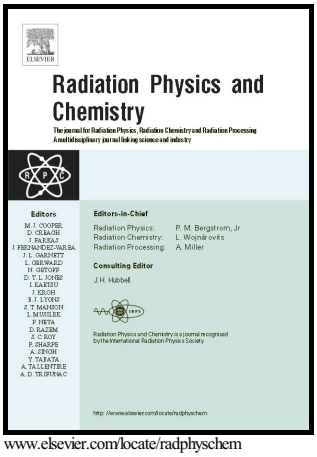

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Mechanism of the radiation-induced transformations of fluoroform in solid noble gas matrixes

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Abstract

The X-ray induced transformations in the CHF_3/Ng systems (Ng = Ne, Ar, Kr or Xe) at 6 K were studied by FTIR spectroscopy. The radiation-induced decomposition of CHF_3 was found to be rather inefficient in solid xenon with low ionization energy, which suggests primary significance of the positive hole transfer from matrix to the fluoroform molecule. $CF_3^{\bullet}$, $:CF_2$, $CHF_2^{\bullet}$ and CF_4 were identified as the products of low-temperature radiolysis in all the noble gas matrixes. In addition, the anionic complex $HF \ldots CF_2^-$ was detected in Ne and Ar matrixes. The radiolysis also resulted in formation of noble gas compounds (HArF in argon, HKrF in krypton, and XeF_2 in xenon). While XeF_2 and HArF were essentially formed directly after irradiation (presumably due to reactions of 'hot' fluorine atoms), HKrF mainly resulted from annealing of irradiated samples below 20 K due to thermally induced mobility of trapped fluorine atoms. In both krypton and xenon matrixes, the thermally induced reactions of F atoms occur at lower temperatures than those of H atoms, while the opposite situation is observed in argon. The mechanisms of the radiation-induced processes and their implications are discussed.

Keywords: fluoroform, matrix isolation, radiolysis, thermal reactions, mobility of fluorine atoms, mobility of hydrogen atoms

1. Introduction

Fluoroform is one of the 'haloforms', a class of compounds with the formula CHX_3 (X = halogen). Due to low reactivity and low toxicity it is used as refrigerant and fire suppressant. In particular, the application of fluoroform is considered as an ecologically acceptable alternative to chlorofluorocarbons (CFCs). Recently it was found that emission of fluoroform increased significantly during the last three decades, so it makes contribution to global warming process. Moreover, it was shown that the photolytic degradation of fluoroform in upper atmosphere is inefficient, so the average lifetime of this molecules was estimated as 270 years [1]. Thus, it is natural that this substance should, to a certain extent, spread to the upper layers of atmosphere and outer space, where it is subjected to the high-energy radiation.

To our knowledge, the radiation chemistry of fluoroform is poorly studied. The products of photoionization of this substance in an argon matrix were first characterized by Prochaska and Andrews using FTIR spectroscopy [2, 3]. These authors reported formation of $CF_3^{\bullet}$, $:CF_2$, $CHF_2^{\bullet}$, CF_4 and CF_3^+. It was also shown that the concentration of radicals and carbene decreases, whereas the concentration of tetrafluoromethane increases as a result of annealing at 30–35 K. In addition, an experimental evidence for formation of a hydrogen-bonded anionic complex of CF_2^- with HF was obtained [3]. The assignment was based on isotopic substitution experiments with both ^{13}C and D enriched substances. Nevertheless, the available data do not allow us to make definite conclusions on the mechanism of the radiation-induced degradation of fluoroform molecules in solid matrixes since the cited works were mainly focused on spectroscopic identification of the species generated by photoionization.

An approach to simulation of the primary radiation effects on isolated molecules in solid inert environment developed in our laboratory is based on using noble gas matrixes with different electronic characteristics [4, 5]. Also, monitoring the dose dependence is important to discriminate between primary and secondary processes [6]. Recently, this approach was applied to simple CFC molecules ($CFCl_3$ and CF_2Cl_2) [7]. The main issue of the present work concerns similarity and difference in the radiation-induced transformations of fluoroform and CFCs, which is an important from both fundamental and practical viewpoint. Considering basic aspects, one may note that fluoroform is characterized by high ionization energy (IE $\approx$ 13.9 eV, i.e., substantially higher than those of most popular CFCs) [8]. As shown in our previous studies [4, 5], IE is a crucial characteristics in the radiation chemistry of matrix isolated molecules, because the transformations of guest species in solid matrixes are mainly initiated by the positive hole transfer. Also, the presence of H atom in the fluoroform molecule is significant since it may strongly affect the reaction pathways for both ionic and excited states. Regarding more practical aspects, a comparative radiation stability of CFC and CHF_3 molecules is significant as they are considered as possible alternative solutions for some applications.

Here we report a systematic study on the radiation-induced

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