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Matrix isolation model studies on the radiation-induced transformations of small molecules of astrochemical and atmospheric interest

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HIGHLIGHTS

- Matrix isolation was used to simulate the radiation-induced transformations in ices.
- Recent results on the radilolysis of astrochemically relevant molecules are reviewed.
- Reactions of thermally mobilized O and H atoms in solid noble gases are discussed.
- Comparison between photolysis and radiolysis in matrices is presented.
- The role of weak intermolecular interactions in the ice radiolysis is demonstrated.

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ABSTRACT

The radiation-induced transformations of small molecules at low temperatures play an important role in the interstellar, planetary and atmospheric chemistry. This work presents a review of our recent model studies on the radiation chemistry of relevant molecules in solid noble gas (Ng) matrices, including some preliminary new results. Among the triatomic molecules, water and carbon dioxide were studied in detail. The radiation-induced degradation of isolated H_2O yields hydrogen atoms and OH radicals, while oxygen atoms are produced at higher doses. Isolated CO_2 molecules are decomposed to yield CO and trapped oxygen atoms. Upon annealing the trapped O and H atoms are mobilized selectively at different temperatures and react with other trapped species. The formation of HCO and HOCO radicals was observed in the mixed $H_2O/CO_2/Ng$ systems. Other studies were concerned with the radiation-induced degradation of simple organic molecules (methanol, formic acid) and chlorofluorocarbons ($CFCl_3$, CF_2Cl_2). Preliminary results for methanol revealed deep dehydrogenation yielding HCO and CO, whereas CO_2, CO and HOCO were detected as primary products for formic acid. In the case of chlorofluorocarbons, significance of ionic channels was demonstrated. The implications of the results for modeling the processes in astrochemical ices and atmosphere are discussed.

1. Introduction

A continuously growing interest to the behavior of chemical species in stratosphere, planetary atmospheres, and outer space is determined by both fundamental and practical aspects, ranging from urgent ecologic issues to the problems of prebiotic evolution of matter and challenges for the future ambitious space missions. In fact, the fields of astrochemistry and atmospheric chemistry are essentially related to the chemical evolution of small molecules in a cold environment affected by light and high-energy radiation. Despite an impressive recent progress in these fields, there is still an evident lack of basic understanding of the mechanisms of such processes, particularly in such complicated systems as interstellar and planetary ices. Direct evidences coming from stratospheric probes and radioastronomical observations are not sufficient to get a clear picture, which implies an important role of laboratory simulation. In this aspect one could refer, for example, to recent works on degradation of small organic molecules in icy films induced by different types of radiation (Andrade et al., 2013; Chen et al., 2013). However, the studies of "realistic" ices (particularly, mixed systems) usually cannot provide unequivocal proof of the reaction mechanism, because the spectroscopic identification of

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reactive intermediates is often not straightforward due to overwhelming absorption of parent substance and severe line broadening. Furthermore, such studies typically require very high absorbed doses. Thus, these experiments should be complemented by spectroscopically informative model studies, which can be done using a classical matrix isolation technique.

Matrix isolation is a powerful tool for elucidation of basic mechanisms in solid-state photochemistry and radiation chemistry. The mechanistic aspects of photochemical reactions studied by matrix isolation through several decades are covered by a number of reviews (e.g., Dunkin, 2004; Bondybey et al., 1999). To a certain extent, the matrix isolation works provide a bridge between gas-phase and solid-phase photochemistry, as well as between theory and experiment. Meanwhile, the radiation chemistry of isolated molecules in noble-gas matrices was not studied so extensively. During the last fifteen years we have developed and implemented a systematic approach to the matrix isolation studies of the radiation-induced transformations of organic molecules in solid noble gas media using a combination of FTIR and EPR spectroscopy, which may be referred to as "matrix isolation for radiation chemistry" (Feldman, 1997, 1999, 2014). The principal feature of radiolysis, as applied to the matrix isolation conditions, is that the energy of ionizing radiation is primarily absorbed by the matrix, and the guest molecules are affected mainly by the positive hole and excitation transfer (see Feldman, 1999, 2014 for detailed scheme of primary events). This means that the matrix should be considered not only as a cage to trap reactive species, but also as a simple model medium for elucidation of the basic environment effect in the radiation chemistry. In particular, this approach made it possible to shed some light on the most spurious issues of the condensed-phase radiation chemistry, namely, effect of excess energy and selectivity of the primary processes (Feldman, 1999, 2014; Feldman et al., 2000, 2003a, 2006). The main focus of our previous works was the study of formation and degradation of the primary ionized species (radical cations) produced from relatively large organic molecules. Recently we turned to detailed characterization of reactive intermediates and reaction pathways occurring under irradiation of selected small molecules in noble gas matrices motivated primarily by modeling the astrochemical and atmospheric processes. Here we present an overview of first results and prospects for further studies.

2. Experimental approach and design

The experimental approach for the combined matrix isolation studies using FTIR and EPR spectroscopy was described in detail elsewhere (Feldman, 1997, 1999) and a modern version of our complex of cryostats is presented in recent papers (Kobzarenko et al., 2012; Feldman, 2014.). In general, the premixed gases in a required ratio (typically, between 1/300 and 1/2500) were deposited onto a cooled KBr plate (for FTIR spectroscopy) or sapphire rod (for EPR spectroscopy) at the temperatures of 7–30 K, depending on the matrix used. The deposited samples were irradiated by X-rays (effective energy ca. 20 keV) at 6–10 K for different time in the range of 3–120 min. Evaluation of the absorbed dose was carried out taking into account mass absorption coefficients for a specific photon energy, as described previously (Kameneva et al., 2015a). It is worth noting that the irradiation was quite efficient in the cases of krypton and xenon, because of very high values of the mass absorption coefficients for these matrices. The degradation of the parent molecules was monitored by FTIR spectroscopy, whereas the products were characterized by both FTIR and EPR spectroscopy. The FTIR spectra were measured using commercial spectrometers (Perkin Elmer 1720X and Bruker Tensor II) and EPR spectra were recorded with a custom-made X-band spectrometer (SPIN, Russia).

3. Results and discussion

3.1. Triatomic molecules

Among the triatomic species, H_2O and CO_2 molecules are of particular relevance to both atmospheric chemistry and astrochemistry. These species are the most widely occurring chemical compounds in the Earth atmosphere and they are found in planetary and interstellar ices. The radiation chemistry of water ice has been extensively investigated, mainly by EPR spectroscopy (Ershov and Pikaev, 1969). Meanwhile, to our knowledge, up to recently, the radiation-induced transformations of isolated water and carbon dioxide molecules in noble gas matrices were not studied in detail.

3.1.1. Water

In an earlier work (Khriachtchev et al., 2002) it was shown that the water molecules undergo rather effective dissociation upon fast electron irradiation in solid xenon to yield trapped OH radicals and H atoms, similar to the process occurring under UV photolysis at 193 nm:

$$H_2O^* \rightarrow H + OH. \quad (1)$$

It is worth noting that the concentrations of hydroxyl radicals and hydrogen atoms are nearly balanced at low absorbed doses, whereas the relative yield of H atoms increases at higher doses, which indicates the occurrence of a secondary process:

$$OH^* \rightarrow H + O. \quad (2)$$

Our recent detailed study (Ryazantsev and Feldman, 2015a) revealed that this scheme is basically applicable also to argon and krypton matrices. It is worth noting that, in fact, direct identification of very simple products of reactions (1) and (2) in matrices is a rather complicated task. Certainly, trapped H atoms are easily detected by EPR spectroscopy. Meanwhile, the OH radical is a species difficult to observe by EPR in weakly interacting media because of orbital degeneracy. A broad, poorly resolved anisotropic doublet signal was assigned to this radical in xenon, presumably due to partial lifting of orbital degeneracy in this relatively polarizable medium (Khriachtchev et al., 2002). Meanwhile, no direct evidences were reported for other noble gas media. As to IR spectroscopy, OH radical is known to be a relatively weak absorber; furthermore, its absorption arises in a strongly contaminated "water region" of the IR spectrum. Nevertheless, we were able to detect weak absorptions of the OH radicals resulting from water radiolysis in all the three matrices (features at 3548, 3539, and 3531 cm^{-1}, in Ar, Kr, and Xe respectively, Ryazantsev and Feldman, 2015a). Detection of O atom in matrices is difficult since it is invisible by both EPR and IR spectroscopy. The way to trace the formation of this species is based on its annealing-induced mobility, which occurs at lower temperature, in comparison with other diffusion processes in matrices (Danilychev and Apkarian, 1993; Kiviniemi et al., 2004). This mobility results in chemical reactions yielding the IR-detectable products:

$$O + OH \rightarrow HO_2, \quad (3)$$

$$O + O_2 \rightarrow O_3. \quad (4)$$

The latter process involves an impurity oxygen, which usually occurs in matrices in small amounts. In addition, the formation of HXeO radical is observed in a xenon matrix: