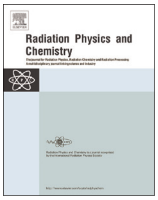
Radiation Physics and Chemistry 110 (2015) 17–23

Contents lists available at ScienceDirect

Radiation Physics and Chemistry

journal homepage: www.elsevier.com/locate/radphyschem



Kinetics and mechanism of the radiation-chemical synthesis of krypton hydrides in solid krypton matrices

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HIGHLIGHTS

- Reactions of radiolytic H atoms in solid krypton were monitored by EPR and FTIR spectroscopy.
- The role of “local” and “global” mobility of H atoms was established.
- HKrCCH and HKrCl were prepared by the radiation-chemical method.

ARTICLE INFO

Article history:
Received 15 December 2014
Accepted 6 January 2015
Available online 7 January 2015

Keywords:
Matrix isolation
X-ray radiolysis
FTIR spectroscopy
EPR
Hydrogen atoms
Kinetics of low-temperature reactions
Noble gas hydrides

ABSTRACT

The processes occurring in the X-irradiated C_2H_2/Kr and HCl/Kr systems in the temperature range of 7–30 K were studied using a combination of FTIR and EPR spectroscopy. In both cases, irradiation results in effective decomposition of isolated molecules (C_2H_2 or HCl) and production of trapped H atoms. The thermal decay of trapped atoms in solid krypton was attributed to “local” reactions (below 21 K) and long-range mobility activated in the temperature range of 23–27 K. Two krypton hydrides, HKrCCH and HKrCl, were synthesized from the radiation-induced hydrogen atoms. In the case of C_2H_2/Kr system, competitive reaction channels of H atoms at various absorbed doses were investigated in details, and HKrCCH was found to be one of the main reaction products. The X-ray radiolysis in krypton matrices was concluded to be a promising method to obtain krypton hydrides.

1. Introduction

The noble gas hydride of general formula HNgY (Ng—a noble gas atom, Y—an electronegative fragment) represent an interesting class of novel compounds with unusual chemical bonds, which attract considerable interest from both theoretical and experimental viewpoint. The molecules of this kind were first discovered in the studies of UV photolysis of hydrogen halides in solid xenon and krypton followed by annealing the samples at ca. 30–50 K (Pettersson et al., 1995). Soon after that, it was demonstrated that xenon dihydride (HXeH) could be produced with high yields using radiolysis of various hydrocarbons in solid xenon at 16 K with subsequent annealing of the samples up to 40 K (Feldman and Sukhov, 1996). The identification of noble gas hydrides is based on very strong characteristic IR absorptions corresponding to the H—Ng stretching vibrations (Pettersson et al., 1999). According to the data of combined FTIR/EPR studies (Feldman et al., 1997) and IR photodecomposition experiments (Pettersson et al., 1997), the mechanism of formation of HNgY molecules includes dissociation of appropriate precursor molecules (HY) in solid xenon or krypton followed by thermally induced reaction involving a matrix atom

$$HY^* \rightarrow H^\bullet + Y^\bullet \quad (1)$$

$$H^\bullet + Ng + Y^\bullet \rightarrow HNgY \quad (2)$$

It should be understood that reaction (2) is certainly not a real trimolecular process. It implies interaction of thermally mobilized H atom with Y fragment trapped in the matrix cage. Thus, the HNgY species corresponds to a local minimum at the potential energy surface, separated from the global minimum corresponding to HY by a sufficiently high barrier (Pettersson et al., 1999). Currently more than thirty noble gas hydrides were characterized by spectroscopic methods and quantum chemical calculations. It is worth noting that the noble gas hydrides may be considered as unique probes of local dynamics and molecular interactions in the noble gas hosts due to extremely large intensity of their vibrational bands and high sensitivity of the corresponding modes to environment effects. Thus, in addition to novel and fascinating chemistry, the studies of formation and properties of such molecules have important implications for the solid-state

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http://dx.doi.org/10.1016/j.radphyschem.2015.01.007

photochemistry, radiation chemistry and chemical physics. The state-of-art of this field is presented in recent reviews (Khriachtchev et al., 2009; Gerber et al., 2012).

It should be noted that the topic is really "hot" from the viewpoint of theoretical chemistry, including both efforts on description of the stability and bonding nature in the HNgY species (Cohen et al., 2014) and prediction of novel molecules of this kind (Ma et al., 2014), while the experimental studies are still limited and come from few groups. In most cases, the noble gas hydrides were obtained using UV photolysis for dissociation of the precursor molecules. Only a few xenon hydrides were prepared by radiolysis (Feldman and Sukhov, 1996, Feldman et al., 2003; Feldman et al., 2005, Ryazantsev et al., 2013) and up to now this method was not used for obtaining krypton hydrides. The main difference between photolysis and radiolysis results from different mechanism of radiation effect on the isolated precursor molecules. In the case of photolysis, the HY molecules directly absorb the UV light, whereas in the case of radiolysis, the energy of ionizing radiation is primarily absorbed by the matrix and the isolated precursor molecules undergo dissociation due to indirect action (charge and energy transfer). The latter mechanism was found to be very efficient, even at high dilutions (Feldman et al., 1996). Basically the radiation-chemical method is more universal, because it can be applied to any kind of precursor molecules, independent of their optical absorption spectra. On the other hand, the effect of radiolysis may be more complicated due to involvement of high-energy ionic reaction channels, in particular, in the cases of argon and krypton matrices with high ionization potentials (Feldman, 1999, Feldman et al., 2003, Kobzarenko et al., 2012). Furthermore the spatial distribution of the dissociation fragments in photolysis and radiolysis may be different (Komaguchi et al., 2007).

In this work, we first report the preparation of krypton hydrides from two precursors (C_2H_2 and HCl) using the radiation-chemical method. The main focus of this study is mechanism and kinetics of the processes leading to the formation of krypton hydrides as monitored by a combination of FTIR and EPR spectroscopy.

2. Experimental

An original complex of close-cycle helium cryostats based on the SHI RDK-101E cryocoolers used in this study was described in more detail elsewhere (Kobzarenko et al., 2012; Feldman, 2013). Acetylene (grade A) and hydrogen chloride obtained by reaction between H_2SO_4 and NaCl were mixed with krypton (Akela-M, 99.999%) in the mole ratios of 1:1500 and 1:780, respectively. The gaseous mixtures were deposited onto a cold KBr plate (for the IR studies) or sapphire road (for the EPR experiments) at 21 K. The deposition temperature was adjusted according to the common criteria used for matrix isolation procedure to compromise between absence of clusterization and acceptable optical properties of the matrix. The thickness of deposited layer were about 60–90 μm in the case of IR-experiment (as determined from the interference picture) and up to 0.5 mm in the case of EPR-experiment (visually controlled).

Irradiation of the deposited samples with X-rays was carried out throw thin aluminum foil windows in the corresponding cryostats at ca. 7 K. A 5-BKhW-6 X-ray tube with tungsten anode (maximum energy 32 keV, effective energy 20 keV). The half-attenuation length for 20 keV X-rays in solid krypton is ca. 80 μm as calculated from the mass attenuation coefficient of 55.5 cm^2/g (Hubbel and Seltzer, 1996). This implies that the dose distribution is essentially inhomogeneous, in particular, in the samples used for the EPR experiment. Nevertheless, we have roughly estimated the effective absorbed dose rate in krypton based on the measurements with Fricke dosimeter applied in the same irradiation geometry and taking into account the mass absorption coefficients of dosimeter and krypton for $E=20$ keV (0.55 and 35 cm^2/g, respectively, Hubbel and Seltzer, 1996). It was found to be ca. 50 and 102 Gy/s for the IR and EPR experiments, respectively.

After irradiation the samples were gradually annealed at different temperatures (up to 35 K).

IR spectra were measured by Perkin Elmer 1720X FTIR spectrometer (MCT detector, resolution of 1 cm^{-1}, averaging by 200 scans) at 7.5 K. EPR spectra were measured using X-band (9.4 GHz) spectrometer manufactured by SPIN (St. Petersburg, Russia) at 6.5 K. Microwave power was kept low (2–5 μW) to avoid the signal saturation.

The relative concentrations of the isolated species were determined by integration of the absorptions in IR experiment and double integration of the first derivative signals in EPR experiment. The inaccuracy of the determination of relative concentrations within the same experiment did not exceed 10%.

3. Results and discussion

3.1. Acetylene-krypton system

Fragment of the IR spectrum of deposited sample C_2H_2/Kr is presented in Fig. 1a. This spectrum reveals characteristic absorptions from isolated monomeric acetylene molecules (bands at 733, 3279, and 3294 cm^{-1}) and weak features from acetylene dimers or associates (bands at 742, 3233, and 3260 cm^{-1}) (assignment in accordance with previous reports, taking into account reasonable matrix shifts (Tanskanen et al., 2006, Feldman et al., 2005, Golovkin et al., 2013).

Irradiation results in significant decomposition of monomers and virtually complete disappearance of associates. The dependence of relative concentration of acetylene monomer on irradiation time is shown in Fig. 2. An estimation of the initial radiation-chemical yield gives the value of ca. 1 molecule per 100 eV of absorbed energy. Because of dosimetric uncertainty mentioned above, this value should be considered as a rough estimate. However, in any case, it reveals high efficiency of energy transfer from krypton matrix to the isolated acytelene molecules under radiolysis, comparable to those found previously for radiolysis of some other organic molecules in solid argon and xenon matrices (Feldman, 1999). As follows from Fig. 2, the rate of acetylene radiolysis decreases rapidly with increasing conversion degree.

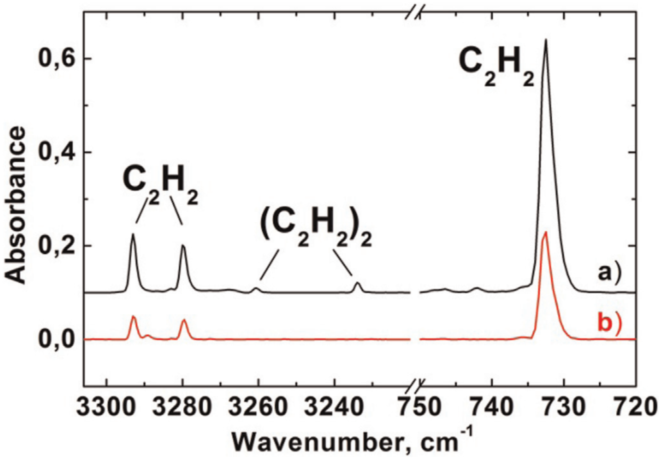

Fig. 1. FTIR spectra of C_2H_2/Kr (1:1500): (a) after deposition; (b) after irradiation with X-rays for 15 min at 7 K.