

Reactions of H atoms produced by electron irradiation of benzene in solid xenon: IR spectrum of cyclohexadienyl radical and possible involvement of HXeC_6H_5

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Received 4 November 2006; in final form 9 February 2007

Available online 16 February 2007

Abstract

Chemical reactions induced by fast electron irradiation of benzene in solid xenon were studied by EPR and FTIR spectroscopy. Irradiation at 16 K leads to H atoms and phenyl radicals. Annealing at 45 K results in formation of HXeH and cyclohexadienyl radical (C_6H_7). A strong IR absorption at $618/620\text{ cm}^{-1}$ and several weaker bands were assigned to cyclohexadienyl radical from comparison with EPR data and DFT calculations. A computationally stable molecule HXeC_6H_5 was not found experimentally, which means that it is either not formed or not stabilized under the experimental conditions used.

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1. Introduction

Matrix isolation technique, a powerful tool for studies of reactive intermediates, is commonly based on the assumption of matrix inertness. However, recent studies of photolysis and radiolysis of various molecules in xenon and krypton matrices revealed formation of novel-type chemical species including matrix atoms. The rare gas hydrides of general structure HRgY ($\text{Rg} = \text{Xe}$ or Kr , Y is an electronegative fragment) were first detected in photochemical experiments [1], and a number of inorganic hydrides of this kind has been characterized by IR spectroscopy [2]. Formation of xenon dihydride upon annealing of the xenon–hydrocarbon systems irradiated with fast electrons was found in our laboratory [3]. More

recently, Lundell et al. [4] reported a computational prediction for a number of organic molecules of similar structure. First experimental evidence for an organoxenon hydride formed from acetylene (HXeCCH) was reported independently by two groups [5,6]. The photochemical data [5] also suggested formation of HXeCC radical and HXeCCXeH (confirmed in later works [7,8]). Further studies led to identification of HKrCCH , HXeC_4H and HKrC_4H [9,10]. Meanwhile, one of the most interesting theoretical results [4] and a great challenge for experimental verification is xenon insertion into benzene molecule.

As shown by comparative FTIR/EPR studies [11] and IR photodecomposition experiments [12], the rare gas hydrides are formed by annealing-induced reactions of hydrogen atoms. Thus, the first step is dissociation of a precursor molecule HY to H and Y in a solid matrix at 7–20 K, either by UV photolysis [1,2,5,7,9,10,12] or by irradiation with fast electrons [3,6,8,11]. The latter approach is not limited by optical absorption spectrum of precursor and makes it possible to populate the states, which are not attainable by direct optical excitation. This may be

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important for benzene, because direct photolysis of C_6H_6 at different wavelengths mainly results in isomerization [13].

In this work, we have studied the reactions induced by fast electron irradiation of benzene in solid xenon using a combination of EPR and FTIR spectroscopy.

2. Experimental

A custom-made complex of continuous-flow helium cryostats for EPR and FTIR studies was described previously [14]. Gaseous mixtures were deposited onto a KBr window (for FTIR studies) or a sapphire rod (for EPR studies). Typical deposition time was 1–2 h at 30 K. After the deposition the samples were irradiated with fast electrons (1 MeV) at 15–17 K using a EG-2.5 Van-de-Graaff type accelerator. The absorbed dose was 40–80 kGy. IR spectra (4000–450 cm^{-1}) were measured at 15–20 K with a Perkin–Elmer 1710 FTIR spectrometer (MCT detector, 100 scans, 1 cm^{-1} resolution). EPR spectra were recorded using an X-band spectrometer with a 100 kHz high-frequency modulation (SPIN, St.-Petersburg, Russia). High purity xenon (99.995%), reagent grade benzene and deuterobenzene (99% D, Aldrich) were used as received.

3. Results

IR spectrum of the solid deposited benzene–xenon mixture exhibits principal absorptions of C_6H_6 (Fig. 1). Irradiation with fast electrons results in noticeable decay of these bands (by ca. 40% at the dose of 40 kGy) and appearance of a number of new features (Fig. 1). The most intense new band at 703 cm^{-1} and weaker absorptions at 3056, 1437, 1429, 1023 and 655 cm^{-1} should be assigned to the $\cdot C_6H_5$ (phenyl) radical, which has been characterized comprehensively in solid argon [15]. All the absorptions observed in

xenon are red-shifted by 3–4 cm^{-1} as compared to argon [15]. Weak bands at 732 and 843 cm^{-1} result from Xe_2H^+ [16].

EPR spectrum of irradiated xenon–benzene system (Fig. 2) shows a characteristic signal from trapped H atoms with basic separation of ca. 50.6 mT and a well-defined additional structure due to interaction of unpaired electron with magnetic xenon nuclei [6,11]. An anisotropic, poorly resolved signal at $g \approx g_e$ should be reasonably ascribed to phenyl radical (the counterpart of H atom in the case of benzene). The EPR spectra of phenyl radical were reported previously in different matrices [17]. Detailed assignment of A and g tensors was made in solid argon [18]. According to these data, phenyl radical is characterized by hyperfine coupling with two *ortho*-H ($a_{xx} = 2.19$ mT, $a_{yy} = 1.54$ mT, $a_{zz} = 1.49$ mT), two *meta*-H ($a_{xx} = 0.66$ mT, $a_{yy} = 0.61$ mT, $a_{zz} = 0.50$ mT), and *para*-H ($a_{xx} = 0.20$ mT, $a_{yy} = 0.25$ mT, $a_{zz} = 0.12$ mT). The spectrum in xenon is severely broadened due to magnetic interactions with matrix. Nevertheless, the spectral pattern and total spread are consistent with those expected for phenyl radical, as shown by powder simulation using the parameters taken from Ref. [18] (weak coupling with *p*-proton was neglected) and Gaussian linewidth of 0.5 mT (Fig. 2). Thus, IR and EPR data show that dissociation to phenyl radical and H atom is the principal process upon fast electron irradiation of benzene in solid xenon.

Decomposition of C_6D_6 upon irradiation in solid xenon was very small (ca. 10%) at the doses up to 80 kGy and the product absorptions were extremely weak.

It is known [1–8,10–12] that hydrogen atoms become mobile and undergo chemical reactions in solid xenon at ca. 40 K. As seen from Figs. 1 and 3, annealing at 45 K results in decrease of the bands of $\cdot C_6H_5$ (ca. 1.8 times) and small decay of benzene absorption (by ca. 10%) with simultaneous appearance of several new bands. The strongest absorption (doublet) was found at 618/620 cm^{-1} , and weaker bands appeared at 2768, 1387, 1287, 1166, 1180,

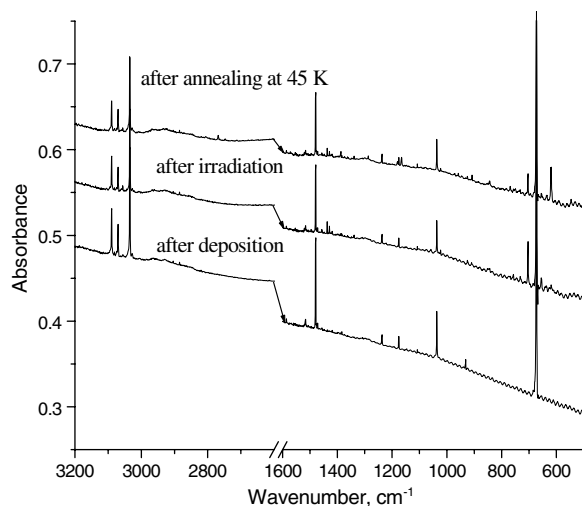


Fig. 1. Effect of irradiation at 16 K and subsequent annealing (5 min at 45 K) on the IR spectra of deposited mixture $C_6H_6/Xe = 1/1500$. The spectra were measured at 20 K.

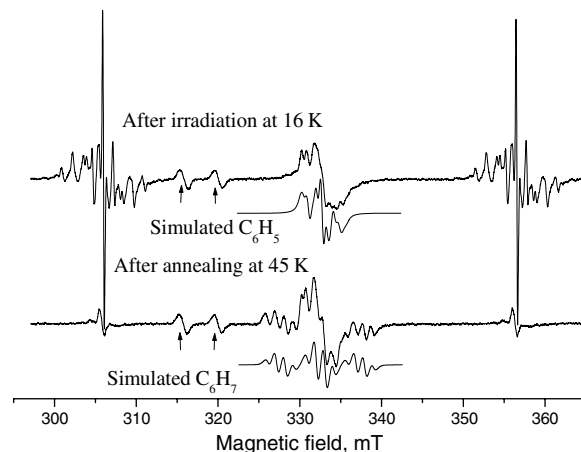


Fig. 2. EPR spectra of deposited C_6H_6/Xe mixture (1/1500) after irradiation at 16 K and subsequent annealing at 45 K (5 min). Arrows show signals from sapphire rod.

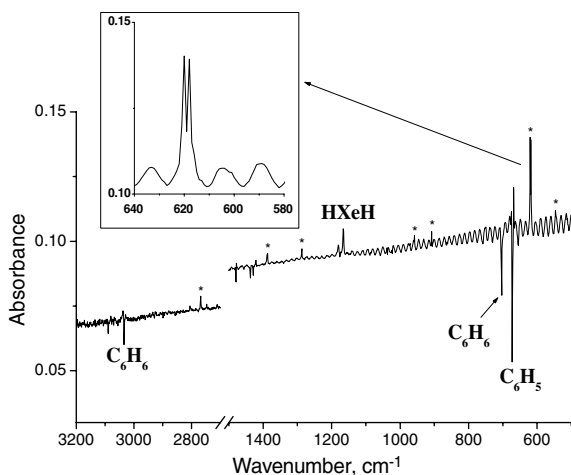


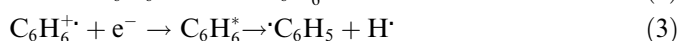
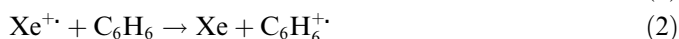
Fig. 3. Detailed view of the annealing-induced changes in the difference IR spectrum (asterisks show the lines ascribed to cyclohexadienyl radical).

958, 908 and 546 cm^{-1} . Among these features, absorptions at 1166 and 1180 cm^{-1} should be assigned to XeH_2 [2,3]. The origin of other new bands will be discussed below.

EPR spectra of the annealed samples (Fig. 2) show drastic decay of H atoms and appearance of a signal from cyclohexadienyl radical ($\cdot\text{C}_6\text{H}_7$), which is known in different media [17]. This radical gives a triplet of quartets due to large hyperfine coupling with two CH_2 protons [$a(2\text{H}) = 4.85\text{ mT}$] and weaker coupling to three roughly equivalent C–H protons [$a(2\text{H}) \approx 1.05\text{ mT}$] (the splitting resulting from two other protons is unresolved). Isotropic simulation is shown in Fig. 2. Note that the central quartet [$M_1(\text{CH}_2) = 0$] overlaps with the signal of $\cdot\text{C}_6\text{H}_5$, whereas two outer components [$M_1(\text{CH}_2) = \pm 1$] are nicely reproduced by simulation.

4. Discussion

In the case of electron irradiation, the energy is primarily absorbed by matrix, and the transformations of isolated molecules occur due to charge and excitation transfer. As shown previously [3,14], the positive hole transfer leading to formation of solute radical cations is the principal process for organic molecules with ionization potentials below 10 eV. This mechanism has been proved by observation of benzene radical cations in solid rare gas matrices doped with electron scavengers [19,20]. In the absence of scavengers, the radical cations undergo recombination with secondary electrons yielding neutral excited states, which decay to form observed products:



High yield of benzene dissociation (in contrast with photochemical data [13]) implies that the recombination leads to population of specific excited states, which are not attainable by direct photoexcitation. In particular, one could ex-

pect formation of high triplet states (expected ratio of triplets to singlets is 3:1 for recombination of uncorrelated ion pairs) and large contribution of vibrationally excited states. From practical point of view, it is worth noting that the method used in this work allows one to break the C–H bonds in aromatic molecules in solid xenon, with minor contribution of other channels. This may be useful for the low-temperature preparation of organoxenon hydride compounds from benzene derivatives.

New IR bands resulting from annealing belong to the products of reactions of thermally mobilized H atoms. In addition to XeH_2 (see above), one could expect formation of HXeC_6H_5 molecule (known only in theory) and cyclohexadienyl radical (product of H addition to benzene ring found by EPR spectroscopy). First, it is clear that the strongest band at 618/620 cm^{-1} cannot belong to HXeC_6H_5 . The calculated harmonic frequency for the strongest absorption corresponding to the H–Xe stretching in HXeC_6H_5 is 1317 cm^{-1} at the MP2 level [4]. The MP2 harmonic calculations tend to overestimate the H–Xe stretching frequencies due to imperfections in theory and neglect of anharmonism; nevertheless, the difference between experiment and calculation cannot exceed 200–300 cm^{-1} [2,5,6,10]. Furthermore, even weakly bound xenon hydrides show H–Xe stretching above 1000 cm^{-1} [2]. The assignment of absorption at 618/620 cm^{-1} to cyclohexadienyl radical looks logical since thermal behaviour of this band correlates with that of $\cdot\text{C}_6\text{H}_7$ as monitored by EPR. The cyclohexadienyl radical has been studied extensively by EPR [17] and UV/vis spectroscopy [21]; however, to our knowledge, its IR spectrum is unavailable. Some information on vibrational frequencies of $\cdot\text{C}_6\text{H}_7$ was obtained in recent gas-phase laser-induced fluorescence (LIF) studies, which revealed fundamentals at 1571, 1174, 981, 559, and 600 cm^{-1} assigned to various in-plane modes [22]. Meanwhile, the strongest response in IR absorption spectra is expected from the out-of-plane C–H bending.

The analysis of LIF data [22] was based on the MP2/6-31G* calculations of harmonic vibrational frequencies. However, reliable interpretation of IR absorption spectra requires also theoretical IR intensities. Moreover, the open-shell systems (radicals) often present a problem for the MP2 method, whereas the density functional theory (DFT) works well enough in these cases [23,24]. To clarify the identification we have performed a series of DFT calculations of harmonic frequencies, IR intensities, and magnetic resonance parameters for the cyclohexadienyl radical.

The calculations were performed with a PRIRODA package [25] using an original procedure of fast evaluation of density functional exchange–correlation terms [26]. A L22 basis set [27] was used in B3LYP [28] and PBE0 [29] DFT calculations. The results obtained with two functionals were very close, so we present here only the data obtained with B3LYP. The radical has a C_{2v} symmetry with a cyclic C_6 plane, and the calculated bond lengths agree reasonably with the MP2 data [22]. The calculated isotropic hyperfine coupling constants are $a(2\text{H}) =$

Table 1

Comparison of calculated harmonic frequencies (cm^{-1}) and IR intensities (km/mol) of C_6H_7 with experimental characteristics of the annealing-induced IR absorptions (vs – very strong, m – medium, mw – medium weak)

| Calculated characteristics (B3LYP) ^a | | | Experiment |
|------------------------------------------------------|-----------|--------------|----------------------|
| Approximate mode description | Frequency | IR intensity | |
| Out-of-plane C–C–C bend, CH_2 wag | 531.5 | 9.6 | 546 (mw) |
| Out-of-plane C–H bend, CH_2 wag | 637.4 | 72.8 | 618/620 (vs) |
| C_m –H out-of-plane bend, CH_2 wag | 937.9 | 6.5 | 908 (mw) |
| C–C–C in-plane bend, CH_2 wag | 967.0 | 7.3 | 958 (mw) |
| C_p –H and C–C–C in-plane bend | 1306.0 | 5.1 | 1287 (mw) |
| CH_2 scissor | 1439.6 | 6.7 | 1387 (mw) |
| CH_2 asym. stretch | 2898.2 | 18.9 | |
| CH_2 sym. stretch | 2915.2 | 39.2 | 2768 (m) (tentative) |
| C–H sym. stretch | 3147.4 | 8.3 | |
| C–H asym. stretch | 3168.5 | 46.6 | |

Only the features with calculated intensities $>5 \text{ km/mol}$ are presented.

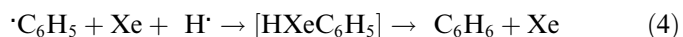
^a The calculated bond lengths in C_6H_7 (nm): $r(\text{C}_o\text{--CCH}_2) = 0.1497$; $r(\text{C}_o\text{--C}_m) = 0.1359$; $r(\text{C}_m\text{--C}_p) = 0.1414$; $r(\text{CCH}_2\text{--H}) = 0.1103$; $r(\text{C}_o\text{--H}) = r(\text{C}_m\text{--H}) = 0.1083$; $r(\text{C}_p\text{--H}) = 0.1081$. C_o , C_m and C_p denote carbon atoms in *ortho*, *meta* and *para* positions to CH_2 group, respectively.

5.45 mT (CH_2), $a(2\text{H}) = 0.99 \text{ mT}$ (*o*-H), $a(1\text{H}) = 1.35 \text{ mT}$ (*p*-H), and $a(2\text{H}) = 0.35 \text{ mT}$ (*m*-H), in agreement with the experimental data (see above), which shows proper description of electronic structure.

We will not present detailed vibrational analysis, because reliable assignment of all modes would require further experimental and theoretical work, which is out of the scope of this Letter. Only the computationally strong features among the calculated 33 fundamentals are shown in Table 1. The calculated frequency of the most intense transition (637 cm^{-1}) is very close to the experimental value of $618/620 \text{ cm}^{-1}$ supporting assignment of this band to the cyclohexadienyl radical (small doublet may be of matrix origin). This feature may be compared with the strongest absorptions for benzene (673 cm^{-1}) and phenyl radical (703 cm^{-1}) in the same matrix. Furthermore, as shown in table, weaker annealing-induced bands also can be attributed to cyclohexadienyl radical. The difference between experimental and theoretical values is obviously within approximately 50 cm^{-1} . Only the band at 2767 cm^{-1} ascribed to the CH_2 symmetrical stretching shows relatively large deviation from the calculated value (ca. 150 cm^{-1}), probably due to neglect of anharmonism, so its assignment to C_6H_7 is tentative. Some computationally strong features (in particular, an asymmetrical C–H stretching predicted at 3168.5 cm^{-1}) were not found, possibly due to overlap with the absorptions of C_6H_6 or due to effect of condensed medium on relative intensities of different bands.

Since virtually all the new bands may be assigned to C_6H_7 is (at least, tentatively), there is little opportunity for further speculations about other species. Thus, HXeC_6H_5 was not found in our experiments. There are two possible reasons for this failure: (1) HXeC_6H_5 cannot be obtained from H^\bullet , Xe and C_6H_5 due to endothermic nature of this reaction or (2) it is kinetically unstable under the experimental conditions used. Regarding the first opportunity, it is worth mentioning that the MP2 calculations [4] predict marginal stability of HXeC_6H_5 vs dissoci-

ation to fragments (computed dissociation limit of only 0.21 eV , which can be compared, e.g., with 1.5 eV for experimentally stable HXeCCH). As discussed recently [30], the MP2 calculations often overestimate the stability of rare gas hydrides (probably due to the problem of spin contamination in radical fragments) and comparison with the DFT data may be helpful. We have performed the DFT calculations of thermochemical stability of HXeC_6H_5 in respect to dissociation to $\text{H}^\bullet + \text{Xe} + \text{C}_6\text{H}_5$. According to preliminary results obtained with scalar-relativistic DFT using B3LYP and PBE0 functionals with a L22 basis set, the formation of HXeC_6H_5 is almost thermoneutral or slightly endothermic (e.g., B3LYP gives that HXeC_6H_5 lies 0.03 eV above the energy of fragments). The applicability of different functionals for the DFT calculations of xenon hydrides was not tested systematically, so final clarification of the problem of theoretical stability of HXeC_6H_5 would require further work and more demanding approaches. Nevertheless, most probably, we deal with the boundary case and the second explanation (kinetic instability) should be also considered. Indeed, EPR and IR data reveal a reaction channel taking away both H atoms and C_6H_5 . This annealing-induced reaction is responsible for the observed loss of about 40% of phenyl radicals and H atoms produced by irradiation. At first glance, it might be prompt recombination yielding C_6H_6 . However, recovery of the parent molecules was not observed in our previous studies in solid xenon [6,11], as well as in experiments of Eberlein and Creuzburg [31]. In all the cases, mobile H atoms in xenon either form xenon hydrides (e.g., HXeH , HXeCCH) or react with organic molecules by abstraction or addition. Recombination is highly exothermic, so this should be some kinetic reason resulting from R/Xe interactions. Therefore, we may suggest tentatively that recovery of C_6H_6 proceeds via intermediate formation of a metastable xenon-containing compound (local minimum on the potential energy surface):



Therefore, in principle, HXeC_6H_5 may exist as an intermediate undergoing either reversible dissociation or transformation to $\text{C}_6\text{H}_6/\text{Xe}$ at 45 K.

5. Conclusions

The results obtained in this study show that benzene molecules undergo effective C–H bond scission upon electron irradiation in solid xenon. Annealing of the irradiated sample at 45 K results in formation of cyclohexadienyl radical, which was clearly revealed by EPR. The assignment of major new IR absorptions to this species was made on the basis of correlation with EPR data and DFT calculations. The data on vibrational spectrum of this species may present interest for various fields of benzene-related chemistry (catalysis, oxidation, etc.). We failed to obtain direct evidence for formation of HXeC_6H_5 , so its stability is questionable. Meanwhile, consideration of the reaction scheme suggests that HXeC_6H_5 might exist as an intermediate in the reaction between H atoms and phenyl radicals in solid xenon. Thus, we cannot fully rule out that this molecule could be prepared at lower temperature in another host. Finally, we may note that the method used in this work can be applied for obtaining xenon hydrides from substituted benzene derivatives.

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