

Experimental Evidence for the Formation of HXeCCH: The First Hydrocarbon with an Inserted Rare-Gas Atom

Vladimir I. Feldman,* Fedor F. Sukhov, Aleksei Yu. Orlov, and Irina V. Tyulpina

*Karpov Institute of Physical Chemistry, 10 Vorontsovo Pole Street, Moscow 105064, Russia, and
Institute of Synthetic Polymeric Materials of RAS, 70 Profsoyuznaya Street, Moscow 117393, Russia*

Received February 10, 2003; E-mail: feldman@cc.nifhi.ac.ru

The rare-gas chemistry pioneered by Bartlett¹ revealed remarkable progress in the past decade. One of the most interesting findings was the discovery of rare-gas hydrides HRgY in low-temperature matrices.² To date, a number of such species have been characterized by IR spectroscopy,³ including the first ground-state argon compound HARF.⁴ A common way of preparing xenon hydrides includes dissociation of an appropriate precursor HY in solid xenon by UV light^{2,3} or fast electrons⁵ followed by subsequent annealing. The formation of HXeY molecules is determined by the long-range mobility of H atoms occurring at around 40 K.⁶ In general, this approach can be also used for the synthesis of novel organic species, if Y is an organic radical with sufficient electronegativity. This may be the way to a new, diverse, and potentially useful area. Recently, Lundell et al.⁷ reported theoretical studies of stability and spectroscopic properties of unusual organic molecules with an Xe atom inserted at the C–H and O–H bonds. They found that certain molecules of this type (e.g., HXeCCH, HXeC₆H₅, and HXeOC₆H₅) could exist from a computational viewpoint. Among these species, HXeCCH is very stable (dissociation barrier of ca. 1.5 eV), which makes its experimental finding quite plausible. Here we report experimental evidence for the formation of HXeCCH in solid xenon.

The method developed in our laboratory^{5,8} is based on the use of fast electrons for the dissociation of guest molecules in solid xenon. In contrast with UV photolysis, this technique is free of limitations imposed by optical absorption spectra of precursors. A combination of FTIR and EPR spectroscopy provides detailed knowledge on the formation of new species. A custom-made complex of cryostats and experimental techniques were described previously.⁸ Various isotopomers of acetylene were prepared by the reaction of CaC₂ with H₂O and D₂O, respectively. Gaseous mixtures of xenon/acetylene were deposited at 30 K onto a cooled KBr plate (for FTIR studies) or a sapphire rod (for EPR studies). After the deposition, the samples were irradiated with fast electrons (ca. 1 MeV) at 15–17 K to the dose of 40 kGy using a Van-de-Graaff accelerator. IR spectra in the range from 4000 to 450 cm⁻¹ were obtained with a Perkin-Elmer 1710 instrument (MCT detector, 100 scans, 1 cm⁻¹). EPR spectra were recorded with an X-band (9.4 GHz) spectrometer (SPIN, St. Petersburg, Russia).

The deposited xenon/acetylene matrix shows principal IR absorptions at 728.0 cm⁻¹ (bending), 3280 cm⁻¹ (C–H stretching), and 1317 cm⁻¹ (combination), consistent with the gas-phase data.⁹ Irradiation at 16 K results in a strong decrease in the intensity of the parent bands. Weak new bands at 731.5 and 843 cm⁻¹ indicate the formation of Xe₂H⁺.¹⁰ The feature appearing at 1767.0 cm⁻¹ (medium, sharp) was assigned to the CCH⁻ anion (cf. 1772.8 and 1770.5 cm⁻¹ in Ne and Ar, respectively^{11,12}), and the band of the CCH radical was found near 1852 cm⁻¹ (weak, broad, structured; cf. 1837.9/1835.7 cm⁻¹ in neon, 1845.8 cm⁻¹ in argon^{11,12}).

Annealing of the irradiated sample at 40–45 K (i.e., when H atoms become mobile) results in substantial changes (Figure 1).

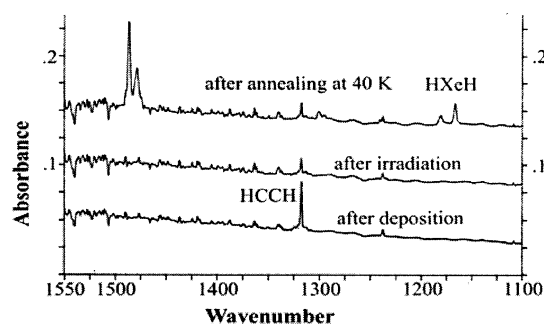


Figure 1. Effect of irradiation and annealing (5 min) on the IR spectra of a deposited mixture of C₂H₂/Xe = 1/2000. The spectra were measured at 16 K.

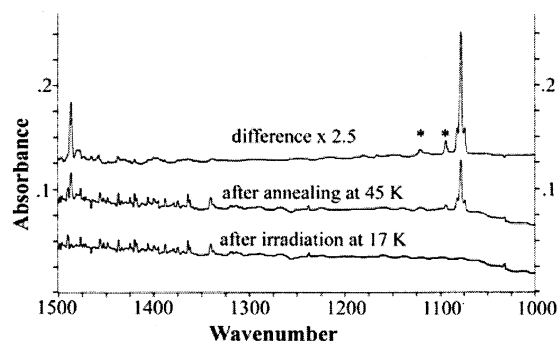


Figure 2. Formation of a new species upon annealing of an irradiated deposited mixture (C₂HD + C₂D₂)/Xe = 1/2000, C₂D₂/C₂HD ≈ 2. All of the spectra were recorded at 17 K. Asterisks show the bands of HXeD.³

The most intense new absorption is found at 1486.0 cm⁻¹, accompanied by a satellite at 1478.1 cm⁻¹. Other weak bands appear at 1165.9 and 1180.4 cm⁻¹ (XeH₂^{3,5,6}), 891.0 cm⁻¹ (vinyl radical, cf. 895.4 cm⁻¹ in neon¹²), and 3273 and 626 cm⁻¹. Focusing on the strongest feature at 1486 cm⁻¹, we should note that it falls in the typical H–Xe stretching region (comparable with HXeBr²), in rough agreement with the theoretical prediction for HXeCCH.⁷

Experiments with isotopic substitution give further support for this assignment. In the case of partially deuterated acetylene, the IR spectrum of the deposited matrix exhibits absorptions of C₂D₂ (2429 and 536 cm⁻¹) and C₂HD (3322, 2573, and 674 cm⁻¹). All of these bands decrease upon irradiation. Subsequent annealing results in the formation of new species as shown in Figure 2. The most prominent absorptions resulting from annealing are positioned at 1486 cm⁻¹ (with sideband at 1478) and 1077.4 cm⁻¹ (accompanied by satellites at 1081.2 and 1073.2 cm⁻¹). As the former band was assigned to H–Xe stretching in the undeuterated sample, the latter one should be ascribed to the D–Xe vibration in the deuterated analogue, DXeCCH and/or DXeCCD. The isotopic

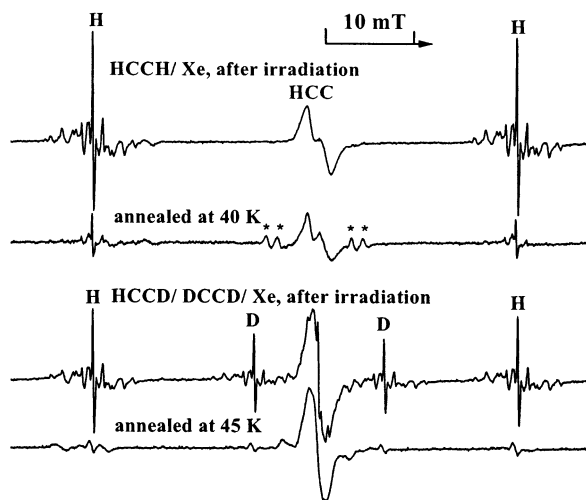


Figure 3. EPR spectra of deposited acetylene/xenon mixtures (1/2000) irradiated at 16 K. Asterisks show lines from vinyl radicals.

frequency ratio of 1.379 is typical for HXeY compounds^{2,3} and inconsistent with other possible candidates containing only C–H bonds.

Thus, FTIR studies give an indication of the formation of a novel molecule containing an H–Xe bond. To obtain more consistent proof of the nature of this species, we have carried out EPR experiments, which make it possible to follow the fate of H atoms and radicals in the system under study. EPR spectra of irradiated deposited samples (Figure 3) show that acetylene dissociates to yield H atoms and the CCH radicals. Trapped H atoms yield a basic doublet with a characteristic hyperfine splitting of 50.6 mT and a well-defined structure due to the interaction of the unpaired electron with the xenon nuclei (¹²⁹Xe and ¹³¹Xe).^{6a,c}

A poorly resolved anisotropic signal at $g \approx g_e$ results from CCH radicals. A sharp anisotropic doublet with an average hyperfine splitting of ca. 1.6 mT was reported for this radical in solid argon.¹³ The signal in xenon is severely broadened due to the presence of matrix magnetic nuclei; however, the hyperfine splitting is nearly the same. The yield of radicals is by 20–30% lower than that of H atoms, as estimated from the integrated intensities of the corresponding signals. This may reflect secondary reactions of CCH (e.g., conversion to C₂ and/or CCH⁻).

Annealing at 40 K (5 min) results in the decay of H atoms (down to ca. 15% of their initial amount). Simultaneously, we observed a decrease in the amount of CCH radicals (by ca. 35%) and the appearance of weak signals, which should be ascribed to vinyl radicals.¹⁴ A rough estimate shows that the formation of vinyl radicals (H addition to acetylene) accounts for less than 10% of the decay of H atoms, so the main channels are combination reactions yielding diamagnetic species. The observation of simultaneous decay of H and CCH is especially significant. Diffusion of CCH at 40 K can be excluded (these species survive at 60 K after the decay of H atoms), so the loss of CCH results from their reaction with H atoms. EPR cannot distinguish between the direct combination to yield acetylene and the reaction with xenon yielding HXeCCH. However, the IR results show that there is no recovery of parent acetylene molecules; on the contrary, we found a small decrease in acetylene bands at 40 K due to the formation of vinyl radicals.

Similar consequences result from the EPR experiments with deuterated acetylene. Irradiation leads to trapping of H atoms, D atoms (triplet with basic separation of ca. 7.8 mT, i.e., 6.51 times

smaller than for H (in line with the μ_H/μ_D ratio)), and CCD radicals (unresolved central signal). The decay of H and D atoms is again accompanied by the decay of CCD radicals and the formation of small amounts of vinyl radicals (various isotopomers).

Both IR and EPR studies provide strong evidence for the formation of HXeCCH and its isotopomers. Comparing these results with the theoretical prediction, one may note that the computed harmonic frequencies for H–Xe stretching⁷ (1735.9 and 1620.8 cm⁻¹ at the MP2 and CCSD(T) levels of theory, respectively) are somewhat higher than the experimental value (1486.0 cm⁻¹). However, this difference is typical for substantially anharmonic, strongly polar H–Xe vibrations in HXeY molecules³. For example, for HXeOH absorbing at 1577.6 cm⁻¹, the MP2 and CCSD(T) computed harmonic frequencies are 1822.7 and 1677.9 cm⁻¹, respectively.¹⁵ Taking into account this scaling, one can find that the agreement for HXeCCH is quite reasonable. Intensities of other bands for this species should be much lower⁷ (at least, by the factor of 50), so their experimental detection is problematic.

In conclusion, we have presented experimental arguments for the characterization of a novel-type rare-gas compound. This may strongly encourage further efforts in the field of organoxenon chemistry (still developed mainly for ionic salts and some fluorinated compounds¹⁶). The insertion of the Xe atom at the C–H bond suggests wide prospects for preparing new unusual reagents and intermediates. Thus, acetylene, known to be a “bridge” between classic inorganic and organic molecules, may now open the “gate” to a new field, organic chemistry of rare-gas hydrides.

Acknowledgment. M. Räsänen is thanked for making us aware of the independent finding of his group, when this manuscript was in preparation. We acknowledge the technical help of V. Ivanchenko and N. Nekhoroshev. The work was supported by the Russian Foundation for Basic Research (project no. 00-03-32041).

References

- (1) Bartlett, N. *Proc. Chem. Soc.* **1962**, 218.
- (2) Pettersson, M.; Lundell, J.; Räsänen, M. *J. Chem. Phys.* **1995**, *102*, 6423–6431.
- (3) For review: Pettersson, M.; Lundell, J.; Räsänen, M. *Eur. J. Inorg. Chem.* **1999**, 729–737.
- (4) Khriachtchev, L.; Pettersson, M.; Runeberg, N.; Lundell, J.; Räsänen, M. *Nature (London)* **2000**, *406*, 874–876.
- (5) Feldman, V. I.; Sukhov, F. F. *Chem. Phys. Lett.* **1996**, *255*, 425–430.
- (6) (a) Feldman, V. I.; Sukhov, F. F.; Orlov, A. Yu. *Chem. Phys. Lett.* **1997**, *280*, 507–512. (b) Pettersson, M.; Nieminen, J.; Khriachtchev, L.; Räsänen, M. *J. Chem. Phys.* **1997**, *107*, 8423–8431. (c) Khriachtchev, L.; Tanskanen, H.; Pettersson, M.; Räsänen, M.; Feldman, V.; Sukhov, F.; Orlov, A.; Shestakov, A. F. *J. Chem. Phys.* **2002**, *116*, 5708–5716 and references therein.
- (7) Lundell, J.; Cohen, A.; Gerber, B. *J. Phys. Chem. A* **2002**, *106*, 11950–11955.
- (8) Feldman, V. I. *Acta Chem. Scand.* **1997**, *51*, 181–192.
- (9) Simanouchi, T. *Tables of Molecular Vibrational Frequencies. Consolidated Volume I*; National Bureau of Standards: Washington, DC, 1972; pp 1–160.
- (10) Kunttu, H.; Seetula, J.; Räsänen, M.; Apkarian, A. *J. Chem. Phys.* **1992**, *96*, 5630–5638.
- (11) Andrews, L.; Kusho, G. P.; Zhou, M.; Wilson, S. P.; Souter, P. F. *J. Chem. Phys.* **1999**, *110*, 4457–4466.
- (12) Forney, J.; Jacox, M. E.; Thompson, W. E. *J. Mol. Spectrosc.* **1995**, *170*, 178–214 and references therein.
- (13) Graham, W. R. M.; Dismuke, K. I.; Weltner, W., Jr. *J. Chem. Phys.* **1974**, *60*, 3817–3823.
- (14) (a) Kasai, P. H.; Whipple, E. B. *J. Am. Chem. Soc.* **1967**, *89*, 1033–1034. (b) Fessenden, R. W.; Schuller, R. H. *J. Chem. Phys.* **1963**, *39*, 2147–2195.
- (15) Pettersson, M.; Khriachtchev, L.; Lundell, J.; Räsänen, M. *J. Am. Chem. Soc.* **1999**, *121*, 11904–11905.
- (16) (a) Christe, K. O. *Angew. Chem., Int. Ed.* **2001**, *40*, 1419–1421. (b) Brel, V. K.; Pirkuliev, N. Sh.; Zefirov, N. S. *Russ. Chem. Rev.* **2001**, *70*, 231–266.

JA034585J