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A Gate to Organokrypton Chemistry: HKrCCH

Leonid Khriachtchev,*,† Hanna Tanskanen,† Arik Cohen,‡ R. Benny Gerber,‡,§ Jan Lundell,†
Mika Pettersson,† Harri Kiljunen,‖ and Markku Räsänen†

Department of Chemistry, P.O. Box 55, FIN-00014 University of Helsinki, Finland, Department of Physical Chemistry, Hebrew University, Jerusalem 91904, Israel, Department of Chemistry, University of California, Irvine, California 92697, and VERIFIN, P.O. Box 55, FIN-00014 University of Helsinki, Finland

Received April 8, 2003; E-mail: Leonid.Khriachtchev@Helsinki.Fi

Since Bartlett's discovery of the first Xe-containing molecule in 1962,[1] a large number of neutral ground-state species containing chemically bound rare-gas (Rg) atoms have been prepared. The vast majority of these molecules are xenon compounds.[2] Far fewer compounds of krypton have been synthesized, and no neutral Kr-containing organic compounds are known.[3] A family of HRgY molecules has been prepared using photolysis of HY (where Y is an electronegative fragment) isolated in a rare-gas matrix and subsequent thermal mobilization of H atoms.[4] Examples of such molecules include an argon compound (HArF),[5,6] a molecule with a Kr−C bond (HKrCN),[7] and a chemical compound formed from water and Xe (HXeOH).[8] Here we report the preparation of HKrCCH, an organic molecule containing krypton. The HKrCCH molecule and its deuterated isotopologues are identified by IR absorption spectroscopy supported by extensive ab initio calculations. A series of similar organokrypton molecules are predicted.

Upon 193-nm irradiation of H_2C_2/Kr (1/300−1/2000) samples, the IR absorption spectra show decomposition of acetylene[9] (see the upper curve in Figure 1) and appearance of C_2H radicals (1842 cm^{-1}).[10] The C_2H radicals are the primary photolysis products of H_2C_2, and photodissociation of C_2H produces C_2 molecules.[11] Accordingly, the C_2H concentration first rises during photolysis, reaches its maximum, and then decreases. The C_2 molecules are IR-inactive in a Kr matrix, which is different from the case of Xe matrixes where complexation with Xe activates its absorption.[11] Formation of $KrHKr^+$ (852 and 1008 cm^{-1})[12] and C_4 clusters (1539 cm^{-1})[13] is also observed especially in samples with a higher initial acetylene concentration.

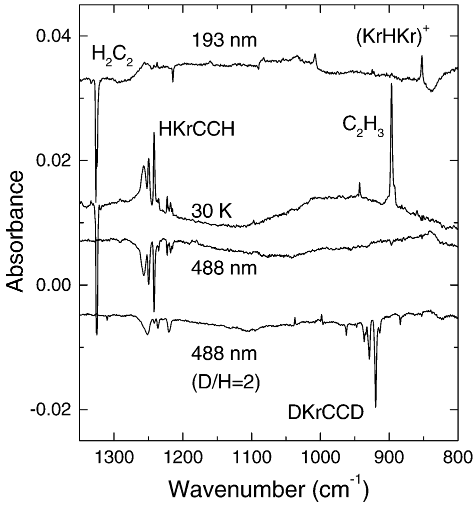

Figure 1. Difference IR absorption spectra of HKrCCH in solid Kr. Shown are the result of 193 nm photolysis ($\sim$2000 pulses with 10 mJ/cm^2) of acetylene in solid Kr (the upper trace), the result of annealing at 30 K of the photolyzed sample (the second upper trace), and the result of 488 nm irradiation (Ar^+ laser, 100 mW/cm^2, 2 h) of the annealed samples (the two lower traces). Note that the irradiation at 488 nm destroys the Kr-containing species selectively. The degree of deuteration in the lowest trace is $\sim$70%. The H−Kr stretching absorption in the partially deuterated sample presumably originates from the HKrCCD isotopologue, which explains some modification of its H−Kr stretching bands as compared with HKrCCH. The H−Kr stretching spectral feature disappears upon full deuteration. The H_2C_2/Kr (1/1000) matrix was deposited onto a CsI window at 20 K and photolyzed at 8 K by 193-nm light pulses from an excimer laser (MSX-250, MPB). The spectra were measured at 8 K with a Nicolet 60 SX FTIR spectrometer in the 4000−400 cm^{-1} spectral region using a resolution of 1 cm^{-1}.

The formation of the Kr-containing molecules with charge-transfer character requires a strongly electronegative fragment to be present in the matrix after photolysis.[4,7,14] In the present study, the electronegative fragment is HC_2 (electron affinity of $\sim$3 eV),[15] and an H atom can react with the Kr + CCH center upon thermal mobilization at $\sim$30 K. Accordingly, we observed the annealing-induced formation of a previously unreported set of IR absorption bands with the strongest components at 1241.5, 1249.5, and 1257 cm^{-1} (see Figure 1). Importantly, no corresponding bands with normal matrix shifts are found in analogous experiments in an Ar matrix (even though HC_2 was produced), suggesting that these bands originate from the H−Kr stretching absorption of a novel Kr-containing species. The observed extensive site splitting of the absorption bands is very characteristic for the HRgY molecules.[4−6,14] Furthermore, the HRgY molecules usually decompose easily upon irradiation by light due to excitation to the repulsive states. The same characteristic property was found for the present absorber: It decomposed upon Ar^+-laser irradiation at 488 nm as presented in the two lower traces in Figure 1. Other products of annealing such as C_2H_3 (891 cm^{-1})[16] and C_4H (2055 cm^{-1})[17] decompose much less efficiently at 488 nm. Using this selective photodissociation, two additional bands are found to belong to the same Kr species: a narrow band at 3290 cm^{-1} and a doublet at 610 and 608 cm^{-1}. The 488-nm photodissociation of the species under discussion partially recovers HC_2 radicals (10−20% of the amount produced by the 193-nm photolysis). Our experiments with D_2C_2/Kr samples give the strongest D−Kr stretching bands of the novel absorber at 920, 929, and 936 cm^{-1} (see the lowest trace in Figure 1) and the weaker bands at 2555.5 and 482.5 cm^{-1}. With certainty, the bands at 3290 (2555.5) and 610 (482.5) cm^{-1} originate from the H−C≡ (D−C≡) stretching and H−CC (D−CC) bending modes. On the basis of these data, we assign the novel absorber to HKrCCH (see Table 1). Remarkably, a similar compound with Xe (HXeCCH) was predicted.[18] In experiments with acetylene in a Xe matrix, we have recently identified HXeCCH with the H−Xe stretch at 1486 cm^{-1}, the H−C≡ stretch at 3273 cm^{-1}, and the H−CC

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† Department of Chemistry, University of Helsinki.
‡ Hebrew University.
§ University of California.
‖ VERIFIN, University of Helsinki.

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Table 1. Experimental and Calculated Vibrations (cm^{-1}) of HKrCCH[a]

	experiment[b]	calculation[c]
C−H stretch	3290 (1.287) [0.06]	3418 (1.305) [0.013]
H−Kr stretch	1241.5 (1.350) [1]	1575 (1.407) [1]
CC−H bend	610 (1.264) [0.07]	616 (1.266) [0.033]

[a] The H/D ratios are given in parentheses. The relative IR intensities are given in brackets. [b] The frequencies are given for the strongest component of the site-split absorption. [c] The other modes that are either IR inactive or outside the experimental range are C−C stretch (1936 cm^{-1}), H−KrCC−H bend (723 cm^{-1}), Kr−C stretch (306 cm^{-1}), and H−Kr−CC−H bend (192 cm^{-1}).

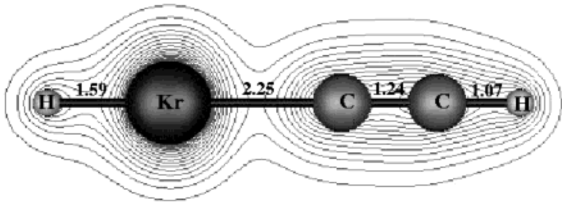

Figure 2. Computational equilibrium structure and electronic density distribution of HKrCCH. The distances are in Å.

bend at 626 cm^{-1},[19] which is similar to the present data on the krypton species. An important difference between the results obtained in Kr and Xe matrixes should be emphasized: HXeCC and HXeCCXeH have been reported,[19] whereas no sign of the analogous Kr species is found in the present study.

Figure 2 shows the linear equilibrium geometry of HKrCCH and the electronic density distribution of the molecule for that configuration calculated at the MP2=full/aug-cc-pVDZ level of theory. The H−Kr and Kr−C distances are 1.59 and 2.25 Å, respectively, which are similar to the corresponding values for HKrCN (1.47 and 2.34 Å).[7] The natural bond orbital analysis suggests a strong ionic character of HKrCCH, with a positive charge on the Kr atom (+0.535) and negative charges on the C atoms (−0.444 and −0.331). Inspection of the electronic density distribution indicates that the H−Kr bond is predominantly covalent. Even though the Kr−C bond is mostly ionic in character, a part of this bond (∼20%) is due to covalent interactions. Importantly, HKrCCH is computationally lower in energy than H + Kr + CCH by ∼0.7 eV, which allows, in agreement with the experiment, its annealing-induced formation from these constituents. Similarly to other HRgY compounds, HKrCCH is a metastable species being much higher in energy than Kr + HCCH. The computed harmonic H−Kr stretching frequency is 1575 cm^{-1}, which is larger than the measured values (1240−1250 cm^{-1}). However, too-high frequencies obtained with the harmonic approximation are common for the HRgY species.[4] The harmonic calculations of HKrCCH and DKrCCD molecules yield H/D ratios of 1.407, 1.305, and 1.266 for the H−Kr stretching, H−C≡ stretching, and H−CC bending vibrations, respectively, and this is in good agreement with the experimental data (see values in parentheses in Table 1). The agreement between the experimental and theoretical IR intensities of these bands is remarkable (see values in brackets in Table 1). It is worth mentioning that HKrCC, an analogue of the observed HXeCC radical,[19] was found to be 1.38 eV higher in energy than H + Kr + CC, which explains its absence in the present experiments.

The preparation of HKrCCH reported here is important in several aspects. First of all, it demonstrates the photochemical insertion of Kr into an H−C bond of a hydrocarbon giving an example of a proper organokrypton compound. So far, the species possessing a Kr−C bond are the CH_3Kr^+ cation[20] and the inorganic HKrCN molecule.[7] It is expected that insertion of Kr can be similarly accomplished for many hydrocarbons with an H−C≡ group. Indeed, we performed ab initio studies (MP2=full/aug-cc-pVDZ) on $HKrC_4H$ and $HKrC_3H_3$ species that can be prepared by insertion of Kr into diacetylene and propyne, respectively, and found that these compounds are computationally stable. For $HKrC_3H_3$, the H−Kr and Kr−C distances are 1.61 and 2.25 Å, respectively, and the H−Kr (harmonic) stretching absorption is 1477 cm^{-1}. The corresponding numbers for $HKrC_4H$ are 1.57 Å, 2.27 Å, and 1613 cm^{-1}. With certainty, a fairly large field of organokrypton molecules can be expected. The stability of these novel organic compounds features a new way for activating chemically the H−C≡ group. Since the H−Kr−C≡ group is expected to be far more reactive than H−C≡, this may lead to new synthetic applications of the krypton catalysis. Our work develops a fluorine-free approach to promote krypton chemistry in general. It is important because nearly all known krypton chemistry has been derived from KrF_2,[3] and our work presents an interesting alternative.

In summary, the experimental and theoretical data presented here allow us to claim the identification of an organic molecule containing krypton, HKrCCH. The molecule was prepared by using 193-nm photolysis of H_2C_2/Kr solid mixtures at 8 K and subsequent thermal mobilization of hydrogen atoms at ≥30 K. The ab initio calculations show intrinsic stability of HKrCCH owing to sufficient ionic and covalent contributions to the bonding. We believe that a series of similar organokrypton molecules can be prepared, and we computationally demonstrated this idea for $HKrC_4H$ and $HKrC_3H_3$.

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