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Theoretical Prediction of Chemically Bound Compounds Made of Argon and Hydrocarbons

Li Sheng,[†] Arik Cohen,[†] and R. Benny Gerber*,[†,‡]
Department of Physical Chemistry, The Hebrew University, Jerusalem 91904, Israel, and Department of Chemistry, University of California, Irvine, California 92697-2025

Received February 24, 2006; E-mail: benny@fh.huji.ac.il

The field of noble gas chemistry has expanded greatly since the preparation by Bartlett of the first noble gas compound xenon hexafluoroplatinate in 1962.[1,2] Of particular interest is the discovery in recent years of novel families of noble gas compounds. A class of such new compounds that is related to the present paper consists of molecules of the form HNgY, where Ng is a noble gas atom and Y denotes an electronegative atom or group of atoms.[3−8] Räsänen and co-workers discovered these compounds by photolysis of HY in matrices of the noble gases.[3−7] With one exception, all the HNgY compounds prepared so far are of the heavy noble gas elements xenon and krypton. Ar, with its highly stable outer electronic shell, is much harder to bind chemically than Kr or Xe. The important exception is HArF, made by Khriachtchev et al.,[3] which is to date the only experimentally known, chemically bound neutral molecule of any of the lighter noble gases, argon, neon, and helium. Theoretical calculations have predicted several new compounds of argon, such as FArCCH and $FArSiF_3$,[9] but the existence of these is yet to be experimentally confirmed. A very interesting challenge is the search for an organic molecule of argon. Theory has played an important role in predicting compounds, such as HXeCCH and HXeCCXeH,[10] made of xenon and a hydrocarbon (acetylene, in this case). Following these predictions, HXeCCH was made by Khriachtchev and co-workers[5] and by Feldman et al.,[8] and HXeCCXeH was also prepared by Khriachtchev et al.[5] Most recently, HKrCCH,[6] $HXeC_4H$,[7] and $HKrC_4H$[7] were also obtained experimentally in all cases by photolysis of a hydrocarbon in the noble gas matrix.[5−8]

These new developments in “ogano-noble chemistry” and the experience of the useful role of theoretical calculations also for others noble gas compounds[11−14] are the motivation of the present paper. It is intriguing to ask whether molecules made of argon and a hydrocarbon can exist. Here, the prediction of fluorine-free organic compounds of argon, $HArC_4H$ and $HArC_6H$, is reported.

All ab initio calculations were carried out at the MP2=full/6-311++G(2d,2p) level of theory, which was used in the successful prediction of HXeCCH and HXeCCXeH and gave results in good agreement with experiments for spectroscopy and stability.[15] The electronic structure package GAMESS[16] was used for all geometry optimizations and harmonic vibrational frequency calculations, and Gaussian 03[17] was used to analyze the partial charges of $HArC_4H$ and $HArC_6H$ by the natural bond orbital (NBO) approach.[18]

The linear equilibrium structure and the partial atomic charges (NBO) of $HArC_4H$ are shown in Figure 1. The short H−Ar and Ar−C distances, 1.495 and 2.170 Å, are the first indication of strong chemical bonding. The NBO analysis suggests a strong ionic character of $HArC_4H$, with a positive charge of +0.489 on Ar and negative charges of −0.340 and −0.259 on C_1 and C_2. The results show that the extremely stable outermost electronic shell of isolated Ar is opened in the bonding and the substantial negative charge is transferred to the C_4H group. The charge transfer character is in analogy with the recently prepared HNgY molecules.[5−8]

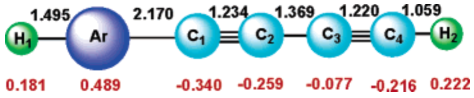

Figure 1. Equilibrium structure and NBO charges of $HArC_4H$ at MP2=full/6-311++G(2d,2p) level of theory. The bond lengths are in angstroms.

Table 1. Calculated Vibrational Frequencies and IR Intensities of $HArC_4H$ at MP2=full/6-311++G(2d,2p) Level of Theory

assignment	frequency[a] (cm^{-1})	IR intensity (km mol^{-1})
C−H stretch	3494.6	101.2
C−C stretch	2147.7	9.1
	1988.3	15.7
H−Ar stretch	1136.2	5747.1
C−Ar−H bend[b]	717.9	1.8
C−C−H bend[b]	619.2	42.7
C−C−C bend[b]	556.3	6.3
C−Ar stretch	274.0	359.9

[a] Only the key frequencies are presented. [b] Doubly degenerate.

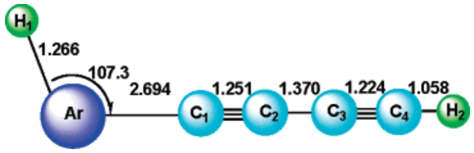

Figure 2. Transition state structure for the $HArC_4H \rightarrow Ar + HC_4H$ dissociation channel at MP2=full/6-311++G(2d,2p) level of theory. The bond lengths are in angstroms; the angle is in degrees.

The calculated harmonic frequencies and infrared intensities of $HArC_4H$ are listed in Table 1. The results show that the $HArC_4H$ is a true local minimum on the potential energy surface. The H−Ar and Ar−C stretching vibrations are at 1136.2 and 274.0 cm^{-1}, respectively. These are relatively stiff frequencies, corresponding to a chemically bound molecule, rather than to weakly interacting van der Waals complex. The H−Ar stretching vibration is predicted to be very intense, and the calculated infrared intensity is about 5747.1 km mol^{-1}, which may serve as an identifying fingerprint of the $HArC_4H$ molecule.

The transition state structure for the $HArC_4H \rightarrow Ar + HC_4H$ reaction is shown in Figure 2, and it has only one imaginary frequency with a value of 608.7 cm^{-1}. Similar to all prepared HNgY molecules, $HArC_4H$ is a metastable species, being 6.56 eV above the global energy minimum $Ar + HC_4H$. Once formed, however, the metastable species is protected from decay by high barrier, 1.15 eV. Zero-point energy correction reduces this value only slightly by 0.01 eV. The results indicate that the $HArC_4H$ molecule is kinetically stable with respect to the $Ar + HC_4H$ exoergic decomposition channel. $HArC_4H$ is by 0.45 eV more stable than the three separate fragments $H + Ar + C_4H$, which should allow its annealing-induced formation from these fragments.[6,7] So far,

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[†] The Hebrew University.
[‡] University of California, Irvine.

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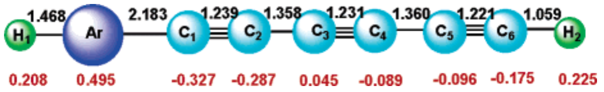

Figure 3. Equilibrium structure and NBO charges of $HArC_6H$ at MP2=full/6-311++G(2d,2p) level of theory. The bond lengths are in angstroms.

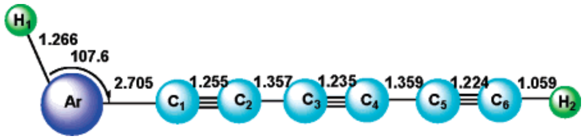

Figure 4. Transition state structure for the $HArC_6H \rightarrow Ar + HC_6H$ dissociation channel at MP2=full/6-311++G(2d,2p) level of theory. The bond lengths are in angstroms; the angle is in degrees.

almost all of the experimentally observed HNgY molecules have been found computationally to lie below the energy limit of the H + Ng + Y; the barrier of HNgY against its three-body dissociation channel is not a determining factor for the stability of HNgY.[15] Thus, $HArC_4H$ is a gateway to organo-argon chemistry. We speculate that a possible synthetic route is based on the photochemistry of HC_4H in a low-temperature argon matrix, in analogy to the preparation of $HNgC_4H$ molecules (Ng = Xe, Kr).[7]

The motivation to study $HArC_6H$ molecule came from the further stabilization of molecule $HNgC_{2n}H$ with increasing n. This trend was supported by experimental and theoretical results of $HNgC_4H$ and $HNgC_2H$ molecules (Ng = Xe, Kr).[5−8,10] The equilibrium structure and NBO charges of the $HArC_6H$ molecule are shown in Figure 3. The predicted H−Ar and Ar−C distances are 1.468 and 2.183 Å, respectively, similar to the corresponding values of $HArC_4H$. The calculated NBO partial charges of $HArC_6H$ are +0.208 on H_1, +0.495 on Ar, and −0.703 on the C_6H group. Comparing the charge values of $HArC_6H$ with the ones of $HArC_4H$ (+0.181 on H_1, +0.489 on Ar, and −0.670 on the C_4H group), it can be seen that $HArC_6H$ molecule has stronger ionic character and appears to be more strongly bound. This trend is further indicated by the large blue shift of H−Ar stretching vibration for $HArC_6H$. The calculated harmonic vibrational frequencies are presented in the Supporting Information. The H−Ar stretching vibration of $HArC_6H$ is 1227.0 cm^{-1}, which is predicted to be shifted +90.8 cm^{-1} compared with the one of $HArC_4H$. The large blue shift is attributed to the enhanced ion-pair character of the $HArC_6H$ molecule. Similar to the $HArC_4H$ molecule, the H−Ar stretching mode of $HArC_6H$ may be an experimental fingerprint of this molecule, and the computed infrared intensity is about 5333.8 km mol^{-1}.

The $HArC_6H$ molecule is computationally lower by about 1.14 eV than the separated fragments H + Ar + C_6H. This stabilization energy steeply increases by 0.69 eV as compared with the $HArC_4H$ analogue. Even then, this molecule is still a metastable species with energy of 6.52 eV above the energy limit of separated Ar + HC_6H. The transition state structure for the $HArC_6H \rightarrow Ar + HC_6H$ dissociation channel is presented in Figure 4. It has an imaginary frequency with value of 589.5 cm^{-1}. The barrier at the MP2 level is about 1.07 eV, which indicates high kinetic stability of $HArC_6H$ against two-body decomposition. There is thus a good prospect to produce and characterize this molecule experimentally.

The obvious question is what is the situation with regard to HArCCH, given that HKrCCH and HXeCCH exist. Our calculations show that HArCCH lies well above H + Ar + CCH, the three-body decomposition channel products. Experience shows that when the three-body channel is highly exothermic, the HNgY molecule does not seem to exist. This may be due to the fact that formation from the three fragments by annealing is unfavorable then. The instability with respect to the products for HArCCH is due to insufficient electronegativity of the CCH group. Clearly the situation for C_4H and C_6H is much improved. The electron affinities of C_4H and C_6H are 3.6 and 3.8 eV, respectively, larger than that of C_2H group (about 3.0 eV).[19] As a result, the computed partial charges of the HAr group and of the carbon atoms increase for $HArC_6H$ compared with those of $HArC_4H$. Further, the stabilization energy of $HArC_6H$ against three-body dissociation is greater than for $HArC_4H$. The same trend was found for $HXeC_nH$ (n = 2, 4).[7] The electronegativity of C_nH is essential for the stability of $HArC_nH$ (n = 4, 6).

In conclusion, the fluorine-free argon organic compounds $HArC_4H$ and $HArC_6H$ have been studied by the MP2 method. The predicted stability of two molecules is in analogy with the prepared noble gas hydrocarbon compounds, which suggests that these molecules should be very likely candidates for experimental observation. The familiar molecules $HNgC_4H$ (Ng = Xe, Kr) were prepared in noble gas matrices by UV photolysis of HC_4H; such an experimental approach is very encouraging for the preparation of $HArC_4H$ and $HArC_6H$. At present, only one argon compound, HArF, was experimentally observed. The compounds predicted here suggest a new class of argon compounds that widen the scope of argon chemistry. It is hoped that the organic chemistry of the light noble gases will begin to emerge soon.

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Supporting Information Available: The frequencies of $HArC_6H$ and complete ref 17. This information is available free of charge via the Internet at http://pubs.acs.org.

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