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Putting Helium Inside Dodecahedrane

R. James Cross,*,† Martin Saunders,*,† and Horst Prinzbach*,‡

Department of Chemistry, Yale University, Box 208107, New Haven, Connecticut 06520-8107, and Chemisches Laboratorium der Universität Freiburg, Chemisches Laboratorium der Universität Freiburg, Freiburg, Germany

james.cross@yale.edu

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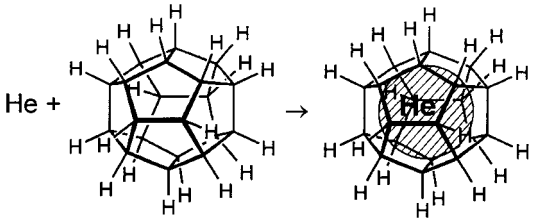
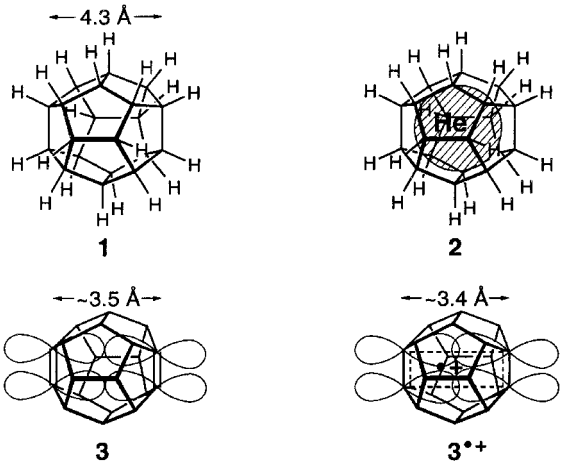
ABSTRACT



By shooting a beam of helium ions at a continuously deposited surface of dodecahdrane, $C_{20}H_{20}$, we can incorporate a helium atom into the molecular cage, where it remains trapped. The experiment produces ~100 μg/h of $C_{20}H_{20}$, doped at levels up to 0.01%.

The "outside chemistry" of $C_{20}H_{20}$ dodecahedrane **1** has been intensively investigated,[1−3] more recently—after significant synthetic improvements[4−7]—in pursuit of the C_{20} fullerene.[4−11] Early in the dodecahedrane story, the "inside chemistry" of cage **1** was addressed and stabilization energies for the inclusion of various atoms and ions (e.g. H^+, He) were calculated.[12−14] Experimental evidence for "inner life" in C_{20} cages came from 1,16-diene **3** and particularly its radical cation $\mathbf{3}^{\bullet+}$ (Scheme 1). At π,π distances of 3.5−3.4 Å there is significant through-cage electron delocalization (PE, CV, ESR).[15−17] This paper reports the preparation of **1** enclosing helium atom **2**. For the last 5 years, we have been studying

Scheme 1



† Yale University.
‡ Universität Freiburg.

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compounds formed by introducing the noble gas atoms into Buckminsterfullerene, its derivatives, and higher relatives.[18,19] Our principal method of preparing these substances involves heating the fullerene under a high pressure of the gas.[20]

Dodecahedrane is significantly smaller and has a much smaller internal cavity. The distance between opposing carbons is 7.1 Å in C_{60} but is only 4.3 Å in dodecahedrane. The van der Waals diameter of helium is approximately 2.6 Å. Calculations show that helium is slightly bound inside C_{60} by a weak van der Waals interaction,[21] but it costs around 27 kcal/mol to put it into $C_{20}H_{20}$.[12,13,22,23] The predicted equilibrium constant is so unfavorable that, even if a process for overcoming the high barrier for entry were provided, the amount which could possibly be introduced by a high-temperature, high-pressure process would be exceedingly small. Does another method exist for preparing significant amounts of dodecahedrane containing helium?

We have recently shown that shooting beams of He^+ and Ne^+ at surfaces of C_{60} produces $He@C_{60}$ and $Ne@C_{60}$.[24] The reaction takes place on a rotating aluminum cylinder. On one side is an oven producing a continuous beam of fullerene, which condenses on the cylinder. A source of helium ions is mounted on the other side of the target. After a few hours, the apparatus is opened, and the target is removed. The fullerene is dissolved off and analyzed by pyrolyzing it at about 1000 °C in order to release the noble gas which is analyzed in a mass spectrometer.

We have now applied this beam process to putting helium inside dodecahedrane. The apparatus is similar to the one used for fullerenes[24] and is shown in Figure 1. A continuous beam of $C_{20}H_{20}$ effuses from the oven and condenses on the rotating target. Helium ions are produced when electrons from the filament strike the helium gas leaked into the ionization chamber. The ions are extracted by an ion lens, bent by 30°, focused, and decelerated to the desired energy. The bend separates the ions from the neutral species, such as UV light and metastable atoms, formed in the ion source. Both sources produce a slit beam about 2 cm wide. The ion source is designed to give a high intensity of ions rather than a well-focused or monoenergetic beam.

The product is dissolved off the target using toluene. The solution is then transferred to a sealed Pyrex tube, where the solvent is removed. The tube is then evacuated for a few hours and sealed. This process removes all helium not trapped inside a dodecahedrane molecule. The helium is released from the product by pyrolizing it at 600 °C for 2 h in the Pyrex ampule. Hot glass is permeable to helium, and so there is a blank signal caused by the diffusion of atmospheric helium into the ampule. To reduce this, the ampule is pyrolized in an evacuated chamber. After cooling, the ampule is placed in a breaker apparatus and broken under vacuum. The resulting gas is passed through a liquid nitrogen trap and a getter pump into a quadrupole mass spectrometer. During the analysis, the spectrometer is closed off from the diffusion pump so that the partial pressure of the noble gas can be measured in a static system. This gives us much more sensitivity than the usual arrangement where the gas to be analyzed flows past the ionizer into a pump. The spectrometer was standardized using a known pressure and volume of helium. The uncertainty in this measurement is about 20%, mostly due to errors in the gas standard.

The results of the analysis are shown in Table 1, showing the energy and charge state of the beam, the amounts of $C_{20}H_{20}$ and helium, and the fraction of $C_{20}H_{20}$ incorporating

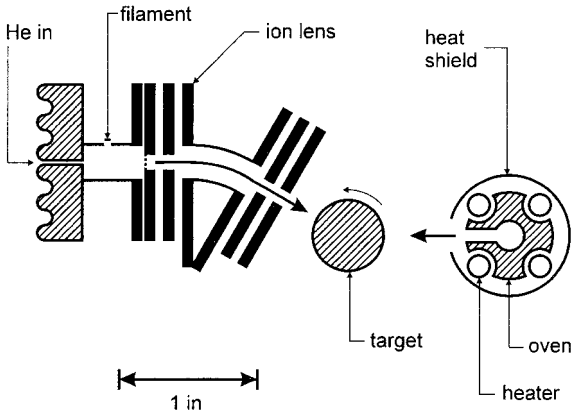

Figure 1. Schematic of the Apparatus. A continuous beam of dodecahedrane $C_{20}H_{20}$ emerges from the oven and condenses on the rotating target. Helium enters the ionizing regions from the left and is ionized by electrons emitted by the filament. Ions are extracted by the grid and focused, bent, and decelerated by the ion lens system. The bend separates the ions from the neutral species, UV light, and metastable atoms, produced in the ionizing region.

Table 1. Incorporation of Helium in $C_{20}H_{20}$

	E (eV)	$C_{20}H_{20}$ (μg)	He (pmol)	incorpn[a]
He^+	150	339	120	9.2×10^{-5}
He^0	150	199	77	1.0×10^{-4}
He^+	100	602	27	1.2×10^{-5}
blank[b]		0	1.9	
background[c]		0	1.4	

[a] Fraction of $C_{20}H_{20}$ molecules containing helium. [b] The amount of helium in a pyrolized, empty ampule, not including the background. [c] The signal in the mass spectrometer with no sample.

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a helium atom. The amount of $C_{20}H_{20}$ was determined by proton NMR, comparing the signal intensity to that of a known sample. The uncertainty in this number is about 20%. The helium blank, the amount of helium diffusing into an empty ampule plus the background in the mass spectrometer, was 3.3×10^{-12} mol, an order of magnitude or more below that of the signals recorded for the filled ampules.

A problem in this experiment is that the He^+ picks up an electron from the surrounding hydrocarbon and a net positive charge builds up with time on the outside of the dodecahedrane film. Since dodecahedrane is an insulator, the charge cannot be readily neutralized by conduction. As the target becomes charged, the ion beam is decelerated and deflected away from the target. To solve this problem, we built a small chamber on the end of the ion lens system to neutralize the beam. Helium is admitted to the chamber through a leak valve until the intensity of the ion beam is reduced by a factor of 2. Part of the ion beam is converted into a beam of fast atoms by resonant charge exchange. The target is then held at a positive voltage to repel any ions. We have no way to measure the intensity of the fast neutral beam, but it must be well under half the intensity of the initial ion beam. Using neutral helium, the amount incorporated is slightly higher than with the ion beam, despite the much lower beam intensity. This observation supports the idea that the surface is charged by the ion beam. To eliminate the surface charging without the loss of ion beam intensity, we tried to neutralize the charge of the ions from the outside of the film by using a beam of low-energy electrons produced by a filament mounted near the target. The electrons and/or the UV light from the filament completely destroyed the dodecahedrane.

We conducted a series of runs at 50, 75, and 100 eV using a neutralized beam to determine the approximate threshold for the reaction. The results showed no signal above background for 50 and 75 eV and only a small signal at 100 eV. The threshold is therefore about 100 eV. In contrast, the measured threshold for putting helium into C_{60} is 30 eV.[24] These, of course, are upper limits to the actual threshold, since the experiment requires a modest signal in order to see the product.

We have shown that helium can penetrate the five-membered rings of dodecahedrane and that the resulting $He@C_{20}H_{20}$ is stable for weeks. In effect, we have made the world's smallest helium balloons. Because of the very small cavity in dodecahedrane, the effective pressure inside must be extremely high, and it will be interesting to see how this affects such properties as the rate of decomposition.

The availability of $He@C_{20}H_{20}$ will allow us to monitor chemical reactions of dodecahedrane in a novel way. We will be able to tell whether the cage structure is intact at every reaction stage. We would expect that any permanent or temporary opening of the cage should release the trapped helium. If the pyrolysis of any product or even of any reaction mixture releases helium, we can proceed confident that the cage has not been destroyed.

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