Some thermal decomposition reactions of C\textsubscript{60}H\textsubscript{36}

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Abstract—C\textsubscript{60}H\textsubscript{36} starts to thermally dehydrogenate at 199.3°C. Vaska’s compound can catalyze the thermal dehydrogenation of C\textsubscript{60}H\textsubscript{36} at low temperature. When nickel powder was used as the catalyst, C\textsubscript{60}H\textsubscript{36} can reduce anthracene by heating, and C\textsubscript{60}H\textsubscript{36} can reduce the silver ion and ammonia complex in solution as well as C\textsubscript{60} itself. © 2001 Elsevier Science Ltd. All rights reserved.

After it had become possible to produce fullerenes in gram quantities,\textsuperscript{1} these compounds were the subject of intensive research. One of the first reactions of Fullerene[60] was the Birch reduction\textsuperscript{2} that gave hydrofullerene C\textsubscript{60}H\textsubscript{36}. Since only conjugated double bonds are involved in reactions of this type, it was assumed that all the double bonds in the product, C\textsubscript{60}H\textsubscript{36}, were isolated from each other.

The synthesis of fullerene hydrides is an area of considerable interest.\textsuperscript{3–10} Speculation concerning the use of fullerene hydrides in batteries has appeared in numerous articles. Both the properties of fullerene hydrides and methods for their large-scale preparation are of considerable interest,\textsuperscript{11} particularly products with the formula C\textsubscript{60}H\textsubscript{36}. Other methods to produce C\textsubscript{60}H\textsubscript{36} have been reported, such as hydrogen transfer\textsuperscript{12} and hydrogen radical-induced hydrogenation.\textsuperscript{13} APCI, CI, FAB, and EI mass spectra of the products of Li/NH\textsubscript{3} Birch reduction of C\textsubscript{60} immediately after work-up show the major constituent to be C\textsubscript{60}H\textsubscript{36}.\textsuperscript{14} The precise structures of these compounds have not yet been established, although the structures of four C\textsubscript{60}H\textsubscript{36} isomers with the symmetry T, T\textsubscript{d}, D\textsubscript{3d} and S\textsubscript{6} have been considered.\textsuperscript{15–18} Yoshida et al.\textsuperscript{19} examined C\textsubscript{60}H\textsubscript{2n} (n=1–30) using molecular mechanics (MM2/P2) and the PM3 method; they reported that C\textsubscript{60}H\textsubscript{36} has the lowest strain energy of 30 hydrogenated fullerenes. Recently, Okotrub et al.\textsuperscript{20} reported the X-ray, spectroscopic and quantum-chemical characterization of hydrofullerene C\textsubscript{60}H\textsubscript{36}.

Fullerene hydrides may have the potential to provide the hydrogen resources. We have found that thermal decomposition of C\textsubscript{60}H\textsubscript{36} at 199.3°C for 11 h produced hydrogen: C\textsubscript{60}H\textsubscript{36} (48 mg) in 1,2-dichlorobenzene-d\textsubscript{4} in an NMR tube was inserted into liquid nitrogen to solidify the solution under vacuum, and then degassed. After degassing three times, the NMR tube was sealed and heated at 199.3°C for 11 h. 1H NMR showed a broad new peak appearing at δ 5.62. After the sealed NMR tube was opened and N\textsubscript{2} was passed through for 10 min, the broad hydrogen peak had disappeared completely (again using 1H NMR detection). Combined with Evans’ work,\textsuperscript{21} this peak was assigned to hydrogen lost from C\textsubscript{60}H\textsubscript{36}. When the C\textsubscript{60}H\textsubscript{36} sample was heated at 248°C for 3 h, the 1H NMR spectrum showed a much higher and broader peak appearing at δ 5.6 and mass spectroscopy showed that the main product is C\textsubscript{60}H\textsubscript{18} (yield 65%) after C\textsubscript{60}H\textsubscript{36} was thermally decomposed under these conditions.

It is reported that Vaska’s compound [trans-carbonyl(chloro)bis(triphenylphosphine)iridium(I)] can be used as a hydrogen-transfer catalyst, for example, from formic acid to α,β-enones using a catalytic amount of Vaska’s compound.\textsuperscript{22} Vaska’s compound readily forms adducts with H\textsubscript{2},\textsuperscript{23–26} O\textsubscript{2},\textsuperscript{27} MeI,\textsuperscript{28} and SO\textsubscript{2}, CO, HCl, CS\textsubscript{2}, etc.\textsuperscript{29} To further explore the decomposition reaction with Vaska’s compound [trans-carbonyl(chloro)bis(triphenylphosphine)iridium(I)] as catalyst, pure C\textsubscript{60}H\textsubscript{36} (20 mg) and Vaska’s compound (15 mg) were dissolved in C\textsubscript{6}D\textsubscript{4}Cl\textsubscript{2} (1,2-dichlorobenzene-d\textsubscript{4}) in an NMR tube after first being bubbled with nitrogen to remove traces of oxygen. Since Vaska’s compound is stable in air but readily takes up oxygen in solution, the NMR tube was inserted into liquid nitrogen to solidify the solution under vacuum, and then degassed. After degassing three times, the NMR tube was sealed. The reaction mixture in the NMR tube was heated at 60°C for 18 h, then the 1H NMR spectrum was taken and a
broad, new, H₂ peak appeared at δ 5.69 ppm. This illustrates that hydrogen can be removed from C₆₀H₃₆ at 60°C using a catalytic amount of Vaska’s compound. Actually, the hydrogen decomposed from C₆₀H₃₆ can also form a dihydro compound with Vaska’s compound, but this is very sensitive and readily decomposes on heating under these conditions. It has been reported that a number of alkenes and activated alkenes can be hydrogenated in the presence of a catalytic amount of Vaska’s compound, and thus we tried to use C₆₀H₃₆ to hydrogenate cyclohexene using Vaska’s compound as catalyst. A mixture of C₆₀H₃₆ (35 mg), cyclohexene (20 mg), Vaska’s compound (15 mg), and the solvent (1,2-dichlorobenzene-d₆ and benzene-d₆, 0.7 ml) was sealed in an NMR tube and then the sample was heated at 80°C for 8 h. The results showed that C₆₀H₃₆ can hydrogenate cyclohexene to give cyclohexane (yield 28%) using Vaska’s compound as catalyst. However, it is very difficult for C₆₀H₃₆ to hydrogenate cyclohexene using Raney nickel as catalyst. We used anthracene as the hydrogen acceptor reacting with C₆₀H₃₆ in the presence of nickel powder catalyst. C₆₀H₃₆ (240 mg, 0.3175 mmol), anthracene (67.81 mg, 0.381 mmol, 1.2 equiv.) and nickel powder (20 mg) were put into a grinder and the resulting mixture ground and then sealed in an ampoule under an inert gas atmosphere. The sample was heated at 298°C for 16 h, extracted with chloroform-d (4 ml) with super-sonication and centrifuged in a glass tube. After filtration, the mixture was separated by a silica-gel chromatography column using toluene and hexane (1:1) as eluent to give pure product (yield 35%); TLC (Rf = 0.556, toluene and hexane: 1:1); 1H NMR (CDCl₃, TMS, 250 MHz): δ 6.90 (m, 4H), 6.78 (m, 4H), and 4.5 (s, 4H); MS (EI): 180 [M-1]+. These results show this reduced product is dihydroanthracene (DHA), the starting material C₆₀H₃₆ becoming C₆₀H₁₈, the mass spectrum showed only one strong signal at 738 [M-1]+.

It has been reported that treatment of a toluene solution of DDQ with C₆₀H₃₆ caused rapid discharge of the red color of the DDQ–toluene complex and formation of a dark brown solution that was indistinguishable from authentic C₆₀. We found that aqueous potassium permanganate was discolored when a little C₆₀H₃₆ was added. C₆₀H₃₆ can be dissolved in benzene, toluene, hexane, etc., and a more concentrated C₆₀H₃₆ solution can be obtained by using C₆₅ as solvent, but C₆₀H₃₆ reacts with this solvent; however, dichlorobenzene is a good solvent for C₆₀H₃₆. We found that C₆₀H₃₆ can be dissolved in DMSO. It is very interesting that a metallic silver mirror deposited on the walls of the reaction vessel of [Ag(NH₃)₂]⁺ and C₆₀H₃₆. To an aqueous silver nitrate solution, ammonia water (NH₃, 15%) was added. A clear [Ag(NH₃)₃]OH complex solution was obtained, and then a DMSO solution of C₆₀H₃₆ was added into the silver ion and ammonia complex solution. The resulting mixture was heated on a burner and a silver mirror was deposited on the reaction vessel. The reaction solution was extracted with toluene and washed thoroughly with water. The toluene solution was then concentrated, and mass spectral analysis confirmed that product is C₆₀H₁₈, a strong molecular ion peak being detected, which may be described by the following equation:

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\text{C}_{60}\text{H}_{36} + 18\text{[Ag(NH}_3\text{)]}_2\text{OH} = \text{C}_{60}\text{H}_{18} + 18\text{Ag} + 18\text{H}_2\text{O} + 36\text{NH}_3
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The silver ion and ammonia complex [Ag(NH₃)₂]⁺ is a fairly specific oxidizing agent. It can oxidize C₆₀H₃₆. Can C₆₀ itself be reduced by C₆₀H₃₆? It is very interesting that we obtained C₆₀H₃₆ as the reduced product: C₆₀H₃₆ (120.96 mg, 0.160 mmol) and C₆₀ (116 mg, 0.161 mmol) were put into a grinder and the mixture was ground. The sample was then placed in a glass tube, covered, heated at 250°C for 1 h, extracted with benzene-d₆ (4 ml), and filtered; 1H NMR (250 MHz, C₆D₆, TMS): δ 6.8 (s, 2H); MS-FD: 722 [M⁺], 721 [M-1]⁺, 720 [C₆₀], HPLC analysis was carried out on a Bucky-clutcher I column using toluene and hexane solution (70:30) as eluent. The results showed that the yield of C₆₀H₃₆ was 13%, and that very little C₆₀H₃₆ was found by HPLC. However, the experiment confirmed that C₆₀H₃₆ cannot reduce C₆₀ at room temperature. C₆₀ is an acceptor and it can be reduced with C₆₀H₃₆ under certain conditions. Consideration of the electronic structure of C₆₀ has naturally focused on the surface π-orbitals. There are 30 filled π-type orbitals with 5-fold degenerate orbitals which are HOMOs. The LUMOs are the triply degenerate t₁₂ orbitals, and a second set of triply degenerate orbitals of t₁₈ symmetry are the LUMO+1’s. Since the LUMO is relatively low in energy, C₆₀ is readily reduced. It should be pointed out that the C₆₀H₃₆ we used in this paper is a mixture of isomers. Research on the thermal decomposition of the separated C₆₀H₃₆ isomers will be more interesting.

References


