Preparation and Decomposition of C 60 H 36

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Preparation and Decomposition of C₆₀H₃₆

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$C_{60}H_{36}$ was prepared by the Benkeser reaction with a much milder procedure. Thermal dehydrogenation of $C_{60}H_{36}$ with $IrCl(CO)(PPh_3)_2$, Pd/C, and Ni−Al alloy and photochemical catalytic dehydrogenation with $RhCl(CO)(PPh_3)_2$ were studied. Pd/C catalyst was more effective for the thermal decomposition of $C_{60}H_{36}$ till now.

Hydrogen, as a clean, convenient, versatile fuel source, is considered to be an ideal energy carrier in the foreseeable future. To date, much effort has been put into storage of hydrogen including physical storage via compression or liquefaction, chemical storage in hydrogen carriers, metal hydrides and gas-on-solid adsorption.[1] But no one satisfies all of the efficiency, size, weight, cost and safety requirements for transportation or utility use.

$C_{60}H_{36}$, first synthesized by the method of the Birch reduction, was loaded with 4.8 wt % hydrogen. If a 100% conversion of $C_{60}H_{36}$ were achieved, 18 mol of H_2 gas would be liberated from each mole of fullerene hydride. It indicated that [60]-fullerene might be a potential hydrogen storage material compared to the metals, and Drewello et al. reported that $C_{60}H_{36}$ was used as the source of hydrogen for the in situ hydrogenation of $(C_{59}N)_2$, leading to $C_{59}NH_5$ as the main reaction product.[2] Pure $C_{60}H_{36}$ is very stable below 500 °C under nitrogen atmosphere and it releases hydrogen accompanying by other hydrocarbons under high temperature.[3] It is a great challenge to explore effective catalysts to decompose $C_{60}H_{36}$ to generate H_2.

Many routes of hydrogenating fullerenes were established including Birch reduction,[4] hydroboration,[5] hydrzirconation,[6] solid-phase hydrogenation,[7] transfer hydrogenation,[8] electrochemical reduction,[9] dissolving metal reduction[10] as well as chemical reduction with diimides.[11] Hydrogenation of C_{60} was carried out in toluene using Ni/Al_2O_3 catalyst in the temperature range 150−250 °C with the hydrogen pressure range 25−75 Kgf cm⁻² . Other methods include hydrogen radical induced hydrogenation,[12] direct hydrogenation when C_{60} was exposed to H_2 gas at 673 K and 50−100 bar, and photoinduced electron transfer.[13]

Hydrogenation of [60]fullerene with Birch reduction by using liquid ammonia is inconvenient to handle and work up, which often requires low temperature and a long period of waiting for the ammonia to evaporate. Benkeser[14] and Michael et al.[15] made several attempts to minimize some of these problems by using of alkylamine solvents instead of liquid ammonia to reduce aromatic substrates such as benzene and naphthalane. Billups prepared a complex mixture of $C_{60}H_{38}$ to $C_{60}H_{44}$ by Benkeser reaction to reduce $C_{60}H_{36}$ obtained by Birch reduction of C_{60}.[16]

We used the Benkeser reaction to synthesize $C_{60}H_{36}$ and good results were obtained.[2]

In our experiments C_{60} was treated with lithium in aliphatic amines, such as ethylenediamine, 1,3-propanediamine, 1,2-propanediamine, *n*-propylamine and 2,2′-diaminodiethylamine,
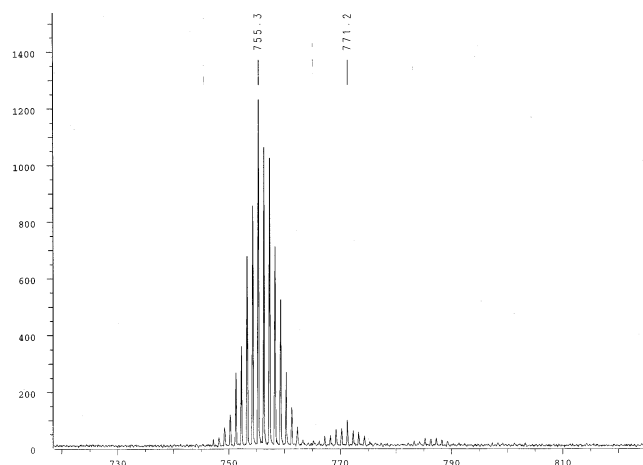

Figure 1. MALDI-TOF mass spectrum of $C_{60}H_{36}$.

as well as with potassium and sodium in ethylenediamine, and *tert*-butyl alcohol was used as a proton source.

The matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrum of crude product showed strong signals at *m/z* = 755.3, which correspond to the $C_{60}H_{35}{}^+$ ion (Figure 1). The ¹H NMR spectrum in ODCB-d_4 (1,2-dichlorobenzene-d_4) showed a broad group of signals between δ = 2.60 and 4.40 with two distinct maxima at δ = 3.10 and 3.40, which was consistent with the result of literature.[4,8]

The infrared spectrum (KBr) has three strong C−H stretching absorptions at 2913, 2847, and 2824 and a weaker band at 1492 cm⁻¹ . The presence of bands at 697, 1024, 1097, 1260, and 1453 cm⁻¹ would indicate the spherical fullerene structure is still present but considerably distorted.

From the experiments we found that the purity of the products depended on the solubility of C_{60} and alkali metals in aliphatic amines. The reduction of C_{60} with lithium in 1,3-propanediamine, 1,2-propanediamine and *n*-propylamine resulted in the augment of amine adducts.

The solubilities of lithium, potassium, and sodium in liquid ammonia at its boiling point are (per 100 g of liquid ammonia) 10.4, 47.8, and 24.5 g, which correspond to mole ratios of 1.49, 1.23, and 1.07 mol, respectively.[17] Like the solubility of alkali metals in liquid ammonia, solubility in ethylenediamine is Li > K > Na. Although they have very negative potentials (Li, −3.0 V; K, −2.9 V; Na, −2.7 V), different solubilities lead to different results. For example, examining from the changes of the color of the reaction mixture, it was so rapid for lithium to
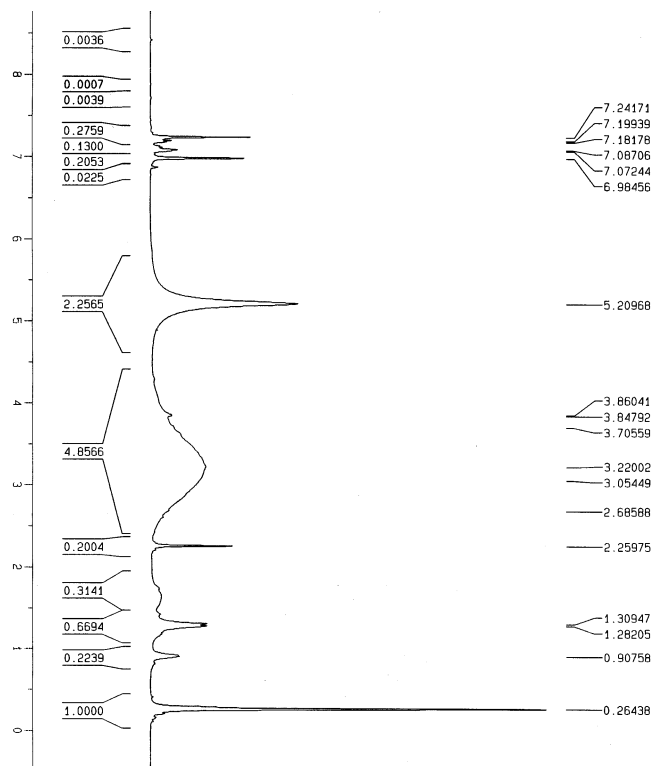
Figure 2. ^{1}H NMR spectra of catalytic dehydrogenation of C$_{60}$H$_{36}$ (20 mg) in 0.5 mL of ODCB-d_4, Pd/C (15 mg), 100 °C, 16 h.

Figure 3. ^{1}H NMR spectra of catalytic dehydrogenation of C$_{60}$H$_{36}$ (20 mg) in 0.5 mL of ODCB-d_4, RhCl(CO)(PPh$_3$)$_2$ (15 mg), 365 nm, room temperature, 6 h.

complete the reaction in 15 min, but 2 h for potassium, and there were no obvious reaction phenomena for sodium for 24 h.

We found that hydrogen can be produced catalytically from C$_{60}$H$_{36}$ by Vasks's compound (IrCl(CO)(PPh$_3$)$_2$) under mild conditions.[18] The sample was dissolved in ODCB-d_4 (1, 2-dichlorobenzene-d_4) in an NMR tube, and the NMR tube was inserted into liquid nitrogen to solidify the solution under vacuum and then degassed. After being degassed three times, the NMR tube was sealed and heated for definite hours. Then the ^{1}H NMR was processed to determine the signal of hydrogen; the signal is at δ 5.69 ppm.[18,19] RhCl(CO)(PPh$_3$)$_2$ as a catalyst, having a structure similar to that of IrCl(CO)(PPh$_3$)$_2$, was also examined for thermal dehydrogenation of C$_{60}$H$_{36}$, but it showed low catalytic activity.

To find a better catalyst, 10 wt % palladium carbon (Pd/C) was tried and good results were obtained. A very big peak for hydrogen appeared at δ 5.2 ppm in the ^{1}H NMR spectrum (Figure 2) at 100 °C over a 10 wt % Pd/C catalyst for 16 h. It showed that hydrogen could be produced from C$_{60}$H$_{36}$ using a catalytic amount of Pd/C.

Very cheap Ni−Al alloy (containing 40−50% of Ni) was used as a catalyst in our experiments. A broad small peak of hydrogen at δ 5.6 ppm in ^{1}H NMR spectrum at 100 °C over a Ni−Al alloy catalyst for 20 h shows that Ni−Al alloy has catalytic activity for thermal dehydrogenation of C$_{60}$H$_{36}$ (Figure S1). We think that C$_{60}$H$_{36}$ was solubilized well in ODCB-d_4 (1, 2-dichlorobenzene-d_4) under our experimental conditions.

RhCl(CO)(PPh$_3$)$_2$ has been used to catalyze photochemical dehydrogenation of alkanes.[20,21] We examined catalytic dehydrogenation of C$_{60}$H$_{36}$ over RhCl(CO)(PPh$_3$)$_2$ catalyst under photoirradiated conditions. A hydrogen peak at δ 5−7 ppm appeared in the ^{1}H NMR spectrum (Figure 3), but at 505 nm it showed no catalytic activity. IrCl(CO)(PPh$_3$)$_2$ was also investigated at both 365 and 505 nm, and the results are not good. It
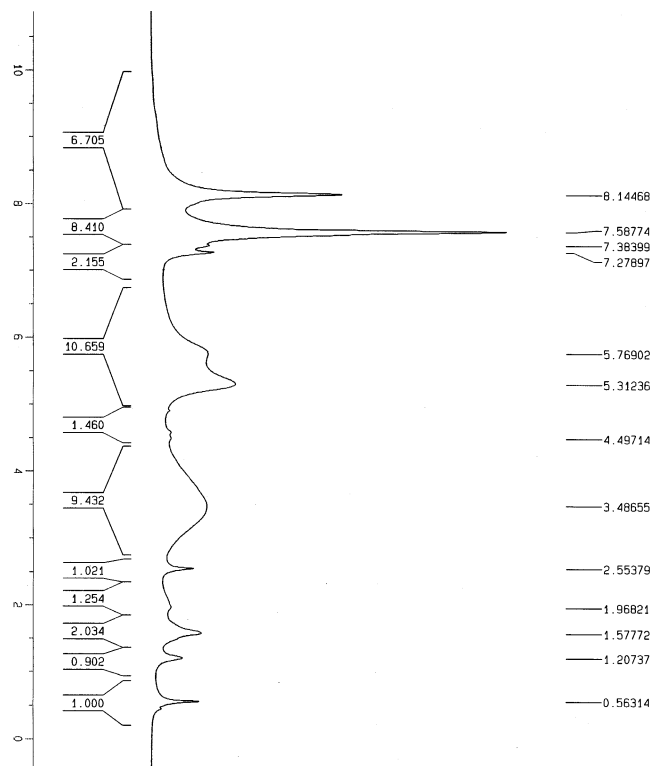
is explained that an effective wavelength for the metal-to-ligand charge-transfer (MLCT) bands of RhCl(CO)(PPh$_3$)$_2$ is limited to the region of 340−420 nm and the MLCT is excited at a range of 365 and 505 nm.[21]

Hydrogen could be generated catalytically from C$_{60}$H$_{36}$, and this result could be considered as a new progress in possible application of fullerenes for hydrogen storage, but how much H$_2$ could be generated from C$_{60}$H$_{36}$? We developed a cylindrical stainless steel reactor based on Dumesic's work[22] to measure the amount of hydrogen catalytically generated from C$_{60}$H$_{36}$. The volume of the reactor is 20 mL with 22 mm of depth and 34 mm of diameter. The reactor has a high temperature silicone rubber gasket and a stainless steel cover plate (with 50 mm hole). After the sample was added, the reactor was sealed. Then the sample was bubbled by He removing air. The reactor was subsequently heated for 16 h at 100 °C and then cooled to room temperature.

The gas was sampled with a syringe inserted through the hole in the cover plate, and the gas was injected into a GC (equipped with thermal conductivity detector TCD) to determine the amount of H$_2$.

The decomposition ratio of C$_{60}$H$_{36}$ in ODCB (1, 2-dichlorobenzene) at 100 °C for 16 h was 33% with Pd/C catalyst and 22% with IrCl(CO)(PPh$_3$)$_2$ under our experimental conditions. The Pd/C catalyst is a more effective one for the thermal decomposition of C$_{60}$H$_{36}$ and Pd/C is also cheaper than IrCl-(CO)(PPh$_3$)$_2$ catalyst till now based on our experiments.

Mass spectroscopy showed that the main solid product is C$_{60}$H$_{18}$ after C$_{60}$H$_{36}$ was thermally decomposed under our conditions,[18] C$_{60}$ was not generated and C$_{60}$H$_{36}$ was decomposed just by half because the temperature of decomposition was not high.

Experimental Section

All reactions were carried out under nitrogen, IR spectra were recorded as KBr pellets, ^{1}H NMR spectra were recorded with a 300 and 400 MHz spectrometer, chemical shifts are given as δ values (internal standard: TMS), MALDI-TOF mass spectra (positive ion mode) were recorded with N_2 laser ($\lambda_{exc} = 337$ nm) in the reflection mode. All of the amines were redistilled before use.

In a topic procedure, *tert*-butyl alcohol and alkali metals were added into a solution of C_{60} in aliphatic amines. The mixture was stirred vigorously under a N_2 atmosphere. When the solution turned from blue to white, the reaction was complete. Then the mixture was poured into ice water, extracted with toluene, and then washed with brine. The toluene solution was dried over Na_2SO_4, and solvent was evaporated; a light-yellow solid was obtained. The crude product was purified by column chromatography with a mixture of silica gel (0.10−0.15 mm) and ion-exchange resin (003 × 7, styrene−DVB, 0.3−0.4 mm) as packing material. ^{1}H NMR (400 MHz, *o*-$C_6D_4Cl_2$): δ 2.60−4.20 (a broad band), 3.10, 3.40. FT-IR ν (KBr, cm^{-1}): 2913, 2847, 2824, 1605, 1492, 1453, 1260, 1097, 1024, 803, 697. MS *m/z* (MALDI-TOF): 755.3 ($C60H_{35}{}^+$).

Pure $C_{60}H_{36}$ (20 mg) and $IrCl(CO)(PPh_3)_2$ (15 mg) were dissolved in ODCB-d_4 (1,2-dichlorobenzene-d_4) in an NMR tube; after air was removed by freeze−pump−thaw in liquid nitrogen, the NMR tube was sealed. Then the reaction mixture was heated at 60 °C for 18 h and the signal of hydrogen dissolving in ODCB-d_4 in the ^{1}H NMR spectrum is at δ 5.69 ppm.

A sealed NMR tube with 20 mg of $C_{60}H_{36}$, 15 mg of $RhCl(CO)(PPh_3)_2$ and 0.5 mL of ODCB-d_4 after air was removed was irradiated at 365 nm for 6 h, and an obvious peak of hydrogen in the range δ 5−7 appeared in the ^{1}H NMR spectrum.

The amounts of hydrogen produced from 100 mg of $C_{60}H_{36}$ in 1 mL of ODCB at 100 °C for 16 h were 0.78 mmol (17.47 mL) and 0.52 mmol (11.73 mL) with decomposition ratios of 33% and 22% for 50 mg of Pd/C catalyst and 50 mg of $IrCl(CO)(PPh_3)_2$.

Supporting Information Available: General procedure of synthesis of $C_{60}H_{36}$ and data of $C_{60}H_{36}$, materials, methods and the GC chromatogram of sample gas. This material is available free of charge via the Internet at http://pubs.acs.org.

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