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Mechanism of hydrogenation of [60]fullerene with Zn-conc. HCl

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A plausible mechanism for hydrogenation of [60]fullerene with Zn-conc. HCl is given and it is confirmed by synthesis of $C_{60}H_{36}$ by reaction of [60]fullerene and Zn–$ZnCl_2$–H_2O.

Keywords: fullerene hydrides, hydrogenation, mechanism

The possible use of fullerene hydrides in hydrogen storage[1, 2] and batteries[3] has made their preparation of considerable interest. Many hydrogenation methods[4-10] for fullerene have been developed in the past. Darwish et al[10] obtained $C_{60}H_{36}$ using Zn-conc. HCl, but no mechanism was proposed. Herein we wish to clarify the mechanism of hydrogenation of [60]Fullerene with Zn-conc. HCl and have confirmed our proposed by synthesis of $C_{60}H_{36}$ by reaction of [60]fullerene and Zn–$ZnCl_2$–H_2O.

A plausible mechanism for hydrogenation of [60]fullerene with Zn-conc. HCl is shown in Scheme 1. It is proposed that $ZnCl_2$ is produced by the reaction of conc. HCl and Zn powder, then by coordination of $ZnCl_2$ to fullerene (1), the fullerene cation (2) is produced, which is protonated to give the free fullerene cation (3). Two electron reduction of the cation (3) by Zn gives the anion (4), which is protonated to give the hydrogenated fullerene.

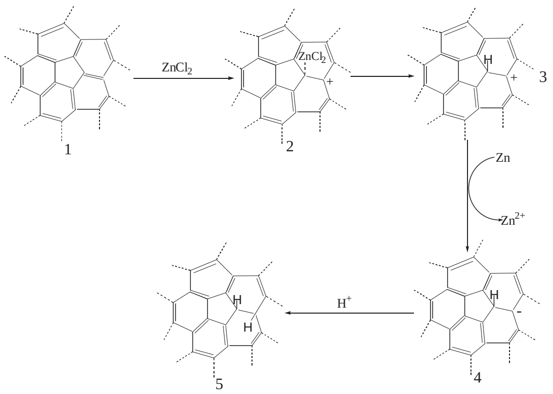
The presence of $ZnCl_2$ is necessary during the course of hydrogenation in the reaction. The production of an activated complex between $ZnCl_2$ and fullerene allow the hydrogenation to be successfully accomplished. Meier *et al.*[9] used Zn-6 mol dm^{-3} HCl and obtained a mixture of 7% $C_{60}H_2$, 3% $C_{60}H_4$ and 1% $C_{60}H_6$ and Darwish *et al.*[10] obtained $C_{60}H_{36}$ using Zn-conc. HCl. Although there is no $ZnCl_2$ in the starting materials, $ZnCl_2$ is produced by the reaction of HCl and Zn during the course of the reaction.

To confirm the rationality of the mechanism, we carried out the following experiment. Zn powder and anhydrous zinc chloride were added to a saturated solution of [60]fullerene in toluene under nitrogen gas at room temperature, then water was added to the rapidly stirred mixture and stirring was continued for a further 16 h. A red-brown solid was obtained finally.

The matrix-assisted laser desorption/ionisation time-of-flight (MALDI-TOF) mass spectrum of the product showed that $C_{60}H_{36}$ (*m/z*=755.3) was the major product (Fig. 1). Simultaneously, small satellite peaks of some lower fullerene hydrides and oxides were observed because of the sensitivity of $C_{60}H_{36}$ to light and oxygen.[10]

The IR spectrum exhibited bands at 2919, 2850, 1651, 1492cm^{-1}, strongly suggesting the presence of C–H and C=C bonds in the reduced product. The presence of bands at 523, 694, 728, 854, 1029, 1178, 1460 cm^{-1} would indicate the spherical fullerene structure is still present but considerably distorted.

In summary, a plausible mechanism for hydrogenation of [60]Fullerene with Zn-conc. HCl has been proposed and confirmed by obtaining $C_{60}H_{36}$ with [60]fullerene and Zn–$ZnCl_2$–H_2O. It should be pointed out that the reduction by Zn–$ZnCl_2$–H_2O is less effective than by Zn–conc. HCl, so the mechanism presented in this paper is one possible mechanism.



Scheme 1 The possible mechanism for hydrogenation of fullerene.

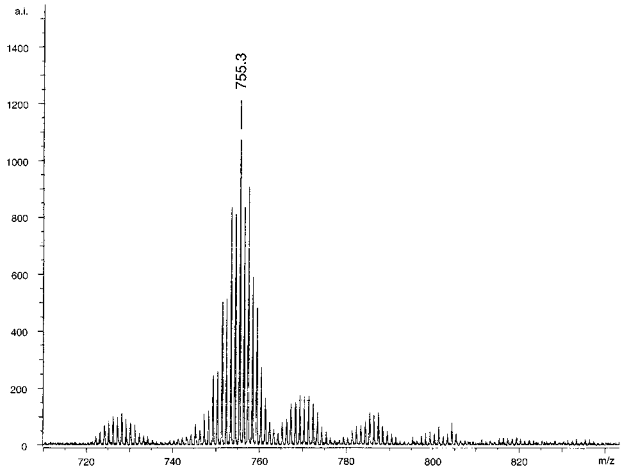


Fig. 1 The MALDI TOF-MS of crude product hydrogenated fullerene with Zn-$ZnCl_2$-H_2O.

Experimental

To a solution of 50 mg (0.07 mmol) of C_{60} in 35 ml of toluene was added 1.75 g (27 mmol) of zinc powder and 1.0 g (7 mmol) of anhydrous zinc chloride, then 1 ml of water was added over 5 min to the rapidly stirred mixture and stirring was continued for a further 16 h under a di-nitrogen atmosphere. The organic layer was extracted, washed with water and dried over Na_2SO_4, and the solvent was evaporated under reduced pressure to give 31 mg of a red-brown solid. FT-IR v (KBr, cm^{-1}): 3423, 2919, 2850, 1651, 1457, 1178, 1029, 854, 728, 697, 523. MS *m/z* (MALDI-TOF): 755.3 ($C_{60}H_{35}^+$).

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