

Catalytic Behaviour of Alkali-metal Fullerenes, $C_{60}M_6$ and $C_{70}M_6$ ($M = Cs, K, Na$), in H_2-D_2 Exchange and Olefin Hydrogenation

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The alkali-metal fullerenes $C_{60}M_6$ and $C_{70}M_6$ ($M = Cs, K, Na$) exhibit remarkable catalytic activities in H_2-D_2 exchange at 173–273 K and ethene hydrogenation at 273–373 K which resemble that of noble metals such as Pt and Pd; uncombined fullerenes and alkali metals are inactive.

Since the initial discovery and subsequent development of the large-scale synthesis of fullerenes (C_{60} and C_{70}), they have been of fundamental interest owing to their unique properties, e.g. incorporation of magnetic metals in their interiors¹ and low-temperature superconductivity when combined with metals.² Of particular interest is that fullerenes display unique types of π -conjugated carbon cages, which could serve as electron acceptors enabling the formation of charge-transfer complexes with alkali metals such as Cs and K which can act as electron donors. Here we report that alkali-metal fullerenes, $C_{60}M_6$ and $C_{70}M_6$ ($M = Cs, K, Na$) exhibit remarkable catalytic activities in H_2-D_2 exchange and olefin hydrogenation at low temperatures. Their catalytic behaviour is strongly associated with the fullerenes structure and the nature of the alkali metals.

The high purity (>99%) crystalline fullerenes C_{60} and C_{70} (Scientific Lab.) were obtained by extraction from toluene-hexene through an alumina column. Their purity was checked by high-performance liquid-gas chromatography using a μ -Bondsphere C-18 column (Waters Chromatography: 3.9×150 mm). The compounds $C_{60}M_6$ and $C_{70}M_6$ ($M = Cs, K, Na$) were prepared by reaction of Cs, K or Na (>99.95%, 25–85 mg) with stoichiometric quantities of C_{60} or C_{70} (20–60 mg) at 498 K for 3 d followed by 7 d at 673 K in sealed capillaries (Rare Metallic Co.) into which the metals had been distilled, according to the literature method.³ The stoichiometry of the fullerenes of C_{60} with Cs and K were established by X-ray data.^{2,3} The resulting greenish-black alkali-metal fullerenes were charged *in vacuo* in a Pyrex-glass reactor equipped with a

closed circulating reaction system (250 ml). The products in H_2-D_2 exchange reactions and olefin hydrogenation were analysed with a QP mass spectrometer (ANELVA AQA-100MPX) and by TCD GC using VZ-7 and Porapak Q columns, respectively.

When a $H_2 + D_2$ (1 : 1 v/v, total pressure 200 Torr) mixture was admitted onto the complexes $C_{60}Cs_6$ or $C_{70}Cs_6$, it was found that the H_2-D_2 exchange reaction proceeded readily to form HD even at low temperatures *i.e.*, 173–273 K, as shown in Fig. 1. By contrast, exchange did not occur on uncombined C_{60} (or C_{70}) film (60 mg) and Cs metal (200 mg) deposited on a wall of the Pyrex-glass reactor under similar reaction conditions even at high temperatures 373 K). The specific activities (TOF = turnover frequency on carbon-cluster base) of $C_{70}Cs_6$ in H_2-D_2 exchange are comparable with those found for noble metals such as Pt and Rh. The catalytic activities of $C_{60}Cs_6$ and $C_{70}Cs_6$ completely vanished on exposure to O_2 (100 Torr) at 300 K due to destruction of the charge-transfer complexation. Similar catalytic behaviour has been reported for electron acceptor-donor complexes of aromatic hydrocarbons and graphite with alkali metals.^{4–6}

It is suggested that the fullerenes act as the sites for dissociative chemisorption of molecular hydrogen upon formation of the charge-transfer complexes with alkali metals. It is of interest that $C_{70}Cs_6$ exhibits remarkable activity in H_2-D_2 exchange ($E_a = 11.1$ kJ mol⁻¹) closely resembling that of platinum metals. The first-order rate constants at 273 K for $C_{70}Cs_6$ are five times higher than for $C_{60}M_6$ ($E_a = 14.5$ kJ mol⁻¹), and much higher than for other electron donor-acceptor complexes *e.g.* with tetracene and graphite, under similar reaction conditions (Table 1). The results imply that the fullerene C_{70} provides more active sites on its cluster core upon charge-transfer complexation with alkali metals compared to C_{60} or other planer aromatic acceptor molecules. The catalytic activities of $C_{60}M_6$ ($M = Cs, K, Na$) and in H_2-D_2 exchange was strongly dependent on the metal, with a reactivity decreasing in the order; $Cs \gg K \gg Na$, in line with the size of the alkali cations [$r = 1.70$ (Cs⁺), 1.33 (K⁺), 0.97 Å (Na⁺)] in the fullerenes. Trends of catalytic activity for hydrogen dissociation on the $C_{60}M_6$ species ($M = Cs, K, Na$) showed no correlation with their superconductivity behaviour.²

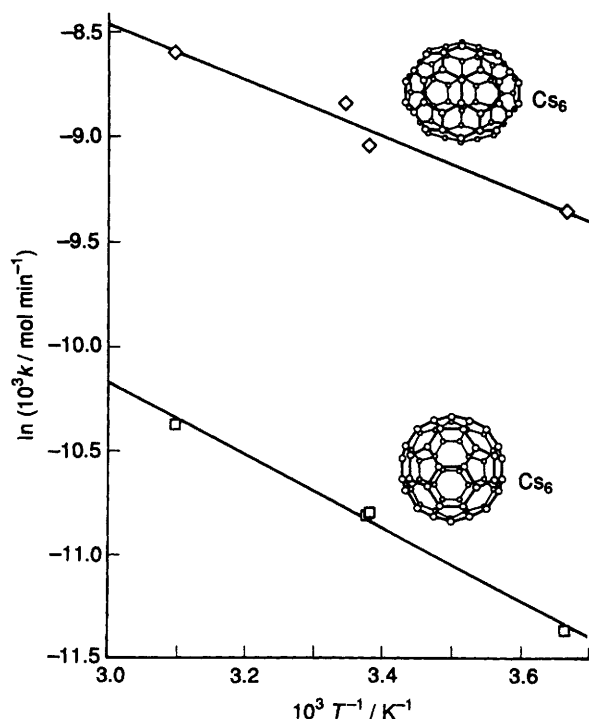


Fig. 1 Arrhenius plots of rates of H_2-D_2 exchange for $C_{60}Cs_6$ and $C_{70}Cs_6$, $p(H_2) = p(D_2) = 11$ kPa

Table 1 Catalytic activities of alkali-metal fullerenes $C_{60}M_6$ and $C_{70}M_6$ ($M = Cs, K, Na$), $Cs_2C_{18}H_{12}$ and Cs-Graphite in H_2-D_2 exchange and ethene hydrogenation reactions

Complex	Rate of hydrogen ^a exchange $H_2 + D_2 \rightleftharpoons 2HD$	Rate of ethane formation ^b $C_2H_4 + H_2 \rightleftharpoons C_2H_6$
$C_{70}Cs_6$	10	0.45
$C_{60}Cs_6$	2	0.008
$C_{60}K_6$	0.08	—
$C_{60}Na_6$	0.001	—
$Cs_2C_{18}H_{12}^c$	0.002	0.035
Cs-Graphite ($C_{24}Cs$)	0.16	—

^a First-order rate constant: mol(HD)/mol (carbon cluster) min⁻¹ $p(H_2) = p(D_2) = 50$ Torr, at 300 K. ^b First-order rate constant of ethane formation: mol (C_2H_6)/mol (carbon cluster) min⁻¹; $p(C_2H_4) = p(H_2) = 100$ Torr at 373 K. ^c $C_{18}H_{12}^{2-}$ = tetracene dianion.

Hydrogenation of ethene proceeded catalytically on $C_{70}Cs_6$ and $C_{60}Cs_6$ at 293–373 K. As shown in Table 1, it is notable that $C_{70}Cs_6$ was much more active (*ca.* 50 times) for ethylene hydrogenation than $C_{60}Cs_6$, possibly due to stronger interaction of ethene on $C_{70}Cs_6$.

IR spectra for $C_{60}Cs_6$ and $C_{70}Cs_6$ films were studied with a specially designed Pyrex-glass cell, enabling preparation and recording *in vacuo* and also measurement during chemisorption. The IR spectra were recorded on a Shimadzu FTIR-8100 single-beam spectrometer with 25–100 scans and a resolution of 2 cm^{-1} . The C_{60} film gave four intense peaks at 1429, 1183, 577 and 526 cm^{-1} [Fig. 2(a)] due to the stretching and deformation modes of C=C and C–C in the cluster framework.⁶ The IR bands at 1429 and 576 cm^{-1} for C_{60} undergo broadening and were shifted to lower frequencies, 1340 and 566 cm^{-1} , respectively upon charge-transfer complexation.

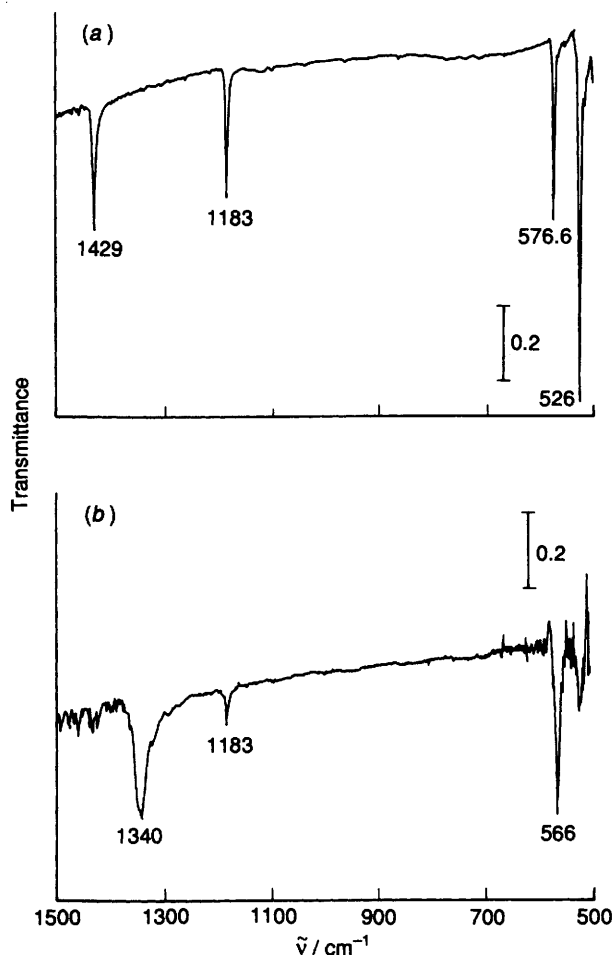


Fig. 2 FTIR spectra of (a) a C_{60} film on KBr disc and (b) after exposure to Cs vapour at 300 K *in vacuo*

Furthermore, the bands at 1183 and 526 cm^{-1} in C_{60} were strongly diminished [Fig. 2(b)]. The formulation $C_{60}Cs_6$ is supported from previous IR data.⁷ For the C_{70} film (IR $\tilde{\nu}/\text{cm}^{-1}$ 1430s, 1415w, 1133m, 1087w, 796s, 674s, 642m, 577s, 567m, 534s)⁸ similar modification of bands due to charge-transfer interaction was observed upon exposure to Cs vapour at 300 K, with appearance of broadened bands at 1366s, 1326m, 821m (sh), 807m, 759m, 554s, 544s (sh) and 528s (sh) cm^{-1} , (sh denotes a sharp peak). When H_2 (and/or D_2) (100 Torr) was admitted onto the $C_{60}Cs_6$ or $C_{70}Cs_6$ films at 273–323 K, no appreciable changes in the IR spectra were observed (indicating negligible contribution of C–H or C–D bond formation), despite the fact that H_2 – D_2 exchange occurred readily to form HD in the gas phase, as monitored by mass spectrometry. This suggests that hydrogen is dissociated on $C_{60}Cs_6$ without formation of a stable hydrogenated fullerene $C_{60}H_mD_n$ [$m+n=36$, $\nu(\text{C–H})=2925, 2855\text{ cm}^{-1}$].⁹ Accordingly, it is proposed that the $H_2 + D_2 \rightarrow 2HD$ reaction proceeds *via* an adsorption–desorption mechanism of molecular hydrogen on the surface of the alkali–metal fullerenes, *i.e.* similarly to the reaction with noble metals such as Pt and Pd.

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Received, 31st December 1993; com. 3107639C

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