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Hydrogenation of Fullerene Cations in the Gas Phase: Reactions of Fullerene Cations and Dications with Atomic and Molecular Hydrogen

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The recent discovery[1] and synthesis[2] of the fullerene series of carbon allotropes has opened up many exciting vistas in chemistry.[3] So far, hydrogenation of fullerenes has been achieved in solution by the Birch reduction, but only with C_{60}.[4] $C_{60}H_{36}$ was the observed product, and ab initio calculations have predicted that $C_{60}H_{60}$ should also be stable.[5] A previous attempt to hydrogenate the monocation of C_{60} in the gas phase was unsuccessful—$C_{60}^{\bullet+}$ has been found to be unreactive toward molecular hydrogen[6]—but the monohydrogenated C_{60} and C_{70} cations have been formed by gas-phase proton transfer.[7] Here we report results of an experimental study which demonstrate that both the monocations and the dications of C_{60} and C_{70} can be hydrogenated in the gas phase by reactions with atomic hydrogen. We have studied the reactions of $C_{60}^{\bullet+}$, C_{60}^{2+}, $C_{70}^{\bullet+}$, and C_{70}^{2+} with H and with H_2 and can report that all of these fullerene ions are observed to add atomic hydrogen with remarkably high efficiency. Hydrogenation of fullerene cations in this manner has importance in the chemistry of sooting flames[8] and in the chemistry which leads to partially hydrogenated fullerane molecules in interstellar clouds and circumstellar envelopes.[9,10]

Atomic hydrogen (atomic deuterium) was produced by the action of a microwave discharge upon a dilute mixture, ~3%, of H_2 (D_2) in He. The discharge source and the method of calibrating the dissociation efficiency have been described previously,[11,12] as has the selected ion flow tube (SIFT) apparatus used in these experiments to measure reaction kinetics.[13] Fullerene ions were produced by electron bombardment (at 50 eV) of C_{60} and C_{70} vapor entrained in argon carrier gas. The fullerene sample was obtained from Strem Chemicals Co. and was a mixture of C_{60} and 2–12% C_{70}. All of the kinetic measurements were performed at 294 ± 2 K in helium buffer gas at a pressure of 0.40 ± 0.01 Torr.

Table I. Rate Coefficients and Thermodynamics for Reactions of Fullerene Ions with H, D, H_2, and D_2 at 294 ± 2 K

reactants	products	k_{obsd} [a]	k_L [b]	$\Delta H°$ [c]
$C_{60}^{\bullet+} + H^\bullet$	$C_{60}H^+$	>0.1[d]	1.9	−67
$C_{60}^{\bullet+} + D^\bullet$	$C_{60}D^+$	>0.3[d]	1.35	−67
$C_{60}^{2+} + H^\bullet$	$C_{60}H^{\bullet 2+}$	>0.3	3.8	
$C_{60}^{2+} + D^\bullet$	$C_{60}D^{\bullet 2+}$	>0.3	2.7	
$C_{60}D^+ + D^\bullet$	$C_{60}D_2^{\bullet+}$	obsd[e]	1.35	
$C_{60}D^{\bullet 2+} + D^\bullet$	$C_{60}D_2^{2+}$	inf[f]	2.7	
$C_{60}D_2^{2+} + D^\bullet$	$C_{60}D_3^{\bullet 2+}$	inf[f]	2.7	
$C_{60}D_3^{\bullet 2+} + D^\bullet$	$C_{60}D_4^{2+}$	inf[f]	2.7	
$C_{70}^{\bullet+} + H^\bullet$ ($D^\bullet$)	$C_{70}H(D)^+$	obsd[e]	1.9 (1.35)	−67
$C_{70}^{2+} + H^\bullet$ ($D^\bullet$)	$C_{70}H(D)^{\bullet 2+}$	obsd[e]	3.8 (2.7)	
$C_{60}^{\bullet+} + H_2$ (D_2)	none	<0.001	1.5 (1.0)	
$C_{70}^{\bullet+} + H_2$ (D_2)	none	<0.001	1.5 (1.0)	
$C_{60}^{2+} + H_2$ (D_2)	none	<0.001	2.9 (2.1)	
$C_{70}^{2+} + H_2$ (D_2)	none	<0.001	2.9 (2.1)	

[a] Observed rate coefficient in units of 10^{-9} cm^3 $molecule^{-1}$ s^{-1}. [b] Calculated Langevin collision rate coefficient, in units of 10^{-9} cm^3 $molecule^{-1}$ s^{-1}. For reactions of the dications C_{60}^{2+} and C_{70}^{2+}, the Langevin collision rate calculated according to the method of Gioumousis and Stevenson instead yields an upper limit to the expected collision rate, because the expression used assumes a point source of charge[14] whereas the charges on molecular C_{60} and C_{70} dications are likely to be spatially separate. [c] Standard enthalpy of reaction in kcal mol^{-1}. Thermochemical quantities used here include $\Delta H_f°(C_{60}^{\bullet+}) = 720$ kcal mol^{-1}, from $\Delta H_f°(C_{60}) = 545$ kcal mol^{-1} and $IE(C_{60}) = 7.61$ eV;[15,16] $\Delta H_f°(C_{60}H^+) = 705$ kcal mol^{-1}, from $\Delta H_f°(C_{60})$ and $PA(C_{60}) = 204$ kcal mol^{-1};[7] $IE(C_{70}) = 7.61$ eV;[16] and $PA(C_{70}) = 204$ kcal mol^{-1}.[7] $\Delta H_f°(C_{60}^{2+})$ is uncertain given the current disagreement regarding $IE(C_{60}^{\bullet+})$,[17,18] and no information is available regarding the heats of formation of hydrogenated fullerene dications. [d] Very probably, $k(H) \geq k(D)$; a lower value for $k(H)$ indicates that the resolution between $C_{60}^{\bullet+}$ and $C_{60}H^+$ is poorer than that between $C_{60}^{\bullet+}$ and $C_{60}D^+$. [e] Reaction observed, but rate coefficient not obtained. [f] Existence of reaction inferred from products observed.

The results of the measurements are summarized in Table I. The rate coefficients obtained for the reactions with H and D atoms are regarded as lower limits for two reasons. Firstly, the downstream quadrupole mass spectrometer could not resolve perfectly between signals differing only by 1 or 2 *m/z* at the high mass range needed for these experiments.[19] Secondly, the reactant ion may be formed as a secondary product in a reaction of type 1, which is exothermic by 37 kcal mol^{-1} for $n = 1$. Reactions

$$C_{60}H_n^+ + H^\bullet \rightarrow C_{60}H_{n-1}^+ + H_2 \qquad (1)$$

with $n > 1$, as well as the analogous reactions for dicationic species, are also expected to be exothermic by virtue of the high enthalpy of formation of atomic hydrogen. Product channels of this type have been observed in the reactions of hydrocarbons and other ions with $H^\bullet$.[20] In the present case, the occurrence of reactions of type 1 cannot be assessed unless the ion $C_{60}H_n^+$ can be introduced into the flow tube as a reactant. This cannot be achieved with our SIFT apparatus in its present configuration.

All of the fullerene ions were found to be unreactive with H_2. The failure of $C_{60}^{\bullet+}$ to react with H_2 has been noted previously in an FT-ICR experiment,[6] and a similar finding for $C_{70}^{\bullet+}$ is not surprising given the structural similarity of $C_{60}^{\bullet+}$ and $C_{70}^{\bullet+}$. The absence of any reaction of the dications C_{60}^{2+} and C_{70}^{2+} with H_2 presumably indicates the absence of any exothermic product channels between these reactants.

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$C_{60}^{\bullet+}$ and C_{60}^{2+} were both observed to add $H^{\bullet}$ (and $D^{\bullet}$) rapidly, with addition occurring upon at least 10% of the collisions at 0.4 Torr of helium. The primary products were also observed to react further according to reactions 2 and 3. Reaction 2 occurs for

$$C_{60}H_n^{+} + H^{\bullet} \rightarrow C_{60}H_{n+1}^{+} \quad (2)$$

$$C_{60}H_n^{2+} + H^{\bullet} \rightarrow C_{60}H_{n+1}^{2+} \quad (3)$$

$n = 1$, 2, and possibly 3 (a tentative identification of $C_{60}D_4^{+}$ was made), while reaction 3 occurs for at least $n = 1–3$. At high flows of D atoms, the major product peak seen for the sequence of reactions initiated by C_{60}^{2+} was at m/z 364, corresponding to $C_{60}D_4^{2+}$: we are unable to deduce whether the "buildup" of this signal is due to the low reactivity of $C_{60}D_4^{2+}$ with $D^{\bullet}$ or due to the occurrence of a rapid D atom transfer reaction of type 1 involving $C_{60}D_5^{\bullet 2+}$ and $D^{\bullet}$. The addition reactions of $C_{60}^{\bullet+}$ and C_{60}^{2+} with $H^{\bullet}$ and $D^{\bullet}$ are extraordinarily rapid; they are at least as efficient as any ion/$H^{\bullet}$ atom addition reactions which have been reported previously.[20] This can be rationalized in terms of the long collision complex lifetime expected for a species as large as $(C_{60}H^{+})^{*}$, resulting in a high probability of collisional stabilization instead of complex dissociation. Indeed, the fullerene ions are sufficiently large and have enough internal modes of energy dispersal that radiative stabilization of the collision complex is also feasible.[21]

Ion signals obtainable for $C_{70}^{\bullet+}$ and C_{70}^{2+} were about 1 order of magnitude lower in intensity than the signals obtainable for $C_{60}^{\bullet+}$ and C_{60}^{2+}. For this reason, it was not possible to quantify the extent of reaction of $C_{70}^{\bullet+}$ and C_{70}^{2+} with $H^{\bullet}$ and with $D^{\bullet}$. At moderate H/D atom flows, however, the decrease in the m/z 840 and 420 ion signals appeared to parallel the decrease seen for m/z 720 and 360, so that we can suggest that the reactivity of the C_{70} monocation and dication is analogous to that of their C_{60} counterparts.

Rapid reactions of fullerene cations with $H^{\bullet}$ are likely to play a significant role in the chemistry of sooting flames, especially in view of the nonreactivity of $C_{60}^{\bullet+}$ with closed-shell species.[22] Conversion of $C_{60}^{\bullet+}$ to $C_{60}H^{+}$ is likely to enhance the production of neutral C_{60} as shown in the reaction sequence 4–6. Proton transfer from $C_{60}H^{+}$ to a species of high PA (such as cyclopropenylidene, which is easily formed within flames)[26] and dissociative recombination of protonated C_{60} are likely to be more efficient processes within sooting flames than are charge transfer from $C_{60}^{\bullet+}$ (since C_{60} has a lower IE than most smaller hydrocarbon species)[27] and the recombination reaction $C_{60}^{\bullet+}$ + e (which may not have any accessible fragmentation product channels).[28] The reactivity of $C_{60}^{\bullet+}$, and C_{60}^{2+}, with $H^{\bullet}$ can be of similar significance to interstellar chemistry, as we shall discuss elsewhere.[29] The reactivity of $H^{\bullet}$ with $C_{60}H^{+}$ to regenerate $C_{60}^{\bullet+}$, and thus the possible role of $C_{60}^{\bullet+}$ as a catalyst for the recombination of H atoms, remains to be explored. Also, since neutralization may proceed by the electron–ion recombination and proton-transfer reactions 7 and 8, the observations reported here clearly point toward the possible presence of slightly hydrogenated fulleranes in interstellar and circumstellar gases. These fulleranes may then provide a signatures for the corresponding fullerenes which are being sought spectroscopically in these regions.[10]

$$C_{60}^{\bullet+} + H^{\bullet} \rightarrow C_{60}H^{+} \quad (4)$$

$$C_{60}H^{+} + M \rightarrow MH^{+} + C_{60} \quad (5)$$

$$C_{60}H^{+} + e \rightarrow C_{60} + H^{\bullet} \quad (6)$$

$$C_{60}H_n^{2+} + e\ (M) \rightarrow C_{60}H_{n-x}^{+} + xH\ (MH^{+}) \quad (7)$$

$$C_{60}H_n^{+} + e\ (M) \rightarrow C_{60}H_{n-x} + xH\ (MH^{+}) \quad (8)$$

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A Stable Crystalline (Alkylperoxy)iodinane: 1-(*tert*-Butylperoxy)-1,2-benziodoxol-3(1*H*)-one

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(Alkylperoxy)iodinanes have not been synthesized probably because of their high tendency to decompose.[1] Milas and Plesnicar reported the reaction of iodosylbenzene with *tert*-butyl hydroperoxide in dichloromethane and proposed the in situ generation of [bis(*tert*-butylperoxy)iodo]benzene, which decomposes even at −80 °C to *tert*-butyl peroxy radical and iodobenzene.[2,3] This ready decomposition of the (alkylperoxy)iodinane will be attributed to the small dissociation energy of the apical hypervalent peroxy–iodine(III) bond and be facilitated by conjugative overlap of the breaking hypervalent bond with π-orbitals of the aromatic nucleus.[4] Thus, it appears that fixation of an apical hetero ligand and an equatorial aromatic ligand on iodine(III) by the formation of five-membered heterocycles such as an iodoxolone, which makes

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