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Reactions of $C_{60}^{\bullet+}$, C_{60}^{2+} and $C_{60}^{\bullet3+}$ with C_2H_2 and C_2H_4 in the Gas Phase: Polymerization Initiated by $C_{60}^{\bullet3+}$.

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Abstract: Reactions of the C_{60} cations $C_{60}^{\bullet+}$, C_{60}^{2+} and $C_{60}^{\bullet3+}$ have been investigated with C_2H_2 and C_2H_4 in the gas phase using the Selected-Ion Flow Tube (SIFT) technique at 295±2 K and 0.35±0.02 Torr of helium. Although $C_{60}^{\bullet+}$ was found to be unreactive ($k < 1x10^{-12}$ cm^3 molecule^{-1} s^{-1}), and C_{60}^{2+} reacted only slowly ($k \leq 2x10^{-12}$ cm^3 molecule^{-1} s^{-1}) by adduct formation, $C_{60}^{\bullet3+}$ reacted rapidly with C_2H_2 by adduct formation ($k = 6.6x10^{-11}$ cm^3 molecule^{-1} s^{-1}) and with C_2H_4 by adduct formation (30%) and electron transfer (70%) ($k = 1.7x10^{-9}$ cm^3 molecule^{-1} s^{-1}). $C_{58}^{\bullet3+}$, which was present as an impurity ion, was observed to react 10 times faster than $C_{60}^{\bullet3+}$ with C_2H_2, $k = 6.0x10^{-10}$ cm^3 molecule^{-1} s^{-1} and this was attributed to a greater sp^3 character of the reacting C site. Higher-order addition reactions were observed with $C_{60}^{\bullet3+}$ and $C_{58}^{\bullet3+}$ and these were interpreted as the first example of cation-induced "ball-and-chain" polymerization by triply-charged fullerene cations. Mechanisms have been proposed for this polymerization without and with an intramolecular hydride shift in the derivatized fullerene cation. Also, $C_{60}C_2H_4^{\bullet3+}$ was observed to undergo proton transfer with C_2H_4 and this is the first example of such a reaction with a triply-charged C_{60} derivative.

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