Collision-Induced Dissociation Evidence for Charge Separation and "Ball-and-Chain" Propagation in the Addition of 1-Butene to C_{60}^{2+}

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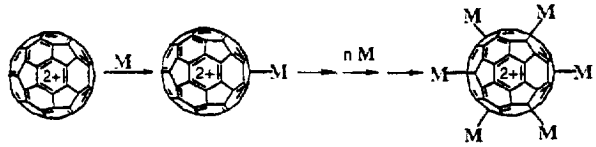
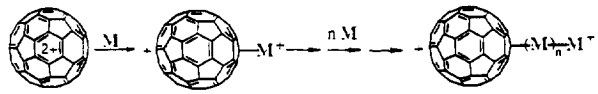
The collision-induced dissociation of the adduct ions $C_{60}(C_4H_8)_2^{2+}$ and $C_{60}(C_4H_8)_3^{2+}$ formed by sequential reactions of C_{60}^{2+} with 1-butene has been investigated by using a selected-ion flow tube (SIFT) apparatus. Experiments at 295 ± 2 K in 0.35 ± 0.02 torr of helium indicated that C_{60}^{2+} adds at least five molecules of 1-butene in a sequential fashion with rates that decrease with the number of molecules added. Collision-induced dissociation experiments in which the downstream sampling nose cone of the SIFT was biased with respect to the flow tube indicated that the adduct ions $C_{60}(C_4H_8)_2^{2+}$ and $C_{60}(C_4H_8)_3^{2+}$ dissociate into $C_{60}^{+\cdot}$ and $(C_4H_8)_2^{+\cdot}$ and $(C_4H_8)_3^{+\cdot}$, respectively. These observations provide evidence for the occurrence of charge separation in the derivatization of C_{60} dications and support the "ball-and-chain" mechanism first proposed by Wang et al. in 1992 for the sequential multiple addition of 1,3-butadiene to C_{60}^{2+} and C_{70}^{2+}. *(J Am Soc Mass Spectrom 1996, 7, 261–265)*

The C_{60} molecule is remarkable in its stability as a multiply charged cation against Coulombic explosion. To date it has been possible to remove up to seven electrons from C_{60} by electron impact in the gas phase [1]. Multiply charged C_{60} cations are derivatized readily by ion–molecule association reactions in the gas phase. The derivatized cations are interesting in the context of multiply charged polyatomic cations generally from the point of view of intramolecular charge separation that may occur in these ions [2]. Previous experimental studies in our Ion Chemistry Laboratory with the selected-ion flow tube (SIFT) technique have identified a number of reactions of multiply charged fullerene cations with unsaturated hydrocarbons that lead to sequential multiple additions. The number of molecules that have been observed to add, the kinetics of their sequential addition, and the occurrence of competing reactions that lead to bimolecular products such as electron transfer all have been found to depend on the nature of the added molecule. This is evident from the results that we have reported previously for the reactions of C_{60}^{2+} and C_{70}^{2+} with 1,3-butadiene [3], of C_{60}^{2+} with ethylene oxide [4], of $C_{58}^{+\cdot 3+}$ and $C_{60}^{+\cdot 3+}$ with acetylene [3], and of $C_{60}^{+\cdot 3+}$ with ethylene (Wang, J.; Javahery, G.; Baranov, V.; Bohme, D. K., *Tetrahedron*, in press). In the interpretation of these results we have considered two types of addition mechanisms: formation of a "fuzzy ball" according to reaction 1,



(1)

and a "ball-and-chain" mechanism [3, 5], as shown in reaction 2:



(2)

In the former mechanism the two charges remain on the C_{60} surface as sequential bonding of the molecules to the C_{60} surface proceeds. In the latter mechanism the initial electrophilic addition leaves one charge on the substituent and subsequent addition leads to further charge separation in the derivatized C_{60} cation driven by intramolecular Coulombic repulsion. As the chain grows, the charge on the substituent will continue to be propagated, and in this way chain growth can be driven by Coulombic repulsion away from the C_{60} surface. Until now we have had no direct evidence for either mechanism, although we have preferred mechanism 2 [3]. Also, we recognized early on that collision-induced dissociation experiments with multiple-adduct ions would be required to distinguish between the two possible mechanisms: collision-induced dissociation of the "fuzzy ball" should lead to the detachment of individual molecules, whereas

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