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Fullerene Dications as Initiators of Polymerization with 1,3-Butadiene in the Gas Phase: Chemistry Directed by Electrostatics?

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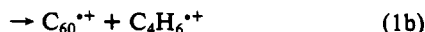
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One of the many emerging frontiers in fullerene chemistry is in the field of polymer chemistry. This is evidenced, for example, by the recent report of the synthesis of the first copolymer containing C_{60} , based on the reaction of the xylylene diradical with C_{60} dissolved in toluene.¹ We report here results of experiments which indicate that the dications of C_{60} and C_{70} may initiate the polymerization of the conventional polymerization monomer 1,3-butadiene in the gas phase. The results suggest a potential role for fullerene dications generally as initiators of polymerization. A novel feature of the proposed mechanism of this polymerization is the role which Coulombic repulsion between the two positive charges may play in driving the direction of polymerization.

Reactions of C_{60}^{2+} , C_{70}^{2+} , C_{60}^{2+} , and C_{70}^{2+} with 1,3-butadiene were monitored with a selected-ion flow tube (SIFT) apparatus.^{2,3} The fullerene cations were produced by electron bombardment (at 50 eV) of C_{60} and C_{70} vapor entrained in argon carrier gas. They were selected with a quadrupole mass filter, injected into helium buffer gas at 295 ± 2 K and 0.40 ± 0.01 Torr, allowed to thermalize by collisions with helium atoms, and finally exposed to 1,3-butadiene further downstream. The progress of the reactions was followed with a second quadrupole mass filter further downstream in the usual fashion.^{2,3} The 1,3-butadiene had a purity of $\geq 99.0\%$ (Matheson, C.P. grade). The fullerene powder was a mixture of C_{60} and C_{70} containing 2-12% C_{70} (Strem Chemicals Co.).

While C_{60}^{2+} and C_{70}^{2+} were found to be unreactive toward 1,3-butadiene, both C_{60}^{2+} and C_{70}^{2+} were observed to react rapidly with 1,3-butadiene with rate coefficients both equal to $(1.0 \pm 0.3) \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, corresponding to nearly unit reaction efficiency (see Table I). Two primary product channels, charge-transfer and adduct formation, were identified, and these are elucidated in reaction 1 for C_{60}^{2+} . The observed variations



of individual ion signals are shown in Figure 1. The branching ratio for adduct formation (1a) to charge transfer (1b) was found to be 4:1 for C_{60}^{2+} and $>1:1$ for C_{70}^{2+} at the operating conditions of the experiments.

The best current value for the ionization energy of C_{60}^{2+} , $11.39 \pm 0.05 \text{ eV}$,^{4,5} makes charge transfer to 1,3-butadiene, which has an ionization energy of 9.07 eV ,⁶ exothermic by 2.32 eV . This

Table I. Kinetic Data for Reactions of $\text{C}_{60}/\text{C}_{70}$ Cations with 1,3-Butadiene at 294 ± 2 K in Helium Buffer Gas at a Pressure of 0.40 ± 0.01 Torr

reactions	BR ^a	k_{obsd}^b	k_c^c
$\text{C}_{60}^{2+} + \text{C}_4\text{H}_6 \rightarrow$ none		<0.001	0.97
$\text{C}_{70}^{2+} + \text{C}_4\text{H}_6 \rightarrow$ none		<0.001	0.97
$\text{C}_{60}^{2+} + \text{C}_4\text{H}_6 \rightarrow \text{C}_{60}\text{C}_4\text{H}_6^{2+}$	0.8	1.0	1.94
$\rightarrow \text{C}_{60}^{2+} + \text{C}_4\text{H}_6^{+}$	0.2		
$\text{C}_{70}^{2+} + \text{C}_4\text{H}_6 \rightarrow \text{C}_{70}\text{C}_4\text{H}_6^{2+}$	>0.5	1.0	1.93
$\rightarrow \text{C}_{70}^{2+} + \text{C}_4\text{H}_6^{+}$	<0.5		

^a Branching ratio with an uncertainty of about $\pm 30\%$. ^b Apparent bimolecular rate coefficient in units of $10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ with an uncertainty of about $\pm 30\%$. ^c Theoretical collision rate coefficient in units of $10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ based on the ADO model of Su, T.; Bowers, M. T. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 1, Chapter 3, pp 83-118.

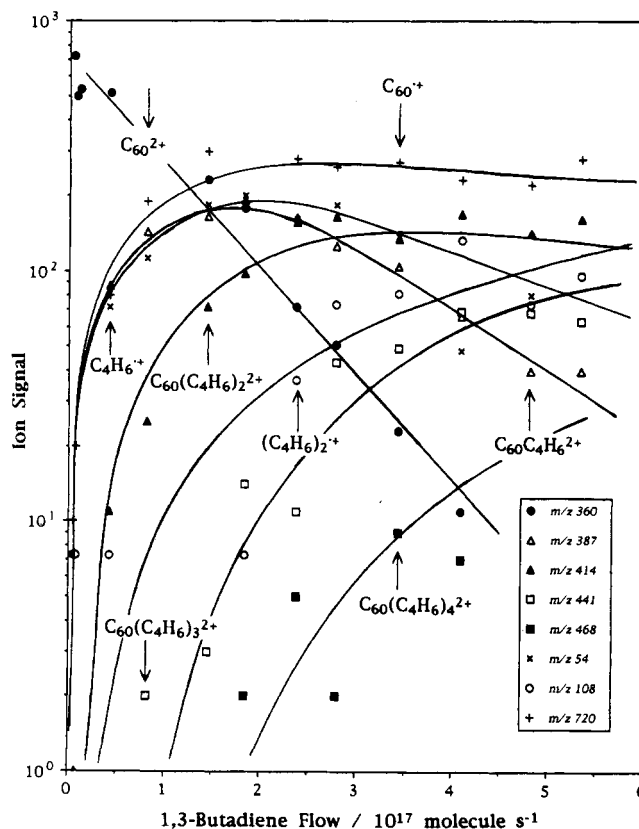
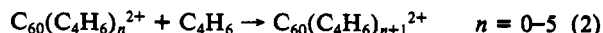


Figure 1. Observed variation in ion signals with the addition of 1,3-butadiene into the reaction region of the SIFT apparatus in which C_{60}^{2+} has been established as the dominant ion in helium buffer gas: $P = 0.40$ Torr, $\bar{v} = 6.9 \times 10^3 \text{ cm s}^{-1}$, nominal reaction length = 47 cm , and $T = 294 \text{ K}$. C_{60}^{2+} is produced by electron impact at 50 eV on C_{60} vapor entrained in argon carrier gas.

exceeds the 2.06 eV which can be computed for the maximum height of the energy barrier to charge transfer which arises from Coulombic repulsion,⁷ so that the occurrence of some charge transfer is not surprising. Formation of the adduct presumably arises from collisional stabilization by helium atoms prior to dissociation to C_{60}^{2+} and C_4H_6^{+} .

Figure 1 displays the observation of the occurrence of rapid sequential addition reactions which attach up to six molecules of butadiene to C_{60}^{2+} :



The butadiene radical cation produced in reaction 1b reacts with butadiene to form the dimer ion $(\text{C}_4\text{H}_6)_2^{+}$. The trimer of bu-

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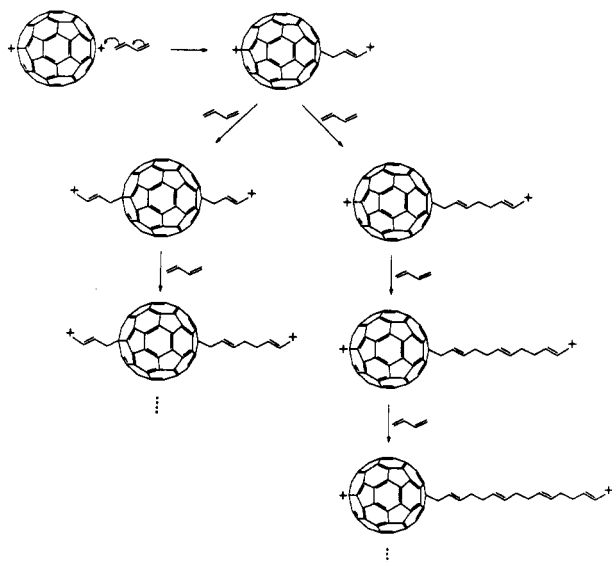


Figure 2. Proposed mechanism for the polymerization of 1,3-butadiene initiated by C₆₀²⁺.

tadiene was also observed, but its formation proceeded at a much slower rate. The formation of the dimer ion has been noted previously in an ICR study, and collision-activated decomposition experiments with a tandem mass spectrometer have indicated that an acyclic branched chain structure is preferred at high pressures.⁸ We have also observed that C₇₀²⁺ reacts with C₄H₆ in a manner which is analogous to that of C₆₀²⁺. This is not surprising given the structural similarity of C₆₀²⁺ and C₇₀²⁺. However, because of lower ion signals (C₇₀ constitutes only a small portion (2–12%) of the fullerene mixture used in the ion source), association products of C₇₀²⁺ with C₄H₆ were observed only up to C₇₀-(C₄H₆)₃²⁺.

With regard to the mechanism of reaction 2, we propose that the initiation step involves addition of butadiene to C₆₀²⁺ by C–C covalent bond formation with the concomitant propagation of one of the two positive charges on the fullerene cage to a distance of four carbon atoms away from the fullerene surface to the terminal carbon of butadiene. Although this appears counterintuitive because a charge becomes less delocalized, via delocalization energy is lost, the energy gained by the Coulombic repulsion between the two positive charges should favor the bond formation described. The Coulombic repulsion between the two positive charges will be relaxed further as more butadiene monomers are added. Two ways in which a polymer chain can be propagated, viz. on one side of the cage, in a tadpole-like fashion, or on both the sides, in a spindle-like fashion, are shown in Figure 2. Sequential addition by direct bonding to the π -system of the fullerene cage cannot be ruled out, but appears less favorable since it does not involve Coulombic relaxation and since we have found that C₆₀²⁺ does not react with 1,3-butadiene. It appears, therefore, that the fullerene cage may become a pendant on, or be blocked in, the polybutadiene chain. The electrostatic driving force, which should be critical in determining the direction of propagation, can be expected to decrease sharply with the number of molecules added since the Coulombic potential varies inversely with the distance of charge separation. This may account for the gradual decrease in the rate of the sequential addition of butadiene which was observed.

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Registry No. C₆₀ fullerene dication, 120329-57-9; C₇₀ fullerene dication, 133869-47-3; 1,3-butadiene, 106-99-0; C₆₀ fullerene cation radical, 108739-25-9; C₇₀ fullerene cation radical, 134932-61-9.

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A Mononuclear Nickel(II) Complex with [NiN₃S₂] Chromophore That Readily Affords the Ni(I) and Ni(III) Analogues: Probe into the Redox Behavior of the Nickel Site in [FeNi] Hydrogenases

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Hydrogenases (H₂ase), the enzymes that catalyze the reversible oxidation of hydrogen,^{1–5} are broadly divided into Fe-only and [FeNi] H₂ases, depending on their metal contents. Most of the [FeNi] H₂ases in their as-isolated forms display rhombic EPR signals (termed as Ni-A, $g = 2.31, 2.23, 2.02$, and Ni-B, $g = 2.33, 2.16, 2.02$).^{1–3} Upon reduction, these signals disappear and further reduction affords a new rhombic signal (Ni-C, $g = 2.19, 2.14, 2.02$). These three signals (Ni-A, Ni-B, and Ni-C) are believed to be associated with the “unready”, “ready”, and “catalytically active” states of the enzymes, respectively. Several attempts have been made to establish the oxidation states of the nickel center at the active site of the enzyme during the catalytic cycle.^{1,6–8} To date, two working mechanisms have been proposed on the basis of physicochemical studies. One mechanism supports the existence of Ni(III) in all three stages of the deactivation/activation processes.^{1c,f,6} Quite in contrast, the other mechanism involves Ni(III) (Ni-A/Ni-B), Ni(II) (EPR silent), and Ni(I) (Ni-C) in the processes of H₂ utilization/evolution.^{1a,2a,b,7,8} Rapid binding of H[–] (substrate) and CO (an inhibitor) to the reduced form of the enzyme and the photoactivity of the substrate-bound species support this mechanism.⁷

In our synthetic analogue approach to the biological nickel site of [FeNi] H₂ase, we have isolated and structurally characterized

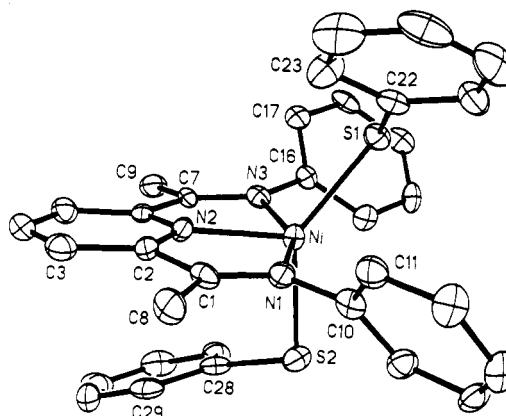


Figure 1. Thermal ellipsoid plot (50% probability level) of 1. Hydrogen atoms are omitted for clarity. Selected bond distances (in Å): Ni–S(1), 2.263 (2); Ni–S(2), 2.351 (2); Ni–N(1), 2.110 (7); Ni–N(2), 1.936 (5); Ni–N(3), 2.131 (6); C(1)–N(1), 1.293 (9); N(3)–C(7), 1.317 (8); S(1)–C(22), 1.768 (8); N(1)–C(10), 1.431 (10). Selected bond angles (in deg): S(1)–Ni–S(2), 138.2 (1); N(1)–Ni–N(2), 78.3 (2); N(2)–Ni–N(3), 78.1 (2); N(1)–Ni–N(3), 156.4 (2); Ni–S(1)–C(22), 111.2 (2); Ni–S(2)–C(28), 105.3 (2); N(1)–Ni–S(2), 92.5 (1); S(1)–Ni–N(3), 90.5 (1); C(1)–C(2)–N(2), 114.6 (6).