Fullerene Dications as Initiators for Gas-Phase "Ball-and-Chain" Polymerization of Ethylene Oxide; Termination by Cyclization**

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Multiply charged cations of buckminsterfullerene, C_{60}^{n+}, are remarkably stable, easily generated (up to at least $n = 3$), and readily subjected to chemical reaction in the gas phase.[1] This control over the number of charges on a molecule is unique and provides an unprecedented opportunity for exploring the role of charge in directing intramolecular reactions. For example, Coulombic repulsion between two positive charges has been postulated to drive the "ball-and-chain" polymerization of 1,3-butadiene initiated by C_{60}^{2+} away from the surface of C_{60} into the surrounding space.[2, 3] An almost exponential decrease in the rate of polymerization is observed at 294 ± 2 K in helium at 0.40 ± 0.01 Torr for the proposed sequential addition leading to a chain of six units of 1,3-butadiene.[2] We report here on a second possible feature of such polymerization: termination by cyclization at chain lengths at which Coulombic repulsion is weaker than chemical forces. We have chosen to investigate this possibility experimentally with the C_{60}^{2+}-initiated polymerization of ethylene oxide which, unlike butadiene, has a strong tendency for cyclization.

Figure 1 displays the remarkable observation that a series of rapid sequential addition reactions attach up to six molecules of ethylene oxide to C_{60}^{2+} in helium buffer gas at 0.35 Torr and 294 K [Eq. (a)]. The initiation reaction of C_{60}^{2+} with ethylene

$$C_{60}(C_2H_4O)_n^{2+} + C_2H_4O \longrightarrow C_{60}(C_2H_4O)_{n+1}^{2+} \quad n = 0-5 \qquad (a)$$

oxide proceeds relatively slowly with a rate constant of $(5.3 \pm 1.6) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, which corresponds to a reaction efficiency of 0.019.[4] The subsequent oligomerization reactions are characterized by larger rate coefficients: we estimate the second step to be more than ten times faster than the first step, and the rate constants drop by a factor of 2 to 3 with each successive step (in the reaction of C_{60}^{2+} with butadiene the rate constants drop by a factor of 3 to 4). Also, more significantly and unlike the case of 1,3-butadiene, the observed rate of addition of ethylene oxide shows a sharp drop at $n = 5$ by about a factor of 10. In contrast to the dication, the monocation of C_{60} did not react with ethylene oxide with a measurable specific rate ($k \leq 3 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}).

The slow first step, which is presumed to proceed in a termolecular fashion by collisional stabilization (He is the stabilizing third body) under our experimental conditions, is not atypical: we have found other oxygen-containing compounds to add slowly to C_{60}^{2+} under similar conditions. In analogy to these reactions we expect the first step to be nucleophilic addition leading to the formation of a product **I** in which the charge is formally localized on the oxygen atom.[1d] This addition is accompanied by a loss in charge delocalization energy of the C_{60}^{2+}, which will act to disfavor association, as will the accompanying distortion at the C_{60} bonding site, which is required for tetrahedral coordination with the nucleophile.[6] If the excess energy associated with C–O bond formation is sufficiently large, we can expect subsequent ring opening and a hydride shift to generate structure **II**.[7]

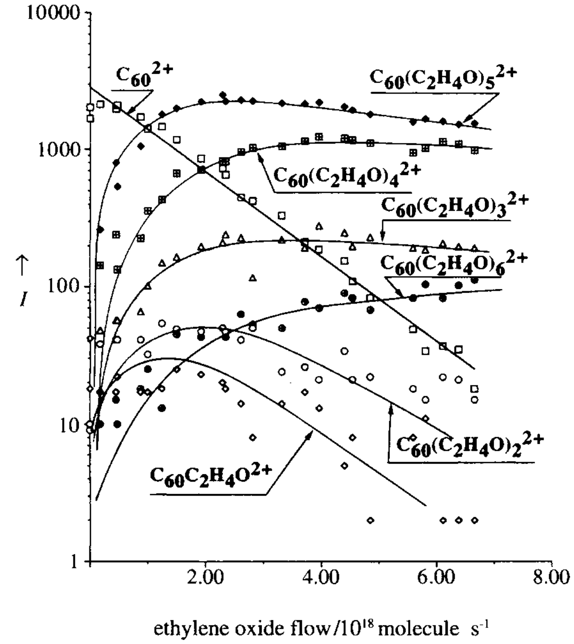
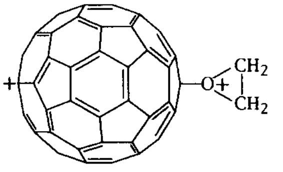
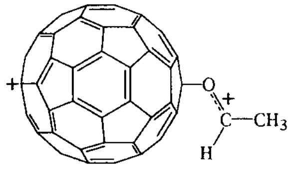


Fig. 1. Variation in the ion signals I upon addition of ethylene oxide into the reaction region of the SIFT apparatus in which C_{60}^{2+} has been established as the dominant ion in helium buffer gas. $p = 0.35$ Torr, $\bar{v} = 6.4 \times 10^3$ cm s^{-1}, $L = 47$ cm, and $T = 294$ K. C_{60}^{2+} is produced by electron impact at 60 eV of C_{60} vapor entrained in argon carrier gas. Signal intensities for the first three adducts $C_{60}(C_2H_4O)_n^{2+}$ ($n = 1, 2, 3$) at low ethylene oxide flows, suggest that the rate constants for reaction of these adducts substantially exceed that for reaction of "bare" C_{60}^{2+}. However, the signal intensities observed for these adducts at high flows ($\geq 4 \times 10^{18}$ molecules^{-1}) are substantially higher than would be expected if these adducts reacted rapidly with ethylene oxide. This apparent discrepancy suggests that higher order adducts may undergo chemical or thermal dissociation. Alternatively, fragmentation may be induced by the electric field gradient in the vicinity of the product ion sampling nosecone, or different isomeric forms of the adducts may be present, some of which react rapidly while others remain essentially unreacted. A detailed kinetic model would require a better understanding of these factors.



I



II

Addition of the second molecule of ethylene oxide can now occur at a site with a localized charge without a distortion requirement, which is more favorable than addition at the site of the remaining charge on the C_{60} surface (recall also that C_{60}^{+} is unreactive).[9] This would explain the considerably higher rate of addition of the second, third, and fourth molecules of ethylene oxide leading either to the propagation of a chain as indicated in structure **III** (for addition to structure **I**)[10] or as indicated in structure **IV** (for addition to structure **II**).

Coulombic repulsion between the propagated charge and the remaining charge on the surface of C_{60} will tend to drive the

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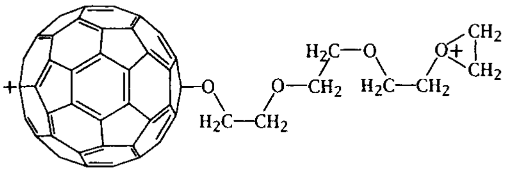
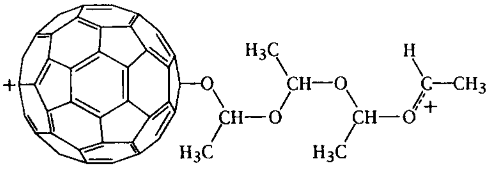
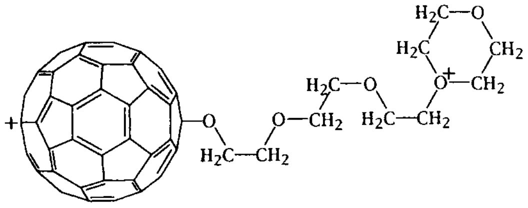


III

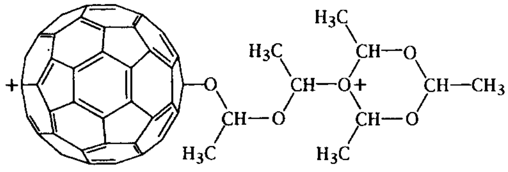


IV

molecular growth away from the surface in a similar fashion to that envisaged for the C_{60}^{2+}-induced polymerization observed with 1,3-butadiene; however, ethylene oxide oligomers should show an increasing tendency for unimolecular cyclization to form a relatively stable six-membered ring at the end of the chain as Coulombic repulsion weakens with increasing charge separation. Structures **V** and **VI** show the products of this cyclization which would inhibit further chain propagation.



V



VI

The observed discontinuity in the addition rate between the fifth and sixth addition is consistent with such a mechanism. However, while the data indicates that most chains do not contain more than five ethylene oxide units, some have six units, and termination after four and perhaps even three additions is probable also. Moreover we cannot rule out cyclization beyond dimers and trimers, to form larger rings, and the dissociation to form cyclic oligomers.

The mechanism of cationic cyclooligomerization of ethylene oxide with BF_3 in CH_2Cl_2 has been investigated in detail by Dale and Daasvatn.[11] These authors have demonstrated the requirement of a minimum chain length for direct cyclization (in the absence of Coulombic repulsion), the termination of the growing chain by direct cyclization beyond dimers and trimers, the competition between formation of a cyclic trimer and dimer, and the possible expulsion of cyclic oligomers. We are currently investigating the chemistry of C_{60}^{n+} with other small epoxides.

Experimental Procedure

The reaction of C_{60}^{2+} with ethylene oxide was monitored with a Selected-Ion Flow Tube (SIFT) apparatus [12, 13]. C_{60}^{2+} was produced by the electron bombardment of 60 eV of C_{60} vapor entrained in argon carrier gas. The dications were selected with a quadrupole mass filter, injected into a flowing helium gas at 295 ± 2 K and 0.35 ± 0.01 Torr, allowed to reach thermal equilibrium by collisions with helium atoms, and finally exposed to ethylene oxide further downstream. The progress of the reactions was followed with a second quadrupole mass filter in the usual fashion [12, 13]. The ethylene oxide had a purity of ≥99.0% (Matheson). The fullerene powder was a mixture of C_{60} and 2–12% C_{70} (Strem Chemicals).

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[4] The reaction efficiency is taken to be equal to the ratio of the measured reaction rate constant to the calculated collision rate constant. The collision rate constant was calculated according to the Average Dipole Orientation (ADO) theory [5].

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[7] It is interesting to note that acetaldehyde, which might be expected to form the secondary carbocation adduct **II** directly, was observed not to add to C_{60}^{2+} with a measurable rate ($k < 1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}) [8].

[8] S. Petrie, G. Javahery, H. Wincel, J. Wang, D. K. Bohme, *Int. J. Mass Spectrom. Ion Processes* **1993**, submitted.

[9] The observed 10-fold increase in the rate of addition of the second ethylene oxide molecule compared to the first suggests very strongly that the first addition activates the dication in some manner. The first addition most likely generates an activated site because the C_{60} substituent carries a localized charge. Previous experiments in our laboratory have shown that sequential addition to the surface of the C_{60} (to form a double-handled adduct) is characterized by essentially identical rates for the first and second addition steps [1].

[10] Addition in this manner is considered to involve concomitant ring opening of the ethylene oxide monomer previously added.

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$[(Ph_3PAu)_6(dppeAu_2)(AuCl)_4Pd]$, an Icosahedral Au_{12} Cluster with a Central Pd Atom**

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The photolysis of $[Ph_3PAuN_3]$ leads to the formation of homometallic gold clusters by reductive elimination of the azide group.[1, 2] The heterodimetal clusters $[(Ph_3PAu)_xM(CO)_y]^{n+}$ (n = 0,1,2) are formed in the presence of metal carbonyls. The composition of the cluster is governed by the electron requirements of the transition metal M, that tries to achieve a stable noble-gas electron configuration. This simple approach to the synthesis of new clusters, encouraged us to carry out the photolytic reaction on other azide complexes. Although the photol-

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