

# Isomer-Specific Trends with Charge State in Gas-Phase Reactions of Fullerene Cations, $C_{60}^{x+}$ ( $x = 1-3$ ), with Nitromethane and Methyl Nitrite: Polymethoxylation of $C_{60}$ Dications

Vladimir Baranov, Alan C. Hopkinson, and Diethard K. Bohme\*

Contribution from the Department of Chemistry and Centre for Research in Earth and Space Science, York University, North York, Ontario, Canada M3J 1P3

Received July 22, 1996<sup>⊗</sup>

**Abstract:** Rate coefficients and product distributions have been measured for the gas-phase reactions of  $C_{60}^{+}$ ,  $C_{60}^{2+}$ , and  $C_{60}^{3+}$  with nitromethane and methyl nitrite which show a strong dependence of reactivity on the charge state of the fullerene cation and on the nature of the neutral reactant isomer. Furthermore, sequential bimolecular methoxy-radical transfer reactions were observed with methyl nitrite leading to the polymethoxylation of  $C_{60}^{2+}$  with up to 12 methoxy groups, far more than the number of charges on the  $C_{60}$  surface. Unusual periodicities were seen in the reaction kinetics, and these are correlated with the radical and aromatic character of the derivatized  $C_{60}(OCH_3)_n^{2+}$  cations. The measurements were performed in helium buffer gas at  $0.35 \pm 0.01$  Torr and  $294 \pm 3$  K with use of the Selected-Ion Flow Tube (SIFT) technique. Multicollision induced dissociation experiments with the derivatized  $C_{60}(OCH_3)_n^{2+}$  ( $n = 1-4$ ) cations indicated sequential loss of single methoxy radicals, which is consistent with direct bonding of the methoxy groups to the  $C_{60}$  cage. Polymethoxylation was not observed with  $C_{60}^{3+}$ . Instead,  $C_{60}^{3+}$  reacts with methyl nitrite by dissociative electron transfer.  $C_{60}^{2+}$  is unreactive with nitromethane, but  $C_{60}^{3+}$  adds one molecule and the  $C_{60}(CH_3NO_2)^{3+}$  adduct ion reacts further only by proton transfer.  $C_{60}^{+}$  is unreactive with both nitromethane and methyl nitrite.

## Introduction

Since buckminsterfullerene,  $C_{60}$ , first became available in macroscopic quantities in 1990,<sup>1</sup> much exciting progress has been made in the “three-dimensional” derivatization of this molecule in the condensed phase to form new, polyfunctional addition products.<sup>2</sup> Also, singly- and multiply-charged cations of  $C_{60}$  became routinely available in the gas phase in conventional mass-spectrometer ion sources and it became possible to investigate the derivatization of this molecule also as a function of charge state. Systematic experiments in our laboratory have shown that addition reactions of singly- and multiply-charged  $C_{60}^{x+}$  cations occurring in helium bath gas at 0.35 Torr and room temperature show a strong dependence on the charge state of the cation for  $x = 1, 2$ , and  $3$ .<sup>3</sup> Briefly, monocations of  $C_{60}$  have been found to add selectively to only a few molecules. In contrast, a rich addition chemistry was observed with  $C_{60}^{2+}$ , although electron transfer becomes an important competitive reaction channel. With  $C_{60}^{3+}$  this competition often favors

electron transfer or even dissociative electron transfer, but addition is still observed.

The chemistries of  $C_{60}^{x+}$  cations have not yet been characterized in solution, although persistent singly- and multiply-charged cations of  $C_{60}$  have now also been observed in this medium, specifically in super acids.<sup>4,5</sup> Observations of the intrinsic reactivities of these cations in the gas phase in the absence of solvent should provide a useful guide for making progress in this regard.

With the dication  $C_{60}^{2+}$ , we have found that polyfunctionalization by sequential addition often predominates in the gas phase and can lead to “ball-and-chain” propagation away from the surface of  $C_{60}$  driven by Coulombic repulsion.<sup>3a,6</sup> Polyfunctionalization on the  $C_{60}^{x+}$  cage itself is also possible but, so far, has appeared to be limited to additions corresponding to the number of charges on the  $C_{60}^{x+}$  cation,<sup>3</sup> although polyhydrogenation of  $C_{60}^{x+}$  by multiple addition of H atoms has been observed.<sup>7</sup> Here we report the first observation of the multiple derivatization of a fullerene cation with a molecular substituent to an extent far beyond the number of charges on the fullerene surface. This observation was part of a general exploration of the reactivity and polyfunctionalization of  $C_{60}^{x+}$  cations with the isomeric molecules  $CH_3NO_2$  and  $CH_3ONO$  as a function of charge state with  $x = 1, 2$ , and  $3$ . A Selected-Ion Flow Tube/

<sup>⊗</sup> Abstract published in *Advance ACS Abstracts*, July 15, 1997.

(1) Krätschmer, W.; Lamb, L. D.; Fostiropoulis, K.; Huffman, D. R. *Nature* **1990**, *347*, 354.

(2) See, for example: (a) Hirsch, A. *Synthesis* **1995**, *8*, 895. (b) Hirsch, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1138. (c) Taylor, R.; Walton, R. W. *Nature* **1993**, *363*, 685. (d) Wudl, F. *Acc. Chem. Res.* **1992**, *25*, 157.

(3) (a) For a review, see: Bohme, D. K. In *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*; Ruoff, R. S., Kadish, K. M., Eds.; Electrochemical Society Proceedings 95-10; Electrochemical Society, Inc.: Pennington, NJ, 1995; p 1465. (b) Petrie, S.; Javahery, G.; Wang, J.; Bohme, D. K. *J. Am. Chem. Soc.* **1992**, *114*, 9177. (c) Petrie, S.; Javahery, G.; Bohme, D. K. *J. Am. Chem. Soc.* **1993**, *115*, 1445. (d) Javahery, G.; Petrie, S.; Wincel, H.; Wang, J.; Bohme, D. K. *J. Am. Chem. Soc.* **1993**, *115*, 5716. (e) Javahery, G.; Petrie, S.; Wincel, H.; Wang, J.; Bohme, D. K. *J. Am. Chem. Soc.* **1993**, *115*, 6295. (f) Javahery, G.; Petrie, S.; Wang, J.; Wincel, H.; Bohme, D. K. *J. Am. Chem. Soc.* **1993**, *115*, 9701. (g) Petrie, S.; Javahery, G.; Wincel, H.; Wang, J.; Bohme, D. K. *Int. J. Mass Spectrom. Ion. Processes* **1994**, *138*, 187. (h) Petrie, S.; Bohme, D. K. *Can. J. Chem.* **1994**, *72*, 577.

(4) (a) Kukolich, S. G.; Huffman, D. R. *Chem. Phys. Lett.* **1991**, *182*, 263. (b) Thomann, H.; Bernardo, M.; Miller, G. P. *J. Am. Chem. Soc.* **1992**, *114*, 6593.

(5) Miller, G. P.; Hsu, C. S.; Thomann, H.; Chiang, L. Y.; Bernardo, M. *Mater. Res. Soc. Symp. Proc.* **1992**, *247*, 293.

(6) (a) Wang, J.; Javahery, G.; Petrie, S.; Bohme, D. K. *J. Am. Chem. Soc.* **1992**, *114*, 9665. (b) Wang, J.; Javahery, G.; Petrie, S.; Hopkinson, A. C.; Bohme, D. K. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 206. (c) Wang, J.; Baranov, V.; Bohme, D. K. *J. Am. Soc. Mass Spectrom.* **1996**, *7*, 261.

(7) (a) Petrie, S.; Becker, H.; Baranov, V.; Bohme, D. K. *Int. J. Mass Spectrom. Ion Processes* **1995**, *145*, 79. (b) Petrie, S.; Javahery, G.; Wang, J.; Bohme, D. K. *J. Am. Chem. Soc.* **1992**, *114*, 6268.

Collision-Induced Dissociation (SIFT/CID) mass spectrometer, in which the reactions of interest occur in helium carrier gas at  $0.35 \pm 0.01$  Torr and  $294 \pm 3$  K, was used to take the measurements. This apparatus permits the products and the kinetics of both primary and higher-order reactions of the  $C_{60}^{x+}$  cations to be monitored quantitatively. Furthermore, the polyfunctionalized  $C_{60}$  cations may systematically be stripped after their formation by multicollision-induced dissociation (CID). Taken together, the kinetic and CID results provide insight into intrinsic reactive features of the bare and derivatized  $C_{60}^{x+}$  cations as well as into the nature of the polyfunctionalization of the  $C_{60}^{x+}$  cations, viz. whether functionalization occurs on the surface of  $C_{60}$  or in a "ball-and-chain" fashion. Insight into the former is provided by trends or the occurrence of unusual periodicities in the magnitudes of the rate coefficients for sequential addition. Insight into the bond connectivities of the polyfunctionalized  $C_{60}^{x+}$  cations is provided by the dependence of the collision-induced dissociation spectrum on collision energy.

The isomeric molecules  $CH_3NO_2$  and  $CH_3ONO$  were chosen as neutral reagents, in part to explore the influence of bond connectivities on chemical reactivity. It will be seen that the observed buckminsterfullerene ion chemistry with these two isomers is very much isomer specific.

## Experimental Section

The SIFT apparatus and SIFT-CID techniques have been described previously.<sup>8,9</sup>  $C_{60}^{x+}$  cations were produced in an ion source by electron impact ionization ( $\sim 50$  V for  $C_{60}^{+}$ , 70 V for  $C_{60}^{2+}$ , 100 V for  $C_{60}^{3+}$ ) of fullerene vapor. The fullerene sample used ( $\sim 90\%$   $C_{60}$ ,  $\sim 9\%$   $C_{70}$ ) was obtained from Termusa Inc. and was introduced into the ion source without further purification. After being selected with a quadrupole mass filter and injected into the flow tube, the  $C_{60}^{x+}$  ions were allowed to thermalize by collisions (ca.  $4 \times 10^5$  collisions) with the He buffer gas atoms prior to entering the reaction region. Nitromethane (Spectranalyzed Grade, Fisher Scientific Co.) and deuterated nitromethane-*d*<sub>3</sub> (99% D, Stohler Isotope Chemicals) were admitted into the flow tube as vapors diluted with helium. Methyl nitrite was synthesized by using the method developed by Slater<sup>10</sup> and added as a pure gas. Reaction products were analyzed with a second quadrupole mass filter downstream. The rate coefficients for primary reactions reported here are estimated to have an uncertainty of  $\pm 30\%$ . Higher-order rate coefficients were obtained by fitting the experimental data to the solutions of the system of differential equations for successive forward reactions. The accuracy of this fitting procedure depends on the stability, and uncertainties in the magnitude, of the ion signals. Reverse reactions have been assumed to be negligible. Also, the standard error in the rate coefficient is propagated to higher-order rate coefficients because they appear in the exponent of exponential terms in the solutions of the differential rate equations. The estimated uncertainty is reported separately for each calculated high-order rate coefficient.

The multicollision-induced dissociation (CID) of sampled ions was investigated by raising the potential of the sampling nose cone to  $-80$  V and taking care not to introduce mass discrimination as the potential of the nose cone is varied. This technique was developed in our laboratory primarily for the qualitative determination of bond connectivities and is described in detail elsewhere.<sup>9</sup>

## Results and Discussion

Table 1 provides a summary of the rate coefficients and product distributions measured for the primary and higher-order

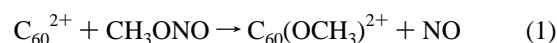
**Table 1.** Rate Coefficients (in units of  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) and Product Channels Measured for Reactions of  $C_{60}^{x+}$  Cations with Nitromethane and Methyl Nitrite in Helium Buffer Gas at  $0.35 \pm 0.01$  Torr and  $294 \pm 3$  K with Use of the SIFT Technique

reaction	rate coefficient
$C_{60}^{+} + CH_3NO_2 \rightarrow \text{products}$	$< 5 \times 10^{-14}$
$C_{60}^{+} + CH_3ONO \rightarrow \text{products}$	$< 5 \times 10^{-14}$
$C_{60}^{2+} + CH_3NO_2 \rightarrow \text{products}$	$< 5 \times 10^{-14}$
$C_{60}^{2+} + CH_3ONO \rightarrow C_{60}(\text{OCH}_3)^{2+} + \text{NO}$	$(5.8 \pm 1.7) \times 10^{-11}$
$C_{60}(\text{OCH}_3)_n^{2+} + CH_3ONO \rightarrow C_{60}(\text{OCH}_3)_{n+1}^{2+} + \text{NO}$	
$n = 1$	$(3.1 \pm 1.2) \times 10^{-10}$
$n = 2$	$(5.2 \pm 2.6) \times 10^{-11}$
$n = 3$	$(3.5 \pm 1.8) \times 10^{-10}$
$n = 4$	$(2.0 \pm 1.5) \times 10^{-11}$
$C_{60}^{3+} + CH_3NO_2 \rightarrow C_{60}(\text{CH}_3\text{NO}_2)^{3+}$	$(3.8 \pm 1.1) \times 10^{-9}$
$C_{60}^{3+} + CH_3ONO \rightarrow C_{60}^{2+} + \text{NO}^+ + \text{CH}_3\text{O}^*$	$(3.0 \pm 0.9) \times 10^{-9}$

reactions of  $C_{60}^{+}$ ,  $C_{60}^{2+}$  and  $C_{60}^{3+}$  with nitromethane and methyl nitrite which were observed in this study.

**Reactions of  $C_{60}^{+}$ .** The monocation  $C_{60}^{+}$  was observed not to react with either nitromethane or methyl nitrite,  $k < 5 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . This is in keeping with our previous observations with other molecules which indicate that  $C_{60}^{+}$  is generally unreactive under our SIFT conditions.<sup>3a</sup> Neither electron transfer nor covalent bond formation is observed. Electron transfer is endothermic since the recombination energy of  $C_{60}^{+}$ ,  $\text{RE}(C_{60}^{+}) = 7.64 \pm 0.02 \text{ eV}$ ,<sup>11</sup> is considerably smaller than the ionization energy of either nitromethane,  $\text{IE}(\text{CH}_3\text{NO}_2) = 11.02 \pm 0.04 \text{ eV}$ ,<sup>12</sup> or methyl nitrite,  $\text{IE}(\text{CH}_3\text{ONO}) = 10.38 \pm 0.03 \text{ eV}$ ,<sup>12</sup> and so is not expected to occur. We have previously attributed the failure to observe the derivatization of  $C_{60}^{+}$  with other molecules to an energy barrier between the electrostatically-bound collision complex and the covalently-bound adduct that arises as a consequence of the transformation from largely  $sp^2$  hybridization to  $sp^3$  hybridization which is required at the C atom on the  $C_{60}$  surface which is derivatized.<sup>3b</sup>

**Reactions of  $C_{60}^{2+}$ .** The dication  $C_{60}^{2+}$  was observed not to react with nitromethane,  $k < 5 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . This is in sharp contrast to the moderately fast methoxy-addition reaction observed with the methyl nitrite isomer, reaction 1, for which a rate coefficient of  $(5.8 \pm 1.7) \times 10^{-11} \text{ cm}^3$



$\text{molecule}^{-1} \text{ s}^{-1}$  was measured. Again, electron transfer was not observed with either molecule although in this case it is exothermic by 0.34 and 0.98 eV with nitromethane and methyl nitrite, respectively, since  $\text{RE}(C_{60}^{2+}) = 11.36 \pm 0.05 \text{ eV}$ .<sup>13</sup> However, we have shown previously that the failure of electron transfer in reactions of this kind can be attributed to an energy barrier arising from Coulombic repulsion between the two singly-charged product ions.<sup>14</sup> The failure of a methoxy-addition reaction analogous to reaction 1 with  $CH_3NO_2$  is more intriguing since the overall change in standard enthalpy of reaction 1 should be similar for the two isomers since the standard enthalpy of formation of  $\text{CH}_3\text{O}^+ + \text{NO}^+$  from  $\text{CH}_3\text{ONO}$  and  $\text{CH}_3\text{NO}_2$  is 41 and 43  $\text{kcal mol}^{-1}$ ,<sup>12</sup> respectively. We propose here that the failure to observe derivatization with nitromethane can be understood in terms of a high barrier to methyl migration required with this molecule.

(11) Lichtenberger, D. L.; Rempe, M. E.; Gogosha, S. B. *Chem. Phys. Lett.* **1992**, *198*, 454.

(12) Lias, S. G.; Liebman, J. E.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *365*, Suppl. 1.

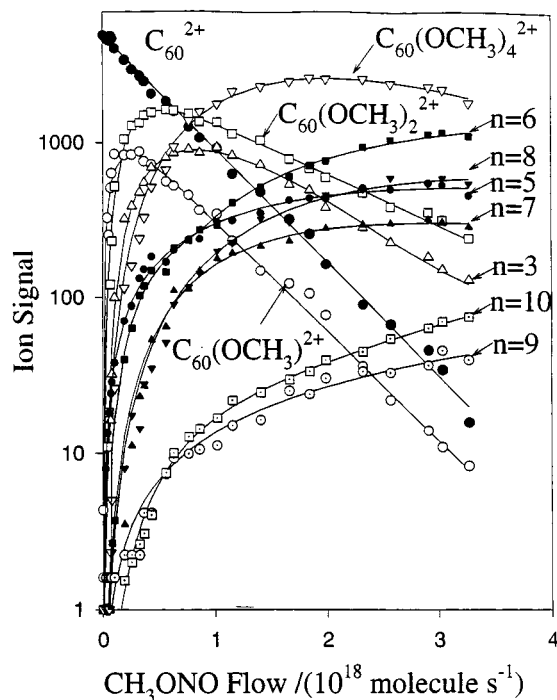
(13) Bohme, D. K. *Int. Rev. Phys. Chem.* **1994**, *13*, 163.

(14) Petrie, S.; Wang, J.; Bohme, D. K. *Chem. Phys. Lett.* **1993**, *204*, 473.

(8) (a) Mackay, G. I.; Vlachos, G. D.; Bohme, D. K.; Schiff, H. I. *Int. J. Mass Spectrom. Ion Phys.* **1980**, *36*, 259. (b) Raksit, A. B.; Bohme, D. K. *Int. J. Mass Spectrom. Ion Processes* **1983/84**, *55*, 69.

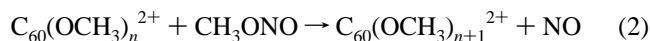
(9) Baranov, V.; Bohme, D. K. *Int. J. Mass Spectrom. Ion Processes* **1996**, *154*, 71.

(10) Slater, W. K. *J. Chem. Soc.* **1920**, *117*, 587.



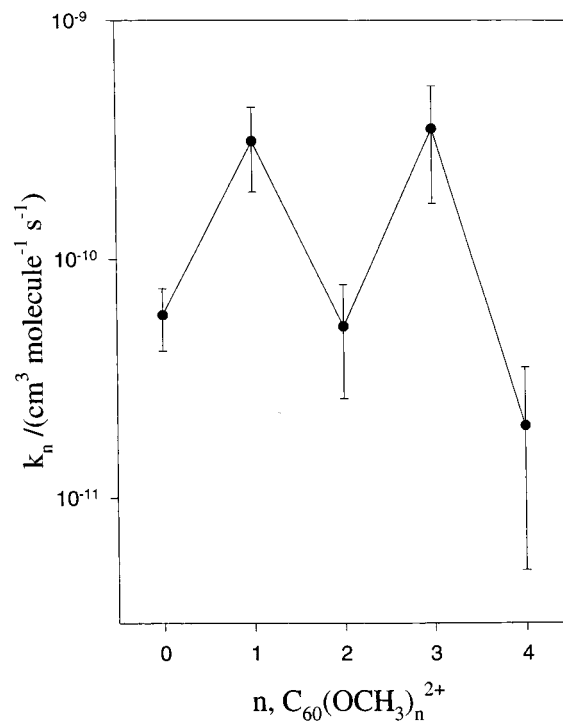
**Figure 1.** Experimental data for the chemistry initiated by the reaction of  $C_{60}^{2+}$  with methyl nitrite. The  $C_{60}^{2+}$  was produced in a low-pressure ion source by electron impact at 70 eV with  $C_{60}$  vapor derived from a fullerene powder. The methyl nitrite was admitted to the flow tube as a pure gas. The measurements were made at  $294 \pm 2$  K in helium buffer gas at a total pressure of  $0.35 \pm 0.01$  Torr. The variations in the adduct ion signals for  $C_{60}(OCH_3)_n^{2+}$  with  $n = 1$  to 4 are fitted with the solutions of the system of differential equations appropriate for the observed sequential reactions. All other lines are drawn for clarity.

Up to twelve methoxy radicals added sequentially to  $C_{60}^{2+}$  according to reaction 2, leading to the polymethoxylation of

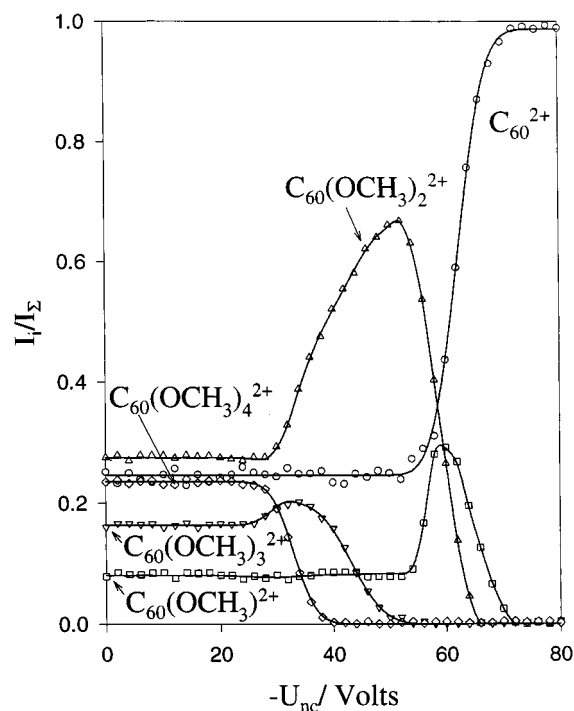


$C_{60}^{2+}$ . Ten additions are apparent in the kinetic data shown in Figure 1. Small signals corresponding to the next two adducts were also seen in the mass spectrum but were not monitored as a function of reactant flow. The rate coefficients determined for the first five steps clearly exhibit an alternation in magnitude (see Figure 2):  $k_0 = (5.8 \pm 1.7) \times 10^{-11}$ ,  $k_1 = (3.1 \pm 1.2) \times 10^{-10}$ ,  $k_2 = (5.2 \pm 2.6) \times 10^{-11}$ ,  $k_3 = (3.5 \pm 1.8) \times 10^{-10}$ , and  $k_4 = (2.0 \pm 1.5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . This observed periodicity should provide a clue regarding the intrinsic reactive features of the derivatized  $C_{60}(OCH_3)_n^{2+}$  cations (vide infra). We note here that the polymethoxylation of neutral  $C_{60}$  with up to 26 methoxy groups has been achieved previously in solution by treating a polychlorofullerene mixture with methanol/KOH.<sup>15</sup>

**Structures of  $C_{60}(OCH_3)_n^{2+}$ .** Figure 3 shows the CID spectrum for the methoxy adducts up to the fourth,  $C_{60}(OCH_3)_4^{2+}$ , taken at a  $CH_3ONO$  flow of  $7.7 \times 10^{17} \text{ molecule s}^{-1}$ . It is clear from this spectrum that the methoxy groups are removed one by one with increasing collision energy. This result is consistent with a "fuzzy-ball" structure involving direct bonding of the methoxy groups to the carbon atoms of the carbon cage of  $C_{60}$ . The observed order of dissociation thresholds in the laboratory frame,  $DT(n = 1) > DT(n = 2) > DT(n = 3) > DT(n = 4)$ , is more difficult to interpret quantitatively as it is determined not only by relative bond-dissociation energies but



**Figure 2.** Alternation in the rate coefficient observed for the sequential addition of methoxy groups in the reaction of  $C_{60}(OCH_3)_n^{2+}$  with  $CH_3ONO$  at  $294 \pm 2$  K in helium buffer gas at a total pressure of  $0.35 \pm 0.01$  Torr (see Figure 1).

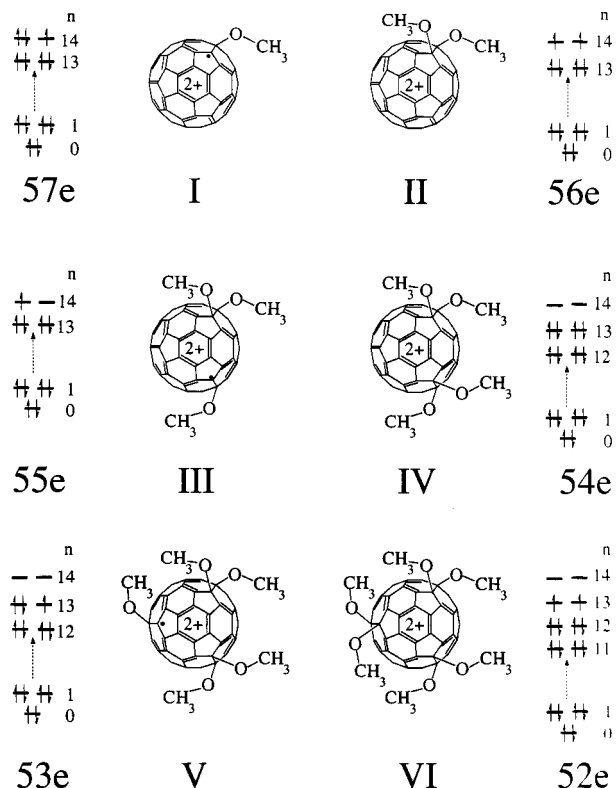


**Figure 3.** CID spectrum recorded for the polymethoxylated  $C_{60}(OCH_3)_n^{2+}$  cations with  $n = 1-4$  at a total pressure of argon (10%)–helium buffer/collision gas of  $0.35 \pm 0.01$  Torr and a flow of methyl nitrite of  $7.7 \times 10^{17} \text{ molecules s}^{-1}$ .

also by the efficiencies of intermolecular and intramolecular energy transfer which are influenced both by the size and by the degrees of freedom of the methoxylated cations.<sup>9</sup> The observation of reaction 2 at room temperature implies that  $D((OCH_3)_n C_{60} - OCH_3^{2+}) > D(CH_3O^* - NO^*) = 41 \text{ kcal mol}^{-1}$  (calculated from known standard enthalpies of formation).<sup>12</sup>

Taken together, the kinetic and CID results lead us to propose the surface-derivatized structures for the polymethoxylated  $C_{60}$ -

(15) Olah, G. A.; Bucsi, I.; Lambert, C.; Aniszfeld, R.; Trivedi, N. J.; Sensharma, D. K.; Surja Prakash, G. K. *J. Am. Chem. Soc.* **1991**, *113*, 9385.



**Figure 4.** Proposed surface-derivatized structures and orbital diagrams for the polymethoxylated  $C_{60}(OCH_3)_n^{2+}$  cations.

$(OCH_3)_n^{2+}$  cations shown in Figure 4. We assume that methoxy addition to  $C_{60}^{2+}$  occurs to 6–6 bonds as is the case in the fluorination<sup>16</sup> and chlorination<sup>15</sup> of  $C_{60}$ .<sup>17</sup> The addition of the first methoxy radical via reaction 2 reduces the symmetry of  $C_{60}^{2+}$  from  $C_{5v}$  (in which the HOMOs are triply degenerate)<sup>18</sup> to  $C_3$  and removes all the orbital degeneracies. However, we chose here to retain orbital degeneracies consistent with the Hückel rule.  $C_{60}^{2+}$  has a delocalized 58-electron  $\pi$ -system, and abstraction of a methoxy radical from  $CH_3ONO$  removes one of these electrons to form an O– $C_{60}$  bond. Our measurements indicate that this bond formation proceeds relatively slowly,  $k = (5.8 \pm 1.7) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The resulting dication,  $C_{60}(OCH_3)_2^{2+}$  (**I** in Figure 4), is a  $\pi$ -radical that reacts more rapidly with another methyl nitrite molecule,  $k = (3.1 \pm 1.2) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , again by radical abstraction, producing  $C_{60}(OCH_3)_2^{2+}$  (**II**), an ion which may have a closed-shell electronic configuration but which we have chosen to depict as a triplet in the orbital diagram accompanying structure **II**. This latter ion again reacts relatively slowly,  $k = (5.2 \pm 2.6) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , to produce **III**. Indeed, all the ions  $C_{60}(OCH_3)_n^{2+}$  for which  $n$  is an odd number are radicals (see **I**, **III**, and **V** in Figure 4), and these were all observed to add  $CH_3O^\bullet$  more rapidly than ions for which  $n$  is even (see Figure 2).

For the  $C_{60}(OCH_3)_n^{2+}$  ions in which  $n$  is even, there is a further interesting periodicity in reaction kinetics, with adducts having  $n = 2$  and 6 being more reactive than those with  $n = 4$  and 8 (based on the appearance of product ions in Figure 1). The  $n = 2$  (**II**) and 6 (**VI**) adducts have 56 and 52  $\pi$ -electrons while those with  $n = 4$  (**IV**) and 8 have 54 and 50  $\pi$ -electrons,

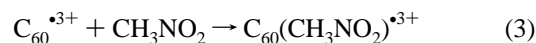
(16) (a) Holloway, J. H.; Hope, E. G.; Taylor, R.; Langley, G. J.; Avent, A. G.; Dennis, T. J.; Hare, J. P.; Kroto, H. W.; Walton, D. R. M. *J. Chem. Soc., Chem. Commun.* **1991**, 966. (b) Selig, H.; Lifshitz, C.; Peres, T.; Fisher, J. E.; McGhie, A. R.; Romanov, J. W.; McCauley, J. P.; Smith, A. B. *J. Am. Chem. Soc.* **1991**, *113*, 5475.

(17) Hirsch, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1138.

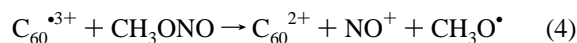
(18) Hrusak, J.; Schwarz, H. *Chem. Phys. Lett.* **1993**, *205*, 187.

respectively. The enhanced stability of the  $n = 4$  and 8 adducts is reminiscent of the extra stability of “aromatic” hydrocarbons which also contain  $(4n + 2)$   $\pi$ -electrons. Also, it is interesting to note that, in the methylation of  $C_{60}^{x-}$  by  $CH_3I$  in  $Li/THF-d_8$  solution, the number of  $CH_3$  groups added varies from 1 to 24, with the number being predominantly even and most commonly 6 and 8.<sup>19</sup>

**Reactions of  $C_{60}^{3+}$ .** The  $C_{60}^{3+}$  cation was observed to react rapidly with both nitromethane and methyl nitrite, but in distinctly different ways. The former reaction was also investigated with fully deuterated nitromethane with similar results, and there was no significant isotope effect in the measured rate coefficients. Representative data are shown in Figures 5 and 6.  $CH_3NO_2$  rapidly adds to  $C_{60}^{3+}$  under SIFT conditions according to reaction 3 with  $k = (3.8 \pm 1.1) \times 10^{-9}$



$\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , while  $CH_3ONO$  reacts by dissociative electron transfer,  $k = (3.0 \pm 0.9) \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , according to reaction 4. Electron transfer was not observed with



$CH_3NO_2$ ; we can set a limit of <1% for the branching ratio of electron transfer. Depending on the value of  $RE(C_{60}^{3+})$ ,  $15.6 \pm 0.5 \text{ eV}^{20}$  or  $16.6 \pm 1 \text{ eV}$ ,<sup>21</sup> electron transfer from nitromethane and methyl nitrite is exothermic by 4.6 or 5.6 eV and 5.2 or 6.2 eV, respectively. It appears that the failure to observe electron transfer with  $CH_3NO_2$  may be attributed to the energy barrier arising from Coulombic repulsion among product ions within the uncertainty of the estimated threshold in exothermicity of  $4.5 \pm 0.4 \text{ eV}$ .<sup>14</sup> In contrast, electron transfer from methyl nitrite to  $C_{60}^{3+}$  seems to overcome this barrier and leads to the dissociation of  $CH_3ONO^+$  into  $CH_3O^\bullet + NO^+$ . This dissociation requires only about 0.5 eV.<sup>22</sup> It is interesting to note that dissociation into  $CH_3O^+ + NO^\bullet$  is even more exothermic but does not occur, apparently because it requires a transition from one diabatic surface to another.<sup>23</sup> We should also note that a previous low-pressure FT-ICR study of the reaction of  $C_{60}^{3+}$  with nitromethane indicated the occurrence of  $O^\bullet$  transfer.<sup>24</sup> We did not observe such a reaction, perhaps because of the greater probability of collisional stabilization of the reaction intermediate at the much higher pressures of our SIFT technique. Also, it should be noted that our failure to see electron transfer between  $C_{60}^{3+}$  and  $CH_3NO_2$  is not totally consistent with our earlier observations of an electron-transfer channel of ca. 10%.<sup>20</sup> The experiments in the present study were performed with a redesigned electron-impact ion source with superior definition of the ionization region and higher signal intensities and they did not show the production of  $C_{60}^{2+}$  from electron transfer with  $CH_3NO_2$  (see Figure 5) observed to a small extent previously. It is likely that the earlier experiments were contaminated with an initial signal of  $C_{58}^{3+}$  as was the case,

(19) Bausch, J. W.; Surya Prakash, G. K.; Olah, G. A.; Tse, D. S.; Lorents, D. C.; Bae, Y. K.; Malhotra, R. *J. Am. Chem. Soc.* **1991**, *113*, 3205.

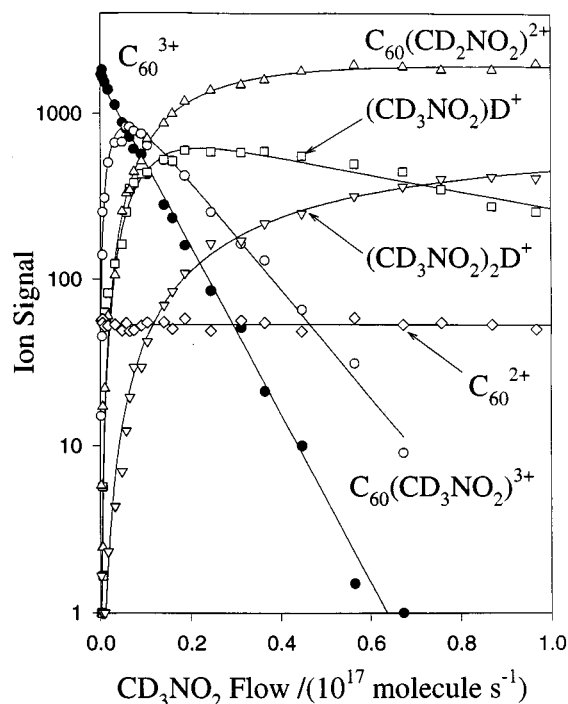
(20) Javahery, G.; Wincel, H.; Petrie, S.; Bohme, D. K. *Chem. Phys. Lett.* **1993**, *204*, 467.

(21) Wörgötter, W.; Dünser, B.; Scheier, P.; Märk, T. D. *J. Chem. Phys.* **1994**, *101*, 8674.

(22) Baer, T.; Haas, J. R. *J. Phys. Chem.* **1986**, *90*, 451.

(23) Leyh-Nihant, B.; Lorquet, J. C. *J. Chem. Phys.* **1988**, *88*, 5606.

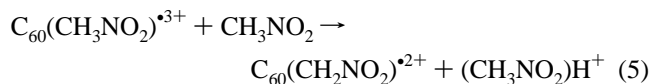
(24) McElvany, S. W.; Bach, S. B. H. *ASMS Conf. Mass Spectrom. Allied Top.* **1991**, *39*, 422.



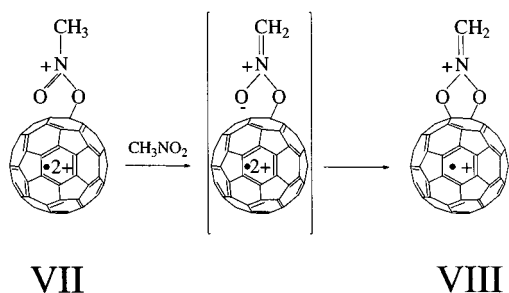
**Figure 5.** Experimental data for the chemistry initiated by the reaction of C<sub>60</sub><sup>3+</sup> with CD<sub>3</sub>NO<sub>2</sub>. The C<sub>60</sub><sup>3+</sup> was produced in a low-pressure ion source by electron impact at 100 eV with C<sub>60</sub> vapor derived from a fullerene powder. The CD<sub>3</sub>NO<sub>2</sub> was admitted into the flow tube as a (4%) mixture in helium. The measurements were made at 294 ± 2 K in helium buffer gas at a total pressure of 0.35 ± 0.01 Torr. The lines represent a fit to the experimental data with the solutions of the system of differential equations appropriate for the observed reactions. The small C<sub>60</sub><sup>2+</sup> initially present can be attributed to the occurrence of electron transfer between impurities and C<sub>60</sub><sup>3+</sup> upstream in the injection region before thermalization downstream.

for example, in our measurements of the reaction of C<sub>60</sub><sup>3+</sup> with acetylene.<sup>25</sup>

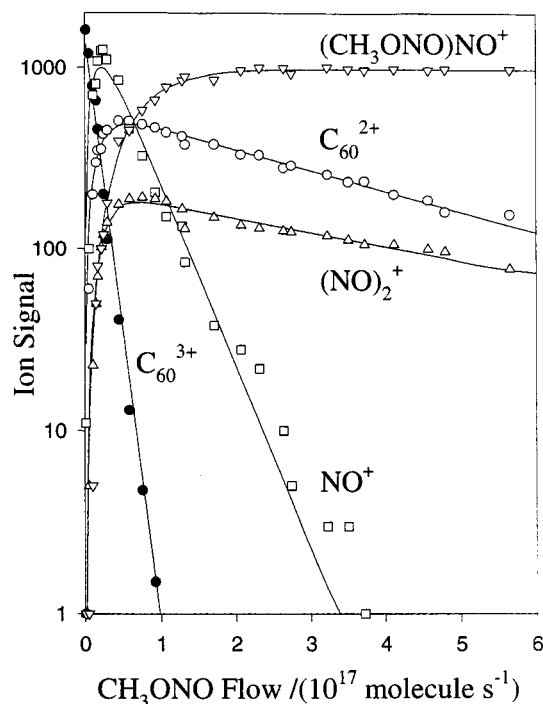
The higher-order reactions apparent in Figures 5 and 6 are also of interest. The adduct ion produced in reaction 3 was observed to react again with nitromethane in a bimolecular proton-transfer reaction as shown in reaction 5 with  $k_5 = (4.0 \pm 1.2) \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . We have observed



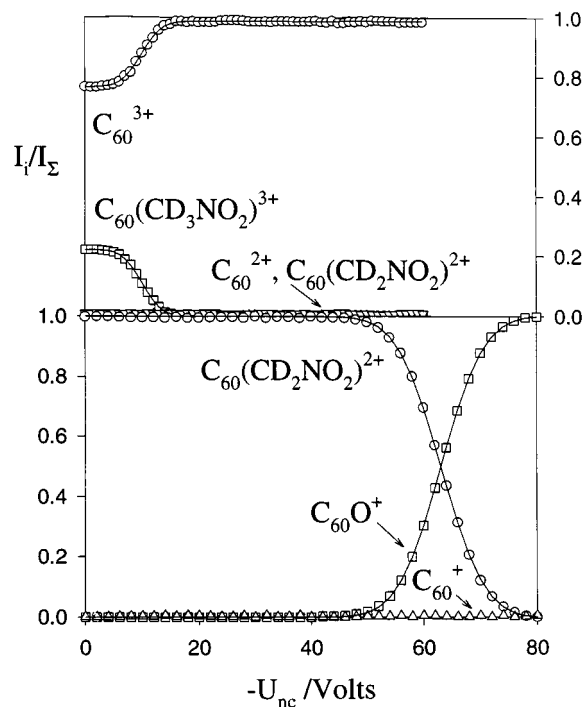
previously a number of analogous proton-transfer reactions of derivatized doubly-charged C<sub>60</sub> cations,<sup>26</sup> and this is one of a growing number of proton-transfer reactions we have encountered with derivatized triply-charged C<sub>60</sub> cations.<sup>3e,g,25</sup> It is likely that the proton transfer reaction 5 converts structure VII to the bridged structure VIII. The CID spectra shown in Figure 7



are consistent with this conjecture. The product ion of reaction 5 has a much higher threshold for dissociation and so is much

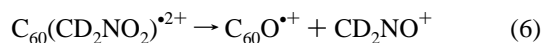


**Figure 6.** Experimental data for the chemistry initiated by the reaction of C<sub>60</sub><sup>3+</sup> with methyl nitrite. The C<sub>60</sub><sup>3+</sup> was produced in a low-pressure ion source by electron impact at 100 eV with C<sub>60</sub> vapor derived from a fullerene powder. The methyl nitrite was admitted into the flow tube as a pure gas. The measurements were made at 294 ± 2 K in helium buffer gas at a total pressure of 0.35 ± 0.01 Torr. The lines represent a fit to the experimental data with the solutions of the system of differential equations appropriate for the observed reactions. The secondary chemistry observed for C<sub>60</sub><sup>2+</sup> and (NO)<sub>2</sub><sup>+</sup> is not shown for clarity. (NO)<sub>2</sub><sup>+</sup> reacts with methyl nitrite to form the adduct ion.

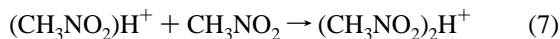


**Figure 7.** CID spectra recorded for the C<sub>60</sub>(CD<sub>3</sub>NO<sub>2</sub>)<sup>3+</sup> cation (top) and its deprotonated form (bottom) at a total pressure of argon (26%)–helium buffer/collision gas of 0.30 ± 0.01 Torr and a flow of nitromethane of 1.3 × 10<sup>15</sup> (top) and 8.2 × 10<sup>16</sup> (bottom) molecules s<sup>-1</sup>.

more strongly bound. It dissociates by the elimination of CD<sub>2</sub>NO<sup>+</sup> according to reaction 6.

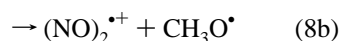


The data in Figure 5 also show the further reaction of protonated nitromethane to form the protonated dimer according to reaction 7. This is presumably a termolecular association



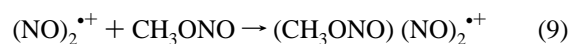
reaction under our experimental operating conditions with He acting as the third body.

The  $\text{NO}^+$  produced in dissociative electron-transfer reaction 4 was observed to rapidly react further with methyl nitrite,  $k = (8.2 \pm 2.5) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , to form both the adduct ion and the dimer ion,  $(\text{NO})_2^{\bullet +}$ , according to reaction 8 in a



ratio of 7 to 3, respectively. The latter channel is endothermic at room temperature by about  $27 \text{ kcal mol}^{-1}$  if the  $\text{NO}^+\cdot\text{NO}^{\bullet}$  cluster ion is formed, given that  $D(\text{NO}^+-\text{NO}^{\bullet}) = 14 \text{ kcal mol}^{-1}$  and  $D(\text{CH}_3\text{O}^{\bullet}-\text{NO}^{\bullet}) = 41 \text{ kcal mol}^{-1}$ ,<sup>12,27</sup> but its occurrence is not so surprising given the large exothermicity of charge-separation reaction 4 which produces  $\text{NO}^+$ , much of which will appear as kinetic energy of the product ions. The  $(\text{NO})_2^{\bullet +}$  ion produced in reaction 8b reacts only slowly with  $\text{CH}_3\text{ONO}$ ,  $k =$

$3.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , to form an adduct according to reaction 9.



## Conclusions

Our gas-phase measurements of reaction products and reaction kinetics have revealed a remarkable diversity in the reactivity of singly- and multiply-charged  $\text{C}_{60}^{x+}$  cations toward nitromethane and methyl nitrite in helium bath gas at 0.35 Torr and room temperature. They clearly show a strong dependence of reactivity on the charge state of the cation for  $x = 1, 2,$  and  $3$  ranging from non-reaction, to derivatization and dissociative electron transfer. The observed reactivity is also *isomer specific*, and this suggests the use of  $\text{C}_{60}^{2+}$  and  $\text{C}_{60}^{\bullet 3+}$  in the analysis for nitromethane and methyl nitrite by chemical-ionization mass spectrometry.

Polymethoxylation of  $\text{C}_{60}^{2+}$  has been observed under SIFT conditions and characterized with multicollision-induced dissociation. This is the first example of multiple derivatization of the surface of a fullerene cation with a molecular substituent to an extent far beyond the number of charges on the fullerene surface. Unusual periodicities have been observed in the kinetics of sequential methoxy addition, and these have been interpreted in terms of the electronic and aromatic nature of the methoxylated  $\text{C}_{60}(\text{OCH}_3)_n^{2+}$  cations.

**Acknowledgment.** The authors thank Alwin Cunje for technical assistance and D.K.B. thanks the Natural Sciences and Engineering Research Council of Canada for the financial support of this research.

JA962530U

(25) Wang, J.; Javahery, G.; Baranov, V.; Bohme, D. K. *Tetrahedron* **1996**, *52*, 5191.

(26) Petrie, S.; Javahery, G.; Bohme, D. K. *Int. J. Mass Spectrom. Ion Processes* **1993**, *124*, 145.

(27) Linn, S. H.; Ono, Y.; Ng, C. Y. *J. Chem. Phys.* **1981**, *74*, 3342.