

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

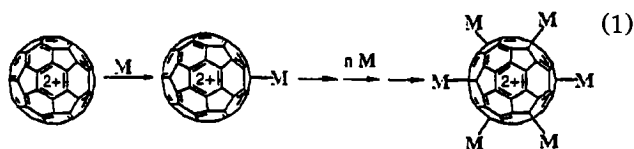
Jinru Wang, Vladimir Baranov, and Diethard K. Bohme

Department of Chemistry and Centre for Research in Earth and Space Science, York University, North York, Ontario, Canada

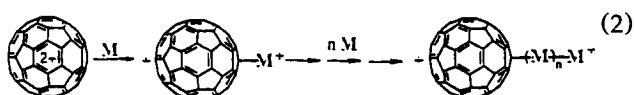
The collision-induced dissociation of the adduct ions $C_{60}(C_4H_8)_2^{2+}$ and $C_{60}(C_4H_8)_3^{2+}$ formed by sequential reactions of C_{60}^{2+} with 1-butene has been investigated by using a selected-ion flow tube (SIFT) apparatus. Experiments at 295 ± 2 K in 0.35 ± 0.02 torr of helium indicated 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}^{+} and $(C_4H_8)_2^{+}$ and $(C_4H_8)_3^{+}$, 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}^{3+} and C_{60}^{3+} with acetylene [3], and of C_{60}^{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,



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

Address reprint requests to D. K. Bohme, Department of Chemistry, York University, North York, Ontario, M3J 1P3 Canada.

collision-induced dissociation of the "ball-and-chain" adduct could lead to the detachment of a molecular chain.

Here we report the results of collision-induced dissociation experiments via the SIFT technique for multiple adducts of 1-butene and C_{60}^{2+} that provide direct evidence for the occurrence of intramolecular charge separation in derivatized multiply charged fullerene ions and support the "ball-and-chain" mechanism 2 for higher order addition.

Experimental

The reaction of C_{60}^{2+} with 1-butene was investigated by using a selected-ion flow tube (SIFT) apparatus [6, 7]. The C_{60}^{2+} was produced in a conventional low pressure ion source by electron impact of C_{60} vapour at an electron energy of 60 eV. The fullerene powder was a mixture of C_{60} and C_{70} that contained 2-12% C_{70} (Strem Chemical Co., Newburyport, MA). The C_{60}^{2+} cations produced in the source were selected with a quadrupole mass filter and injected into the flow tube where they were thermalized by collisions ($\sim 4 \times 10^4$) with helium buffer gas at 295 ± 2 K and 0.35 ± 0.02 torr. The 1-butene was introduced into the flow tube downstream. The 1-butene was obtained commercially and was of high purity (Matheson, Whitby, Ontario; CP grade, > 99.0%). The progress of the reaction was monitored with a second quadrupole mass filter and detector as a function of the flow of the neutral reagent. The rate data were analyzed in the usual manner [6, 7]. The rate coefficients for the observed 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 solution of the system of differential equations for a chain of successive reactions. The accuracy for these procedures of fitting depends on many parameters and is given separately for every calculated high order rate coefficient reported in the text.

In the collision-induced dissociation (CID) experiments argon was used as the collision gas at a pressure of 0.30 ± 0.01 torr. The downstream sampling nose cone of the SIFT was biased with respect to the flow tube from 0 to -80 V. After traversing the nose-cone orifice, the sampled ions are exposed to a series of electric fields that includes a front-lens voltage ($V_{fl} = 0$ to -500 V), a quadrupole field (rf/dc), and an exit-lens voltage ($V_{el} = 0$ to -500 V). The nose-cone voltage V_{nc} , V_{fl} , and V_{el} were varied by using a computer-controlled power supply (model TD9500, Spectrum Solutions Inc., Russelton, PA). V_{nc} was used as a reference voltage. V_{fl} and V_{el} were varied to ensure constant ion-signal ratios I_i/I_Σ , where I_i are the observed ion intensities and I_Σ is the sum of the detected ions. Ar^+/Fe^+ and $Fe^+/C_{60}^+/(C_{60})Fe^+$ were used for adjustment and calibration in helium buffer-collision gas. Ion-signal ratios could be kept constant within 1-3% over a range in V_{nc} from 0 to -80 V. The voltages

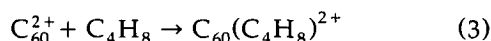
required to maintain constant ion-signal ratios were determined manually, parametrized, and incorporated into the control program for the power supply.

At the Ar pressure employed in the CID experiments reported here, dissociation occurs as a consequence of multiple rather than single collisions. This CID mode of operation of the SIFT is newly developed in our laboratory. We have now explored in detail the collision-induced dissociation of a large variety of positive ions. Results of these studies are reported elsewhere (Baranov, V.; Bohme, D. K., submitted).

Results and Discussion

SIFT Results for the Sequential Addition of 1-Butene

The ion-signal profiles measured for the reaction of C_{60}^{2+} with 1-butene are shown in Figure 1. C_{60}^{2+} reacts rapidly with 1-butene to form exclusively the adduct ion according to reaction 3 with a rate



coefficient of $9.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Electron transfer was not observed even though it is exothermic by 1.78 eV. The ionization energies of 1-butene and C_{60}^+ are 9.58 ± 0.02 eV [8] and 11.36 ± 0.05 eV [9], respec-

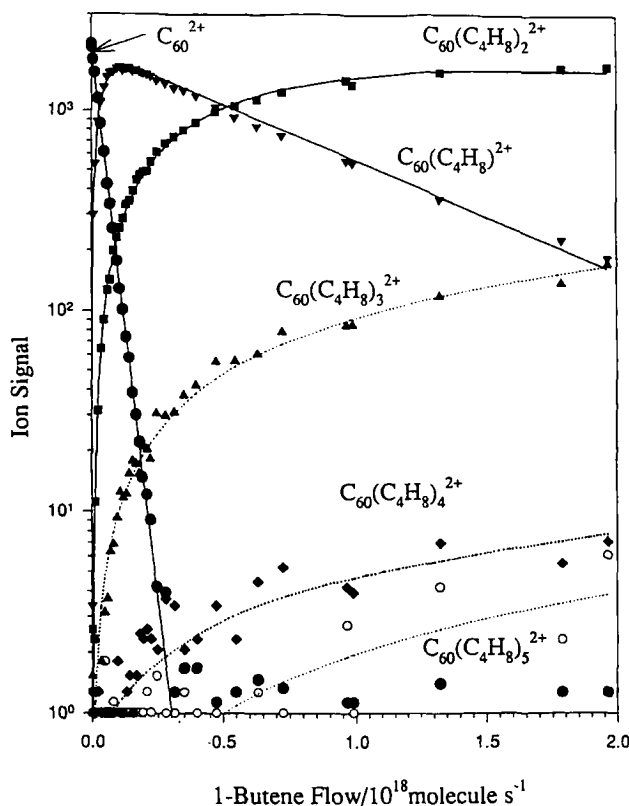
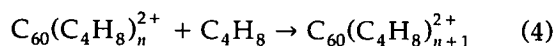


Figure 1. Variation in ion signals recorded for the reaction of C_{60}^{2+} with 1-butene in helium buffer gas at 295 ± 2 K and 0.36 ± 0.01 torr. The C_{60}^{2+} was produced by electron impact on C_{60} vapor at 60 eV. The solid lines represent a fit to the experimental data with the solution of the differential equations appropriate for this reaction. The dotted lines are drawn by hand.

tively. Apparently the energy barrier that arises from Coulombic repulsion between the singly charged product ions of the electron-transfer reaction impedes the electron transfer reaction [10]. The barrier is 1.80 ± 0.16 eV [8], which is just slightly higher than the exothermicity of electron transfer. The association reaction 3 involves a rehybridization of the bonding C atom on C_{60} from largely sp^2 to sp^3 . Adduct formation presumably occurs under our experimental operating conditions via the collisional stabilization of the chemically bonded intermediate complex by helium atoms.

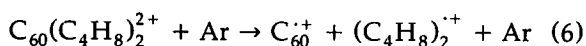
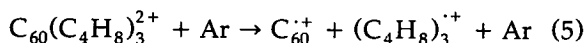
Figure 1 also provides evidence for the sequential addition of up to five molecules of 1-butene according to the following reaction ($n = 0$ to 4):



A kinetic fit to the profiles for the first and second adduct ions provided rate coefficients for their reactions of $(4.0 \pm 1.2) \times 10^{-11}$ and $(1.0 \pm 0.6) \times 10^{-11}$ cm^3 molecule $^{-1}$ s $^{-1}$, respectively. Clearly, the rate of sequential addition decreases with n and there is a sharp drop in rate, by a factor of about 20, between the first and second addition.

Multiple Collision-Induced Dissociation of Adduct Ions

Our multiple collision-induced dissociation studies began with an unsuccessful attempt to dissociate the adduct ions $C_{60}(C_4H_8)^{2+}$, $C_{60}(C_4H_8)_2^{2+}$, and $C_{60}(C_4H_8)_3^{2+}$ in helium buffer gas by raising the nose-cone voltage up to -80 V. Argon was found to be much more suitable for this purpose because of its higher mass. Figure 2 displays the multiple CID spectra recorded for $C_{60}(C_4H_8)_2^{2+}$ and $C_{60}(C_4H_8)_3^{2+}$ in argon buffer gas. The appearance of C_{60}^+ at high nose-cone voltages and the observation that $C_{60}(C_4H_8)^{2+}$ and $C_{60}(C_4H_8)_2^{2+}$ do not increase as those for the third and second adducts decrease and $(C_4H_8)_3^+$, $(C_4H_8)_2^+$, and $(C_4H_8)^+$ are produced one after the other, indicate that the third adduct breaks up directly into C_{60}^+ and $(C_4H_8)_3^+$ and that the second adducts breaks up directly into C_{60}^+ and $(C_4H_8)_2^+$. The multiple CID chemistry can therefore be represented by the following two equations:



There was no evidence for fragmentation of the fullerene itself. The $(C_4H_8)_n^+$ ($n = 2, 3$) fragments produced in reactions 5 and 6 dissociated further by losing C_4H_8 until eventually $(C_4H_8)^+$ itself began to decompose, but these latter results are not included in Figure 2. Figure 2 shows that the collision-induced dissociation of $C_{60}(C_4H_8)_3^{2+}$ begins at slightly above

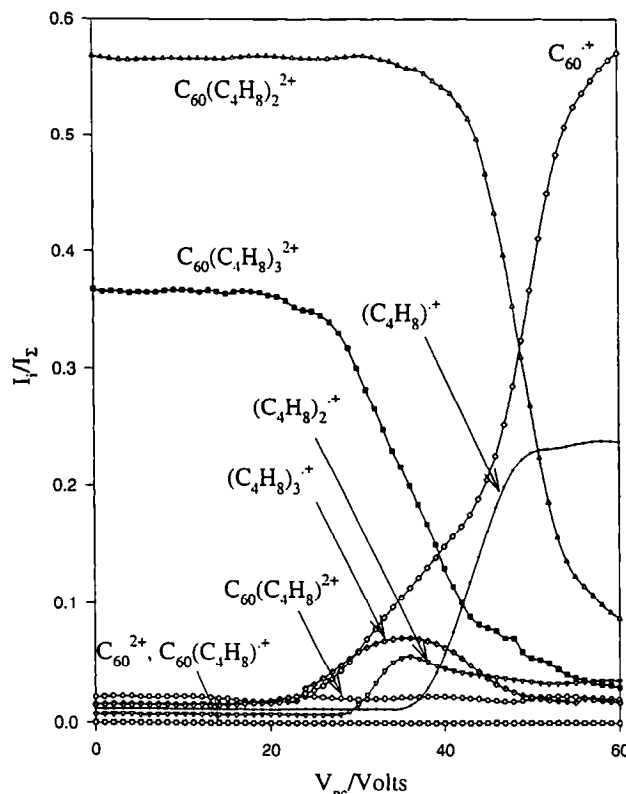


Figure 2. Variation in ion signals recorded as a function of the negative nose-cone voltage V_{nc} , for ions formed in the sequential reaction of C_{60}^{2+} with 1-butene. Experimental conditions were similar as in Figure 1, except that argon was used as the buffer gas at 0.30 ± 0.01 torr. The 1-butene was added into the reaction region as a 10% mixture in argon.

-20 V, which is about 20 V before that of $C_{60}(C_4H_8)_2^{2+}$. A close look at the CID profile for the appearance of C_{60}^+ reveals a break at slightly above -40 V that matches the onset of the collision-induced dissociation of $C_{60}(C_4H_8)_2^{2+}$. Both of these features are more readily apparent in Figure 3, which shows the Gaussian fits to the variation in the differential ion signal as a function of the nose-cone voltage. There are clearly two contributions to the formation of C_{60}^+ and these correspond to the collision-induced dissociation of $C_{60}(C_4H_8)_3^{2+}$ and $C_{60}(C_4H_8)_2^{2+}$ according to reactions 5 and 6.

Charge Separation and Chain Propagation

The CID results clearly establish that $(C_4H_8)_2$ and $(C_4H_8)_3$ are attached to C_{60}^{2+} as a dimer and trimer, respectively, and that the multiple derivatization of C_{60}^{2+} by 1-butene is accompanied by charge separation. They rule out the "fuzzy-ball" mechanism 1 and favor the "ball-and-chain" mechanism 2. This latter mechanism is illustrated in Scheme I in which it is assumed that electrophilic addition of the 1-butene occurs at the electron-rich double bond of this molecule, namely, at the 1 position. This leaves the positive charge nominally on the 2 position. Sequential addition in this

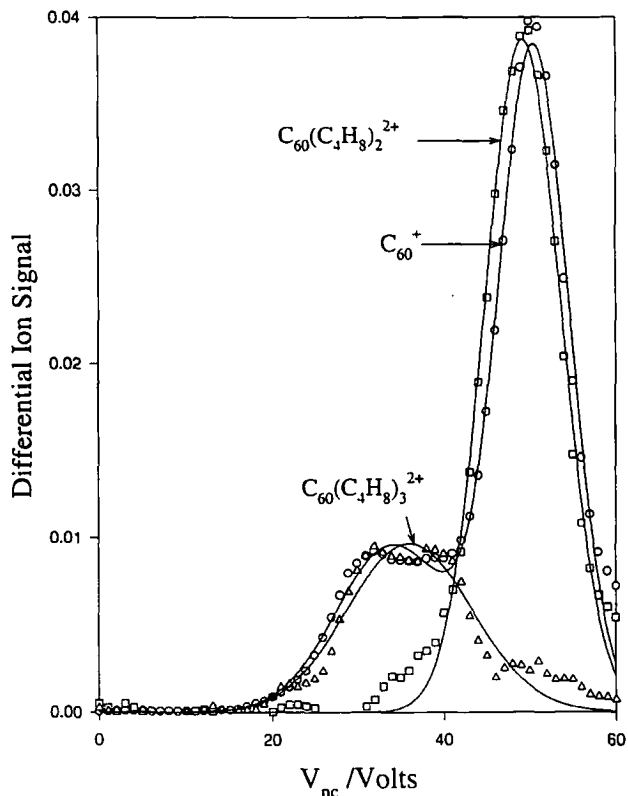
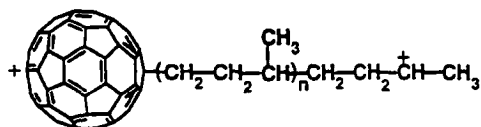
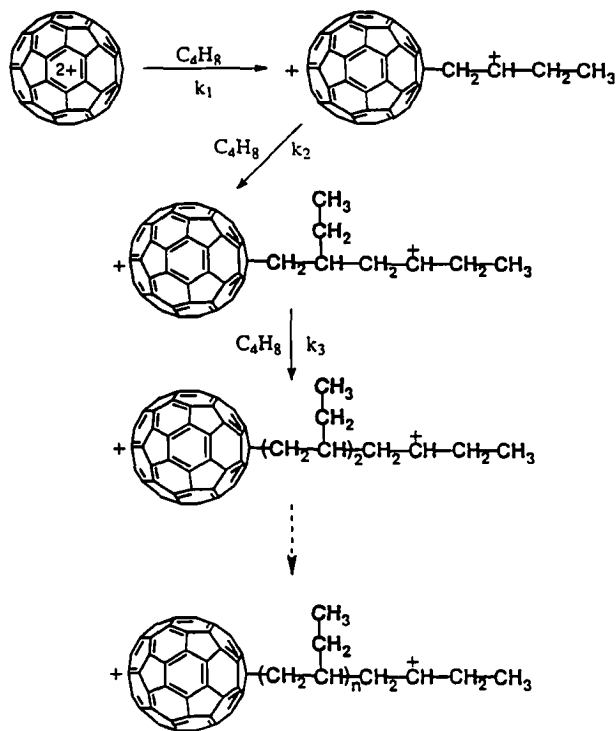


Figure 3. Variation in the differential ion signal as a function of the negative nose-cone voltage V_{nc} , for the data in Figure 2. The solid lines represent Gaussian fits to the experimental points. The differential signals of the declining ions $C_{60}(C_4H_8)_2^{2+}$ and $C_{60}(C_4H_8)_3^{2+}$ have been multiplied by -1 .

manner leads to the formation of a branched chain as indicated in Scheme I. A hydride shift from the 3 to the 2 position, driven by Coulombic repulsion between the two positive charges, would move the positive charge on the first substituent from the 2 to the 3 position. Subsequent polymerization initiated and driven in this fashion would lead to the following branched chain:



A further hydride shift from the 4 position of the first substituent is less likely because the resulting primary carbonium ion should be less stable than the secondary carbonium ion with the charge on the 3 position. If we take, for example, the computed energy difference of about 20 kcal mol^{-1} between the 1-propyl and 2-propyl $C_3H_7^+$ cations [11] as typical of the energy difference between a primary and secondary carbonium ion and compare this to $2.5 \text{ kcal mol}^{-1}$, which can be estimated for the electrostatic Coulomb relaxation energy for moving the charge from the 3 to the 4 position, we see that the hydride shift from the 4 to the 3 position is energetically unfavorable.



Scheme I

The observation of reactions 5 and 6 also indicates that the C—C bond with the C_{60} is the weakest link in the ball-and-chain structure. This is perhaps not surprising because the formation of this bond involves strain that accompanies the rehybridization of the bonding carbon on C_{60} from mainly sp^2 to mainly sp^3 .

The difference in the onset of collision-induced dissociation of $C_{60}(C_4H_8)_3^{2+}$ and $C_{60}(C_4H_8)_2^{2+}$ is difficult to rationalize. Although the same bond is broken in both cases, the barrier for dissociation with respect to the bonding well for these two dissociations will be different due to differences in the Coulombic repulsion between product ions. Coulombic repulsion will have more of an effect on the bonding well of the diadduct and could make the barrier for its dissociation smaller than that for the triadduct. Also, there are differences in the energy transfer that accompanies multiple CID because of differences in mass, size, and the number of degrees of freedom in the side chain. With regard to the latter, we can expect the probability for bond dissociation under multiple collision conditions to increase with the number of degrees of freedom because of the increase in total internal energy that accompanies this increase in molecular complexity. A higher probability of dissociation will translate into a lower measured onset of dissociation. The diadduct should therefore have an earlier onset for dissociation. We cannot be more quantitative than this at this time because our multiple collision-induced dissociation technique has not yet been calibrated and the theory of multiple CID is not yet fully developed.

Our rate coefficient measurements indicate that the rate of chain propagation decreases as the chain grows. The rate of chain propagation should be influenced by the availability of the charge near the end of the chain described in Scheme I. Intuitively, one might expect the charge to become less accessible as the chain grows. However, the exact dynamics for such a reaction sequence remains uncertain and should provide a worthwhile and interesting challenge for future calculations.

Acknowledgments

D. K. B. is grateful to the Natural Sciences and Engineering Research Council of Canada for the financial support of this research.

References

1. Scheier, P.; Märk, T. D. *Phys. Rev. Lett.* **1994**, *73*, 54.
2. See, for example, (a) Gross, D. S.; Williams, E. R. *J. Am. Chem.*

- Soc.* **1995**, *117*, 883; (b) Rockwood, A. L.; Busman, M.; Smith, R. D. *Int. J. Mass Spectrom. Ion Processes* **1991**, *111*, 103.
3. Wang, J.; Javahery, G.; Petrie, S.; Bohme, D. K. *J. Am. Chem. Soc.* **1992**, *114*, 9665.
4. Wang, J.; Javahery, G.; Petrie, S.; Hopkinson, A. C.; Bohme, D. K. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 206.
5. "Ball-and-chain" molecules in which the C₆₀ unit has been functionalized with a rigid polycyclic chain recently have been synthesized by Khan, S. I.; Oliver, A. M.; Paddon-Row, M. N.; Rubin, Y. *J. Am. Chem. Soc.* **1993**, *115*, 4919.
6. Mackay, G. I.; Vlachos, G. D.; Bohme, D. K.; Schiff, H. I. *Int. J. Mass Spectrom. Ion Phys.* **1980**, *36*, 259.
7. Raksit, A. B.; Bohme, D. K. *Int. J. Mass Spectrom. Ion Processes* **1983/84**, *55*, 69.
8. Lias, S. G.; Liebman, J. E.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *365*, Suppl. 1.
9. Bohme, D. K. *Int. Rev. Phys. Chem.* **1994**, *13*, 163.
10. Petrie, S.; Wang, J.; Bohme, D. K. *Chem. Phys. Lett.* **1993**, *204*, 473.
11. See, for example, Koch, W.; Liu, B. *J. Am. Chem. Soc.* **1989**, *111*, 3479.