Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Direct Observation of C_{60}^{-} Nano-ion Gas Phase Ozonation via Ion Mobility-Mass Spectrometry

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Supporting Information

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Information Available

- A schematic diagram of the experimental setup used in this study
- Mobility spectra for THA^+ and C_{60}^-
- Method of calculation for the collision rate between C_{60}^- and O_3
- Mass peaks at high ozone mixing ratio

Experimental Setup

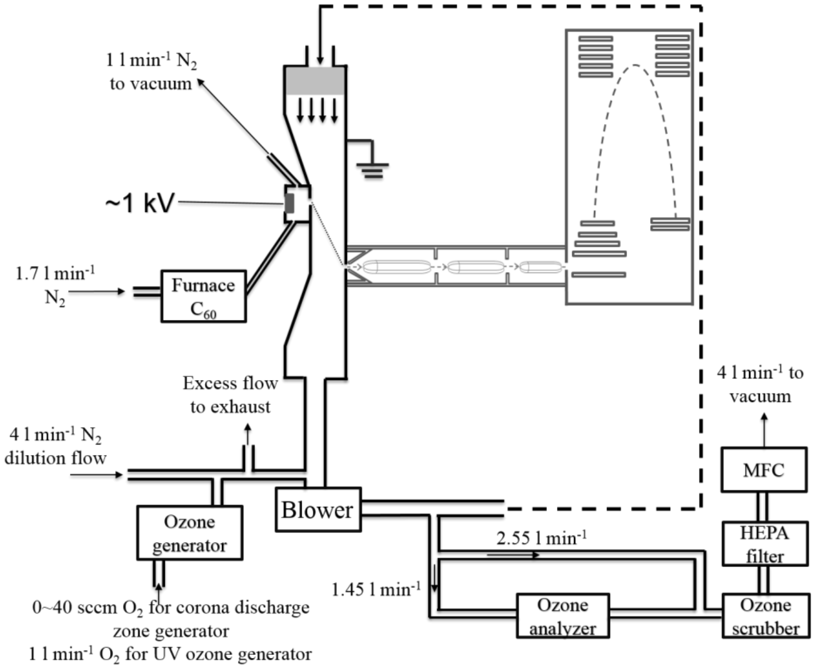

Figure S1. A schematic diagram of the experimental setup of the DMA-MS system, including flow rates.

Mobility spectra for THA$^+$ and C_{60}^-

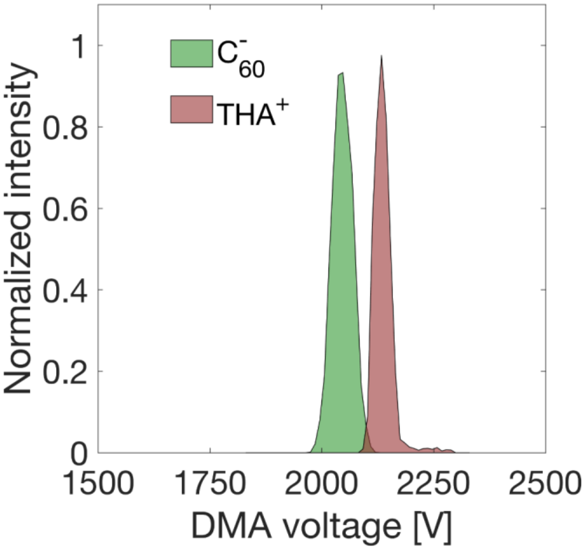

Figure S2. The mobility spectra for THA$^+$ and C_{60}^-; the THA$^+$ spectrum is used in instrument calibration.

Calculation of collision rate between C_{60}^{-} and O_3

The collision rate coefficient (β) between C_{60}^{-} and O_3 is approximated with the following equations:

$$\beta = \sqrt{\frac{8k_BT}{\pi m_r}} \cdot \pi(r_{O_3} + r_{C_{60}})^2 \, \eta(\psi_D) \tag{S1}$$

$$\eta(\psi_D) = 1 + C\psi_D \tag{S2}$$

$$\psi_D = \frac{ze\mu_D}{4\pi\varepsilon_0 k_B T(r_{O_3}+r_{C_{60}})^2} \tag{S3}$$

where k_B is the Boltzmann constant, T is system temperature, m_r is the reduced mass of an ozone and a fullerene molecule, $\eta(\psi_D)$ is the enhancement factor of the collision rate due to ion-dipole interaction, ψ_D is the ion–dipole energy to thermal energy ratio, μ_D is the dipole moment of ozone (0.53D), and ε_0 is the vaccum permittivity . r_{O_3} and $r_{C_{60}^{-}}$ are radii of ozone and C_{60}^{-} and they were estimated to be 1.099 nm and 0.483 nm, respectively. The condensed phase bulk densities of ozone (1354 kg m^{-3})[1] and C_{60} (1720 kg m^{-3}) were utilized in this calculation, assuming that both ozone and C_{60} can be treated as spheres without inducing significant errors in the final collision rate calculation. With these radii values, ψ_D has a value of 0.248, indicating the influence of the ion-dipole potential is modest. *C* is approximated with a value 0.6, i.e. we approximate that the ozone dipole moment is aligned with the directional vector between O_3 and C_{60}^{-} for 60% of its trajectory. While this is a rough approximation, it vastly simplifies estimation of the collision rate coefficient, and is intermediate to its upper and lower limits (1.0 and 0.0, respectively).

Mass Peaks at High Ozone Mixing Ratio

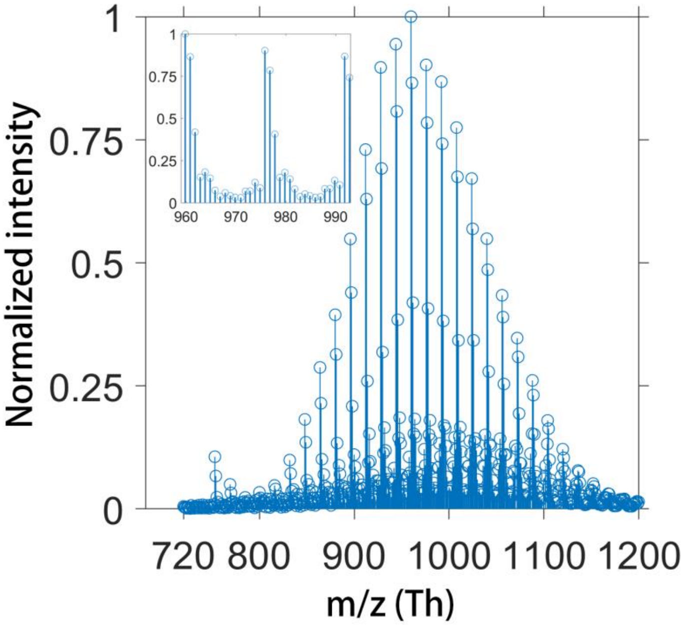

Figure S3. An example mass spectrum at an ozone mixing ratio of 171 ppm, with circles indicating local maxima of signal intensities (as opposed to integrated ion signals). The inset figure shows a portion of the main figure to illustrate the pattern of the mass peaks.

Reaction mechanisms other than sequential oxygen addition become more important as ozone concentration increases. To illustrate this, Figure S3 shows the local intensity maxima of the mass spectra at an ozone mixing ratio of 171 ppm. Since the ion signals are not integrated, Figure S3 exhibits deviations from isotropic patterns expected from integrated ion signals. However, peaks corresponding to $C_{60}O_n^-$, $C_{60}O_n^-$+4 Da, $C_{60}O_n^-$+8 Da, $C_{60}O_n^-$+12 Da and $C_{60}O_n^-$ +14 Da are clearly present in the spectra. As is explained in the main text, formation of $C_{60}O_n^-$+4 Da, $C_{60}O_n^-$+8 Da, $C_{60}O_n^-$+12 Da peaks can be (partially) attributed to the loss of CO or CO_2 from the reaction products, while the $C_{60}O_n^-$+14 Da peaks may arise from reactions involving contaminants within the DMA sheath tubing.

1. R. I. Brabets and J. M. McDonough, *The Journal of Chemical Physics*, 1957, **27**, 880-882.