Interactive comment on “Acid-yield measurements of the gas-phase ozonolysis of ethene as a function of humidity using Chemical Ionisation Mass Spectrometry (CIMS)” by K. E. Leather et al.

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The only competition for the nascent CBs is between prompt unimolecular reaction and collisional stabilisation. Bimolecular reactions are much too slow to compete at such a timescale (one collision!). All studies agree that a substantial fraction (about half) of the nascent CBs from C₂H₄+O₃ undergoes prompt unimolecular reaction, most probably isomerisation to dioxirane (Kroll et al., JPCA 105, 4446, 2001). The rest (which I termed SCIs in my previous comment) is composed of a fraction which was formed vibrationally “cold”, and a fraction which is stabilised. Only the SCIs can undergo reaction with H₂O.

It is simply absurd to state (as in C. Percival’s reply to my previous comment) that “the
unimolecular decomposition rate of CB that we include is the total decomposition (i.e. both Hot and SCI)". Summing the first-order loss rates of hot CBs and SCI is just meaningless. The CBs cannot be simultaneously cold and hot.

Therefore, the Equation (R4) in Leather et al. cannot be used as such to model the experimental yields. And it cannot be used to extrapolate the observed HCOOH yields to e.g. isoprene or MVK or MACR.

Note that the relative importance of the possible reactions for a given CB is dependent on the system in which it is generated (Jenkin et al., Atmos. Environ. 31, 81–104, 1997). In particular, the stabilisation fraction is expected to increase for larger precursors, because the internal energy gained from the reaction is distributed among a larger number of vibration modes. For example for the C\textsubscript{12}-C\textsubscript{14} compounds investigated by Donahue et al. (PCCP 13, 10848–10857), the stabilisation fraction is 100%, even at 100 Torr.

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