

Interactive comment on “Estimation of rate coefficients and branching ratios for reactions of organic peroxy radicals for use in automated mechanism construction” by Michael E. Jenkin et al.

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Prof. Wennberg notes that "Teng was the first to point out that for multifunctional compounds, the nitrate branching ratios should (and do) scale more closely with heavy atoms than just carbon."

Historically, that is not quite accurate, as this has been discussed as far back as the turn of the century, and several models incorporated nitrate yields that are based on the number of heavy atoms, or even estimates that try to account for rigidity and other

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factors affecting quantum state density and hence lifetime/pressure dependence. Much of this was based on theoretical state density and partition function calculations, and this data was exchanged e.g. during Eurotrac meeting around the years 2000.

Mechanistically, it is clear that the pressure dependence is due to collisional stabilisation which, given that the energetics are not all that different between different RO₂+NO reactions, is thus directly linked to the state density of the peroxy nitrite intermediate. This is mostly governed by the low-frequency modes, i.e. the number of modes generated by the molecular skeleton containing the heavy atoms, whereas the H-atoms only contribute by providing a bit of mass, a high-frequency modes that are barely excited at room temperature and thus don't contribute significantly to the state density. These theoretical state density calculations were used by e.g. Jozef Peeters to construct more complex models that weighted for e.g. double bonds and rings that do not contribute to high-density internal rotations and are thus not as effective as single-bonded chains in increasing the lifetime and hence nitrate yields.

In our work, such models were used as far back as 2001 (a-pinene oxidation, Peeters et al.), and as recent as 2012 (b-pinene oxidation, Vereecken and Peeters) where the nitrate yields used do not match the Arey et al. model exactly, but rather are based at least on the number of heavy atoms, and sometimes accounted for double bonds and other effects. An example would be one of the first nitrate formation steps in Peeters et al. 2001, figure 1, formation of RO₃, C₁₀ Arey et al. tert nitrate yield 10% 10.45%; C₁₀+O₂ tert nitrate yield 11.11%, used yield is rounded 11%.

At that time, it was felt to be sufficient to refer to Arey et al., as the theory-based model was due to be published in full, and it was in many respects a theory-based reparameterization of the Arey et al. model. An unfortunate choice, as ultimately Peeters never published his model, despite extensive hints in in our papers that this was due to happen; the main block was that no theoretical characterization of the nitrite to nitrate interconversion process was ever available, suggested now to be either a roaming reaction or a singlet-triplet-singlet double surface hop, both of which are very hard to

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do computationally, and thus not characterized even today. Other authors did publish some work on this, e.g. Barker et al. 2003 probed the required energetic and rovibrational characteristics of the nitrite-nitrate interconversion process, but no computationally supported solution was ever found. Other scientists in those days likewise attempted to come up with models based on a quantification of the microscopic mechanism, but all faltered on the lack of a characterization of the nitrite-nitrate conversion step, as well as the odd differences in yields between primary, secondary and tertiary nitrates, which from a theoretical-mechanistic point of view remains unexplained. It may be that some models were presented as talks or posters at some conference, describing these efforts, but my memory does not stretch back that far, and I have only printed proceedings from this period, making searches too time-consuming for a merely historic reminiscence.

While it is possible that Teng et al. were the first to *explicitly* publish this finding in a peer-reviewed paper, the use of heavy atom number instead of carbon number in the prediction of nitrate yields thus dates back about 2 decades. Technically, for theoreticians, Barker et al. 2003 already indicates clearly that heavy atom count is more appropriate than carbon number, as that analysis is based on state density, and essentially only lacks a good description of the nitrite-nitrate conversion. The upcoming results on nitrate yields obtained at NCAR could likewise solve some of the conceptual problems related to prim/sec/tert yields that hampered development of theory-based models.

Feeling old, Luc Vereecken

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