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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Evaluated kinetic and photochemical data for atmospheric chemistry: Volume VII – Criegee intermediates" *by* R. Anthony Cox et al.

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This work assesses kinetics for the fast-moving field of carbonyl oxide chemistry. The evaluation is thorough and thoughtful and accurately captures and accounts for most of the questions and disagreements that arise from the available studies. The evaluation makes insightful recommendations of the key points for additional research (including branching fractions for some key reactions). The manuscript, although an experiment-based evaluation, also points out the key role of advanced theoretical methods, which now can produce highly accurate kinetics values for experimentally inaccessible reactions. This is an excellent work that will be very useful to modelers and as a guide

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to experimental kineticists. There are just a few improvements that I would suggest, focused on the aspect I am most familiar with, reaction kinetics of carbonyl oxides.

First, new investigations have continued since the evaluation that forms the basis of this paper, especially in the reaction kinetics of the stabilized carbonyl oxides. That is unavoidable. However, the authors may consider the newest investigations (PNAS 117 (18), 9733-9740 (2020)) of the kinetics of the C4 carbonyl oxide methyl vinyl ketone oxide, because here theory and direct experiments suggest that the bimolecular reactions of the conjugated carbonyl oxides may differ from the reactions used as analogies in the evaluation. For example, direct kinetics measurements show that the reaction of methyl vinyl ketone oxide with SO2 is a factor of three or so slower than the reactions of non-conjugated carbonyl oxides of similar size.

Second, as the manuscript acknowledges, measuring thermal kinetics for unimolecular reactions of carbonyl oxides is often experimentally difficult because of the need to correct for competing bimolecular processes. In this case the theoretical characterizations, especially those for which microcanonical rate coefficients and the related tunneling parameters have been corroborated by direct energy-specific dynamics measurements, provide valuable information about the unimolecular processes (see Int. Rev. Phys. Chem. 39 (1), 1-33 (2020)). The evaluation already makes good use of theory in interpreting the unimolecular kinetics, but the authors might consider emphasizing experimentally validated calculations (J. Chem. Phys. 146, 134307 (2017)) for acetone oxide (k298 = 276 s-1), where the tunneling-adjusted microcanonical rate coefficients match experiment over a wide energy range, and J. Chem. Phys. 145, 234308 (2016) that treats the unimolecular decay of Z-acetaldehyde oxide with similar tests of tunneling parameters against direct experiment (k298 = 122 s-1). These values are slightly lower than the recommendations. I note that the unimolecular decay kinetics for some methyl vinyl ketone oxide conformers (J. Am. Chem. Soc., 140 (34), 10866–10880 (2018)) have also been compared to energy-resolved dynamics measurements.

Third, in the discussion of the atmospheric role of carbonyl oxides, are there other non-

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kinetics uncertainties (e.g., in the alkene source inventory) that should be mentioned? The development of sensitive measurement methods for carbonyl oxides (e.g., J. Am. Chem. Soc. 139 (38), 13387–13392 (2017)) that may eventually constrain the concentration of these intermediates in the field should possibly be mentioned as an important area for continued effort.

Finally – is there a reference to verify a unity quantum yield of O (1D) from UV excitation of carbonyl oxides (section 5)?

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