Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2019-1138-RC1, 2020
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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Chemical loss processes of isocyanic acid, HNCO, in the atmosphere" *by* Simon Rosanka et al.

Anonymous Referee #1

Received and published: 6 March 2020

This is a well-written paper with two main parts, (i) computational characterization of HNCO reactions with OH (a refinement which confirms what is known already that that this is very slow) and new data for Cl, NO3 and O3, and (ii) modeling of predicted surface concentrations of HNCO based on the results combined with literature information. My focus will be on the first part.

The dominant source of HNCO is biomass burning, and it has a long lifetime in the atmosphere, so this is a relevant topic for Atm. Chem. Phys. Fairly standard and usually reliable computational chemistry techniques are applied to characterize reactants, intermediates, products and barriers for a variety of HNCO reaction pathways. The methodology is described in sufficient detail, along with information such as molecular geometries, to allow others to reproduce the results. I see no errors in the work and

the conclusions are sound. The ms. is suitable for publication once some areas are addressed.

1. Page 3, lines 7-13. In this brief discussion of photochemistry, given the various known bond strengths in HNCO, what are the threshold wavelengths at which photodissociation could occur? 2. The uncertainty in barrier heights of 0.5 kcal/mol is quite small. How was this estimated? What are the magnitudes of the room temperature tunneling factors? I would expect large factors to be less reliable. 3. Page 6. The agreement on Fig. 2, at elevated temperatures of the order of 1000 K, is somewhat fortuitous because the slopes of computed and observed rate constants are different, but the agreement is noted favorably. Therefore factors like hindered internal rotations in the TS do need to be taken into account, even if they are not very important under atmospheric conditions. 4. Page 6 line 30 and the following line. Here and elsewhere the lifetime is described as "several decades" or 50 years. But 10ˆ10 s is about 300 years. 5. In the discussion of Cl + HNCO on p. 7 the dominant path is addition. I imagine the calculations are for the high-pressure limit, but is this reached everywhere over 200-450 K? The pressure dependence should be investigated via RRKM theory, especially as data are provided at up to 450 K where falloff is more likely than at room temperature. 6. On Line 1 of page 8 redissociation of HNC(Cl)O is stated to be its most likely fate, but given the rate quoted is the addition of molecular oxygen potentially competitive, especially below room temperature? 7. On page 8 there is no mention of the complications of describing the vibronic structure of NO3 accurately with the kinds of computational approaches used here. As studied, for example, by Okumura and Stanton, Jahn-Teller effects break symmetry and change the vibrational energy levels significantly, so that standard evaluation of partition functions may be significantly in error.

Minor typographical errors: Page 3 line 3 "…data are available…" Page 6 line 26. "an" should be "a" and there is a double comma Page 10 line 2 insert a space in "whereasthe"

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