

We thank the reviewers for their constructive comments. Our responses to both reviews follows, with one section per review. We shall address reviewer 2 first as their comments were more substantial. The reviewer comments are in bold and our responses are in a normal font.

1 Reviewer 2

- 5 **The provided manuscript discusses a VBS-based model for pure organic neutral and ion-induced nucleation, including its formulation, assumptions, and comparison with CLOUD measurements. The authors claim that their model reproduces experimental nucleation rates across various conditions. The topic of the manuscript is important and well within the scopes of ACP. However, several critical issues need to be addressed before publication consideration in ACP.**

Major Concerns:

- 10 1. **The assumption that the critical cluster for both neutral and ion nucleation is always a dimer (see Equations BR5 and BR14) is likely invalid. This assumption raises fundamental questions about the model's physical accuracy and consistency. According to nucleation thermodynamics and kinetics, the critical cluster is defined as a cluster with equal forward and backward evaporation rates. As shown in Figure 9 and other figures, the evaporation rates of neutral dimers are 3-4 orders of magnitude higher than the forward rate, indicating that dimers are not yet critical clusters. Additionally, the size of the critical cluster should depend on monomer concentrations; a constant size regardless of concentration (as in Figure 9) is unphysical. Furthermore, charged clusters tend to be more stable, implying that the critical cluster size for ion-induced nucleation should be smaller than that for neutral nucleation. The authors should at minimum explicitly acknowledge the unphysical nature of this assumption and discuss its impact on the predicted nucleation rates.**

20 This comment reflects a misunderstanding our central ansatz. We do not *assume* anything (directly) about a critical cluster. We instead observe that, for numerous VOCs studied at CLOUD, the mass spectrometry data reveal a spectrum of oxidation products with decreasing volatility with increasing oxidation state. For the many systems explored at CLOUD, the molecules formed include ones with sufficiently low volatility that the dimer is thermodynamically stable, allowing those species to form particles at a rate equal to their kinetic collision rate. Although the concentrations of those exceptionally low volatility species may be too low for appreciable growth by condensation of the same species, they serve as condensation nuclei for somewhat more volatile species. Particle inception does not involve a free energy barrier as hypothesized in the classical nucleation theory, allowing cluster growth through successive condensation of increasingly volatile species as described in Tröstl et al. [2021]. This mechanism does not preclude the classical nucleation mechanism, but rather bypasses it when atmospheric reactions decrease volatility of oxidized organic molecules to enable kinetic cluster formation before any of the more volatile species build sufficient supersaturation to nucleate as described by the classical theory. We thus indirectly assume that any free-energy maximum after the separated vapors is lower than the free energy of those separated vapors, at which point it is the assumptions of classical nucleation theory that break down.

35 Classical nucleation theory is a thermodynamic framework that applies to a continuum fluid, and it has been bodged to permit consideration of small clusters containing only an integer number of monomer molecules. We do not use classical nucleation theory here, but that does not mean our theory is “unphysical”; instead, continuum physics is without any doubt unphysical for molecular dimers. We consider the kinetic, rather than thermodynamic limit of particle formation. Pedants may thus consider this to be “new-particle formation” and not “nucleation”, as there is no free energy maximum above the free energy of the separated vapor monomers. That, in fact, is the critical distinction: at some point, the maximum free energy becomes the free energy of the vapor molecules (whether or not there is a secondary, local, free-energy maximum corresponding to the “critical cluster” of classical nucleation theory). As long as the rate-limiting step is the dimer formation, then the kinetic limit applies.

We already address this in the original manuscript, near line 155: “For organic vapors consisting of a rich mixture, we can surmise that there will be some constituents of sufficiently low volatility that they will nucleate on every collision; once they collide to form a cluster it will never evaporate. This suggests intrinsically bimolecular (kinetic) nucleation where binary vapor collisions are rate limiting and the nucleation rate varies as the square of the nucleator concentration.”

To this we shall add “This differs from classical nucleation theory, where a free-energy maximum for some cluster defines a point of equal condensation and evaporation rates. Here we assume that for this rich mixture (which includes some exceptionally low volatility species) the free-energy maximum is the ensemble of vapors. The problem then becomes to identify this subset of vapors and then find their collision rate to define the particle formation rate.”

Rick Flagan (a co-author of this manuscript) addressed this in the paper “A thermodynamically consistent kinetic framework for binary nucleation.” *J. Chem. Phys.*, 127 (doi:10.1063/1.2800001), which we shall cite with an added discussion in the revised manuscript.

The comment above, “As shown in Figure 9 and other figures, the evaporation rates of neutral dimers are 3-4 orders of magnitude higher than the forward rate, indicating that dimers are not yet critical clusters. Additionally, the size of the critical cluster should depend on monomer concentrations; a constant size regardless of concentration (as in Figure 9) is unphysical.” makes it evident that we have not described what we are doing, and assuming, with sufficient clarity. The reviewer appears to be in a mindset, inspired by classical nucleation theory, where nucleation occurs in a homogeneous vapor (i.e. Argon). The organics we are considering here are about as far from this as one could imagine. Instead, they are an incredibly complex mixture with a huge range of individual (pairwise) dimer free energies ($\Delta G_{i,j}$). It is important that we write with sufficient clarity to knock readers with a classical nucleation theory expectation bias out of their reverie. Our hope is that the added sentences quoted above will help.

Regarding the dimer evaporation in Fig. 9, that is more or less exactly the point. The (kinetic) nucleators are a subset of the ULVOCs. It would be incorrect to view the ULVOCs as a whole to be the nucleating species (or for that matter for there to be a sharp cutoff at the semi-arbitrary definition of the ULVOC-ELVOC boundary. Instead, we surmise that a subset of the ULVOCs constitute the nucleators. We also assert that this is more or less obvious – there are almost certainly *some* species that form dimers which, for all practical purposes, never evaporate. Equally, of course, there are other species that form dimers that evaporate rapidly. The key assumption of this theory is that we can use a “nucleation efficiency” to describe the transition from species that stick forever and those that evaporate instantly: it is again self-evident that such a function must exist and be monotonic, extending from 1.0 at the low end to 0.0 at the high end, and we simply invoke a sigmoid (with a gain) as a reasonable approximation of reality.

The key difference with these mixtures vs a classical homogeneous system is that, instead of the critical cluster changing size as concentrations increase, the number (volatility) of species that nucleate more or less kinetically increases as concentrations increase, while the rate-limiting step all the while remains dimer formation. Of course this is an approximation, but the consequence is a nucleation rate that slightly exceeds c_{ULVOC}^2 because the nucleators represent a larger and larger fraction of the total ULVOC as concentrations rise. For those wedded to classical nucleation theory, the observed particle formation rates are very nearly quadratic in c_{ULVOC} , again consistent with dimers being rate limiting.

- 2. Regarding Equations 16 and B4, clarification is needed on how the value of the kinetic (collision) rate coefficient, k_{kin} , was obtained as 10^{-10} cm³ s⁻¹. According to Figure 13.5 in Seinfeld and Pandis (2016), the typical collision rate coefficient for organic molecules (700 amu) should be approximately 7×10^{-10} cm³ s⁻¹, about seven times higher than the value used. Since the neutral nucleation rate is proportional to k_{kin} , adopting the higher value would likely lead to deviations from CLOUD measurements. This discrepancy suggests that other parameters might need adjustment to reconcile the model with experimental data.**

It is a good point that we need to be clear here. This is a semi-empirical theory, and we pick 10^{10} entirely because it makes for easy mental math. In practice this makes no difference (we have tried many different values, but in our opinion actually presenting some sort of sensitivity analysis is simply not useful). Because the theory is semi-empirical, if we increase k^{kin} we will simply lower the empirical saturation ratio threshold for the nucleation efficiency, and the results will be the same. It *does* matter what the ΔH values are, and so we present this sensitivity study in the Appendix; the

90 differences are not exceptional, but there is a clear winner in the “NMD” enthalpies with a minimum nucleation rate near 253 K in our theory and in the observations.

3. **In Figure 2, the criteria for determining neutral and charged threshold values are unclear. Clarification on the methodology used for these determinations is necessary for proper interpretation.**

They are empirical. In the revised manuscript we will make this clearer.

- 95 4. **In lines 300-301 and Figure 7, the manuscript omits comparison with CLOUD measurements at higher ionization rates, such as those achieved with π beams (see Fig. 4 in Kirkby et al., 2016). Including such comparisons would strengthen the validation of the model against experimental data.**

How we wish we could do this. Unfortunately, the key variable here is temperature, and we have yet to obtain and analyze a dataset with variable (beam) ionization rates over the full temperature range presented in Simon *et al.*

- 100 5. **At line 669 and Equation B9, the authors neglect ‘other losses’ or ‘wall losses’ in the final nucleation rate equation. It is important to justify this omission and clarify whether these losses are considered in the results presented in Figure 9, as they can significantly influence nucleation rates.**

105 Point well taken. The nucleation rates presented in Simon et al. are $J_{1.7}$, for $d_{\text{mob}} = 1.7$ nm, corresponding roughly to a physical size $d_p \simeq 1.4$ nm. We do indeed assume that the measured J are at a size close enough to the dimer (or trimer) for wall losses to be safely neglected; however, consideration of wall losses (or indeed coagulation) is crucial for generalization, and we will make this clear in the revised manuscript.

6. **The rates used in lines 739-740 pertain to small molecules or charged clusters (~ 100 amu). For larger organic molecules (~ 700 amu), these rates are expected to differ substantially. The authors should justify their choice of these rates and analyze the sensitivity of the predicted ion-induced nucleation (IIN) rates to these assumptions.**

110 In the end we use a semi-empirical ion-induced nucleation coefficient, much as we use a semi-empirical neutral kinetic coefficient. For the same reasons as discussed above, the exact values are not consequential, but it is important to make this clear in the text.

- 115 7. **In line 741, the method for determining the wall loss rate should be explained. The sensitivity of model predictions to this parameter must be assessed. As I understand, wall loss for neutral and charged clusters are quite different. The authors should also discuss how different wall loss rates for neutral and charged clusters might affect the model performance.**

120 As discussed above, wall losses in this presentation are neglected (but they are not neglected in the determination of $J_{1.7}$ in the cited work of Simon *et al.*). The reviewer notes: “As I understand, wall loss for neutral and charged clusters are quite different”. Here the reviewer seems to be drawing from the many studies that have used Teflon or other dielectric chambers in which charge accumulates on the chamber walls and enhances the deposition of charged particles as described in Rader and McMurry [McMurry, P.H. and Rader, D.J. (2007) “Aerosol Wall Losses in Electrically Charged Chambers”, *Aerosol Sci. Tech.* 4: 249–268. doi:10.1080/02786828508959054]. One additional feature of the CLOUD chamber is that, being made from stainless steel, deposited charge is conducted away from the surface, eliminating the local field. Only image-charge effects are present within the chamber, greatly reducing the range of the wall effect on particle losses. Thus for the conductive CLOUD chamber with the high-voltage clearing field off, we do not expect (or observe) any difference in wall loss beyond that expected based on mobility (diffusion coefficients).

Minor Concerns:

1. **Lines 19-21 should include references to other groups’ studies on organic nucleation, such as Zhang et al. (2004) and Yu et al. (2017), to provide a more comprehensive and balanced perspective.**

We shall.

130 2. **Lines 27-29 contain a statement that may not fully reflect the current understanding. Several studies (e.g., Lee et al., 2003; Yu et al., 2010) have demonstrated the importance of ion-induced or ion-mediated nucleation in the global atmosphere. The introduction should acknowledge these differing viewpoints for a balanced discussion.**

135 Be a little careful what you wish for – that line is in essence a negative citation asserting that those early studies were incorrect, but we will gladly add the suggested references to the list. To be clear, we did *not* intend to assert that neutral acid-base nucleation was even thought to predominate, and so we will also make it clear in revision that neutral and ion induced acid-base nucleation were thought to be the major pathways. it remains true that many climate models use a sulfate proxy for nucleation.

3. **In Figure 9, including error or uncertainty bars for the measured data would improve the clarity and robustness of the comparison.**

140 This is a reasonable suggestion, but we in fact removed the abundant error bars from the original Simon *et al.* presentation for this figure. Those can still be seen in the original published figure, but there is a real issue embedded here – it is not always straightforward to separate the precision of the individual measurements from the precision of the variability (i.e. the temperature dependence in this case). It is our judgement that the precision of the temperature dependence in these data is much higher than their overall accuracy, and here the main point of comparison is that temperature dependence. We therefore feel that presenting the data without the published error bars is more useful

145 4. **Lines 304-305. Similar general shape has been observed and predicted for H₂SO₄-NH₃-H₂O ternary nucleation (Dunne et al., 2016, Yu et al., 2018). The authors may want to point this out as well.**

150 The shape is an inevitable consequence of ion-induced nucleation being (potentially) rate-limited by ion-pair formation, a result far older than the suggested citations. However, we shall include those as well as the original literature in our revised manuscript - we are making no claims that this is an original finding here.

Overall, addressing these issues will enhance the physical consistency, clarity, and robustness of the manuscript, making it more suitable for publication in ACP.

2 Reviewer 1

155 Donahue et al. present a very interesting and detailed study on how nucleation can be described within the previously established volatility basis set (VBS). In a first part, the thermodynamic principles of nucleation are introduced alongside a description of the VBS and subsequently extended to the nucleation of organic vapors. In the second part, the application of the VBS to nucleation is discussed in a general manner and applied in the following to previously published results from chamber nucleation experiments. The paper is well-written and follows a clear flow and logic. The presented method allows a more detailed investigation of the contribution of organic vapors to nucleation and might

160 have substantial impact in the field.

I have some minor comments and suggestion to consider prior to publication.

– **Caption Figure 1. The two panels are described as ‘a)’ and ‘b)’ which is not detailed on the plots.**

Fixed.

165 – **l. 107 The term ‘aerosol-phase activity’ is used here to explain decreased tendency of organic vapors to condense on very small particles, but is not well defined in this context. As I understand the reduced interaction with the particle surface due to the contribution of the particle curvature is the reason for this tendency, I suggest a brief introduction of the activity term.**

We shall add a brief discussion of the Kelvin term along with the existing references.

170 – **l. 147 The temperature dependency is introduced very briefly here, although it is the basis for large sections of the conclusions in this paper. I understand that this was largely introduced in the cited studies, but I would suggest**

adding a few more points on the assumptions necessary and maybe limitations of this approach. This might help to judge the robustness of the derived conclusions.

The Appendices address this in depth, and we shall refer the reader to that discussion in the revised manuscript.

- 175
- **I. 152 Here, the authors link nucleation with the saturation ratio of a mixture based on the VBS. The assumption being, that the formation of a cluster is driven by volatility alone and detailed chemical structure is statistically similar enough across the mixture of vapors. In section 3.3, the authors introduce a gain to describe nucleation efficiency, motivating it in part with different functional groups and the resulting different bonding situation. Is the chemical nature of a mixture and its influence on nucleation something that could be parametrized using the approach presented in this manuscript if enough comparable experimental datasets would be available?**

180 In our opinion this boils down to the discussion that the free energy of evaporation for the dimers is somewhere between a factor of 2 and 3 lower than the free energy of vaporization of the bulk (sub-cooled) liquids. The difference between a factor of 2 and a factor of 3 is vast. Ultimately, the “VBS gestalt” is that if the mixture is sufficiently rich, average properties such as those presented here will likely be more accurate than (somewhat randomly selected) specific properties for one or two surrogate molecules. Put another way, we *agree* that nucleation is a rare phenomenon that selects
185 for special properties of the nucleating mixture, but at the end of the day we assert that the best guess for that special property (absent acid-base reactions) is the vapor pressure itself.

- **I. 231 should read ‘sensitive to the chemical identity’**

Done.

- 190
- **I. 368 the minimum is could as well be outside this window, above 278 K or below 263 K, right? More to that point, the measurements seem to have large uncertainties. Did the authors attempt to apply the temperature dependence to estimate the nucleation rate from the chemical composition experiments at another temperature? I understand this might inflate the manuscript too much, but maybe an example case could help to understand how different the chemical composition actually contributes to the nucleation rate.**

195 The minimum (or a minimum) could well fall outside this temperature range, but we observe a minimum within it, and the model confirms this minimum. In fact, it is almost certain that the nucleation rate will go through a maximum at some higher temperature, though use of the ULVOC concentration for the independent variable makes this a little less obvious. It is just true that both the data and the theory show a minimum in the (neutral) nucleation somewhere between 263 and 243 K. Here we are taking the published experimental results as a given – it was the job of the authors then (admittedly including many of the authors here) as well as the reviewers then to vet those results. That is not to assert that
200 our work is absolved of any discussion of uncertainty. Instead, we do this parametrically (for example by considering the performance of the model with different vaporization enthalpy parameterizations). We are simply not claiming that the specific parameters here are “correct”, only that they result in a pleasing correspondence with the published nucleation rates. Somewhere down the line we may have a sufficiently robust dataset to try to find values that deserve a rigorous error analysis.