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Atmospheric Chemistry and Physics Discussions

Interactive comment on "From quantum chemical formation free energies to evaporation rates" *by* I. K. Ortega et al.

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We want to thank the referee for the useful discussion.

Once again, we agree with the referee. The steric hindrance will be larger in the case of collisions of two clusters which both contain DMA molecules. Experimental studies (Okada and George 1999, Mulcahy et al. 2000) show how the sticking coefficient of DMA to different surfaces (initially 0.7) decreases dramatically when a monolayer of DMA is formed on the surface. When DMA forms hydrogen bonds with the surface, it uses the N-H functional group. As a result, both of the methyl groups point upward from the surface. After the first monolayer is formed, the next molecules colliding with the surface therefore encounter a layer of non-polar and very weakly bonding methyl groups, so the chances of bonding to it decreases dramatically. We can see some

clear parallels to our clusters. If we have enough DMA molecules interacting with each sulfuric acid molecule, the next DMA colliding won't have any other place to bind but the methyl groups, and that will lead to a very weak interaction, and probably to a non-sticking collision. (As a side note, the DMA evaporation rates from such clusters will also be relatively high, so this may not be crucial in terms of the final cluster distribution.) Probably this will be a major effect when enough DMA molecules per sulfuric acid are present in the cluster. Just by inspecting the geometries of different clusters (figure 1r), is easy to see how this will have a major effect in collisions involving clusters like H2SO4((CH3)2NH)3 or H2SO4((CH3)2NH)4 , but is hard to say how big will be the effect for (H2SO4)2((CH3)2NH)2 collisions, since there are still two free (and quite easily accessible) hydrogen atoms for forming new H-bonds. A study of how the sticking factor depends on the DMA-sulfuric acid ratio in the cluster would certainly be interesting, but as we do not currently have any information about sticking factors of our clusters, we have modified the text again to add a further note of caution about this issue.

"Steric hindrance can have some effect in the case of collisions with DMA molecules or DMA – containing clusters, since the molecule contains two methyl groups which do not participate in hydrogen bonding. The effect of this on the overall sticking factor is likely to be small for clusters with a small number of DMA molecules compared to the number of sulfuric acid molecules. For clusters with the same amount of DMA and sulfuric acid molecules, the steric hindrance may be higher. In the case of clusters containing more DMA than sulfuric acid molecules, the steric hindrance may become an important issue. In any case, clusters containing more DMA than sulfuric acid molecules are not thermodynamically stable, so the error associated with assuming a sticking factor of one for all clusters will likely be smaller than the error associated with the calculation of formation free energies."

References

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Interactive comment on Atmos. Chem. Phys. Discuss., 11, 27327, 2011.

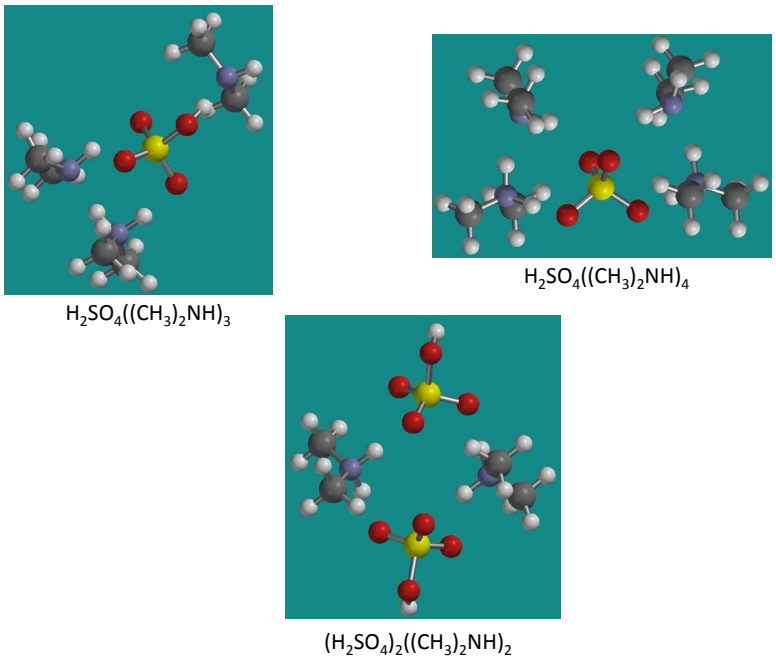

Figure1r, structure of clusters with differen DMA/H_2SO_4 ratio

Fig. 1.