We thank the referee for the constructive comments, which are added in full below (in black font). Our replies are given in blue font directly after the comments; text that has been added to the manuscript is shown in red font.

Anonymous Referee #3

In this study, formation rates published by Almeida et al. (2013) for ternary sulfuric acid (SA) nucleation with dimethylamine (DMA) in the CLOUD chamber are re-analyzed with a method that takes into account self-coagulation. The authors argue that particle formation rates at 1.7 nm are more than a factor of 10 higher than those reported by Almeida et al. (2013), which would imply that SA-DMA new particle formation is significant at lower DMA gas-phase concentrations than previously thought. The revised formation rates agree well with rates calculated by a kinetic aerosol model at different particle diameters. Therefore, the authors conclude that nucleation for the conditions studied here proceeds at rates that are collision-controlled.

General comments:

I think this manuscript is well written and contains some interesting results and conclusions that makes it suitable for publication in ACP. However, since the manuscript focuses mainly on a re-evaluation of particle formation rates from the paper by Almeida et al. (2013), I think more information needs to be given on the approach used by Almeida et al. for extrapolating their formation rates. I suggest that the authors add a schematic diagram or a table illustrating how 1) Almeida et al. have calculated their formation rates and 2) how the authors of the present study have calculated their formation rates. Such a diagram should also include information on what instruments were used when deriving the particle formation rates, and the necessary corrections. For instance, the authors state on lines 335-338 that Almeida et al. (2013) made an extrapolation from 3 to 1.7 nm when deriving their formation rates at 1.7 nm. How was this extrapolation done?

Furthermore, the authors of the present study use data from the smallest SMPS size channel to calculate the formation rate. As the authors admit on lines 344-345, “the smallest SMPS size channels need to be corrected by large factors to account for losses and charging probability, which introduces uncertainty”. How were these corrections made, and how large were the corrections relative to the actual measured number concentrations? In addition, the authors assume on line 366 that the growth rate is independent of size which adds more uncertainty. How large are these uncertainties compared to the “error” resulting from the extrapolation method used by Almeida et al. (2013)?

Another general comment I have is related to the fact that there is another recent study focusing on nanoparticle growth for the SA-DMA system in the CLOUD chamber by Ahlm et al. (2016), where most authors of this manuscript were co-authors. In that study, model simulations and measurements with three different instruments indicated an increasing particle-phase DMA/SA molar ratio with increasing particle size due to a decreasing Kelvin-effect of DMA with increasing size, from ~1.5 to 20 nm. The results of that study appear, at least to this reviewer, to be inconsistent with the view provided in this manuscript that nucleation and growth up to ~80 nm are completely collision-controlled. I think there needs to be some explanation, or at least, discussion of this issue.

The first comment refers to the different methods used by Almeida et al. (2013) and in the present study. To add further information regarding the Almeida et al. (2013) method was requested also by reviewer 2 (comment 9). To address this comment, the following paragraph was added to section 2.3:

"The method introduced here explicitly takes into account losses that occur between particles with d_{p1} and d_{p2} (self-coagulation). These losses have not been taken into account by Almeida et al. (2013). Almeida et al. (2013) derived $J_{3.2nm}$ from CPC and SMPS measurements by including the corrections for wall loss, dilution and coagulation above 3.2 nm (see also Kürten et al., 2016a). However, the extrapolation to 1.7 nm was made by using the Kerminen and Kulmala equation (Kerminen and Kulmala, 2002), which does not include the effect of self-coagulation. For the system of sulfuric acid and dimethylamine, where a significant fraction of particles reside in the small size range, this process is, however, important."

We think this additional information sufficiently addresses the first part of the question and would therefore not like to add another figure to illustrate the methods.

SMPS measurements and uncertainties:

The second part of the comment addresses the SMPS measurements and the uncertainties in the Almeida et al. (2013) and the present study (especially related to the uncertainty in the growth rate).

The SMPS measurements, including the necessary corrections, are further described in the context of comment 2 (see further below).

When discussing uncertainties and errors it is important to note that Almeida et al. (2013) neglected an important process in their derivation of new particle formation rates. When particles grow from small sizes to larger sizes they are subject to several loss processes. For a chamber experiment such as CLOUD three loss processes are important: 1) coagulation, 2) wall loss, and 3) dilution. Due to these losses, the particle number concentrations (and the formation rates) decrease with particle size. Therefore, when retrieving formation rates at small diameters (d_{p1}) from measurements made at larger sizes (d_{p2}), the loss processes need to be accounted for. While Almeida et al. (2013) considered, in principle, all three loss processes; coagulation was only considered with the particles larger than d_{p2}. However, since a large fraction of particles reside in the size range between d_{p1} and d_{p2} for the sulfuric acid-dimethylamine system, their coagulation (self-coagulation) needs to be taken into account as well. The Kerminen and Kulmala equation (Kerminen and Kulmala, 2002) that was used for the correction by Almeida et al. (2013) does, however, not include this effect. This leads to a significant underestimation of the formation rates at J_{dp1} ($J_{1.7nm}$). For this reason, the method from Almeida et al. (2013) could not yield accurate formation rates, which was not known, however, at the time when the analysis was performed (see also comment 2) by referee #2). The differences between the formation rates from Almeida et al. (2013) and the ones calculated with the reconstruction method (section 2.3) can be as high as a factor of 50 (see Fig. 1).

In contrast, the error on the formation rates J_{dp1} ($J_{1.7nm}$) from the method in the present study is not of a systematic nature but is rather due to the uncertainties in the required parameters such as the growth rate. The error on the growth rate is ±20%. On the other hand, the growth rate size-dependency found for kinetic nucleation is relatively small in the relevant diameter range

(Kürten et al., 2015a). Therefore, the systematic error caused by this effect does not cause significant deviations. For a sulfuric acid concentration > 2×10^6 cm^{-3} and collision-controlled nucleation the size dependent growth rate leads to factor of less than 2 uncertainty (Kürten et al., 2015a), which is much smaller than the factor of 50 due to the use of an incomplete method.

Comparison to Ahlm et al. (2016):

The Ahlm et al. (2016) study showed that the small particles (< ~5 nm) grow by maintaining a 1:1 ratio between base and acid. At least that is the result of the MABNAG model that was used in their study. The APi-TOF and CI-APi-TOF measurements for the charged and neutral clusters support this assumption since the number of acid and DMA molecules do roughly match each other up to a size of ca. 2 nm (see also Almeida et al., 2013; Kürten et al., 2014; Bianchi et al., 2014). For the larger particles (d_p > 5 nm) and high amine mixing ratios (above ca. 40 pptv) the MABNAG model predicts base to acid ratios between 1.5 and 2, i.e., the particles are rather dimethylaminium-sulfate (2:1 ratio) than dimethylaminium-bisulfate (1:1 ratio. The Ahlm et al. (2016) simulation therefore predicts a transition from a 1:1 to a 2:1 ratio when DMA is sufficiently high and the particles reach > 5 nm.

The model used in the present study makes use of the assumption that a 1:1 ratio between base and acid is maintained over the full size range. In order to test how the predicted size distribution would change for a 2:1 ratio, this scenario was modeled and the results are shown in the revised version of the manuscript (new panel in Fig. 2, panel c). As expected, the results for the 2:1 ratio simulation indicate a somewhat faster growth. However, the effect is relatively small and makes the comparison between measured and simulated size distribution less good compared to the base-case scenario (1:1 ratio between base and acid). Therefore, we do not think that from the perspective of the kinetic model it makes a significant difference whether a 1:1 or a 2:1 ratio is assumed. As for the new particle formation rates, these are almost certainly better represented by the 1:1 ratio because there is direct evidence from the measurements with the mass spectrometers that the clusters and small particles maintain this ratio up to ~2 nm.

The following discussion was added to section 4:

"It is not yet clear what exact base to acid ratio the particles have for a given diameter. The clusters and small particles (< ~2 nm) seem to grow by maintaining a 1:1 ratio between base and acid, which follows from measurements using mass spectrometers (Almeida et al., 2013; Kürten et al., 2014; Bianchi et al., 2014). The larger particles could eventually reach a 2:1 ratio between base and acid, especially at the DMA mixing ratios relevant for this study (Ahlm, et al., 2016). However, even when a 2:1 ratio is assumed in the model (Fig. 2c) the expected size distributions would not change significantly compared with the base-case scenario (1:1 ratio). Therefore, it is not possible from our comparisons to find out if and at what diameter a transition from 1:1 to 2:1 base to acid ratio takes place."

Specific comments:

1. In the Almeida et al. (2013) paper, the ACDC model reproduced ternary SA-ammonia formation rates almost perfectly, but somewhat over-predicted ternary SA-DMA formation rates compared to observations in the CLOUD chamber. I think it could be worth mentioning that the conclusion within this manuscript, that ternary SA-DMA formation rates in the CLOUD

chamber were underestimated by Almeida et al., brings the formation rates much closer to predictions by the ACDC model.

We thank the referee for pointing this out. We have added the lines from the ACDC calculation in Almeida et al. (2013) to Fig. 1 for a comparison.

Furthermore, the following discussion was added to section 3.3:

"The higher formation rates are also consistent with calculations from the ACDC (Atmospheric Cluster Dynamics Code) model (McGrath et al., 2012) that were previously published in Almeida et al. (2013). Figure 1 shows the rates calculated by the ACDC model (black lines). It should be noted that these values refer to a mobility diameter of 1.2 to 1.4 nm and therefore, somewhat higher rates are expected due to the smaller diameter compared to $J_{1.7\mathrm{nm}}$. However, the agreement between the measured and predicted rates from ACDC are now in much better agreement than before."

2. Sect. 2.1: Please describe the SMPS measurements including corrections.

The differential mobility analyzer used for the SMPS measurements is a home-built instrument with a Kr^{85} neutralizer. The corrections required to retrieve the true particle number density for each of the size channels take into account a) the charging efficiency of the particles and b) the diffusion losses within the sampling lines, charger and the differential mobility analyzer as a function of the particle diameter.

The first correction (charging efficiency) yields a factor of ~50, while the second correction (transmission efficiency) requires a factor of ~3.6 for the smallest diameter (4.3 nm). The values for the charging efficiency can be determined from Wiedensohler and Fissan (1988) and the transmission can be calculated from Karlsson and Martinsson (2003) using an effective length of 8.1 m and a flow rate of 1.5 liters per minute for this SMPS system.

The following was added to section 2.1:

"The SMPS uses a differential mobility analyzer built by the Paul Scherrer Institute; it includes a Kr^{85} charger to bring the particles into a charge equilibrium before they are classified. The retrieval of the particle size distributions requires corrections for the charging and the transmission efficiency, which were performed according to the literature (Wiedensohler and Fissan, 1988; Karlsson and Martinsson, 2003)."

3. Line 35: The word "advanced" is not very useful for the reader. It is better to try to explain as clearly as possible the difference between the approach used here and the method used by Almeida et al.

In principle, we agree. However, in the abstract we would not like to include too many details about the method. Therefore, the information that it is currently provided:

"…due to earlier approximations in correcting particle measurements made at larger detection threshold."

should be sufficient. However, further information about the method used by Almeida et al. (2013) was added to the end of section 2.3.

4. Line 40: “modeled and measured size distributions show good agreement”. I think it should be mentioned that this was for one nucleation event that you studied in detail, unless you have analyzed other events as well.

Other events were tested as well and the comparison between model and measurement yielded similar results. The one nucleation event that was studied in further detail (Fig. 2) was chosen because it was one of the longest ones (duration of ~6h) and it was carried out at relatively high sulfuric acid concentrations. Therefore, the particles could grow to large diameters and the comparison between model and experiment covered a wide size range.

The following information was added to section 3.4:

“Comparison between modeled and measured size distributions yielded similar results for other experiments from CLOUD7. However, the experiment shown in Fig. 2 was carried out over a relatively long time (6 h) at high sulfuric acid concentrations. Therefore, the particles could grow to large diameters and the comparison between model and experiment covers a wide size range.”

5. Lines 137-138: To what extent was dimethylamine oxidized by OH within the chamber during these events? Were any oxidation products detected and may these have contributed to new particle formation?

To answer this question we will first estimate the expected OH concentration during the experiments (we refer to the experiment shown in Fig. 2):

The sulfuric acid monomer production rate is

$$P_1 = k_{OH+SO2} \cdot [OH] \cdot [SO_2] \qquad (1)$$

Using a value of $P_1 = 2.9\times10^5$ cm^{-3} s^{-1} (see section 3.4), $k_{OH+SO2} = 9\times10^{-12}$ cm^3 s^{-1} (Atkinson et al., 2004) and $[SO_2] = 1.5\times10^{12}$ cm^{-3} (60 ppbv of SO_2 were used in the experiment) the estimated OH concentration is 2.1×10^4 cm^{-3}.

This value of OH can be used to estimate the concentration of products from the reaction between DMA and OH (assuming steady-state conditions):

$$C_{DMA+OH\ products} = \frac{k_{OH+DMA} \cdot [OH] \cdot [DMA]}{k_w} \qquad (2)$$

Here it is assumed that the products are “sticky”, i.e., they are irreversibly lost to the chamber walls with the rate k_w. The DMA mixing ratio (concentration) is 40 pptv (1×10^9 cm^{-3}), the reaction rate between OH and DMA is 6.5×10^{-11} cm^3 s^{-1} (Carl and Crowley, 1998) and the wall loss rate is 2×10^{-3} s^{-1}. This results in a concentration of the products of 7×10^5 cm^{-3}.

Compared with the concentration of DMA (1×10^9 cm^{-3}), the concentration of the products is less than one per mille; compared with the sulfuric acid monomer the products amount ca. 7%.

In fact, if the products would contribute to nucleation and growth, this would even lower their concentration since an additional loss term in the denominator of equation (2) would need to be included. The low concentrations of the DMA oxidation products should therefore rule out a significant contribution to aerosol nucleation and growth during CLOUD.

This is further supported by the fact that no DMA oxidation products were detected in the sulfuric acid clusters measured by the CI-APi-TOF.

In the atmosphere, [OH] can be a factor of ~100 times higher than in the current study. This can lead to higher concentrations of oxidation products of DMA. However, as these products were not observed in CLOUD we have no evidence of their impact on nucleation on growth.

6. Line 321: How high is “relatively high”, and how do the authors know there was no sulfuric acid in the chamber? Do the authors think this is a general problem with using a CIMS for measuring sulfuric acid?

The sulfuric acid background was sometimes higher than 1×10^{6} cm^{-3}, while it is usually in the range of 1×10^{5} cm^{-3} for the CIMS instrument. During the DMA experiments in CLOUD 7 there was, however, an instrumental problem with the CIMS, which caused the high background. The measurements made with the CI-APi-TOF verified that the high background was not real, i.e., it did not originate from the CLOUD chamber. This is now mentioned in section 3.1 and the value of the high sulfuric acid background is provided. In principle, however, the CIMS is a great instrument that measured H_2SO_4 reliably during many CLOUD experiments.

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