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Heterogeneous chemistry involving methanol in tropospheric clouds

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[1] In this report we analyze airborne measurements to suggest that methanol in biomass burning smoke is lost heterogeneously in clouds. When a smoke plume intersected a cumulus cloud during the SAFARI 2000 field project, the observed methanol gas phase concentration rapidly declined. Current understanding of gas and aqueous phase chemistry cannot explain the loss of methanol documented by these measurements. Two plausible heterogeneous reactions are proposed to explain the observed simultaneous loss and production of methanol and formaldehyde, respectively. If the rapid heterogeneous processing of methanol, seen in a cloud impacted by smoke, occurs in more pristine clouds, it could affect the oxidizing capacity of the troposphere on a global scale. *INDEX TERMS*: 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry. **Citation**: Tabazadeh, A., R. J. Yokelson, H. B. Singh, P. V. Hobbs, J. H. Crawford, and L. T. Iraci (2004), Heterogeneous chemistry involving methanol in tropospheric clouds, *Geophys. Res. Lett.*, *31*, L06114, doi:10.1029/2003GL018775.

1. Introduction

[2] After methane, methanol (CH₃OH) is the second most abundant organic trace gas in the Earth's atmosphere [Singh *et al.*, 2000, 2001]. In the troposphere CH₃OH reacts directly with OH in the gas and aqueous phases, contributing to sources of reactive species such as formaldehyde (HCHO), ozone and hydrogen radicals. Currently, the sources and sinks of methanol are not well understood [Singh *et al.*, 2000; Heikes *et al.*, 2002; Galbally and Kirstine, 2002]. The mass of methanol lost in the atmosphere due to gas and aqueous phase OH oxidation is estimated to be ~100 and ~10 Tg/year [Heikes *et al.*, 2002], respectively, which is smaller than the total estimated source. According to these estimates, the lifetime of methanol in the atmosphere is primarily controlled by gas phase

oxidation. Below the possibility of a heterogeneous sink for methanol is explored.

2. Measurement Summary

[3] The SAFARI 2000 (S2K) field project employed a combination of ground, airborne, and satellite instruments to study the atmospheric effects of biomass burning [Hobbs *et al.*, 2003]. The mixing of clouds and smoke was common during the S2K experiment (see auxiliary photos¹). The bottom figure in the auxiliary file shows a smoke plume mixing with a capping cumulus cloud on August 18, 2000. The latter situation provides a unique opportunity to explore how various trace gases, particularly oxygenated organics, interact with clouds.

[4] A number of trace gases were measured with an airborne FTIR (AFTIR) instrument [Yokelson *et al.*, 1999, 2003a] during the S2K field experiment. Laboratory studies indicate that the inlet has a good passing efficiency for a large number of molecules, including CH₃OH, HCHO, and C₂H₄ [Yokelson *et al.*, 2003b]. Most reactive and stable trace gases present above 5–20 ppbv (e.g., the CH₃OH detection limit is ~5 ppb) were measured by the AFTIR.

[5] On August 18, 2000 the University of Washington's Convair-580 aircraft penetrated a fresh biomass-burning plume at various altitudes below and within a capping cumulus cloud. The AFTIR measured rapid loss and production of CH₃OH and HCHO, respectively, which correlated with increased exposure to the cloud [Yokelson *et al.*, 2003a]. Isolated, and cloud-free, plumes from three other fires were sampled at different stages in their evolutions, ranging in age from 5–45 minutes, but no significant changes of CH₃OH and HCHO were detected in these cases [Yokelson *et al.*, 2003a; Hobbs *et al.*, 2003]. This is consistent with the stability of these two compounds for the first 2–3 hours of "cloud-free" smoke aging for a biomass fire observed in Alaska [Goode *et al.*, 2000].

[6] The smoke plume was penetrated and sampled at three altitudes: once below the cloud, and twice within the cumulus cloud at different altitudes above the cloud base (Table 1). We assume that the degree of cloud processing of the smoke increases with altitude above the cloud base. From the rate of the observed ozone recovery in the smoke [Yokelson *et al.*, 2003a], the horizontal dimensions of the cloud (~3 km), the measured horizontal windspeed ($5 \pm 1 \text{ m s}^{-1}$), and typical updraft velocities (~1–2 m s⁻¹), we can estimate how long the smoke sampled was cloud-processed. The results are summarized in Table 1. We use CO as a conserved tracer to account for the dilution of

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Table 1. Observations of Chemical Changes Due to Cloud Processing of Smoke^a

Sample	H(m)	Excess Mixing Ratio (ppb)				
		CH ₃ OH	HCHO	NO ₂	NO	CO
1	1945	68 (0.0135)	102 (0.0202)	191 (0.0379)	185 (0.0367)	5043
2a	3866	36 (0.0135)	54 (0.0202)	101 (0.0370)	98 (0.0367)	2663
2b	3866	15 (0.0056)	59 (0.0222)	86 (0.0323)	122 (0.0458)	2663
2c	3866	-21	+5	-15	+24	2663
3a	4166	30 (0.0135)	45 (0.0202)	84 (0.0379)	81 (0.0367)	2215
3b	4166	< 5	76 (0.0343)	58 (0.0262)	121 (0.0546)	2215
3c	4166	-25 to +31		-26	+40	2215

^aExcess mixing ratio (EMR) is defined as ppbv in the smoke minus ppbv in the background. Numbers in parentheses are dimensionless quantities, which are obtained by dividing the species EMR by the CO EMR. Sample 1 gives the EMR measured below the cloud base in a diluting column. Trace gas-to-CO ratios in sample 1 (cloud free) provide the benchmark for detecting chemical changes in samples 2 and 3, which were taken after the smoke intersected a cumulus cloud. 2a and 3a give the calculated EMR at different heights, due to dilution only, which were obtained by multiplying trace gas to CO ratios in sample 1 by the EMR of CO in samples 2 and 3, respectively. 2b and 3b give the measured EMR after ~ 3 and ~ 10 mins of smoke exposure to the cloud, respectively. 2c and 3c give the inferred chemical changes (sample (b)-sample (a)) due to cloud processing of the smoke. AFTIR precision and calibration accuracy are better than 1% and 5%, respectively (1σ). The detection limits, which dominate the uncertainty (2σ) in this data are: CH₃OH and CO (~ 5 ppbv); NO, NO₂, and HCHO (15–20 ppbv).

the smoke [Hobbs *et al.*, 2003]. The CH₃OH gas-phase concentration measured by the AFTIR in the lowest in-cloud sample (sample 2) was not close to 36 ppb, which would occur from dilution alone, but was 15 ppb after only ~ 3 minutes of exposure to cloudy conditions (Figure 1). After ~ 10 minutes of exposure (Table 1, sample 3), the methanol concentration was below the AFTIR detection [Yokelson *et al.*, 1999, 2003a].

3. Gas- and Aqueous-Phase Oxidation

[7] Biomass burning emits large quantities of chlorine species into the atmosphere [Li *et al.*, 2003]. We performed some simple calculations to explore the possibility of oxidation chemistry involving chlorine radicals. A drop in CH₃OH concentration by more than one-half in ~ 3 mins (Figure 1) requires a steady state concentration of Cl in the gas phase of $\sim 7 \times 10^7 \text{ cm}^{-3}$ (rate constant for Cl reaction with CH₃OH is $5.5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$) [Atkinson *et al.*, 1997]. At such high Cl levels, C₂H₄ oxidation would have been complete, since it reacts with Cl about 5 times faster than methanol (rate constant for C₂H₄ reaction with Cl is $3 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$) [Atkinson *et al.*, 1997]. Clearly, this did not happen since no significant loss in C₂H₄/CO ratio was measured with the AFTIR during even the first 10 mins of exposure to the cloud [see Yokelson *et al.*, 2003a, Table 1]. In addition, in cloud-free smoke, produced by another fire in the same region, the rate of oxidation in the gas phase for a large number of species was consistent with OH chemistry [Hobbs *et al.*, 2003].

[8] Having ruled out chlorine chemistry, the rapid decrease in the CH₃OH concentration cannot be explained by “standard” gas and aqueous phase chemistry (see Appendix A in the auxiliary file, reactions 1–4). In 3 mins (Figure 1), less than 0.1 ppb of CH₃OH can be lost through gas-phase reaction with OH. The maximum aqueous phase loss, where we assumed water droplets to be in thermodynamic equi-

librium with the gas phase, can account for only ~ 7 ppb loss of CH₃OH in 3 mins. In fact, more than 3 times as much CH₃OH was lost during this time period (Table 1). Overall, measurable loss through bulk aqueous phase chemistry is highly unlikely due to mass transport limitations, since significant gas transfer into the bulk of water droplets cannot occur in 3 to 10 mins of exposure [Jacob, 1986] (see auxiliary file (Appendix A), for more details). Below we propose a few plausible heterogeneous chemical processes involving OH and NO₂ that may help to explain the rapid loss of gaseous CH₃OH in the cloud.

4. Possible Heterogeneous Reactions

[9] Here we use the measured rate of change in the CH₃OH gas phase concentration, as well as typical microphysical properties of cloud drops, to determine a pseudo first-order rate constant for methanol reaction on cloud droplet surfaces. In deriving the pseudo first-order rate constants below, we assumed only the gas phase supplied the oxidant to the surface of cloud drops. However, in reality, the steady state oxidant concentration at the surface is also affected by supply from the bulk phase as well as possible in situ conversion mechanisms at the surface (e.g., the reaction of O(¹D) with surface water to produce in situ OH). Some recent molecular dynamics simulations suggest that the OH concentration is enriched at the interface of aqueous salt solutions [Roeselova *et al.*, 2003]. Whether this conclusion applies to water droplets in clouds requires

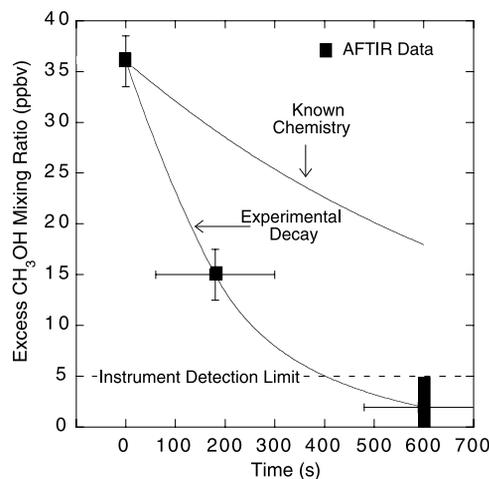


Figure 1. The measured chemical decrease in the CH₃OH gas-phase concentration as a function of exposure time to the cloud. The AFTIR data point at time zero gives the CH₃OH concentration just below the cloud base. The error bars indicate the range of measurement uncertainties. The upper line shows the maximum calculated decrease in the CH₃OH gas-phase concentration based on known aqueous phase chemistry since the gas phase loss due to the reaction with OH is negligible. The lower line shows a fit to the experimental data. The experimental decay curve was used to derive a range of possible heterogeneous rate constants, which are given in the auxiliary file (Appendix A). See caption to Table 1 and the auxiliary file (Appendix A) for more details.

further investigation. However, it is beyond the scope of this paper to distinguish what processes may have contributed to the oxidant concentration at or near the surface.

[10] The most likely heterogeneous process to consider here is the reaction of adsorbed CH_3OH with OH:



This heterogeneous process may also help to explain why a rapid production of HCHO was simultaneously observed in the cloud (Table 1). Laboratory measurements indicate that CH_3OH on dry ammonium sulfate surfaces (relative humidity (RH) $\sim 35\%$) can react with OH to yield formaldehyde [Oh and Andino, 2000, 2001]. According to these measurements, the rate of gas phase methanol reaction with OH is enhanced by about 30% in the presence of dry ammonium sulfate surfaces at $\sim 35\%$ RH. However, no yield for CH_3OH reaction with OH on dry ammonium sulfate was measured at $\sim 3\%$ RH [Sorensen *et al.*, 2002]. Since the RH conditions were different in the above experiments, we suspect that the rate of this reaction may have a dependence on the RH and/or the physical phase of the particles. In the Sorensen *et al.* study, it was assumed that OH was only supplied to the surface from the gas phase. While this assumption may hold at 3% RH, at higher RHs other mechanisms (noted above) may also supply OH to the surface of particles, thereby enhancing the overall rate of this surface oxidation process. More experimental work is needed to investigate whether the above reaction can occur at a faster rate on cloud drop surfaces.

[11] To obtain a pseudo first-order rate constant for the heterogeneous CH_3OH reaction with OH, the measurements shown in Figure 1 were used. Assuming a constant concentration for gas phase OH in the smoke ($[\text{OH}] = 2 \times 10^7 \text{ cm}^{-3}$) [Hobbs *et al.*, 2003], the change in the CH_3OH gas-phase concentration can be calculated from,

$$\ln \frac{[\text{CH}_3\text{OH}]_f}{[\text{CH}_3\text{OH}]_i} = -[k_g + k_{aq}^* + k_{het}^{\text{OH}}][\text{OH}]_g \Delta t$$

where, $[\text{CH}_3\text{OH}]_i$ is the expected concentration of CH_3OH in sample 2 (~ 36 ppbv), and $[\text{CH}_3\text{OH}]_f$ is the measured concentration of CH_3OH in sample 2. We set $[\text{CH}_3\text{OH}]_f = 15$ ppbv and $\Delta t = 180$ s (see Table 1) to derive a value for the rate of this heterogeneous process (k_{het}^{OH}) at -5°C . The rest of the parameters in the above equation are constant and are given in the auxiliary file (Appendix A).

[12] The normalized pseudo first-order heterogeneous rate constant obtained here ($\sim 3.7 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1} \text{ cm}$, see Appendix A in the auxiliary file) is about 300 times larger than the gas-phase rate constant for the conditions sampled in this cloud ($S = 0.0063 \text{ cm}^2 \text{ cm}^{-3}$, where S is the surface area of cloud droplets per unit volume of air). Although this relative increase appears to be too large, it is perhaps more useful to compare the heterogeneous and aqueous phase loss rates to assess whether the inferred rates derived here are plausible. To do so we analyze the loss rates calculated and measured for sample 2 (Table 1). The maximum aqueous phase methanol loss for sample 2 is 7 ppb (Figure 1). On the other hand, the observed loss for

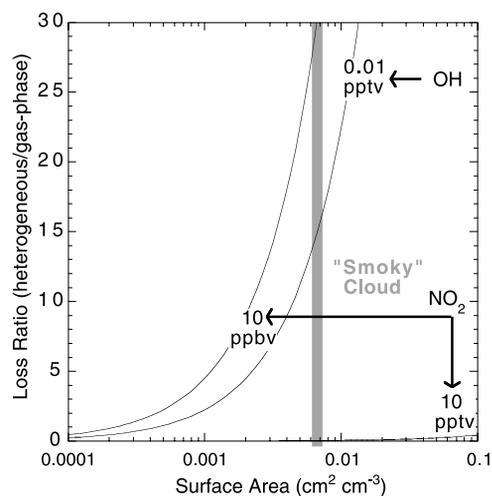
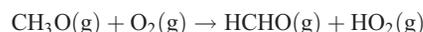
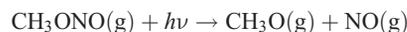
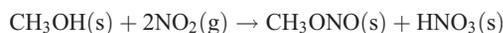


Figure 2. The ratio of heterogeneous-to-gas phase loss of CH_3OH as a function of surface area of cloud drops for an assumed range of oxidant concentrations. The gas-phase and heterogeneous rate constants used in the calculations are given in the auxiliary file (Appendix A). The heterogeneous loss is calculated for a period of 1 h (rate = $1 \times k_{het} \times S$ [oxidant] [CH_3OH]). The gas phase loss is calculated for a period of 24 h (rate = $24 \times k_{gas}$ [OH] [CH_3OH]). Gas-phase OH concentration was set to 10^6 cm^{-3} for all calculations. See text for more details. The surface area of the particles in the cloud affected by smoke, which was sampled on August 18, 2000, is indicated on the plot by the shaded vertical line.

sample 2 is 21 ppb (Table 1), indicating that the heterogeneous loss is ~ 3 times faster ($21/7$) than the maximum aqueous phase loss. In a recent study, the reaction of $\text{Cl}_2^{\bullet-}$ radical anion with ethanol was found to be at least two times faster at the air-water interface than in the bulk [Strekowski *et al.*, 2003]. Thus the inferred loss rate calculated here for the methanol reaction with OH on the cloud surface is consistent with current information (admittedly limited) on reactions of radicals with small alcohols on aqueous surfaces.

[13] Another possible heterogeneous process is the reaction of adsorbed methanol with gas phase NO_2 :



where methyl nitrite (CH_3ONO) photolyzes in the gas phase, as shown above, to yield NO and formaldehyde. Taylor *et al.* [1980] showed that the photochemical lifetime of CH_3ONO is nearly independent of altitude and is ~ 2 mins. Laboratory studies indicate that the reaction of CH_3OH with NO_2 is enhanced catalytically on various surfaces, including stainless steel, Pyrex and smog chamber walls [Takagi *et al.*, 1986]. We used pseudo first-order kinetics to derive a normalized rate constant ($\sim 4.3 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1} \text{ cm}$, see Appendix A in the auxiliary file) for the CH_3OH reaction with NO_2 . The procedure used is identical to that described above for the reaction with OH.

[14] Of the two reactions proposed above, the OH reaction is more plausible since methanol loss ($\sim 25\text{--}30$ ppb) and HCHO production in sample 3 (31 ppb) are nearly identical (see Table 1). However, the measurements seem to indicate that NO_2 and methanol were consumed as NO and HCHO were produced in the cloud (Table 1), which provides some support for the NO_2 surface reaction.

5. Atmospheric Implications

[15] In Figure 2 the ratio of heterogeneous-to-gas phase loss of CH_3OH is shown using the rate constants given in Appendix A for typical ranges of oxidant concentrations. The heterogeneous loss is calculated assuming that an air mass spends on average ~ 1 h in cloudy air each day [Jacob, 1999]. The gas phase loss is calculated for 24 h. If the heterogeneous rate constants derived in this work from field data are applicable to the global troposphere, then clouds can provide a major sink for gas-phase CH_3OH through reaction with OH. For the NO_2 reaction, the effect could be significant only for polluted conditions.

[16] In clouds affected by smoke there might be significant organic coverage on the surface. This might, in turn, promote the methanol uptake and oxidation on the surface. In clouds unaffected by smoke, the surface tension of water droplets is lower than pure water due to organic contamination [Facchini et al., 2000]. Partial or complete organic coatings may provide a more suitable medium for CH_3OH uptake and for reactions to occur in the global atmosphere [Djikaev and Tabazadeh, 2003]. However, the rate of heterogeneous CH_3OH oxidation in the global atmosphere may be lower than that determined here for a “dirty” cloud, since organic layers on aqueous surfaces are probably thicker and more prominent in smoky environments.

[17] Clearly, future targeted laboratory and fieldwork are needed to determine whether the heterogeneous CH_3OH loss, reported here to occur rapidly in a cloud affected by smoke, also occurs in more pristine clouds. The mixing of clouds and smoke is quite common throughout the tropics [e.g., Reid et al., 1998]. If the heterogeneous reactions proposed here occur in cleaner environments, then oxidation of methanol on cloud drops would be a more important process, since methanol and clouds are globally distributed in the Earth’s atmosphere. Thus, heterogeneous oxidation in clouds has the potential to provide a major global source for reactive organic species (e.g., HCHO, CH_3ONO), as well as a sink for CH_3OH .

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