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Atmospheric Chemistry and Physics Discussions

Suppression of chlorine activation on aviation-produced volatile particles

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Abstract

We examine the effect of nm-sized aircraft-induced aqueous sulfuric acid (H_2SO_4/H_2O) particles on atmospheric ozone as a function of temperature. Our calculations are based on a previously derived parameterization for the regional-scale perturbations of the sulfate surface area density due to air traffic in the North Atlantic Flight Corridor (NAFC) and a chemical box model. We confirm large scale model results that at temperatures $T > 210$ K additional ozone loss – mainly caused by hydrolysis of $BrONO_2$ and N_2O_5 – scales in proportion with the aviation-produced increase of the background aerosol surface area. However, at lower temperatures (< 210 K) we isolate two effects which efficiently reduce the aircraft-induced perturbation: (1) background particles growth due to H_2O and HNO_3 uptake enhance scavenging losses of aviation-produced liquid particles and (2) the Kelvin effect efficiently limits chlorine activation on the small aircraft-induced droplets by reducing the solubility of chemically reacting species. These two effects lead to a substantial reduction of heterogeneous chemistry on aircraft-induced volatile aerosols under cold conditions. In contrast we find contrail ice particles to be potentially important for heterogeneous chlorine activation and ozone depletion. These features have not been taken into consideration in previous global studies of the atmospheric impact of aviation. Therefore, to parameterize them in global chemistry and transport models, we propose the following parameterisation: scale the hydrolysis reactions by the aircraft-induced surface area increase, and neglect heterogeneous chlorine reactions on liquid plume particles but not on ice contrails and aircraft induced ice clouds.

1. Introduction

In view of the present and anticipated growth rates of commercial aviation, there is increasing concern about the environmental impact of the associated emissions on atmospheric ozone (O_3) chemistry. While recent assessments concentrated on the re-

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sponse of O_3 to gaseous nitrogen compounds (NO_x) and water vapor (H_2O) emissions (WMO, 1994; Brasseur et al., 1998), aerosols and contrails formed in aircraft exhaust plumes may also play an important role (IPCC, 1999; Kawa et al., 1999). Such particles can significantly enhance the aerosol surface area available for heterogeneous reactions (Hofmann et al., 1998; Anderson et al., 1999). Global model calculations suggest the additional heterogeneous chemistry in the perturbed aerosol layer to have a net O_3-depleting effect (Weisenstein et al., 1998; Pitari et al., 2001). These model calculations indicate that the O_3-depleting effect of aircraft particle emissions depends on temperature (T), with the highest values predicted in the cold regions north of the NAFC. In addition, Weisenstein et al. (1998) show that the impact of aircraft emissions on ozone appears to be sensitive to the size and number densities of the emitted particles at plume breakup (time τ after which the plume can be considered a regional-scale perturbation). However, these simulations did not account for the temperature feedback on particle number densities at plume breakup nor the different chemical reactivity of the nm-sized aircraft particles, compared to the background aerosols of typical size 100 nm, due to the Kelvin effect (exponential decrease of solubility due to surface curvature following $\exp[-\text{const.}/r]$, where r is the particle radius).

In general, the rate of a given heterogeneous reaction, $k \propto \gamma A$, is determined by the reactive uptake coefficient γ and the aerosol surface area density A (in units of $cm^2 cm^{-3}$), both of which depend on T. While the T-dependence of A is independent of the chemical reaction under consideration, that of γ ranges from weak for concentration-independent reactions (e.g. hydrolyses of N_2O_5 or $BrONO_2$) to pronounced for reactions depending on the reactants solubilities, e.g. for $ClONO_2$+HCl (Hanson et al., 1994). Due to the Kelvin effect, the reactive uptake of aircraft particles (subscript a) might be limited in comparison to background particles (subscript b), i.e. $\gamma_a < \gamma_b$. Furthermore, the Kelvin effect limits the solubility of H_2O and HNO_3 and thus the growth of the small particles ($|dA_a/dT| < |dA_b/dT|$). In addition, scavenging losses of aircraft particles may increase as background aerosols grow more readily in cooling air masses. This may significantly reduce the aircraft-induced surface area at

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plume breakup, $A_a(\tau)$, leading to $A_a(\tau) \ll A_b$ at low temperatures. Therefore reliable estimates for liquid surface area perturbations due to air traffic are required that can account for such dependences. Introducing the concept of an "average plume decay time" as a criterion for plume breakup, we have previously derived such estimates of size spectrum and surface area perturbation of the volatile plume particles as a function of air traffic density and background aerosol surface area density (Kärcher and Meilinger, 1998) among other parameters, and employ these results in the present study. Using a stationary photochemical box model (Grooß, 1996; Meilinger et al., 2001), we examine heterogeneous ozone chemistry on aircraft-produced particles as a function of temperature including the Kelvin effect and coagulation processes between aircraft-induced H_2SO_4/H_2O and background particles. Our results apply best to the stratospheric part of the NAFC, where relatively long particle residence times (days to weeks) cause surface area perturbations from subsonic aircraft to be largest (IPCC, 1999). We will show that at cold lowermost stratospheric conditions enhanced scavenging and Kelvin effect render heterogeneous chlorine chemistry on nm-sized aircraft particles largely inefficient. Further, our results allow for a simple parameterization scheme for heterogeneous hydrolysis and halogen chemistry on aviation-produced liquid aerosols suited for implementation in global models.

2. Model description

We employ an extended version (Meilinger et al., 2001) of the Mainz Photochemical Box Model (see Grooß, 1996, for details). Net ozone production rates, $P(O_3)$, are averaged over 24 hours to account for the diurnal cycle, assuming constant latitude (50 °N) and applying the O_3 profile of the U.S. standard atmosphere. The model includes complete diurnal chemistry for NO_y, Cl_y, Br_y, HO_x, O_x, methane, ethane, acetone and their oxidation products. For gas phase reactions, we used the kinetic reaction rates recommended by Atkinson et al. (1999) and DeMore et al. (1997) considering the update by Sander et al. (2000). Photolysis rates were calculated with an update (Becker et al.,

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2000) of the scheme by Lary and Pyle (1991).

More importantly, the model includes heterogeneous reactions of N_2O_5, bromine and chlorine species on liquid and ice particles. The liquid particles are assumed to be composed of aqueous H_2SO_4, which may take up H_2O, HNO_3, HCl, HOCl, HBr and HOBr at sufficiently low temperatures. The new model version accounts for heterogeneous processes on background as well as on aviation-produced aerosols. In the evaluation of heterogeneous reaction rates, we distinguish reactive uptake coefficients and available surface area densities of both particle types.

While background aerosol surface area density is calculated according to Carslaw et al. (1995), the size distribution and surface area density of the aircraft-induced liquid particles are calculated according to the parameterization of Kärcher and Meilinger (1998). Their estimates account for a variety of parameters controlling the aircraft aerosol at the average plume decay time: the conversion of fuel sulfur into ultrafine sulfate particles, the plume mixing with ambient air, and the background aerosol surface area, which – due to uptake of HNO_3 – is T-dependent.

Uptake coefficients, γ_{ij}^{eff}, for heterogeneous reactions of molecules i adsorbed on the surface and reacting with molecules of species j are calculated according to $1/\gamma_{ij}^{eff}(r) = 1/\alpha_i + 1/\gamma_{ij}^{react} + 4\,\mathrm{Kn}/3$, where the first term describes pure physisorption (with the mass accommodation coefficient α_i), γ_{ij}^{react} is the reaction probability of the adsorbed molecules, and the last term describes the case when vapor transport to the particle surface is limited by gas phase diffusion (with the Knudsen number Kn, only important for large particles, i.e. in the case of ice particle formation). While constant γ_{ij}^{react} is assumed for heterogeneous reactions on ice, for liquid phase reactions γ_{ij}^{react} generally depends on the reactants solubilities H_{ij} (Hanson et al., 1994; Peter, 1997). Due to the Kelvin barrier, the solubilites depend exponentially on particle radius ($H_{ij}(r) \propto \exp[-r_{cr}/r]$). This exponential dependence strongly limits the uptake coefficient γ_{ij} for particles smaller than or about equal to the critical radius $r_{cr} = 2\sigma v_{i,j}/(RT)$. Using the typical values $\sigma = 0.08\,\mathrm{J/m^2}$, $v_{\mathrm{HCl}} = 28.56\,\mathrm{cm^3/mol}$,

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$T = 200\,\mathrm{K}$, and $R = 8.314\,\mathrm{JK^{-1}mol^{-1}}$ yields $r_{cr} \simeq 2\,\mathrm{nm}$, which is comparable to the mean radius of aviation-produced liquid particles (Kärcher et al., 2000). We averaged γ_{ij} over the respective size distribution of liquid aerosol particles to account for the fraction of larger particles which dominate the effective uptake.

3. Effects of aviation-produced aerosols on ozone

3.1. Particle scavenging

Depending on the variability of the background aerosol surface area density, A_b, typical ranges of the relative surface area perturbation at the average plume decay time, $A_a(\tau)/A_b$, in the NAFC are 0.03 – 20% for the present subsonic air traffic in the tropopause region (Kärcher and Meilinger, 1998). The magnitude of this perturbation is mainly determined by the size and number concentration of the background particles which scavenge the smaller aircraft particles. The coagulation efficiency becomes strongly enhanced when the background particles grow due to condensation of H_2O and HNO_3 at temperatures below the HNO_3 dew point, T_d (the temperature at which the liquid HNO_3 mass fraction becomes equal to that of H_2SO_4).

Figure 1 shows $A_a(\tau)$ and A_b as a function of T starting with $A_a(\tau)/A_b = 10\%$ at $T = 220\,\mathrm{K}$, which is the value after an average plume decay time of 1–2 days, representative for the traffic density in the NAFC (we use 45.8 h in this study, following Kärcher and Meilinger, 1998). Note that without scavenging by the background aerosols (i.e. allowing only for self-coagulation and dilution of the aircraft aerosols) there would be about 30% more aircraft-derived liquid particles (at 220 K).

At temperatures above T_d (here 205.5 K), surface area densities of background and aircraft aerosols vary only weakly (Fig. 1). However, below T_d the background particles take up H_2O and a substantial fraction of the total HNO_3 (34% at 205 K), yielding larger particles. Consequently, coagulation rates increase and the surface area density of the aviation-produced particles decreases by more than an order of magnitude at 200 K.

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3.2. Kelvin effect

Figure 2 shows the dominant heterogeneous reaction rates k_a and k_b for aircraft (red) and background (green) particles, respectively. It illustrates the leading role of the hydrolysis of $BrONO_2$ (dashed) and N_2O_5 (dotted) at high and moderate temperatures. These reactions are assumed to be independent of the educt solubilities, but depend mainly on surface area densities. Consequently, there is little dependence on T above T_d, and $k_a/k_b \simeq 10\%$, which is in agreement with the surface area ratio. The decrease in k_a below T_d corresponds to the reduction in A_a due to enhanced scavenging (Fig. 1), while the increase of k_b is mainly caused by growth of A_b (but reduced due to the consumption of the educts).

As temperatures approach T_d, however, solubility-dependent chlorine activation gains importance and $ClONO_2$+HCl (solid curves) becomes the most important reaction path. However, due to the Kelvin effect, the solubility of HCl in aviation-induced aerosols remains low, and hence $k_a/k_b < A_a(\tau)/A_b$.

3.3. Ozone destruction on liquid aircraft particles

Figure 3 summarizes these results in terms of net effects on ozone. The black dash-dotted curve in Fig. 3a shows the net ozone production rates $P(O_3)$ for gas phase chemistry only. The green solid curve additionally considers heterogeneous chemistry on the background aerosol (Meilinger et al., 2001). The violet dashed curve and the red circles additionally include the liquid aircraft aerosols, with (red circles) and without (violet dashed curve) the Kelvin effect, while the blue diamonds show the effect after including contrail ice particles assuming number densities and surface areas which correspond to the same degree of entrainment that was assumed for the non-contrail plume. At temperatures above ~ 214 K (corresponding roughly to the zonal mean value at 200 hPa and 50° N), heterogeneous chemistry increases gas phase O_3 destruction by $\sim 500\,cm^{-3}s^{-1}$. At low temperatures ($T < 210$ K) $P(O_3)$ takes on large negative values, which are up to a factor of 20 larger than the gas phase-driven production. This

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is due to heterogeneous activation of chlorine caused by the enhanced solubility of HCl in the liquid background aerosol particles which grow as T approaches T_d.

In contrast, liquid aircraft-induced particles show a completely different temperature effect on O_3 loss than the background particles. Figure 3b contains the same information as Fig. 3a but expressed as the fraction of O_3 change due to heterogeneous chemistry on aviation particles normalized by the heterogeneous effect of the background aerosols only, i.e. $P_a^{het}(O_3)/P_b^{het}(O_3)$, where $P_b^{het}(O_3) = P_b(O_3) - P_{gas}(O_3)$ and $P_a^{het}(O_3) = P_{a+b}(O_3) - P_b^{het}(O_3) - P_{gas}(O_3)$.

At high T, the additional effect of aviation aerosols on O_3 rates is about 10%, close to the size of the surface area perturbation A_a/A_b. Under these conditions, the Kelvin effect becomes unimportant, as the N_2O_5 and $BrONO_2$ hydrolysis reactions are independent of solubilities, but rather are surface contact-driven. At low T, however, the relative impact of H_2SO_4/H_2O particles from aircraft decreases to below 1% when neglecting the Kelvin effect, and even below 0.1% when including the Kelvin effect.

Thus both, temperature-enhanced scavenging and the Kelvin effect limit the relative effect of aviation-produced aerosol on heterogeneous chemistry under cold conditions (Fig. 3b), while O_3 depletion increases by more than two orders of magnitude as T decreases from 210 to 203 K (Fig. 3a). In contrast, under warmer conditions the heterogeneous effect of aviation-produced droplets scales in proportion to the surface area perturbation.

3.4. Ozone destruction on contrail ice particles

In the tropopause region, T_d lies several Kelvin below the ice frost point (T_{ice}), so that freezing and cirrus cloud formation may occur before the air becomes chemically processed by the liquid particles (Kärcher and Solomon, 1999). Persistent contrails form in ice-supersaturated air. This may pave the way for efficient regional-scale heterogeneous chemistry (Borrmann et al., 1996; Kärcher, 1997).

The blue diamonds in Fig. 3 show the effect of ice particles (originating, for example,

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from an aged contrail) on O_3 loss below the frost point at 207.6 K (while all other curves ignore transient or persistent ice formation). The increase of heterogeneous O_3 loss is caused by chlorine activation on ice surfaces and exceeds the effect of supercooled ternary background aerosol by up to a factor of 10. At the same time, the presence of ice diminishes the effect of heterogeneous chemistry on the liquid particles (not shown) due to gas phase dehydration and accelerated scavenging.

In summary, at temperatures below the frost point, enhanced O_3 loss due to additional aircraft-induced chlorine activation on contrails or contrail-cirrus is important; in comparison, chlorine activation due to liquid particles from aircraft emissions can be neglected.

4. Conclusions

We have shown for temperatures $T > 210$ K in the lowermost stratosphere, that the effect of aircraft-induced H_2SO_4/H_2O aerosols on heterogeneous ozone chemistry is dominated by the hydrolysis of $BrONO_2$ and N_2O_5, which – because they are solubility independent – scale directly with the increase of available aerosol surface area. This highlights the importance of reliable estimates of the surface area perturbation in global model simulations.

Relative to background aerosols, the chemical effects of aircraft-emitted volatile particles on atmospheric ozone decreases with decreasing temperature (Fig. 3b). Below the dew point of HNO_3, chlorine activation caused by the new liquid particles is limited by reduced solubilities of reacting gases (Kelvin effect) and by enhanced scavenging losses due to the swelling background particles. Therefore, additional chlorine activation due to aircraft-produced volatile particles can be neglected. Below the ice frost point, O_3 loss rates caused by chlorine activation in persistent contrails or contrail-induced ice clouds exceed those on supercooled droplets by as much as an order of magnitude.

This suggests the following simple parameterization for the heterogeneous N_2O_5 and

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halogen chemistry on aviation-produced particles:

- for $T > T_{ice}$ scale $BrONO_2$ and N_2O_5 hydrolysis by $(A_a + A_b)/A_b$ without Kelvin effect;
- for $T < T_{ice}$ take chlorine activation on ice particles into account.

This parameterization can be easily applied in large-scale atmospheric models.

Similar calculations (not discussed here) reveal that these mechanisms also work under lower stratospheric conditions at the cruising altitude of supersonic aircraft (above 16 km). As a consequence, the strong sensitivity of stratospheric O_3-losses on the size and number of aircraft-produced H_2SO_4/H_2O particles as suggested by global chemical transport models (Weisenstein et al., 1998) is likely to be removed. Simulations including our proposed parameterization scheme are needed to confirm this conjecture. Especially in the polar regions, contrails may develop into long-lived polar stratospheric clouds (PSCs).

Recent assessments emphasized that for a future supersonic aircraft fleet, the impact of particle emissions may nearly double the calculated O_3 loss relative to NO_x and H_2O emissions alone (Kawa et al., 1999). However, under cold conditions such as the winter polar stratosphere, scavenging and Kelvin effect limit the chemistry on aviation-produced liquid aerosols, whereas the formation of aircraft-induced PSCs (likewise not yet being considered in global assessment studies) might enhance chlorine activation (Peter et al., 1991). At moderate and high temperatures the aviation-induced surface area increase (up to about a factor of two in supersonic flight corridors; Kärcher and Meilinger, 1998) would also considerably affect heterogeneous chemistry.

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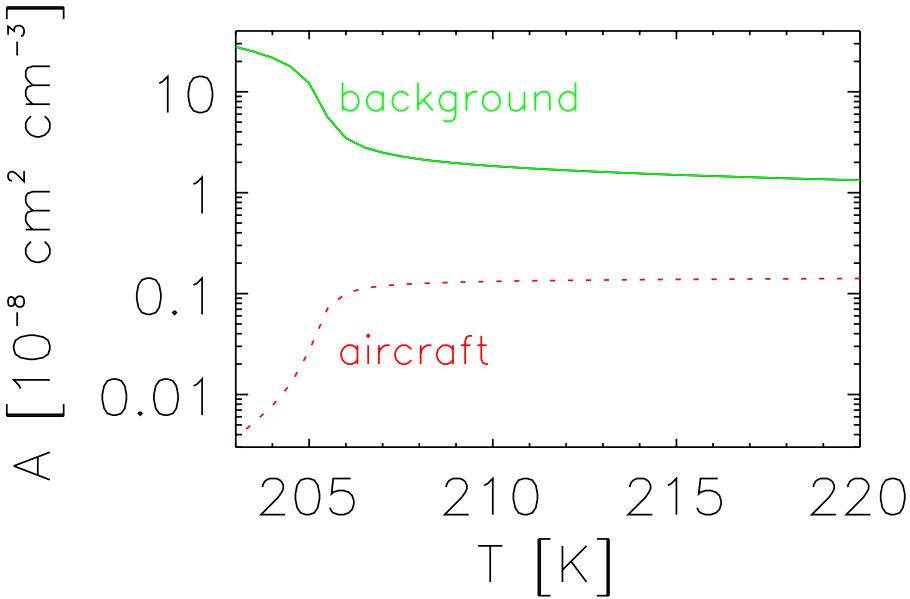

Fig. 1. Surface area densities [$\mu m^2 cm^{-3}$] of background (green solid curve) and aircraft-generated (red dotted curve) H_2SO_4/H_2O particles in the NAFC as a function of temperature, the latter calculated according to the method of Kärcher and Meilinger (1998) using temperature-dependent background aerosol surface areas (Carslaw et al., 1995) assuming 25 ppmv H_2O, 0.87 ppbv HNO_3 and a background number density of 50 cm^{-3} containing 100 pptv H_2SO_4.

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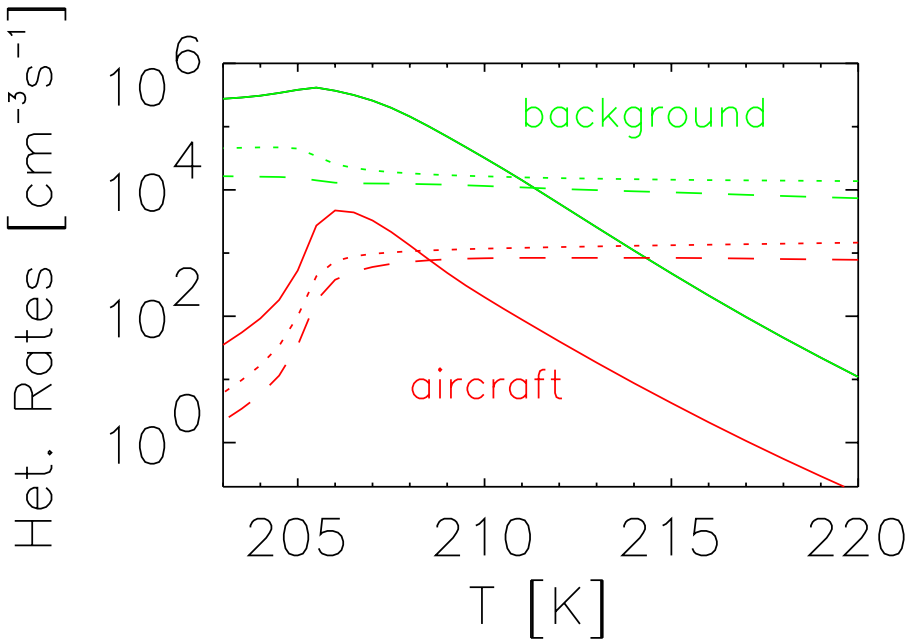

Fig. 2. Heterogeneous reaction rates of $ClONO_2$+HCl (solid curves), N_2O_5+H_2O (dotted) and $BrONO_2$+H_2O (dashed curves) due to background aerosol (green curves) and due to particles from aircraft (red curves). Same conditions as in Fig. 1, assuming typical lowermost stratospheric concentrations (Hendricks et al., 1999) with 325 pptv Cl_y, 2.78 pptv Br_y, 275 ppbv O_3, 44 ppbv CO, and 1.7 ppmv CH_4. Typical NO_x mixing ratios of 0.2 ppbv for the NAFC were taken from Ziereis et al. (2000). NMHC levels of 100 pptv C_2H_6 and 100 pptv acetone were taken from Singh et al. (1997).

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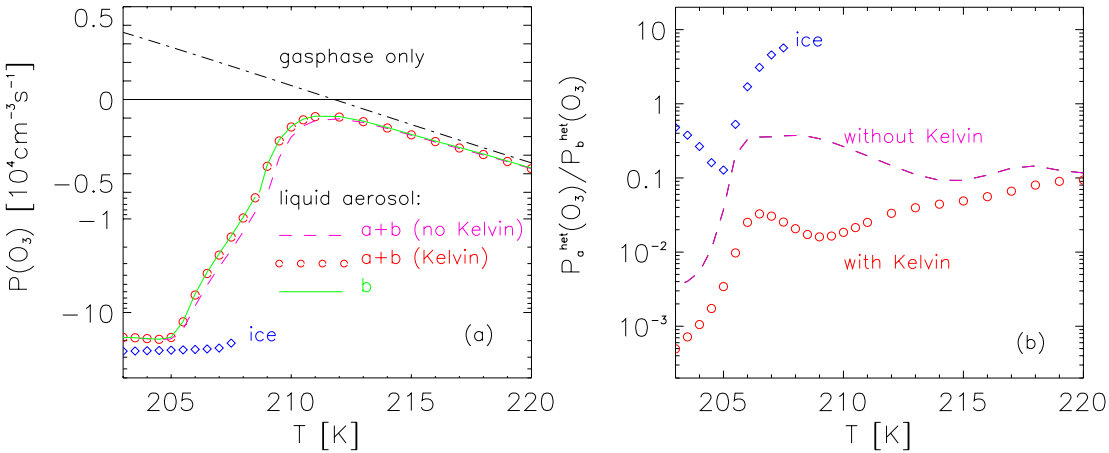

Fig. 3. **(a)** Averaged net ozone production rates $P(O_3)$ at 200 hPa and 50 °N as a function of temperature assuming no aerosol (black dash-dotted curve), 50 cm^{-3} background aerosol particles containing 100 pptv H_2SO_4 (green solid curve), background aerosol mixed with aviation-induced aqueous H_2SO_4 particles in the North Atlantic flight corridor with (red circles) and without (violet dashed curve) Kelvin effect, and 4.2 cm^{-3} ice particles from an aged contrail or cirrus (blue diamonds). **(b)** Heterogeneous ozone production rates relative to background aerosol (green solid curve in (a)). Symbols as in Fig. 2 showing the relative effect of liquid aircraft particles with (red circles) and without (violet dashed curve) Kelvin effect, and for ice particles (blue diamonds). Same conditions as Figs. 1 and 2.

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