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The influence of in-cloud chemical reactions on ozone formation in polluted areas

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Abstract

Aqueous reactions among dissolved radicals and trace metals have been incorporated into a comprehensive gas-phase chemical reaction mechanism in order to quantify the chemical influences of clouds on ozone (O_3) formation in the lower troposphere. In-cloud reactions of dissolved HO_2 with itself, the reaction of dissolved O_3 and HO_2, and reactions of dissolved HO_2 with copper dramatically reduce total HO_2 and other free-radical concentrations in clouds, thereby reducing the rate at which O_3 is produced from anthropogenic NO_x and hydrocarbons. Under typical urban or moderately polluted conditions, local ozone formation rates are reduced by 30-90% when aqueous reactions are occurring. However, the rate at which NO_x, Non-Methane HydroCarbons (NMHC), and O_3 are oxidized is also reduced, resulting in longer atmospheric chemical lifetimes of O_3, NO_x, and NMHC. When NO_x concentrations are less than about 200 ppt, in-cloud reactions reducing HO_2 concentrations decrease the rate at which O_3 is destroyed. Over a longer time scale, aqueous reactions can reduce or enhance the total O_3 produced per molecule of NO_x emitted, depending on the concentration conditions under which NO_x is emitted into the atmosphere. Longer-term impacts of clouds on O_3 formation are much smaller than their local impacts, in the range of a few 10's of percent increase or decrease, due to compensating chemical processes under high and low NO_x conditions. The effects of cloud chemistry on O_3 formation are highly dependent on the concentrations of NO_x and hydrocarbons.

1 Introduction

Most urban or regional-scale models of ozone pollution ignore effects associated with clouds, probably because undesirable ozone buildup is usually associated with "sunny" conditions. However, clouds are nearly always present in the planetary boundary layer in some amounts (Walcek[1]), even during relatively clear "ozone episodes" (Ching et al.[2]). Past studies of in-cloud chemical processes have either not investigated ozone (e. g. Jacob et al.[3]), or have studied ozone from a global perspective (Lelieveld & Crutzen[4]), and not addressed ozone formation in polluted urban areas. In this study, we focus on how aqueous-phase chemical processes influence ozone formation in the lower troposphere for a wide range of pollutant concentration conditions. The radiative and dynamic effects of clouds on O_3 photochemistry are not addressed here, even though these additional cloud effects are very important.

2 Ozone formation model

The Stockwell et al.[5] mechanism is used to simulate gas-phase chemical reactions. This mechanism includes over 160 reactions among 60 constituents. 21 photolysis reactions, and 40 categories of reactive organic compounds. Over 70 important aqueous-phase reactions and dissolution equilibria identified by Lelieveld & Crutzen[4], Jacob et al.[3], and Jacob[6] have been added to the gas-phase mechanism. The integrated *heterogeneous* reaction mechanism thus simulates the chemistry of both cloudy and clear air over a wide range of pollutant concentrations. The model includes equilibria and reactions among all soluble longer-lived chemicals of the Stockwell mechanism, and also includes solubility and reaction of HO_2, HO, and CH_3O_2 radicals. Both gas and droplet-side mass transfer limitations are considered when calculating heterogeneous effects, and trace metal reactions of iron, copper and manganese are included.

The mechanism is initialized with a pollutant mix whose relative concentrations are representative of air within industrialized urban areas. Initial concentrations for each constituent considered for one set of initial conditions are listed in Table 1. Numerous simulations are performed over a wide range of initial NO_x and NMHC concentrations, but the relative concentrations of the various NMHC are the same as shown in Table 1. Carbon monoxide (CO) is usually co-emitted with organic pollutants. Therefore, initial CO concentrations are linearly scaled to the initial concentration of other anthropogenic organics as described in the footnote of Table 1. The model also is initialized with a small concentration of isoprene, although its concentration is not included in the concentration of NMHC, since this is not an anthropogenically-emitted hydrocarbon. Therefore, "NMHC" in this study means anthropogenic hydrocarbons, and also includes CO, although CO concentrations are not included in the NMHC concentration numbers presented.

Photolysis rates are derived from the two-stream radiative transfer model (Madronich[7]) for 40° north latitude, summer solstice conditions at the surface. Clear-sky photolysis rates are used in this study, even though we recognize that clouds significantly modify photolysis rates. In this study, we are not addressing radiative impacts of clouds on photochemistry, but are analyzing the chemical effects only. Also, as noted in earlier studies (Lelieveld and Crutzen[4]; Madronich[7]), photolysis rates are generally lower than clear-sky values near the

Table 1. Chemical conditions for simulations: 10 ppb NO_x; 100 ppb (carbon) NMHC[1]

constituent	symbol	initial concentration (ppb)[1]
inorganic		
ozone	O_3	50
hydrogen peroxide	H_2O_2	1
nitrogen oxides	$NO+NO_2$	10
nitric acid	HNO_3	0
sulfur dioxide	SO_2	1
carbon monoxide[2]	CO	220.[2]
chloride	Cl	0.33
trace metals		
iron	Fe	3.19 (ppt)
copper	Cu	0.121 (ppt)
manganese	Mn	0.234 (ppt)
organic		
formaldehyde	HCHO	4.00
acetaldehyde	ALD	3.33
alkanes low-reactive	HC3	5.86
alkanes mid-reactive	HC5	3.33
alkanes high-reactive	HC8	2.41
ethane	ETH	1.0
ethene	OL2	2.5
terminal alkenes	OLT	0.79
internal alkenes	OLI	0.21
toluene	TOL	1.27
xylene	XYL	1.01
ketone	KET	1.79
isoprene[3]	ISO	0.05
methane[3]	CH_4	1700.

[1] For other concentrations of NO_x or NMHC, concentrations are scaled linearly with respect to these concentrations. E. g., at 10 ppbC, NMHC concentrations are divided by 10. 1 ppb carbon (ppbC)= actual molar mixing ratio ppb x carbon number

[2] CO scaled with respect to total NMHC. [CO] ppb = 100 + 1.2 [NMHC(ppbC)]

[3] Isoprene and methane, naturally occurring hydrocarbons, are not included in NMHC.

base of clouds, but can become greater than clear-sky values in the upper regions of clouds. Thus, for shallow clouds there will be compensating radiative effects when averaging over the entire cloud layer. Therefore, the clouds in this study crudely represent shallow planetary boundary layer clouds.

The model uses an exponentially-assisted, iterative integration technique of the total (gas + liquid phase) concentrations of all constituents. Concentrations of fast-reacting radicals are calculated assuming chemical steady-state between destruction and production in both phases. Miscellaneous physical properties of the simulations are listed in Table 2.

Table 2. Additional simulation conditions

Factor	simulation value
temperature (°K)	288
pressure (mb)	1013.25
water vapor	
(g kg^{-1})	7.2
% Rh	100
(ppm)	11,600
cloud liquid water content (g m^{-3})	0.5
cloud drop radius (μm)	10
sticking coefficient for gas uptake to droplets	0.1
pH of cloudwater	4

3 Short-term, local impacts

In order to assess local-scale, short-term impacts of heterogeneous reactions, O_3 formation rates are averaged during the last 10 minutes of a 30 minute integration. By integrating for a short period, a photochemical balance is established among fast-reacting radicals and NO_x, and the calculated O_3 formation rates are representative of the initial NO_x and NMHC concentrations, which do not change appreciably during the short simulation. By only considering the last 10 minutes of the simulation, uncertainties introduced by initially specifying concentrations of fast-reacting NO_x and radicals that deviate from photochemical balance are avoided. Essentially, this portion of the study is designed to represent the chemistry of a "point" in the lower troposphere under the specified chemical and meteorological conditions.

Fig. 1 shows the calculated O_3 formation rate as a function of the concentration of controllable pollutants NO_x and NMHC calculated by ignoring (Fig. 1a) or including (Fig. 1b) aqueous-phase reactions. Diagrams like Fig. 1 have been used to quantify how changes in concentrations of pollutants resulting from emission controls will modify the rate of ozone formation in polluted areas. Comparing of Fig. 1a and 1b show that there is a dramatic shift in the rate at which ozone is formed in the atmosphere within a cloud relative to a cloud-free environment. There is a general decrease in ozone formation rates under those regimes where O_3 is formed most rapidly. Fig. 2 shows the absolute difference between Figs. 1a-b. Aqueous-phase reactions induce their most dramatic change in ozone formation rates when the NO_x:NMHC ratio is in the 40-100 range, and the change is a function of the concentrations of NO_x and NMHC. In a relative sense, the most dramatic changes in ozone formation

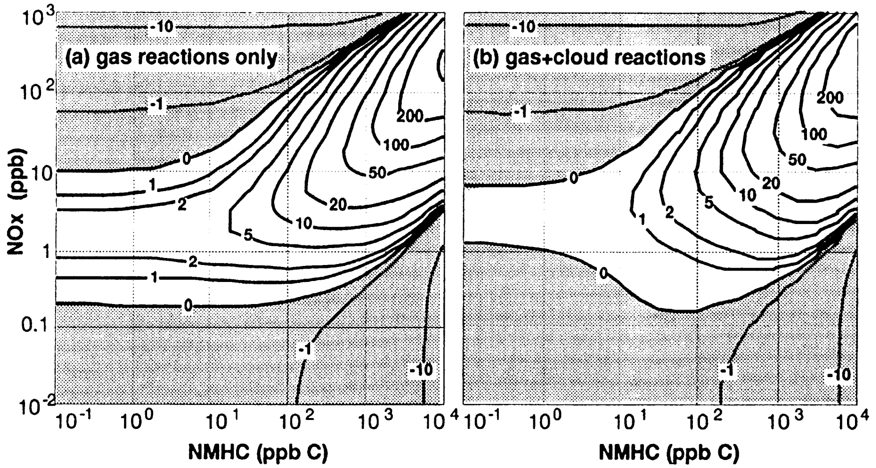

Figure. 1: O_3 formation rate (ppb hour^{-1}) as a function of NMHC and NO_x concentrations considering: (a) only gas-phase reactions; and (b) both gas and aqueous reactions. Gray areas denote chemical conditions where ozone is destroyed by chemical processes.

induced by aqueous-phase reactions occur under low NO_x and NMHC concentrations, when absolute ozone formation rates are low. In particular, the "threshold" NO_x concentration below which ozone is slowly destroyed in the atmosphere increases by a factor of 2-5, from 0.1-0.2 ppb when only gas-phase chemical reactions are considered, to 0.5 - 1 ppb when aqueous-phase reactions are occurring. In the concentration regimes typical of regionally polluted areas ($[NO_x] \approx$ 1-100 ppb; $[NMHC] \approx$ 10-1000 ppbC), local ozone formation rates are reduced by 20-90% when cloud reactions are occurring.

Diagnostic analysis of our heterogeneous reaction mechanism shows that the dominant reactions affecting ozone formation rates are the following reactions destroying aqueous-phase HO_2 in clouds. In a cloud, HO_2 dissolves into two species: $HO_2 + O_2^-$, and the sum of these is referred to as $HO_2(aq)$.

$$Cu^{2+} + O_2^- \text{-->} Cu^+ + O_2 \quad , \tag{1}$$

$$Cu^+ + O_2^- \text{-->} Cu^{2+} + H_2O_2 + 2HO^- \quad , \tag{2}$$

$$Fe(II) + HO_2(aq) \text{-->} Fe(III) + H_2O_2 \quad , \tag{3}$$

$$O_3 + O_2\text{-} \text{-->} HO + O_2 \quad \text{, and} \tag{4}$$

$$HO_2 + O_2^- \text{-->} H_2O_2 + O_2 \quad . \tag{5}$$

Nearly all other aqueous reactions have a nearly negligible influence on ozone chemistry. The reactions with trace metals copper and iron (1-3) exert the strongest influence on ozone formation, and the impact of these reactions is directly proportional to the concentrations of these metals. Trace metal concentrations used in this study (Table 1) are derived from measurements and used in an earlier cloud chemistry study (Jacob[6]). However, measurements of the concentration and speciation of trace metals in clouds are highly uncertain and not widely available. Even without trace metals, ozone formation rates are dramatically inhibited within clouds by reactions 4-5. Reactions 1-5 dramatically reduce HO_2 concentrations by a factor of 2-10. Since the reaction NO + HO_2 in the gas phase is a major source of HO radical in the atmosphere, HO concentrations are also reduced in a cloudy environment.

4 Longer-term, regional impacts

The results shown in Figs. 1-2, derived from looking at essentially individual "points" in the atmosphere, are consistent with earlier studies of the influence of clouds on O_3 formation: aqueous reactions reduce HO_2 concentrations and ozone formation rates in clouds. However, since concentrations of HO and HO_2 are so dramatically reduced by aqueous-phase reactions, there will be corresponding reductions in the rate at which longer-lived NO_x, O_3 and NMHC are oxidized in the atmosphere, and therefore there is a significant feedback between the occurrence of aqueous-phase reactions in the atmosphere and the concentrations of ozone and ozone precursors. By integrating our chemical reaction mechanism for a longer time period, it is possible to obtain some qualitative or semi-quantitative insights into the longer-term or larger-scale impacts of clouds on ozone formation in the troposphere.

Fig. 3 shows how concentrations of O_3 evolve over a two-day integration for two pollutant concentration conditions: "pristine" (0.01 ppb NO_x, 0.1 ppbC NMHC); and more "polluted" conditions (1 ppb NO_x; 10 ppbC NMHC). The solid curves show the time evolution considering gas-phase reactions only, and

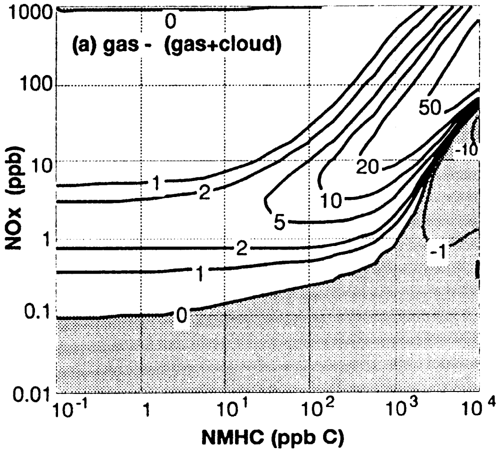

Figure 2: Difference (ppb $hour^{-1}$) between ozone formation rates calculated with and without aqueous-phase chemical reactions. Gray area denotes ozone tendency (∂C/∂t) greater when aqueous-phase reactions considered.

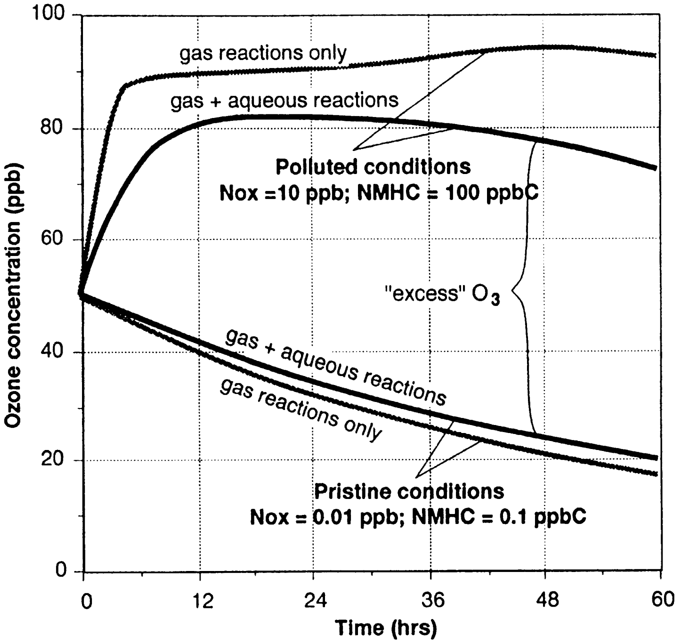

Figure 3: Ozone concentration within air parcels during 60 hours of continuous noon photolysis conditions. Both "pristine" and "polluted" conditions with and without heterogeneous reactions are shown. "Excess O_3" is defined as the additional O_3 that exists in the polluted air above the O_3 that would exist without additional NO_x and NMHC pollutants.

the gray curves show the evolution when gas and aqueous reactions occur. Under very clean conditions, ozone is not even produced, and is slowly destroyed by its photolysis and reaction with HO_2. Under polluted conditions, there is a burst of ozone formation during the first three - four hours when NO_x concentrations are high. After NO_x is oxidized, ozone concentrations fall off as in the extremely clean case. Initially, ozone is much more rapidly formed under cloud-free conditions, but NO_x is also oxidized much faster without cloudy reactions. NO_x concentrations are depleted after 3-4 hours with only gas-phase reactions occurring. In contrast, when both gas and aqueous reactions are occurring, it takes 8-9 hours for NO_x to become oxidized. During those additional 3-4 hours, ozone tendencies are elevated when aqueous reactions are occurring relative to the simulation where aqueous reactions are neglected. For this study, the "excess O_3" shown on Fig. 3 is defined as the additional ozone in the atmosphere that results from the addition of NO_x and NMHC pollutants above pristine conditions. As shown in Fig. 3, this excess O_3 builds up to an approximately constant value after one or two days, during which the NO_x and NMHC pollutants are naturally oxidized in the atmosphere down to "background" values.

Fig. 4 shows the excess ozone (ppb) produced after two days under a wide range of NO_x and hydrocarbon concentration conditions for simulations where aqueous reactions are ignored. The lower left corner of Fig 4 is defined to have "zero" excess ozone. When aqueous reactions are allowed to occur for the entire two day period, excess ozone contours look qualitatively similar to Fig. 4, and are therefore not shown.

The differences between the excess ozone calculated with and without heterogeneous reactions are shown in Fig. 5. For high initial NO_x:NMHC concentration ratios, net ozone accumulations are reduced by 10-50 ppb, while Fig. 4 shows the total ozone accumulations are 50-200 ppb. Thus, longer-term ozone accumulations are reduced by 20-50% when heterogeneous reactions occur. However, the gray areas on Fig. 5 show initial chemical regimes where aqueous-phase reactions increase ozone concentrations in the atmosphere by 0-20 ppb, depending on the initial pollution mix. This increase in ozone accumulations results from compensating effects. When concentrations of initial pollutants are high, ozone formation rates are suppressed by aqueous reactions. However, when concentrations of pollutants (primarily NO_x) are low, ozone destruction rates are reduced by aqueous reactions, as shown in Fig 2. In addition, NO_x and NMHC concentrations remain higher when aqueous-phase reactions are occurring in the atmosphere, since their oxidation rate is reduced. Therefore, while ozone forms at a slower rate within clouds, the slow formation persists for a longer time when aqueous reactions occur. Thus, in contrast to earlier studies of the influence of aqueous-phase chemical processes on O_3 formation, aqueous-phase reactions can both reduce *or enhance* ozone concentrations in the atmosphere, depending on the chemical conditions under which ozone precursors are emitted into the atmosphere and when clouds occur during the oxidation of these precursors. For the regimes of pollutant concentrations typical of polluted industrial areas, ozone accumulations are reduced or enhanced by ±10-20% when aqueous reaction are occurring.

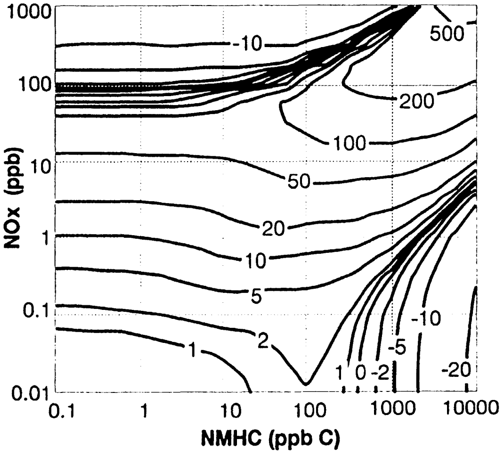

Figure 4: "Excess O_3" (ppb) within polluted air parcel after 48 hours, calculated considering only gas-phase reactions. Lower left point of figure is *defined* to have zero excess O_3.

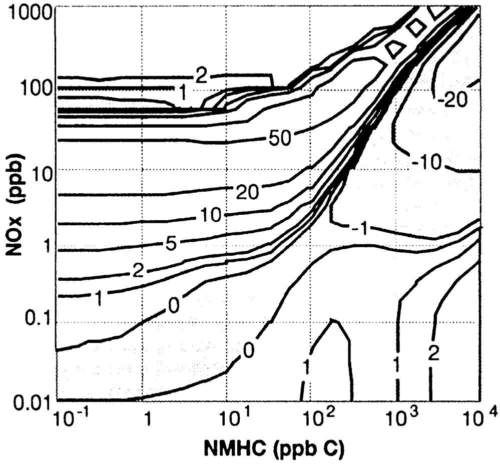

Figure 5: Difference between excess ozone (ppb) calculated considering or neglecting heterogeneous reactions. Gray areas denote regimes where in-cloud reactions enhance ozone formation during the oxidation of primary NO_x and NMHC pollutants.

The changes in ozone concentrations shown in Fig. 5 are calculated assuming continuous cloudiness during the entire 2-day simulation period and thus overestimates the influence of clouds on ozone formation. Clouds typically occupy 10-30% of polluted atmosphere, and relative residence times of air parcels in cloudy air are approximately proportional to the cloud fractional area or volume. If the numbers shown in Fig. 5 are scaled by the 10-30% frequency or area of cloud occurrence, we expect to see ozone concentration changes on the order of less than ±5%.

5 Conclusions

Current models of ozone formation that neglect heterogeneous chemistry probably overestimate ozone formation in polluted areas when even small cloud amounts are present. At high concentrations of pollutants, ozone formation in cloudy portions of polluted areas are locally reduced by 20-90%. However, when considering accumulations of ozone over several hours to perhaps a day in polluted areas, cloud effects have both positive and negative impacts on ozone formation. While O_3 formation rates are largely reduced by in-cloud reactions, the oxidation rates of O_3 precursors is simultaneously reduced, leading to higher concentrations of O_3 precursors when considering longer term or regional-scale impacts of clouds on ozone formation.

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