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PHOTOCHEMICAL PRODUCTION OF CARBOXYLIC ACIDS IN A REMOTE CONTINENTAL ATMOSPHERE

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ABSTRACT. Model calculations are conducted to investigate the production of carboxylic acids from photochemical decomposition of isoprene, one of the main natural hydrocarbons emitted from vegetation. Both gas-phase and aqueous-phase chemical reaction pathways are examined. A simple dynamical model is proposed to simulate the boundary layer of the Amazon rain forest, and model predictions are compared to measurements made in that region in July 1985. It is found that formic acid, methacrylic acid, and pyruvic acid can be produced in significant quantities by gas-phase decomposition of isoprene. In the Amazon basin, this source may yield concentrations of these acids in the order of 1 ppb, 0.1 ppb, and 0.02 ppb, respectively. Production of formic acid in cloud by aqueous-phase oxidation of CH_2O does not greatly increase the formic acid concentration predicted from the gas-phase mechanism; cloud droplets with $pH > 4$ are actually expected to constitute net sinks for formic acid. No significant production of acetic acid is expected from the photochemical decomposition of isoprene. Comparisons of model predictions with field data indicates that isoprene could be a major source of formic acid and pyruvic acid observed in the gas phase and in rainwater; however, acetic acid must originate from another source.

1. INTRODUCTION

Carboxylic acids have been recognised as major contributors to the acidity of precipitation in remote atmospheres (Keene et al., 1983), but little is known of their sources. Keene and Galloway (1986) observed that concentrations of HCOOH and CH_3COOH in rainwater of Central Virginia are much higher in May-September than in October-March, and noted a sharp drop in October coinciding with the senescence of the vegetation. They further noted that the HCOOH/CH_3COOH concentration ratios in rainwater collected at a number

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of rural and remote continental sites were remarkably similar. They inferred that emissions from vegetation are the main atmospheric source of these two acids. Organic acids are emitted directly by vegetation (Graedel et al., 1986), but they can also be produced in the atmosphere by photochemical decomposition of natural hydrocarbons released from vegetation, in particular isoprene. The relative contributions of these two types of sources is uncertain. The object of this paper is to examine the importance of isoprene as a possible atmospheric source of carboxylic acids. Both gas-phase and aqueous-phase chemical reaction pathways will be investigated. A simple dynamical model will be used to simulate concentrations observed during a recent field study in the Amazon rain forest.

Formic acid is generally the most abundant organic acid found in rainwater (Keene et al., 1983; Keene and Galloway, 1986). It is released directly by vegetation, both naturally and during biomass burning (Graedel et al., 1986; Talbot et al., 1987). It is also produced in the atmosphere by reaction of CH_2O with HO_2 (Su et al., 1979), but this reaction is very slow at atmospheric concentrations (Jacob, 1986). A more important atmospheric source appears to be the reaction of olefins with O_3 (Atkinson and Lloyd, 1984). In particular, HCOOH has been observed as a product of the irradiation of isoprene-NO_x mixtures (Arnts and Gay, 1979). Formation of HCOOH in this system is thought to proceed by ozonation of the C=C bonds producing the Criegee biradical $\cdot CH_2OO\cdot$, followed by reaction of $\cdot CH_2OO\cdot$ with H_2O to give HCOOH (Hatakeyama et al., 1981). The atmospheric chemistry of Criegee biradicals has been reviewed by Atkinson and Lloyd (1984).

Some recent papers have argued that aqueous-phase oxidation of formaldehyde in clouds may represent a major global source of formic acid (Chameides, 1984; Adewuyi et al., 1984). Formaldehyde scavenged by cloud droplets hydrolyzes to $H_2C(OH)_2$, which is then rapidly oxidized by OH(aq) to HCOOH. Formate is in turn rapidly oxidized by OH(aq), so that the fate of formic acid in a cloud is strongly dependent on cloudwater pH (Jacob, 1986). Concentrations of HCOOH predicted solely from this aqueous-phase mechanism are consistent with measurements in rainwater at remote marine sites (Jacob, 1986; Keene and Galloway, 1986).

However, as pointed out by Keene and Galloway (1986), the above aqueous-phase model studies do not account for the much larger HCOOH concentrations often observed at continental sites. Possibly this difference could be due to direct emissions of HCOOH from vegetation; however, it is of interest to explore whether the source could be explained from the atmospheric chemistry of isoprene. Isoprene is the main natural hydrocarbon emitted by deciduous trees (Lamb et al., 1985), and its reaction with O_3 may be a substantial source of HCOOH. Further, the photochemical decomposition of isoprene yields large amounts of CH_2O, which may then be oxidized to HCOOH in cloud. The photochemical decomposition of isoprene may produce other carboxylic acids by hydrolysis of higher Criegee biradicals, and may produce acetic acid in cloud by aqueous-phase oxidation of acetaldehyde. The importances of these pathways will be evaluated.

Our discussion will be based on simulations of boundary layer chemistry in the Amazon rain forest. Extensive data on atmospheric

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concentrations have recently been collected in this region as part of the Amazon Boundary Layer Experiment (ABLE-2A). Isoprene was found to be by far the main non-methane hydrocarbon, with daytime concentrations typically in the range 1-5 ppb (Rasmussen and Khalil, 1987; Zimmerman et al., 1987). Average gas-phase concentrations of formic and acetic acids at ground level were 1.6 and 2.2 ppb, respectively (Andreae et al., 1987a). Data on NO_x and O_3 concentrations, and their fluxes at the ground (Kaplan et al., 1987) were collected. These data provide means to calibrate the model and compare its predictions to actual measurements.

We will begin by a brief description of the model, in particular the gas-phase and aqueous-phase chemistry determining the production and removal of carboxylic acids. We will then present simulations of isoprene chemistry in the Amazon basin, with emphasis on the behaviour of carboxylic acids. The effect of cloud formation on acid production will be investigated. Predicted acid concentrations will be compared to observations.

2. MODEL DESCRIPTION

2.1. Gas-phase chemistry

The gas-phase chemistry of the remote troposphere is simulated with a standard H_xO_y - N_xO_y - CH_4 - CO mechanism (Logan et al., 1981). The photochemistry of isoprene has been added, with the mechanism proposed by Lloyd et al. (1983) and the rate constants of Lurmann et al. (1986). The rate constant for the isoprene + OH reaction has been set to $2.5 \times 10^{11} \exp(409/T)$, following the recommendation by Atkinson (1986). Some necessary alterations have been made to the Lloyd et al. mechanism, in particular the reactions of RO_2 radicals with HO_2 are included and the production of organic acids is explicitly considered. Isoprene reacts with OH, O_3, and NO_3 to produce methylvinylketone and methacrolein. Criegee biradicals are produced following addition of O_3 to the C=C double bonds of isoprene, methylvinylketone, and methacrolein, and subsequent cleavage of the C-O and O-O bonds (Lloyd et al., 1983):

$$\underset{\text{(isoprene)}}{CH_2CHC(CH_3)CH_2} + O_3 \rightarrow 0.5\ CH_2O + 0.2\ \underset{\text{(methylvinylketone)}}{CH_2CHC(O)CH_3}$$

$$+ 0.3\ \underset{\text{(methacrolein)}}{CH_2C(CH_3)CHO} + 0.2\ \cdot CH_2OO\cdot + 0.06\ HO_2$$

$$+ 0.2\ \underset{\text{(MVKO)}}{CH_2CHC(\dot{O}\dot{O})CH_3} + 0.3\ \underset{\text{(MAOO)}}{CH_2C(CH_3)\cdot CHOO\cdot} \qquad \text{(RG1)}$$

$$\underset{\text{(methylvinylketone)}}{CH_2CHC(O)CH_3} + O_3 \rightarrow 0.5\ CH_2O + 0.2\ \cdot CH_2OO\cdot + 0.21\ HO_2$$

$$+ 0.2\ \underset{\text{(MCRG)}}{CH_3C(O)\cdot CHOO\cdot} + 0.15\ CH_3CHO$$

$+ 0.5\ CH_3C(O)CHO + 0.15\ CH_3C(O)O_2$ (RG2)

$CH_2C(CH_3)CHO + O_3 \rightarrow 0.5\ CH_2O + 0.2\ \cdot CH_2OO\cdot + 0.21\ HO_2 + 0.15\ CH_3O_2$
(methacrolein)

$+ 0.5\ CH_3C(O)CHO + 0.2\ CH_3C(\dot{O}\dot{O})CHO$ (RG3)
(MGLYO)

The thermalized Criegee biradicals $\cdot CH_2OO\cdot$, MVKO, MAOO, MCRG and MGLYO react rapidly with NO, NO_2, SO_2, aldehydes, and H_2O. Except under very polluted conditions, reaction with H_2O is the dominant sink. The hydrolysis of $\cdot CH_2OO\cdot$ produces HCOOH (Hatakeyama *et al.*, 1981). It is likely that MCRG and MAOO are hydrolyzed by a similar mechanism to form pyruvic acid and methacrylic acid, respectively:

$\cdot CH_2OO\cdot + H \longrightarrow HCOOH + H_2O$ (RG4)

$MCRG + H_2O \longrightarrow H_3CC(O)COOH + H_2O$ (RG5)
(pyruvic acid)

$MAOO + H_2O \longrightarrow H_2CC(CH_3)COOH + H_2O$ (RG6)
(methacrylic acid)

A rate constant $k = 3.4\times10^{-18}\ cm^3\ sec^{-1}$ has been recommended for (RG4) (Atkinson and Lloyd, 1984), and the same rate constant will be assumed for (RG5) and (RG6). In the case of MGLYO and MVKO, the radical carbon is fully substituted and reaction with H_2O (if it occurs) would not produce a carboxylic acid. We assume here that MGLYO and MVKO decompose to unreactive products.

Therefore, the gas-phase oxidation of isoprene may produce formic pyruvic acid, and methacrylic acid. One notes that acetic acid is not an expected product. Formic acid is mostly removed by dry deposition and washout. It does not photolyze (Calvert and Pitts, 1966), and its reaction with OH is very slow ($k = 4.5 \times 10^{13}\ cm^3\ sec^{-1}$; Wine *et al.*, 1985). On the other hand, pyruvic acid photolyzes in the atmosphere on a time scale of the order of a day (Grosjean, 1984). Pyruvic acid absorbs radiation up to 370 nm with a near-unity quantum yield for photodissociation to CO_2 (Yamamoto and Black, 1985). Methacrylic acid does not appear to photolyze at tropospheric wavelengths (Rosenfeld and Weiner, 1983), but it probably reacts rapidly with OH by addition to the C=C bond. It is assumed here that the reaction of OH with methacrylic acid proceeds with the same rate constant as the reaction of OH with 2-methyl propene ($k = 6\times10^{-11}\ cm^3\ sec^{-1}$; Atkinson, 1986).

2.2 Aqueous-phase chemistry

The mechanism used is that presented by Jacob (1986). The aqueous-phase chemical reactions of sulfur, NO_x, chloride, and carbonate originally present in the Jacob (1986) mechanism have not

$CH_3C(O)O_2$
(RG2)

$+ 0.21\ HO_2 + 0.15\ CH_3O_2$

$CH_3C(\dot{O}\dot{O})CHO$ (RG3)
(MGLYO)

MVKO, MAOO, MCRG and
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been included since they do not significantly affect the chemistry of interest here. Formic acid is rapidly produced in cloud droplets during the day following the hydrolysis of $CH_2O(aq)$ and oxidation of $H_2C(OH)_2$ by OH(aq):

$$CH_2O(g) === CH_2O(aq) \qquad (H1)$$

$$CH_2O(aq) + H_2O === H_2C(OH)_2 \qquad (RA1)$$

$$H_2C(OH)_2 + OH \rightarrow HC(OH)_2 \longrightarrow HCOOH + HO_2 \qquad (RA2)$$

Production of HCOOH by this pathway is very fast because of the high hydration constant of CH_2O ($K_{A1} = 1.4x10^3$) and because (RA2) is very rapid ($k_{A2} = 2x10^9\ M^{-1}\ sec^{-1}$). In the aqueous phase, HCOOH is rapidly oxidized by OH(aq):

$$HCOOH ==== HCOO^- + H^+ \qquad (RA3)$$

$$HCOOH + OH \longrightarrow CO_2 + H_2O + HO_2 \qquad (RA4)$$

$$HCOO^- + OH \longrightarrow CO_2 + H_2O + O_2^- \qquad (RA5)$$

with $k_{A4} = 2x10^8\ M^{-1}\ sec^{-1}$, $k_{A5} = 2.5x10^9\ M^{-1}\ sec^{-1}$. Removal of $HCOO^-$ by (RA5) is fast, therefore a cloud is not an efficient source of HCOOH if the HCOOH produced remains in the aqueous phase (Jacob, 1986). However, HCOOH produced in the aqueous phase can be stabilized by volatilizing to the gas phase. The volatilization of HCOOH depends on the degree of HCOOH(aq)/$HCOO^-$ dissociation in the droplet (pK_{A3} = 3.75) and thus is strongly pH dependent. Figure 1 shows the

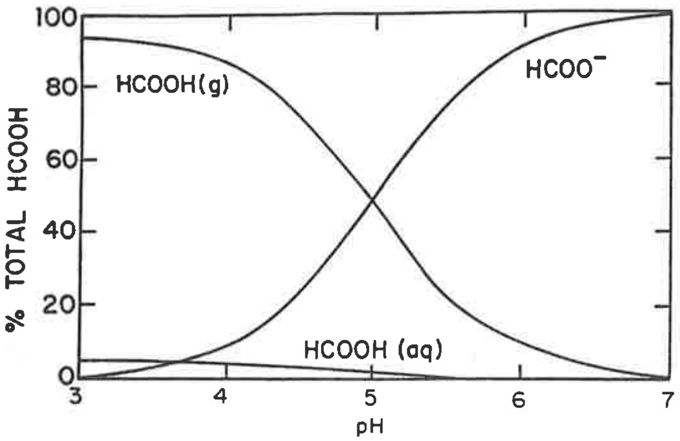

Figure 1. Equilibrium speciation of HCOOH in cloud (liquid water content 0.5 $g\ m^{-3}$, T = 291K).

Table 1. Aqueous-phase mechanism: acetaldehyde, peroxyacetic acid, acetic acid.

a) Henry's Law constants

		K_H M atm^{-1}	ΔH kcal mole^{-1}	Reference
(H2)	CH_3CHO	13.	-11.	Snider and Dawson (1985)
(H3)	$CH_3C(O)OOH$	4.4(2)	-12.3	Lind and Kok (1986)
(H4)	CH_3COOH	8.8(3)	-12.8	CRC (1986)
(H5)	$CH_3C(O)OO$	12.	-12.3	footnote a

b) Aqueous-phase equilibrium constants

		K M atm^{-1}	ΔH kcal mol^{-1}	Reference
(RA6)	$CH_3COOH = CH_3COO^- + H^+$	1.7(-5)	-0.1	Sillen and Martell (1964)
(RA7)	$CH_3CHO \overset{H_2O}{====} CH_3CH(OH)_2$	1.2^b	-5.	Bell (1966)

c) Aqueous-phase reaction rate constants

		k sec^{-1},M^{-1}sec^{-1}	E_a kcal mole^{-1}	Reference
(RA8)	$CH_3CHO + OH \xrightarrow{O_2} CH_3C(O)OO + H_2O$	5.(8)	3.*	Merz and Waters (1949)
(RA9)	$CH_3C(O)OO + HO_2 \longrightarrow CH_3C(O)OOH + O_2$	4.3(5)	6.*	$\frac{1}{2}kHO_2{+}HO_2$
(RA10)	$CH_3C(O)OO + O_2^- \xrightarrow{H_2O} CH_3C(O)OOH + OH^- + O_2$	5.(7)	3.2*	$\frac{1}{2}kHO_2{+}O_2^-$
(RA11)	$CH_3C(O)OOH \xrightarrow{H_2O} CH_3COOH + H_2O_2$	< 5.(-6)^b		Koubek and Edwards (1963)
(RA12)	$CH_3CH(OH)_2 + OH \longrightarrow CH_3COOH + H_2O + HO_2$	5.(8)	3.*	Merz and Waters (1949)
(RA13)	$CH_3COOH + OH \longrightarrow \cdots$	2.(7)	3.7*	Fahrataziz and Ross (1977)
(RA14)	$CH_3COO^- + OH \longrightarrow \cdots$	7.(7)	3.*	ibid.
(RA15)	$CH_3C(O)OOH + OH \longrightarrow \cdots$	2.(7)	3.7*	estimated

(a) calculated from K_{H3} scaled to the ratio of Henry's Law constants of HO_2 and H_2O_2 (Jacob, 1986).

(b) This upper limit value is used in the simulation.

* These activation energies are estimated following the method of Jacob (1986).
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ic acid, acetic acid.

ΔH kcal mole^{-1}	Reference
-11.	Snider and Dawson (1985)
-12.3	Lind and Kok (1986)
-12.8	CRC (1986)
-12.3	footnote a

ΔH kcal mol^{-1}	Reference
-0.1	Sillen and Martell (1964)
-5.	Bell (1966)

c^{-1}	E_a kcal mole^{-1}	Reference
	3.*	Merz and Waters (1949)
	6.*	½kHO_2+HO_2
	3.2*	½kHO_2+O_2^-
		Koubek and Edwards (1963)
	3.*	Merz and Waters (1949)
	3.7*	Fahratazlz and Ross (1977)
	3.*	ibid.
	3.7*	estimated

constants of HO_2 and H_2O_2

hod of Jacob (1986).

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speciation of HCOOH at 291K, as a function of pH. It is clear that the efficiency of a droplet as a source of HCOOH increases with the droplet acidity. This effect will be quantitatively demonstrated in the model simulations.

An issue of interest is whether CH_3COOH may be produced in the aqueous phase from acetaldehyde or peroxyacetic acid. Both of these species are major products of the gas-phase photochemical decomposition of isoprene (Jacob and Wofsy, 1987). A mechanism for aqueous-phase production and loss of CH_3COOH was added to the model of Jacob (1986), and is shown in Table 1. Acetic acid may be produced in the same way as formic acid following hydration of CH_3CHO. In addition, it may be produced by hydrolysis of peroxyacetic acid, however this process is quite slow at the pH values found in cloudwater. Peroxyacetic acid may be either scavenged from the gas phase or produced within the aqueous-phase from the reaction of $CH_3CHO(aq)$ with OH. Note that the intermediate $CH_3CHO(aq)$ does not react with NO or NO_2 because of the low solubility of these species.

2.3 Dynamical model

We attempt to simulate undisturbed conditions in the planetary boundary layer (PBL) over the Amazon rain forest during the dry season (Gregory et al., 1987). The depth of the mixed layer was found during ABLE-2A to respond quickly to the radiation balance. At night, the inversion was based a few tens of meters above the canopy top; at sunrise, the mixed layer deepened rapidly, and grew at a rate of 5-10 cm sec^{-1} during the morning hours. On a typical day, the inversion stabilized at noon at an altitude of about 1500 m, and remained at that level until late afternoon. The mixed layer then decayed very rapidly. A simple two-box model extending from canopy top to 1500 m (Figure 2) is used here to describe the boundary layer dynamics. At night, an inversion based 50 m above the canopy top is assumed, separating layer 1 (mixed layer) from layer 2 (remnant PBL). Eddy diffusion exchange between layers 1 and 2 is allowed, with an eddy diffusion coefficient of $2x10^3$ cm^2 sec^{-1}. This exchange is necessary to account for the observed persistence of O_3 near the canopy top at night (Kaplan et al., 1987). In the morning, air from layer 2 is entrained into layer 2 as the mixed layer grows, until layer 2 disappears at noon. Layer 2 is reconstituted at sunset with the concentrations of layer 1. A typical diurnal temperature profile for the mixed layer (D.R. Fitzjarrald, personal communication, 1986) is adopted and is shown in Figure 2. The temperature of layer 2 is assumed constant at 296K.

Other model conditions are listed in Table 2. Kaplan et al. (1987) have found that the soil of the Amazon forest is a strong source of NO; their reported value for the emission flux is used here, where it is assumed (as observed by Kaplan et al.) that NO has been entirely converted to NO_2 by the time it reaches the top of the canopy (at night) or has reached a steady state with respect to NO_2 (in the day). Isoprene emissions are assumed to proceed from sunrise to sunset only, and to be unsensitive to changes in the intensity of solar radiation during the day (Sanadze and Kalandadze, 1965). An exponential

Table 2. Model conditions.

Radiation field:	0° latitude (equator), clear sky, surface albedo = 0.18, solar declination = 20°; vertical columns of ozone, water vapor, and aerosol from Logan et al. (1981).
Temperature:	See text and Figure 2.
Water vapor:	16 g/kg air
Condensation nuclei:	NH_4^+, H^+, NO_3^-, SO_4^{2-} (see text)
Cloud physics:	Liquid water content: 0.5 g m^{-3} Droplet radius: 10 µm Sticking coefficient: 0.1
Species with fixed concentrations:	CH_4: 1700 ppb (Logan et al., 1981) C_2H_6: 2 ppb ibid. CO: 140 ppb (S.C. Wofsy, unpublished data, 1986).
Emission fluxes:	NO: 5.2×10^{10} molecules $cm^{-1}s^{-1}$ (Kaplan et al., 1987) Isoprene: $5 \times 10^{11} e^{0.2(T-298)}$ molecules $cm^{-2}s^{-1}$ (Lamb et al., 1985; see text)
Deposition velocities:	V_d (cm s^{-1}):

Species	V_d	Species	V_d
O_3	2	HCOOH	0.5
Isoprene	2	pyruvic acid	0.5
HNO_3	3	methacrylic acid	0.5
NO_3	3	peroxyacetic acid	0.5
CH_2O	0.5	H_2O_2	0.5
		CH_3CHO	0.5

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= 20°; vertical columns of
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5 g m^{-3}

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text)

Species	V_d
HCOOH	0.5
pyruvic acid	0.5
methacrylic acid	0.5
peroxyacetic acid	0.5
H_2O_2	0.5
CH_3CHO	0.5

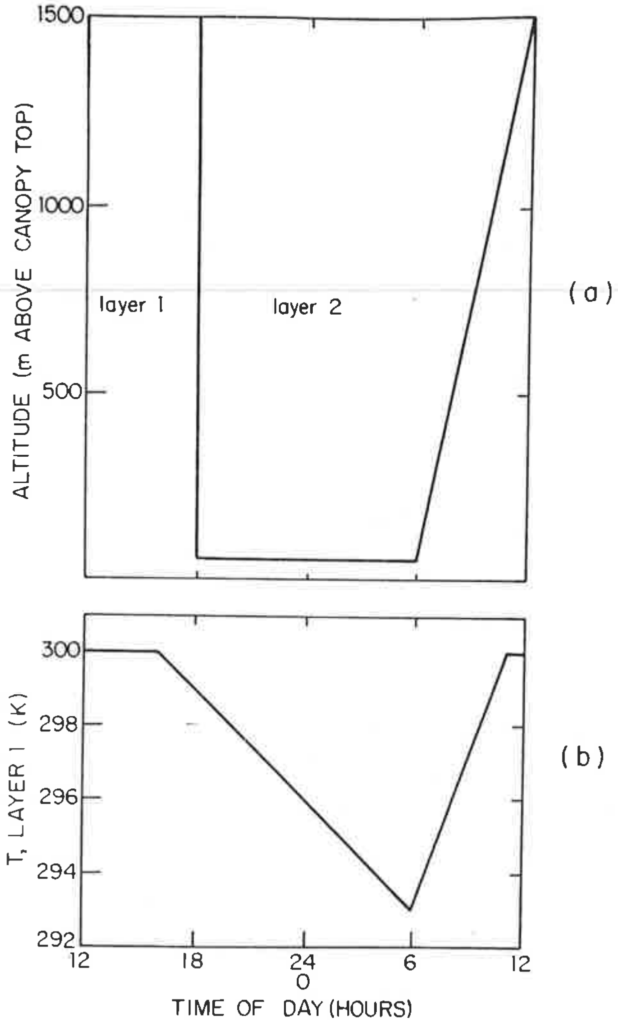

Figure 2 (a) Height of the mixed layer as a function of time of day. (b) Diurnal cycle of temperature in the mixed layer (layer 1).

dependence of the isoprene emission rate on temperature is assumed from Lamb et al. (1985, 1986), and the emission rate at 298K is selected as an adjustable parameter to best fit the data. We thus find a flux of $5x10^{11}$ molecules cm^{-2} sec^{-1} at 298K, which is in the range reported by Lamb et al. (1985) for forests in the United States. The sensitivity of model predictions to the isoprene emission rate will be discussed.

A deposition velocity for O_3 of 2 cm sec^{-1} was taken from Kaplan et al. (1987). The vertical gradient of O_3 was found by Kaplan et al. to be mostly confined to the lower ten meters above the ground, even at night, indicating little aerodynamic resistance to deposition at the top of the canopy. The nighttime isoprene concentration profiles measured in ABLE-2A (Rasmussen and Khalil, 1987) show evidence of a rapid sink for isoprene at the ground. The nature of this nighttime sink is uncertain; in particular, reaction of isoprene with NO_3 should be slow in view of the low nighttime NO and O_3 concentrations measured near the ground by Kaplan et al. (1987). We elect to simulate the nighttime isoprene sink as a deposition velocity at the top of the canopy, which is the lower boundary of our model. Based on the observed nighttime gradients within the canopy and an eddy diffusion coefficient of $2x10^3$ cm^2 sec^{-1}, we estimate a deposition velocity for isoprene of 2 cm sec^{-1}, similar to that of O_3.

Model simulations in the absence of cloud were iterated over 10 successive diurnal cycles, starting from reasonable initial conditions. After 10 days of simulation most of the species were in steady state, i.e. the same diurnal pattern was repeated from day to day. Separate simulations of cloud chemistry were conducted by cooling noontime boundary layer air down to a temperature at which a liquid water content of 0.5 g m^{-3} was achieved (Table 2). The cloud droplets were assumed to reach instantaneously a size of 10 μm radius, and the sticking coefficient for all species was assumed to be 0.1. The model results are not very sensitive to these assumptions, as discussed by Jacob (1986). An accurate treatment of gas-droplet transfer was used in the cloud chemistry model; this treatment includes consideration of both gas-phase and aqueous-phase gradients of concentrations near the gas-droplet interface. For further details the reader is referred to Jacob (1986).

3. RESULTS

3.1. Gas-phase production of carboxylic acids.

We show in Figure 3 some daily patterns of concentrations obtained after iterating the gas-phase model over 10 successive diurnal cycles. The concentrations and diurnal variations of NO, O_3, and isoprene reproduce observations fairly well. Detailed comparisons of model predictions with observations are presented in a separate paper (Jacob and Wofsy, 1987). Ozone is produced in the boundary layer during the day, reflecting the influence of isoprene photochemistry and high NO emissions from soils; a maximum concentration of 26 ppb is predicted in late afternoon, which is consistent with observations. At night, O_3 is depleted near the ground, but remains at over 20 ppb in the remnant PBL. Maxima in isoprene concentrations are predicted in the early morning and late afternoon, when the source is on and the main sink (reaction with OH) is slow. At night, isoprene is depleted from layer 1 by deposition, but remains at a high concentration aloft because the nighttime chemical sinks (reactions with O_3 and NO_3) are slow.

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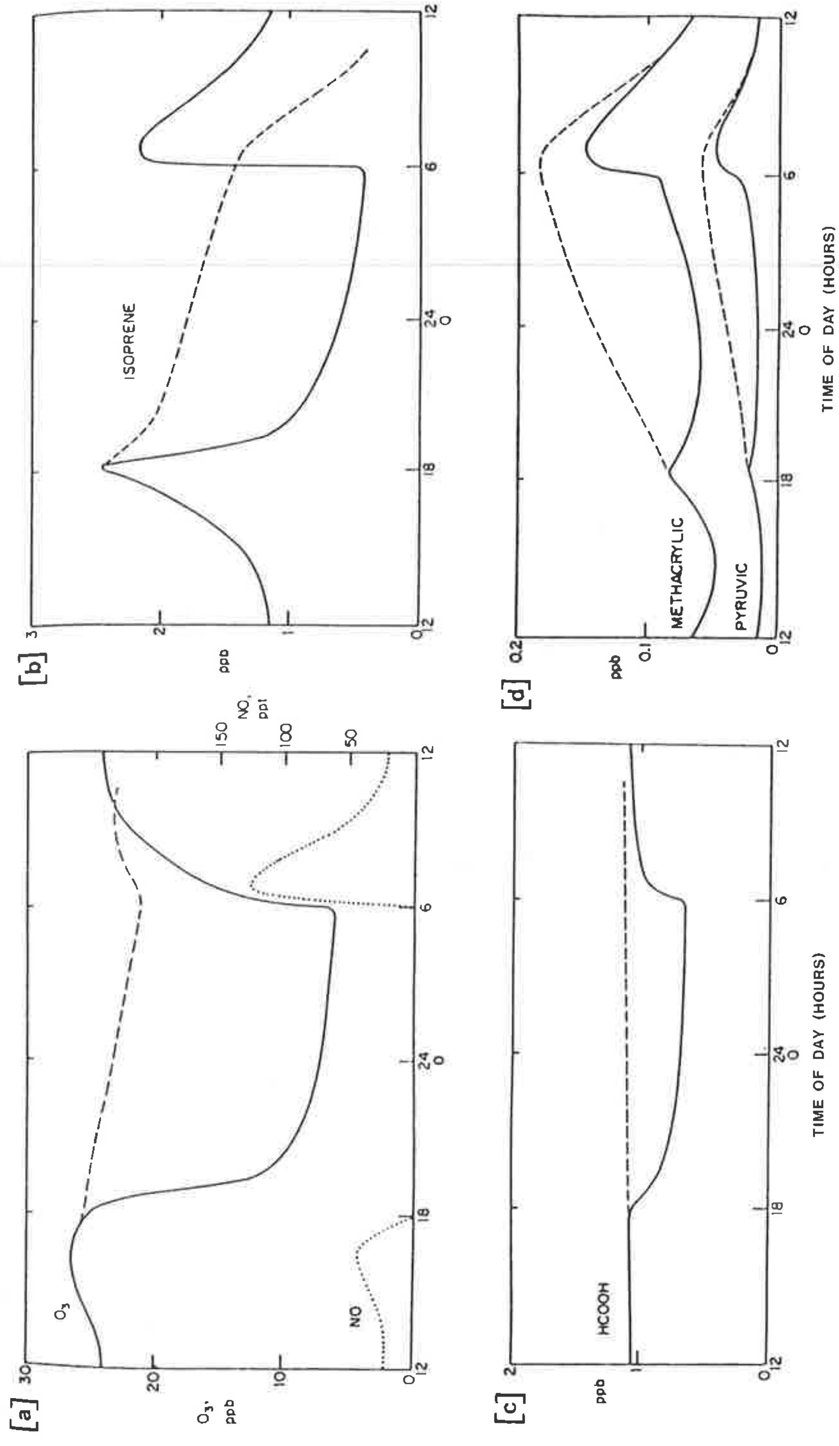

Figure 3. Diurnal variations in the concentrations of (a) ozone, (b) isoprene, (c) formic acid, and (d) methacrylic and pyruvic acids, for layer 1 (solid line) and layer 2 (dashed line), with the conditions of Table 2 and no cloud present. Dotted line is the concentration of NO in layer 1.

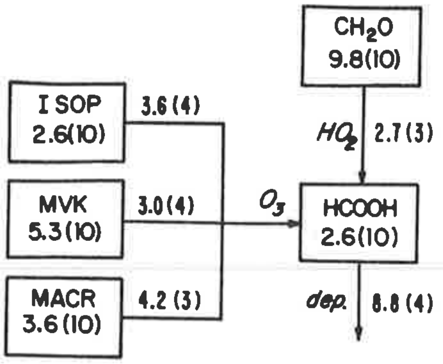

Figure 4 Formic acid production and loss rates at noon, with the model conditions of Table 2 and no cloud present. Concentrations are in units of molecules cm^{-3}, and transformation rates are in units of molecules cm^{-3} sec^{-1}.

The isoprene source yields a formic acid concentration of about 1 ppb (Figures 3 and 4). Predicted concentrations of methacrylic acid and pyruvic acid are lower, of the order of 0.1 and 0.02 ppb, respectively. Concentrations of methacrylic acid and pyruvic acid are highest at night because of rapid daytime sinks from reaction with OH and photolysis, respectively. Formic acid does not show such a diurnal variation because of its long chemical lifetime; the main feature in the diurnal concentration pattern of HCOOH is the nighttime removal in layer 1 by deposition. It should be noted that the predicted concentrations of HCOOH scale almost linearly to the deposition velocity, a quantity difficult to estimate. The deposition velocity assumed here (0.5 cm sec^{-1}) is probably uncertain to about a factor of 5, and a similar uncertainty would apply to predicted HCOOH concentrations.

Andreae *et al.* (1987a) have reported measurements of gas-phase HCOOH within the forest canopy during ABLE-2A. The HCOOH concentrations observed by Andreae *et al.* were approximately constant during the daylight hours, and dropped to low values at night, a result in harmony with model predictions. Daytime concentrations were in the range 1-3ppb, in fair agreement with simulated values. Therefore, it appears that isoprene could be a major source of HCOOH in continental atmospheres.

According to our mechanism, photochemical decomposition of isoprene should produce methacrylic acid and pyruvic acid in addition to HCOOH. Both methacrylic acid and pyruvic acid have fairly rapid photochemical sinks, which would tend to control their concentrations. We are not aware of any measurements of methacrylic acid in the atmosphere, but measurements of pyruvic acid were made by Andreae *et al.* (1987b) during ABLE-2A. Pyruvic acid was present ubiquitously in

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gas-phase, aerosol, and precipitation samples. The formic-to-pyruvic ratios in precipitation were in the range 13 to 62, with a mean value of 40. Gas-phase concentrations of pyruvic acid within the canopy ranged from 90 to 400 ppt, with a mean value of 180 ppt. These results are roughly consistent with an isoprene source for pyruvic acid as simulated by the model. Observed gas-phase concentrations are higher than predicted, but the significance of this discrepancy is difficult to assess in view of the uncertainties on the rate of (RG5) and the yield of MCRG from (RG2). Pyruvic acid is unlikely to be

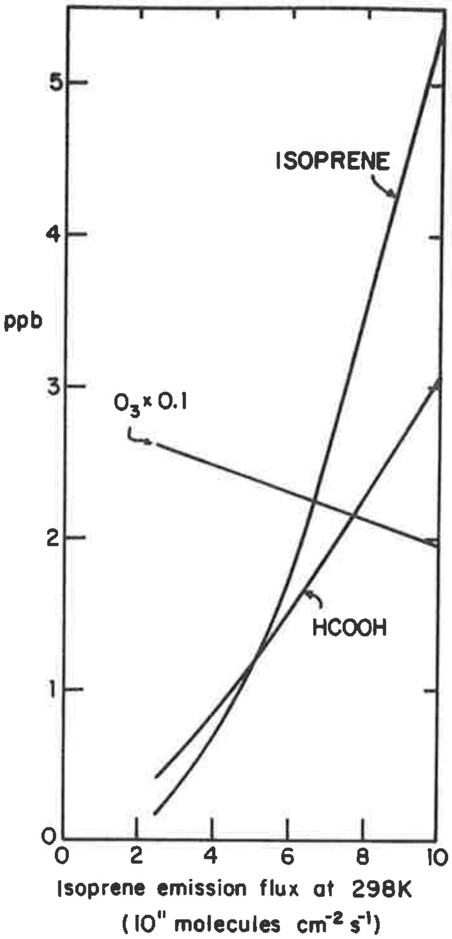

Figure 5 Noontime isoprene, HCOOH, and O_3 concentrations, as a function of the isoprene source strength. The isoprene source E is given as $E = A\ e^{0.2(T-298)}$ molecules cm^{-2} s^{-1}, where the preexponential constant (isoprene flux at 298K) is the adjustable parameter.

released from vegetation because of its high acidity constant (pK 2.4), and appears to have no significant atmospheric sources other than the oxidation of isoprene. Grosjean (1984) has reported the photochemical production of pyruvic acid from o-cresol, but this source should be significant only in polluted urban atmospheres.

Isoprene fluxes from forests have been observed to vary over a wide range, although the exponential dependence on temperature as given by Table 2 appears to be universal (Lamb *et al.*, 1985). The sensitivity of the HCOOH concentration to the isoprene source strength was explored by a series of simulations where various values of the preexponential constant (value of the isoprene flux at 298K) were considered (Figure 5). The dependence of the isoprene concentration on the isoprene emission flux is strongly non-linear because OH, which provides the dominant isoprene sink, is depleted by isoprene and its decomposition products (methylvinylketone, methacrolein, aldehydes, organic peroxides). The concentration of formic acid also shows a strong dependence on the isoprene emission flux.

3.2 The role of cloud chemistry

We now consider a cloud forming under noontime conditions and with initial gas-phase concentrations obtained from the 10-day standard gas-phase simulation discussed above. Cloud formation enhances radiation in the upper region of the cloud (because of scattering from

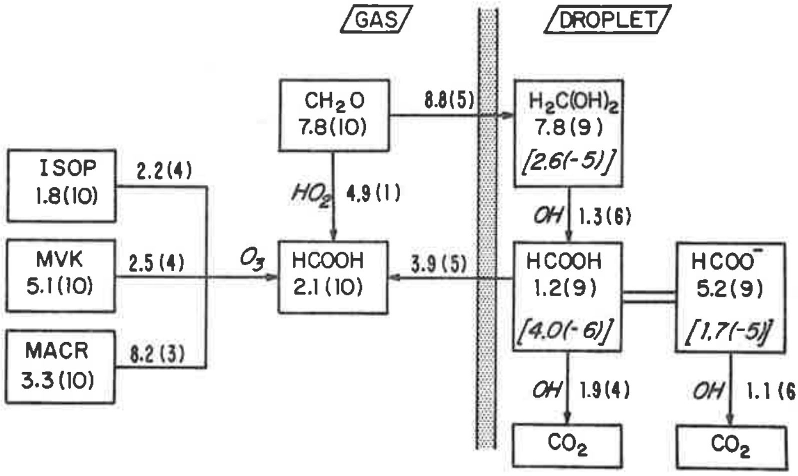

Figure 6 Production and loss rates of HCOOH one hour after cloud formation, with the conditions of Table 2 and a noontime radiation field. Concentrations are in units of molecules cm^{-3}, and transformation rates are in units of molecules cm^{-3} sec^{-1}. Aqueous-phase concentrations (M) are given in brackets. Gas-droplet transfer rates are given as net fluxes.

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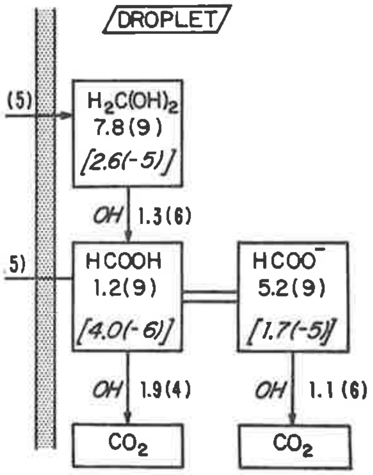

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below), and weakens radiation in the lower region of the cloud (because of increased optical depth). An intermediate level is considered here where cloud formation causes no net change in the radiation field. The cloud is assumed to be decoupled from the ground, i.e. emission and deposition fluxes are set to zero upon cloud formation. The condensation nuclei are assumed to be (H^+, NH_4^+, NO_3^-, SO_4^{2-}) mixtures, initially at equilibrium with $HNO_3(g)$ (specified from the gas-phase model) and $NH_3(g)$. Various initial nuclei acidities and $NH_3(g)$ concentrations are used in the different simulations, in order to investigate a range of cloudwater pH regimes and study the sensitivityof the aqueous-phase chemistry to droplet pH.

Figure 6 shows the production and removal of HCOOH in cloud one hour after cloud formation. In this simulation the condensation nuclei were assumed to be acid-base neutral, and the initial $NH_3(g)$ concentration was set to zero. The pH of the droplets one hour after cloud formation is 4.39, and is still decreasing slowly because of continuing production of HCOOH which is a major component of the droplet acidity. Comparison of Figures 4 and 6 indicates that the aqueous-phase source of HCOOH in cloud is about 20 times faster than the gas-phase source; however, the aqueous-phase sink is also much faster than the gas-phase sink. Let $HCOOH_T$ represent total HCOOH in cloud ($HCOOH(g) + HCOOH(aq) + HCOO^-$); we see from Figures 4 and 6 that the $HCOOH_T$ concentration one hour after cloud formation is close to the initial HCOOH(g) concentration.

The concentration of HCOOH in cloud is strongly dependent on cloudwater pH, mainly because the partitioning of HCOOH between the gas and aqueous phases has a major effect on its removal rate. Figure 7 shows the concentrations of CH_2O and HCOOH species one hour after cloud formation for a range of cloudwater pH values. At low pH, most of the HCOOH produced in the aqueous phase volatilizes to the gas phase, where it has a long lifetime against oxidation by OH(g). As the pH increases, however, an increasing fraction of the HCOOH produced remains in the aqueous phase as $HCOO^-$, and is oxidised by the reaction $HCOO^- + OH$. As a result, the $HCOOH_T$ concentration decreases with increasing cloudwater pH; at high pH, the cloud is a net sink for HCOOH. A maximum in the aqueous-phase concentration of $HCOO^-$ is found at pH 5.5. Keene and Galloway (1986) have reported average $HCOO^-$ concentrations in rainwater over central Brazil of 17 µeq l^{-1}, with an average pH of 4.63; our simulations predict a cloudwater concentration of 23 µeq l^{-1} for that pH. This good agreement indicates that the aqueous-phase mechanism for HCOOH production could explain the observed concentrations in precipitation at continental sites.

Compared to marine clouds (Chameides, 1984; Jacob, 1986), the relative effect of aqueous-phase chemistry on HCOOH concentrations in continental clouds is much less dramatic. Even under acidic conditions, where net production is maximum, the $HCOOH_T$ concentration one hour after cloud formation is 1.2 ppb, as compared to the initial concentration of 1 ppb. Although CH_2O concentrations are much higher in continental clouds than in marine clouds, aqueous-phase production of HCOOH is not correspondingly faster because the reaction $H_2C(OH)_2$ + OH is the dominant sink for OH(aq) at high CH_2O concentrations;

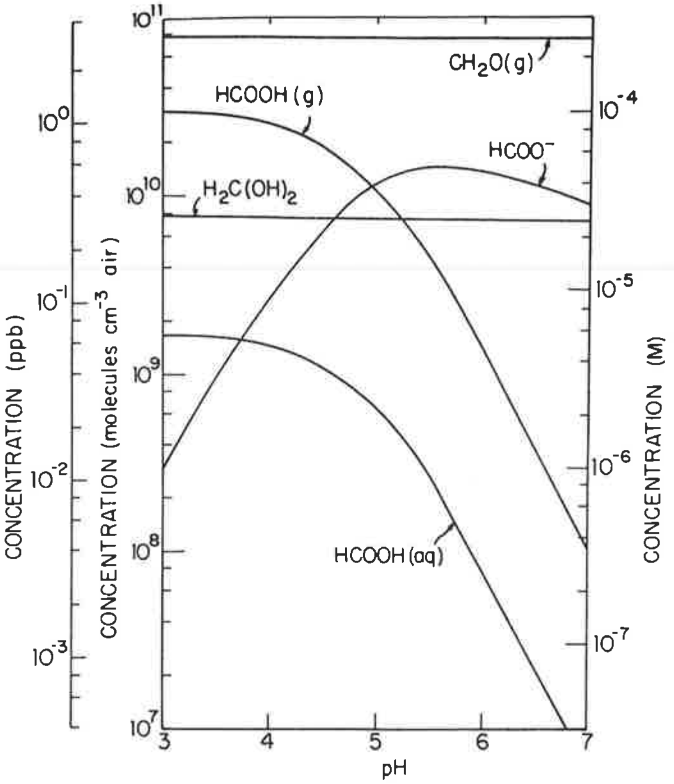
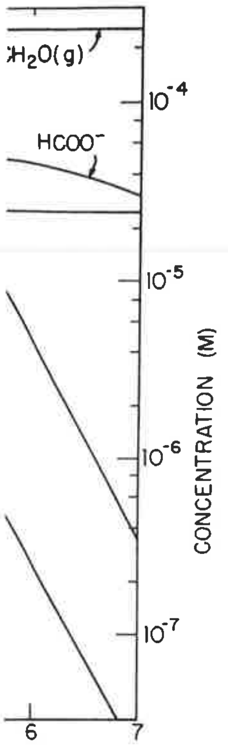


Figure 7 Concentrations of CH_2O and HCOOH species, one hour after cloud formation, as a function of cloudwater pH. Model conditions are those of Table 2 with a noontime radiation field. Gas-phase concentrations are in units of molecules cm^{-3} air and ppb (left-hand scales), and aqueous-phase concentrations are in units of M (right-hand scale).

therefore, increasing the CH_2O concentration leads to a corresponding decrease in the OH(aq) concentration, with little change in the rate of HCOOH production. The OH(aq) concentrations predicted in the present simulations range fromn 1.0×10^{-13} M at pH 3 to 3.3×10^{-13} M at pH 7, and are much lower than the concentrations predicted in a remote marine cloud under similar radiation conditions (from 3.8×10^{-13} M at pH 3 to 1.5×10^{-12} M at pH 7; Jacob, 1986).

Figure 8 shows the concentration of acetic acid one hour after cloud formation, as a function of cloudwater pH. Production from aceltaldehyde oxidation and peroxyacetic acid hydrolysis is very slow. Aqueous-phase oxidation of CH_3CHO is much slower than for CH_2O becaus the hydration constant for CH_3CHO is three orders of magnitude small



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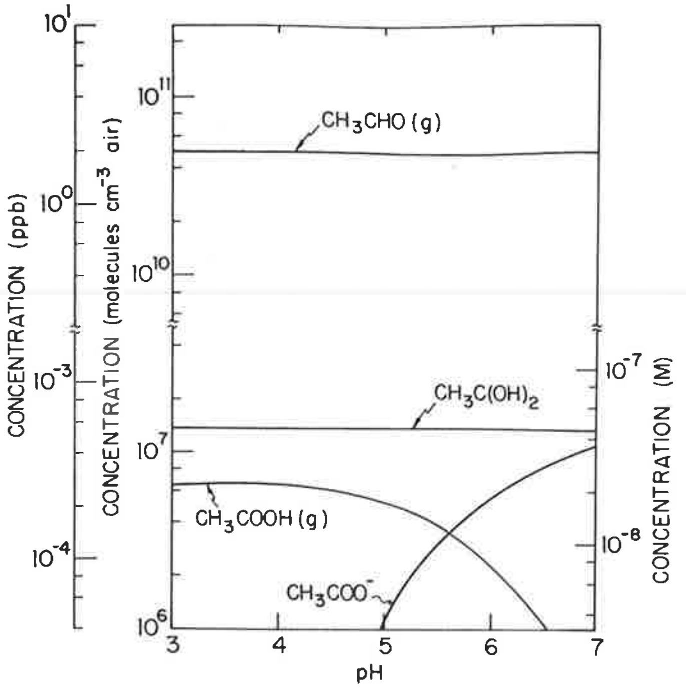

Figure 8 Concentrations of CH_3CHO and CH_3COOH species, one hour after cloud formation, as a function of cloudwater pH. Model conditions are those of Table 2 with a noontime radiation field. Gas-phase concentrations are in units of molecules cm^{-3} air and ppb (left-hand scales), and aqueous-phase concentrations are in units of M (right-hand scale).

than that of CH_2O. The predicted concentrations of CH_3COO^- can be compared to the average concentration of 3.7 µeq l^{-1} measured by Keene and Galloway (1986) in rainwater over central Brazil. Clearly, photochemical decomposition of isoprene appears to be a negligible source of CH_3COOH. Other sources of acetic acid, probably direct emissions from vegetation, must be present to produce the concentrations observed in the gas phase by Andreae _et al_. (1987a) and in rainwater by Keene and Galloway (1986).

4. CONCLUSIONS

The production of carboxylic acids from atmospheric oxidation of isoprene in a remote continental atmosphere has been studied with a detailed chemical model. The model was applied to a simulation of atmospheric chemistry in the boundary layer of the Amazon basin, and predictions were compared to field measurements made during ABLE-2A. The model reproduces fairly well the observed diurnal pattern in the concentrations of isoprene, O_3, and NO; therefore, it should provide a fairly realistic representation of the boundary layer chemistry. The reader is referred to Jacob and Wofsy (1987) for a detailed discussion of the photochemistry of biogenic emissions over the Amazon Basin.

According to our chemical mechanism, the gas-phase photochemical decomposition of isoprene produces formic acid, methacrylic acid, and pyruvic acid. Concentrations of these acids predicted from the isoprene source in the Amazon basin are of the order of 1 ppb, 0.1 ppb, and 0.02 ppb, respectively. Production of formic acid in cloud by aqueous-phase oxidation of CH_2O does not greatly increase the formic acid concentration predicted from the gas-phase mechanism; cloud droplets with $pH > 4$ are actually expected to constitute net sinks for formic acid. No significant production of acetic acid is expected from the photochemical decomposition of isoprene, either in the gas phase or in the aqueous phase. Comparison of model predictions with field data indicates that isoprene could be a major source of formic acid and pyruvic acid observed in the gas phase and in rainwater; however, acetic acid must originate from another source.

ACKNOWLEDGEMENTS

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