

## Multi-Phase Chemistry of C<sub>2</sub> and C<sub>3</sub> Organic Compounds in the Marine Atmosphere

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**Abstract.** A box model is used to explore the detailed chemistry of C<sub>2</sub> and C<sub>3</sub> organic compounds in the marine troposphere by tracing the individual reaction paths resulting from the oxidation of ethane, ethene, acetylene, propane, propene and acetic acid. The mechanisms include chemical reactions in the gas phase and in the aqueous phase of clouds and aerosol particles at cloud level under conditions resembling those in the northern hemisphere. Organic hydroperoxides are found to be important intermediate products, with subsequent reactions leading partly to the formation of mixed hydroxy or carbonyl hydroperoxides that are readily absorbed into cloud water, where they contribute significantly to the formation of multifunctional organic compounds and organic acids. Organic hydroperoxides add little to the oxidation of sulfur dioxide dissolved in the aqueous phase, which is dominated by H<sub>2</sub>O<sub>2</sub>. Next to acetaldehyde and acetone, glycol aldehyde, glyoxal, methyl glyoxal and hydroxy propanone are prominent oxidation products in the gas and the aqueous phase. Acetaldehyde is not efficiently converted to acetic acid in clouds; the major local sources of acetic acid are gas-phase reactions. Other acids produced include hydroperoxy acetic, glycolic, glyoxylic, oxalic, pyruvic, and lactic acid. The mechanism of Schuchmann *et al.* (1985), which derives glycolic and glyoxylic acid from the oxidation of acetate, is found unimportant in the marine atmosphere. The principal precursors of glyoxylic acid are glyoxal and glycolic acid. The former derives mainly from acetylene and ethene, the latter from glycolaldehyde, also an oxidation product of ethene. The oxidation of glyoxylic acid leads to oxalic acid, which accumulates and is predicted to reach steady state concentrations in the range 30–90 ng m<sup>-3</sup>. This is greater, yet of the same magnitude, than the concentrations observed over the remote Pacific Ocean.

**Key words:** oxidation of C<sub>2</sub> and C<sub>3</sub> hydrocarbons, aqueous phase chemistry of C<sub>2</sub> and C<sub>3</sub> organic compounds, acetaldehyde, glycol aldehyde, glyoxal, methyl glyoxal, hydroxy propanone, acetic acid, hydroperoxy acetic acid, glycolic acid, glyoxylic acid, oxalic acid, pyruvic acid

### Introduction

The oxidation of hydrocarbons is the origin of a great variety of oxygen-containing organic compounds in the troposphere. In the marine atmosphere, the leading hydrocarbon precursors next to methane are ethane, acetylene and propane. Ethene and propene occur with smaller abundance, but this is compensated by their greater reactivity (for a review of marine hydrocarbons see Warneck, 2000). The alkanes and acetylene are endowed with longer life times. They originate mainly on the

Table I. Initial conditions used in the model<sup>a</sup>

Gas-phase mixing ratios (nmol mol <sup>-1</sup> )			
Ozone, O <sub>3</sub>	40	Ethane, C <sub>2</sub> H <sub>6</sub>	1.30
Hydrogen peroxide, H <sub>2</sub> O <sub>2</sub>	0.30	Ethene, C <sub>2</sub> H <sub>4</sub>	0.077
Nitrogen dioxide, NO <sub>2</sub>	0.06	Acetylene, C <sub>2</sub> H <sub>2</sub>	0.30
Nitric oxide, NO	–	Propane, C <sub>3</sub> H <sub>8</sub>	0.80
Nitrous acid, HNO <sub>2</sub>	0.01	Propene, C <sub>3</sub> H <sub>6</sub>	0.026
Nitric acid, HNO <sub>3</sub>	0.08	Methanol, CH <sub>3</sub> OH	0.80
PAN, CH <sub>3</sub> CO <sub>3</sub> NO <sub>2</sub>	0.18	Ethanol, C <sub>2</sub> H <sub>5</sub> OH	0.08
Sulfur dioxide, SO <sub>2</sub>	0.045	Formaldehyde, HCHO	0.20
Ammonia, NH <sub>3</sub>	0.035	Acetaldehyde, CH <sub>3</sub> CHO	0.077
Methane, CH <sub>4</sub>	1700	Acetone, CH <sub>3</sub> COCH <sub>3</sub>	0.80
Hydrogen, H <sub>2</sub>	575	Formic acid, HCOOH	0.25
Carbon monoxide, CO	125	Acetic acid, CH <sub>3</sub> COOH	0.20
		Methyl hydroperoxide, CH <sub>3</sub> OOH	0.20
Aqueous phase species (nmol m <sup>-3</sup> ) <sup>b</sup>			
Sulfate, SO <sub>4</sub> <sup>2-</sup>	15.27	Sodium, Na <sup>+</sup>	126.55
Chloride, Cl <sup>-</sup>	133.25	Magnesium, Mg <sup>2+</sup>	14.24
Nitrate, NO <sub>3</sub> <sup>-</sup>	6.5	Ammonium, NH <sub>4</sub> <sup>+</sup>	7.635
Hydroxyl ion, OH <sup>-</sup>	0.00012	Hydrogen ion, H <sup>+</sup>	7.635

<sup>a</sup>Assembled from the data of Atlas and Ridley (1996), Blake and Rowland (1986), Blake *et al.* (1996, 1997, 2003), Ehhalt *et al.* (1986), Rudolph (1995), Rudolph and Jonen (1990), Singh *et al.* (1994, 1995, 2000), and the compilation of Warneck (2000).

<sup>b</sup>Concentrations refer to air volume.

continents and reach the remote troposphere by global transport. The same holds for methanol, ethanol, formic acid and acetic acid. The presence of short-lived alkenes in the marine atmosphere is largely due to emissions from the ocean surface. Spatial distributions and abundances of all these precursor substances are reasonably well known from a variety of measurements. Important oxidation products, such as acetaldehyde, acetone, or peroxy acetyl nitrate (PAN) have also been observed in marine air, and mixing ratios have been determined. Table I provides an overview of characteristic mixing ratios adopted here for the northern hemisphere and appropriate references. It is important to note that some of the values can vary widely so that the selection is, to some extent, arbitrary.

A great many laboratory studies have established mechanisms for the oxidation of C<sub>1</sub>-C<sub>3</sub> hydrocarbons (see reviews of Atkinson, 1994, 1997; Calvert *et al.*, 2000). Rate coefficients for most gas-phase reactions are well known, although gaps still exist for hydroperoxides. In addition, kinetic parameters for chemical reactions occurring in the aqueous phase of aerosols and clouds have recently been assembled (Herrmann *et al.*, 2000; Ervens *et al.*, 2003a), and it has been shown that aqueous phase reactions are important for the formation of some species, such as oxalic

acid (Ervens *et al.*, 2003a; Warneck, 2003). The information currently available thus makes it possible to construct a fairly comprehensive chemical model, which includes processes occurring in the gas phase as well as in the aqueous phase, to obtain a detailed description of reaction pathways and product distributions resulting from the oxidation of the above-mentioned hydrocarbons under conditions existing in the marine atmosphere. The present paper presents such a model and explores the consequences of the chemistry involved. Herrmann *et al.* (2000) and Ervens *et al.* (2003a), in their CAPRAM model, have concentrated the effort on the aqueous radical chemistry, which was coupled to the RADM gas-phase lumped species reaction scheme of Stockwell *et al.* (1990, 1997). This model is better suited to describe the situation over the continents, where the number of species is too great to allow individual treatment.

### Chemical Mechanisms and Model

The study is based on the extension of a previous chemical model (Warneck, 1999), which was used to determine the relative importance of various pathways for the oxidation of sulfur dioxide and nitrogen dioxide in sun-lit continental clouds. This box model involves 27 species and 47 reactions in the gas phase, and 50 species and 113 reactions in the aqueous phase. It describes the oxidation of C<sub>1</sub> organic compounds, the basic chemistry of O<sub>3</sub>, HO<sub>x</sub>, NO<sub>x</sub> and SO<sub>2</sub> and the associated intermediate compounds. In the present application, 19 aqueous reactions involving transition metals are deleted because of their almost negligible abundance in the marine atmosphere. The two phases are coupled by gas-aqueous exchange processes describing the approach to Henry's law equilibria. Coefficients for the forward and reverse transfer processes are explicitly calculated assuming a uniform cloud drop size. The cloud parameters used previously are typical for continental fair weather clouds: drop radius  $r = 5 \mu\text{m}$ , number density  $n = 320 \text{ cm}^{-3}$ , and liquid water to air volume ratio  $L = 1.7 \times 10^{-7}$ . For the simulation of clouds in the marine atmosphere the conditions are changed to  $r = 12 \mu\text{m}$ ,  $n = 69 \text{ cm}^{-3}$  and  $L = 5.0 \times 10^{-7}$ . These values are typical for small marine cumulus clouds (Pruppacher and Klett, 1997), whereas marine stratus clouds feature higher number densities and somewhat lower liquid water contents. The parameters for elevation ( $z \approx 900 \text{ m}$ ), air pressure ( $p_{\text{air}} = 908 \text{ hPa}$ ), temperature ( $T = 285 \text{ K}$ ), and water vapor pressure (1.4 kPa for a relative humidity  $\sim 100\%$ ) are retained.

Tables II–V present additional reactions and photochemical processes needed to incorporate C<sub>2</sub> and C<sub>3</sub> chemistry. Gas-phase reactions are summarized in Table II. Here, the numbering of reactions continues where the previous list had ended. The main scheme describes the oxidation of the source gases ethane, ethene, acetylene, propane and propene. Methanol, ethanol and acetic acid are added as source gases. Most of the oxidation mechanisms and reaction rate coefficients are known. Rate values for several reactions of peroxy radicals with HO<sub>2</sub> radicals that produce hydroperoxides are not available and had to be estimated. The protocol of Jenkin *et al.*

Table II. Supplementary gas-phase reactions and rate coefficients

Reaction	$k_{298}$ ( $\text{cm}^3 \text{s}^{-1}$ or $\text{s}^{-1}$ )	$-E_a/R_g$ (K)	Ref. <sup>a</sup>
Photolyses <sup>b</sup>			
$\text{CH}_3\text{COCH}_3 + h\nu (+\text{O}_2)$ $\rightarrow \text{CH}_3\text{OO} + \text{CH}_3\text{CO}_3$	$1.0 \times 10^{-6}$		a
$\text{CH}_3\text{COCHO} + h\nu (+\text{O}_2)$ $\rightarrow \text{CH}_3\text{CO}_3 + \text{HO}_2 + \text{CO}$	$1.2 \times 10^{-4}$		b
$\text{HOCH}_2\text{CHO} + h\nu (+\text{O}_2)$ $\rightarrow \text{HCHO} + \text{CO} + 2\text{HO}_2$	$1.3 \times 10^{-5}$		b
$\text{OCHCHO} + h\nu (+\text{O}_2)$ $\rightarrow \text{HCHO} + \text{CO} \rightarrow 2\text{CO} + 2\text{HO}_2$	$1.9 \times 10^{-5}$ $6.1 \times 10^{-5}$		b b
$\text{OCHCOOH} + h\nu (+\text{O}_2)$ $\rightarrow \text{CO} + \text{CO}_2 + 2\text{HO}_2$	$8.7 \times 10^{-5}$		c
$\text{CH}_3\text{COCO} + h\nu (+\text{O}_2)$ $\rightarrow \text{CH}_3\text{CHO} + \text{CO}_2$	$1.3 \times 10^{-4}$		d
$\rightarrow \text{CH}_3\text{CO}_3 + \text{CO}_2 + \text{HO}_2$	$1.1 \times 10^{-4}$		d
Oxidation of alkenes			
G36 $\text{OH} + \text{C}_2\text{H}_6 (+\text{O}_2) \rightarrow \text{C}_2\text{H}_5\text{OO} + \text{H}_2\text{O}$	$2.5 \times 10^{-13}$	1030	e
G37 $\text{C}_2\text{H}_5\text{OO} + \text{NO} (+\text{O}_2)$ $\rightarrow \text{CH}_3\text{CHO} + \text{NO}_2 + \text{HO}_2$	$9.2 \times 10^{-12}$	-380	e
G38 $\text{C}_2\text{H}_5\text{OO} + \text{HO}_2 \rightarrow \text{C}_2\text{H}_5\text{OOH} + \text{O}_2$	$7.7 \times 10^{-12}$	-900	e
G39a $\text{OH} + \text{C}_2\text{H}_5\text{OOH} \rightarrow \text{C}_2\text{H}_5\text{OO} + \text{H}_2\text{O}$	$1.0 \times 10^{-12}$		x
G39b $\rightarrow \text{CH}_3\text{CHO} + \text{OH}$	$5.0 \times 10^{-12}$		x
G40a $\text{OH} + \text{C}_3\text{H}_8 (+\text{O}_2)$ $\rightarrow \text{CH}_3\text{CH}(\text{OO})\text{CH}_3 + \text{H}_2\text{O}$	$8.5 \times 10^{-13}$	330	e
G40b $\rightarrow \text{C}_2\text{H}_5\text{CH}_2\text{OO} + \text{H}_2\text{O}$	$3.0 \times 10^{-13}$	841	e
G41 $\text{CH}_3\text{CH}(\text{OO})\text{CH}_3 + \text{NO} (+\text{O}_2)$ $\rightarrow \text{CH}_3\text{COCH}_3 + \text{NO}_2 + \text{HO}_2$	$9.0 \times 10^{-12}$	-360	e
G42 $\text{C}_2\text{H}_5\text{CH}_2\text{OO} + \text{NO} (+\text{O}_2)$ $\rightarrow \text{C}_2\text{H}_5\text{CHO} + \text{NO}_2 + \text{HO}_2$	$9.4 \times 10^{-12}$	-350	e
G43 $\text{CH}_3\text{CH}(\text{OO})\text{CH}_3 + \text{HO}_2$ $\rightarrow \text{CH}_3\text{CH}(\text{OOH})\text{CH}_3 + \text{O}_2$	$9.0 \times 10^{-12}$	-700	x
G44 $\text{C}_2\text{H}_5\text{CH}_2\text{OO} + \text{HO}_2$ $\rightarrow \text{C}_2\text{H}_5\text{CH}_2\text{OOH} + \text{O}_2$	$8.0 \times 10^{-12}$	-700	x
G45a $\text{OH} + \text{CH}_3\text{CH}(\text{OOH})\text{CH}_3$ $\rightarrow \text{CH}_3\text{CH}(\text{OO})\text{CH}_3 + \text{H}_2\text{O}$	$1.0 \times 10^{-12}$		x
G45b $\rightarrow \text{CH}_3\text{COCH}_3 + \text{OH} + \text{H}_2\text{O}$	$8.0 \times 10^{-12}$		x
G46a $\text{OH} + \text{C}_2\text{H}_5\text{CH}_2\text{OOH}$ $\rightarrow \text{C}_2\text{H}_5\text{CH}_2\text{OO} + \text{H}_2\text{O}$	$1.0 \times 10^{-12}$		x
G46b $\rightarrow \text{C}_2\text{H}_5\text{CHO} + \text{OH} + \text{H}_2\text{O}$	$5.0 \times 10^{-12}$		x
G47 $\text{OH} + \text{CH}_3\text{CHO} (+\text{O}_2) \rightarrow \text{CH}_3\text{CO}_3 + \text{H}_2\text{O}$	$1.5 \times 10^{-11}$	-307	e

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Table II. (Continued)

Reaction	$k_{298}$ (cm <sup>3</sup> s <sup>-1</sup> or s <sup>-1</sup> )	$-E_a/R_g$ (K)	Ref. <sup>a</sup>
G48	NO <sub>3</sub> + CH <sub>3</sub> CHO (+O <sub>2</sub> ) → CH <sub>3</sub> CO <sub>3</sub> + HNO <sub>3</sub>	2.7 × 10 <sup>-15</sup>	1860 b
G49a	OH + CH <sub>3</sub> COCH <sub>3</sub> (+O <sub>2</sub> ) → CH <sub>3</sub> COOH + CH <sub>3</sub> OO	7.0 × 10 <sup>-14</sup>	-423 f
G49b	→ CH <sub>3</sub> COCH <sub>2</sub> OO + H <sub>2</sub> O	1.0 × 10 <sup>-13</sup>	1320 f
G50	CH <sub>3</sub> COCH <sub>2</sub> OO + NO (+O <sub>2</sub> ) → CH <sub>3</sub> CO <sub>3</sub> + HCHO + NO <sub>2</sub>	8.0 × 10 <sup>-12</sup>	-300 g
G51	CH <sub>3</sub> COCH <sub>2</sub> OO + HO <sub>2</sub> → CH <sub>3</sub> COCH <sub>2</sub> OOH + O <sub>2</sub>	9.0 × 10 <sup>-12</sup>	-1250 g
G52a	OH + CH <sub>3</sub> COCH <sub>2</sub> OOH → CH <sub>3</sub> COCH <sub>2</sub> OO + H <sub>2</sub> O	1.0 × 10 <sup>-12</sup>	x
G52b	→ CH <sub>3</sub> COCHO + OH + H <sub>2</sub> O	5.0 × 10 <sup>-12</sup>	x
G53	OH + CH <sub>3</sub> COCHO (+O <sub>2</sub> ) → CH <sub>3</sub> CO <sub>3</sub> + CO + H <sub>2</sub> O	1.5 × 10 <sup>-11</sup>	-830 b
G54	CH <sub>3</sub> CO <sub>3</sub> + NO (+O <sub>2</sub> ) → CO <sub>2</sub> + CH <sub>3</sub> OO + NO <sub>2</sub>	2.0 × 10 <sup>-11</sup>	-270 g
G55a	CH <sub>3</sub> CO <sub>3</sub> + HO <sub>2</sub> → CH <sub>3</sub> C(O)OOH + O <sub>2</sub>	1.1 × 10 <sup>-11</sup>	-1040 g
G55b	→ CH <sub>3</sub> COOH + O <sub>3</sub>	2.8 × 10 <sup>-12</sup>	-1040 g
G56	CH <sub>3</sub> CO <sub>3</sub> + CH <sub>3</sub> OO (+O <sub>2</sub> ) → CO <sub>2</sub> + HCHO + CH <sub>3</sub> OO + HO <sub>2</sub> + O <sub>2</sub>	1.1 × 10 <sup>-11</sup>	-500 g
G57	CH <sub>3</sub> CO <sub>3</sub> + CH <sub>3</sub> CO <sub>3</sub> (+O <sub>2</sub> ) → 2CH <sub>3</sub> OO + 2CO <sub>2</sub>	1.4 × 10 <sup>-11</sup>	-500 g
G58	CH <sub>3</sub> CO <sub>3</sub> + NO <sub>2</sub> → PAN	1.0 × 10 <sup>-11</sup>	g
G59	PAN → CH <sub>3</sub> CO <sub>3</sub> + NO <sub>2</sub>	4.8 × 10 <sup>-4</sup>	13580 g
G60	OH + CH <sub>3</sub> COOH (+O <sub>2</sub> ) → CH <sub>3</sub> OO + CO <sub>2</sub> + H <sub>2</sub> O	8.0 × 10 <sup>-13</sup>	e
G61	OH + CH <sub>3</sub> OH (+O <sub>2</sub> ) → HCHO + H <sub>2</sub> O + HO <sub>2</sub>	9.0 × 10 <sup>-13</sup>	415 h
G62 <sup>c</sup>	OH + C <sub>2</sub> H <sub>5</sub> OH (+O <sub>2</sub> ) → CH <sub>3</sub> CHO + H <sub>2</sub> O + HO <sub>2</sub>	3.2 × 10 <sup>-12</sup>	85 h
G63 <sup>c</sup>	OH + C <sub>2</sub> H <sub>5</sub> CHO (+O <sub>2</sub> ) → C <sub>2</sub> H <sub>5</sub> CO <sub>3</sub> + H <sub>2</sub> O	2.0 × 10 <sup>-11</sup>	-405 e
G64	C <sub>2</sub> H <sub>5</sub> CO <sub>3</sub> + NO → C <sub>2</sub> H <sub>5</sub> OO + CO <sub>2</sub> + NO <sub>2</sub>	2.1 × 10 <sup>-11</sup>	-340 e
G65a	C <sub>2</sub> H <sub>5</sub> CO <sub>3</sub> + HO <sub>2</sub> → C <sub>2</sub> H <sub>5</sub> C(O)OOH + O <sub>2</sub>	1.2 × 10 <sup>-11</sup>	i
G65b	→ C <sub>2</sub> H <sub>5</sub> COOH + O <sub>3</sub>	2.6 × 10 <sup>-12</sup>	i
G66	C <sub>2</sub> H <sub>5</sub> CO <sub>3</sub> + NO <sub>2</sub> → C <sub>2</sub> H <sub>5</sub> C(O)ONO <sub>2</sub>	1.0 × 10 <sup>-11</sup>	x
G67	C <sub>2</sub> H <sub>5</sub> C(O)ONO <sub>2</sub> → C <sub>2</sub> H <sub>5</sub> CO <sub>3</sub> + NO <sub>2</sub>	5.0 × 10 <sup>-4</sup>	14073 j
G68 <sup>c</sup>	OH + C <sub>2</sub> H <sub>5</sub> COOH (+O <sub>2</sub> ) → CH <sub>3</sub> CH(OO)COOH + H <sub>2</sub> O	1.2 × 10 <sup>-12</sup>	k
G69a	CH <sub>3</sub> CH(OO)COOH + NO (+O <sub>2</sub> ) → CH <sub>3</sub> CHO + CO <sub>2</sub> + HO <sub>2</sub> + NO <sub>2</sub>	6.3 × 10 <sup>-12</sup>	x
G69b	→ CH <sub>3</sub> COCO <sub>3</sub> + HO <sub>2</sub> + NO <sub>2</sub>	2.7 × 10 <sup>-12</sup>	x

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Table II. (Continued)

Reaction	$k_{298}$ ( $\text{cm}^3 \text{s}^{-1}$ or $\text{s}^{-1}$ )	$-E_a/R_g$ (K)	Ref. <sup>a</sup>
G70	$\text{CH}_3\text{CH}(\text{OO})\text{COOH} + \text{HO}_2$ $\rightarrow \text{CH}_3\text{CH}(\text{OOH})\text{COOH} + \text{O}_2$	$9.0 \times 10^{-12}$	x
G71 <sup>c</sup>	$\text{OH} + \text{CH}_3\text{CH}(\text{OOH})\text{COOH}$ $\rightarrow \text{CH}_3\text{COCO}(\text{OOH}) + \text{OH} + \text{H}_2\text{O}$	$5.0 \times 10^{-12}$	x
G72	$\text{OH} + \text{CH}_3\text{COCO}(\text{OOH}) (+\text{O}_2)$ $\rightarrow \text{CH}_3\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O}$	$1.2 \times 10^{-13}$	-276 1
G73a	$\text{OOCH}_2\text{COOH} + \text{NO} (+\text{O}_2)$ $\rightarrow \text{OCHCOOH} + \text{NO}_2 + \text{HO}_2$	$4.5 \times 10^{-12}$	x
G73b	$\rightarrow \text{HCHO} + \text{CO}_2 + \text{HO}_2$	$4.5 \times 10^{-12}$	x
G74	$\text{OOCH}_2\text{COOH} + \text{HO}_2$ $\rightarrow \text{HOOCH}_2\text{COOH} + \text{O}_2$	$9.0 \times 10^{-12}$	x
G75a	$\text{OH} + \text{HOOCH}_2\text{COOH}$ $\rightarrow \text{OOCH}_2\text{COOH} + \text{H}_2\text{O}$	$1.0 \times 10^{-12}$	x
G75b	$\rightarrow \text{OCHCOOH} + \text{OH} + \text{H}_2\text{O}$	$5.0 \times 10^{-12}$	x
G76	$\text{OH} + \text{OCHCOOH} (+\text{O}_2)$ $\rightarrow \text{CO} + \text{CO}_2 + \text{HO}_2 + \text{H}_2\text{O}$	$1.5 \times 10^{-11}$	x
G77	$\text{OH} + \text{HOCH}_2\text{COOH} (+\text{O}_2)$ $\rightarrow \text{OCHCOOH} + \text{HO}_2 + \text{H}_2\text{O}$	$5.0 \times 10^{-12}$	x
G78	$\text{OH} + \text{CH}_3\text{CH}(\text{OH})\text{COOH} (+\text{O}_2)$ $\rightarrow \text{CH}_3\text{COCO}(\text{OOH}) + \text{HO}_2$	$5.0 \times 10^{-12}$	x
Oxidation of alkenes			
G79	$\text{OH} + \text{C}_2\text{H}_4 (+\text{O}_2) \rightarrow \text{HOCH}_2\text{CH}_2\text{OO}$	$8.5 \times 10^{-12}$	-438 b
G80a	$\text{HOCH}_2\text{CH}_2\text{OO} + \text{NO} (+\text{O}_2)$ $\rightarrow 2 \text{HCHO} + \text{NO}_2 + \text{HO}_2$	$7.0 \times 10^{-12}$	b
G80b	$\rightarrow \text{HOCH}_2\text{CHO} + \text{NO}_2 + \text{HO}_2$	$2.0 \times 10^{-12}$	b
G81	$\text{HOCH}_2\text{CH}_2\text{OO} + \text{HO}_2$ $\rightarrow \text{HOCH}_2\text{CH}_2\text{OOH} + \text{O}_2$	$1.5 \times 10^{-11}$	b
G82a	$\text{OH} + \text{HOCH}_2\text{CH}_2\text{OOH}$ $\rightarrow \text{HOCH}_2\text{CH}_2\text{OO} + \text{H}_2\text{O}$	$1.0 \times 10^{-12}$	x
G82b	$\rightarrow \text{HOCH}_2\text{CHO} + \text{OH} + \text{H}_2\text{O}$	$5.0 \times 10^{-12}$	x
G82c	$\text{OH} + \text{HOCH}_2\text{CH}_2\text{OOH} (+\text{O}_2)$ $\rightarrow \text{OCHCH}_2\text{OOH} + \text{HO}_2 + \text{H}_2\text{O}$	$3.0 \times 10^{-12}$	x
G83a	$\text{OH} + \text{OCHCH}_2\text{OOH}$ $\rightarrow \text{CO} + \text{HCHO} + \text{H}_2\text{O} + \text{OH}$	$1.2 \times 10^{-11}$	x
G83b	$\rightarrow \text{OCHCHO} + \text{OH} + \text{H}_2\text{O}$	$5.0 \times 10^{-12}$	x
G84a	$\text{OH} + \text{HOCH}_2\text{CHO} (+\text{O}_2)$ $\rightarrow \text{HCHO} + \text{CO} + \text{HO}_2$	$1.0 \times 10^{-11}$	b
G84b	$\rightarrow \text{OCHCHO} + \text{HO}_2$	$2.5 \times 10^{-12}$	b
G85	$\text{O}_3 + \text{C}_2\text{H}_4 \rightarrow \text{HCHO} + \text{CH}_2\text{OO}^*$	$1.6 \times 10^{-18}$	2580 b

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Table II. (Continued)

Reaction	$k_{298}$ (cm <sup>3</sup> s <sup>-1</sup> or s <sup>-1</sup> )	$-E_a/R_g$ (K)	Ref. <sup>a</sup>
G86a	CH <sub>2</sub> OO* (+M, H <sub>2</sub> O) → HCOOH	47.0%	b
G86b	CH <sub>2</sub> OO* (+O <sub>2</sub> ) → CO + HO <sub>2</sub> + OH	12.0%	b
G86c	→ CO <sub>2</sub> + 2HO <sub>2</sub>	10.6%	b
G86d	→ CO <sub>2</sub> + H <sub>2</sub>	13.8%	b
G86e	→ CO + H <sub>2</sub> O	12.4%	b
G86f	→ HCOOH	4.2%	
G87a	OH + C <sub>3</sub> H <sub>6</sub> (+O <sub>2</sub> ) → CH <sub>3</sub> CH(OO)CH <sub>2</sub> OH	1.9 × 10 <sup>-11</sup>	-504 b
G87b	OH + C <sub>3</sub> H <sub>6</sub> (+O <sub>2</sub> ) → CH <sub>3</sub> CH(OH)CH <sub>2</sub> OO	7.0 × 10 <sup>-12</sup>	-504 b
G88a	CH <sub>3</sub> CH(OO)CH <sub>2</sub> OH + NO (+O <sub>2</sub> ) → HCHO + CH <sub>3</sub> CHO + NO <sub>2</sub> + HO <sub>2</sub>	9.0 × 10 <sup>-12</sup>	b
G88b	CH <sub>3</sub> CH(OH)CH <sub>2</sub> OO + NO (+O <sub>2</sub> ) → HCHO + CH <sub>3</sub> CHO + NO <sub>2</sub> + HO <sub>2</sub>	9.0 × 10 <sup>-12</sup>	b
G89a	CH <sub>3</sub> CH(OO)CH <sub>2</sub> OH + HO <sub>2</sub> → CH <sub>3</sub> CH(OOH)CH <sub>2</sub> OH + O <sub>2</sub>	1.4 × 10 <sup>-11</sup>	x
G89b	CH <sub>3</sub> CH(OH)CH <sub>2</sub> OO + HO <sub>2</sub> → CH <sub>3</sub> CH(OH)CH <sub>2</sub> OOH + O <sub>2</sub>	1.4 × 10 <sup>-11</sup>	x
G90a	OH + CH <sub>3</sub> CH(OOH)CH <sub>2</sub> OH → CH <sub>3</sub> CH(OO)CH <sub>2</sub> OH + H <sub>2</sub> O	1.0 × 10 <sup>-12</sup>	x
G90b	→ CH <sub>3</sub> COCH <sub>2</sub> OH + H <sub>2</sub> O + OH	8.0 × 10 <sup>-12</sup>	x
G90c	OH + CH <sub>3</sub> CH(OOH)CH <sub>2</sub> OH (+O <sub>2</sub> ) → CH <sub>3</sub> CH(OOH)CHO + HO <sub>2</sub> + H <sub>2</sub> O	5.0 × 10 <sup>-12</sup>	x
G91	OH + CH <sub>3</sub> COCH <sub>2</sub> OH (+O <sub>2</sub> ) → CH <sub>3</sub> COCHO + HO <sub>2</sub> + H <sub>2</sub> O	3.0 × 10 <sup>-12</sup>	x
G92a	OH + CH <sub>3</sub> CH(OH)CH <sub>2</sub> OOH → CH <sub>3</sub> CH(OH)CH <sub>2</sub> OO + H <sub>2</sub> O	1.0 × 10 <sup>-12</sup>	x
G92b	→ CH <sub>3</sub> CH(OH)CHO + H <sub>2</sub> O + OH	5.0 × 10 <sup>-12</sup>	x
G92c	OH + CH <sub>3</sub> CH(OH)CH <sub>2</sub> OOH (+O <sub>2</sub> ) → CH <sub>3</sub> COCH <sub>2</sub> OOH + HO <sub>2</sub> + H <sub>2</sub> O	7.0 × 10 <sup>-12</sup>	x
G93a	OH + CH <sub>3</sub> CH(OH)CHO (+O <sub>2</sub> ) → CH <sub>3</sub> COCHO + HO <sub>2</sub> + H <sub>2</sub> O	7.0 × 10 <sup>-12</sup>	x
G93b	→ CH <sub>3</sub> CHO + CO + HO <sub>2</sub>	1.4 × 10 <sup>-11</sup>	x
G94a	OH + CH <sub>3</sub> CH(OOH)CHO → CH <sub>3</sub> CH(OO)CHO + H <sub>2</sub> O	1.0 × 10 <sup>-12</sup>	x
G94b	→ CH <sub>3</sub> COCHO + OH + H <sub>2</sub> O	7.0 × 10 <sup>-12</sup>	x
G94c	→ CH <sub>3</sub> CHO + CO + OH	1.0 × 10 <sup>-11</sup>	x
G95	CH <sub>3</sub> CH(OO)CHO + NO (+O <sub>2</sub> ) → CH <sub>3</sub> COCHO + NO <sub>2</sub> + HO <sub>2</sub>	9.0 × 10 <sup>-12</sup>	x
G96	CH <sub>3</sub> CH(OO)CHO + HO <sub>2</sub> → CH <sub>3</sub> CH(OOH)CHO	1.4 × 10 <sup>-11</sup>	x

(Continued on next page)

Table II. (Continued)

Reaction	$k_{298}$ ( $\text{cm}^3 \text{s}^{-1}$ or $\text{s}^{-1}$ )	$-E_a/R_g$ (K)	Ref. <sup>a</sup>	
G97a	$\text{O}_3 + \text{C}_3\text{H}_6 \rightarrow \text{CH}_3\text{CHO} + \text{CH}_2\text{OO}^*$	$3.0 \times 10^{-17}$	1878	b
G97b	$\rightarrow \text{HCHO} + \text{CH}_3\text{CHOO}^*$	$7.0 \times 10^{-17}$		b
G98a	$\text{CH}_3\text{CHOO}^* (+\text{M}, \text{H}_2\text{O}) \rightarrow \text{CH}_3\text{COOH}$	43%		b
G98b	$\text{CH}_3\text{CHOO}^* (+\text{O}_2) \rightarrow \text{CH}_3 + \text{CO} + \text{OH}$	16%		b
G98c	$\rightarrow \text{CH}_3 + \text{CO}_2 + \text{HO}_2$	18%		b
G98d	$\rightarrow \text{CH}_4 + \text{CO}_2$	16%		b
G98e	$\rightarrow \text{CH}_3\text{OH} + \text{CO}$	7%		b
Oxidation of acetylene				
G99a	$\text{OH} + \text{C}_2\text{H}_2 (+\text{O}_2) \rightarrow \text{OCHCHO} + \text{OH}$	$4.8 \times 10^{-13}$		k
G99b	$\rightarrow \text{HCOOH} + \text{CO} + \text{HO}_2$	$3.2 \times 10^{-13}$		k
G100	$\text{OH} + \text{OCHCHO} (+\text{O}_2)$ $\rightarrow 2\text{CO} + \text{HO}_2 + \text{H}_2\text{O}$	$1.1 \times 10^{-11}$		b

<sup>a</sup>References: a, Warneck (2001); b, Calvert *et al.* (2000); c, estimate of Beck (1998) based on the absorption spectrum of Back and Yamamoto (1985); d, Berges and Warneck (1992); e, Atkinson *et al.* (1997); f, Wollenhaupt and Crowley (2000), Wollenhaupt *et al.* (2000); g, Tyndall *et al.* (2001); h, Jiménez *et al.* (2003); i, Lightfoot *et al.* (1992); j, Schurath and Wipprecht (1980); k, Atkinson (1994); l, Mellouki and Mu (2003), the reaction path was assumed to be like that of acetic acid; x, estimate, see text.

<sup>b</sup>Photodissociation coefficients are noon time values.

<sup>c</sup>Only the most prominent reaction channel is considered.

(1997) was used as a guide. Hydroperoxides, in turn, can react with OH radicals. These reactions are assumed to have two channels, similar to the reaction of OH with  $\text{CH}_3\text{OOH}$ . One, the abstraction of the peroxidic hydrogen atom, was assigned a rate coefficient of  $1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  in all cases. Rate coefficients for the other channels, which involve the abstraction of a hydrogen atom from the neighboring carbon atom, were estimated by analogy to the corresponding alcohol augmented by 50% to account for the presence of the peroxy group. Photochemical decomposition of organic hydroperoxides was not considered. These processes should be less important than reactions with OH radicals. The reaction scheme in Table II includes the self-reaction of acetyl peroxy and its combination with methyl peroxy. The self-reaction of methyl peroxy was included previously and is retained. The combinatory interactions of all other alkyl peroxy radicals are neglected, because they occur at lower concentrations and the rate coefficients are much smaller than those for their reactions with NO and  $\text{HO}_2$ . The interactions of alkyl peroxy with acetyl peroxy radicals may possibly be important, if the rate coefficients had values similar to that for the reaction between methyl peroxy and acetyl peroxy. The results of this study indicate, however, that the concentrations of acetyl peroxy radicals are low enough to allow these reactions to be neglected as well. Finally, the



additional reactions in Table II do not take into account processes involving NO<sub>3</sub> radicals, except the reaction with acetaldehyde. As NO<sub>3</sub> radicals are active mainly at night, the night-time chemistry clearly is incomplete.

Table III lists Henry's law constants and mass accommodation coefficients for a number of substances involved in the mechanism. The dissolution in water of ethane, propane, ethene, propene and acetylene, like that of methane, is neglected because these gases are poorly soluble. Hydroperoxides not listed in Table III are C<sub>2</sub>H<sub>5</sub>CH<sub>2</sub>OOH, CH<sub>3</sub>CH(OOH)CH<sub>3</sub> and CH<sub>3</sub>COCH<sub>2</sub>OOH. They are treated like C<sub>2</sub>H<sub>5</sub>OOH. HOCH<sub>2</sub>CH<sub>2</sub>OOH was estimated to behave similar to ethane diol, and

Table III. Supplement of gas-liquid partition coefficients,  $K_H$  (mol dm<sup>-3</sup> atm<sup>-1</sup>, 1 atm = 101.325 kPa), the associated heats of solution  $\Delta H_{\text{soln}}/R_g$  (K) divided by the gas constant, and the mass accommodation coefficients,  $\alpha$ , at 285 K

	$K_H(298)$	$\Delta H_{\text{soln}}/R_g$	$\alpha(285)$	Ref. <sup>a</sup>
C <sub>2</sub> H <sub>5</sub> OH	$1.9 \times 10^2$	6290	0.021	a, b
CH <sub>3</sub> CHO <sup>b</sup>	13.4	5880	0.02	c, x
C <sub>2</sub> H <sub>5</sub> CHO <sup>b</sup>	13.1	5940	0.02	d, x
CH <sub>3</sub> COCH <sub>3</sub>	26.9	5230	0.01	c, b
CH <sub>3</sub> COCHO <sup>b</sup>	$3.7 \times 10^3$	7540	0.02	e, x
HOCH <sub>2</sub> CHO <sup>b</sup>	$4.1 \times 10^4$	4630	0.02	e, x
OHCCHO <sup>b</sup>	$3.6 \times 10^5$		0.02	e, x
CH <sub>3</sub> COCH <sub>2</sub> OH	$4.7 \times 10^2$	7200	0.02	f, x
CH <sub>3</sub> COOH	$4.1 \times 10^3$	6200	0.037	g, b
OCHCOOH <sup>b</sup>	$2.7 \times 10^6$		0.02	h, x
HOCH <sub>2</sub> COOH	$4.2 \times 10^5$		0.02	i, x
CH <sub>3</sub> COCO <sup>b</sup>	$3.1 \times 10^5$	5100	0.02	j, x
C <sub>2</sub> H <sub>5</sub> OOH	$3.4 \times 10^2$	5990	0.02	k, x
CH <sub>3</sub> C(O)OOH	$8.4 \times 10^2$	5310	0.02	k, x
HOOCH <sub>2</sub> COOH	$4.2 \times 10^5$		0.02	i, x
CH <sub>3</sub> CO <sub>3</sub>	40.5	3830	0.02	l, x
OOCH <sub>2</sub> COOH	$2.0 \times 10^4$		0.02	l, x
HOCH <sub>2</sub> CH <sub>2</sub> OOH	$4.0 \times 10^5$		0.02	i, x
PAN	2.8	6550	0.02	m, x

<sup>a</sup>The first entry refers to the partition coefficient, the second to the accommodation coefficient: a, Snider and Dawson (1985); b, Duan *et al.* (1993), Davidovits *et al.* (1995); c, Benkelberg *et al.* (1995); d, Zhou and Mopper (1990); e, Betterton and Hoffmann (1988), for OCHCHO only a lower limit value is available; f, assumed to be similar to 1-propanol, Snider and Dawson (1985); g, Johnson *et al.* (1996); h, Saxena and Hildemann (1996); i, assumed to be similar to values for diols, Saxena and Hildemann (1996); j, Khan *et al.* (1995); k, O'Sullivan *et al.* (1996); l, it was assumed that  $K_H(\text{peroxy}) = K_H(\text{hydroperoxide}) \times K_H(\text{HO}_2)/K_H(\text{H}_2\text{O}_2)$ ; m, Kames *et al.* (1991), Kames *et al.* (1995); x, estimate for mass accommodation coefficient.

<sup>b</sup>Value for the sum of hydrated and non-hydrated compound in the aqueous phase.

the hydroxy-hydroperoxides  $\text{CH}_3\text{CH}(\text{OOH})\text{CH}_2\text{OH}$  and  $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{OOH}$  (not listed in Table III) are taken to behave similar to 1,2 propane-diol,  $K_{\text{H}} \approx 9.0 \times 10^5 \text{ mol dm}^{-3} \text{ atm}^{-1}$  (Saxena and Hildemann, 1996). The partition coefficients for  $\text{HOCH}_2\text{COOH}$ ,  $\text{HOCH}_2\text{COOH}$ ,  $\text{CH}_3\text{CHOHCOOH}$  and  $\text{CH}_3\text{CH}(\text{OOH})\text{COOH}$  are likewise assumed to have values similar to diols, whereas the hydroperoxy-carbonyl compounds  $\text{OCHCH}_2\text{OOH}$ ,  $\text{CH}_3\text{CH}(\text{OOH})\text{CHO}$  and  $\text{CH}_3\text{CH}(\text{OOH})\text{CHO}$  are treated like hydroxy-ethanal. The partition coefficient for peroxy propionic acid,  $\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{OOH}$ , was modeled like that of peroxy acetic acid,  $\text{CH}_3\text{C}(\text{O})\text{OOH}$ , which has been measured (O'Sullivan *et al.*, 1996).

Note that it is necessary to distinguish between the two peroxy acids  $\text{CH}_3\text{C}(\text{O})\text{OOH}$  and  $\text{HOCH}_2\text{COOH}$ . The former is commonly called peroxy acetic acid, whereas according to IUPAC terminology it should be named ethane peroxy acid. The latter must be designated hydroperoxy ethanoic acid. Similarly,  $\text{C}_2\text{H}_5\text{C}(\text{O})\text{OOH}$  is designated propane peroxy acid in order to distinguish it from 2-hydroperoxy propanoic acid,  $\text{CH}_3\text{CH}(\text{OOH})\text{COOH}$ . Ethane peroxy acid has a fairly high pK value (pK  $\approx 7.7$ ). In the acidic pH regime of clouds it behaves like a hydroperoxide because dissociation can be neglected. In contrast, the carboxyl group of hydroperoxy acetic acid is expected (and was assumed) to have a pK value similar to that of glycolic acid (pK  $\approx 3.8$ ). Likewise, the pK value of 2-hydroperoxy propanoic acid was assumed to be similar to that of lactic acid (pK  $\approx 3.8$ ).

Among the peroxy radicals produced in the gas phase, only  $\text{CH}_3\text{CO}_3$  is considered to enter the aqueous phase in addition to  $\text{CH}_3\text{OO}$  and  $\text{HO}_2$ , which were previously included. Other species that are present with much lower abundances were neglected. Their aqueous reactions with  $\text{HO}_2$  and  $\text{O}_2^-$  would form hydroperoxides, but these reactions are unimportant compared to the corresponding reactions with  $\text{HO}_2$  in the gas phase. The source of  $\text{OOCH}_2\text{COOH}$  is the oxidation of acetic acid in aqueous solution. This peroxy radical is estimated to have a partition coefficient similar to that of acetic acid. It is partly transferred to the gas phase, where it undergoes additional reactions. All substances resulting from reactions in aqueous solution with the exception of oxalic acid are released to the gas phase when the cloud dissipates. Oxalic acid is assumed to remain associated with deliquescent aerosol particles, because it remains fully dissociated at the pH attained (pH 2–3).

Table IV provides data for additional aqueous phase equilibria that need consideration. The species  $\text{OHCCHO}$  and  $\text{CH}_3\text{COCHO}$ , are almost fully hydrated in aqueous solution (Betterton *et al.*, 1988), and it is assumed that hydration occurs rapidly in both cases. Undissociated pyruvic acid,  $\text{CH}_3\text{COCOCH}_3$ , also is fully hydrated, whereas the anion, which is preponderant in the pH range considered, occurs largely in the non-hydrated form (Fischer and Warneck, 1991). Table IV includes dissociation constants for several acids involved. Values for  $\text{HOCH}_2\text{COOH}$  and  $\text{OOCH}_2\text{COOH}$ , which are not known and are not listed, are arbitrarily set equal to that for  $\text{HOCH}_2\text{COOH}$ .

Table V presents additional reactions in the aqueous phase. Whereas in the gas phase oxygen is present in large excess and its concentration is constant, the  $\text{O}_2$

Table IV. Supplement of aqueous phase equilibria: equilibrium constants and forward reaction rate coefficients (units: mol, dm<sup>3</sup>, s)

Reaction	$K(298)$	$\Delta H_{\text{diss}}/R_g$	$k_f$	$k_r$	Ref. <sup>a</sup>
CH <sub>3</sub> CHO (+H <sub>2</sub> O) ⇌ CH <sub>3</sub> CH(OH) <sub>2</sub>	1.06	1213	0.0042 + 346 [H <sup>+</sup> ] <sup>b</sup>	0.0043 + 279 [H <sup>+</sup> ] <sup>b</sup>	a
CH <sub>3</sub> COOH ⇌ CH <sub>3</sub> COO <sup>-</sup> + H <sup>+</sup>	1.75 × 10 <sup>-5</sup>	-50.3	7.9 × 10 <sup>5b</sup>	4.5 × 10 <sup>10</sup>	b, c
(HO) <sub>2</sub> CHCOOH ⇌ (HO) <sub>2</sub> CHCOO <sup>-</sup> + H <sup>+</sup>	3.47 × 10 <sup>-4</sup>	267	6.7 × 10 <sup>6b</sup>	2.0 × 10 <sup>10c</sup>	b
OCHCOOH ⇌ (HO) <sub>2</sub> CHCOOH	300		7.5	0.025	d
OCHCOO <sup>-</sup> ⇌ (HO) <sub>2</sub> CHCOO <sup>-</sup>	15.1		0.083	0.0055	d
HOCH <sub>2</sub> CHO ⇌ HOCH <sub>2</sub> CH(OH) <sub>2</sub>	9.0		0.086	0.0096	d
CH <sub>3</sub> CO (+H <sub>2</sub> O) ⇌ CH <sub>3</sub> C(OH) <sub>2</sub>	1.5		2.0 × 10 <sup>4</sup>	3.0 × 10 <sup>4</sup>	e
HOCH <sub>2</sub> COOH ⇌ HOCH <sub>2</sub> COO <sup>-</sup> + H <sup>+</sup>	1.48 × 10 <sup>-4</sup>	80.5	2.9 × 10 <sup>6b</sup>	2.0 × 10 <sup>10c</sup>	b
CH <sub>3</sub> CHOHCOOH ⇌ CH <sub>3</sub> CHOHCOO <sup>-</sup> + H <sup>+</sup>	1.38 × 10 <sup>-4</sup>	40.3	2.7 × 10 <sup>6b</sup>	2.0 × 10 <sup>10c</sup>	b
CH <sub>3</sub> COCO <sup>+</sup> OH ⇌ CH <sub>3</sub> COCO <sup>-</sup> + H <sup>+</sup>	3.26 × 10 <sup>-3</sup>	1418	5.2 × 10 <sup>7b</sup>	2.0 × 10 <sup>10c</sup>	f
HC <sub>2</sub> O <sub>4</sub> <sup>-</sup> ⇌ C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> + H <sup>+</sup>	5.42 × 10 <sup>-5</sup>	-805	1.2 × 10 <sup>6b</sup>	2.0 × 10 <sup>10c</sup>	b
H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> ⇌ HC <sub>2</sub> O <sub>4</sub> <sup>-</sup> + H <sup>+</sup>	5.59 × 10 <sup>-2</sup>	-453	1.0 × 10 <sup>9b</sup>	2.0 × 10 <sup>10c</sup>	b

<sup>a</sup>a, Kurz (1967), Kurz and Coburn (1967); b, Smith and Martell (1977); c, Eigen *et al.* (1964); d, Sørensen *et al.* (1974); e, Schuchmann and von Sonntag (1988); f, Fischer and Warneck (1991).

<sup>b</sup>At 285 K.

<sup>c</sup>Value adopted in the present study.

concentration in the aqueous phase is diffusion-controlled and may be depleted by oxidation reactions. Allowance is made for this possibility by separating addition reactions between O<sub>2</sub> and organic radicals from other reactions in the oxidation mechanisms. The results indicate, however, that the exchange of O<sub>2</sub> with the gas phase and aqueous diffusion are sufficiently rapid to maintain an almost constant concentration of oxygen also in the aqueous phase. The oxidation mechanisms of ethanol, acetaldehyde and acetone are largely equivalent to those occurring in the gas phase. The known rate coefficients for the two channels of the reaction between methyl peroxy radicals are equivalent to those in the gas phase. If acetyl peroxy radicals were treated in the same manner, the respective rate coefficients would approach the diffusion limit. Therefore, the values were reduced by a factor of

Table V. Supplementary aqueous phase reactions

Reaction	$k_{298}$ (dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> or s <sup>-1</sup> )	$-E_a/R_g$ (K)	Ref. <sup>a</sup>
Photolysis			
$\text{CH}_3\text{COCH}_3 + h\nu \rightarrow \text{CH}_3 + \text{CH}_3\text{CO}$	$1.0 \times 10^{-6}$		a
General reactions			
A98 $\text{OH} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{CH}_3\text{CHOH} + \text{H}_2\text{O}$	$1.9 \times 10^9$	1200	c, s
A99 $\text{CH}_3\text{CHOH} + \text{O}_2 \rightarrow \text{CH}_3\text{CHO} + \text{HO}_2$	$2.0 \times 10^9$		d
A100 $\text{OH} + \text{CH}_3\text{CHO} \rightarrow \text{CH}_3\text{CO} + \text{H}_2\text{O}$	$3.6 \times 10^9$		e
A101 $\text{CH}_3\text{CO} + \text{O}_2 \rightarrow \text{CH}_3\text{CO}_3$	$2.0 \times 10^9$		d
A102 $\text{OH} + \text{CH}_3\text{CH}(\text{OH})_2$ $\rightarrow \text{CH}_3\text{C}(\text{OH})_2 + \text{H}_2\text{O}$	$1.2 \times 10^9$		e
A103 $\text{CH}_3\text{C}(\text{OH})_2 + \text{O}_2$ $\rightarrow \text{CH}_3\text{COOH} + \text{HO}_2$	$2.0 \times 10^9$		d
A104 $\text{CH}_3\text{CO}_3 + \text{HO}_2$ $\rightarrow \text{CH}_3\text{C}(\text{O})\text{OOH} + \text{O}_2$	$5.0 \times 10^6$		x
A105 $\text{CH}_3\text{CO}_3 + \text{O}_2^-$ $\rightarrow \text{CH}_3\text{C}(\text{O})\text{OOH} + \text{OH}^- + \text{O}_2$	$1.0 \times 10^9$		e
A106 $\text{CH}_3\text{CO}_3 + \text{CH}_3\text{CO}_3$ $\rightarrow 2\text{CH}_3 + 2\text{CO}_2 + \text{O}_2$	$2.0 \times 10^9$		x
A107 $\text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{O}_2$	$3.2 \times 10^9$		f
A108 $\text{CH}_3\text{CO}_3 + \text{CH}_3\text{O}_2$ $\rightarrow \text{CH}_3\text{O} + \text{CH}_3 + \text{CO}_2 + \text{O}_2$	$2.0 \times 10^9$		x
A109a $\text{CH}_3\text{O}_2 + \text{CH}_3\text{O}_2$ $\rightarrow \text{HCHO} + \text{CH}_3\text{OH} + \text{O}_2$	$1.3 \times 10^8$		g
A109b $\rightarrow 2\text{CH}_3\text{O} + \text{O}_2$	$0.7 \times 10^8$		g
A110 $\text{CH}_3\text{O} \rightarrow \text{CH}_2\text{OH}$	$5.0 \times 10^5$		g
A111 <sup>b</sup> $\text{CH}_2\text{OH} + \text{O}_2 \rightarrow \text{HCHO} + \text{HO}_2$	$4.5 \times 10^9$		g
A112 $\text{OH} + \text{CH}_3\text{COOH}$ $\rightarrow \text{CH}_2\text{COO}^- + \text{H}^+ + \text{H}_2$	$1.7 \times 10^7$	1330	h
A113 $\text{OH} + \text{CH}_3\text{COO}^-$ $\rightarrow \text{CH}_2\text{COO}^- + \text{H}_2$	$7.3 \times 10^7$	1770	h
A114 $\text{CH}_2\text{COO}^- + \text{O}_2 \rightarrow \text{OOCH}_2\text{COO}^-$	$1.7 \times 10^9$		i
A115 $\text{OOCH}_2\text{COO}^- + \text{HO}_2$ $\rightarrow \text{HOOCH}_2\text{COO}^- + \text{O}_2$	$1.0 \times 10^6$		x
A116 $\text{OOCH}_2\text{COO}^- + \text{O}_2^-$ $\rightarrow \text{HOOCH}_2\text{COO}^- + \text{OH}^- + \text{O}_2$	$1.0 \times 10^7$		i
A117a $\text{OH} + \text{HOOCH}_2\text{COO}^-$ $\rightarrow \text{OOCH}_2\text{COO}^- + \text{H}_2\text{O}$	$1.4 \times 10^8$		x
A117b $\rightarrow \text{OCHCOO}^- + \text{OH} + \text{H}_2\text{O}$	$7.0 \times 10^8$		x

(Continued on next page)

Table V. (Continued)

Reaction	$k_{298}$ (dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> or s <sup>-1</sup> )	$-E_a/R_g$ (K)	Ref. <sup>a</sup>
A118a	2OCH <sub>2</sub> COO <sup>-</sup> → HOCH <sub>2</sub> COO <sup>-</sup> + OCHCOO <sup>-</sup> + O <sub>2</sub>	4.2 × 10 <sup>7</sup>	i
A118b	→ 2 HOCHCOO <sup>-</sup> + O <sub>2</sub>	1.8 × 10 <sup>7</sup>	i
A118c	→ 2 HCHO + 2 CO <sub>2</sub> + H <sub>2</sub> O <sub>2</sub> + 2OH <sup>-</sup>	4.2 × 10 <sup>7</sup>	i
A118d	→ 2 OCHCOO <sup>-</sup> + H <sub>2</sub> O <sub>2</sub>	3.9 × 10 <sup>7</sup>	i
A119	HOCHCOO <sup>-</sup> + O <sub>2</sub> → OCHCOO <sup>-</sup> + HO <sub>2</sub>	2.0 × 10 <sup>9</sup>	d
A120a	CH <sub>3</sub> OO + OCH <sub>2</sub> COO <sup>-</sup> → HCHO + HOCH <sub>2</sub> COO <sup>-</sup> + O <sub>2</sub>	6.0 × 10 <sup>7</sup>	x
A120b	→ CH <sub>3</sub> OH + OCHCOO <sup>-</sup> + O <sub>2</sub>	6.0 × 10 <sup>7</sup>	x
A120c	→ CH <sub>3</sub> O + HOCHCOO <sup>-</sup> + O <sub>2</sub>	8.0 × 10 <sup>7</sup>	x
A121	CH <sub>3</sub> CO <sub>3</sub> + OCH <sub>2</sub> COO <sup>-</sup> → CH <sub>3</sub> + CO <sub>2</sub> + HOCHCOO <sup>-</sup> + O <sub>2</sub>	2.0 × 10 <sup>9</sup>	x
A122	OH + HOCH <sub>2</sub> COOH → HOCHCOO <sup>-</sup> + H <sup>+</sup> + H <sub>2</sub> O	6.0 × 10 <sup>8</sup>	c
A123	OH + HOCH <sub>2</sub> COO <sup>-</sup> → HOCHCOO <sup>-</sup> + H <sub>2</sub> O	8.6 × 10 <sup>8</sup>	c
A124	OH + (HO) <sub>2</sub> CHCOOH → (HO) <sub>2</sub> CCOO <sup>-</sup> + H <sub>2</sub> O + H <sup>+</sup>	2.8 × 10 <sup>8</sup>	1000 s
A125	OH + (HO) <sub>2</sub> CHCOO <sup>-</sup> → (HO) <sub>2</sub> CCOO <sup>-</sup> + H <sub>2</sub> O	1.5 × 10 <sup>9</sup>	4500 j, s
A126	OH + OCHCOO <sup>-</sup> → CO + CO <sub>2</sub> + H <sub>2</sub> O	3.6 × 10 <sup>9</sup>	k
A127	(HO) <sub>2</sub> CCOO <sup>-</sup> + O <sub>2</sub> → HC <sub>2</sub> O <sub>4</sub> <sup>-</sup> + HO <sub>2</sub>	2.0 × 10 <sup>9</sup>	d
A128	OH + HC <sub>2</sub> O <sub>4</sub> <sup>-</sup> → CO <sub>2</sub> + CO <sub>2</sub> <sup>-</sup> + H <sub>2</sub> O	4.7 × 10 <sup>7</sup>	c
A129	OH + C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> → CO <sub>2</sub> + CO <sub>2</sub> <sup>-</sup> + OH <sup>-</sup>	7.7 × 10 <sup>6</sup>	c
A130	OH + CH <sub>3</sub> COC(OH) <sub>2</sub> → CH <sub>3</sub> COC(OH) <sub>2</sub> + H <sub>2</sub> O	1.1 × 10 <sup>9</sup>	1600 s
A131	CH <sub>3</sub> COC(OH) <sub>2</sub> + O <sub>2</sub> → CH <sub>3</sub> COCOO <sup>-</sup> + H <sup>+</sup> + HO <sub>2</sub>	2.0 × 10 <sup>9</sup>	d
A132a	OH + HOCH <sub>2</sub> CH(OH) <sub>2</sub> → HOCHCH(OH) <sub>2</sub> + H <sub>2</sub> O	5.0 × 10 <sup>8</sup>	x
A132b	→ HOCH <sub>2</sub> C(OH) <sub>2</sub> + H <sub>2</sub> O	1.0 × 10 <sup>9</sup>	x
A133	OH + HOCH <sub>2</sub> CHO → CH <sub>2</sub> OH + CO + H <sub>2</sub> O	1.0 × 10 <sup>9</sup>	x
A134	HOCH <sub>2</sub> C(OH) <sub>2</sub> + O <sub>2</sub> → HOCH <sub>2</sub> COOH + HO <sub>2</sub>	2.0 × 10 <sup>9</sup>	d
A135	HOCHCH(OH) <sub>2</sub> + O <sub>2</sub> → OCHCH(OH) <sub>2</sub> + HO <sub>2</sub>	2.0 × 10 <sup>9</sup>	d

(Continued on next page)

Table V. (Continued)

Reaction	$k_{298}$ (dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> or s <sup>-1</sup> )	$-E_a/R_g$ (K)	Ref. <sup>a</sup>
A136 OH + OCHCH(OH) <sub>2</sub> → OCHC(OH) <sub>2</sub> + H <sub>2</sub> O	1.1 × 10 <sup>9</sup>		1
A137 OCHC(OH) <sub>2</sub> + O <sub>2</sub> → OCHCOOH + HO <sub>2</sub>	1.4 × 10 <sup>9</sup>		1
A138a OH + CH <sub>3</sub> COCH <sub>3</sub> → CH <sub>3</sub> COCH <sub>2</sub>	6.5 × 10 <sup>7</sup>	2200	c, s
A138b → CH <sub>3</sub> COOH + CH <sub>3</sub>	4.5 × 10 <sup>7</sup>	2200	m
A139 CH <sub>3</sub> COCH <sub>2</sub> + O <sub>2</sub> → CH <sub>3</sub> COCH <sub>2</sub> OO	2.0 × 10 <sup>9</sup>		d
A140 CH <sub>3</sub> COCH <sub>2</sub> OO + HO <sub>2</sub> → CH <sub>3</sub> COCH <sub>2</sub> OOH + O <sub>2</sub>	1.0 × 10 <sup>6</sup>		x
A141 CH <sub>3</sub> COCH <sub>2</sub> OO + O <sub>2</sub> <sup>-</sup> → CH <sub>3</sub> COCH <sub>2</sub> OOH + OH <sup>-</sup> + O <sub>2</sub>	2.0 × 10 <sup>7</sup>		x
A142a OH + CH <sub>3</sub> COCH <sub>2</sub> OOH → CH <sub>3</sub> COCH <sub>2</sub> OO + H <sub>2</sub> O	1.4 × 10 <sup>7</sup>		x
A142b → CH <sub>3</sub> COCH(OH) <sub>2</sub> + OH	7.0 × 10 <sup>8</sup>		x
A143a OH + HOCH <sub>2</sub> CH <sub>2</sub> OOH → HOCHCH <sub>2</sub> OOH + H <sub>2</sub> O	5.0 × 10 <sup>8</sup>		x
A143b → HOCH <sub>2</sub> CH(OH) <sub>2</sub> + OH	5.0 × 10 <sup>8</sup>		x
A144 HOCHCH <sub>2</sub> OOH + O <sub>2</sub> → (HO) <sub>2</sub> CHCH <sub>2</sub> OOH + HO <sub>2</sub>	2.0 × 10 <sup>9</sup>		x
A145a OH + (HO) <sub>2</sub> CHCH <sub>2</sub> OOH → (HO) <sub>2</sub> CCH <sub>2</sub> OOH + H <sub>2</sub> O	1.0 × 10 <sup>9</sup>		x
A145b → OCHCH(OH) <sub>2</sub> + OH + H <sub>2</sub> O	8.0 × 10 <sup>8</sup>		x
A146 (HO) <sub>2</sub> CCH <sub>2</sub> OOH + O <sub>2</sub> → HOOCH <sub>2</sub> COOH + HO <sub>2</sub>	2.0 × 10 <sup>9</sup>		x
A147a OH + CH <sub>3</sub> CH(OOH)CH <sub>2</sub> OH → CH <sub>3</sub> CH(OOH)CHOH + H <sub>2</sub> O	5.0 × 10 <sup>8</sup>		x
A147b → CH <sub>3</sub> COCH <sub>2</sub> OH + OH + H <sub>2</sub> O	5.0 × 10 <sup>8</sup>		x
A148 CH <sub>3</sub> CH(OOH)CHOH + O <sub>2</sub> → CH <sub>3</sub> CH(OOH)CH(OH) <sub>2</sub> + HO <sub>2</sub>	2.0 × 10 <sup>9</sup>		x
A149 OH + CH <sub>3</sub> COCH <sub>2</sub> OH → CH <sub>3</sub> COCHOH + H <sub>2</sub> O	1.0 × 10 <sup>9</sup>		x
A150 CH <sub>3</sub> COCHOH + O <sub>2</sub> (+H <sub>2</sub> O) → CH <sub>3</sub> COCH(OH) <sub>2</sub> + HO <sub>2</sub>	2.0 × 10 <sup>9</sup>		d
A151a OH + CH <sub>3</sub> CH(OOH)CH(OH) <sub>2</sub> → CH <sub>3</sub> CH(OOH)C(OH) <sub>2</sub> + H <sub>2</sub> O	1.0 × 10 <sup>9</sup>		x
A151b → CH <sub>3</sub> COCH(OH) <sub>2</sub> + OH + H <sub>2</sub> O	5.0 × 10 <sup>8</sup>		x
A152 CH <sub>3</sub> CH(OOH)C(OH) <sub>2</sub> + O <sub>2</sub> → CH <sub>3</sub> CH(OOH)COOH + HO <sub>2</sub>	2.0 × 10 <sup>9</sup>		x
A153 OH + CH <sub>3</sub> CH(OOH)COOH → CH <sub>3</sub> COCO <sub>2</sub> H + OH + H <sub>2</sub> O	5.0 × 10 <sup>8</sup>		x

(Continued on next page)

Table V. (Continued)

Reaction	$k_{298}$ (dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> or s <sup>-1</sup> )	$-E_a/R_g$ (K)	Ref. <sup>a</sup>
A154a	OH + CH <sub>3</sub> CHOHCH <sub>2</sub> OOH → CH <sub>3</sub> COHCH <sub>2</sub> OOH + H <sub>2</sub> O	5.0 × 10 <sup>8</sup>	x
A154b	→ CH <sub>3</sub> CHOHCH(OH) <sub>2</sub> + OH	5.0 × 10 <sup>8</sup>	x
A155	CH <sub>3</sub> COHCH <sub>2</sub> OOH + O <sub>2</sub> → CH <sub>3</sub> COCH <sub>2</sub> OOH + HO <sub>2</sub>	2.0 × 10 <sup>9</sup>	x
A156a	OH + CH <sub>3</sub> CHOHCH(OH) <sub>2</sub> → CH <sub>3</sub> CHOHC(OH) <sub>2</sub> + H <sub>2</sub> O	1.0 × 10 <sup>9</sup>	x
A156b	→ CH <sub>3</sub> COHCH(OH) <sub>2</sub> + H <sub>2</sub> O	8.0 × 10 <sup>8</sup>	x
A157	CH <sub>3</sub> CHOHC(OH) <sub>2</sub> + O <sub>2</sub> → CH <sub>3</sub> CHOHCOO <sup>-</sup> + H <sup>+</sup> + HO <sub>2</sub>	2.0 × 10 <sup>9</sup>	x
A158	CH <sub>3</sub> COHCH(OH) <sub>2</sub> + O <sub>2</sub> → CH <sub>3</sub> COCH(OH) <sub>2</sub> + HO <sub>2</sub>	2.0 × 10 <sup>9</sup>	x
A159	OH + CH <sub>3</sub> CHOHCOO <sup>-</sup> → CH <sub>3</sub> COHCOO <sup>-</sup> + H <sub>2</sub> O	5.0 × 10 <sup>8</sup>	x
A160	CH <sub>3</sub> COHCOO <sup>-</sup> + O <sub>2</sub> → CH <sub>3</sub> COCOO <sup>-</sup> + HO <sub>2</sub>	2.0 × 10 <sup>9</sup>	x
A161	CH <sub>3</sub> C(OH) <sub>2</sub> COOH + OH → products	1.2 × 10 <sup>8</sup>	2800 s
A162	CH <sub>3</sub> COCOO <sup>-</sup> + OH → products	7.0 × 10 <sup>8</sup>	2300 s
Reactions involving sulfur-oxygen species			
A163	SO <sub>4</sub> <sup>-</sup> + CH <sub>3</sub> CHO → HSO <sub>4</sub> <sup>-</sup> + CH <sub>3</sub> CO	5.0 × 10 <sup>7</sup>	n
A164	SO <sub>4</sub> <sup>-</sup> + CH <sub>3</sub> CH(OH) <sub>2</sub> → HSO <sub>4</sub> <sup>-</sup> + CH <sub>3</sub> C(OH) <sub>2</sub>	1.7 × 10 <sup>7</sup>	n
A165	SO <sub>4</sub> <sup>-</sup> + CH <sub>3</sub> COO <sup>-</sup> → CH <sub>3</sub> + CO <sub>2</sub> + SO <sub>4</sub> <sup>2-</sup>	2.8 × 10 <sup>7</sup>	1210 o
A166	SO <sub>4</sub> <sup>-</sup> + HOCH <sub>2</sub> COO <sup>-</sup> → CH <sub>2</sub> OH + CO <sub>2</sub> + SO <sub>4</sub> <sup>2-</sup>	2.3 × 10 <sup>7</sup>	x
A167a	SO <sub>4</sub> <sup>-</sup> + (HO) <sub>2</sub> CHCOO <sup>-</sup> → (HO) <sub>2</sub> CCOO <sup>-</sup> + SO <sub>4</sub> <sup>2-</sup> + H <sup>+</sup>	1.7 × 10 <sup>7</sup>	p
A167b	→ CH(OH) <sub>2</sub> + CO <sub>2</sub> + SO <sub>4</sub> <sup>2-</sup>	2.3 × 10 <sup>7</sup>	p
A168 <sup>b</sup>	CH(OH) <sub>2</sub> + O <sub>2</sub> → HCOOH + HO <sub>2</sub>	2.0 × 10 <sup>9</sup>	d
A169	SO <sub>4</sub> <sup>-</sup> + (HO) <sub>2</sub> CHCOOH → (HO) <sub>2</sub> CCOO <sup>-</sup> + SO <sub>4</sub> <sup>2-</sup> + 2H <sup>+</sup>	1.7 × 10 <sup>7</sup>	p
A170a	SO <sub>4</sub> <sup>-</sup> + OCHCOO <sup>-</sup> → CH(OH) <sub>2</sub> + CO <sub>2</sub> + SO <sub>4</sub> <sup>2-</sup>	2.3 × 10 <sup>7</sup>	p
A170b	→ CO + CO <sub>2</sub> + SO <sub>4</sub> <sup>2-</sup> + H <sup>+</sup>	5.0 × 10 <sup>7</sup>	p
A171	HSO <sub>3</sub> <sup>-</sup> + C <sub>2</sub> H <sub>5</sub> OOH → C <sub>2</sub> H <sub>5</sub> OH + HSO <sub>4</sub> <sup>-</sup>	7.8 × 10 <sup>6</sup> [H <sup>+</sup> ]	q
A172	HSO <sub>3</sub> <sup>-</sup> + CH <sub>3</sub> CHOHCH <sub>3</sub> → CH <sub>3</sub> CHOHCH <sub>3</sub> + HSO <sub>4</sub> <sup>-</sup>	8.0 × 10 <sup>6</sup> [H <sup>+</sup> ]	x

(Continued on next page)

Table V. (Continued)

Reaction	$k_{298}$ (dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> or s <sup>-1</sup> )	$-E_a/R_g$ (K)	Ref. <sup>a</sup>
A173	$\text{HSO}_3^- + \text{C}_2\text{H}_5\text{CH}_2\text{OOH}$ $\rightarrow \text{C}_2\text{H}_5\text{CH}_2\text{OH} + \text{HSO}_4^-$	$8.0 \times 10^6[\text{H}^+]$	x
A174	$\text{HSO}_3^- + \text{CH}_3\text{COCH}_2\text{OOH}$ $\rightarrow \text{CH}_3\text{COCH}_2\text{OH} + \text{HSO}_4^-$	$8.0 \times 10^6[\text{H}^+]$	x
A175	$\text{HSO}_3^- + \text{HOCH}_2\text{CH}_2\text{OOH}$ $\rightarrow \text{HOCH}_2\text{CH}_2\text{OH} + \text{HSO}_4^-$	$8.0 \times 10^6[\text{H}^+]$	x
A176	$\text{HSO}_3^- + (\text{HO})_2\text{CHCH}_2\text{OOH}$ $\rightarrow \text{HOCH}_2\text{CH}(\text{OH})_2 + \text{HSO}_4^-$	$25 + 9.0 \times 10^6[\text{H}^+]$	x
A177	$\text{HSO}_3^- + \text{CH}_3\text{CHOHCH}_2\text{OOH}$ $\rightarrow \text{CH}_3\text{CHOHCH}_2\text{OH} + \text{HSO}_4^-$	$8.0 \times 10^6[\text{H}^+]$	x
A178	$\text{HSO}_3^- + \text{CH}_3\text{CH}(\text{OOH})\text{CH}_2\text{OH}$ $\rightarrow \text{CH}_3\text{CHOHCH}_2\text{OH} + \text{HSO}_4^-$	$8.0 \times 10^6[\text{H}^+]$	x
A179	$\text{HSO}_3^- + \text{HOCH}_2\text{COO}^-$ $\rightarrow \text{HOCH}_2\text{COO}^- + \text{HSO}_4^-$	$25 + 9.0 \times 10^6[\text{H}^+]$	x
A180	$\text{HSO}_3^- + \text{CH}_3\text{C}(\text{O})\text{OOH}$ $\rightarrow \text{CH}_3\text{COO}^- + \text{HSO}_4^- + \text{H}^+$	$555 + 4.9 \times 10^7[\text{H}^+]$	q
A181	$\text{HSO}_3^- + \text{C}_2\text{H}_5\text{C}(\text{O})\text{OOH}$ $\rightarrow \text{C}_2\text{H}_5\text{COO}^- + \text{HSO}_4^- + \text{H}^+$	$25 + 9.0 \times 10^6[\text{H}^+]$	x
A182	$\text{HSO}_3^- + \text{CH}_3\text{CH}(\text{OOH})\text{COO}^-$ $\rightarrow \text{CH}_3\text{CH}(\text{OH})\text{COO}^- + \text{HSO}_4^-$	$25 + 9.0 \times 10^6[\text{H}^+]$	x
A183	$\text{HSO}_3^- + \text{CH}_3\text{CH}(\text{OOH})\text{CH}(\text{OH})_2 \rightarrow$ $\text{CH}_3\text{CHOHCH}(\text{OH})_2 + \text{HSO}_4^-$	$25 + 9.0 \times 10^6[\text{H}^+]$	x
Reactions involving nitrogen-oxygen species			
A184	$\text{CH}_3\text{CO}_3 + \text{NO}_2 \rightarrow \text{PAN}$	$5.0 \times 10^9$	x
A185a	$\text{PAN} \rightarrow \text{CH}_3\text{CO}_3 + \text{NO}_2$	$7.1 \times 10^{-5}$	x
A185b	$\rightarrow \text{CH}_3\text{COOH} + \text{HOONO}_2$	$3.4 \times 10^{-4}$	x
A186	$\text{NO}_3 + \text{HC}_2\text{O}_4^-$ $\rightarrow \text{CO}_2 + \text{CO}_2^- + \text{NO}_3^- + \text{H}^+$	$6.8 \times 10^7$	r
A187	$\text{NO}_3 + \text{C}_2\text{O}_4^{2-} \rightarrow \text{CO}_2 + \text{CO}_2^- + \text{NO}_3^-$ $+ \text{CO}_2^- + \text{NO}_3^-$	$2.2 \times 10^8$	r

<sup>a</sup>a, Similar to that for the gas phase; b, Zuo (1992); c, Buxton *et al.* (1988); d, undetermined rate coefficients of association reactions involving O<sub>2</sub> were assigned a value of  $2 \times 10^9$  dm<sup>-3</sup> mol s<sup>-1</sup>; e, Schuchmann and von Sonntag (1988); f, Marchaj (1991); g, Schuchmann and von Sonntag (1984), the channel leading to CH<sub>3</sub>OOCH<sub>3</sub> was neglected; h, Chin and Wine (1994); i, Schuchmann *et al.* (1985); j, estimated from the data of Vel Leitner and Doré (1997); k, analogous to reaction A100; l, Buxton *et al.* (1997); m, branching ratio taken to be similar to that of reaction G48; n, estimated by setting  $k(\text{SO}_4^- + \text{CH}_3\text{CHO}) = k(\text{OH} + \text{CH}_3\text{CHO}) \times k(\text{SO}_4^- + \text{HCHO})/k(\text{OH} + \text{HCHO})$ ; o, Huie and Clifton (1990), p, similar to reactions A155 and A156 q, Wannowius (2001); r, Raabe (1996); s, Ervens *et al.* (2003b); x = estimated.

<sup>b</sup>In the previous description (Warneck, 1999a) reaction A111 was part of compound reaction A16, and reaction A159 was part of compound reaction A17.



four. The mechanism for the oxidation of acetic acid follows that of Schuchmann *et al.* (1985), which is here expanded to include the cross combination reactions of O<sub>2</sub>CH<sub>2</sub>COOH with methyl peroxy and acetyl peroxy. The rate coefficients for these reactions were estimated by analogy with the reactions of methyl peroxy and acetyl peroxy with each other. The oxidation of glyoxal and glycolaldehyde, which are largely entrained from the gas phase, is modeled like that of formaldehyde. Glycolic acid, glyoxylic acid and hydroperoxy ethanoic acid are intermediate oxidation products in the overall mechanisms leading to oxalic acid. Most of the hydroperoxides are only lightly soluble in water, so that their reactions in the aqueous phase can be neglected. However, they readily oxidize sulfur(IV) species, especially HSO<sub>3</sub><sup>-</sup>, which is the dominant S(IV) component in the pH range frequently encountered in atmospheric water drops. These reactions also are included.

As Table V shows, a greater number of rate coefficients of reactions in the liquid phase have not been measured and had to be estimated. Addition reactions of organic radicals with oxygen, where known, are rapid, and a standard rate coefficient of  $2 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  is adopted in cases where data are not available. Rate coefficients for all other reactions were estimated by analogy to known reactions whenever possible. For the majority of reactions, the temperature dependence has not been studied so that values reported at room temperature are mostly used.

In contrast to the previous study, which considered chemical reactions only in the presence of a cloud, the present application is designed to explore the development of the system for several days, with clouds being present twice a day, from 11.00 to 11.30 h and from 15.00 to 15.30 h, respectively. At all other times the liquid water content of the air is assumed to be that of aqueous aerosol particles ( $L = 5.0 \times 10^{-11}$ , approximately). The diurnal variation of solar radiation is approximated by a sine function with additional tails to simulate 1 h dawn and dusk periods before sunrise and after sunset. Sunrise is set at 6.00 h and sunset at 18.00 h. Noon values of the photodissociation coefficients are similar to those used previously, approximating conditions of early summer near 50° northern latitude. Photodissociation coefficients for additional processes (see Tables II and V) are adjusted accordingly. In the aqueous phase the photodissociation coefficients are raised by a factor of 1.8 compared to those in the gas phase to make allowance for the increase in light intensity in atmospheric water drops (Madronich, 1987).

Table I presents initial conditions used in the computer program. The gas phase species include not only the source gases, but also intermediates such as peroxy acetyl nitrate (PAN), acetaldehyde and acetone with mixing ratios approximating observations. The concentrations of most species were found to remain reasonably constant when running the program over time periods of several days, but ethene and propene became seriously depleted, and hydrogen peroxide and methyl hydroperoxide increased significantly. To compensate for the loss of ethene and propene due to reactions with OH radicals, surrogate sources simulating their emissions from the ocean surface were included, making allowance for the observation that both species are photochemically induced and their emissions feature a diurnal

variation with maxima at noon (Ratte *et al.*, 1993). The sources of ethene and propene required to compensate the losses were found to be about three times greater than the fluxes observed by Plass-Dülmer *et al.* (1995), but the exact values depend on the mixing ratios assumed for these source gases. The photochemical production of  $\text{H}_2\text{O}_2$  was kept in balance by a sink of appropriate magnitude in lieu of dry deposition to the ocean surface, corresponding to a deposition velocity of  $5 \times 10^{-3} \text{ cm s}^{-1}$ . The rise in the concentration of methyl hydroperoxide was tolerated.

### Results and Discussion

Initially the program was run for 48 h in the absence of cloud water to explore the behavior of the gas-phase chemical system and to establish the concentrations of species occurring as intermediates in the oxidation mechanisms. The results showed that PAN serves as source of  $\text{NO}_2$ , and that nitric acid, the oxidation product of  $\text{NO}_2$ , increases at the expense of PAN. The sum of  $\text{NO}_2$  and  $\text{NO}$ , which are intermediates in this reaction sequence, is kept in steady state and remains nearly constant. The decomposition of PAN also induces a night-time chemistry via reactions of acetyl peroxy radicals, G56 and G57, that generate  $\text{CH}_3\text{OO}$  and  $\text{HO}_2$ . The concentration of  $\text{NO}$  is insignificant at night, but the reactions of ozone with  $\text{HO}_2$ ,  $\text{C}_2\text{H}_4$  and  $\text{C}_3\text{H}_6$  still provide sources of  $\text{OH}$  radicals that induce further reactions. The ensuing chemistry is much slower than that during daylight as indicated by the smaller concentrations of important radicals. Night-time concentrations of  $\text{OH}$ ,  $\text{HO}_2$ ,  $\text{CH}_3\text{OO}$ ,  $\text{CH}_3\text{CO}_3$ , in units of molecule  $\text{cm}^{-3}$ , are approximately  $1.4 \times 10^4$ ,  $9.0 \times 10^6$ ,  $8.2 \times 10^7$  and  $7.5 \times 10^6$ , respectively. The corresponding noon time values are  $3.5 \times 10^6$ ,  $4.3 \times 10^8$ ,  $1.2 \times 10^8$  and  $8.0 \times 10^6$ . The concentrations of acetyl peroxy radicals are comparable, but they are at least one order of magnitude smaller than those of methyl peroxy radicals.

Table VI lists important products resulting from the oxidation of  $\text{C}_2$  and  $\text{C}_3$  compounds and shows mixing ratios obtained after 48 h periods in the absence and in the presence of aqueous aerosol particles. In many cases the mixing ratios differ little for the two conditions, but five product compounds are formed primarily in the aqueous phase: hydroperoxy acetic acid, glycolic acid, glyoxylic acid, oxalic acid and lactic acid. With the exception of oxalic acid, these species occur overwhelmingly in the gas phase, because the liquid volume of the aqueous aerosol is too small to retain much of these substances despite favorable Henry's law partition coefficients. Oxalic acid remains associated with the aqueous phase, but the mixing ratio is formally calculated as if the substance were present uniformly within the entire volume.

Following these initial calculations, the mixing ratios for the products shown in column 2 of Table VI were added to those in Table I to complete the spectrum of species assumed to be initially present in the full computer program. Product mixing ratios occurring on the third day shortly before noon, following the first cloud

Table VI. Gas-phase molar mixing ratios of products from C<sub>2</sub> and C<sub>3</sub> organic compounds after 48 h and after the first cloud event on the third day

Compound (origin)	Gas phase only	Aqueous aerosol present	After cloud event
Hydroperoxides			
C <sub>2</sub> H <sub>5</sub> OOH (ethane)	1.8 (−11) <sup>a</sup>	1.9 (−11) <sup>a</sup>	1.9 (−11) <sup>a</sup>
CH <sub>3</sub> C(O)OOH (acetaldehyde)	1.1 (−10)	1.1 (−10)	1.4 (−10)
CH <sub>3</sub> CH(OOH)CH <sub>3</sub> (propane)	2.9 (−11)	2.9 (−11)	2.9 (−11)
C <sub>2</sub> H <sub>5</sub> CH <sub>2</sub> OOH (propane)	1.1 (−11)	1.1 (−11)	1.1 (−11)
C <sub>2</sub> H <sub>5</sub> C(O)OOH (propane)	6.8 (−12)	6.4 (−12)	7.4 (−12)
CH <sub>3</sub> COCH <sub>2</sub> OOH (acetone, propene)	1.1 (−11)	1.1 (−11)	1.3 (−11)
HOCH <sub>2</sub> CH <sub>2</sub> OOH (ethene)	4.5 (−11)	4.5 (−11)	3.1 (−11)
OCHCH <sub>2</sub> OOH (ethene)	6.1 (−12)	6.1 (−12)	1.0 (−11)
CH <sub>3</sub> CH(OOH)CH <sub>2</sub> OH (propene)	2.7 (−11)	2.7 (−11)	1.8 (−11)
CH <sub>3</sub> CH(OH)CH <sub>2</sub> OOH (propene)	1.0 (−11)	1.0 (−11)	6.7 (−12)
CH <sub>3</sub> CH(OOH)CHO (propene)	5.9 (−12)	5.9 (−12)	7.5 (−12)
Aldehydes and ketones			
CH <sub>3</sub> CHO <sup>b</sup> (ethane, ethanol, propene)	6.1 (−11)	6.0 (−11)	6.7 (−11)
HOCH <sub>2</sub> CHO (ethene)	1.4 (−11)	1.4 (−11)	1.9 (−11)
OCHCHO (ethene, acetylene)	5.4 (−12)	5.5 (−12)	7.1 (−12)
C <sub>2</sub> H <sub>5</sub> CHO (propane)	6.5 (−12)	6.5 (−12)	8.4 (−12)
CH <sub>3</sub> COCH <sub>3</sub> <sup>b</sup> (propane)	8.1 (−10)	8.1 (−10)	8.2 (−10)
CH <sub>3</sub> COCHO (propane, propene)	3.1 (−12)	3.0 (−12)	4.3 (−12)
CH <sub>3</sub> COCH <sub>2</sub> OH (propene)	1.7 (−11)	1.8 (−11)	2.6 (−11)
CH <sub>3</sub> CH(OH)CHO (propene)	2.2 (−12)	1.9 (−12)	2.4 (−12)
Acids			
CH <sub>3</sub> COOH <sup>b</sup> (ethane, propane, propene)	2.2 (−10)	2.2 (−10)	2.2 (−10)
C <sub>2</sub> H <sub>5</sub> COOH (propane)	1.5 (−12)	1.5 (−12)	1.7 (−12)
CH <sub>3</sub> CH(OOH)COOH (propane)	5.1 (−14)	5.4 (−14)	1.2 (−12)
HOCH <sub>2</sub> COOH (acetic acid, ethene)	—	3.3 (−18)	2.9 (−12)
HOCH <sub>2</sub> COOH (acetic acid)	—	1.3 (−18)	1.6 (−12)
OCHCOOH (acetic acid, ethene)	—	3.5 (−18)	1.6 (−12)
(COOH) <sub>2</sub> (glyoxylic acid)	—	1.7 (−21)	5.4 (−13)
CH <sub>3</sub> COCOOH (propane, propene)	5.6 (−15)	5.9 (−15)	3.5 (−13)
CH <sub>3</sub> CH(OH)COOH (propene)	—	2.2 (−18)	3.8 (−13)

<sup>a</sup>Numbers in parentheses indicate powers of 10.

<sup>b</sup>Mixing ratio is prescribed by the initial conditions and shows little change.

event, are given in the third column of Table VI to show that products resulting predominantly from gas-phase reactions exhibit small changes, whereas most acids become significantly enhanced compared to those found in the absence of clouds. The behavior of several compounds has been analyzed in more detail, and the results will be discussed individually in the following.

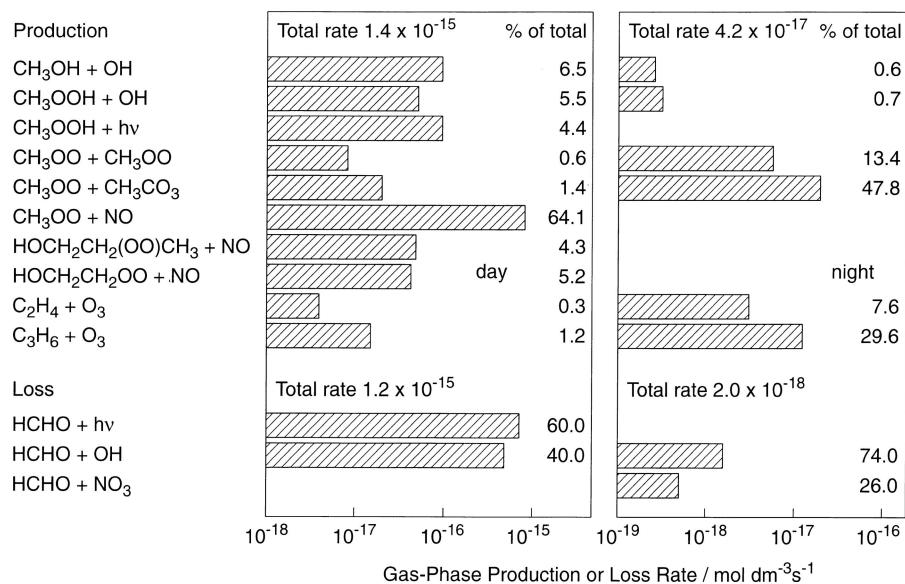


Figure 1. Relative contributions of important reactions to the gas-phase production and loss of formaldehyde. Left: Daylight shortly before noon; the reactions shown contribute 93% to the total rate. Right: At midnight; the reactions contribute 99% to the total rate.

#### FORMALDEHYDE (METHANAL)

The substance has multiple gas-phase sources. The oxidation of C<sub>2</sub> and C<sub>3</sub> compounds adds 13 reactions to those that result from the oxidation of methane and methanol, but each additional reaction contributes fairly little to the total rate of HCHO formation so that the oxidation of methane remains the major source. Figure 1 shows a bar graph indicating the relative contributions during the day and at night. In the first case, approximately 64% of HCHO is formed by the reaction CH<sub>3</sub>OO + NO; the reactions of other peroxy radicals with NO contribute another 11.5%. These reaction pathways are closed at night. At nighttime the reactions of CH<sub>3</sub>OO radicals with each other and with CH<sub>3</sub>C(O)OO assume a leading role in the production of formaldehyde. In addition, the reactions of ozone with ethene and propene become relatively more prominent, although their rates remain essentially unchanged from those during the day. In the aqueous phase, the oxidation of methanol is the most important reaction leading to HCHO, but the effect on the total rate is insignificant because the dissolution of methanol in cloud water reduces its concentration in the gas phase by the same amount. The major loss reactions are photolysis of HCHO and reaction with OH radicals. Their rates do not compensate the total rate of HCHO formation. This causes formaldehyde to accumulate as Figure 2 shows. The imbalance between production and loss is more pronounced at night, but then the rates are reduced so that formaldehyde accumulates at a lower rate. The imbalance indicates a missing sink, which may be due to

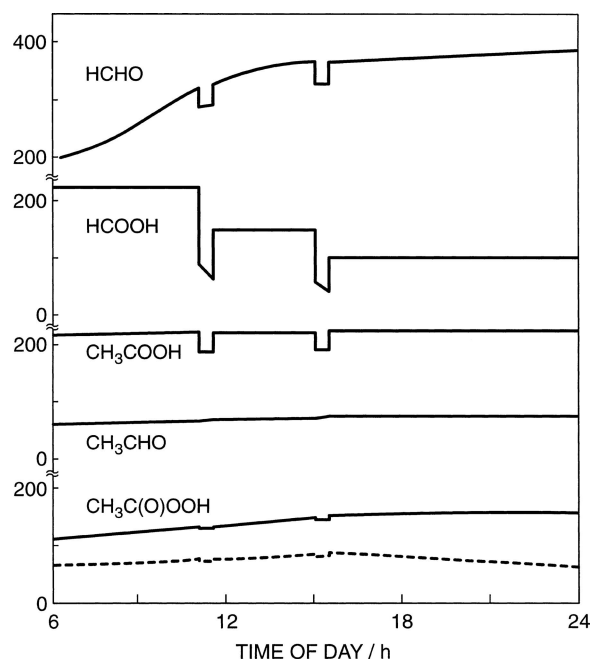


Figure 2. Development of gas-phase mixing ratios ( $\text{pmol mol}^{-1}$ ) for formaldehyde, formic acid, acetaldehyde, acetic acid, and ethane peroxy acid on the first day with cloud events. The dashed line gives the mixing ratio of  $\text{CH}_3\text{C}(\text{O})\text{OOH}$  assuming a dry deposition rate similar to that of  $\text{H}_2\text{O}_2$ .

dry deposition. The assumption of a dry deposition rate similar to that for  $\text{H}_2\text{O}_2$  largely eliminates the imbalance, keeping the HCHO mixing ratio below  $300 \text{ pmol mol}^{-1}$ . Model comparisons with measurements reported in the literature have been found to overpredict as well as underpredict observations (for a review see Fried *et al.*, 2003). The present study is not centered on formaldehyde, however, and the problem was not further pursued.

#### FORMIC ACID (METHANOIC ACID)

Compared to C<sub>1</sub> chemistry, where formic acid is produced only in the aqueous phase (from formaldehyde), the addition of C<sub>2</sub> compounds to the system leads to the gas phase production of formic acid from ozone reacting with ethene and of OH reacting with acetylene (reactions G86a, G86f and G99b, respectively). During the day, the combined production rates of  $\sim 1.6 \times 10^{-17} \text{ mol dm}^{-3} \text{ s}^{-1}$  are approximately balanced by the only gas-phase loss reaction,  $\text{OH} + \text{HCOOH}$  (G34, see Warneck, 1999). In the presence of cloud water, however, formic acid partly dissolves in the aqueous phase, where it undergoes additional reactions involving the radicals OH,  $\text{SO}_4^-$ ,  $\text{Cl}_2^-$  and  $\text{NO}_3$ . Here, the reactions of OH with undissociated and dissociated

formic acid are dominant, whereas the other reactions are negligible in the marine atmosphere. Figure 2 indicates that the mixing ratio of formic acid declines after a cloud event. As it turns out, the loss rate in the aqueous phase is not only by an order of magnitude greater than the aqueous production rate (by oxidation of formaldehyde), but it also is more than two orders of magnitude greater than the production rate in the gas phase. Thus, the losses during a 30 min cloud event cannot be compensated by gas phase production in the following cloud-free period. Note, however, that the gas and aqueous phase chemistry discussed here represents only a small part of the overall cycle of formic acid, which is dominated by advection from the continents to the marine atmosphere and dry deposition to the ocean surface. These processes are not part of the box model used. The loss rate associated with dry deposition has been estimated as  $3.5 \times 10^{-3} \text{ m s}^{-1}$  (Warneck, 2000). In the present box model this would be equivalent to a loss rate of  $3.3 \times 10^{-14} \text{ mol dm}^{-3} \text{ s}^{-1}$ , or twenty times the loss rate due to in-cloud reactions.

#### ACETALDEHYDE (ETHANAL)

Gas phase reactions leading to the production of acetaldehyde include the oxidation of ethane, hydroperoxy ethane and ethanol by OH radicals (reactions G36/37 G39b, G62), and the reactions of propene with OH radicals and with ozone (reactions G87/G88, G93b, G94c and G97a). Figure 3 shows the relative contributions. The first four reactions are dominant during the day, the last reaction, which in daylight contributes only 1.5%, takes over at night. The total production rate of  $\sim 1.8 \times 10^{-16} \text{ mol dm}^{-3} \text{ s}^{-1}$  is nearly balanced by the rate of the predominant gas-phase loss reaction:  $\text{OH} + \text{CH}_3\text{CHO}$  (G47). Photolysis of acetaldehyde is negligible in

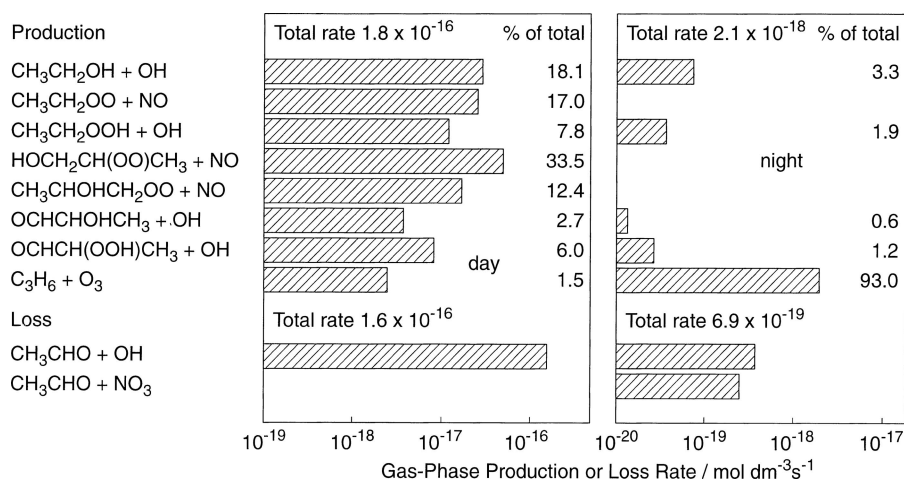


Figure 3. Relative contributions of gas-phase reactions to the production and destruction of acetaldehyde. Left: Daylight shortly before noon. Right: At midnight.

comparison. At night, the production of acetaldehyde exceeds losses, but the rates are much reduced compared to those during the day.

Acetaldehyde is less well soluble in water than formaldehyde. In contrast to HCHO, which is essentially fully hydrated in the aqueous phase, only about 55% of CH<sub>3</sub>CHO exist in the hydrated form, CH<sub>3</sub>CH(OH)<sub>2</sub>. In addition, whereas the hydration of formaldehyde occurs rapidly with a time constant of  $\tau \sim 0.1$  s (Schecker and Schulz, 1969), that of acetaldehyde proceeds more slowly ( $\tau \sim 40$  s, Kurz and Coburn, 1967). The reaction with OH radicals leads to acetic acid only when acetaldehyde is hydrated (A102/103), in the other case acetyl peroxy radicals are produced (A100/A101) as in the gas phase, and these radicals tend to equilibrate between the two phases. The reactions of sulfate radicals with acetaldehyde (A163/164) are ineffective because SO<sub>4</sub><sup>-</sup> concentrations are too small. The major source of acetaldehyde in the aqueous phase is the oxidation of ethanol (A98/99), occurring at a rate of  $\sim 8.0 \times 10^{-18}$  mol dm<sup>-3</sup> s<sup>-1</sup>. This is only 6% of the total rate of CH<sub>3</sub>CHO formation in the gas phase in the presence of cloud water ( $\sim 1.3 \times 10^{-16}$  mol dm<sup>-3</sup> s<sup>-1</sup>), and 44% of that resulting from the oxidation of ethanol in the gas phase. On the other hand, the production rate of CH<sub>3</sub>CHO in the aqueous phase is by a factor of ten greater than the loss rate, so that clouds represent a net source.

#### ACETIC ACID (ETHANOIC ACID)

There are three gas-phase sources of acetic acid: the reactions of OH with acetone (G49a), of acetyl peroxy with HO<sub>2</sub> radicals (G55b), and of propene with ozone (G97b/98a). In daylight, they contribute approximately 29%, 62% and 9%, respectively, to a total rate of  $\sim 3.2 \times 10^{-17}$  mol dm<sup>-3</sup> s<sup>-1</sup>. At night, the relative contributions are 1%, 15%, and 84%, respectively, and the total rate is  $\sim 2.4 \times 10^{-18}$  mol dm<sup>-3</sup> s<sup>-1</sup> (compare Figure 4). The only gas-phase loss process is the reaction of

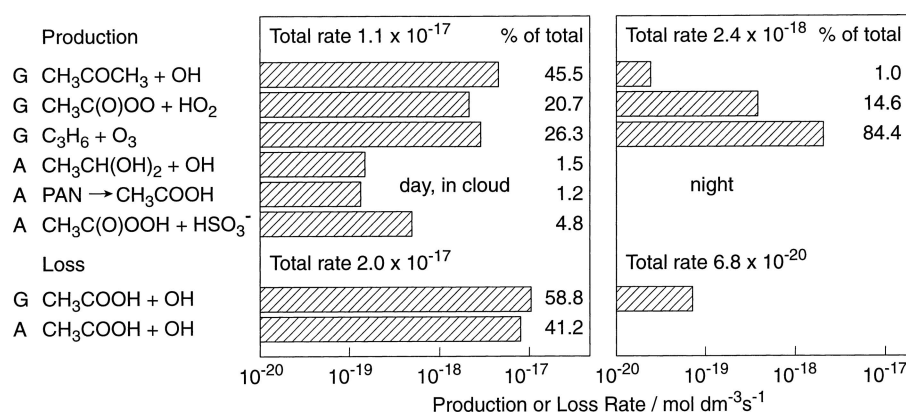


Figure 4. Relative contributions of reactions leading to the production and loss of acetic acid. Left: Reactions in the gas phase and in the aqueous phase of a cloud, daylight shortly before noon. Right: Gas-phase reactions at midnight.

acetic acid with OH radicals (G60). During the day, this process nearly compensates the rate of formation, at night it does not.

In the presence of clouds, the gas-phase formation of acetic acid declines to one third of the rate in cloud-free air because of the scavenging effect of clouds on OH and HO<sub>2</sub> radicals. Reactions responsible for the formation of acetic acid in the aqueous phase are the oxidation of acetaldehyde (A102/103), the reaction of ethane peroxy acid with hydrogen sulfite (A180) and the decomposition of PAN (reaction A185b). The major loss reaction in the aqueous phase is that of acetate with OH. As in other cases, the effect of SO<sub>4</sub><sup>-</sup> radicals is negligible. The left-hand side of Figure 4 shows daylight contributions of all reactions under cloud conditions. The gas-phase reactions remain dominant, but losses of acetic acid due to reaction with OH radicals become equivalent in both phases. Figure 2 shows that the mixing ratio of acetic acid rises only slightly with time, indicating that production and losses are approximately balanced. The loss rate of acetic acid in the aqueous phase of clouds is much smaller than that of formic acid. Again, the present model does not include dry deposition as a sink. A dry deposition velocity similar to that of formic acid would make this process the dominant sink also for acetic acid.

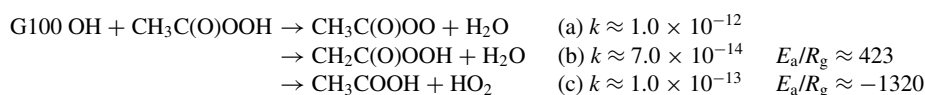
The aqueous phase reaction of OH radicals with acetate leads to the formation of peroxy acetate radicals that react either with each other or with CH<sub>3</sub>OO, CH<sub>3</sub>C(O)OO, HO<sub>2</sub> and O<sub>2</sub><sup>-</sup> radicals. According to the mechanism of Schuchmann *et al.* (1985), the self-reaction produces glycolic acid and glyoxylic acid in addition to formaldehyde and hydrogen peroxide (reactions A118/119). The discussion further below will show, however, that these reactions are fairly unimportant as sources of glycolic acid and glyoxylic acid when compared to other pathways for their formation. The reasons are that the reactions of peroxy acetate, OOCCH<sub>2</sub>COO<sup>-</sup>, with HO<sub>2</sub> and O<sub>2</sub><sup>-</sup>, which produce hydroperoxy ethanoic acid, dominate over all other reactions with peroxy radicals. In addition, peroxy acetate equilibrates with hydrogen ions to form the corresponding peroxy acetic acid radical. Because of an unfavorable gas-liquid partition coefficient (see Table II) this species tends to escape to the gas phase, where it enters into reactions with NO or HO<sub>2</sub> to form glyoxylic acid and hydroperoxy acetic acid, respectively. Both products are reabsorbed into the aqueous phase, where they undergo further reactions. The reaction of hydroperoxy acetic acid with OH also generates glyoxylic acid (in both phases). Thus, glyoxylic acid is the major product resulting from the oxidation of acetic acid in cloud water.

#### HYDROPEROXIDES

Table VI provides a list of hydroperoxides resulting from the (partial) oxidation of C<sub>2</sub> and C<sub>3</sub> hydrocarbons in the marine atmosphere. Hydroperoxides, in general, are formed by reaction of the corresponding peroxy radical precursors with HO<sub>2</sub>. Losses are due to reactions with OH radicals, which lead mainly to the corresponding aldehydes or ketones and keep the mixing ratios of most hydroperoxides in the range



of a few pmol mol<sup>-1</sup>. CH<sub>3</sub>C(O)OOH, is an exception. The derived mixing ratio, in the order of 100 pmol mol<sup>-1</sup>, makes this hydroperoxide a major species in addition to methyl hydroperoxide. Figure 2 shows that the mixing ratio of CH<sub>3</sub>C(O)OOH increases with time. The reaction scheme in Tables II and IV assumes only one loss process: the interaction with HSO<sub>3</sub><sup>-</sup> in the aqueous phase to give SO<sub>4</sub><sup>2-</sup> and acetic acid, which is effective only in the presence of clouds. Orlando and Tyndall (2003) have recently discussed photolysis and reaction with OH as possible gas-phase loss processes for ethane peroxy acid. From the measured spectrum, and assuming a quantum yield of unity, they estimated a photodissociation coefficient on the order of 5 × 10<sup>-7</sup> s<sup>-1</sup>, which is insufficient to compensate the production rate under the present conditions. The rate coefficient for the reaction with OH has not been measured. Comparison with the behavior of acetone suggests that the reaction may proceed by three pathways



where the rate coefficient for the first channel should have one half the value of that for the reaction OH + H<sub>2</sub>O<sub>2</sub>, and the rate coefficients for the other two channels should be similar to those for acetone (reaction G49). However, the inclusion of these reactions, assuming the indicated rate coefficients, has only a small effect on the mixing ratio of ethane peroxy acid and its change with time. More effective is dry deposition at a rate equal to that for H<sub>2</sub>O<sub>2</sub> (5 × 10<sup>-3</sup> cm s<sup>-1</sup>). When this loss process is included in the model, the mixing ratio adjusts to steady state values in the vicinity of 6.5 × 10<sup>-11</sup>. The variation with time is shown in Figure 2 for comparison with conditions assuming no dry deposition.

Of special interest are reactions of C<sub>2</sub> and C<sub>3</sub> hydroperoxides with hydrogen sulfite in the aqueous phase of clouds and their contribution to sulfur(IV) oxidation. These reactions are proton-catalyzed. The reaction rate increases with decreasing pH, but the effect is largely compensated by the concurrent decrease in solubility of SO<sub>2</sub> (at pH > 2). For the initial conditions indicated in Table I, the pH of aqueous aerosol particles adjusts to pH ≈ 3.0, and to pH ≈ 4.5 under cloud conditions. Figure 5 shows important oxidants and their contributions to S(IV) oxidation. Four of the hydroperoxides listed in Table VI have a marked effect, yet each contributes only in the low percentage range. Hydrogen peroxide remains the most important oxidant, followed by OH radicals in the gas phase and ozone in the aqueous phase. Nitric peroxy acid, HOONO<sub>2</sub>, has previously been recognized to be an important oxidant in continental clouds (Warneck, 1999). It remains significant in the marine atmosphere despite the lower NO<sub>2</sub> precursor concentrations compared to continental air. The contribution of ethane peroxy acid is significant because of an appreciable concentration in the gas phase. The hydroxy-hydroperoxides (and the mixed carbonyl hydroperoxides) are endowed with larger Henry's law coefficients

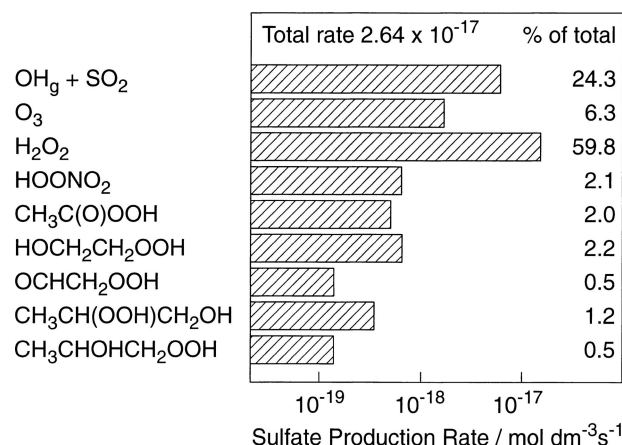


Figure 5. Relative contributions of (daylight) reactions to the oxidation of  $\text{SO}_2$  in the gas phase and in the aqueous phase of a cloud, especially contributions of hydroperoxides.

than ordinary hydroperoxides, so that their concentrations in aqueous solution are higher than those of other hydroperoxides. Accordingly, their contributions are more favorable. Altogether, the processes shown in Figure 5 contribute 99% to the total oxidation rate. The remainder is due to other organic hydroperoxides. The individual contributions of all organic hydroperoxides sum to 9.5% of the total oxidation rate, and to 15.8% of that associated with  $\text{H}_2\text{O}_2$ . The same reactions occur in the absence of a cloud in the aqueous phase of aerosol particles. Their impact is fairly small, however. The total loss of  $\text{SO}_2$  calculated for a full 24 h period, with the occurrence of two 1/2 h cloud events daily, is  $3.2 \times 10^{-13} \text{ mol dm}^{-3}$ , to which the gas phase reaction  $\text{OH} + \text{SO}_2$  contributes 82%, reactions in sunlit cloud water contribute 17.7%, and reactions in the aqueous phase of aerosol particles contribute 0.3%, approximately. The radical-driven oxidation of sulfite in the aqueous phase is entirely negligible.

#### GLYCOLALDEHYDE (2-HYDROXY ETHANAL)

This compound is a product resulting from the OH-induced oxidation of ethene. Figure 6 shows an oxidation scheme. Glycolaldehyde arises from the reaction of  $\text{HOCH}_2\text{CH}_2\text{OO}$  with NO (G80b) as well as from the reaction of OH with hydroperoxy ethanol (G82b) produced in the reaction of  $\text{HOCH}_2\text{CH}_2\text{OO}$  with  $\text{HO}_2$  (G81). The former reaction has been considered previously as part of the mechanism leading to the formation of oxalic acid, (Warneck, 2003), yet the latter reaction appears to be more significant, because ~65% of glycolaldehyde are formed along this channel. The further oxidation of glycolaldehyde leads partly to glyoxal, which is discussed further below. The gas-phase loss of glycolaldehyde occurs by photolysis and by reaction with OH radicals (G84). Daytime production and loss rates are approximately balanced at  $\sim 4.0 \times 10^{-17} \text{ mol dm}^{-3} \text{ s}^{-1}$  (noon time value).

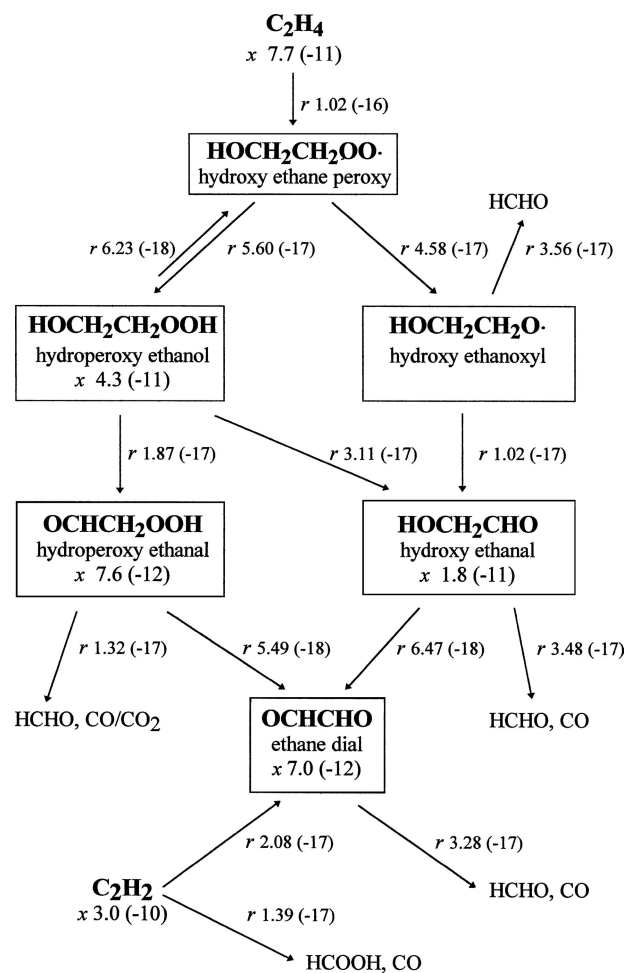


Figure 6. Gas-phase oxidation scheme for ethene leading to glycol aldehyde and glyoxal to show the importance of hydroperoxides as intermediates. Mixing ratios,  $x$ , and reaction rates,  $r$ , ( $\text{mol dm}^{-3} \text{ s}^{-1}$ ) represent noon-time steady state values for  $n(\text{OH}) = 3.7 \times 10^6$ ,  $n(\text{HO}_2) = 4.3 \times 10^6$ ,  $n(\text{NO}) = 5.9 \times 10^6$ , and total number density  $n(\text{M}) = 2.3 \times 10^{19}$  ( $\text{molecule cm}^{-3}$ ) based on the rate coefficients given in Table II (reactions G79-G84 and G100). The formation of glyoxal from acetylene, reaction G99a, is included to indicate the relative contributions to glyoxal from both precursors.

In the presence of cloud water, HOCH<sub>2</sub>CH<sub>2</sub>OOH is partly absorbed into the aqueous phase, whereupon the contribution of reaction G82b is greatly reduced and the corresponding aqueous reaction A143b takes over in generating HOCH<sub>2</sub>CHO. Much less significant is the reaction of HOOCH<sub>2</sub>CH(OH)<sub>2</sub> with hydrogen sulfite (A176). Figure 7 shows gas-phase mixing ratios for HOCH<sub>2</sub>CH<sub>2</sub>OOH and HOCH<sub>2</sub>CHO during three consecutive days with cloud events. Both species decline gradually toward new steady state mixing ratios due to in-cloud reactions,

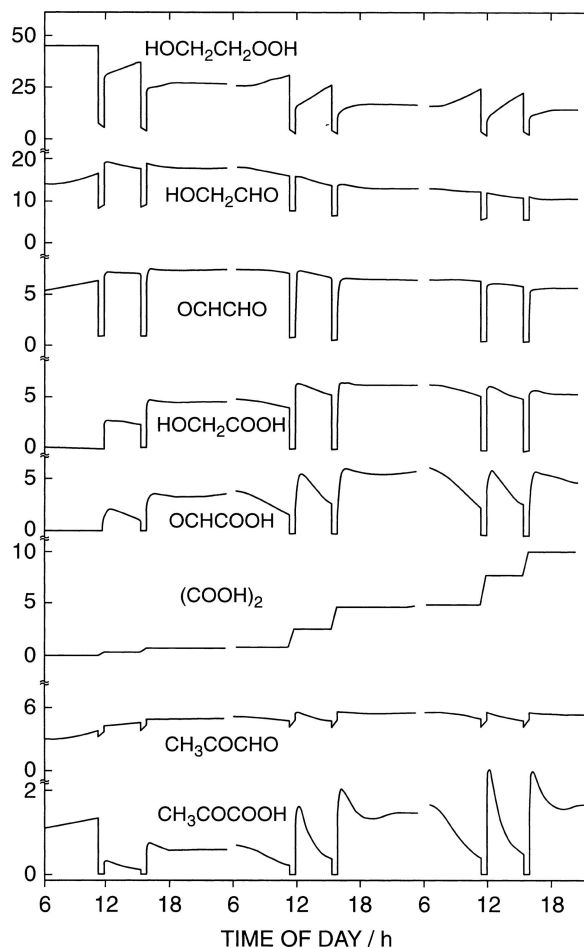


Figure 7. Development of gas-phase mixing ratios ( $\text{pmol mol}^{-1}$ ) for hydroxy ethane hydroperoxide, hydroxy ethanal, glyoxal, hydroxy ethanoic acid, oxo-ethanoic acid, oxalic acid, methyl glyoxal and pyruvic acid on three consecutive days with two cloud events each.

although hydroperoxy ethanol shows greater fluctuations because of repeated gas-phase formation and in-cloud destruction. Glycolaldehyde in the aqueous phase exists in the hydrated and non-hydrated form and both undergo reactions with OH radicals (A132 and A133). The first reaction is dominant because most glycolaldehyde exists in the hydrated form. Figure 8 shows the relative contributions of these reactions. The results indicate that in-cloud production and loss of glycol aldehyde occur at three times the rate of gas-phase reactions in the absence of a cloud.

#### GLYOXAL (ETHANE DIAL)

Figure 6 shows that glyoxal arises from reactions of OH radicals with  $\text{OCHCH}_2\text{OOH}$  (G83b), with glycol aldehyde (G84b), and with acetylene (G99a).

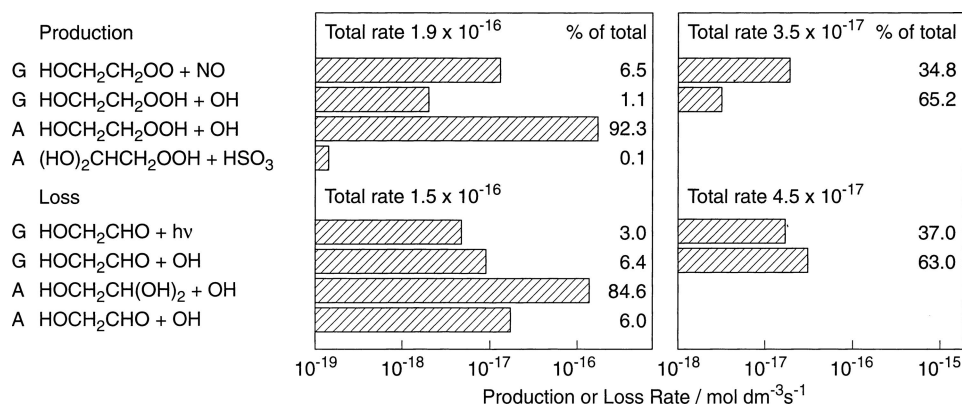


Figure 8. Relative contributions of reactions leading to the production and loss of glycol aldehyde, daylight shortly before noon. Left: Reactions in the gas phase and in the aqueous phase of a cloud. Right: Gas-phase reactions after the cloud event.

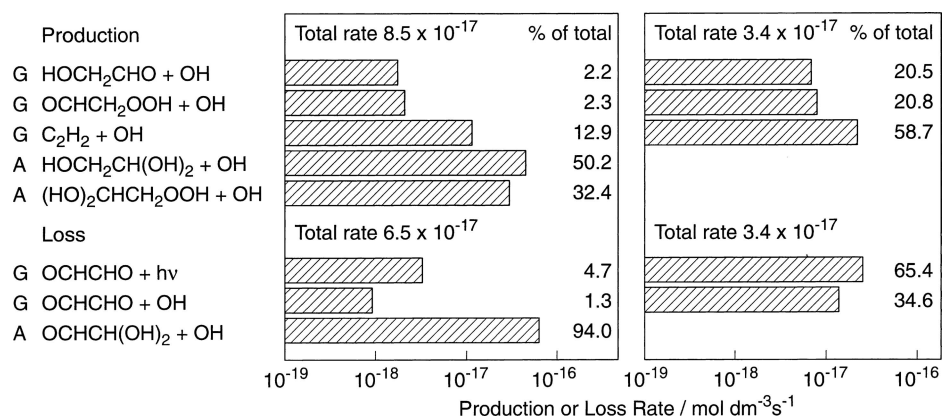


Figure 9. Relative contributions of reactions leading to the production and loss of glyoxal, daylight shortly before noon. Left: Reactions in the gas phase and in the aqueous phase of a cloud. Right: Gas-phase reactions after the cloud event.

Gas-phase losses of glyoxal occur by reaction with OH radicals (G100) and by photolysis. Figure 7 includes gas-phase mixing ratios of glyoxal for three consecutive days, and Figure 9 shows relative contributions of reactions to the formation and loss of glyoxal. The reaction with acetylene contributes approximately 60% to the total rate of the gas-phase formation of glyoxal for the conditions assumed. Production and loss reactions are essentially balanced. The same reactions take place in the presence of cloud water. In this case, the gas-phase production and loss rates are reduced as the precursors OCHCH<sub>2</sub>OOH and HOCH<sub>2</sub>CHO as well as OCHCHO are largely partitioned into the aqueous phase. Production of glyoxal from acetylene continues at the same rate as before because C<sub>2</sub>H<sub>2</sub> is only slightly absorbed into cloud water. In the aqueous phase, reaction G83b and G84b are replaced by

the equivalent reactions A145b and A132a/135. Figure 9 shows that the rates of these reactions, as well as the loss of glyoxal by reaction with OH radicals, exceed considerably the corresponding reactions in the gas phase. The total production rate inside a cloud is approximately three times greater than outside. Excess glyoxal is released to the gas phase when the cloud dissipates. Table VI and Figure 7 indicate that the gas phase mixing ratio is raised by about 30% after the first cloud event, but the mixing ratio stabilizes on the following days.

#### GLYCOLIC ACID (HYDROXY ETHANOIC ACID)

This compound is produced only in the aqueous phase of clouds. Four reactions are responsible for its formation (A118a, A120a, A132b/134 and A175). Of these, the reaction of OH with  $\text{HOCH}_2\text{CH}(\text{OH})_2$  (A132b, followed by A134) dominates all others, contributing 99.5% to a total rate of  $\sim 9.0 \times 10^{-17} \text{ mol dm}^{-3} \text{ s}^{-1}$ . The two reactions A118a and A120a that involve the  $\text{OOCH}_2\text{COO}^-$  radical and the reaction of hydroperoxy acetate with hydrogen sulfite (A175) contribute less than 1% to the total production rate. Thus, ethene is the principal source of glycolic acid in the marine atmosphere. The major loss processes are the reaction of glycolic acid and its anion with OH radicals (A122/123). As in other cases, the reaction with  $\text{SO}_4^-$  radicals (A166) is not important. The production rate of glycolic acid is 3 to 5 times greater than the loss rate. The excess material is released when the cloud dissipates. In the gas phase, glycolic acid is subject to attack by OH radicals, but the resulting losses are comparatively minor. Figure 7 shows that the abundance of glycolic acid rises until after a few days a steady state mixing ratio of  $\sim 6.5 \times 10^{-12}$  is reached.

#### GLYOXYLIC ACID (OXOETHANOIC ACID)

Figure 10 summarizes reactions responsible for the production and the loss of glyoxylic acid. Production in the gas-phase results from the interaction of peroxy acetic acid radicals with NO (G73a) and the oxidation by OH radicals of hydroperoxy acetic acid (G75b) and glycolic acid (G77). The latter two processes are dominant, contributing approximately 35% and 63%, respectively, to the total. In the aqueous phase, which is more effective as a medium for the production of glyoxylic acid, the major precursors are glyoxal (reactions A136/137), glycolic acid (reactions A122, A123 followed by A119), and hydroperoxy acetic acid (reaction A117). The relative contributions are 67%, 23%, 9%, approximately. Cross combination reactions of the peroxy acetic acid radical with itself (A118) and with methyl peroxy and acetyl peroxy radicals (A120, A121) contribute less than 1% to the total rate of glyoxylic acid formation in the aqueous phase. Thus, the mechanism of Schuchmann *et al.* (1985), in which acetate is oxidized to glyoxylic acid, is unimportant as a source of glyoxylic acid in marine clouds.

As glycolic acid is formed only in the aqueous phase of clouds and its mixing ratio rises for two consecutive days, the mixing ratio of glyoxylic acid rises as well.

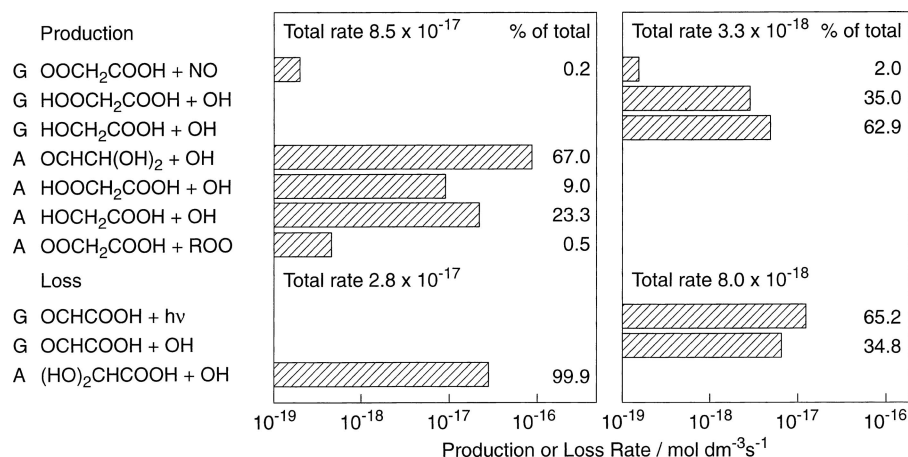


Figure 10. Relative contributions of reactions leading to the formation and loss of glyoxylic acid, daylight shortly before noon. Left: Reactions in the gas phase and in the aqueous phase of a cloud. Right: Gas-phase reactions after the cloud event.

Figure 7 shows this effect. Losses of glyoxylic acid occur by photolysis and by reaction with OH radicals. Losses exceed production by a factor of about three, so that the mixing ratio of glyoxylic acid fluctuates considerably between in-cloud production and gas-phase destruction. The major loss process of glyoxylic acid in the aqueous phase is oxidation by reaction with OH radicals. The interaction of glyoxylic acid with SO<sub>4</sub><sup>-</sup> radicals can be neglected.

#### HYDROPEROXY ACETIC ACID (HYDROPEROXY ETHANOIC ACID)

As was shown in Figure 10, a significant fraction of glyoxylic acid derives from hydroperoxy acetic acid. This compound is formed by two reactions in the aqueous phase of clouds. One is the interaction of peroxy acetate radicals with HO<sub>2</sub> and its anion O<sub>2</sub><sup>-</sup> (A115, A116), as discussed above. These reactions, however, generate only 10% of HOCH<sub>2</sub>COOH. The dominant process, contributing about 90%, is the reaction of OH radicals with hydroperoxy ethanal, OCHCH<sub>2</sub>OOH, which is here assumed to exist in aqueous solution mainly in its hydrated form, HOCH<sub>2</sub>CH(OH)<sub>2</sub> (reaction A145a followed by A146). Hydroperoxy ethanal is a product arising from the oxidation of ethene (compare Figure 6). This demonstrates that hydroperoxy acetic acid also arises mainly as a product from the oxidation of ethene rather than of acetic acid.

#### OXALIC ACID (ETHANE DIOIC ACID)

Oxalic acid is formed by reactions of OH radicals with glyoxylic acid and its anion in the aqueous phase (A124/125 followed by A127). The *pK*<sub>1</sub> value for

oxalic acid is  $pK_1 \approx 1.25$  (Smith and Martell, 1977), which keeps the acid fully dissociated in clouds and in the aqueous aerosol as well. The two anions  $\text{HC}_2\text{O}_4^-$  and  $\text{C}_2\text{O}_4^{2-}$  react with OH and  $\text{NO}_3$  radicals, reactions A128, A129 and A186, A187, respectively. The reactions with nitrate radicals are found to be negligible due to their relatively small concentrations. The reactions with OH radicals also are slow, so that oxalate concentrations build up to appreciable concentrations before losses become effective. Figure 7 shows the rise of oxalic acid for three consecutive days with two  $\frac{1}{2}$  h cloud events each. On this time scale, losses are still negligible. The production rate increases to reach its maximum on the third day, when the gas-phase concentration of glyoxylic acid has built up to a quasi-steady state. The average in-cloud production rate of oxalate then is approximately  $1 \times 10^{-16} \text{ mol dm}^{-3} \text{ s}^{-1}$ , or  $3.8 \times 10^{-10} \text{ mol m}^{-3} \text{ h}^{-1}$ . This corresponds to an increase in the mixing ratio of oxalic acid of  $\sim 1 \times 10^{-11} \text{ d}^{-1}$ . The rate is almost ten times larger than that estimated previously (Warneck, 2003). The main reason is that the rate coefficient  $k_{\text{A136}}$  for the oxidation of glyoxal in the aqueous phase, which leads to glyoxylic acid, is  $1.1 \times 10^9 \text{ dm}^{-3} \text{ mol}^{-1} \text{ s}^{-1}$  (Buxton *et al.*, 1997), whereas previously a value of  $6.6 \times 10^7 \text{ dm}^{-3} \text{ mol}^{-1} \text{ s}^{-1}$  was used. In addition, a slightly larger mixing ratio of ethene was assumed in the present study, and hydroperoxy acetic acid, which represents a source of glyoxylic acid, is now included in the chemical mechanism. On the other hand, the previous estimate did not take into account that a factor of 0.319 must be applied to the production rate in order to average over a 24 h period of sunlight and darkness, when a sine function of solar intensity (for a 12 h period with maximum at noon) is used as in the present model. Furthermore, liquid-water clouds in the troposphere occur only in the region below  $\sim 6$  km, which harbors about 62% of the tropospheric air mass within a vertical column. Keeping this in mind, the previous estimate for the concentrations of oxalic acid in the marine atmosphere must be revised.

The previous study had shown that within the troposphere as a whole ethene as a precursor of oxalic acid is not as effective as acetylene, because ethene is released from the ocean surface and reacts rapidly with OH radicals within the boundary layer, whereas acetylene occurs within the entire tropospheric air space, because it is advected from the continents. The present estimate, therefore, concentrates on oxalic acid as a product from the oxidation of acetylene. Figure 6 shows that 63% of glyoxal derives from acetylene, and Figure 10 shows that 67% of glyoxylic acid derives from glyoxal. Thus, the above rate of oxalic acid production resulting from the oxidation of glyoxylic acid in clouds must be multiplied by  $0.63 \times 0.67 = 0.42$  to obtain the fraction of oxalic acid resulting from the oxidation of acetylene. The rate of oxalic acid formation in clouds then is  $0.42 \times 3.8 \times 10^{-10} \text{ (mol m}^{-3} \text{ h}^{-1}) \times 24 \text{ (h d}^{-1}) \times 0.319 = 1.22 \times 10^{-9} \text{ mol m}^{-3} \text{ d}^{-1}$ , where the factor 0.319 results from the averaging of solar intensity over a 24 h period. If we assume, as previously (Lelieveld *et al.*, 1989), that an air parcel spends 15% of its time in a cloud compared to the total time inside and outside, but consider now that liquid-water clouds are confined to the region below 6 km altitude (62% of total air mass within a vertical



column), the average rate of oxalic acid formation in a tropospheric air column is  $0.15 \times 0.62 \times 1.22 \times 10^{-9} = 1.14 \times 10^{-10} \text{ mol m}^{-3} \text{ d}^{-1}$  (reduced to a constant air density at 900 m altitude). The value must be combined with the residence time of oxalic acid in the troposphere to obtain the average concentration.

The residence time of oxalic acid in the troposphere is determined by the residence time of aerosol particles appropriately reduced by the loss of oxalic acid resulting from its reaction with OH radicals. According to the present model the fractions of the two anions  $\text{HC}_2\text{O}_4^-$  and  $\text{C}_2\text{O}_4^{2-}$  respectively, are approximately 0.3 and 0.7 at pH 5, as applicable for the aqueous phase of cloud drops, and 0.978 and 0.022 at pH 3 for the aqueous phase of aerosol particles. With these fractions, the rate coefficients for reactions A128 and A129 given in Table V lead to average values of  $1.94 \times 10^7$  and  $4.61 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  for the reaction of OH radicals with oxalic acid in cloud drops and aerosol particles, respectively. Noon time values for the concentration of OH radicals in the present model for the aqueous phase of clouds and aerosol particles are approximately  $3.9 \times 10^{-13}$  and  $4.0 \times 10^{-16} \text{ mol dm}^{-3}$ , respectively. A factor of 0.319 must be applied to average over a full day. This leads to a chemical destruction rate for oxalic acid of  $2.08 \times 10^{-1} \text{ d}^{-1}$  in clouds and  $5.07 \times 10^{-4} \text{ d}^{-1}$  outside clouds. Assuming again that an air parcel spends 15% of its time in a cloud and 85% outside, the combined average destruction rate is  $0.15 \times 2.08 \times 10^{-1} + 0.85 \times 5.07 \times 10^{-4} = 3.17 \times 10^{-2} \text{ d}^{-1}$ . The destruction of oxalic acid in clouds is much more effective than that in aerosol particles because aqueous OH concentrations are higher in clouds (the partitioning between gas phase and aqueous phase is more efficient). The associated life time of oxalic acid in the troposphere would be 31.6 d. When it is combined with the residence time for aerosol particles, 6–12 d (Balkanski *et al.*, 1993), which is determined largely by deep cloud formation and rainout, one obtains a reduced residence time for oxalic acid in the range 5.0–8.7 d. The corresponding concentration range for oxalic acid is  $1.14 \times 10^{-10} (5.0 - 8.7) = (5.7 - 9.9) \times 10^{-10} \text{ mol m}^{-3}$  or 51–89  $\text{ng m}^{-3}$ , which is two to five times higher than the previous estimate of Warneck (2003). Ervens *et al.* (2003) have recently published rate coefficients for reactions A128 and A129 that are higher than the values given in Table IV and used here, namely  $k_{\text{A128}} = 2.5 \times 10^{12} \exp(-2800/T)$  and  $k_{\text{A129}} = 4.6 \times 10^{14} \exp(-4300/T)$ . Their application at  $T = 285 \text{ K}$  would lower the time constant for the loss of oxalic acid due to reaction with OH to about 6 d and the overall residence time to 3–4 d. The corresponding steady state oxalic acid concentrations would be 30–40  $\text{ng m}^{-3}$ , approximately, which is in the same order of magnitude. The margin of uncertainty is considerable. Not only has it been assumed that in-cloud conditions resulting from the present model can be extrapolated to all liquid water clouds at mid-latitude, but the cloud statistics, on which the 15% estimate of time spent by an air parcel in a cloud is based, also carries a wide margin of uncertainty. The concentrations of oxalic acid derived here are somewhat higher than those that were observed over the remote Pacific Ocean: 10–25  $\text{ng m}^{-3}$  (Kawamura and Usukura, 1993) and 27  $\text{ng m}^{-3}$  median, 40  $\text{ng m}^{-3}$  average (Kawamura and Sakaguchi, 1999). The

present results, therefore, demonstrate only that the chemical mechanisms provide sufficient room for the generation of observable concentrations of oxalic acid in the marine troposphere.

#### ACETONE (PROPANONE)

Acetone is the principal oxidation product of propane (reactions G40a/41 and G43 followed by G45b). Losses occur via photolysis and reaction with OH radicals. Production and loss reactions keep the mixing ratio of acetone approximately in balance. The reaction of acetone with OH (G49) leads partly to the formation of hydroperoxy propanone (G51), which by reacting further with OH provides a source of methyl glyoxal (G52b). The solubility of acetone in cloud water is moderate, but the concentration in the aqueous phase is nevertheless appreciable owing to the high concentration acetone in the gas phase. In the aqueous phase,  $\text{NO}_x$  is essentially absent so that acetyl peroxy radicals arising from the reaction of acetone with OH are converted entirely to methyl glyoxal via hydroperoxy propanone (reactions A140, A141, A142b). Closer inspection of the reaction rates shows, however, that this source of methyl glyoxal cannot compete with the corresponding process in the gas phase (see further below).

#### HYDROXY PROPANONE

The only gas-phase reaction leading to the formation of  $\text{CH}_3\text{COCH}_2\text{OH}$  is the reaction of OH radicals with 1-hydroxy 2-hydroperoxy-propane (G90b). This compound is a product resulting from the oxidation of propene. The loss of hydroxy propanone also proceeds by reaction with OH radicals (G91). These reactions, occurring at rates of  $\sim 1.5 \times 10^{-17} \text{ mol dm}^{-3} \text{ s}^{-1}$ , keep the mixing ratio of hydroxy propanone essentially constant. The same two reactions take place in the aqueous phase of clouds (A147b, A149/150). Here, the production rate is almost four times greater than that in the gas phase, but a cloud event lasting 30 min does not raise the mixing ratio of hydroxy propanone appreciably after the cloud dissipates (compare Table VI). The rate of in-cloud production by the reaction of  $\text{CH}_3\text{COCH}_2\text{OOH}$  with sulfite (A174) is insignificant in comparison. In both phases,  $\text{CH}_3\text{COCH}_2\text{OH}$  serves as an intermediate to the formation of methyl glyoxal.

#### 2-HYDROXY PROPANAL

In the gas phase, the only reaction leading to the formation of  $\text{CH}_3\text{CHOHCHO}$  is the reaction of OH radicals with 1-hydroperoxy 2-hydroxy-propane (G92b). This compound is a product resulting from the oxidation of propene. Reaction of 2-hydroxy propanal with OH is the only gas-phase loss reaction (G93) considered, photolysis was assumed to be negligible in comparison. 2-Hydroxy propanal is readily absorbed into cloud water and the same reactions as in the gas phase are

effective in the aqueous phase (A154b, A156). An additional production occurs via the reaction of 2-hydroperoxypropanal with sulfite (A183), but as in other cases its contribution is fairly small. The turnover rate in the gas phase is approximately  $5.0 \times 10^{-18} \text{ mol dm}^{-3} \text{ s}^{-1}$ . The production rate in the aqueous phase is five times higher, and this is reflected in a slight rise in the mixing ratio of CH<sub>3</sub>CHOHCHO after the cloud dissipates (see Table VI).

#### METHYL GLYOXAL (2-OXO PROPANAL)

Figure 11 summarizes the budget of methyl glyoxal in the presence and in the absence of cloud water. Important processes causing the formation of CH<sub>3</sub>COCHO, in the gas phase as well as in the aqueous phase, are reactions of the OH radical with hydroperoxy propanone, hydroxy propanone, 2-hydroperoxy propanal and 2-hydroxy propanal (G52b, G91, G93a, G94b and A142b, A149/150, A151b, A156b/158). The gas-phase reaction CH<sub>3</sub>CH(OO)CHO + NO contributes less than 1% to the total rate and is not shown in Figure 11. The mixed hydroxy and hydroperoxy aldehydes are more efficiently absorbed into cloud water than the other two precursors of methyl glyoxal, which causes the aqueous phase reactions of the former two compounds to be favored over those of the latter. Photolysis of methyl glyoxal is the main loss process, assisted by reaction with OH (G53, A130/131). Production and loss are approximately balanced at a rate of  $\sim 3.0 \times 10^{-17} \text{ mol dm}^{-3} \text{ s}^{-1}$ . The large photodissociation coefficient of  $1.2 \times 10^{-4} \text{ s}^{-1}$  keeps the mixing ratio of methyl glyoxal in the low pmol mol<sup>-1</sup> regime (see Table VI and Figure 7).

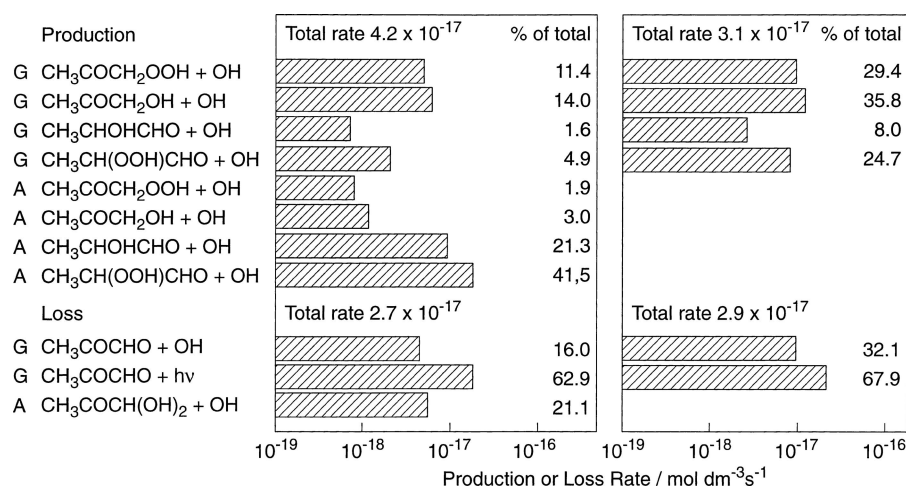


Figure 11. Relative contributions of the major reactions leading to the production and loss of methyl glyoxal, daylight shortly before noon. Left: Reactions in the gas phase and in the aqueous phase of a cloud. Right: Gas-phase reactions after the cloud event.

## PYRUVIC ACID (2-OXO PROPANOIC ACID)

The gas-phase production of pyruvic acid is a consequence of the oxidation of propionic acid formed in the reaction of HO<sub>2</sub> with propionyl peroxy (G65b). This radical arises from the oxidation of propanal (reactions G63–G66), which is an oxidation product of propane. The reaction of propionic acid with OH leads to the 2-peroxy propionic acid radical (G68), which reacts either with NO to form pyruvic acid (G69b), in addition to other products, or with HO<sub>2</sub> to form 2-hydroperoxy propionic acid (G70). This species reacts further with OH to form pyruvic acid (G71) as well. The most prominent pathway for the formation of pyruvic acid is the reaction of 2-hydroperoxy propionic acid with OH (G71), and photolysis is the major gas-phase loss process. The reaction of OH with lactic acid (G78) is negligible as a source of pyruvic acid in the gas phase. Because propionic acid is a minor product of propane oxidation and photolysis of CH<sub>3</sub>COCOOH is efficient, the mixing ratio of pyruvic acid established in the absence of clouds is fairly small (see Table VI). In the presence of clouds the reactions of OH with 2-hydroperoxy propionic acid and lactic acid are largely transferred into the aqueous phase (A153, A159/160), because these acids are efficiently absorbed into cloud water. A third important pathway for the production of pyruvic acid in the aqueous phase is the oxidation of methyl glyoxal by reaction with OH (A130/131). These reactions contribute 40.9, 13.5 and 45.6 percent, respectively, to the total rate of formation of pyruvic acid. Whereas the gas-phase production rate in cloud-free air is  $\sim 1.0 \times 10^{-18}$  mol dm<sup>-3</sup> s<sup>-1</sup>, the rate in the aqueous phase of a cloud is raised to  $\sim 1.3 \times 10^{-17}$  mol dm<sup>-3</sup> s<sup>-1</sup>. This leads to the release into the gas phase of  $\sim 1.5 \times 10^{-14}$  mol dm<sup>-3</sup> of pyruvic acid after the first 30 min cloud event, and an additional  $\sim 1.4 \times 10^{-14}$  mol dm<sup>-3</sup> after the second. The additional material is subsequently photolysed so that the mixing ratio of pyruvic acid fluctuates between 0.7 and 2.8 pmol mol<sup>-1</sup>, as Figure 7 illustrates.

## LACTIC ACID (2-HYDROXY PROPANOIC ACID)

This compound has no gas-phase sources. It is produced in the aqueous phase of clouds by the reaction of OH radicals with 2-hydroxy propanal (A156a/157) and, to a much smaller extent, by the reaction of 2-hydroperoxy propionic acid with sulfite (A182). Losses of lactic acid occur by reaction with OH in both phases. The rate of destruction in the gas phase is fairly small, and that in the aqueous phase is smaller than the production rate, so that lactic acid accumulates toward a quasi-steady state mixing ratio of  $\sim 2.2$  pmol mol<sup>-1</sup>.

**Conclusions**

The present study has explored the chemistry of C<sub>2</sub> and C<sub>3</sub> organic compounds in the marine troposphere by tracing the individual chemical pathways resulting from

the oxidation of ethane, ethene, acetylene, propane, propene, and acetic acid, both in the gas phase and in the aqueous phase of clouds and the marine aerosol. The results lead to the following principal conclusions: (1) Although the chemistry of C<sub>2</sub> and C<sub>3</sub> compounds adds numerous sources of formaldehyde to the system, the oxidation of methane remains the dominant source during the day. At night, the reactions of ethene and propene with ozone contribute substantially to the formation of HCHO. (2) Unlike formaldehyde, acetaldehyde is not efficiently converted to acetic acid in clouds, and the major sources of acetic acid are reactions in the gas phase. (3) Organic hydroperoxides are prominent intermediate products resulting from the oxidation of hydrocarbons in the marine atmosphere. Subsequent reactions lead partly to the formation of mixed hydroxy or carbonyl hydroperoxides that are readily absorbed into cloud water, where they contribute significantly to the formation of multifunctional carbonyl compounds and organic acids. The oxidation of sulfur dioxide by organic hydroperoxides in the aqueous phase is subordinate to that by hydrogen peroxide, which represents the major oxidant. (4) Next to acetaldehyde and acetone, the most prominent oxidation products are glycol aldehyde, glyoxal, methyl glyoxal and hydroxy propanone. In the aqueous phase of clouds these compounds are partly converted to the corresponding organic acids. (5) Whereas formic and acetic acid are primarily due to advection from the continents (this process is not treated here), the gas phase chemistry adds propanoic, 2-hydroperoxy propanoic and pyruvic acid. In-cloud chemistry additionally generates hydroperoxy acetic, glycolic, glyoxylic, oxalic, pyruvic and lactic acid. Most acids are released to the gas phase when the cloud dissipates, attaining mixing ratios in the low pmol mol<sup>-1</sup> regime, corresponding to concentrations in the order of 10 ng m<sup>-3</sup>. Sempéré and Kawamura (1996) have observed concentrations of glyoxal, methyl glyoxal, glyoxylic acid, and pyruvic acid in rainwater samples over the western Pacific Ocean at concentrations similar to those calculated here. (6) Oxalic acid remains associated with the aerosol. As the oxidation of oxalic acid is slow, it accumulates and is predicted to reach concentrations in the range 30–90 ng m<sup>-3</sup>, before it is removed from the atmosphere, mainly by rainout from clouds. These values are comparable in magnitude to those found by Sempéré and Kawamura (1996) in rainwater and by Kawamura and Usukara (1993) in the marine aerosol over the Pacific Ocean.

## References

- Atkinson, R., Baulch, D. L., Cox, R. A., Hampson, R. F., Kerr, J. A., Rossi, M. J., and Troe, J., 1997: Evaluated kinetic, photochemical and heterogeneous data for atmospheric chemistry: Supplement V, IUPAC subcommittee on gas kinetic data evaluation for atmospheric chemistry, *J. Phys. Chem. Ref. Data* **26**, 521–1011.
- Atkinson, R., 1994: Gas-phase tropospheric chemistry of organic compounds. *J. Phys. Chem. Ref. Monograph 2*, American Institute of Physics, New York.
- Atlas, E. L. and Ridley, B. A., 1996: The Mauna Loa observatory photochemical experiment: Introduction, *J. Geophys. Res.* **101**, 14531–14541.

- Back, R. A. and Yamamoto, S., 1985: The gas-phase photochemistry and thermal decomposition of glyoxylic acid, *Can J. Chem.* **63**, 542–548.
- Balkanski, Y. J., Jacob, D. J., Gardner, G. M., Graustein, W. C., and Turekian, K. K., 1993: Transport and residence times of tropospheric aerosols inferred from a global three-dimensional simulation of  $^{210}\text{Pb}$ , *J. Geophys. Res.* **98**, 20573–20586.
- Beck, J., 1998: *Organic Acids in the Atmosphere* (in German), Doctoral Thesis, University Mainz D77, Shaker Verlag, Aachen, Germany.
- Benkelberg, H.-J., Hamm, S., and Warneck, P., 1995: Henry's law coefficients for aqueous solutions of acetone, acetaldehyde and acetonitrile, and equilibrium constants for the addition compounds of acetone and acetaldehyde with bisulfite, *J. Atmos. Chem.* **20**, 17–34.
- Berges, M. G. M. and Warneck, P., 1992: Product quantum yields for the 350 nm photodecomposition of pyruvic acid in air, *Ber. Bunsenges. Phys. Chem.* **96**, 413–416.
- Betterton, E. A. and Hoffmann, M. R., 1988: Henry's law constants of some environmentally important aldehydes, *Environ. Sci. Technol.* **22**, 1415–1418.
- Blake, D. R. and Rowland, F. S., 1986: Global atmospheric concentrations source strength of ethane, *Nature* **321**, 231–233.
- Blake, D. R., Chen, T.-Y., Smith, T. W. Jr., Wang, C. J.-L., Wingenter, O. W., Blake, N. J., and Rowland, F. S., 1996: Three-dimensional distribution of non-methane hydrocarbons and halocarbons over the north-western Pacific during the, 1991 Pacific Exploratory Mission (PEM-West A), *J. Geophys. Res.* **101**, 1763–1778.
- Blake, N. J., Blake, D. R., Simpson, I. J., Meinardi, S., Swanson, A. L., Lopez, J. P., Katzenstein, A. S., Barletta, B., Shirai, T., Atlas, E., Sachse, G. Avery, M., Vay, S., Fuelberg, H. E., Kiley, C. M., Kita, K., and Rowland, F. S., 2003: NMHCs and halocarbons in Asian continental outflow during the transport and chemical evolution over the Pacific (TRACE-P) Field Campaign: Comparison with PEM-West B, *J. Geophys. Res.* **108** (D20), 8806, doi:10.1029/2002JD003367.
- Blake, N. J., Blake, D. R., Chen, T.-Y., Collins, J. E., Sachse, G. W., Anderson, B. E., and Rowland, F. S., 1997: Distribution and seasonality of selected hydrocarbons and halocarbons over the western Pacific basin during PEM-West A and PEM-West B, *J. Geophys. Res.* **102**, 28315–28331.
- Buxton, G. V., Greenstock, C. L., Helman, W. P., and Ross, A. B., 1988: Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals ( $\text{OH}/\text{O}^-$ ) in aqueous solution, *J. Phys. Chem. Ref. Data* **17**, 513–886.
- Buxton, G. V., Malone, T. N., and Slamon, G. A., 1997: Oxidation of glyoxal initiated by OH in oxygenated aqueous solutions, *J. Chem. Soc. Faraday Trans.* **93**, 2889–2893.
- Calvert, J. G., Atkinson, R., Kerr, J. A., Madronich, S., Moortgat, G. K., Wallington, T. J., and Yarwood, G., 2000: *The Mechanisms of Atmospheric Oxidation of the Alkenes*, Oxford University Press,
- Chin, M. and Wine, P.-H., 1994: A temperature-dependent competitive kinetics study of the aqueous phase reactions of OH radicals with formate, formic acid, acetate, acetic acid, and hydrated formaldehyde, in G. R. Helz, R. G. Zepp and D. G. Crosby (eds.), *Aquatic and Surface Photochemistry*, Lewis Publishers, Boca Raton, Florida, pp. 85–96.
- Davidovits, P., Hu, J. H., Worsnop, D. R., Zahniser, M. S., and Kolb, C. E., 1995: Entry of gas molecules into liquids, *Faraday Discuss.* **100**, 65–82.
- Duan, S. X., Jayne, J. T., Davidovits, P., Worsnop, D. R., Zahniser, M. S., and Kolb, C. E., 1993: Uptake of gas-phase acetone by water surfaces, *J. Phys. Chem.* **97**, 2284–2288.
- Ehhalt, D. H., Rudolph, J., and Schmidt, U., 1986: On the importance of light hydrocarbons in atmospheric multiphase systems, in W. Jaeschke (ed.), *Chemistry of Multiphase Atmospheric Systems*, NATO ASI Series **G 6**, Springer-Verlag, Berlin, pp. 321–350.
- Eigen, M., Kruse, W., Maass, G., and De Mayer, L., 1964: Rate constants of protolytic reactions in aqueous solution, *Progr. React. Kinet.* **2**, 285–318.

- Ervens, B., George, C., Williams, J. E., Buxton, G. V., Salmon, G. A., Bydder, M., Wilkinson, F., Dentener, F., Mirabel, P., Wolke, R., and Herrmann, H., 2003a: CAPRAM 2.4 (MODAC mechanism): An extended and condensed tropospheric aqueous phase mechanism and its application, *J. Geophys. Res.* **108** (D14), 4426, doi:10.1029/2002JD002202.
- Ervens, B., Gligorowski, S., and Herrmann, H., 2003b: Temperature-dependent rate constants for hydroxyl radical reactions with organic compounds in aqueous solutions, *Phys. Chem. Phys.* **5**, 1811–1824.
- Fischer, M. and Warneck, P., 1991: The dissociation constant of pyruvic acid: Determination by spectrophotometric measurements, *Ber. Bunsenges. Phys. Chem.* **95**, 523–527.
- Fried, A., Crawford, J., Olson, J., Walega, J., Potter, W., Wert, B., Jordan, C., Anderson, B., Shetter, R., Lefer, B., Blake, D., Blake, N., Meinardi, S., Heikes, B., O'Sullivan, D., Snow, J., Fuelberg, H., Kiley, C. M., Sandholm, S., Tan, D., Sachse, G., Singh, H., Faloon, I., Harward, C. N., and Carmichael, G. R., 2003: Airborne tunable diode laser measurements of formaldehyde during TRACE-P: Distributions and box model comparisons, *J. Geophys. Res.* **108**(D20), 8798, doi:10.1029/2003JD003451.
- Herrmann, H., Ervens, B., Jacobi, H.-W., Wolke, R., Nowacki, P., and Zellner, R., 2000: CAPRAM 2.3: A chemical aqueous phase radical mechanism for tropospheric chemistry, *J. Atmos. Chem.* **36**, 231–284.
- Huie, R. E. and Clifton, C. L., 1990: Temperature dependence of the rate constants for reactions of the sulfate radical, SO<sub>4</sub><sup>-</sup>, with anions, *J. Phys. Chem.* **94**, 8561–8567.
- Jenkin, M. E., Saunders, S. M., and Pilling, M. J., 1997: The tropospheric degradation of volatile organic compounds: A protocol for mechanism development, *Atmos. Environ.* **31**, 81–104.
- Jiménez, E., Gilles, M. K., and Ravishankara, A. R., 2003: Kinetics of the reactions of the hydroxyl radical with CH<sub>3</sub>OH and C<sub>2</sub>H<sub>5</sub>OH between 235 and 360 K, *J. Photochem. Photobiol. A* **157**, 237–245.
- Johnson, B. J., Betterton, E. A., and Craig, D., 1996: Henry's law coefficients of formic and acetic acids, *J. Atmos. Chem.* **24**, 113–119.
- Kames, J. and Schurath, U., 1995: Henry's law constant and hydrolysis-rate constants for peroxyacyl nitrates (PANs) using a homogeneous gas-phase source, *J. Atmos. Chem.* **21**, 151–164.
- Kames, J., Schweighoefer, S., and Schurath, U., 1991: Henry's law constant and hydrolysis of acetylperoxy nitrate (PAN), *J. Atmos. Chem.* **12**, 169–180.
- Kawamura, K. and Usukara, K., 1993: Distribution of low molecular weight dicarboxylic acids in the North Pacific aerosol samples, *J. Oceanogr.* **49**, 271–283.
- Kawamura, K. and Sakaguchi, F., 1999: Molecular distributions of water soluble dicarboxylic acids in marine aerosols over the Pacific Ocean including tropics, *J. Geophys. Res.* **104**, 3501–3509.
- Khan, I., Brimblecombe, P., and Clegg, S. L., 1995: Solubilities of pyruvic acid and the lower (C1–C6) carboxylic acids. Experimental determination of equilibrium vapor pressures above pure aqueous and salt solutions, *J. Atmos. Chem.* **22**, 285–302.
- Kurz, J. L., 1967: The hydration of acetaldehyde. I Equilibrium thermodynamic parameters, *J. Am. Chem. Soc.* **89**, 3524–3528.
- Kurz, J. L. and Coburn, J. I., 1967: The hydration of acetaldehyde II. Transition state characterization, *J. Am. Chem. Soc.* **89**, 3528–3537.
- Lelieveld, J., Crutzen, P. J., and Rodhe, H., 1989: Zonal average cloud characteristics for global atmospheric chemistry modeling, GLOMAC Report UDC 551. 5510.4, CM-76. International Meteorology Institute, Stockholm.
- Lightfoot, P. D., Cox, R. A., Crowley, J. N., Destriau, M., Hayman, G. D., Jenkin, M. E., Moortgat, G. K., and Zabel, F., 1992: Organic peroxy radicals: Kinetics, spectroscopy, and tropospheric chemistry, *Atm. Environ.* **26A**, 1805–1961.
- Madronich, S., 1987: Photodissociation in the atmosphere 1. Actinic flux and the effects of ground reflection and clouds, *J. Geophys. Res.* **92**, 9740–9752.

- Marchaj, A., Kelley, D. G., Bakac, A., and Espenson, J. H., 1991: Kinetics of the reactions between alkyl radicals and molecular oxygen in aqueous solution, *J. Phys. Chem.* **95**, 4440–4441.
- Mellouki, A. and Mu, Y., 2003: On the atmospheric degradation of pyruvic acid in the gas phase, *J. Photochem. Photobiol. A* **157**, 295–300.
- Orlando, J. J. and Tyndall, G. S., 2003: Gas-phase uv absorption spectra for peracetic acid, and for acetic acid monomers and dimers, *J. Photochem. Photobiol. A*, **157**, 161–166.
- O'Sullivan, D. W., Lee, M., Noone, B. C., and Heikes, B. G., 1996: Henry's law constant determinations for hydrogen peroxide, methyl hydroperoxide, hydroxymethyl hydroperoxide, ethyl hydroperoxide, and peroxyacetic acid, *J. Phys. Chem.* **100**, 3241–3247.
- Plass-Dülmer, C., Koppmann, R., Ratte, M., and Rudolph, J., 1995: Light non-methane hydrocarbons in sea water, *Global Biogeochem. Cycles* **9**, 79–100.
- Pruppacher, H. R. and Klett, J. K., 1997: *Microphysics of Clouds and Precipitation*, 2nd edn., Kluwer Academic Publishers, Dordrecht, The Netherlands.
- Ratte, M., Plass-Dülmer, C., Koppmann, R., Rudolph, J., and Denga, J., 1993: Production mechanisms of C2-C4 hydrocarbons in seawater: Field measurements and experiments, *Global Biogeochem. Cycles*, **7**, 369–378.
- Rudolph, J., 1995: The tropospheric distribution and budget of ethane, *J. Geophys. Res.* **100**, 11369–11381.
- Rudolph, J. and Jöni, F. J., 1990: Measurements of light hydrocarbons over the Atlantic in regions of low biological activity, *J. Geophys. Res.* **95**, 20583–20591.
- Saxena, P. and Hildemann, L. M., 1996: Water-soluble organics in atmospheric particles: A critical review of the literature and application of thermodynamics to identify candidate compounds, *J. Atmos. Chem.* **24**, 57–109.
- Schecker, H. G. and Schulz, G., 1969: Untersuchungen zur Hydratationskinetik von Formaldehyd, *Z. Phys. Chem. N. F.* **65**, 221–224.
- Schuchmann, H.-P. and von Sonntag, C., 1984: Methyl peroxy radicals: A study of the  $\gamma$ -radiolysis of methane in oxygenated aqueous solutions, *Z. Naturforsch.* **39B**, 217–221.
- Schuchmann, M. N. and von Sonntag, C., 1988: The rapid hydration of the acetyl radical. A pulse radiolysis study of acetaldehyde in aqueous solution, *J. Am. Chem. Soc.* **110**, 5698–5701.
- Schuchmann, M. N., Zegota, H., and von Sonntag, C., 1985: Acetate peroxy radicals,  $\text{O}_2\text{CH}_2\text{CO}_2^-$ : A study on the  $\gamma$ -Radiolysis and pulse radiolysis of acetate in oxygenated aqueous solutions, *Z. Naturforsch.* **40b**, 215–221.
- Schurath, U. and Wipprecht, V., 1980: Reactions of peroxyacyl radicals, in B. Versino and H. Ott (eds.), *First European Symposium on Physico-Chemical Behaviour of Atmospheric Pollutants*, Ispra, Italy, 1979, CEC, Bruxelles-Luxembourg, pp.157–165.
- Sempéré, R. and Kawamura, K., 1996: Low molecular weight dicarboxylic acids and related polar compounds in the remote marine rain samples collected from the western Pacific, *Atmos. Environ.* **30**, 1609–1619.
- Singh, H. B., Kanakidou, M., Crutzen, P. J., and Jacob, D. J., 1995: High concentrations and photochemical fate of oxygenated hydrocarbons in the global troposphere, *Nature* **378**, 50–54.
- Singh, H. B., O'Hara, D., Herlth, D., Sachse, W., Blake, D. R., Bradshaw, J. D., Kanakidou, M., and Crutzen, P. J., 1994: Acetone in the atmosphere: Distribution, sources and sinks, *J. Geophys. Res.* **99**, 1805–1819.
- Singh, H., Chen, Y., Tabazadeh, A., Fukui, Y., Bey, I., Yantosca, R., Jacob, D., Arnold, F., Wohlfrom, K., Atlas, E., Flocke, F., Blake, D., Blake, N., Heikes, B., Snow, J., Talbot, R., Gregory, G., Sachse, G., Vay, S., and Kondo, Y., 2000: Distribution and fate of selected oxygenated organic species in the troposphere and lower stratosphere over the Atlantic, *J. Geophys. Res.* **105**, 3795–3805.
- Smith, R. M. and Martell, A. E., 1977: *Critical Stability Constants, 3. Other Organic Ligands*, Plenum Press, London.



- Snider, J. R. and Dawson, G. A., 1985: Tropospheric light alcohols, carbonyls, and acetonitrile: Concentrations in the southwestern United States and Henry's law data, *J. Geophys. Res.* **90D**, 3797–3805.
- Sørensen, P. E., Bruhn, K., and Lindeløv, F., 1974: Kinetics and equilibria for the reversible hydration of the aldehyde group on glyoxylic acid, *Acta Chem. Scand.* **A28**, 162–168.
- Stockwell, W. P., Middleton, P., Chang, J. S., and Tang, X., 1990: The second generation regional acid deposition model. Chemical mechanisms for regional air quality modeling, *J. Geophys. Res.* **95**, 16343–16367.
- Stockwell, W. P., Kirchner, R. F., Kuhn, M., and Seefeld, S., 1997: A new mechanism for regional atmospheric chemistry modeling, *J. Geophys. Res.* **102**, 25847–25879.
- Tyndall, G. S., Cox, R. A., Granier, C., Lesclaux, R., Moortgat, G. K., Pilling, M. J., Ravishankara, A. R., and Wallington, T. J., 2001: Atmospheric chemistry of small organic peroxy radicals, *J. Geophys. Res.* **106**, 12157–12182.
- Vel Leitner, N. K. and M. Doré, 1997: Mechanism of the reaction between hydroxyl radicals and glycolic, glyoxylic, acetic, and oxalic acids in aqueous solution: Consequence on hydrogen peroxide consumption in the H<sub>2</sub>O<sub>2</sub>/UV and O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> systems, *Water Res.* **31**, 1383–1397.
- Wannowius, K. J., 2001: Contribution to the chemistry in clouds: A laboratory study on the kinetics and mechanism of the oxidation of sulfur and nitrogen compounds by hydroperoxides in aqueous phase, in R. Jaenicke (ed.), *Dynamics and Chemistry of Hydrometeors*, Wiley VCH Weinheim, Germany, pp. 468–527.
- Warneck, P., 1999: The relative importance of various pathways for the oxidation of sulfur dioxide and nitrogen dioxide in sunlit continental fair weather clouds, *Phys. Chem. Chem. Phys.* **1**, 5471–5483.
- Warneck, P., 2000: *Chemistry of the Natural Atmosphere*, 2nd edn., Academic Press, San Diego, California.
- Warneck, P., 2001: Photodissociation of acetone in the troposphere: An algorithm for the quantum yield, *Atmos. Environ.* **35**, 5773–5777.
- Warneck, P., 2003: In-cloud chemistry opens pathway to the formation of oxalic acid in the marine atmosphere, *Atmos. Environ.* **37**, 2423–2427.
- Wollenhaupt, M. and Crowley, J. N., 2000: Kinetic studies of the reactions CH<sub>3</sub> + NO<sub>2</sub> → products, CH<sub>3</sub>O + NO<sub>2</sub> → products, and OH + CH<sub>3</sub>C(O)CH<sub>3</sub> → CH<sub>3</sub>C(O)OH + CH<sub>3</sub>, over a range of temperature and pressure, *J. Phys. Chem. A* **104**, 6429–6438.
- Wollenhaupt, M., Carl, S. A., Horowitz, A., and Crowley, J. N., 2000: Rate coefficient for reaction of OH with acetone between 202 and 295 K, *J. Phys. Chem. A* **104**, 2695–2705.
- Zhou, X. and Mopper, K., 1990: Apparent partition coefficients of 15 carbonyl compounds between air and sea water and between air and freshwater. Implications for air-sea exchange, *Environ. Sci. Technol.* **24**, 1864–1869.