

# **R&D PROGRAMME ENVIRONMENT AND CLIMATE**

**AREA: 1.2. Atmospheric Physics and Chemistry**

**TOPIC: 1.2.1.2.**

**FINAL REPORT**

**Contract No. ENV4-CT97-0388**

## **Model Development for Tropospheric Aerosol and Cloud Chemistry, (MODAC)**

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**‘Tropospheric Aqueous Phase Radical Chemistry Evaluation, Model construction and Laboratory Studies’**

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**‘Model Development for the Chemistry of the Atmospheric Aqueous Phase with Particular Reference to Sulfur Chemistry and the Influence on it of Organic Pollutants’**

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**‘Modelling and Experimental Study of the Heterogeneous Processes at the Gas/Liquid Interface’**

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**‘Modelling of Cloud and Aerosol Chemistry in a strato-cumulus model containing Microphysics’**

**Key Words (5): Oxidants, Radicals, Aqueous Phase, Multiphase, Modelling**

**Reporting Period: 01/10/1997 - 31/03/2000**

## **Part A: SUMMARY REPORT OF THE PROJECT**

### **I. GENERAL OBJECTIVES**

The performed project MODAC ('Model Development for Tropospheric Aerosol and Cloud Chemistry') is devoted to the development of adequate physico-chemical models for the description of heterogeneous and multiphase chemical processes taking place in the troposphere. The model development performed in the project is limited to the so-called 'tropospheric aqueous phase' which in the following includes aqueous particles dispersed in air, i.e. the droplets of clouds, fog and rain and the aqueous (wet) aerosol. Reactions occurring on solids (i.e. direct gas-solid interactions) are not treated in this project.

The general objectives of this project are:

- To develop an extensive aqueous phase chemical mechanism, including all relevant processes, that will be based on an evaluation of current scientific knowledge ('the overall mechanism'). In particular, the model will include an extended description of organic chemistry and radical processes.
- To apply tools of sensitivity analysis to the above mechanism in order to check which processes are of the highest importance and also which classes of reaction do not contribute significantly to chemical conversions in the tropospheric aqueous phase.
- To couple the overall aqueous phase mechanism with the existing and well accepted gas phase chemical RADM2 mechanism.
- To develop a kinetic description of transport in the aqueous phase, the gas phase and across the gas/liquid interface and to use this description in the model.
- To include heterogeneous gas-aqueous processes in the model and to describe them adequately.
- To develop a reduced chemical mechanism which may in the future be applied in larger (global) models.
- To couple the model to a simple description of cloud dynamics for a stratocumulus cloud and to couple the model to a simple wet aerosol model.
- To introduce into the model emission scenarios which are typical for Europe, i.e. a marine, a continental polluted and a continental rural scenario.
- To perform a limited set of laboratory studies on reaction kinetics and uptake coefficients on systems which are of central importance for the overall model but for which data either do not exist or are inconclusive.

The proposed project complies explicitly with topic 1.2.1.2. 'Tropospheric Physics and Chemistry' of the work programme 'Environment and Climate 1994-1998' under research task 2: 'Tropospheric Aerosols and Clouds'. The project is focused on deepening our understanding of multiphase chemistry of radicals and organic substances in the troposphere. The project will be highly compatible to the priorities for the work programme under the point 'Combating atmospheric pollution - better air quality'. The effects of anthropogenic emissions (e.g. from car traffic) will be better described when multiphase tropospheric conversions are taken into account. Furthermore, the effects of biogenic emissions can probably not be fully understood when only gas phase processes are included in air chemistry models. Consideration of multiphase processes by adequate models which are based on the latest laboratory results will help to develop better tools for understanding the mechanisms and effects of air pollution and possible political measures which might be taken.

## II. SPECIFIC OBJECTIVES FOR THE REPORTING PERIOD

The following achievements have been expected and were achieved during the project:

- (i) A chemical aqueous phase reaction mechanism for tropospheric chemistry based on currently available reviewed literature data as well as data from laboratory experiments performed within the project will be developed.
- (ii) A sub-model description of mass transfer processes and heterogeneous reactions in the multiphase troposphere based on the latest data available will be constructed.
- (iii) A tropospheric chemistry box model will be built which integrates the above chemical reaction schemes and transport descriptions with the accepted up-to-date gas phase chemical RADM2 mechanism, cloud and aerosol microphysics and an array of emission scenarios.
- (iv) Case studies obtained with the model developed in MODAC for the three scenarios of (a) the marine, (b) the continental polluted (i.e. urban) and (c) the continental unpolluted (i.e. rural) troposphere for the effects of strato-cumulus clouds and the wet aerosol will be performed and interpreted.
- (v) A tested condensed mechanism for tropospheric heterogeneous and aqueous phase chemistry for the use in global models will be established.

In conclusion, the proposed studies will yield a number of physico-chemical data which subsequently can be included into tropospheric chemistry models and which are expected to contribute to a more detailed understanding of the complex tropospheric chemistry system.

## III. MAIN RESULTS

### Introduction

Several studies in recent years ([1 - 4]) have shown the influence of aqueous phase processes on tropospheric chemistry. These existing aqueous phase mechanisms are restricted to some selected aspects of cloud chemistry. So, CAPRAM2.3 represents a mechanism exceeds approaches with the treatment of (1) a detailed presentation of the oxidation of organic compounds with one and two carbon atoms, (2) an explicit description of S(IV)-oxidation by radicals and iron(III), as well as by peroxides and ozone, (3) the reactions of OH, NO<sub>3</sub>, Cl<sub>2</sub><sup>-</sup>, Br<sub>2</sub><sup>-</sup>, and CO<sub>3</sub><sup>-</sup> radicals, as well as reactions of the transition metal ions (TMI) iron, manganese and copper. The mechanism is applied for three different scenarios (urban, remote, marine).

The meteorological parameters, such as the temperature and pressure, are constant during the three days of simulation (T = 288.15 K, p = 1 atm). A liquid water content of 0.3 g m<sup>-3</sup> is assumed. For the first set of calculations the gas phase chemistry is described by RADM2 [5]. Furthermore the species CH<sub>3</sub>OH, C<sub>2</sub>H<sub>5</sub>OH, Cl<sub>2</sub> and Br<sub>2</sub> are additionally treated. Within the development of the multiphase scheme the gas phase part was replaced by the newer gas phase mechanisms RACM [6]. In the framework of the project this aqueous phase mechanism was updated and revised using recent values, which are critically revised and updated in close co-operation with contributor 2.

Whereas the original version of CAPRAM (version 2.3) contains 265 aqueous phase reactions and 34 heterogeneous processes, in the updated version (CAPRAM2.4) 438 aqueous phase processes and 34 heterogeneous processes are considered. The phase transfer from the gas phase and vice versa is treated by means of the resistance model by Schwartz [7]. Hence, apart from Henry constants also the mass accommodation coefficients and the gas phase diffusion coefficients are implemented.

### **The resulting Mechanism (CAPRAM 2.4, the MODAC mechanism)**

In the following tables the main result of the MODAC project, i.e. the developed mechanism for tropospheric aqueous phase chemistry is given in full detail. The resulting mechanism is addressed as the Chemical Aqueous Phase Radical Mechanism (CAPRAM) in its version 2.4, as the MODAC mechanism. It has been agreed by all MODAC project partners to address the mechanism generally as:

#### CAPRAM2.4. (MODAC mechanism)

The Tables also contain the processed data implementations of the former version CAPRAM 2.3. which is described by Herrmann et al. (1999, 2000) and which served as a starting point for the further development. It should be noted that also the completion and conclusion of the mechanism version CAPRAM 2.3. has also been supported in the MODAC project because completion of CAPRAM 2.3. fell in the early phase of MODAC.

The references addressed in the Tables are found at the end of part A of this report.

### **References**

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**Table 1:** Initial Concentrations for three scenarios under polluted continental (urban), unpolluted continental (remote) and marine conditions (gas phase species in ppb; aqueous phase species in M)

	urban		remote		marine	
	1 <sup>st</sup> data set	changed in 2 <sup>nd</sup> data set	1 <sup>st</sup> data set	changed in 2 <sup>nd</sup> data set	1 <sup>st</sup> data set	changed in 2 <sup>nd</sup> data set
NO <sub>2</sub>	4.5	a	1.5	a	0.4	a
HNO <sub>3</sub>	1	b	0.3	b	0.15	g
CH <sub>4</sub>	1700	a	1700	a	1700	a
H <sub>2</sub> O <sub>2</sub>	1	d	0.001	a	0.001	a
H <sub>2</sub>	2000		2000		2000	
CO	200		150		140	
O <sub>3</sub>	90	a	60	a	40	a
HCl	6	a	0.7	b	0.5	g
NH <sub>3</sub>	25	a	1.5	b	0.05	g
CO <sub>2</sub>	5 · 10 <sup>5</sup>	a	3.3 · 10 <sup>5</sup>	b	3.3 · 10 <sup>5</sup>	b
SO <sub>2</sub>	10	b	1	h	0.1	h
HCHO	0.1	a	0.1	a	0.01	a
ETH	2	a	1.5	a	1	a
	2	a	1	a	1	a
HC3: Alkanes with OH rate constant between 2.7 · 10 <sup>-13</sup> and 3.4 · 10 <sup>-12</sup> cm <sup>3</sup> s <sup>-1</sup> (298 K, 1 atm)	1	a	0.5	a	0	a
HC5: Alkanes with OH rate constant between 3.4 · 10 <sup>-12</sup> and 6.8 · 10 <sup>-12</sup> cm <sup>3</sup> s <sup>-1</sup> (298 K, 1 atm)	0.1	a	0	a	0	a
HC8: Alkanes with OH rate constant greater than 6.8 · 10 <sup>-12</sup> cm <sup>3</sup> s <sup>-1</sup> (298 K, 1 atm)	1	a	0.5	a	0.1	a
C <sub>2</sub> H <sub>4</sub> (RADM2: OL2; RACM: ETE)	0.1	a	0.1	a	0.1	a
OLT: Terminal alkenes	0.1	a	0.1	a	0.1	a
Isoprene	0.1	a	0.1	a	0.1	a
TOL: Toluene and less reactive aromatics	0.1	a	0.01	a	0	a
CSL: Cresol and other OH-substituted aromatics	0.001	a	0.001	a	0	a
XYL: Xylene and more reactive aromatics	0.1	a	0.01	a	0	a

Table 1 cont.

	urban		remote		marine	
	1 <sup>st</sup> data set	changed in 2 <sup>nd</sup> data set	1 <sup>st</sup> data set	changed in 2 <sup>nd</sup> data set	1 <sup>st</sup> data set	changed in 2 <sup>nd</sup> data set
ALD: Acetaldehyde and higher aldehydes	0.1		0.1		0.01	
Ketones	0.1	1	0.1	0.3	0.01	0.1
Glyoxal	0.1		0.1		0.01	
Methylglyoxal	0.1		0.1		0.01	
PAN	0.01	0.5	0.01	0.001	0.01	0
CH <sub>3</sub> OOH	0.01	1	0.01	0.001	0.01	0
OP2: Higher organic peroxides	0.001	0.1	0.001	0.1	0.001	0.1
CH <sub>3</sub> C(O)OOH	0.001		0.001		0.001	
CH <sub>3</sub> OH	5		2		0.8	0.5
EtOH	1		0.24		2.4 · 10 <sup>-3</sup>	0
API	0.04	0	0.04		0	
LIM	0.02	0	0.02		0	
OH	3.16 · 10 <sup>-10</sup>		3.16 · 10 <sup>-10</sup>		1.6 · 10 <sup>-9</sup>	
pH	4.5		4.5		5.2	
Cl <sup>-</sup>	1 · 10 <sup>-4</sup>		1 · 10 <sup>-4</sup>		5.6 · 10 <sup>-4</sup>	
Br <sup>-</sup>	3 · 10 <sup>-6</sup>		3 · 10 <sup>-7</sup>		1.8 · 10 <sup>-6</sup>	
Fe <sup>3+</sup>	5 · 10 <sup>-6</sup>		5 · 10 <sup>-7</sup>		5 · 10 <sup>-8</sup>	
Mn <sup>2+</sup>	2.5 · 10 <sup>-7</sup>		2.5 · 10 <sup>-8</sup>		1 · 10 <sup>-9</sup>	
Cu <sup>+</sup>	2.5 · 10 <sup>-7</sup>		2.5 · 10 <sup>-8</sup>		1 · 10 <sup>-9</sup>	
Cu <sup>2+</sup>	0		0		3 · 10 <sup>-8</sup>	1 · 10 <sup>-9</sup>
HSO <sub>4</sub> <sup>-</sup>	3 · 10 <sup>-7</sup> *)		3 · 10 <sup>-7</sup>		5.97 · 10 <sup>-6</sup>	
SO <sub>4</sub> <sup>2-</sup>	5.97 · 10 <sup>-5</sup>		5.97 · 10 <sup>-5</sup>		5 · 10 <sup>-8</sup>	
C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	5 · 10 <sup>-6</sup>	2.5 · 10 <sup>-7</sup>	5 · 10 <sup>-7</sup>	2.5 · 10 <sup>-8</sup>		
H <sub>2</sub> O <sub>(g)</sub>			2 · 10 <sup>7</sup>	3 · 10 <sup>7</sup>		
O <sub>2(g)</sub>			2 · 10 <sup>8</sup>	2 · 10 <sup>8</sup>		
N <sub>2(g)</sub>			7.8 · 10 <sup>8</sup>	7.8 · 10 <sup>8</sup>		
H <sub>2</sub> O <sub>(aq)</sub>			55.5	55.5		

Constant during the simulation time [ppb] or [M]:

<sup>a</sup> Zimmermann and Poppe, 1996; <sup>b</sup> Graedel and Weschler, 1981; <sup>c</sup> Saxena and Hildemann, 1996; <sup>d</sup> Matthijsen and Builjes, 1995; <sup>e</sup> Weschler *et al.*, 1986; <sup>f</sup> Leibrock and Slemr, 1996; <sup>g</sup> Jacob, 1986; <sup>h</sup> estimated; <sup>i</sup> Chameides, 1984; <sup>j</sup> Herrmann *et al.*, 1996a; <sup>k</sup> [C<sub>2</sub>O<sub>4</sub>]<sup>2-</sup> = [Fe<sup>3+</sup>], Sedlak and Hoigne, 1992; <sup>l</sup> Rohrer and Brüning, 1992; <sup>m</sup> Fuentes *et al.*, 1996; <sup>n</sup> results from [SO<sub>4</sub><sup>2-</sup>]<sub>0</sub> and [H<sup>+</sup>]<sub>0</sub>

**Table 2a)** Emissions [ $\text{cm}^{-3} \text{s}^{-1}$ ]  $\cdot 10^5$  cm height of layer = [ $\text{cm}^2 \text{s}^{-1}$ ]

	urban		remote		marine	
	1 <sup>st</sup> data set	changed in 2 <sup>nd</sup> data set	1 <sup>st</sup> data set	changed in 2 <sup>nd</sup> data set	1 <sup>st</sup> data set	changed in 2 <sup>nd</sup> data set
CH <sub>3</sub> CHO and higher aldehydes	5.93·10 <sup>5</sup>	1.93·10 <sup>4</sup>	3171		10.41	0
alpha-Pinene	1.88·10 <sup>5</sup>		1.93·10 <sup>4</sup>	1.88·10 <sup>5</sup>	8987	
CH <sub>3</sub> OH	1.16·10 <sup>6</sup>		1.07·10 <sup>4</sup>		0.59	
CO	8.99·10 <sup>7</sup>		3.7·10 <sup>6</sup>		8.53·10 <sup>5</sup>	
CSL: Cresol and other OH-substituted aromatics	1.82·10 <sup>6</sup>		2.88·10 <sup>4</sup>		7.78	0
DIEN	1.24·10 <sup>6</sup>		1.55·10 <sup>4</sup>		11.7	
C <sub>2</sub> H <sub>4</sub> (ETE)	2.61·10 <sup>6</sup>		4.54·10 <sup>4</sup>		45.0	
ETH	1.54·10 <sup>6</sup>		1.5·10 <sup>4</sup>		8.91	
ETOH	4.03·10 <sup>6</sup>		3736		0.415	
HC3: Alkanes with OH rate constant between 2.7·10 <sup>-13</sup> and 3.4·10 <sup>-12</sup> cm <sup>3</sup> s <sup>-1</sup> (298 K, 1 atm)	2.76·10 <sup>6</sup>		1.53·10 <sup>4</sup>		1.73	
HC5: Alkanes with OH rate constant between 3.4·10 <sup>-12</sup> and 6.8·10 <sup>-12</sup> cm <sup>3</sup> s <sup>-1</sup> (298 K, 1 atm)	4.9·10 <sup>6</sup>		6.31·10 <sup>4</sup>		2.653	0
HC8: Alkanes with OH rate constant greater than 6.8·10 <sup>-12</sup> cm <sup>3</sup> s <sup>-1</sup> (298 K, 1 atm)	3.19·10 <sup>6</sup>		4.044·10 <sup>4</sup>		11.72	0
HCHO	2.58·10 <sup>5</sup>		3028		17.8	
Isoprene	0	1.54·10 <sup>5</sup>	0	1.5·10 <sup>6</sup>		
Ketones	9.9·10 <sup>5</sup>		8920		1.59	
Limonene	1.88·10 <sup>5</sup>	1.93·10 <sup>4</sup>	1.93·10 <sup>4</sup>	1.88·10 <sup>5</sup>	8987	0
NH <sub>3</sub>	3.03·10 <sup>6</sup>		9.06·10 <sup>5</sup>		4.57·10 <sup>5</sup>	
NO	1.01·10 <sup>7</sup>		2.86·10 <sup>5</sup>		2.8·10 <sup>4</sup>	
OLT: Terminal alkenes	4.94·10 <sup>5</sup>		7950		7.28	0
CH <sub>3</sub> COOH	8.44·10 <sup>4</sup>		3350		810	
SO <sub>2</sub>	3.27·10 <sup>7</sup>	3.27·10 <sup>6</sup>	2.91·10 <sup>5</sup>		7.92·10 <sup>4</sup>	
TOL: Toluene and less reactive aromatics	1.7·10 <sup>6</sup>		2.108·10 <sup>4</sup>		5.81	
XYL: Xylene and more reactive aromatics	9.88·10 <sup>5</sup>		1.13·10 <sup>4</sup>		0.721	0

**Table 2h):** Depositions [ $\text{cm s}^{-1}$ ] /  $10^5$  cm height of layer = [ $\text{s}^{-1}$ ]

	urban = remote	marine
CH <sub>3</sub> OH	1e-5	1e-5
CO	1e-6	1e-6
EtOH	5e-6	5e-6
H <sub>2</sub> O <sub>2</sub>	1e-5	5e-6
HCHO	1e-5	5e-6
HCl	1e-5	5e-6
HNO <sub>3</sub>	2e-5	5e-6
HOBr	2e-6	2e-6
HOCl	2e-6	2e-6
N <sub>2</sub> O <sub>5</sub>	2e-5	5e-6
NH <sub>3</sub>	1e-5	1e-5
NO <sub>2</sub>	4e-6	1e-6
O <sub>3</sub>	4e-6	4e-7
CH <sub>3</sub> OOH	5e-6	5e-6
HCOOH	1e-5	5e-6
SO <sub>2</sub>	1e-5	5e-6
H <sub>2</sub> SO <sub>4</sub>	2e-5	5e-6

CAPRAM2.3 ⇌ CAPRAM2.4(MODAC mechanism) ⇌ CAPRAM2.4-reduced(MODAC mechanism)

**Legend:**  
 xxx in former version, removed in CAPRAM2.4 (MODAC mechanism)  
 xxx added in CAPRAM2.4 (MODAC mechanism)  
 \* removed in CAPRAM2.4-reduced (MODAC mechanism)  
 k [M<sup>n</sup> s<sup>-l</sup>]; n reaction order - l

**Table 3a:** Henry's Law Constants

red.	No. 2.4	No. 2.3	Species	$K_H^{298}$ M atm <sup>-1</sup>	$\Delta H/R$ , K	References	reason
	1	1	CO <sub>2</sub>	3.11 · 10 <sup>-2</sup> 3.1 · 10 <sup>-2</sup>	-2423	Chameides, 1984	
	2	2	HCl	1.10	-2020	Marsh and McElroy, 1985	
	3	3	NH <sub>3</sub>	60.7	-3920	Clegg and Brimblecombe, 1990	
	4	4	O <sub>3</sub>	1.14 · 10 <sup>-2</sup>	-2300	Kosak-Channing and Helz, 1983	
	5	5	HO <sub>2</sub>	9 · 10 <sup>3</sup>		Weinstein-Lloyd and Schwartz, 1991	
	6	6	OH	25	-5280	Kläning <i>et al.</i> , 1985b	
	7	7	H <sub>2</sub> O <sub>2</sub>	1.02 · 10 <sup>5</sup>	-6340	National Bureau of Standards, 1971	
	8	8	HNO <sub>3</sub>	2.1 · 10 <sup>5</sup>	-8700	Lind and Kok, 1994	
	9	9	NO <sub>3</sub>	0.6		Lelieveld and Crutzen, 1991	
	10	10	N <sub>2</sub> O <sub>5</sub>	1.4		Rudich <i>et al.</i> , 1996	value for N <sub>2</sub> O <sub>5</sub> available
	11	11	NO <sub>2</sub>	1.2 · 10 <sup>-2</sup>	-1263	<i>estimated equal as N<sub>2</sub>O<sub>5</sub></i>	
	12	12	HNO <sub>2</sub>	49	-4880	<b>Schwartz and White, 1983</b>	
	13	13	HNO <sub>4</sub>	1.0 · 10 <sup>5</sup>		Schwartz and White, 1982	
	14	14	SO <sub>2</sub>	1.24	-3247	Park and Lee, 1988	
	15	15	HCHO	3 · 10 <sup>5</sup>	-7216	mean value from Möller and Mauersberger, 1992; Amels, 1996; Jacob <i>et al.</i> , 1989 and Reginbal and Mozurkewich, 1997	$K_H(HNO_4) = K_H(H_2O_2)$ several measurements available
	16	16	CH <sub>3</sub> OOH	2.5 6	-5607	Beilke and Gravenhorst, 1978	physical solubility, not effective Henry's Law Constant
	17	17	CH <sub>3</sub> C(O)OOH	310	-5890	<b>Betterton and Hoffmann, 1988a</b>	measurement, not estimate
*	18	18	CH <sub>3</sub> OH	220	-5390	<i>Jacob, 1986</i>	
	19	19	C <sub>2</sub> H <sub>5</sub> OH	190	-6290	<b>Lind and Kok, 1994</b>	
						Lind and Kok, 1994	
						Betterton, 1992	
						Betterton, 1992	

Table 3a cont.

red.	No. 2,4	No. 2,3	Species	$K_{H298}$ , M atm <sup>-1</sup>	$\Delta H/R$ , K	References	reason
	20	20	CH <sub>3</sub> CHO	11.4 4.8	-6254	Betterton and Hoffmann, 1988a	physical solubility, not effective Henry's Law Constant
	21	21	HCOOH	5530	-5630	Khan and Brimblecombe, 1992	
	22	22	CH <sub>3</sub> COOH	5500	-5890	Khan and Brimblecombe, 1992	
	23	23	CH <sub>3</sub> O <sub>2</sub>	6	-5607	Jacob, 1986	
	24	24	ETHP	310 6	-87	$K_H(CH_3O_2) = K_H(CH_3OOH)$ $K_H(CH_3O_2) = K_H(ETHP)$ estimated equal as CH <sub>3</sub> CH <sub>2</sub> OOH Wilhelm <i>et al.</i> , 1977	better estimate O'Sullivan <i>et al.</i> , 1996
	25	25	Cl <sub>2</sub>	340 $9.15 \cdot 10^{-2}$	20.7	Loomis, 1928	
	26	26	Br <sub>2</sub>	0.758	31.6		
	27	27	H <sub>2</sub> SO <sub>4</sub>	$2.1 \cdot 10^5$ $8.7 \cdot 10^{11}$		$K_H(H_2SO_4) = K_H^{eff}(MSA)/K_A(MSA)$ Brimblecombe and Clegg, 1988 $K_H(H_2SO_4) = K_H(HNO_3)$ $K_H(ACO_2) = K_H(CH_3C(O)OOH)$	better estimate
	28	28	ACO <sub>3</sub>	669	1263 -5893		
	29	29	GLY	1.4	-1700	Betterton and Hoffmann, 1988a Loomis, 1928	
	30	30	O <sub>2</sub>	$1.3 \cdot 10^{-3}$			
	31	31	CINO <sub>2</sub>	0.024		Behnke <i>et al.</i> , 1997	
	32	32	BrNO <sub>2</sub>	0.3		Frenzel <i>et al.</i> , 1998	
	33	33	BrCl	0.94		Bartlett and Margerum, 1998	
	34	34	NO	$1.2 \cdot 10^{-2}$	-1263		
		29	CH <sub>4</sub>	$1.46 \cdot 10^{-3}$	-5893	Mackay and Shan, 1981	removed because no further processes in the aqueous phase
		30	C <sub>2</sub> H <sub>6</sub>	$1.95 \cdot 10^{-3}$		Mackay and Shan, 1981	"
		31	C <sub>3</sub> H <sub>8</sub>	$4.55 \cdot 10^{-3}$	-1700	Mackay and Shan, 1981	"
		32	PAN	5		Holdren <i>et al.</i> , 1984	"
		33	OP2	837		O'Sullivan <i>et al.</i> , 1996	"
		34	OL2P	6		$K_H(OL2P) = K_H(CH_3O_2)$	"

**Table 3b:** Mass accommodation coefficients and Gas Phase Diffusion Coefficients

red.	No 2.4	No 2.3	Species	$\alpha$	References	$\alpha$ (288 K) [ $10^3 \text{ m}^2 \text{ s}^{-1}$ ]	$D_g$ [ $10^5 \text{ m}^2 \text{ s}^{-1}$ ]	References	reason
	1	1	CO <sub>2</sub>	$2 \cdot 10^{-4}$	estimated	<b>1.5</b> $\cdot 10^{-4}$	1.55	McElroy, 1997	
	2	2	HCl	0.064	Davidovits <i>et al.</i> , 1995	<b>0.1158</b>	1.89	Marsh and McElroy, 1985	
	3	3	NH <sub>3</sub>	0.04	Bongartz, 1995	<b>0.091</b>	2.3	Ponche, 1993	
	4	4	O <sub>3</sub>	$5 \cdot 10^{-2}$	Mirabel, 1996	<b>0.1</b>	1.48	Schwartz, 1986	
	5	5	HO <sub>2</sub>	0.01	Hanson, 1992	<b>0.01</b>	1.04	Hanson, 1992	
	6	6	OH	0.05	estimated	<b>0.05</b>	1.53	Hanson, 1992	
	7	7	H <sub>2</sub> O <sub>2</sub>	0.11	Davidovits <i>et al.</i> , 1995	<b>0.1532</b>	1.46	McElroy, 1997	
	8	8	HNO <sub>3</sub>	0.054	Davidovits <i>et al.</i> , 1995	<b>0.0868</b>	1.32	Kirchner, 1990	
	9	9	NO <sub>3</sub>	$4 \cdot 10^{-3}$	Kirchner, 1990 Rudich, 1996	<b>4</b> $\cdot 10^{-3}$	1.00	Thomas, 1998	
	10	10	N <sub>2</sub> O <sub>5</sub>	$3.7 \cdot 10^{-3}$	George <i>et al.</i> , 1994	<b>0.018</b>	1.10	Kirchner, 1990	
	11	11	NO <sub>2</sub>	$1.5 \cdot 10^{-3}$	estimated	<b>0.0015</b>	1.92	Ponche, 1993	
	12	12	HNO <sub>2</sub>	0.5	Bongartz, 1995	<b>0.05</b>	1.30	Kirchner, 1990	
	13	13	HO <sub>2</sub> NO <sub>2</sub>	0.1	Jacob, 1986	<b>0.1</b>	1.30	Schweitzer, 1998	
	14	14	SO <sub>2</sub>	$3.5 \cdot 10^{-2}$	Tang and Lee, 1987 Gardner, 1987	<b>0.11</b>	1.28	McElroy, 1997	
	15	15	HCHO	0.02	estimated	<b>0.02</b>	1.64	Fuller, 1986 <sup>a)</sup>	
	16	16	CH <sub>3</sub> OOH	$3.8 \cdot 10^{-3}$	Davidovits <i>et al.</i> , 1995	<b>6.758</b> $\cdot 10^{-3}$	1.31	Fuller, 1986 <sup>b)</sup>	
	17	17	CH <sub>3</sub> C(O)OOH	0.019	$\alpha = \alpha_{\text{CH}_3\text{COOH}}$	<b>0.019</b>	1.02	Fuller, 1986 <sup>b)</sup>	
	18	18	CH <sub>3</sub> OH	$1.5 \cdot 10^{-2}$	Davidovits <i>et al.</i> , 1995	<b>0.0271</b>	1.16	Schwartz, 1986	
	19	19	C <sub>2</sub> H <sub>5</sub> OH	$8.2 \cdot 10^{-3}$	Davidovits <i>et al.</i> , 1995	<b>0.0176</b>	0.95	Schwartz, 1986	
	20	20	CH <sub>3</sub> CHO	0.03	estimated	<b>0.03</b>	1.22	Fuller, 1986 <sup>b)</sup>	
	21	21	HCOOH	0.012	Davidovits <i>et al.</i> , 1995	<b>0.0229</b>	1.53	Schwartz, 1986	
	22	22	CH <sub>3</sub> COOH	0.019	Davidovits <i>et al.</i> , 1995	<b>0.0322</b>	1.24	Schwartz, 1986	
	23	23	CH <sub>3</sub> O <sub>2</sub>	$3.8 \cdot 10^{-3}$	$\alpha = \alpha_{\text{CH}_3\text{OOH}}$	<b>6.7581</b> $\cdot 10^{-3}$	1.35	Fuller, 1986 <sup>b)</sup>	
	24	24	ETHP	$8.2 \cdot 10^{-3}$	estimated	<b>8.2</b> $\cdot 10^{-3}$	1.08	Fuller, 1986 <sup>b)</sup>	
	25	25	Cl <sub>2</sub>	0.03	estimated	<b>0.08</b>	1.28	Schwartz, 1986	
	26	26	Br <sub>2</sub>	0.03	estimated	<b>0.08</b>	1.00	Schwartz, 1986	
	27	27	H <sub>2</sub> SO <sub>4</sub>	0.07	Davidovits <i>et al.</i> , 1995	<b>0.12</b>	1.30	Schwartz, 1986	
	28	28	ACO <sub>3</sub>	0.019	$\alpha = \alpha_{\text{CH}_3\text{COOH}}$	<b>0.019</b>	1.0	Fuller, 1986 <sup>b)</sup>	
	29	29	<b>GLY</b>	<b>0.023</b>		<b>0.023</b>	<b>1.15</b>	<b>Fuller, 1986<sup>b)</sup></b>	also GLY-chem in aq. phase considered

Table 3b cont.

red.	No 2.4	No 2.3	Species	$\alpha$	References	$\alpha$ (288 K) [ $10^5 \text{ m}^2 \text{ s}^{-1}$ ]	$D_g$ [ $10^5 \text{ m}^2 \text{ s}^{-1}$ ]	References	reason
	30		$\text{O}_2$	0.1	estimated	0.01	1.12	Fuller, 1986 <sup>a)</sup>	no initial conc. For $\text{O}_2$ in the aq. phase formed in the aq. phase
	31		$\text{ClNO}_2$	0.01	Schweitzer, 1998	0.01	1.44	Fuller, 1986 <sup>a)</sup>	formed in the aq. phase
	32		$\text{BrNO}_2$	0.01	Schweitzer, 1998	0.01	1.44	Fuller, 1986 <sup>a)</sup>	formed in the aq. phase
	33		$\text{BrCl}$	0.33	Katrib <i>et al.</i> , 1999	0.33	1.19	Fuller, 1986 <sup>a)</sup>	formed in the aq. phase
	34		$\text{NO}$	0.001		0.001	2.24		formed in the aq. phase
		29	$\text{CH}_4$	$5 \cdot 10^{-5}$	estimated		1.41	Fuller, 1986 <sup>a)</sup>	removed because no further processes in the aqueous phase
		30	$\text{C}_2\text{H}_6$	$1 \cdot 10^{-4}$	estimated		0.95	Fuller, 1986 <sup>a)</sup>	"
		31	$\text{C}_2\text{H}_4$	$1 \cdot 10^{-4}$	estimated		1.01	Fuller, 1986 <sup>a)</sup>	"
		32	$\text{PAN}$	0.019	estimated		0.63	Fuller, 1986 <sup>a)</sup>	"
		33	$\text{OP2}$	0.01	estimated		0.76	Fuller, 1986 <sup>a)</sup>	"
		34	$\text{OL2P}$	$8.2 \cdot 10^{-3}$	estimated		0.82	Fuller, 1986 <sup>a)</sup>	"

a) These values are calculated after the method by Fuller, 1986

Table 4: HO<sub>x</sub>- and TMI-Chemistry

red	No. 2.4	No. 2.3	Reaction	k <sub>298</sub> , M <sup>n</sup> s <sup>-1</sup>	E <sub>a</sub> /R, K	Reference	reason
		1	$H_2O_2 + Fe^{3+} \rightarrow HO_2 + H^+ + Fe^{2+}$	$2 \cdot 10^3$		Walling and Goosen, 1973	no evidence that rxn. takes place
		2	$H_2O_2 + [Fe(OH)]^{2+} \rightarrow HO_2 + H^+ + Fe^{2+} + OH$	$2 \cdot 10^3$		$k_2 = k_1$	no evidence that rxn. takes place
		3	$H_2O_2 + [Fe(OH)]^{2+} \rightarrow HO_2 + H^+ + Fe^{2+} + 2 OH$	$2 \cdot 10^3$		$k_3 = k_1$	no evidence that rxn. takes place
	1	4	$H_2O_2 + Fe^{2+} \rightarrow OH + OH + Fe^{3+}$	76		Walling, 1975	
*	2		$Mn(OH)^{2+} + H_2O_2 \rightarrow MnO_2 + H^+ + H_2O$	$2.8 \cdot 10^3$		Barb et al., 1950	several studies confirm this value
*	3		$Mn^{4+} + H_2O_2 \rightarrow Mn^{2+} + 2 H^+ + O_2$	$1 \cdot 10^6$		Jacobsen et al., 1997	new data available (MnO <sub>2</sub> )
	4	5	$H_2O_2 + Cu^+ \rightarrow OH + OH + Cu^{2+}$	$7.0 \cdot 10^3$		Jacobsen et al., 1997	new data available
*	5	6	$H_2O_2 + Mn^{2+} \rightarrow HO_2 + H^+ + Mn^{2+}$	$7.3 \cdot 10^4$		Berdnikov, 1973	
	6	7	$O_2 + Fe^{3+} \rightarrow O_2 + Fe^{2+}$	$1.5 \cdot 10^8$		Davies et al., 1968	
	7	8	$HO_2 + [Fe(OH)]^{2+} \rightarrow Fe^{2+} + O_2 + H_2O$	$1.3 \cdot 10^5$		Rush and Bielski, 1985	
	8	9	$O_2 + [Fe(OH)]^{2+} \rightarrow O_2 + Fe^{2+} + OH$	$1.5 \cdot 10^8$		Ziajka et al., 1994	
*	9	10	$O_2 + [Fe(OH)_2]^+ \rightarrow O_2 + Fe^{2+} + 2 OH$	$1.5 \cdot 10^8$		Rush and Bielski, 1985	
	10	11	$O_2 + Fe^{2+} \xrightarrow{2H^+} H_2O_2 + Fe^{3+}$	$1.0 \cdot 10^7$		Rush and Bielski, 1985	
	11	12	$HO_2 + Fe^{2+} \xrightarrow{H^+} H_2O_2 + Fe^{3+}$	$1.2 \cdot 10^6$	5050	Jayson et al., 1973b	
	12	13	$OH + Fe^{2+} \rightarrow [Fe(OH)]^{2+}$	$4.3 \cdot 10^8$	1100	Christensen and Sehested, 1981	
*	13		$MnO_2 + HO_2 \xrightarrow{H^+} Mn^{2+} + H_2O_2 + O_2$	$1 \cdot 10^7$		Jacobsen et al., 1997	new data available (MnO <sub>2</sub> )
*	14		$OH + Mn^{2+} \rightarrow OH + Mn^{3+}$	$2.6 \cdot 10^7$		Baral et al., 1986	new data available; consistent to other (new) Mn reactions
	14	14	$O_2 + Mn^{2+} \xrightarrow{2H^+} H_2O_2 + Mn^{3+}$	$2 \cdot 10^7$		Jacobsen et al., 1997	back reaction included => E34
	15	15	$O_3 + Mn^{2+} \xrightarrow{H^+} H_2O_2 + Mn^{3+}$	$1.1 \cdot 10^8$		Pick-Kaplan and Rabani, 1975	back reaction included => E35
	15	16	$O_2 + Cu^+ \xrightarrow{2H^+} H_2O_2 + Cu^{2+}$	$2 \cdot 10^5$		Graedel et al., 1986	measurement instead of computer simulation
	16	17	$HO_2 + Cu^+ \xrightarrow{H^+} H_2O_2 + Cu^{2+}$	$9.4 \cdot 10^9$		von Piechowski et al., 1993	corrected value
*	17	18	$OH + Cu^+ \rightarrow OH + Cu^{2+}$	$1 \cdot 10^{10}$		Rabani et al., 1973	
	18	19	$HO_2 + Cu^{2+} \rightarrow O_2 + Cu^+ + H^+$	$2.2 \cdot 10^9$		Kozlov and Berdnikov, 1973	
	19	20	$O_2 + Cu^{2+} \rightarrow O_2 + Cu^+$	$3 \cdot 10^9$		Goldstein et al., 1992	
				$3 \cdot 10^9$		Cabelli et al., 1987	to be consistent to R19 (pH: 3-6.5; former value: pH = 4.5)
				$1.2 \cdot 10^8$		Rabani et al., 1973	"
				$1 \cdot 10^8$		Cabelli et al., 1987	"
				$8 \cdot 10^8$		Rabani et al., 1973	"

Table 4 cont.

red	No. 2.4	No. 2.3	Reaction	$k_{298}$ , $M^n s^{-1}$	$E_a/R$ , K	Reference	reason
	20	21	$Fe^{3+} + Cu^+ \rightarrow Fe^{2+} + Cu^{2+}$	$3 \cdot 10^7$		Seclak and Hoigné, 1993	measurement instead of estimate
	21	22	$[Fe(OH)]^{2+} + Cu^+ \rightarrow Fe^{2+} + Cu^{2+} + OH^-$	$1.3 \cdot 10^7$		Buxton et al., 1995	measurement instead of estimate
*	22	23	$[Fe(OH)_2]^+ + Cu^+ \rightarrow Fe^{2+} + Cu^{2+} + 2 OH^-$	$3 \cdot 10^7$		Seclak and Hoigné, 1993	measurement instead of estimate
	23	24	$Fe^{2+} + Mn^{3+} \rightarrow Fe^{3+} + Mn^{2+}$	$1.3 \cdot 10^7$		Buxton et al., 1995	
	24	25	$Fe^{2+} + Mn^{3+} \rightarrow Fe^{3+} + Mn^{2+}$	$1.5 \cdot 10^4$		Diebler and Sutin, 1964	
	24	25	$O_3 + O_2 \xrightarrow{H^+} 2 O_2 + OH \rightarrow O_3^- + O_2$	$1.5 \cdot 10^9$	2200	Sehested et al., 1983	split into elementary steps
	25	25	$HO_3 \rightarrow OH + O_2$	330	4500	this work	split into elementary steps
*	26	26	$HO_2 + HO_2 \rightarrow O_3 + H_2O_2$	$8.3 \cdot 10^5$	2720	Bielski et al., 1985	
*	27	27	$HO_2 + O_2 \xrightarrow{H^+} H_2O_2 + O_2$	$9.7 \cdot 10^7$	1060	Bielski et al., 1985	
*	28	28	$HO_2 + OH \rightarrow H_2O + O_2$	$1.0 \cdot 10^{10}$		Elliot and Buxton, 1992	
*	29	29	$O_2 + OH \rightarrow OH + O_2$	$1.1 \cdot 10^{10}$	2120	Christensen et al., 1989	
	30	30	$H_2O_2 + OH \rightarrow HO_2 + H_2O$	$3.0 \cdot 10^7$	1680	Christensen et al., 1982	
*	31	31	$CH_3OOH + OH \rightarrow CH_3O_2 + H_2O$	$3 \cdot 10^7$	1680	31/32: Sum is equal as before	consideration of another reaction pathway
*	32	32	$CH_3OOH + OH \rightarrow HO_2 + HCOOH$	$2.4 \cdot 10^7$	1680	branching ratio 0.8 : 0.2 (correlation for H abstractions)	
	33	32	$HSO_3^- + OH \rightarrow H_2O + SO_3^-$	$2.7 \cdot 10^9$		Buxton et al., 1996a	
*	34	33	$SO_3^{2-} + OH \rightarrow OH^- + SO_3^-$	$4.6 \cdot 10^9$		Buxton et al., 1996a	
*	35	35	$MnO_2^+ + MnO_2^+ \rightarrow 2 Mn^{2+} + H_2O_2$	$6 \cdot 10^6$		Jacobsen et al., 1997	new data available (MnO <sub>2</sub> <sup>+</sup> )
	36	36	$Cu^+ + O_2 \rightarrow Cu^{2+} + O_2^-$	$4.6 \cdot 10^5$		Bjergbakke et al., 1976	
	37	37	$Fe^{2+} + O_3 \rightarrow FeO^{2+} + O_2$	$8.2 \cdot 10^5$		Logager et al., 1992	new data available (FeO <sup>2+</sup> )
*	38	38	$FeO^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO_2 + OH^-$	$9.5 \cdot 10^3$	2766	Jacobsen et al., 1998a	"
*	39	39	$FeO^{2+} + H_2O \rightarrow Fe^{3+} + OH + OH^-$	$2.34 \cdot 10^4$	4089	Jacobsen et al., 1998a	"
*	40	40	$FeO^{2+} + HO_2 \rightarrow Fe^{3+} + O_2 + OH^-$	$2.0 \cdot 10^6$		Jacobsen et al., 1997a	"
*	41	41	$FeO^{2+} + OH \rightarrow Fe^{3+} + H_2O_2$	$1.0 \cdot 10^7$		Logager et al., 1992	"
*	42	42	$FeO^{2+} + HONO \rightarrow Fe^{3+} + NO_2 + OH^-$	$1.1 \cdot 10^4$	4150	Jacobsen et al., 1998b	"
*	43	43	$FeO^{2+} + HSO_3^- \rightarrow Fe^{3+} + SO_3^- + OH^-$	$2.5 \cdot 10^5$		Jacobsen et al., 1998b	"
	44	44	$FeO^{2+} + Cl^- \xrightarrow{H^+} Fe^{3+} + ClOH$	100		Jacobsen et al., 1998b	"

Table 4 cont.

red	No.	No.	Reaction	$k_{298}$ , $M^{-n} s^{-1}$	$E_a / R$ , K	Reference	reason
	2.4	2.3					
*	45		$FeO^{2+} + Mn^{2+} \xrightarrow{2H^+} Mn^{3+} + Fe^{3+} + H_2O$	$1.0 \cdot 10^4$	2562	Jacobsen <i>et al.</i> , 1998b)	"
*	46		$FeO^{2+} + HCOOH \xrightarrow{H^+} Fe^{3+} + COOH + H_2O$	160	2680	Jacobsen <i>et al.</i> , 1998b)	"
*	47		$FeO^{2+} + HCOO^- \rightarrow Fe^{3+} + COOH + OH^-$	$3 \cdot 10^5$		Jacobsen <i>et al.</i> , 1998b)	"
*	48		$FeO^{2+} + C_2H_5OH \rightarrow Fe^{3+} + CH_3CHOH + OH^-$	$2.5 \cdot 10^3$		Jacobsen <i>et al.</i> , 1998b)	"
*	49		$FeO^{2+} + CH_3(OH)_2 \rightarrow Fe^{3+} + OH^- + CH(OH)_2$	400	5352	Jacobsen <i>et al.</i> , 1998b)	"
*	50		$FeO^{2+} + NO_2^- \xrightarrow{H^+} Fe^{3+} + NO_2 + OH^-$	$1 \cdot 10^5$		Jacobsen <i>et al.</i> , 1998b)	"
*	51		$FeO^{2+} + Fe^{2+} \rightarrow 2 Fe^{3+} + 2 OH^-$	$7.2 \cdot 10^4$	842	Jacobsen <i>et al.</i> , 1997a)	"
*	52		$FeO^{2+} + Fe^{2+} \xrightarrow{2H_2O} FeOH_2Fe^{4+} + 2 OH^-$	$1.8 \cdot 10^4$	5052	Jacobsen <i>et al.</i> , 1997a)	"
*	53		$FeOH_2Fe^{4+} + H^+ \rightarrow 2 Fe^{3+} + H_2O$	1.95	5653	Jacobsen <i>et al.</i> , 1997a)	"
*	54		$FeOH_2Fe^{4+} \rightarrow 2 Fe^{3+} + 2 OH^-$	0.49	8780	Jacobsen <i>et al.</i> , 1997a)	"
*	55		$MnO^{2+} + Mn^{2+} \xrightarrow{2H^+} 2 Mn^{3+} + H_2O$	$1 \cdot 10^5$		Jacobsen <i>et al.</i> , 1998a)	new data available
*	56		$Mn^{2+} + O_3 \rightarrow MnO^{2+} + O_2$	$1.65 \cdot 10^3$		Jacobsen <i>et al.</i> , 1998a)	new data available
*	57		$Cu^+ + O_3 \xrightarrow{H^+} Cu^{2+} + OH + O_2$	$3 \cdot 10^7$		Hoigne and Buhler, 1996	new data available
*	58		$OH + O_3 \rightarrow O_2 + HO_2$	$1 \cdot 10^8$		Sehested <i>et al.</i> , 1984	additional sink for $OH/O_3$
*	59		$O^3P + O_2 \rightarrow O_3$	$4 \cdot 10^9$		Kläning <i>et al.</i> , 1984	sink for $O^3P$ ( $NO_3$ photolysis)

Table 5: N-Chemistry

red.	No. 2.4	No. 2.3	Reaction	$k_{298}$ , $M^{-n} s^{-1}$	$E_a / R$ , K	Reference	reason
	60		$N_2O_5 \rightarrow NO_2^+ + NO_3^-$	$1 \cdot 10^9$		<b>estimated</b>	correct formulation
	61		$NO_2^+ + H_2O \rightarrow NO_3^- + 2H^+$	$8.9 \cdot 10^7$		<b>Behnke et al., 1997</b>	correct formulation
*	62	34	$N_2O_5 + H_2O \rightarrow 2H^+ + 2NO_3^-$	$5 \cdot 10^9$		<i>estimated</i>	wrong formulation
*	63	35	$NO_3 + OH^- \rightarrow NO_3^- + OH$	$9.4 \cdot 10^7$	2700	Exner et al., 1992	
*	64	36	$NO_3 + Fe^{2+} \rightarrow NO_3^- + Fe^{3+}$	$8 \cdot 10^6$		Pikaev et al., 1974	
*	65	37	$NO_3 + Mn^{2+} \rightarrow NO_3^- + Mn^{3+}$	$1.1 \cdot 10^6$		Neta and Huie, 1986	
*	66	38	$NO_3 + H_2O_2 \rightarrow NO_3^- + H^+ + HO_2$	$4.9 \cdot 10^6$	2000	Herrmann et al., 1994	
		39	$NO_3 + CH_3OOH \rightarrow NO_3^- + H^+ + CH_3O_2$	$4.9 \cdot 10^6$	2000	$k = k_{H_2O_2}$	
*	67	40	$NO_3 + HO_2 \rightarrow NO_3^- + H^+ + O_2$	$3.0 \cdot 10^9$		Sehested et al., 1994	
*	68	41	$NO_3 + O_2^- \rightarrow NO_3^- + O_2$	$3.0 \cdot 10^9$		$k = k_{HO_2}$	
	69	42	$NO_3 + HSO_3^- \rightarrow NO_3^- + H^+ + SO_3$	$1.3 \cdot 10^9$	2000	Exner et al., 1992	
*	70	43	$NO_3 + SO_3^{2-} \rightarrow NO_3^- + SO_3$	$3.0 \cdot 10^8$		Exner et al., 1992	
*	71	44	$NO_3 + HSO_4^- \rightarrow NO_3^- + H^+ + SO_4$	$2.6 \cdot 10^5$		Raabe, 1996	
		45	$NO_3 + SO_4^{2-} \rightarrow NO_3^- + SO_4$	$5.6 \cdot 10^3$		Logager et al., 1993	corrected value
*	73	46	$NO_2 + OH \rightarrow NO_3^- + H^+$	$1 \cdot 10^5$		Wagner et al., 1980	correct product; in 2.3 for simplification lumped to HNO <sub>3</sub>
			$NO_2 + OH \rightarrow HOONO$				
*	74	47	$NO_2 + O_2^- \rightarrow NO_2^- + O_2$	$1 \cdot 10^8$		Warneck and Wurzinger, 1988	
*	75	48	$NO_2 + NO_2 \xrightarrow{H_2O} HNO_2 + NO_3^- - H^+$	$8.4 \cdot 10^7$	-2900	Park and Lee, 1988	
			$O_2NO_2 \rightarrow NO_2 + O_2$				
*	76	49	$O_2NO_2 \rightarrow NO_2 + OH$	$4.5 \cdot 10^{-2}$		Lammel et al., 1990	measurement in more alkaline solution
		50	$NO_2^- + OH \rightarrow NO_2 + OH$	$1.1 \cdot 10^{10}$		Barker et al., 1970	
*	78	51	$NO_2^- + SO_4^- \rightarrow SO_4^{2-} + NO_2$	$9.1 \cdot 10^9$		Reese, 1997	
*	79	52	$NO_2^- + NO_3 \rightarrow NO_3^- + NO_2$	$7.2 \cdot 10^8$	0	Herrmann and Zellner, 1998	
*	80	53	$NO_2^- + Cl_2^- \rightarrow 2Cl^- + NO_2$	$1.4 \cdot 10^9$		Jacobi, 1996	
*	81	54	$NO_2^- + Br_3^- \rightarrow 2Br^- + NO_2$	$6 \cdot 10^7$	1720	Shoute et al., 1991	
				$1.2 \cdot 10^7$		<b>Jacobi, 1996</b>	

Table 5 cont.

red.	No.	No.	Reaction	$k_{298}$ , $M^n s^{-1}$	$E_a/R$ , K	Reference	reason
	2.4	2.3					
*	82	55	$NO_2^- + CO_3^{2-} \rightarrow CO_3^{2-} + NO_2$	$6.6 \cdot 10^5$	850	Huie <i>et al.</i> , 1991a)	
*	83	56	$NO_2^- + O_3 \rightarrow NO_3^- + O_2$	$5 \cdot 10^5$	7000	Damschen and Martin, 1983	corrected value
	84	57	$HNO_2 + OH \rightarrow NO_2 + H_2O$	$1 \cdot 10^9$	6900	Rettich, 1978	measurement in more alkaline solution
	85		$NO_2^+ + Cl^- \rightarrow ClNO_2$	$1.1 \cdot 10^{10}$		Barker <i>et al.</i> , 1970	
	86		$NO_2^+ + Br^- \rightarrow BrNO_2$	$1 \cdot 10^{10}$		Chr. George, pers. comm., 1999	considering XNO <sub>2</sub> chemistry
	87		$ClNO_2 + Br^- \rightarrow NO_2^- + BrCl$	$5 \cdot 10^6$		Chr. George, pers. comm., 1999	"
	88		$BrNO_2 + Br^- \rightarrow NO_2^- + Br_2$	$2.55 \cdot 10^4$		Chr. George, pers. comm., 1999	"
	89		$BrNO_2 + Cl^- \rightarrow NO_2^- + BrCl$	10		Chr. George, pers. comm., 1999	"

Table 6: S-Chemistry

red	No.	No.	Reaction	$k_{298}$ , $M^{-n} s^{-1}$	$E_a / R$ , K	Reference	reason
	2.4	2.3					
	90	58	$HMS^{\cdot} + OH \rightarrow H_2O + HO_2 + HCOOH + HSO_3^{\cdot}$	$3 \cdot 10^8$		Barlow et al., 1997b)	correct products; split into elementary steps
*	91	59	$H_2O + CHOHSO_3^{\cdot}$ $HMS^{\cdot} + SO_4^{2-} \rightarrow SO_4^{\cdot-} + H^{\cdot} + HCHO + SO_3^{\cdot-}$	$2.8 \cdot 10^6$		Barlow et al., 1997b)	"
*	92	60	$SO_4^{\cdot-} + OHCH_2SO_3$ $HMS^{\cdot} + NO_3 \rightarrow NO_2^{\cdot} + H^{\cdot} + HCHO + SO_3^{\cdot-}$	$1.3 \cdot 10^6$ $4.2 \cdot 10^6$		Herrmann et al., 1996a) Barlow et al., 1997b)	"
*	93	61	$NO_3^{\cdot} + OHCH_2SO_3$ $HMS^{\cdot} + Cl_2^{\cdot-} \rightarrow 2 Cl^{\cdot} + H^{\cdot} + HCHO + SO_3^{\cdot-}$	$5.0 \cdot 10^5$		Jacobi, 1996	"
*	94	62	$2 Cl^{\cdot} + OHCH_2SO_3$ $HMS^{\cdot} + Br_2^{\cdot-} \rightarrow 2 Br^{\cdot} + H^{\cdot} + HCHO + SO_3^{\cdot-}$	$5.0 \cdot 10^4$		Barlow et al., 1997b) estimated as $k = 0.1k(Cl_2^{\cdot-})$	"
*	95	95	$2 Br^{\cdot} + OHCH_2SO_3$ $OHCH_2SO_3 \rightarrow SO_3 + CH_2OH$	$1 \cdot 10^5$		estimated	sink for $OHCH_2SO_3$
*	96	96	$SO_3 + H_2O \rightarrow SO_4^{2-} + 2 H^{\cdot}$	$1 \cdot 10^{10}$		estimated as diffusion controlled	sink for $SO_3$
	97	97	$CHOSOH_3^{\cdot} + O_2 \rightarrow O_2CHOHSO_3^{\cdot}$	$2.6 \cdot 10^9$		Barlow et al., 1997b)	split into elementary steps; consideration of side reactions
	98	98	$O_2CHOHSO_3^{\cdot} \rightarrow HO_2 + CHOSO_3^{\cdot}$	$1.7 \cdot 10^4$		Barlow et al., 1997b)	"
	99	99	$O_2CHOHSO_3^{\cdot} \rightarrow O_2CHO + HSO_3^{\cdot}$	$7.0 \cdot 10^3$		Barlow et al., 1997b)	"
	100	100	$CHOSO_3^{\cdot} + H_2O \rightarrow HSO_3^{\cdot} + HCOOH$	$1.26 \cdot 10^{12}$		Buxton et al., 1997	"
	101	101	$O_2CHO + H_2O \rightarrow HCOOH + HO_2$	44.32		Barlow et al., 1997b)	"
*	102	102	$CHOHSO_3^{2-} + O_2 \rightarrow CHOHSO_3^{\cdot} + O_2^{\cdot-}$	$1.6 \cdot 10^8$		Barlow et al., 1997b)	"
	103	63	$HSO_3^{\cdot} + H_2O_2 + H^{\cdot} \rightarrow SO_4^{2-} + H_2O + 2 H^{\cdot}$	$6.9 \cdot 10^7$	4000	Zellner et al., 1994	to be consistent to R104/105
	104	64	$HSO_3^{\cdot} + CH_3OOH + H^{\cdot} \rightarrow SO_4^{2-} + 2 H^{\cdot} + CH_3OH$	$7.2 \cdot 10^7$	3800	Lind et al., 1987	corrected value
*	105	65	$HSO_3^{\cdot} + CH_3C(O)OOH + H^{\cdot} \rightarrow SO_4^{2-} + 2 H^{\cdot}$ <i>+prod.</i> $+ CH_3COOH$	$4.8 \cdot 10^7$ $5.6 \cdot 10^7$	3990	Lind et al., 1987	correct product; analogous to other $HSO_3^{\cdot}$ + ROOH
*	106	66	$SO_2 + O_3 \xrightarrow{H_2O} HSO_4^{\cdot} + O_2 + H^{\cdot}$	$2.4 \cdot 10^4$		Hoffmann, 1986	
	107	67	$HSO_3^{\cdot} + O_3 \rightarrow HSO_4^{\cdot} + O_2$	$3.7 \cdot 10^5$	5530	Hoffmann, 1986	
	108	68	$SO_3^{2-} + O_3 \rightarrow SO_3^{\cdot-} + O_2$	$1.5 \cdot 10^8$	5280	Hoffmann, 1986	

Table 6 cont.

red.	No. 2.4	No. 2.3	Reaction	$k_{298}$ $M^{-n} s^{-1}$	$E_a / R$ , K	Reference	reason
*	109	69	$[Fe(OH)]^{2+} + HSO_3^- \xrightarrow{H_2O} Fe^{2+} + SO_3^- + H_2O$	39		Ziajka et al., 1994	
	110	70	$Fe^{2+} + SO_5^- \xrightarrow{H_2O} [Fe(OH)]^{2+} + HSO_5^-$	30	5809	Herrmann et al., 1996a	T dependent value
	111	71	$Fe^{2+} + HSO_5^- \rightarrow [Fe(OH)]^{2+} + SO_4^-$	$4.3 \cdot 10^7$		Williams, 1996	
*	112		$Mn^{2+} + HSO_5^- \rightarrow SO_4^- + Mn^{3+} + OH^-$	$3 \cdot 10^4$		Ziajka et al., 1994	
	113	72	$Mn^{2+} + SO_5^- \xrightarrow{H_2O} Mn^{3+} + HSO_5^- + OH^-$	$3 \cdot 10^4$		estimated equal as $k_{(Fe^{2+} + HSO_5^-)}$	completion of Mn chemistry to be consistent to E38
	114	73	$Fe^{2+} + SO_4^- \xrightarrow{H_2O} [Fe(OH)]^{2+} + SO_4^{2-} + H^+$	$4.6 \cdot 10^6$		Herrmann et al., 1996a	
	115	74	$Fe^{2+} + S_2O_8^{2-} \xrightarrow{H_2O} [Fe(OH)]^{2+} + SO_4^{2-} + SO_4^- + H^+$	$1 \cdot 10^{10}$		Berglund et al., 1994	T dependent value
*	116	75	$SO_5^- + SO_5^- \rightarrow S_2O_8^{2-} + O_2$	$3.5 \cdot 10^7$	-2165	Ziajka et al., 1994	measurement instead of estimate
	117	76	$SO_5^- + SO_5^- \rightarrow 2 SO_4^- + O_2$	$4.6 \cdot 10^9$		Buxton et al., 1997	
	118	77	$SO_5^- + HO_2 \rightarrow HSO_5^- + O_2$	17		Herrmann et al., 1995	new evidences about product ratio
*	119		$SO_5^- + O_2 \xrightarrow{H^+} HSO_5^- + OH^- + O_2$	$1.8 \cdot 10^8$	2600	Buxton et al., 1997	"
*	120		$SO_5O_2H^- + HSO_3^- \rightarrow 2 SO_4^{2-} + 2 H^+$	$4.8 \cdot 10^7$	2600	Herrmann et al., 1995	correct product; split into elementary steps
	121		$SO_5O_2^- + HSO_3^- \rightarrow 2 SO_4^{2-} + H^+$	$7.2 \cdot 10^6$		Buxton et al., 1996a	
	122		$SO_5O_2^- \rightarrow SO_5^- + O_2$	$2.2 \cdot 10^8$		Buxton et al., 1997	
	123	76	$SO_5^- + O_2 \rightarrow SO_5^-$	$1.7 \cdot 10^9$		Buxton et al., 1996a	
*	124	77	$SO_5^- + HSO_3^- \rightarrow HSO_5^- + SO_5^-$	$2.34 \cdot 10^8$		Buxton et al., 1997	split into elementary steps; sink reaction
*	125	78	$SO_5^- + HSO_3^- \rightarrow SO_4^{2-} + SO_4^- + H^+$	$3.0 \cdot 10^5$		Buxton et al., 1997	"
*	126	79	$SO_5^- + SO_3^{2-} \xrightarrow{H^+} HSO_5^- + SO_3^-$	$5.2 \cdot 10^6$		Buxton et al., 1997	"
	127	80	$SO_5^- + SO_3^{2-} \rightarrow SO_4^- + SO_4^{2-}$	1200		Buxton et al., 1997	"
*	128	81	$OH^- + HSO_4^- \rightarrow H_2O + SO_4^-$	$2.5 \cdot 10^9$		Buxton et al., 1996a	
				$8.6 \cdot 10^3$		Buxton et al., 1996a	
				$3.6 \cdot 10^2$		Buxton et al., 1996a	
				$2.13 \cdot 10^5$		Buxton et al., 1996a	
				$5.5 \cdot 10^5$		Buxton et al., 1996a	
				$3.5 \cdot 10^5$		Tang et al., 1988	

Table 6 cont.

red.	No. 2.4	No. 2.3	Reaction	$k_{298}$ , $M^{-n} s^{-1}$	$E_a / R$ , K	Reference	reason
*	129		$SO_4^- + SO_4^- \rightarrow S_2O_8^{2-}$	$1.6 \cdot 10^8$	840	<i>Herrmann et al., 1995a)</i> <i>Ervens, 1997</i> <i>Reese, 1997</i>	T dependent value
*	130		$SO_4^- + HSO_3^- \rightarrow SO_4^{2-} + SO_3^- + H^+$	$6.1 \cdot 10^8$ $3.2 \cdot 10^8$ $5.8 \cdot 10^8$		mean value of Reese, 1997; Wine <i>et al., 1989; Buxton et al., 1996a</i> <i>Reese, 1997</i>	mean value of all available data
*	131		$SO_4^- + SO_3^{2-} \rightarrow SO_4^{2-} + SO_3^-$	$3.2 \cdot 10^8$ $3.4 \cdot 10^8$	1200	mean value of Reese, 1997; Wine <i>et al., 1989; Buxton et al., 1996a</i> <i>McElroy and Waygood, 1990</i>	mean value of all available data no evidence that rxn. takes place
*	82		$SO_4^- + Fe^{2+} \rightarrow [Fe(SO_4)]^+$	$3 \cdot 10^8$		<i>Neta and Hite, 1987</i>	T dependent value
*	132		$SO_4^- + Mn^{2+} \rightarrow SO_4^{2-} + Mn^{3+}$	$2 \cdot 10^7$ $1.4 \cdot 10^7$	4089	<i>Buxton et al., 1996b</i>	T dependent value
*	133		$SO_4^- + Cu^+ \rightarrow SO_4^{2-} + Cu^{2+}$	$3 \cdot 10^8$		estimated equal as $k_{(Fe^{2+} + SO_4^- \rightarrow$ $FeSO_4^+)$ ; <i>McElroy and Waygood,</i> <i>1990)</i> <i>Reese, 1997</i>	expresse 1 similarto Fe/ Mn chemistry
*	134		$SO_4^- - H_2O_2 \rightarrow SO_4^{2-} + H^+ + HO_2$	$2.8 \cdot 10^7$ $1.7 \cdot 10^7$		mean value of Reese, 1997; Wine <i>et al., 1989; Maruthamutu and</i> <i>Neta, 1978</i> $k = k_{H_2O_2}$	mean value of all available data
*	135		$SO_4^- + CH_3OOH \rightarrow SO_4^{2-} + H^+ + CH_3O_2$	$2.8 \cdot 10^7$ $1.7 \cdot 10^7$		<i>Jiang et al., 1992</i> $k_{H_2O_2} = k_{O_2}$	equal to $k_{H_2O_2}$
*	136		$SO_4^- + HO_2 \rightarrow SO_4^{2-} + H^+ + O_2$	$3.5 \cdot 10^9$			
*	137		$SO_4^- + O_2^- \rightarrow SO_4^{2-} + O_2$	$3.5 \cdot 10^9$			
*	138		$SO_4^- + NO_3^- \rightarrow SO_4^{2-} + NO_3$	$5.0 \cdot 10^4$		<i>Exner et al., 1992</i>	
*	139		$SO_4^- + OH^- \rightarrow SO_4^{2-} + OH$	$1.4 \cdot 10^7$		<i>Herrmann et al., 1995b</i>	
	140		$SO_4^- + H_2O \rightarrow SO_4^{2-} + H^+ + OH$	11	1110	<i>Herrmann et al., 1995b</i>	
	141		$HSO_3^- + HSO_3^- + H^+ \rightarrow 2 SO_4^{2-} + 3 H^+$	$7.14 \cdot 10^6$		<i>Betterton and Hoffmann, 1988b</i>	
*	142		$HSO_3^- + SO_3^{2-} + H^+ \rightarrow 2 SO_4^{2-} + 2 H^+$	$7.14 \cdot 10^6$		<i>Betterton and Hoffmann, 1988b</i>	
*	143		$HSO_3^- + OH^- \rightarrow SO_3^{2-} + H_2O$	$1.7 \cdot 10^7$		<i>Maruthamutu and Neta, 1977</i>	
*	144		$HNO_4 + HSO_3^- \rightarrow HSO_4^- + NO_3^- + H^+$				
*	145		$OH^- + SO_4^- \rightarrow HSO_5^-$	$1.0 \cdot 10^{10}$		<i>Wilhelm et al., 1977</i>	new sink for $SO_4^-$ /source $HSO_5^-$

Table 6 cont.

red.	No. 2.4	No. 2.3	Reaction	$k_{298}$ , $M^{-n} s^{-1}$	$E_a/R$ , K	Reference	reason
*	146		$MnHSO_3^+ + Mn^{3+} \rightarrow 2 Mn^{2+} + SO_3^- + H^+$	$1.3 \cdot 10^6$		Berglund <i>et al.</i> , 1994	consideration of C <sub>2</sub> - difunctional compounds
*	147		$SO_5^- + HC_2O_4^- \rightarrow HSO_5^- + C_2O_4^-$	$5 \cdot 10^3$		this work	"
*	148		$SO_5^- + C_2O_4^{2-} \rightarrow HSO_5^- + C_2O_4^-$	$1 \cdot 10^4$		this work	"
*	149		$SO_5^- + CH(OH)_2CH(OH)_2 \rightarrow HSO_5^- + C(OH)_2CH(OH)_2$	$5 \cdot 10^5$		this work	"

Table 7: Organic Chemistry

red.	No. 2.4	No. 2.3	Reaction	$k_{255}$ , $M^{-1} s^{-1}$	$E_a / R$ , K	Reference	reason
	150	94	$CH_3OH + OH \xrightarrow{O_2} H_2O + HO_2 + HCHO$ $\rightarrow H_2O + CH_2OH$	$1.0 \cdot 10^9$	580	Elliot and McCracken, 1989	split into elementary steps
*	151	95	$CH_3OH + SO_4^{\cdot-} \xrightarrow{O_2} SO_4^{2-} + H^{\cdot} + HO_2 + HCHO$ $\rightarrow SO_4^{2-} + H^{\cdot} + CH_2OH$	$9.0 \cdot 10^6$	2190	Clifton and Huie, 1989	"
*	152	96	$CH_3OH + NO_3 \xrightarrow{O_2} NO_3^{2-} + HO_2 + HCHO$ $\rightarrow NO_3^{\cdot} + H^{\cdot} + CH_2OH$	$5.4 \cdot 10^5$	4300	Herrmann and Zellner, 1998 <i>Exner et al., 1993</i>	"
*	153	97	$CH_3OH + Cl_2 \xrightarrow{O_2} 2 Cl^{\cdot} + HO_2 + HCHO$ $\rightarrow 2 Cl^{\cdot} + H^{\cdot} + CH_2OH$	1000 $5.1 \cdot 10^4$	5500	Zellner <i>et al.</i> , 1996	"
*	154	98	$CH_3OH + Br_2 \xrightarrow{O_2} 2 Br^{\cdot} + HO_2 + HCHO$ $\rightarrow 2 Br^{\cdot} + H^{\cdot} + CH_2OH$	$5.4 \cdot 10^5$ 1000		<i>Wicktor, 1997</i> Reese, 1997	"
*	155	99	$CH_3OH + CO_3^{\cdot-} \xrightarrow{O_2} CO_3^{2-} + HO_2 + HCHO$ $\rightarrow CO_3^{2-} + H^{\cdot} + CH_2OH$	$2.6 \cdot 10^3$		Zellner <i>et al.</i> , 1996	"
	156	100	$CH_3OH + O_2 \rightarrow O_2CH_2OH$	$2 \cdot 10^9$		von Sonntag, 1987	explicit consideration of alkyl /peroxy radicals
*	157	101	$O_2CH_2OH + OH \rightarrow HCHO + H_2O + O_2^{\cdot-}$	$1.65 \cdot 10^{10}$		von Sonntag, 1987	"
	158	102	$O_2CH_2OH + O_2CH_2OH \rightarrow CH_3OH + O_2 + HCHO$	$1.05 \cdot 10^9$		von Sonntag, 1987	"
	159	100	$EtOH + OH \xrightarrow{O_2} H_2O + HO_2 + CH_3CHO$ $\rightarrow H_2O + CH_3CHOH$	$1.9 \cdot 10^9$		Buxton <i>et al.</i> , 1988a	split into elementary steps
*	160	101	$EtOH + SO_4^{\cdot-} \xrightarrow{O_2} SO_4^{2-} + H^{\cdot} + HO_2 + CH_3CHO$ $\rightarrow SO_4^{2-} + H^{\cdot} + CH_3CHOH$	$4.1 \cdot 10^7$	1760	Clifton and Huie, 1989	"
*	161	102	$EtOH + NO_3 \xrightarrow{O_2} NO_3^{2-} + HO_2 + CH_3CHO$ $\rightarrow NO_3^{\cdot} + H^{\cdot} + CH_3CHOH$	$2.2 \cdot 10^6$	3300	Herrmann and Zellner, 1998	"
*	162	103	$EtOH + Cl_2 \xrightarrow{O_2} 2 Cl^{\cdot} + HO_2 + CH_3CHO$ $\rightarrow 2 Cl^{\cdot} + H^{\cdot} + CH_3CHOH$	$1.2 \cdot 10^5$		Zellner <i>et al.</i> , 1996	"
*	163	104	$EtOH + Br_2 \xrightarrow{O_2} 2 Br^{\cdot} + HO_2 + CH_3CHO$ $\rightarrow 2 Br^{\cdot} + H^{\cdot} + CH_3CHOH$	$3.8 \cdot 10^3$		Reese <i>et al.</i> , 1999	"
*	164	105	$EtOH + CO_3^{\cdot-} \xrightarrow{O_2} CO_3^{2-} + HO_2 + CH_3CHO$ $\rightarrow CO_3^{2-} + H^{\cdot} + CH_3CHOH$	$1.5 \cdot 10^9$		Khuz'min, 1972	"
	165		$CH_3CHOH + O_2 \rightarrow O_2CH_2CHOH$	$2 \cdot 10^9$		estimated	explicit consideration of alkyl /peroxy radicals

Table 7 cont.

red.	No. 2.4	No. 2.3	Reaction	$k_{298}$ , $M^{-1} s^{-1}$	$E_a / R$ , K	Reference	reason
*	166		$O_2CH_3CHOH \rightarrow CH_3CHO + HO_2$	52	7217	von Sonntag, 1987	"
*	167		$O_2CH_3CHOH + OH \rightarrow CH_3CHO + H_2O + O_2$	$8 \cdot 10^9$		von Sonntag, 1987	"
	168	106	$CH_2(OH)_2 + OH \xrightarrow{O_2} H_2O + HO_2 + HCOOH$ $\rightarrow H_2O + CH(OH)_2$	$1.0 \cdot 10^9$	1020	Hart <i>et al.</i> , 1964; Chin and Wine, 1994	split into elementary steps
*	169	107	$CH_2(OH)_2 + SO_4^- \xrightarrow{O_2} SO_4^{2-} + H^+ + HO_2 + HCOOH$ $\rightarrow SO_4^{2-} + H^+ + CH(OH)_2$	$1.4 \cdot 10^7$	1300	Buxton <i>et al.</i> , 1990	"
*	170	108	$CH_2(OH)_2 + NO_3 \xrightarrow{O_2} NO_2 + HO_2 + HCOOH$ $\rightarrow NO_3^- + H^+ + CH(OH)_2$	$1.0 \cdot 10^6$	4500	Exner <i>et al.</i> , 1993	"
*	171	109	$CH_2(OH)_2 + Cl_2 \xrightarrow{O_2} 2 Cl^- + HO_2 + HCOOH$ $\rightarrow 2 Cl^- + H^+ + CH(OH)_2$	$3.1 \cdot 10^4$	4400	Zellner <i>et al.</i> , 1996	"
*	172	110	$CH_2(OH)_2 + Br_2 \xrightarrow{O_2} 2 Br^- + HO_2 + HCOOH$ $\rightarrow 2 Br^- + H^+ + CH(OH)_2$	$3.6 \cdot 10^4$	4330	Jacobi <i>et al.</i> , 1999	more actual data
*	173	111	$CH_2(OH)_2 + CO_3^- \xrightarrow{O_2} CO_3^{2-} + HO_2 + HCOOH$ $\rightarrow CO_3^{2-} + H^+ + CH(OH)_2$	$3 \cdot 10^3$		estimated	split into elementary steps
*	174	114	$CH(OH)_2 + O_2 \rightarrow HO_2 + HCOOH$	$1.3 \cdot 10^4$		Zellner <i>et al.</i> , 1996	"
	175	112	$CH_3CH(OH)_2 + OH \xrightarrow{O_2} H_2O + HO_2 + HAc$ $\rightarrow H_2O + CH_3C(OH)_2$	$2 \cdot 10^9$		estimated	explicit consideration of alkyl /peroxyl radicals
	176	113	$CH_3CHO + OH \xrightarrow{H_2O/O_2} H_2O + HO_2 + HAc$ $\rightarrow H_2O + CH_3C(OH)_2$	$1.2 \cdot 10^9$		Schuchmann and von Sonntag, 1988	split into elementary steps
*	177	114	$CH_3CHO + SO_4^- \xrightarrow{H_2O/O_2} SO_4^{2-} + H^+ + HO_2 + HAc$ $\rightarrow SO_4^{2-} + H^+ + CH_3CO$	$2 \cdot 10^7$		estimated	"
*	178	115	$CH_3CH(OH)_2 + SO_4^- \xrightarrow{O_2} SO_4^{2-} + H^+ + HO_2 + HAc$ $\rightarrow SO_4^{2-} + H^+ + CH_3C(OH)_2$	$2 \cdot 10^7$		estimated	"
*	179	116	$CH_3CH(OH)_2 + NO_3 \xrightarrow{O_2} NO_2 + H^+ + HO_2 + HAc$ $\rightarrow NO_3^- + H^+ + CH_3C(OH)_2$	$1.9 \cdot 10^6$		Zellner <i>et al.</i> , 1996	"

Table 7 cont.

red.	No. 2.4	No. 2.3	Reaction	$k_{298}$ , $M^{-1} s^{-1}$	$E_a/R$ , K	Reference	reason
*	180	117	$CH_3CHO + Cl_2 \xrightarrow{O_2} 2 Cl + H + HO_2 + HAC$ $\rightarrow 2 Cl + H + CH_3CO$	$4 \cdot 10^4$		Jacobi, 1996	"
*	181	118	$CH_3CHO + Br_2 \xrightarrow{O_2} 2 Br + H + HO_2 + HAC$ $\rightarrow 2 Br + H + CH_3CO$	$4 \cdot 10^4$ $4 \cdot 10^3$		<i>estimated</i> <b>estimated: <math>k_{6,2} = 0.1 \cdot k_{Cl}</math></b> <i>estimated</i>	" better estimate split into elementary steps
*	182	119	$CH_3CHO + CO_2 \xrightarrow{O_2} CO_3 + H + HO_2 + HAC$ $\rightarrow CO_3 + H + CH_3CO$	$1 \cdot 10^4$			
	183	120	$HCOOH + OH \xrightarrow{O_2} H_2O + HO_2 + CO_2$ $\rightarrow H_2O + CO_2H$	$1.3 \cdot 10^8$	1000	Buxton <i>et al.</i> , 1988a; Chin and Wine, 1994	"
	184	121	$HCOO + OH \xrightarrow{O_2} OH + HO_2 + CO_2$ $\rightarrow OH + CO_2H$	$10^9$	1000	Buxton <i>et al.</i> , 1988a; Elliot and Simons, 1984 Reese, 1997	"
*	185	122	$HCOOH + SO_4 \xrightarrow{O_2} SO_4 + H + HO_2 + CO_2$ $\rightarrow SO_4 + H + CO_2H$	$3.2 \cdot 10^9$			
*	186	123	$HCOO + SO_4 \xrightarrow{O_2} SO_4 + HO_2 + CO_2$ $\rightarrow SO_4 + CO_2H$	$2.5 \cdot 10^6$			
*	187	124	$HCOOH + NO_3 \xrightarrow{O_2} NO_3 + H + HO_2 + CO_2$ $\rightarrow NO_3 + H + CO_2H$	$2.1 \cdot 10^7$		Reese, 1997	"
*	188	125	$HCOO + NO_3 \xrightarrow{O_2} NO_3 + HO_2 + CO_2$ $\rightarrow NO_3 + CO_2H$	$3.8 \cdot 10^5$	3400	Exner <i>et al.</i> , 1994	"
*	189	126	$HCOOH + Cl_2 \xrightarrow{O_2} 2 Cl + H + HO_2 + CO_2$ $\rightarrow 2 Cl + H + CO_2H$	$5.1 \cdot 10^7$	2200	Exner <i>et al.</i> , 1994	"
*	190	127	$HCOO + Cl_2 \xrightarrow{O_2} 2 Cl + HO_2 + CO_2$ $\rightarrow 2 Cl + CO_2H$	$5500$ $8 \cdot 10^4$	4500 4450	Jacobi <i>et al.</i> , 1999 Jacobi <i>et al.</i> , 1999	" more actual value
*	191	128	$HCOOH + Br_2 \xrightarrow{O_2} 2 Br + H + HO_2 + CO_2$ $\rightarrow 2 Br + H + CO_2H$	$1.3 \cdot 10^6$		Jacobi <i>et al.</i> , 1996 Jacobi <i>et al.</i> , 1999	split into elementary steps
*	192	129	$HCOO + Br_2 \xrightarrow{O_2} 2 Br + HO_2 + CO_2$ $\rightarrow 2 Br + CO_2H$	$4 \cdot 10^3$		Reese <i>et al.</i> , 1999	"
*	193	130	$HCOO + CO_3 \xrightarrow{O_2} CO_3 + H + HO_2 + CO_2$ $\rightarrow CO_3 + H + CO_2H$	$4.9 \cdot 10^3$	3300	Jacobi, 1996	"
	194	131	$CO_2H + O_2 \rightarrow CO_2 + HO_2$	$1.4 \cdot 10^5$		Zellner <i>et al.</i> , 1996	"
	195	132	$HAc + OH \xrightarrow{O_2} H_2O + HO_2 + ACO_3$ $\rightarrow H_2O + CH_3COOH$	$2 \cdot 10^9$		<b>estimated</b>	explicit consideration of alkyl /peroxy radicals split into elementary steps
				$1.5 \cdot 10^7$	1330	Thomas, 1965; Chin and Wine, 1994	

Table 7 cont.

red.	No. 2.4	No. 2.3	Reaction	$k_{298}$ , $M^{-1} s^{-1}$	$E_a / R$ , K	Reference	reason
	196	133	$Ac + OH \xrightarrow{O_2} OH + HO_2 + ACO_3$ $\rightarrow H_2O + CH_3COO^-$	$1 \cdot 10^8$	1800	Fisher and Hamill, 1973; Chin and Wine, 1994	"
*	197	134	$HAc + SO_4 \cdot \xrightarrow{O_2} SO_4^{2-} + H^+ + HO_2 + ACO_3$ $\rightarrow SO_4^{2-} + H^+ + CH_3COOH$	$2.0 \cdot 10^5$		Reese, 1997	"
*	198	135	$Ac + SO_4 \cdot \xrightarrow{O_2} SO_4^{2-} + CH_3O_2 + CO_2$ $\rightarrow SO_4^{2-} + CH_3 + CO_2$	$2.8 \cdot 10^7$	1210	Reese, 1997;	"
*	199	136	$HAc + NO_3 \cdot \xrightarrow{O_2} NO_3^- + H^+ + HO_2 + ACO_3$ $\rightarrow NO_3^- + H^+ + CH_3COOH$	$1.4 \cdot 10^4$	3800	Huie and Clifton, 1990 Exner <i>et al.</i> , 1994	"
*	200	137	$Ac + NO_3 \cdot \xrightarrow{O_2} NO_3^- + CH_3O_2 + CO_2$ $\rightarrow NO_3^- + CH_3 + CO_2$	$2.9 \cdot 10^6$	3800	Exner <i>et al.</i> , 1994	"
*	201	138	$HAc + Cl_2 \cdot \xrightarrow{O_2} 2 Cl + H^+ + HO_2 + ACO_3$ $\rightarrow 2 Cl + H^+ + CH_3COOH$	1950 1500	4800 4930	Jacobi <i>et al.</i> , 1998 Jacobi <i>et al.</i> , 1999	" more actual value
*	202	139	$Ac + Cl_2 \cdot \xrightarrow{O_2} 2 Cl + CH_3O_2 + CO_2$ $\rightarrow 2 Cl + CH_3 + CO_2$	$2.6 \cdot 10^5$	4800	Jacobi <i>et al.</i> , 1996	split into elementary steps
*	203	140	$HAc + Br_2 \cdot \xrightarrow{O_2} 2 Br + H^+ + HO_2 + ACO_3$ $\rightarrow 2 Br + H^+ + CH_3COOH$	10		Reese <i>et al.</i> , 1999	"
*	204	141	$Ac + Br_2 \cdot \xrightarrow{O_2} 2 Br + CH_3O_2 + CO_2$ $\rightarrow 2 Br + CH_3 + CO_2$	100		Jacobi, 1996	"
*	205	142	$Ac + CO_3 \cdot \xrightarrow{O_2} CO_3^{2-} + CH_3O_2 + CO_2$ $\rightarrow CO_3^{2-} + CH_3 + CO_2$	580		Zellner <i>et al.</i> , 1996	"
	206		$CH_3COOH + O_2 \rightarrow ACO_3$	$1.7 \cdot 10^9$		Schuchmann <i>et al.</i> , 1985	explicit consideration of alkyl /peroxyl radicals
	207		$CH_3 + O_2 \rightarrow CH_3O_2$	$4.1 \cdot 10^9$		Marchaj <i>et al.</i> , 1991	"
	208	143	$CH_3O_2 + CH_3O_2 \rightarrow HCHO + CH_3OH + O_2$	$1.7 \cdot 10^8$	2200	Herrmann <i>et al.</i> , 1999b)	consideration of additional reaction pathways (correlation)
	209		$CH_3O_2 + CH_3O_2 \rightarrow CH_3O + CH_3O + O_2$	$3.6 \cdot 10^7$	2200	Herrmann <i>et al.</i> , 1999b)	correct products;
	210		$ACO_3 + ACO_3 \rightarrow 2 CH_3O_2 + 2 CO_2 + O_2$	$1.5 \cdot 10^8$		estimated equal as $k_{AETMPX}$	
	211	144	$CH_3O_2 + HSO_3^- \rightarrow CH_3OOH + SO_3^-$	$5 \cdot 10^5$		Herrmann <i>et al.</i> , 1999b)	

Table 7 cont.

red.	No. 2.4	No. 2.3	Reaction	$k_{298}$ , M <sup>-1</sup> s <sup>-1</sup>	$E_a$ / R, K	Reference	reason
*	212	145	ETHP + ETHP → products → EtOH + CH <sub>3</sub> CHO + O <sub>2</sub>	1.6 · 10 <sup>8</sup> 6 · 10 <sup>7</sup>	-750	Herrmann <i>et al.</i> , 1999	correct products; consideration of different reaction pathways (correlation)
	213		ETHP + ETHP → CH <sub>3</sub> CH <sub>2</sub> O + CH <sub>3</sub> CH <sub>2</sub> O + O <sub>2</sub>	1 · 10 <sup>8</sup>	-750	Herrmann <i>et al.</i> , 1999	correct products; consideration of different reaction pathways (correlation)
*	214		CH <sub>3</sub> CH <sub>2</sub> O + O <sub>2</sub> → HO <sub>2</sub> + CH <sub>3</sub> CHO	6 · 10 <sup>6</sup>		estimated	sink reaction
	215		CH <sub>3</sub> CH <sub>2</sub> O → CH <sub>3</sub> CHOH	1 · 10 <sup>6</sup>		estimated	sink reaction
*	216		Fe <sup>2+</sup> + CH <sub>3</sub> O <sub>2</sub> → FeCH <sub>3</sub> O <sub>2</sub> <sup>2+</sup>	8.6 · 10 <sup>5</sup>		Khaikin <i>et al.</i> , 1996	FeCH <sub>3</sub> O <sub>2</sub> <sup>2+</sup> : new considered
*	217		FeCH <sub>3</sub> O <sub>2</sub> <sup>2+</sup> + H <sup>+</sup> → Fe <sup>3+</sup> + O <sub>2</sub>	3.0 · 10 <sup>4</sup>		Khaikin <i>et al.</i> , 1996	FeCH <sub>3</sub> O <sub>2</sub> <sup>2+</sup> : new considered
*	218		FeCH <sub>3</sub> O <sub>2</sub> <sup>2+</sup> → Fe <sup>3+</sup> + CH <sub>3</sub> OOH + OH <sup>-</sup>	100		Khaikin <i>et al.</i> , 1996	FeCH <sub>3</sub> O <sub>2</sub> <sup>2+</sup> : new considered
	219		OH + HC <sub>2</sub> O <sub>4</sub> <sup>-</sup> → H <sub>2</sub> O + C <sub>2</sub> O <sub>4</sub> <sup>-</sup>	3.2 · 10 <sup>7</sup>		Getoff <i>et al.</i> , 1971	consideration of C <sub>2</sub> -difunctional compounds
*	220		NO <sub>3</sub> + HC <sub>2</sub> O <sub>4</sub> <sup>-</sup> → NO <sub>2</sub> <sup>-</sup> + H <sup>+</sup> + C <sub>2</sub> O <sub>4</sub> <sup>-</sup>	6.8 · 10 <sup>7</sup>		Raabe, 1996	"
*	221		Cl <sub>2</sub> <sup>-</sup> + HC <sub>2</sub> O <sub>4</sub> <sup>-</sup> → 2 Cl <sup>-</sup> + H <sup>+</sup> + C <sub>2</sub> O <sub>4</sub> <sup>-</sup>	1.3 · 10 <sup>6</sup>		estimated (ETR)	"
*	222		Br <sub>2</sub> <sup>-</sup> + HC <sub>2</sub> O <sub>4</sub> <sup>-</sup> → 2 Br <sup>-</sup> + H <sup>+</sup> + C <sub>2</sub> O <sub>4</sub> <sup>-</sup>	3.7 · 10 <sup>3</sup>		estimated (ETR)	"
*	223		SO <sub>4</sub> <sup>-</sup> + HC <sub>2</sub> O <sub>4</sub> <sup>-</sup> → SO <sub>4</sub> <sup>2-</sup> + H <sup>+</sup> + C <sub>2</sub> O <sub>4</sub> <sup>-</sup>	3.35 · 10 <sup>5</sup>		Buxton <i>et al.</i> , 1999	"
	224		OH + C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> → OH <sup>-</sup> + C <sub>2</sub> O <sub>4</sub> <sup>-</sup>	5.3 · 10 <sup>6</sup>		Getoff <i>et al.</i> , 1971	"
*	225		NO <sub>3</sub> + C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> → NO <sub>2</sub> <sup>-</sup> + C <sub>2</sub> O <sub>4</sub> <sup>-</sup>	2.2 · 10 <sup>8</sup>		Raabe, 1996	"
*	226		Cl <sub>2</sub> <sup>-</sup> + C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> → 2 Cl <sup>-</sup> + H <sup>+</sup> + C <sub>2</sub> O <sub>4</sub> <sup>-</sup>	4.0 · 10 <sup>6</sup>		estimated (ETR)	"
*	227		Br <sub>2</sub> <sup>-</sup> + C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> → 2 Br <sup>-</sup> + C <sub>2</sub> O <sub>4</sub> <sup>-</sup>	1.1 · 10 <sup>4</sup>		estimated (ETR)	"
*	228		SO <sub>4</sub> <sup>-</sup> + C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> → SO <sub>4</sub> <sup>2-</sup> + C <sub>2</sub> O <sub>4</sub> <sup>-</sup>	1.05 · 10 <sup>6</sup>		Buxton <i>et al.</i> , 1999a	"
	229		C <sub>2</sub> O <sub>4</sub> <sup>-</sup> + O <sub>2</sub> → CO <sub>2</sub> + CO <sub>2</sub> + O <sub>2</sub> <sup>-</sup>	2.0 · 10 <sup>9</sup>		estimated	"
	230		OH + CH(OH) <sub>2</sub> CH(OH) <sub>2</sub> → H <sub>2</sub> O + C(OH) <sub>2</sub> CH(OH) <sub>2</sub>	1.1 · 10 <sup>9</sup>	1516	Buxton <i>et al.</i> , 1976	"
*	231		NO <sub>3</sub> + CH(OH) <sub>2</sub> CH(OH) <sub>2</sub> → H <sup>+</sup> + NO <sub>2</sub> <sup>-</sup> + C(OH) <sub>2</sub> CH(OH) <sub>2</sub>	1.1 · 10 <sup>6</sup>	3368	Herrmann <i>et al.</i> , 1995c	"
*	232		Cl <sub>2</sub> <sup>-</sup> + CH(OH) <sub>2</sub> CH(OH) <sub>2</sub> → H <sup>+</sup> + 2 Cl <sup>-</sup> + C(OH) <sub>2</sub> CH(OH) <sub>2</sub>	4.0 · 10 <sup>4</sup>		Herrmann <i>et al.</i> , 1995c	"
*	233		Br <sub>2</sub> <sup>-</sup> + CH(OH) <sub>2</sub> CH(OH) <sub>2</sub> → H <sup>+</sup> + 2 Br <sup>-</sup> + C(OH) <sub>2</sub> CH(OH) <sub>2</sub>	500		estimated (H abstr.)	"

Table 7 cont.

red.	No. 2.4	No. 2.3	Reaction	$k_{298}$ , $M^{-1} s^{-1}$	$E_a$ / R, K	Reference	reason
*	234		$SO_4^- + CH(OH)_2CH(OH)_2 \rightarrow H^+ + SO_4^{2-} + C(OH)_2CH(OH)_2$	$2.35 \cdot 10^7$	1395	Mirabel, 1996	"
	235		$C(OH)_2CH(OH)_2 + O_2 \rightarrow O_2C(OH)_2CH(OH)_2$	$1.38 \cdot 10^9$		Mirabel, 1996	"
	236		$O_2C(OH)_2CH(OH)_2 \rightarrow HO_2 + CH(OH)_2COOH$	$2 \cdot 10^9$		estimated	"
	237		$OH + CH(OH)_2COOH \rightarrow H_2O + C(OH)_2COOH$	$1.1 \cdot 10^9$	1516	estimated equal to $k((CH(OH)_2)$	"
*	238		$NO_3 + CH(OH)_2COOH \rightarrow H^+ + NO_3^- + C(OH)_2COOH$	$1.1 \cdot 10^6$	3368	estimated equal to $k((CH(OH)_2)$	"
*	239		$Cl_3^- + CH(OH)_2COOH \rightarrow H^+ + 2 Cl^- + C(OH)_2COOH$	$4.0 \cdot 10^4$		estimated equal to $k((CH(OH)_2)$	"
*	240		$Br_3^- + CH(OH)_2COOH \rightarrow H^+ + 2 Br^- + C(OH)_2COOH$	500		estimated equal to $k((CH(OH)_2)$	"
*	241		$SO_4^- + CH(OH)_2COOH \rightarrow H^+ + SO_4^{2-} + C(OH)_2COOH$	$2.35 \cdot 10^7$	1395	estimated equal to $k((CH(OH)_2)$	"
	242		$C(OH)_2COOH + O_2 \rightarrow O_2C(OH)_2COOH$	$2 \cdot 10^9$		estimated	additional reactions of peroxy radicals
	243		$O_2C(OH)_2COOH \rightarrow HO_2 + H_2C_2O_4$	$2 \cdot 10^9$		estimated	"
*	244		$CH_3CO + O_2 \rightarrow ACO_3$	$2 \cdot 10^9$		estimated	"
*	245		$ACO_3 + O_2^- \rightarrow CH_3C(O)OO^-$	$1 \cdot 10^9$		Schuchmann and v. Sonntag, 1988	"
	246		$CH_3C(OH)_2 + O_2 \rightarrow CH_3C(OH)_2O_2$	$2 \cdot 10^9$		estimated	"
	247		$CH_3C(OH)_2O_2 \rightarrow 2 H^+ + Ac^- + O_2^-$	$1 \cdot 10^5$		estimated	"
*	248		$CH_3O + O_2 \rightarrow HCHO + HO_2$	$1.2 \cdot 10^6$		estimated as in the gas phase	"
	249		$CH_3O \rightarrow CH_2OH$	$1 \cdot 10^6$		estimated	"
	250		$2 O_2CH_2COO^- \xrightarrow{H_2O} 2 CH(OH)_2COO^- + H_2O_2$	$2 \cdot 10^7$		Schuchmann <i>et al.</i> , 1985	"
*	251		$2 O_2CH_2COO^- \rightarrow 2 HCHO + H_2O_2 + 2 OH^- + 2 CO_2$	$1.88 \cdot 10^7$		Schuchmann <i>et al.</i> , 1985	"
*	252		$2 O_2CH_2COO^- \xrightarrow{H_2O} CH(OH)_2COO^- + CH_3COO^- + O_2$	$1.88 \cdot 10^7$		Schuchmann <i>et al.</i> , 1985	"
*	253		$2 O_2CH_2COO^- \xrightarrow{H_2O} 2 O_2^- + CH(OH)_2COO^- + 2 H_2O$	$7.5 \cdot 10^6$		Schuchmann <i>et al.</i> , 1985	"
	254		$CO_2 + O_2 \rightarrow CO_2 + O_2^-$	$4 \cdot 10^9$			"
	255		$CH_3COO^- + O_2 \rightarrow O_2CH_2COO^-$	$2 \cdot 10^9$		estimated	"

Table 8: Chlorine chemistry

red.	No.	No.	Reaction	$k_{298}$ , $M^{-n} s^{-1}$	$E_a / R$ , K	Reference	reason
	256	146	$SO_4^- + Cl^- \rightarrow SO_4^{2-} + Cl^-$	$3.3 \cdot 10^8$	0	Huie and Clifton, 1990; Herrmann et al., 1997	back reaction included => E51
*	257	147	$NO_3 + Cl^- \rightarrow NO_2 + Cl^-$	$1.0 \cdot 10^7$	4300	Exner et al., 1992	back reaction included => E52
	258	148	$Cl_2 + Cl_2^- \rightarrow Cl_2 + 2 Cl^-$	$8.7 \cdot 10^8$		Zellner et al., 1996	
	259	149	$Cl_2 + Fe^{2+} \rightarrow 2 Cl^- + Fe^{3+}$	$1.0 \cdot 10^7$	3030	Thornton and Laurence, 1973	additional reaction channel
*	260		$Cl_2 + Fe^{2+} \rightarrow FeCl^{2+}$	$4 \cdot 10^6$	3490	Thornton and Laurence, 1973	
*	261	150	$Cl_2 + Mn^{2+} \rightarrow 2 Cl^- + Mn^{3+}$	$8.5 \cdot 10^6$	4090	Laurence and Thornton, 1973	additional reaction channel
*	262		$Cl_2 + Mn^{2+} \rightarrow MnCl_2^+$	$2 \cdot 10^7$	4090	Laurence and Thornton, 1973	
*	263		$MnCl_2^+ \rightarrow Mn^{2+} + Cl_2^-$	$3 \cdot 10^5$	4090	Laurence and Thornton, 1973	additional reaction channel
*	264		$MnCl_2^+ \rightarrow Mn^{3+} + 2 Cl^-$	$2.1 \cdot 10^5$		Laurence and Thornton, 1973	following sinks
*	265	151	$Cl_2 + Cu^+ \rightarrow 2 Cl^- + Cu^{2+}$	$1 \cdot 10^7$		Laurence and Thornton, 1973	"
	266	152	$Cl_2 + H_2O_2 \rightarrow 2 Cl^- + H^+ + HO_2$	$1 \cdot 10^8$	3340	$k_{Cu^+} = k_{Fe^{2+}}$ $k_{Cu^+} \cong 10 \cdot k_{Fe^{2+}}$ Elliot, 1989	better estimate (more consistent to other $Fe^{2+}/Cu^+$ ratios)
*	267	153	$Cl_2 + CH_3OOH \rightarrow 2 Cl^- + H^+ + CH_3O_2$	$7 \cdot 10^5$	3340	Jacobi et al., 1999 $k_{CH_3OOH} = k_{H_2O_2}$	more actual value
*	268	154	$Cl_2 + OH^- \rightarrow 2 Cl^- + OH^-$	$4.0 \cdot 10^6$		Jacobi, 1996	
	269	155	$Cl_2 + HO_2 \rightarrow 2 Cl^- + H^+ + O_2$	$1.3 \cdot 10^{10}$		Jacobi, 1996	
*	270	156	$Cl_2 + O_2^- \rightarrow 2 Cl^- + O_2$	$6 \cdot 10^9$		Jacobi, 1996	
	271	157	$Cl_2 + HSO_3^- \rightarrow 2 Cl^- + H^- + SO_3^-$	$1.7 \cdot 10^8$	400	Jacobi et al., 1996	
*	272	158	$Cl_2 + SO_3^{2-} \rightarrow 2 Cl^- + SO_3^-$	$6.2 \cdot 10^7$		Jacobi et al., 1996	
	273	159	$Cl_2 + H_2O \rightarrow H^+ + Cl^- + HOCl$	0.401	7900	Wang and Margerum, 1994	correct rounded
				0.4			
			$Cl_2 + H_2O \rightarrow H^+ + 2 Cl^- + OH^-$	23.4		Buxton et al., 1998	new data available

Table 9: Bromine chemistry

red.	No.	No.	Reaction	$k_{298}$ , $M^{-n} s^{-1}$	$E_a / R$ , K	Reference	reason
	274	160	$SO_4^- + Br^- \rightarrow SO_4^{2-} + Br$	$2.1 \cdot 10^9$		Herrmann <i>et al.</i> , 1997	
	275	161	$NO_3^- + Br^- \rightarrow NO_3^- + Br$	$3.8 \cdot 10^9$		Zellner <i>et al.</i> , 1996	better reference
	276	162	$Br_2^- + Br_2^- \rightarrow Br_2 + 2 Br^-$	$1.7 \cdot 10^9$		Reese, 1998 Reese <i>et al.</i> , 1999	
*	277	163	$Br_2^- + Fe^{2+} \rightarrow 2 Br^- + Fe^{3+}$	$3.6 \cdot 10^6$	3330	Thornton and Laurence, 1973	additional reaction channel
*	278		$Br_2^- + Mn^{2+} \rightarrow MnBr_2^+$	$6.3 \cdot 10^6$	4330	Laurence and Thornton, 1973	
*	279	164	$Br_2^- + Mn^{2+} \rightarrow 2 Br^- + Mn^{3+}$	$6.3 \cdot 10^6$	4330	Laurence and Thornton, 1973	additional reaction channel
*	280		$MnBr_2^+ \rightarrow Br_2^- + Mn^{2+}$	$3 \cdot 10^5$		Laurence and Thornton, 1973	following sink
	281		$MnBr_2^+ \rightarrow 2 Br^- + Mn^{3+}$	$2.2 \cdot 10^5$		$k_{Cu^+} = k_{Fe^{2+}}$ Reese, 1997	
	282	165	$Br_2^- + Cu^+ \rightarrow 2 Br^- + Cu^{2+}$	$3.6 \cdot 10^6$		Reese, 1997	
	283	166	$Br_2^- + H_2O_2 \rightarrow 2 Br^- + H^+ + HO_2$	$1.0 \cdot 10^5$		$k = k_{1202}$ Jacobi, 1996	
*	284	167	$Br_2^- + CH_3OOH \rightarrow 2 Br^- + H^+ + CH_3O_2$	$1.0 \cdot 10^5$			
*	285	168	$Br_2^- + OH^- \rightarrow 2 Br^- + OH$	$1.1 \cdot 10^4$		Rafi and Surton, 1965	
	286	169	$Br_2^- + HO_2 \rightarrow 2 Br^- + H^+ + O_2$	$6.5 \cdot 10^9$		Wagner and Strehlow, 1987	
*	287	170	$Br_2^- + O_2^- \rightarrow 2 Br^- + O_2$	$1.7 \cdot 10^8$		Shoute <i>et al.</i> , 1991; Jacobi, 1996	
	288	171	$Br_2^- + HSO_3^- \rightarrow 2 Br^- + H^+ + SO_3^-$	$5.0 \cdot 10^7$	780	Shoute <i>et al.</i> , 1991; Jacobi, 1996	
*	289	172	$Br_2^- + SO_3^{2-} \rightarrow 2 Br^- + SO_3^-$	$3.3 \cdot 10^7$	650	Shoute <i>et al.</i> , 1991; Jacobi, 1996	
	290	173	$Br_2 + H_2O \rightarrow Br^- + H^+ + HOBr$	1.7	7500	Beckwith <i>et al.</i> , 1996	
	291		$BrOH^- \rightarrow Br^- + OH^-$	$4.2 \cdot 10^6$		Zehavi and Rabani, 1972	completion of BrOH <sup>-</sup> chemistry

Table 10: Carbonate Chemistry

red.	No.	No.	Reaction	$k_{298}$ , $M^{-n} s^{-1}$	$E_a/R$ , K	Reference	reason
*	292	174	$HCO_3^- + OH^- \rightarrow H_2O + CO_3^-$	$1.7 \cdot 10^7$	1900	Exner, 1990	
*	293	175	$CO_3^{2-} + OH^- \rightarrow OH^- + CO_3^-$	$3.9 \cdot 10^8$	2840	Buxton <i>et al.</i> , 1988a,b <i>estimated</i>	measurement instead of estimate
*	294	176	$CO_3^{2-} + SO_4^- \rightarrow SO_4^{2-} + CO_3^-$	$4.1 \cdot 10^7$		Padmaja <i>et al.</i> , 1993	
*	295	177	$HCO_3^- + SO_4^- \rightarrow SO_4^{2-} + CO_3^- + H^+$	$4.1 \cdot 10^6$		Huie and Clifton, 1990	
*	296	178	$CO_3^{2-} + NO_3^- \rightarrow NO_3^- + CO_3^-$	$2.8 \cdot 10^6$	2090	<i>estimated</i>	
*	297		$HCO_3^- + NO_3^- \rightarrow NO_3^- + CO_3^- + H^+$	$4.1 \cdot 10^7$		<i>estimated</i> $k_{HCO_3^-} = k_{CO_3^{2-}}$	reactions of $HCO_3^-$ added for completion
*	298	179	$CO_3^{2-} + Cl_2^- \rightarrow 2 Cl^- + CO_3^-$	$2.7 \cdot 10^6$		<i>estimated</i>	
*	299		$HCO_3^- + Cl_2^- \rightarrow 2 Cl^- + CO_3^- + H^+$	$2.7 \cdot 10^6$		<i>estimated</i>	reactions of $HCO_3^-$ added for completion
*	300	180	$CO_3^{2-} + Br_2^- \rightarrow 2 Br^- + CO_3^-$	$1.1 \cdot 10^5$		Huie <i>et al.</i> , 1991b	
*	301		$HCO_3^- + Br_2^- \rightarrow 2 Br^- + CO_3^-$	$1.1 \cdot 10^5$		<i>estimated</i>	reactions of $HCO_3^-$ added for completion
*	302	181	$CO_3^- + CO_3^- \xrightarrow{O_2} 2 O_2^- + 2 CO_2$	$2.2 \cdot 10^6$		Huie and Clifton, 1990	
*	303	182	$CO_3^- + Fe^{2+} \rightarrow CO_3^{2-} + Fe^{3+}$	$2 \cdot 10^7$		<i>estimated</i>	
*	304	183	$CO_3^- + Mn^{2+} \rightarrow CO_3^{2-} + Mn^{3+}$	$1.5 \cdot 10^7$		Cope <i>et al.</i> , 1978	
*	305	184	$CO_3^- + Cu^+ \rightarrow CO_3^{2-} + Cu^{2+}$	$2 \cdot 10^7$		<i>estimated</i>	
*	306	185	$CO_3^- + H_2O_2 \rightarrow HCO_3^- + HO_2$	$4.3 \cdot 10^5$		Draganic <i>et al.</i> , 1991	
*	307	186	$CO_3^- + CH_3OOH \rightarrow HCO_3^- + CH_3O_2$	$4.3 \cdot 10^5$		$k_{H_2O_2} = k_{CH_3OOH}$	
*	308	187	$CO_3^- + HO_2 \rightarrow HCO_3^- + O_2$	$6.5 \cdot 10^8$		$k_{HO_2} = k_{O_2}$	
*	309	188	$CO_3^- + O_2^- \rightarrow CO_3^{2-} + O_2$	$6.5 \cdot 10^8$		Eriksen <i>et al.</i> , 1985	
*	310	189	$CO_3^- + HSO_3^- \rightarrow HCO_3^- + SO_3^-$	$1 \cdot 10^7$		<i>estimated</i>	
*	311	190	$CO_3^- + SO_3^{2-} \rightarrow CO_3^{2-} + SO_3^-$	$5.0 \cdot 10^6$	470	Exner <i>et al.</i> , 1990;	
						Huie <i>et al.</i> , 1991a	
*	312		$CO_3^- + NO_2^- \rightarrow CO_2 + NO_3^-$	$1 \cdot 10^9$		Lillie <i>et al.</i> , 1978	sinks added for $CO_3^-$
*	313		$CO_3^- + O_3 \rightarrow CO_2 + O_2 + O_2^-$	$1 \cdot 10^5$		Sehested <i>et al.</i> , 1983	sinks added for $CO_3^-$

**Table 11:** Photolysis Rates (Aqueous Phase), geographical latitude of 51° N

red.	No	Reaction	$j_{\max}$ [s <sup>-1</sup> ]	Range of Quantum Yield $\Phi$	References	reason
	2.4					
	2.3					
	314	$\text{H}_2\text{O}_2 + \text{h}\nu \rightarrow 2 \text{OH}$	$7.19 \cdot 10^{-6}$	$0.98 \pm 0.03^a$ $0.96 \pm 0.03^b$	Zellner <i>et al.</i> , 1990 Zellner <i>et al.</i> , 1990	
*	315	$[\text{Fe}(\text{OH})]^{2+} + \text{h}\nu \rightarrow \text{Fe}^{2+} + \text{OH}$	$4.51 \cdot 10^{-3}$	$0.312 \pm 0.03 \dots 0.074 \pm 0.015^c$	Benkelberg and Warneck, 1995	
*	316	$[\text{Fe}(\text{OH})_2]^+ + \text{h}\nu \rightarrow \text{Fe}^{2+} + \text{OH} + \text{OH}^\cdot$	$5.77 \cdot 10^{-3}$	$0.235 \dots 0.07^d$	Benkelberg <i>et al.</i> , 1991	
*	317	$[\text{Fe}(\text{SO}_4)]^+ + \text{h}\nu \rightarrow \text{Fe}^{2+} + \text{SO}_4^\cdot$	$6.43 \cdot 10^{-3}$	$(7.9 \pm 0.34 \dots 1.56 \pm 0.02) \cdot 10^{-3}^e$	Benkelberg and Warneck, 1995	
*	318	$\text{NO}_2^\cdot + \text{h}\nu \rightarrow \text{NO} + \text{OH}$	$2.57 \cdot 10^{-5}$	$0.07 \pm 0.01^a$	Zellner <i>et al.</i> , 1990	
	319	$\text{NO}_3^\cdot + \text{h}\nu \rightarrow \text{NO}_2 + \text{OH}$	$4.28 \cdot 10^{-7}$	$0.046 \pm 0.009^b$	Zellner <i>et al.</i> , 1990	
	320	$2 \text{Fe}(\text{C}_2\text{O}_4)_2^- + \text{h}\nu \rightarrow 2 \text{Fe}^{2+} + 3 \text{C}_2\text{O}_4^{2-} + 2 \text{CO}_2$	$2.47 \cdot 10^{-2}$	$0.017 \pm 0.003$ <b><math>1.0 \pm 0.25</math> (436 nm)</b>	Zellner <i>et al.</i> , 1990 <b>Zuo and Hoigne, 1992</b>	oxalate chemistry
*	321	$2 \text{Fe}(\text{C}_2\text{O}_4)_3^- + \text{h}\nu \rightarrow 2 \text{Fe}^{2+} + 5 \text{C}_2\text{O}_4^{2-} + 2 \text{CO}_2$	$1.55 \cdot 10^{-2}$	<b><math>0.6 \pm 0.46</math> (436 nm)</b>	<b>Zuo and Hoigne, 1992</b>	"
*	322	$\text{CH}_3\text{O}_2\text{H} + \text{h}\nu \rightarrow \text{CH}_3\text{O} + \text{OH}$	$7.19 \cdot 10^{-6}$		$j_{\text{P1}} = j_{\text{P0}}$	analogous to $\text{H}_2\text{O}_2$ (also other reactions treated as being equal)
*	323	$\text{NO}_3 + \text{h}\nu \rightarrow \text{NO} + \text{O}_2$	$2.32 \cdot 10^{-2}$		estimated as in the gas phase	additional sinks for $\text{NO}_3$
*	324	$\text{NO}_3 + \text{h}\nu \rightarrow \text{NO}_2 + \text{O}^3\text{P}$	$2.01 \cdot 10^{-1}$		estimated as in the gas phase	additional sinks for $\text{NO}_3$

<sup>a</sup>  $\lambda = 308 \text{ nm}$ ,  $T = 298 \text{ K}$ ; <sup>b</sup>  $\lambda = 351 \text{ nm}$ ,  $T = 298 \text{ K}$ ; <sup>c</sup>  $\lambda = 280 \dots 370 \text{ nm}$ ; <sup>d</sup>  $\lambda = 290 \dots 365 \text{ nm}$

Table 12: Aqueous equilibria

red.	No 2,4	No 2,3	Reactions	K, M	k <sub>298</sub> , (forward) M <sup>m</sup> s <sup>-1</sup>	E <sub>a</sub> /R, K	Ref.	k <sub>298</sub> (back) M <sup>m</sup> s <sup>-1</sup>	E <sub>a</sub> /R, K	Ref.	reason
	1	1	H <sub>2</sub> O ⇌ H <sup>+</sup> + OH <sup>-</sup>	1.8 · 10 <sup>-14</sup>	2.34 · 10 <sup>-5</sup>	6800	a	1.3 · 10 <sup>11</sup>		c	
	2	2	CO <sub>2</sub> + H <sub>2</sub> O ⇌ H <sub>2</sub> CO <sub>3</sub>	7.7 · 10 <sup>-7</sup>	4.3 · 10 <sup>-2</sup>	9250	b	5.6 · 10 <sup>4</sup>	8500	x	
*	3	3	H <sub>2</sub> CO <sub>3</sub> ⇌ H <sup>+</sup> + HCO <sub>3</sub> <sup>-</sup>	2 · 10 <sup>-4</sup>	1 · 10 <sup>7</sup>		c	5 · 10 <sup>10</sup>		c	
	4	4	HCO <sub>3</sub> <sup>-</sup> ⇌ H <sup>+</sup> + CO <sub>3</sub> <sup>2-</sup>	4.69 · 10 <sup>-11</sup>	2.35	1820	a	5 · 10 <sup>10</sup>		c	
	5	5	HCl ⇌ H <sup>+</sup> + Cl <sup>-</sup>	1.72 · 10 <sup>6</sup>	8.6 · 10 <sup>16</sup>	-6890	d	5 · 10 <sup>10</sup>		c	8.6 · 10 <sup>16</sup> >> diffusion controlled (vibrational freq.); based on K · k <sub>back</sub>
	6	6	NH <sub>3</sub> + H <sub>2</sub> O ⇌ NH <sub>4</sub> <sup>+</sup> + OH <sup>-</sup>	1.77 · 10 <sup>-5</sup> 3.17 · 10 <sup>-7</sup>	6.02 · 10 <sup>5</sup>	560	a	3.4 · 10 <sup>10</sup>		c	new: k <sub>f</sub> = speed of hydrogen bond breaking in water H <sub>2</sub> O included in K
	7	7	HO <sub>2</sub> ⇌ H <sup>+</sup> + O <sub>2</sub> <sup>-</sup>	1.6 · 10 <sup>-5</sup>	8.0 · 10 <sup>5</sup>	0	e,f	5 · 10 <sup>10</sup>	0	y	
	8	8	HNO <sub>3</sub> ⇌ H <sup>+</sup> + NO <sub>3</sub> <sup>-</sup>	22	1.1 · 10 <sup>12</sup>	-1800	g,h	5 · 10 <sup>10</sup>		c	
	9	9	HNO <sub>2</sub> ⇌ H <sup>+</sup> + NO <sub>2</sub> <sup>-</sup>	5.3 · 10 <sup>-4</sup>	2.65 · 10 <sup>7</sup>	1760	i	5 · 10 <sup>10</sup>		c	
	10	10	HO <sub>2</sub> NO <sub>2</sub> ⇌ H <sup>+</sup> + O <sub>2</sub> NO <sub>2</sub> <sup>-</sup>	1 · 10 <sup>-5</sup>	5 · 10 <sup>5</sup>		j	5 · 10 <sup>10</sup>		y	
	11	11	NO <sub>2</sub> + HO <sub>2</sub> ⇌ HO <sub>2</sub> NO <sub>2</sub>	2.2 · 10 <sup>9</sup>	1.0 · 10 <sup>7</sup>		k	4.6 · 10 <sup>-3</sup>		j	
	12	12	SO <sub>2</sub> + H <sub>2</sub> O ⇌ HSO <sub>3</sub> <sup>-</sup> + H <sup>+</sup>	3.13 · 10 <sup>-4</sup>	6.27 · 10 <sup>4</sup>	-1940	l	2.0 · 10 <sup>8</sup>		c	
	13	13	HSO <sub>3</sub> <sup>-</sup> ⇌ SO <sub>3</sub> <sup>2-</sup> + H <sup>+</sup>	6.22 · 10 <sup>-8</sup>	3110	-1960	l	5 · 10 <sup>10</sup>		c	
	14	14	H <sub>2</sub> SO <sub>4</sub> ⇌ HSO <sub>4</sub> <sup>-</sup> + H <sup>+</sup>	1000	5 · 10 <sup>13</sup>			5 · 10 <sup>10</sup>		c	added for completion
	15	15	HSO <sub>4</sub> <sup>-</sup> ⇌ SO <sub>4</sub> <sup>2-</sup> + H <sup>+</sup>	1.02 · 10 <sup>-2</sup>	1.02 · 10 <sup>9</sup>	-2700	g	1 · 10 <sup>11</sup>		c	
	16	16	HCOOH ⇌ HCOO <sup>-</sup> + H <sup>+</sup>	1.77 · 10 <sup>-4</sup>	8.85 · 10 <sup>6</sup>	-12	a	5 · 10 <sup>10</sup>		c	
	17	17	HAc ⇌ Ac <sup>-</sup> + H <sup>+</sup>	1.75 · 10 <sup>-5</sup>	8.75 · 10 <sup>5</sup>	-46	a	5 · 10 <sup>10</sup>		c	
*	18	18	Fe <sup>3+</sup> + H <sub>2</sub> O ⇌ [Fe(OH)] <sup>2+</sup> + H <sup>+</sup>	1.1 · 10 <sup>-4</sup>	4.7 · 10 <sup>4</sup>		m	4.3 · 10 <sup>8</sup>		m	
	19	19	[Fe(OH)] <sup>2+</sup> + H <sub>2</sub> O ⇌ [Fe(OH) <sub>2</sub> ] <sup>+</sup> + H <sup>+</sup>	1.4 · 10 <sup>-7</sup>	1.1 · 10 <sup>3</sup>		n	8.0 · 10 <sup>9</sup>		n	
*	20	20	Fe <sup>3+</sup> + SO <sub>4</sub> <sup>2-</sup> ⇌ [Fe(SO <sub>4</sub> )] <sup>-</sup>	1.8 · 10 <sup>-2</sup>	3.2 · 10 <sup>3</sup>		m	1.8 · 10 <sup>5</sup>		m	
	21	21	HCHO + H <sub>2</sub> O ⇌ CH <sub>2</sub> (OH) <sub>2</sub>	36	0.18	-4030	q	5.1 · 10 <sup>-3</sup>		p	
	22	22	CH <sub>3</sub> CHO + H <sub>2</sub> O ⇌ CH <sub>3</sub> CH(OH) <sub>2</sub>	2.46 · 10 <sup>-2</sup>	1.4 · 10 <sup>-4</sup>	-2500	p	5.69 · 10 <sup>-3</sup>		o	
	23	22	CH <sub>2</sub> (OH) <sub>2</sub> + HSO <sub>3</sub> <sup>-</sup> ⇌ HMS + H <sub>2</sub> O	2 · 10 <sup>8</sup>	790	2990	q	3.95 · 10 <sup>-6</sup>	2990	q	

Table 12 cont.

red.	No	No	Reactions	K,	k <sub>298</sub> , (forward)	E <sub>a</sub> / R, K	Ref.	k <sub>298</sub> (back)	E <sub>a</sub> / R, K	Ref.	reason
	2.4	2.3		M	M <sup>n</sup> s <sup>-1</sup>	K		M <sup>n</sup> s <sup>-1</sup>	K		
	24	23	CH <sub>3</sub> (OH) <sub>2</sub> + SO <sub>3</sub> <sup>2-</sup> ⇌ HMS + OH <sup>-</sup>	3.6·10 <sup>6</sup>	2.5·10 <sup>7</sup>	2450	q	3.95·10 <sup>6</sup>	5530	q	
	25	24	Cl + Cl <sup>-</sup> ⇌ Cl <sub>2</sub> <sup>-</sup>	1.9·10 <sup>5</sup>	2.7·10 <sup>10</sup>		r	1.4·10 <sup>5</sup>		r	new data available
	26	25	Br + Br <sup>-</sup> ⇌ Br <sub>2</sub> <sup>-</sup>	6·10 <sup>5</sup>	1.2·10 <sup>10</sup>		s	1.9·10 <sup>4</sup>		s	
	27	26	Cl <sup>-</sup> + OH <sup>-</sup> ⇌ ClOH <sup>-</sup>	0.7	4.3·10 <sup>9</sup>		t	6.1·10 <sup>9</sup>		t	
	28	27	ClOH <sup>-</sup> + H <sup>+</sup> ⇌ Cl + H <sub>2</sub> O	1.6·10 <sup>7</sup>	2.1·10 <sup>10</sup>		t	1.3·10 <sup>5</sup>		z	new data available
	29	28	ClOH <sup>-</sup> + Cl <sup>-</sup> ⇌ Cl <sub>2</sub> <sup>-</sup> + OH <sup>-</sup>	2.2·10 <sup>4</sup>	1.0·10 <sup>4</sup>		u	4.5·10 <sup>7</sup>		u	
	30	29	Br <sup>-</sup> + OH <sup>-</sup> ⇌ BrOH <sup>-</sup>	333	1.1·10 <sup>10</sup>		v	3.3·10 <sup>7</sup>		v	
	31	30	BrOH <sup>-</sup> + H <sup>+</sup> ⇌ Br + H <sub>2</sub> O	1.8·10 <sup>12</sup>	4.4·10 <sup>10</sup>		y	2.45·10 <sup>-2</sup>		w	
*	32	31	BrOH <sup>-</sup> + Br <sup>-</sup> ⇌ Br <sub>2</sub> <sup>-</sup> + OH <sup>-</sup>	70	1.9·10 <sup>8</sup>		y	2.7·10 <sup>6</sup>		x	
*	33		Mn <sup>3+</sup> + H <sub>2</sub> O ⇌ Mn(OH) <sup>2+</sup> + H <sup>+</sup>	0.93	1.86·10 <sup>10</sup>		y	2·10 <sup>10</sup>		y	detailed formulation of Mn chemistry (new data available)
*	34		O <sub>2</sub> <sup>-</sup> + Mn <sup>2+</sup> ⇌ MnO <sub>2</sub> <sup>+</sup>	2.3·10 <sup>4</sup>	1.5·10 <sup>8</sup>		z	6.5·10 <sup>3</sup>		z	"
*	35		HO <sub>2</sub> <sup>-</sup> + Mn <sup>2+</sup> ⇌ MnO <sub>2</sub> <sup>+</sup> + H <sup>+</sup>	0.17	1.1·10 <sup>6</sup>		z	6.5·10 <sup>6</sup>		z	"
*	36		Mn <sup>2+</sup> + Mn <sup>3+</sup> ⇌ Mn <sup>2+</sup> + Mn <sup>4+</sup>	1·10 <sup>-3</sup>	1·10 <sup>7</sup>		A	1·10 <sup>10</sup>		A	"
*	37		Mn(OH) <sup>2+</sup> + H <sub>2</sub> O ⇌ Mn(OH) <sub>2</sub> <sup>-</sup> + H <sup>+</sup>	1·10 <sup>-5</sup>	2·10 <sup>5</sup>		B	2·10 <sup>10</sup>		B	"
*	38		Mn <sup>2+</sup> + HSO <sub>3</sub> <sup>-</sup> ⇌ MnHSO <sub>3</sub> <sup>+</sup>	3·10 <sup>4</sup>	3.1·10 <sup>7</sup>		C	1.033·10 <sup>3</sup>		C	"
*	39		Cu <sup>2+</sup> + OH <sup>-</sup> ⇌ CuOH <sup>+</sup>	1.17·10 <sup>4</sup>	3.5·10 <sup>8</sup>		D	3·10 <sup>4</sup>		E	
	40		HO <sub>3</sub> <sup>-</sup> ⇌ H <sup>+</sup> + O <sub>3</sub> <sup>-</sup>	5·10 <sup>-9</sup>	330		F	5.2·10 <sup>10</sup>		F	sink for O <sub>3</sub> <sup>-</sup> (see R24/25)
*	41		HOONO ⇌ H <sup>+</sup> + OONO <sup>-</sup>	1·10 <sup>-6</sup>	5·10 <sup>4</sup>		G	5·10 <sup>10</sup>		(E)	HOONO new added (see reaction 73)
	42		CHOHSO <sub>3</sub> <sup>-</sup> ⇌ CHOSO <sub>3</sub> <sup>2-</sup> + H <sup>+</sup>	1.34·10 <sup>-6</sup>	5.9·10 <sup>4</sup>		H	4.4·10 <sup>10</sup>		H	link between acid/anion
	43		SO <sub>5</sub> O <sub>2</sub> H ⇌ SO <sub>5</sub> O <sub>2</sub> <sup>-</sup> + H <sup>+</sup>	1.6·10 <sup>-5</sup>	7.5·10 <sup>5</sup>		(E)	5·10 <sup>10</sup>		(E)	"
	44		H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> ⇌ H <sup>+</sup> + HC <sub>2</sub> O <sub>4</sub> <sup>-</sup>	6.4·10 <sup>-2</sup>	3.2·10 <sup>9</sup>		(E)	5·10 <sup>10</sup>		(E)	consideration of C <sub>2</sub> <sup>-</sup> difunctional compounds
	45		HC <sub>2</sub> O <sub>4</sub> <sup>-</sup> ⇌ H <sup>+</sup> + C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	5.25·10 <sup>-5</sup>	2.6·10 <sup>6</sup>		(E)	5·10 <sup>10</sup>		(E)	"
*	46		CH(OH) <sub>2</sub> COOH ⇌ H <sup>+</sup> + CH(OH) <sub>2</sub> COO <sup>-</sup>	3.16·10 <sup>-4</sup>	6.32·10 <sup>6</sup>		J	2·10 <sup>10</sup>		J	"

Table 12 cont.

red.	No 2.4	No 2.3	Reactions	K, M	k <sub>298</sub> (forward) M <sup>n</sup> s <sup>-1</sup>	E <sub>a</sub> / R, K	Ref.	k <sub>298</sub> (back) M <sup>n</sup> s <sup>-1</sup>	E <sub>a</sub> / R, K	Ref.	reason
	47		$\text{CHOCHO} + \text{H}_2\text{O} \rightleftharpoons (\text{CH}(\text{OH})_2)_2$ $[\text{Fe}(\text{C}_2\text{O}_4)]^+ \rightleftharpoons [\text{Fe}]^{3+} + \text{C}_2\text{O}_4^{2-}$ $[\text{Fe}(\text{C}_2\text{O}_4)_2]^- \rightleftharpoons [\text{Fe}(\text{C}_2\text{O}_4)]^- + \text{C}_2\text{O}_4^{2-}$ $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-} \rightleftharpoons [\text{Fe}(\text{C}_2\text{O}_4)_2]^- + \text{C}_2\text{O}_4^{2-}$ $\text{SO}_4^- + \text{Cl}^- \rightleftharpoons \text{SO}_4^{2-} + \text{Cl}^-$	$3.9 \cdot 10^3$ $2.9 \cdot 10^9$ $6.3 \cdot 10^6$ $3.8 \cdot 10^4$ $1.2$	$21.5$ $3 \cdot 10^{-3}$ $3 \cdot 10^{-3}$ $3 \cdot 10^{-3}$ $2.52 \cdot 10^8$	     	     	     	     	     	     
*	51		$\text{NO}_3 + \text{Cl}^- \rightleftharpoons \text{NO}_3^- + \text{Cl}^-$ $\text{Cl}^- + \text{Fe}^{3+} \rightleftharpoons \text{FeCl}^{2+}$ $\text{CH}_3\text{C}(\text{O})\text{OOH} \rightleftharpoons \text{CH}_3\text{C}(\text{O})\text{OO}^- + \text{H}^+$ $\text{CH}_3\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{C}(\text{OH})_2$	$3.4$ $1.39$ $6.3 \cdot 10^{-9}$ $367$	$3.4 \cdot 10^8$ $3 \cdot 10^3$ $315$ $1.1 \cdot 10^7$	    	    	    	    	    	    
*	52		$2 \text{Br}^- + \text{CO}_3^{2-} \rightleftharpoons \text{Br}_2 + \text{CO}_3^{2-}$ $\text{ACO}_3 \rightleftharpoons \text{O}_2\text{CH}_2\text{COO}^- + \text{H}^+$	$0.34$ $1.75 \cdot 10^{-5}$	$3.4 \cdot 10^4$ $8.75 \cdot 10^5$	  	  	  	  	  	  
*	53										
*	54										
*	55										
*	56										
*	57										

<sup>a</sup> Harned and Owen, 1958; <sup>b</sup> Welch *et al.*, 1969; <sup>c</sup> Graedel and Weschler, 1981; <sup>d</sup> Marsh and McElroy, 1985; <sup>e</sup> Bielski *et al.*, 1985; <sup>f</sup> Baxendale *et al.*, 1971; <sup>g</sup> Redlich, 1946; <sup>h</sup> Redlich and Hood, 1957; <sup>i</sup> Park and Lee, 1988; <sup>j</sup> Lammel *et al.*, 1990; <sup>k</sup> Warneck and Wurzing, 1988; <sup>l</sup> Beilke and Gravenhorst, 1978; <sup>m</sup> Brandt and van Eldik, 1995; <sup>n</sup> Hemmes *et al.*, 1971; <sup>o</sup> Bell and Evans, 1966; <sup>p</sup> Bell *et al.*, 1956; <sup>q</sup> Olson and Hoffmann, 1989; <sup>r</sup> Buxton *et al.*, 1998; <sup>s</sup> Merétyi and Lind, 1994; <sup>t</sup> Jayson *et al.*, 1973; <sup>u</sup> Grigor'ev *et al.*, 1987; <sup>v</sup> Zehavi and Rabani, 1972; <sup>w</sup> Klänning and Wolff, 1985; <sup>x</sup> Fournier de Violet, 1981; <sup>y</sup> Wells and Davies, 1967; <sup>z</sup> Jacobsen *et al.*, 1997b; <sup>A</sup> Rosseinsky, 1963; <sup>B</sup> v. Piechowski *et al.*, 1993; <sup>C</sup> Berglund *et al.*, 1993; <sup>D</sup> Buxton *et al.*, 1988; <sup>E</sup> Meyerstein, 1971; <sup>F</sup> Bühler *et al.*, 1984; <sup>G</sup> Wagner *et al.*, 1980; <sup>H</sup> Barlow *et al.*, 1997b; <sup>I</sup> Sedlak and Hoigne, 1993; <sup>J</sup> Buxton *et al.*, 1997; <sup>K</sup> Betterton and Hoffmann, 1988a; <sup>L</sup> Moorhead and Sutin, 1967; <sup>M</sup> Buxton *et al.*, 1999b; <sup>N</sup> Buxton *et al.*, 1999c; <sup>O</sup> Martell and Sillen; <sup>P</sup> Schuchmann and v. Sonntag, 1988; <sup>Q</sup> Lilie *et al.*, 1978; <sup>S</sup> estimated equal as acetic acid

## IMPACT OF MAIN RESULTS

The mechanism described here is of high interest for a better understanding of multiphase tropospheric chemistry. After dissemination of this mechanism and its first applications for the description of tropospheric cloud chemistry under urban and rural as well as marine conditions, the mechanisms will be used in the modelling community to better assess multiphase phenomena within the troposphere. The mechanism will contribute to solving air pollution problems by use in chemical transport models which will be applied for prediction of the effect of additional anthropogenic emissions and, on the other hand, reducing measures of air pollutants in the future.

## CONCLUSIONS

A mechanism according to the objectives for the first year of MODAC was established and is currently disseminated. Within the project the mechanism was significantly updated and improved and was used for subsystem modelling. A reduced form has been developed which is to be included higher scalar tropospheric models.

## PUBLICATIONS FROM THE MODAC PROJECT

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1. Herrmann, H., Ervens, B., Hesper, J. and Wicktor, F. 1999. *Tropospheric aqueous phase chemistry laboratory and modelling studies*. Fine Particle Science and Environmental Chamber Workshop, Riverside, Oktober 1999.
2. Herrmann, H., Ervens, B., Hesper, J. and Wicktor, F. 1999. *Radical-induced tropospheric multiphase formation and degradation of atmospheric reactive substances (ARS)*. First International Symposium on Atmospheric Reactive Substances (ARS), Bayreuth, 14.-16. April.
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6. 6th FECS Conference on Chemistry and the Atmospheric Chemistry and Air Pollution (VOC, Oxidants/NO<sub>x</sub> and Particulates), 26-28 août, Copenhagen, Danemark.  
F. Schweitzer, Ph. Mirabel, Ch. George (présentation affichée)  
Hydrobromic Acid Reactivity at the Air/Water Interface
7. EUROTRAC2 - Chemical Mechanism Development Workshop, 23-25 septembre, Karlsruhe, Allemagne.  
F. Schweitzer, Ph. Mirabel, Ch. George (présentation affichée)  
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## Part B: DETAILED REPORTS OF THE CONTRACTORS

### Contractor 1:

#### Tropospheric Aqueous Phase Radical Chemistry Evaluation, Model construction and Laboratory Studies

**Contractor:** Institut für Troposphärenforschung, Leipzig  
**Leading Scientist:** Prof. Dr. H. Herrmann  
**Scientific Staff:** B. Ervens, D. Weise, J. Hesper

### Objectives

The main objective of the project was the development of an extensive aqueous phase chemical mechanism. The main part is represented by reactions of radicals and organic compounds in the aqueous phase. The mechanism concerned should describe the heterogeneous and aqueous phase processes of the tropospheric cloud chemistry. The starting point of this mechanism was the Chemical Aqueous Phase Radical Mechanism (CAPRAM2.3 [1, 2]). All currently available kinetic and photochemical data used in this scheme were reviewed in detail. Additional processes were implemented of (i) difunctional C<sub>2</sub> organic compounds (e. g. glyoxal, oxalate) and (ii) species for which data became available during the last few years (e. g. FeO<sup>2+</sup>).

To give a more realistic impression of cloud chemistry emissions and depositions were implemented to the box model. The data sets for these values were evaluated by contributor 3 and 4. Based on these results a reduced version of CAPRAM2.4 was developed in co-operation with the contributor 2 and 3.

With the contributors 2 and 3 an intercomparison of the multiphase scheme was performed checking whether the model results are reproducible with different solvers for the models.

Additional some laboratory measurements were performed to make available kinetic data of essential aqueous phase reactions.

### 1. Development of the mechanism

#### 1.1 Conditions

In first studies [1,2] with the multiphase scheme CAPRAM2.3/ RADM2 a monodisperse droplet radius of 1 µm was assumed, the liquid water content (LWC) was set at 0.3 g m<sup>-3</sup> leading finally to a droplet concentration of 7·10<sup>4</sup> cm<sup>-3</sup>. With this very small droplet radius the maximum effect of cloud chemistry was demonstrated. For the model studies performed with CAPRAM2.4 a droplet radius of 10 µm was used to be more related to realistic cloud conditions.

The initial concentrations for the gas phase chemistry was taken from Zimmermann and Poppe [3], these ones for the aqueous phase are taken from literature ([1], [2]). The initial values for the transition metal ions Fe<sup>3+</sup>, Mn<sup>2+</sup> and Cu<sup>+</sup> were taken from the work by and Matthijsen and Builtjes [3]. It has to be noted that the initial concentrations describe only cloud chemistry during the droplet radius is this one of a aerosol particle. With the initial concentrations it can be differentiated in three environments, urban (continental polluted), rural (continental unpolluted) and marine. The meteorological conditions for the temperature and the pressure are constant (T = 288 K, p = 1 atm). The calculations are performed for four days but only the last three days are considered for the interpretation of the results.

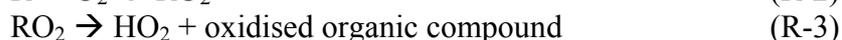
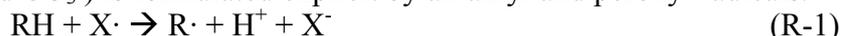
### 1.2 Update and revision of the aqueous phase chemistry

The mechanism CAPRAM2.3 contains 265 aqueous phase processes. In first calculations it was coupled with RADM2 including 158 gas phase reactions [4]. In the frame of the update the more actual version RACM [8] with 237 gas phase processes was used. For 34 species the phase transfers are described. The uptake of the species CH<sub>3</sub>OH, C<sub>2</sub>H<sub>5</sub>OH, NH<sub>3</sub>, HCl, Br<sub>2</sub> and Cl<sub>2</sub> is also included although they are not considered in the gas phase and so they have no further reactions in the gas phase. Photolysis rates at ground level are calculated using a solar radiation flux model [9]. Therefore, the photolysis rates are different for continental and marine conditions. For all regimes a surface albedo of 0.1 is assumed. The calculations are performed for a geographical latitude of 51° N and for the 21<sup>st</sup> of June. Further input parameters, e.g. wavelength-dependent absorption coefficients and quantum yields for aqueous phase species, are taken from Ruggaber [10]. For simplification no scattering light was considered, i. e. the photolysis rates are assumed to be zero between 8:00 pm and 4:00 am.

The phase transfers are described in the model calculations with the resistance model by Schwartz [11] considering mass accommodation, Henry's Law constants and gas phase diffusion coefficients. If gas phase diffusion coefficients are not available from literature they were estimated after the method by Fuller [12].

Not only reactions of primary radicals such as OH and NO<sub>3</sub> which are transported directly from the gas phase into the droplet are considered but also those of secondary radicals such as SO<sub>4</sub><sup>-</sup>, Cl<sub>2</sub><sup>-</sup>, Br<sub>2</sub> and CO<sub>3</sub><sup>-</sup> which are formed from reactions with OH or NO<sub>3</sub>. Even in CAPRAM2.3 a lot of kinetic data measured in our laboratory were implemented. Some reaction rate constants are still unknown, so that such rate coefficients had to be estimated based on other kinetic data and reactivity relationships. If available the temperature dependencies were implemented but a lot of these data are missing until now.

In both versions of CAPRAM the most detailed part is the chemistry of organic compounds considering not only C<sub>1</sub> organics as in the other aqueous phase mechanisms known from literature [13, 14] but also reactions of the C<sub>2</sub> alcohols, aldehydes, carbonic acids and peroxy radicals. Within the update the oxidation of organics by the radicals and radical anions X (OH, NO<sub>3</sub>, SO<sub>4</sub><sup>-</sup>, SO<sub>5</sub><sup>-</sup>, Cl<sub>2</sub><sup>-</sup>, Br<sub>2</sub><sup>-</sup> and CO<sub>3</sub><sup>-</sup>) is formulated explicit by all alkyl and peroxy radicals.



Furthermore the detailed oxidation of glyoxal, glyoxylic acid and oxalate by radicals and radical anions (OH, NO<sub>3</sub>, SO<sub>4</sub><sup>-</sup>, Cl<sub>2</sub><sup>-</sup>, Br<sub>2</sub><sup>-</sup>, CO<sub>3</sub><sup>-</sup>) was added. So the number of reactions in this part was increased from 50 to 110 processes. The uptake of glyoxal linking its chemistry to the gas phase chemistry and further hydration of it was included

The sulfur chemistry considering the reactions of SO<sub>x</sub><sup>-</sup> radical anions (x = 3, 4, 5) has a part of 43 reactions. Here the essential extension was a splitting of the HMS<sup>-</sup> oxidation into elementary steps.

In total 34 reactions of the HO<sub>x</sub>-radicals (OH and HO<sub>2</sub>) and transition metal ions (Cu<sup>+2+</sup>, Fe<sup>2+/3+</sup>, Mn<sup>2+/3+</sup>) are considered. Because a lot of reactions of the ferryl ion (FeO<sup>2+</sup>) and the dynamic behaviour of several manganese species was implemented here the number was extended to 59 reactions.

25 reactions of the nitrogen chemistry are implemented including reactions of the NO<sub>3</sub> radical. This part was completed with 6 additional or split reaction pathways.

The halogen chemistry (Cl<sub>2</sub><sup>-</sup>/Br<sub>2</sub><sup>-</sup>) and the carbonate chemistry (CO<sub>3</sub><sup>-</sup>) changed only in some few points (2, 3 and 4 processes added, respectively).

Six photolysis processes,  $[\text{Fe}(\text{OH})]^{2+}$ ,  $[\text{Fe}(\text{OH})_2]^+$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $[\text{Fe}(\text{SO}_4)]^+$  and  $\text{H}_2\text{O}_2$ , are formulated for the aqueous phase with photolysis rates from Röth [8]. In the updated version the photolysis processes of  $[\text{Fe}(\text{C}_2\text{O}_4)_2]^-$ ,  $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ ,  $\text{NO}_3$  (assumed to be equal as in the gas phase) and  $\text{CH}_3\text{OOH}$  were also considered.

## 2. Results

### 2.1 Comparison between CAPRAM2.3 and CAPRAM2.4

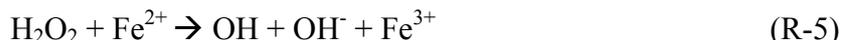
#### 2.1.1 OH and $\text{NO}_3$ radicals

The concentration levels of the OH radical in the aqueous phase were calculated for all three environments with the scheme CAPRAM2.3/RADM2. It is evident that the highest concentration is reached in the marine case ( $4.8 \cdot 10^{-12}$  M), in the other cases it reaches only  $1.9 \cdot 10^{-12}$  M (rural) and  $1.7 \cdot 10^{-12}$  M (urban). In all three cases at noon the phase transfer from the gas phase is the most important source for the OH radical. In the urban and rural case the next important source is the reaction of  $\text{H}_2\text{O}_2$  with  $\text{Fe}^{2+}$  and  $\text{Cu}^+$  while in the marine case nearly 15 % is formed from the photolysis of  $\text{H}_2\text{O}_2$ . Most of the sink reactions are initiated with organic compounds such as  $\text{CH}_2(\text{OH})_2$  and  $\text{HCOOH}/\text{HCOO}^-$ . Since the initial concentrations of the organic compounds in the gas phase in the marine case are nearly one order of magnitude lower than in the other cases, less organics destroy the OH radical.

If larger droplets are considered (= smaller total surface) the OH concentration in the urban case is decreased to  $5.5 \cdot 10^{-13}$  M (CAPRAM2.3/RACM). After the update of the mechanism to CAPRAM2.4 its concentration is more than doubled up to  $1.2 \cdot 10^{-12}$  M in the urban case. The main reasons for this effect are (1) the new implemented reaction



as an effective OH source, (2) a loss of importance of  $\text{CH}_2(\text{OH})_2$  and  $\text{HCOOH}/\text{HCOO}^-$  as sinks due to their smaller concentrations within the droplet (changed Henry's Law Constant for HCHO), (3) the increased importance of the photolysis of  $\text{Fe}(\text{OH})^{2+}$  because more Fe(III) is in the system and (4) the reaction of  $\text{H}_2\text{O}_2$  and  $\text{Cu}^+$  is less effective (see section 3.1.2 'transition metal chemistry'). A remarkable point is that the trend of the OH concentration was inverted compared to CAPRAM2.3: Whereas there in the marine case the highest concentration was found, now the urban concentration is up to a factor of four higher than in the remote case ( $7 \cdot 10^{-13}$  M) and in the marine case ( $3 \cdot 10^{-13}$  M). Here the importance of the Fenton reaction

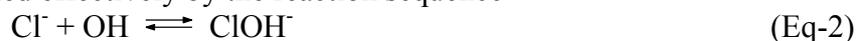


becomes evident. Because of the very effective  $\text{SO}_2$  oxidation in the urban case (section 3.1.3) much more  $\text{H}_2\text{O}_2$  is remaining in the urban case, so that (R-5) overcompensate the decay of OH by organics in the urban case.

Also the  $\text{NO}_3$  radical in the aqueous phase shows essential changes: Whereas in CAPRAM2.3 the diurnal variation of  $\text{NO}_{3(\text{aq})}$  follows that of the corresponding gas phase species, now it shows significant maxima during day. In CAPRAM2.3 the only source for  $\text{NO}_{3(\text{aq})}$  is the uptake from the gas phase with fluxes of  $1.8 \cdot 10^{-11}$  M  $\text{s}^{-1}$  (day) and  $2.7 \cdot 10^{-10}$  M  $\text{s}^{-1}$  (night). The main sinks are the reactions with chloride (>70%) and bromide (>20%). In CAPRAM2.4 also the back reaction of the first mentioned process is included



Because the Cl atom is formed effectively by the reaction sequence



the chlorine atom acts during day - because of high OH concentrations - as an such effective  $\text{NO}_3$  source, that  $\text{NO}_3$  is even transported into the gas phase (at least in the urban case). Since the fraction of  $\text{NO}_3$  in the aqueous phase is so small compared to the total  $\text{NO}_3$  budget, the

influence to the gas phase is small showing only a slightly enhanced day time concentration compared to the former version.

The effect of 'day-time-NO<sub>3</sub>' can be observed partly also in the remote and marine case, but because there the OH concentration is lower the maxima are not so significant as in the urban case.

### 2.1.2 Transition metal chemistry

An essential difference between the two versions of CAPRAM is the treatment of transition metal ions. Whereas in CAPRAM2.3 and in other mechanisms (e. g. [ ]) Fe(III) is reduced by copper within the first few time steps, CAPRAM2.4 represents the highly dynamic redox cycling of iron in the tropospheric aqueous phase. This effect is initialised by the new added reaction



having an effective flux because of the high O<sub>2(aq)</sub> concentration (3·10<sup>-4</sup> M). With this less Cu<sup>+</sup> is available reducing Fe(III),



so that the Fe(III) concentration is higher by about three orders of magnitude. The Fe(III) complexes are photolysed during day time forming Fe<sup>2+</sup> ions,



so that its concentration predominate then, whereas during night Fe(III) species represent the main part of iron.

### 2.1.3 Sulfur oxidation

In CAPRAM2.3 the HSO<sub>3</sub><sup>-</sup> concentration decreases from 9.7·10<sup>-7</sup> M to 5·10<sup>-8</sup> M over a time period of 96 h when 1 μm droplets are considered. Here the sulfur oxidation takes mainly place by radicalic pathways: HSO<sub>3</sub><sup>-</sup> reacts with OH, Cl<sub>2</sub><sup>-</sup> or Br<sub>2</sub><sup>-</sup> forming the SO<sub>3</sub><sup>-</sup> radical anion which is immediately oxidised to SO<sub>5</sub><sup>-</sup>. Transition metal ions (Fe<sup>2+</sup>, Mn<sup>2+</sup>) lead to HSO<sub>5</sub><sup>-</sup> which is further converted to SO<sub>4</sub><sup>-</sup> by the same species. The main sink for SO<sub>4</sub><sup>-</sup> is the reaction with chloride forming finally HSO<sub>4</sub><sup>-</sup>/ SO<sub>4</sub><sup>2-</sup>. Other oxidation pathways, such as the reaction with hydrogen peroxide and ozone have only a contribution of about 20 % to the total loss of HSO<sub>3</sub><sup>-</sup>.

This reaction pattern changes if a larger droplet radius is assumed: Because of the smaller surface higher OH and organics concentrations remain in the gas phase. So, there more HO<sub>2</sub> is formed being in equilibrium with HNO<sub>4</sub>. Its concentration is enhanced by a factor of 10 in the gas phase corresponding to the ratios of the total droplet surfaces. HNO<sub>4</sub> is transported into the droplet where it can act then as a further S(IV) sink (up to 40 % of the total S(IV) loss in CAPRAM2.3).

In CAPRAM2.4 the total S(IV) is oxidised within some few hours of simulation by hydrogen peroxide. This can be ascribed in essential to three different effects: (1) The direct oxidation of copper by oxygen leads to a high O<sub>2</sub><sup>-</sup>/HO<sub>2</sub> concentration. These species form H<sub>2</sub>O<sub>2</sub> by the reactions with Fe<sup>2+</sup>/Cu<sup>+</sup>. (2) The change of the Henry's Law Constant for formaldehyde causes an increase of the OH concentration because HCHO can act as a very effective sink for this radical. Since every oxidation step of an organic compound by OH lead to HO<sub>2</sub> also from this change the HO<sub>2</sub> concentration is enhanced. (3) Due to the consideration of the iron-oxalato-complexes a significant fraction of the iron exists in a complexed form: under urban conditions the concentration of the mono-oxalato-complex is about 1·10<sup>-6</sup> M being 20 % of

the total iron. So, less Fe(II) is available being an important sink for hydrogen peroxide. In total, all these effects lead to a higher H<sub>2</sub>O<sub>2</sub> concentration (a factor of 2 during day, and even a factor of 100 during night) compared to CAPRAM2.3 so that the radical pathways of the sulfur oxidation are compensated.

#### 2.1.4 Difunctional C<sub>2</sub> organic compounds

As mentioned before in CAPRAM2.4 the C<sub>2</sub> organic chemistry was further completed considering the difunctional C<sub>2</sub> compounds glyoxal, oxalate/ oxalic acid and glyoxylic acid. The chemistry of glyoxal in the gas phase is restricted to the formation mainly by peroxy radicals from aromatics and as loss processes the photolysis and the reaction with OH and NO<sub>3</sub>. The latter two processes are very slow so that glyoxal accumulates during night if uptake and further aqueous processes are not considered. It could be shown that these species are oxidised very effectively in the aqueous phase forming glyoxylic acid and oxalate. In the urban case after three days of simulation maximum concentrations for CH(OH)<sub>2</sub>CH(OH)<sub>2(aq)</sub>, CH(OH)<sub>2</sub>COOH<sub>(aq)</sub> and HC<sub>2</sub>O<sub>4</sub><sup>-</sup> of 4·10<sup>-8</sup> M, 4·10<sup>-8</sup> M and 3·10<sup>-8</sup> M, respectively, can be found. It is interesting to note that this oxalate concentration is independent of the fact whether an initial concentration for oxalate is used or not usually estimated equal as iron [16]. So, it can be concluded that oxalate is formed indirectly from the aromatic oxidation in the gas phase. Maybe this could be a hint how to explain high oxalate concentrations found in particles in field measurements [17].

## 2.2 The influence of emissions/depositions

All calculations described until now were based on outputs of simulations with a closed box, i. e. without any exchange processes with the environment. As indicated in section 3.1.3 under these conditions there are species, such as SO<sub>2</sub>, which are oxidised within a short time of simulation. This effect can be also observed for other species (NO<sub>2</sub>, organics) so that the urban scenario is not really polluted anymore after some time of simulation. To avoid this total oxidation emissions and depositions were implemented permitting the renewal of the trace gases in the box and keeping the concentration levels of these species more or less constant during the whole simulation time. If emissions as additional sources are considered several reaction patterns discussed before are changed.

### 2.2.1 pH value

The high SO<sub>2</sub> emission in the urban case (3.27·10<sup>7</sup> cm<sup>-3</sup> s<sup>-1</sup>) and the amount of the emitted organics lead to a very significant acidification of the droplet. The latter effect can be explained with the formation of HO<sub>2</sub> in every oxidation step of organics and then the following reaction in the aqueous phase



The dissociation of SO<sub>2</sub> in the aqueous phase and (R-8) have contributions of 23 % and 58 %, respectively, to the formation of H<sup>+</sup> (urban case, t = 36:00). This observation corresponds to the detailed presentation of the influences of TMI to the pH value [2]. So the pH value is decreased by nearly one unit from 2.8 to 2.0 when emissions are considered.

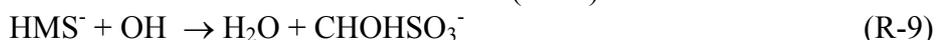
### 2.2.2 OH<sub>(aq)</sub> and NO<sub>3(aq)</sub> radicals

The concentration of the OH<sub>(aq)</sub> radical is decreased from 1.2·10<sup>-12</sup> M to 2·10<sup>-14</sup> M in the urban case after 36 h hours of simulation when emissions and depositions are considered. On the one hand a lot of organics are emitted consuming OH in the gas phase; formaldehyde gains in importance as sink species in the aqueous phase (with emissions 47% of 4.9·10<sup>-6</sup> M s<sup>-1</sup>; without emissions 19% of 1.9·10<sup>-8</sup> M s<sup>-1</sup>). On the other hand the relative high emission of SO<sub>2</sub>

and the additional source of formaldehyde lead to significant concentrations of the HMS<sup>-</sup> complex viz



so that the reaction of HMS<sup>-</sup> acts also as an essential OH sink (19 %).



Due to the very low SO<sub>2</sub> concentration in the studies without emissions there is a high H<sub>2</sub>O<sub>2</sub> concentration. So in this case the Fenton reaction (R-5) is an essential source for OH. But if the SO<sub>2</sub> budget is more or less constant during the simulation the H<sub>2</sub>O<sub>2</sub> concentration is controlled by this species, so that less OH is formed by reaction (R-5). So, the most important source for OH is the photolysis of nitrate (41%) due to the additional emission of NO. The emissions of organics determine the concentration levels of OH<sub>(aq)</sub> in this way that in the remote case a slightly higher concentration can be found (1.2·10<sup>-13</sup> M) and in the marine case the highest (2.7·10<sup>-13</sup> M) because roughly the organic emissions in the urban case are 100 times higher than in the remote case and even 10<sup>4</sup> times higher than in the marine case.

In these second runs of model studies the NO<sub>3(aq)</sub> radical does not show such sharp day time maxima in the urban case because of the significant reduced OH concentration. In total, in all three cases the NO<sub>3</sub> concentration averaged over the simulation time is enhanced up to 1·10<sup>7</sup> cm<sup>-3</sup>, 6·10<sup>6</sup> cm<sup>-3</sup> and 2·10<sup>6</sup> cm<sup>-3</sup> in the three cases, respectively, due to NO emissions leading finally to NO<sub>3</sub>.

### 2.2.3 Sulfur(IV)

For SO<sub>2(g)</sub> emissions were implemented compensating the fast consume of S(IV) by hydrogen peroxide. Having a relative large emission flux of SO<sub>2</sub> in the urban case compared to the other two cases (being about 100 or 400 times higher, respectively) the SO<sub>2</sub> concentration even increases up to a level of 2·10<sup>12</sup> cm<sup>-3</sup> after four days of simulation whereas it is decreased in the remote and marine case to a level of about 10<sup>8</sup> cm<sup>-3</sup> after the first day.

## 2.3 The mechanism reduction

To facilitate the application of the aqueous phase mechanism in a 1D model (contributor 4) the aqueous phase scheme should be reduced from 440 to at most 220 aqueous phase processes. The basis of the reduction was the output of the extended mechanism considering also emissions/depositions. Species were selected for which the concentrations should be equal (± 5 %) in the reduced scheme compared to the complete scheme: OH, S(IV), NO<sub>x</sub> (= NO + NO<sub>2</sub>), NO<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub> and H<sup>+</sup>. Three different non-numerical approaches were used by the three groups performing this part of the project (contributor 1, 2 and 3). The method used here was analysis of sinks and sources of the selected target species in this way that processes were removed with contributions of < 1% to the total production/ loss of the species at t =

$$\frac{d[\text{OH}]}{dt} = -(k_1[\text{OH}][\text{CH}_3\text{OH}] + \underbrace{k_2[\text{OH}][\text{Cu}^+]}_{< 1\% \text{ of } \frac{d[\text{OH}]}{dt}} + \dots)$$

36:00 h and t = 48:00 h:

The removed processes were investigated and such processes were resumed which were either links between acids and their anion or the only sink for a species or essentially for CAPRAM2.4 (e.g. oxidation of C<sub>2</sub> species). This suggested mechanism contained 215 aqueous phase processes. Since every of the three groups suggested different schemes for which also the required conditions were fulfilled a combination of the three schemes was found representing the concentration levels for the selected species very well in the urban case. After some few changes the reduced scheme was also applicable for the other scenarios.

The final 'CAPRAM2.4-reduced' includes 183 aqueous phase processes and 33 phase transfers. (The uptake of peroxy acetic acid could be neglected because all of its reactions in the aqueous phase were removed.) It becomes evident that the chemistry of manganese and the carbonate radical anion  $\text{CO}_3^-$  can be neglected under the conditions chosen for the simulations. An essential part of the organic reactions (59 processes) could be removed because it became clear that in the aqueous phase the organic oxidation can be described by only the reactions of OH.

## 2.4 Consideration of another data set of initial concentrations and emissions/depositions

Additional to the first data set of initial concentrations as used for CAPRAM2.3 [1,2] and the emission/ deposition values another data set was considered in which some of these values were revised. In the urban case the  $\text{SO}_2$  emission was reduced to a tenth and the initial value (10 ppb) was reduced to 5 ppb because the studies made with these values showed that its emission is so high that the amount of sulfur(IV) determines essentially the chemistry in the urban case. Furthermore the initial concentrations for HCl were set in the urban, remote and marine case from 6, 0.7 and 5 ppb to 0.2, 0.1 and 0.5 ppb, respectively. Major revisions were also made in the marine case where several emissions fluxes for organics were set to zero.

### 2.4.1 Effects of the changed input parameters

As mentioned before  $\text{HMS}^-$  represents an important sink for  $\text{OH}_{(\text{aq})}$  in the urban case. With a smaller flux of sulfur(IV) less  $\text{HMS}^-$  is formed so that more  $\text{OH}_{(\text{aq})}$  is remaining in the aqueous phase ( $1 \cdot 10^{-13}$  M). In the marine case less organic material is present in both phases because of 'switching off' their emissions. This leads to the effect that the  $\text{OH}_{(\text{aq})}$  concentration is increased by about 10 % to  $3 \cdot 10^{-13}$  M.

The initialised  $\text{HCl}_{(\text{g})}$  dissociates immediately in the aqueous phase, so that in the former data set it led to a doubling of the initial chloride concentration in the urban case. Also in the other two cases it had an essential contribution to the chloride budget in the droplet. As indicated in section 3.1.1 chloride can be converted by OH to chlorine atoms forming via (Eq-1)  $\text{NO}_3$  radicals. If the chloride concentration is diminished the equilibrium is not shifted anymore to the side of the  $\text{NO}_3$  radicals so that the main maxima of  $\text{NO}_{3(\text{aq})}$  are during night in all three cases.

Using more moderate initial values for SO in the urban case there is no increase in this concentration anymore in the gas phase; it is reduced to  $10^{10}$   $\text{cm}^{-3}$  after three days of simulation. Corresponding to this the  $\text{H}_2\text{O}_{2(\text{g})}$  concentration is enhanced by two orders of magnitude up to  $2 \cdot 10^{10}$   $\text{cm}^{-3}$  during daytime.

The reduced scheme was also tested with these changed input parameters showing that it is also applicable for this data set.

## 2.5 Effects of cloud chemistry to gas phase concentration levels

The main goal of the development an explicit aqueous phase mechanism is clarifying the effects of cloud chemistry having to the gas phase oxidation capacity. Already with the original mechanism CAPRAM2.3 these considerations were made leading to the insight that trace gas concentrations are reduced by uptake processes and further consume of species in the aqueous phase. But there are also examples where gas phase concentrations are increased if aqueous phase chemistry is considered.

The OH concentration is reduced during day by 44 % (47 % in CAPRAM2.4) compared to model simulations with the gas phase scheme RACM. The same is valid for  $\text{NO}_3$  for which the concentration from both schemes is reduced by nearly two orders of magnitude (from  $10^9$   $\text{cm}^{-3}$  to less than  $10^7$   $\text{cm}^{-3}$ ). Both species are not very soluble but their consume within the aqueous phase is so fast that their fluxes into the droplets is very high.

The methyl peroxy radical shows an essential difference between CAPRAM2.3 and CAPRAM2.4 influencing the gas phase: whereas its concentration level is enhanced by 113 % (day time, after 36 h hours) considering CAPRAM2.3 it is reduced by 48 % when the aqueous phase scheme is replaced by CAPRAM2.4. On the one hand a higher Henry's Law Constant is responsible and on the other hand - to a smaller extent - the further sink for the radical with  $\text{Fe}^{2+}$ .

The most evident difference can be seen in the  $\text{SO}_2$  level, for which after 36 h the concentration level is decreased to 71 % in CAPRAM2.3 but to 100 % by CAPRAM2.4.

It is understandable that unsloube organic species (alkanes, alkenes) are also influenced essentially if aqueous phase is considered: Their only sink are reactions with OH,  $\text{NO}_3$  and  $\text{O}_3$  so that more of these organics remain in the gas phase when their sink species are consumed by uptake processes (e.g. up to + 92 % for alkanes during day and even +3650 % for internal alkenes during night).

If emissions are considered these general trends change for some species, e. g. an enhanced NO concentration can be found (+5 % vs. -57 %) in presence of the aqueous phase because of much lower ozone concentrations (-54 %) being the main sink species for NO in the gas phase. Also the  $\text{SO}_2$  concentration decreases more moderately (-17 % vs. -100 %) because of the continuous emission flux of  $\text{SO}_2$ .

## 2. Laboratory studies

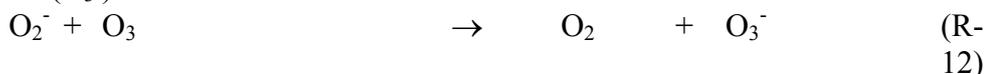
Because it is known [18] that the ozone concentrations are reduced when cloud chemistry was included. In aqueous solution the reaction of  $\text{O}_2^-$  with ozone are of interest for the decomposition of ozone and for recycling of OH-radicals in the tropospheric droplets. This reaction leads to  $\text{O}_3^-/\text{HO}_3$  which decays in the last step to O/OH [19].

The reaction of  $\text{O}_2^-$  radical anion with ozone and the following decay of the  $\text{O}_3^-$  radical anion including its temperature dependence in the range of 278 – 308 K was investigated with a laser photolysis-long path absorption apparatus (LP/LPA). The absorption spectrum of the ozonide radical in aqueous solution was measured with a diode-array-absorption-apparatus.

$\text{O}_2^-$  was generated at pH = 10.0 by laser photolysis of sodium acetate according to:



The superoxide radical anion formed in this reaction reacts with added ozone to form the ozonide radical anion ( $\text{O}_3^-$ ):



For the kinetic investigations  $\text{O}_3^-$  has been monitored by using the output of a high power halogen lamp at 430 nm recorded with a monochromator/photomultiplier combination. To increase the sensitivity of the experiment the light beam was reflected eight times through the reaction cell by the use of two aluminium coated mirrors in White configuration. In this study the rate coefficients of the formation (12) and the decay of  $\text{O}_3^-$  (13) were measured in the temperature interval between 278 and 318K. The following Arrhenius-expressions are derived

$$k_{12} (T) = (2.3 \pm 0.3) \cdot 10^{12} \cdot \exp [-(2200 \pm 1100)\text{K}/T] \text{ l} \cdot (\text{mol} \cdot \text{s})^{-1}$$

$$k_{13} (T) = (7 \pm 1) \cdot 10^9 \cdot \exp [-(4500 \pm 1000)\text{K}/T] \text{ s}^{-1}$$

corresponding to activation energies of  $E_A$  (12) =  $(18 \pm 9) \text{ kJ} \cdot \text{mol}^{-1}$  and  $E_A$  (13) =  $(37 \pm 9) \text{ kJ} \cdot \text{mol}^{-1}$ , respectively.

### 3. Conclusion

In close co-operation with contributor 2 the aqueous phase mechanism CAPRAM2.3 was revised, updated and further completed. The main revised parts are the organic chemistry and the transition metal (TMI) chemistry where on the one hand difunctional compounds were added and on the other hand reactions were added representing the high dynamic behaviour of TMI.

With the resulting aqueous phase mechanism CAPRAM2.4., coupled to the gas phase RACM and a set of uptake processes an intercomparison between the three groups (contributor 1, 2 and 3) was performed confirming same results from the model studies with different model programs.

The main part of the work performed was the interpretation and elucidation of differences between the former and the actual version and the effects caused by implementation of emissions/depositions in the box model.

With the new aqueous phase scheme a dynamic redox cycling of iron depending of the time of day is represented. Furthermore significant oxalate concentrations (in the range of  $10^{-8}$  M) in the droplet can be explained by aromatic oxidation in the gas phase forming glyoxal which is transported into the aqueous phase which is oxidized in the aqueous phase by radicals to glyoxylic acid and finally to oxalate. In CAPRAM2.4 the sulfur oxidation is much more effective than in CAPRAM2.3, so that sulfur is totally oxidized after some hours of oxidation. To avoid such effects emissions and depositions were implemented allowing renewal of trace gases. Because of higher fluxes of organic species, SO<sub>2</sub> and NO<sub>2</sub> reaction patterns changed so that e. g. the OH concentration was influenced in this way that in the urban case more is present (due to less loss by HMS<sup>-</sup>) and in the marine case it is increased because of lower organic emissions compared to the other cases.

In close co-operation with contributor 2 and 3 a reduced aqueous phase scheme was created allowing the implementation of the aqueous phase scheme developed in a 1D model. There it became evident that organic oxidation can be described proper exclusively by reactions of OH and that manganese and CO<sub>3</sub><sup>-</sup> reactions can be neglected under the conditions used here.

Finally it was shown that the cloud chemistry described by CAPRAM2.4 can influence essentially gas phase concentration levels of trace gases and radicals.

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## Contractor 2:

### **Model Development for the Chemistry of the Atmospheric Aqueous Phase with Particular Reference to Sulfur Chemistry and the Influence on it of Organic Pollutants.**

**Contractor:** The University of Leeds  
**Leading Scientists:** Drs G. V. Buxton and G. A. Salmon.

**Scientific Staff:** Dr J. E. Williams (1.4.98 to 30.9.99), Mr J. Wang (1.10.98 to 30.9.99), Dr M. Bydder (1.10.99 to 31.3.00) and Dr F. Wilkinson (1.10.99 to 31.3.00, 40% FTE).

#### **1. Objectives for reporting period.**

The overall objective of the project was to develop a box model to describe tropospheric chemistry occurring in the gas and aqueous phases. The model was to incorporate the gas phase model RACM of Stockwell *et al.*<sup>1)</sup> and also an extensive aqueous phase mechanism which was to be developed from the CAPRAM 2.3 scheme of Herrmann *et al.*<sup>2)</sup> The scheme was to take particular account of the reactions of free radicals and their reactions with C1 and C2 organic pollutants and the products of these reactions.

Specific objectives were:

- i). To continue the construction of the aqueous phase reaction scheme and the review of the rate constants and other kinetic data.
- ii). To incorporate into the model the diurnal variation in photolysis rates of the gas and aqueous phase photolysis processes.
- iii). To incorporate in the model emissions and depositions into, and from, the gas phase that are appropriate to the remote, urban and marine scenarios in a European context.
- iv). To describe the mass transfer of species between the gas phase and the aqueous droplets by the Schwartz model.<sup>3)</sup>
- v). To carry out thorough checks of the consistency between the output of the program modules developed in Leeds, Leipzig and Strasbourg/Lyon.
- vi). To develop a reduced aqueous phase mechanism suitable for use in the 1-D cloud modelling associated with this project and which may be applied in larger regional and global models.
- vii). To apply the model to some case studies, particularly the generation of S(VI) in cloud droplets.
- viii). Where gaps are identified in existing knowledge of the rate parameters required for a proper formulation of the aqueous phase reaction scheme, experiments were to be performed, where feasible, to acquire the relevant data

#### **2. Main activities and results**

##### **2.1 Modelling and data review.**

As described in the interim report, the decision was taken to use the FACSIMILE code<sup>4)</sup> as the integrator for the computation of the model and the Stockwell RACM scheme<sup>1</sup> to represent the gas phase chemistry since this is a well defined state-of-the-art model. The version of RACM utilises 23 photolysis reactions and 214 thermal reactions for 78 species. In addition, emissions to, and depositions from the gas phase were implemented. The emissions were represented by 22 zero-order processes and the depositions by 15 first-order processes. The kinetic data for these were reviewed by, and obtained from, contractors 3 and 4.

The full aqueous phase mechanism, which is designated CAPRAM 2.4 (MODAC), comprises 11 photolysis reactions and 437 thermal reactions involving 153 species. Photolysis rates in both phases were computed using the photon flux algorithm of Roth.<sup>5)</sup>

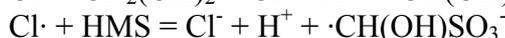
Mass transfer between the gas and aqueous phases was represented by 34 equilibria, the rate parameters for which were calculated using the Schwartz model.<sup>3</sup> The parameters required, namely the gas phase diffusion coefficients and the mass accommodation coefficients were assembled, reviewed and provided by Contractor 3. Most model runs used a drop radius of 10  $\mu\text{m}$  and a liquid water content of  $0.3\text{g m}^{-3}$ .

Considerable effort was expended in achieving consistency between the model modules developed in Leeds, Leipzig and Strasbourg/Lyon (Objective (v)).

Reduction of the aqueous phase mechanism and the establishment of which were the most important reactions were tackled together. The method followed was to run the model with the complete reaction scheme with cloud 'ON' for 24 hours using dummy products to give the throughput for each reaction. For example, for the urban scenario, these throughputs ranged over 30 orders of magnitude. Reactions with throughputs less than 15 orders of magnitude below those of the most significant reactions were excluded from the mechanism. Interaction between the groups involved in the box modelling (Leeds, Leipzig and Strasbourg/Lyon) resulted in the formulation of a reduced aqueous phase reaction scheme which is very robust to changes in the initial scenarios. This reduced version of CAPRAM 2.4(MODAC) retained 4 photolysis reactions and 179 thermal reactions.

## 2.2 Extensions to CAPRAM 2.4.

During the course of this work, other studies from our Laboratory<sup>6), 7)</sup> indicated that some of the rate parameters for the reactions of  $\text{Cl}_2^-$  radical are in error and that reactions of the Cl-atom are likely to be more relevant than those of  $\text{Cl}_2^-$ , with the consequence that the predictions by the model of the effect of  $[\text{Cl}^-]$  will be erroneous. This possibility was examined in detail by the addition of 28 reactions each for Cl and Br. Unfortunately, many of the rate constants for the reactions of Br have not been measured and estimates of these were, therefore, made. The most significant effects were reductions in  $[\text{Cl}_2^-]$  by a factor of  $\sim 2$  and of  $[\text{Br}_2^-]$  by  $\sim 100$  for the urban scenario. In general  $\text{Br}_2^-$  is of minor importance to the overall scheme. However, we recommend the addition of the Cl-atom reactions to the full scheme, with corresponding modifications to the rate constants for the  $\text{Cl}_2^-$  reactions. For the reduced mechanism we recommend the addition of the following reactions:



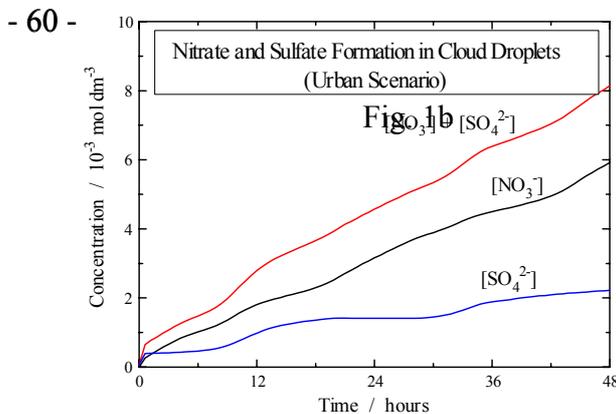
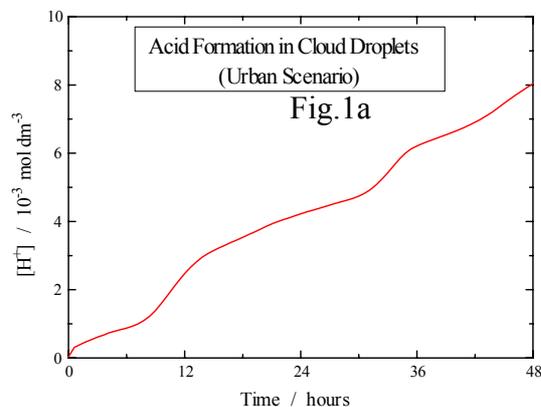
and



The rate constant for the reaction of  $\text{Cl}\cdot$  with  $\text{H}_2\text{O}_2$  has not been measured, but is likely to be close to the diffusion controlled limit.

## 2.3 Case Studies.

a) **Production of S(VI) and acidity.** The computed increases in  $[\text{H}^+]$ ,  $[\text{SO}_4^{2-}]$  and  $[\text{NO}_3^-]$  with time for the urban scenario with permanent cloud and using the full scheme (CAPRAM 2.4(MODAC)) are shown in Figs 1a and 1b. These data indicate that high acidities ( $\text{pH} < 2.1$ ) are attained. In addition, it is clear that, for the urban scenario, nitric acid is also an important source of acidity.



Figs. 2a and 2b show the sources of S(VI) for the urban and remote scenarios. For the urban scenario, the main oxidant is pernitric acid, but hydrogen peroxide and ozone also make significant contributions. For the remote scenario, however, hydrogen peroxide is the main contributor (~88%). These results are in agreement with the recent modelling study by Warneck<sup>8)</sup>

Fig. 2a

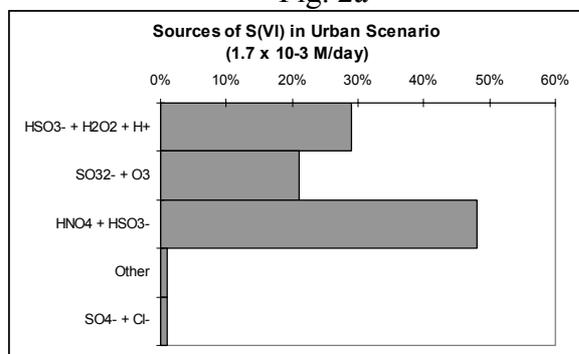
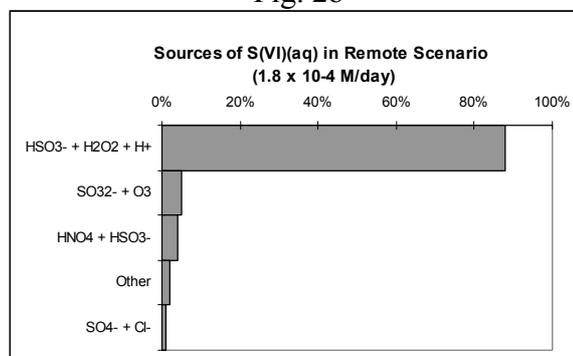


Fig. 2b

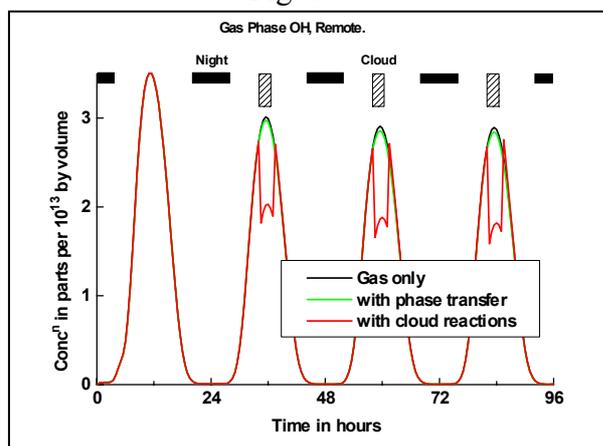


It is clear that for these scenarios free-radical induced oxidation of S(IV) to S(VI) is a minor process. This is due to the efficient scavenging of  $\cdot\text{OH}$  and  $\text{SO}_4^{\cdot-}$  by organic pollutants. This was demonstrated by running the model for the remote scenario with the transfer of organic species from the gas phase to the aqueous phase 'switched off'. Under these conditions hydrogen peroxide contributed ~57% to the oxidation of S(IV) while the reaction of  $\text{SO}_4^{\cdot-} + \text{Cl}^-$  contributed ~20%.

### b). Influence of cloud on the gas phase.

In fig. 3 is shown the time profile of  $\cdot\text{OH}$  concentration in the gas phase for the remote scenario and the influence of the presence of cloud on it. In this example the cloud is 'switched on' for periods of three hours from 10.0am. to 1.00pm. on the second and subsequent days.

Fig. 3



Time profiles have also been obtained for  $\text{HO}_2^{\cdot}$ ,  $\text{NO}_3^{\cdot}$  (cloud at night),  $\text{H}_2\text{O}_2$ ,  $\text{O}_3$ , HONO and HCOOH under remote and urban conditions. Those for formic acid and HONO are of particular interest since they show that cloud can act as a source of these species to the gas phase, see Figs 4 and 5.

"

Fig. 4

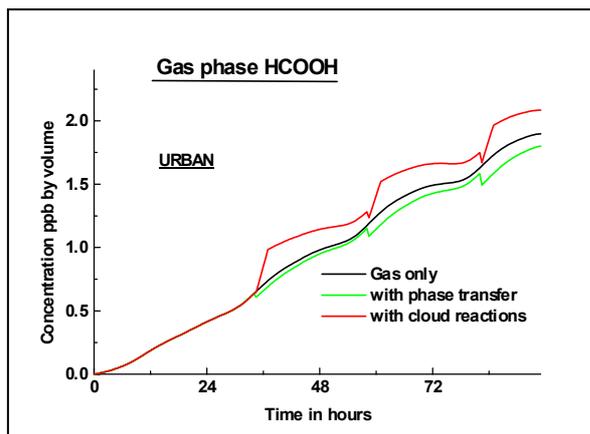
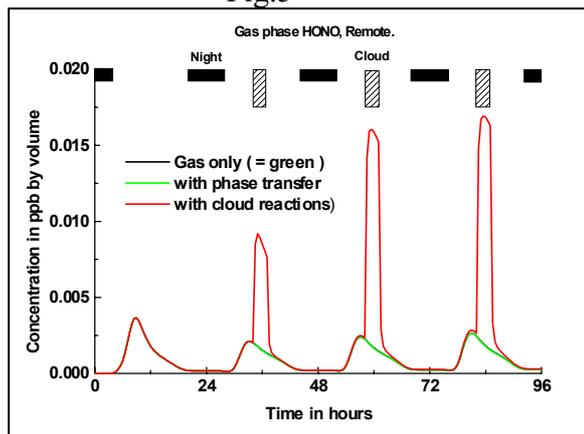


Fig.5



The effect of cloud on the gas phase concentrations of the above species is summarised in Table 1.

Table 1

Effect of cloud on Gas Phase Concentrations. <sup>a</sup>		
	$\Delta c/c_{\text{No Cloud}} \times 100$	
	Remote	Urban
OH	-32.2	-59.5
HO <sub>2</sub>	-73.1	-61.4
NO <sub>3</sub> <sup>b</sup>	-97.3	-96.5
O <sub>3</sub>	-4.1	-10.1
H <sub>2</sub> O <sub>2</sub>	-58.9	-99.9
HCOOH	+37.5	+20.8
HONO	+457.3	-71.8

<sup>a</sup> At midday.

<sup>b</sup> At midnight (cloud on 10.0 pm to 1.00 am.)

#### 2.4 Experimental Studies.

A number of rate constants were measured which were considered to be central to the requirements of the modelling. They were determined either by the pulse radiolysis or laser flash photolysis techniques and are listed in Table 2.

**Table 2**  
**Rate constants, k, for some Reactions of Free Radicals**  
**in Aqueous solution**

Reaction	$k^a/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	comments
$\text{Cl} + \text{NO}_3^-$	$(1.02 \pm 0.04) \times 10^8$	$I^b \rightarrow 0$
$\text{NO}_3 + \text{Cl}^-$	$(3.4 \pm 0.1) \times 10^8$	$I \rightarrow 0$
$\text{NO}_3 + \text{HCOOH}$	$(1.9 \pm 0.1) \times 10^4$	$[\text{HNO}_3] = 2.0 \text{ mol dm}^{-3}$ $E_a = 36 \pm 2 \text{ kJ mol}^{-1}$
$\text{NO}_3 + \text{HCOO}^-$	$(4.2 \pm 0.1) \times 10^7$	$I = 1.0 \text{ mol dm}^{-3}$
$\text{NO}_3 + (\text{COOH})_2$	$(2.4 \pm 0.2) \times 10^4$	$[\text{HNO}_3] = 2.0 \text{ mol dm}^{-3}$ $E_a = 41 \pm 2 \text{ kJ mol}^{-1}$
$\text{NO}_3 + \text{HC}_2\text{O}_4^-$	$(6.8 \pm 0.7) \times 10^6$	$I = 1.0 \text{ mol}$
$\text{NO}_3 + (\text{COO}^-)_2$	$(2.2 \pm 0.1) \times 10^8$	$I = 1.0 \text{ mol dm}^{-3}$
$\text{OH} + \text{GMBS}^c$	$(1.7 \pm 0.4) \times 10^9$	$I \leq 3 \times 10^{-2} \text{ mol dm}^{-3}$
$\text{OH} + \text{GDBS}^d$	$(7.3 \pm 2.3) \times 10^7$	$I \leq 3 \times 10^{-2} \text{ mol dm}^{-3}$
$\text{SO}_4^- + \text{GMBS}$	$(2.6 \pm 0.5) \times 10^8$	$I = 3.0 \text{ mol dm}^{-3}$
$\text{SO}_4^- + \text{GDBS}$	$(1.8 \pm 0.9) \times 10^6$	$I = 3.0 \text{ mol dm}^{-3}$
$\text{Cl} + \text{Glyoxal}$	$(6.2 \pm 0.4) \times 10^8$	$I \sim 0$
$\text{Cl} + \text{GMBS}$	$(1.9 \pm 0.7) \times 10^8$	$I \leq 10^{-2} \text{ mol dm}^{-3}$
$\text{Cl} + \text{GDBS}$	$(1.5 \pm 0.4) \times 10^8$	$I \leq 10^{-2} \text{ mol dm}^{-3}$
$\text{SO}_4^- + \text{HC}_2\text{O}_4^-$	$(3.4 \pm 0.1) \times 10^5$	$I \rightarrow 0$
$\text{SO}_4^- + (\text{COO}^-)_2$	$(1.03 \pm 0.05) \times 10^6$	$I \rightarrow 0$
$\text{SO}_5^- + \text{HC}_2\text{O}_4^-$	$\leq 2.5 \times 10^4$	
$\text{SO}_5^- + (\text{COO}^-)_2$	$\sim 5 \times 10^4$	

<sup>a</sup>  $20 \pm 2^\circ\text{C}$     <sup>b</sup> Ionic strength    <sup>c</sup> Glyoxal mono-bisulfite<sup>complex</sup>

<sup>d</sup> Glyoxal di-bisulfite complex.

### 3. Deviations from technical annex.

There were no substantive deviations from the technical annex. Staff for the project were not appointed until 1.4.98, thus resulting in slippage on the timetable and subsequent extension of the period of the contract.

### 4. Conclusions.

A box model, CAPRAM 2.4(MODAC), has been developed to describe tropospheric chemistry in the presence of cloud and fog. The model provides a useful tool for elucidating which reactions are important in the tropospheric aqueous phase and which areas require further research. A version of the model with a reduced sub-set of aqueous phase reactions has also been formulated. This may be used in larger scale regional and global models and should also be a valuable tool for policy makers. For the model to be satisfactorily extended to wet aerosols, much more research on ionic strength effects is needed.

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**Contractor 3:****Modelling and Experimental Study of the Heterogeneous Processes  
at the Gas/Liquid Interface**

**Contractor:** Centre de Géochimie de la Surface - Equipe de Physico-chimie de l'Atmosphère,  
Centre National de la Recherche Scientifique, Strasbourg (F)

**Leading Scientists:** Christian George and Philippe Mirabel

**Scientific Staff:** Géraldine Deiber, Stéphane Lecalve and Francis Schweitzer

**1) Main Objectives**

The main objectives of our group were to evaluate data found in the literature, perform (when necessary) experimental studies in order to close gaps in existing data and finally to implement uptake process according to the current state-of-the-art in the model developed within MODAC.

As will be stated below, these objectives have been mainly achieved during the reporting period.

**2) Main results obtained****2-1) Evaluation of data**

Measurements of mass transfer across the gas/liquid interface (i.e., uptake kinetics) is still a scientific field in its infancy. Nevertheless, several organisations (NASA-JPL or IUPAC) tried to collect and evaluate existing data in this field. These compilations are mostly up to date (NASA-JPL) or on the way to be revised (IUPAC). But it must be underlined that none of these compilations is focused on the processes on liquid water. These latter only represent a small fraction of existing studies despite their central importance for cloud and/or fog chemistries which are, of course, related to air pollution. It finally appears that only a limited number of groups (in Europe but also in the United States) are delivering data that are potentially useful for model devoted to the simulation of wet chemistry. However, the existing data set is far from sufficient in regard to the large variety of species involved in wet chemistry (see other contributions in this project), therefore it is important to close the gap by experimentally measuring these mass accommodations or to find a way to correctly estimates their values.

**2-2) Modelling the mass accommodation process**

The rate of uptake of a trace gas by a liquid is a multi-step process that can be related to fundamental properties of the gas, interface and of the condensed phase such as mass accommodation coefficient, solubility and reactivity.

The uptake process can be summarised as follows:

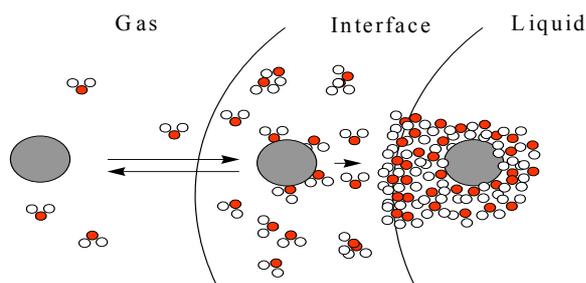
- 1 - diffusion of the molecules in the gas phase toward the liquid interface,
- 2 - transfer across the interface (accommodation process),
- 3 - diffusion and reaction in the condensed phase,
- 4 - eventually, diffusion out and desorption of the reaction products.

The rate at which a trace gas molecule may be transferred, from a well mixed gas phase at a given concentration  $n_{\text{mixed}}$ , into the condensed phase can be obtained from the kinetic theory of gases. This allows the calculation of the maximum flux  $\Phi_{\text{max}}$  that may cross the interface:

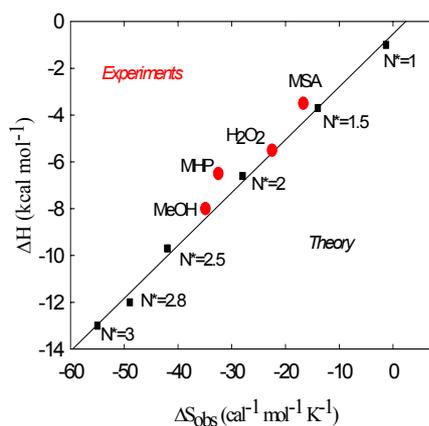
$$\Phi_{\text{max}} = \frac{1}{4} \langle c \rangle n_{\text{mixed}} \alpha \quad (1)$$

where  $\langle c \rangle$  is the trace gas average thermal velocity and  $\alpha$  is the mass accommodation coefficient that characterises the gas/liquid efficiency for the accommodation process. It represents the probability that a molecule, impinging on the interface, will be transferred into the condensed phase.

In order to explain the generally observed negative temperature dependence of  $\alpha$ , Davidovits *et al.* [Davidovits *et al.*, 1991] developed a model, later modified by Nathanson *et al.* [Nathanson *et al.*, 1996] in order to improve the description of the dynamics at the interface. They considered that mass accommodation can be viewed as a multi-step process where the trace gas first thermally accommodates on the droplet surface, with unit probability, and remains adsorbed until it undergoes a further step into the liquid or until it is released back to the gas phase. The step into the liquid being depicted as a continuous nucleation process, at the interface, where only clusters reaching a critical size (defined as  $N^*$ ) by condensation are taken up by the nearby liquid phase (see Figure 1). The critical size is defined as the number of molecules in the cluster or more precisely the number of hydrogen bonds used to form the cluster. In this theory, there is a direct relationship, governed by  $N^*$ , between the changes of enthalpy and entropy when going from the surface state into the bulk i.e.,  $\Delta H_{\text{obs}}$  and  $\Delta S_{\text{obs}}$ . It is interesting to note, from our experiments, that the values of  $\Delta H_{\text{obs}}$  and  $\Delta S_{\text{obs}}$  found for  $\text{CH}_3\text{OOH}$  (MHP) are between those reported for methanol and for hydrogen peroxide indicating that  $N^*$  is related to the chemical structure of the incoming gas (see Figure 2).



**Figure 1:** schematic diagram of the dynamic nucleation processes at the interface (see text for explanations).



**Figure 2:** Theoretical (solid line and squares) and experimental (circle) relationship between  $\Delta H_{\text{obs}}$  and  $\Delta S_{\text{obs}}$  governed by  $N^*$ .

From existing data (such as those measured at Strasbourg), we calculated mass accommodation coefficient as a function of temperature. For this purpose, we made the

following assumption:  $N^*$  is the sum of the contribution of the functional groups present in a molecule, i.e.:

$$N^* = \sum_i N_i^* \quad (3)$$

where  $N_i^*$  is the contribution of the  $i^{\text{th}}$  chemical group in a given molecule. Taking this assumption as a starting point, we tried to obtain values for different chemical structures.

If we consider that  $N^*$  for HOOH is two times the contribution of OH (already note that this does not take care of the peroxy function), it becomes possible to determine the contribution of the OH function as:

$$N_{\text{OH}}^* = N_{\text{H}_2\text{O}_2}^* / 2 \quad (4)$$

**Afterwards, it is possible to calculate the contribution of the methyl, ethyl and peroxy function from  $N^*$  reported for methanol, ethanol and methyl hydroperoxide as listed in table I.**

**Table I: group contribution to  $N^*$**

OH	0.88
CH <sub>3</sub>	1.44
<b>1.1 CH<sub>3</sub>CH<sub>2</sub></b>	1.67
C(O)	0.52
OOH	0.66
H	1.52
COOH	0.84

Then it becomes easy to estimate a mass accommodation coefficient. In fact, for ethyl hydroperoxide,  $N^*$  can be calculated according to:

$$\begin{aligned} N_{\text{EtOOH}}^* &= N_{\text{CH}_3\text{CH}_2}^* + N_{\text{OOH}}^* \\ &= 1.67 + 0.66 \\ &= 2.33 \end{aligned} \quad (5)$$

The changes of entropy and enthalpy can then be determined by using the equation reported by Nathanson *et al.*

$$\Delta H_{\text{obs}} = -10 \times (N^* - 1) + 7.53 \times (N^{2/3} - 1) - 0.1 \times 10 \quad (\text{kcal.M}^{-1}) \quad (6)$$

$$\Delta S_{\text{obs}} = -13 \times (N^* - 1) - 19 \times (N^* - 1) + 9.21 \times (N^{2/3} - 1) - 0.1 \times 13 \quad (\text{cal.M}^{-1}.\text{K}^{-1}) \quad (7)$$

**The mass accommodation coefficient  $\alpha$  is then calculated using:**

$$\frac{\alpha}{1-\alpha} = \exp\left(\frac{-\Delta G_{obs}^*}{RT}\right) \quad (8)$$

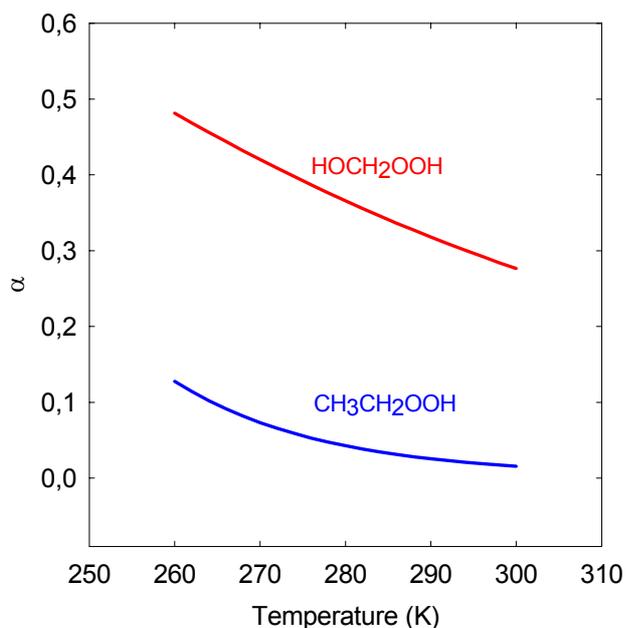
and  $\Delta G_{obs} = \Delta H_{obs}$  et  $\Delta S_{obs}$ .

The corresponding temperature dependent mass accommodation coefficient is depicted in Figure 3 with values for ethyl and hydroxy methyl hydroperoxide. Note that in the current state of knowledge such estimates are to be considered with great care. In fact experimental values should be preferred when available. As shown in table 2, estimated values for  $\alpha$  are relatively close to measured ones, but since the current database is limited, the above described estimation method relies on a weak basis.

**Table 2: Comparison between experimentally determined and estimated mass accommodation coefficients**

	$\alpha_{exp}$ at 288K	Calculated N*	$\alpha_{Estimated}$ at 288K
ethylene glycol	0.0446	2.22	0.038
1-propanol	0.0110	2.76	0.0085
EtOOH		2.33	0.028
CH <sub>2</sub> (OH)OOH		1.46	0.33

However, within this project we developed a framework for estimating mass accommodation coefficients in order to use a systematically derived input data for modelling tasks as described elsewhere in this report. This is the first time that such an approach as been employed for modelling purposes. Of course that method can be generalised in a near future once the database of measured values will have grown substantially.



**Figure 3:** estimated mass accommodation coefficients for ethyl and hydroxy methyl hydroperoxides as a function temperature

### 1.1.1 2-3) Uptake of Hydrogen Halides by Water Droplets

Most of the recent available data have been implemented in up-to-date box model in which chemistry is simulated with great details. However there is still a lack of knowledge concerning the rate of mass transfer at the air/water interface. Therefore, we focussed our attention during this study to the measurement of mass accommodation coefficients of different hydrogen halides i.e., HCl, HBr and HI which are presumably produced during halogen activation episodes. Note that the data derived here have a larger spectrum of applications since, for example, HCl is present in all the troposphere due to volcanoes emissions and/or emissions from a variety of industrial sources ranging from incinerators to perchlorate-fueled space vehicles!

#### 1.1.1.1.1 Experimental section

As already mentioned previously, the rate of uptake of a trace gas by a liquid is a multi-step process related to the mass accommodation coefficient ( $\alpha$ ), the solubility and the reactivity of the trace gas in the liquid phase. The rate at which a trace gas molecule may be transferred into the condensed phase can be obtained from the kinetic theory of gases. This allows the calculation of the net flux  $\Phi_{net}$  that may cross the interface :

$$\Phi_{net} = \frac{1}{4} \langle c \rangle n \gamma \quad (9)$$

where  $\langle c \rangle$  is the trace gas average thermal velocity,  $\gamma$  is the uptake coefficient (taking into account all processes potentially affecting the uptake rate and therefore including  $\alpha$ ) and  $n$  is the gas phase density of the trace gas.

The technique used to measure the uptake rates has already been described elsewhere [Magi *et al.*, 1997; Schweitzer *et al.*, 1998a] and therefore we will only provide a brief summary of its principle of operation. The uptake coefficient is measured by the decrease of the gas phase concentration of the trace species, due to their exposure to a monodispersed train of droplets. These latter are generated by a vibrating orifice (75  $\mu\text{m}$  diameter) leading to droplet diameters in the range 80-150  $\mu\text{m}$ .

The apparatus, where the contact between both phases takes place, is a vertically aligned flowtube which internal diameter is 1.8 cm. Its length can be varied up to 20 cm, in order to change the gas/liquid interaction time (0 - 20 ms) or the surface exposed by the droplet train (0 - 0.2  $\text{cm}^2$ ). Since the uptake process is directly related to the total surface  $S$  exposed by the droplets, any change  $\Delta S$  in this surface results in a change  $\Delta n$  of the trace gas density at the exit ports of the flowtube. Considering the kinetic theory of gases and since we are measuring the averaged signal during the transit time due to changes in the exposed surface, it becomes possible to calculate the uptake rate as: [Worsnop *et al.*, 1989]

$$\gamma = \frac{4F_g}{\langle c \rangle \Delta S} \ln \left( \frac{n}{n - \Delta n} \right) \quad (10)$$

where  $F_g$  is the carrier gas volume flow rate through the system,  $n$  is the trace gas density at the inlet of the flowtube and  $\Delta n = n - n'$  where  $n'$  is the trace gas density at the outlet port of the interaction chamber. By measuring the fractional changes in concentration  $[n/(n-\Delta n)]$  as a function of  $\langle c \rangle \Delta S / 4F_g$ , it becomes possible to determine the overall uptake coefficient  $\gamma$  as shown in Figure 4.

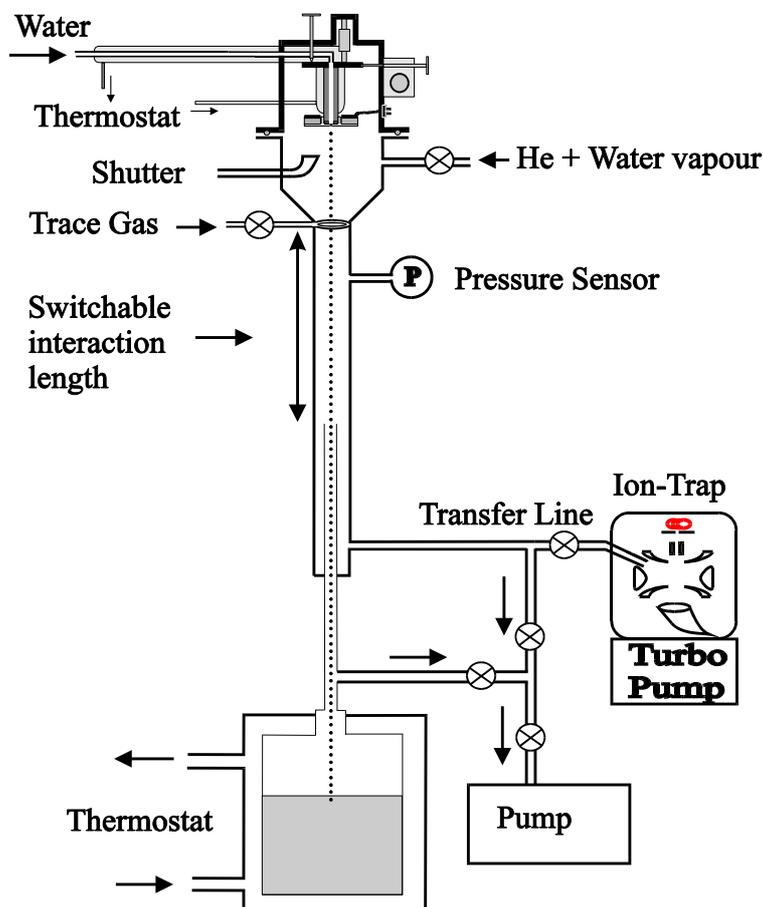


Figure 4 Schematic representation of our droplet train apparatus

Aqueous solutions used to prepare the droplets were made from Milli-Q water (18 MΩ cm) and reagent grade salts when necessary. The different gaseous hydrogen halides were obtained simply by bubbling a known flux of He in an aqueous solution of the corresponding acid. If the latter was not enough concentrated, the solution was acidified with sulphuric acid in order to enhance the amount of hydrogen halide swept out of the solution by the helium flux. The resulting concentrations in the helium flux were in the range  $10^{12} - 10^{14}$  cm<sup>-3</sup> with most experiments performed with a density of about  $10^{13}$  cm<sup>-3</sup>. The gas phase concentration was monitored using an ion-trap mass spectrometer (Varian model Saturn 4D) connected to the exit ports of the flowtube. For that purpose, a small flux of helium (ca. 1cm<sup>3</sup> STP) is continuously sampled through a 50 μm pinhole, diluted with pure Helium and then directly injected in the high vacuum chamber of the ion trap through a ca. 15 cm long heated glass tube (i.d., 1 cm). The gases were then ionised with an electron beam with an energy of 70 eV. A full mass spectrum was taken every second.

All gases used during this study are highly sticky. Therefore in order to achieve a rapid steady-state of the adsorption-desorption processes at the flowtube wall's, all the gas delivery system (including the flowtube itself) were heated at 310-320 K. With such experimental conditions, any change of the gas-phase density, as monitored by mass spectrometry, were simply related to the uptake by the droplets as shown by the first order kinetics we measured. It must also be underlined that due to the moveable outlet of the flowtube, we systematically varied its inner glass surface to volume ratio by a factor of 2 which lead to an easy detection of any wall effects (which were not observed in the course of this work).

#### 1.1.1.1.1 Results

All acids studied here have large effective Henry's law constant due to their dissociation according to:



where X is either Cl, Br or I. Table I lists the effective Henry's law constant found in the literature. It should be mentioned that despite the large solubility of these acids, physical Henry's law (i.e., just referring to gas/liquid partitioning without dissociation) constants may be quite small. In fact, for HCl the physical Henry's law constant was estimated to be of the order of  $1 \text{ M atm}^{-1}$  whereas the chemical dissociation increases this value by several orders of magnitude.[*Clegg and Brimblecombe, 1986; VanDoren et al., 1990*] It was found experimentally that the uptake rates of these acids were not dependent on the interaction time meaning that saturation effects were absent. In such a case, the uptake coefficient may be described according to: [*Worsnop et al., 1989*]

$$\frac{1}{\gamma} = \frac{\langle c \rangle d_{\text{eff}}}{8D_g} - \frac{1}{2} + \frac{1}{\alpha} \quad (12)$$

where  $d_{\text{eff}}$  is the effective droplet diameter [*Worsnop et al., 1989*]. The diffusion coefficient ( $D_g$ ) is not known and therefore had to be estimated by the method presented by Reid et al.

[Reid *et al.*, 1987]. In addition, since our carrier gas is a mixture of helium and water vapour, it was necessary to compute the diffusion coefficient in this background. This was done according to the following equation :

$$\frac{1}{D_g} = \frac{P_{H_2O}}{D_{g-H_2O}} + \frac{P_{He}}{D_{g-He}} \quad (13)$$

where  $P_{H_2O}$  and  $P_{He}$  are the partial pressures of water and helium respectively,  $D_{g-H_2O}$  and  $D_{g-He}$  are the binary diffusion coefficients of the trace gases in water and helium respectively (see Table II for numerical values).

Uptake rate measurements were performed on pure water but also on 1M NaOH solutions. It was found that the uptake kinetics were strictly identical on pure water or on NaOH solutions i.e. independent of the interaction time. This means that the measured uptake rates were not affected by any saturation effects which could have been introduced by a too strong acidification of the surface, due to the in-coming acid, nor to a low dissociation process. In fact, it can be safely assumed that reaction 11 is faster in alkaline solutions meaning that if the uptake is limited by the dissociation kinetics, these effects should vanish at pH 14 used in some of our experiments. Therefore, the observed uptake rates should have been larger on solutions with pH = 14 than on pure water. Since this was not the case, we assume that we are measuring only the forward rate of the entry of the trace gas into a liquid and that equation 12 fully applies to our system.

Figure 5 shows the mass accommodation coefficients obtained, as a function of temperature, once the uptake coefficients have been corrected for diffusion limitations using equation 12. The ratio between measured uptake coefficients and the calculated mass accommodation coefficients were in the range 1.3 - 1.7 highlighting the strong interplay between diffusion and interfacial transports. Also, by lowering the temperature we affected the mixed diffusion coefficient but we believe that this introduces only a slight error because the temperature range is restricted (due to both the properties of water and experimental set-up) meaning that the influence of the changes of water partial pressure is also limited. However, in all cases we could estimate that the diffusion coefficients and partial pressures of the gases are known to within 30%. Such an uncertainty will in turn introduce an additional error in  $\alpha$  of about the same level. Please note that the errors given below are just reflecting the experimental uncertainties given at the  $2\sigma$  level.

The  $\alpha$  values exhibit a clear negative dependence with temperature. For example, in the case of HBr,  $\alpha$  decreases from 0.16 to 0.068 when the temperature increases from 262 to 281 K. It is also apparent that the mass accommodation coefficients exhibit the following trend:  $\alpha_{HCl} > \alpha_{HBr} \sim \alpha_{HI}$ . Figure 5 also shows the excellent agreement with the previously published results obtained by Van Doren *et al.* [VanDoren *et al.*, 1990] on HCl, leading to an increased level of confidence in the reported mass accommodation coefficients in both studies. The agreement with other studies [Abul-haj *et al.*, 1987; Adewuyi and Carmichael, 1982; Kirchner *et al.*, 1990] is also satisfactory despite different experimental conditions. In fact, Abul-Haj *et al.* [Abul-haj *et al.*, 1987] reported 0.1 as an upper limit for the mass accommodation coefficient of HCl on water whereas Kirchner *et al.* [Kirchner *et al.*, 1990] measured a lower limit for  $\alpha$  of 0.01 at room temperature i.e., our measured value lies between these two limits. These restricted set of experiments were performed on water but many more data were published for the uptake on ice or sulphuric acid [Abbatt *et al.*, 1992; Abbatt and Molina, 1992a; Abbatt and Molina, 1992b; Chu *et al.*, 1993; Elrod *et al.*, 1995; Fluckiger *et al.*, 1998;

[Hanson and Ravishankara, 1992; Hanson and Ravishankara, 1993; Henson *et al.*, 1997; Hitchcock *et al.*, 1980; Luo *et al.*, 1994] that cannot be directly compared with the results given here.

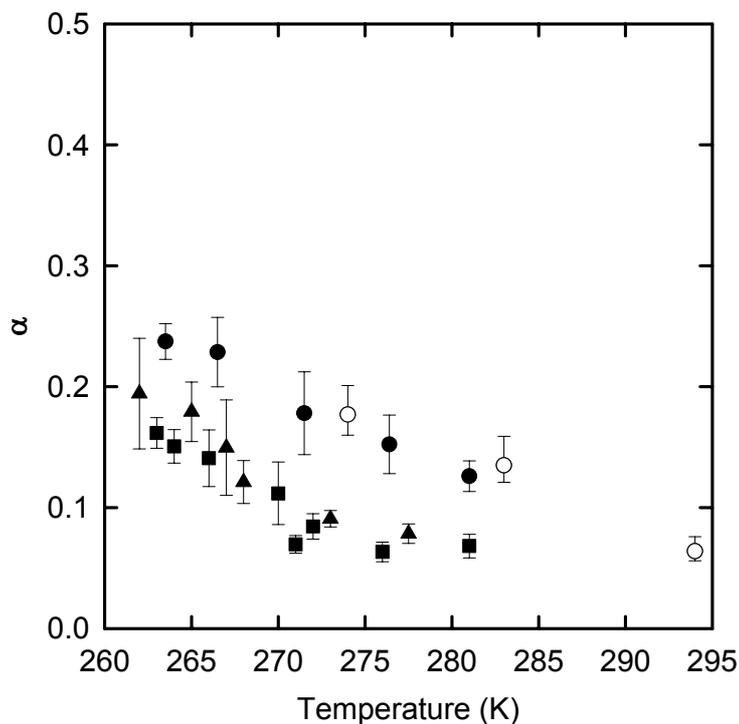


Figure 5: Plot of  $\alpha$  versus temperature for HCl, HBr and HI. The error bars are given at the  $2\sigma$  level. (circles : HCl ; Squares: HBr ; triangles : HI ; Filled symbols this work ; hollow circles : HCl from [VanDoren *et al.*, 1990]).

### 1.1.2 2-4) Modelling of the chemistry in a marine environment

The above described data and the framework for estimating mass accommodation coefficients were used as input data for box modelling studies using the chemical code developed within MODAC. This chemical scheme is described in more detail elsewhere in this report and therefore is not presented here.

We focussed mainly our attention on the halogen activation occurring in an air mass under a polluted marine environment. Figure 6 shows briefly some of the obtained outputs. Whereas in a clean marine environment the nitrogen oxides levels are low, in a polluted case this is sharply different and so is the subsequent chemistry. The halogen chemistry in a "clean case" or in the arctic has already been the focus of different studies but less attention has been given to the simulation in a polluted marine air mass despite the fact that field experiments were and are still reporting unexpected high levels of halogenated species [Keene *et al.*, 1990; Spicer *et al.*, 1998]. The results depicted in Figure 6 show the diurnal variation of some photolytical precursors of atomic Cl and Br. The main difference with the processes occurring at the Arctic is introduced by the fact that now the multiphase chemistry of  $N_2O_5$  is an important source for these precursors with nearly no induction time as observed for other activation/cycling processes. In fact, Behnke *et al.* [Behnke *et al.*, 1997] and Schweitzer *et al.* [Schweitzer *et al.*, 1998b] (and references cited therein) showed that the interaction of gaseous

$\text{N}_2\text{O}_5$  with dilute solutions of NaX produce rapidly nitryl halides. In solutions representative of real sea-salt aerosols, the main product is  $\text{ClNO}_2$  (mainly due to the large abundance of chloride compared to bromide). The uptake kinetics of  $\text{N}_2\text{O}_5$  were shown to be independent of the amount of water available for the reaction, therefore it was postulated that dinitrogen pentoxide first dissociates, in a rate limiting step, according to:



Such a reaction was previously observed as a decomposition pathway for  $\text{N}_2\text{O}_5$  in concentrated protic inorganic solvents as demonstrated by Raman spectroscopy [Colburn, 1966]. In addition, Behnke *et al.* [Behnke *et al.*, 1997] showed that it is followed by reaction of the highly reactive nitronium ion with  $\text{X}^-$  (where X is Cl and Br) or water according to :



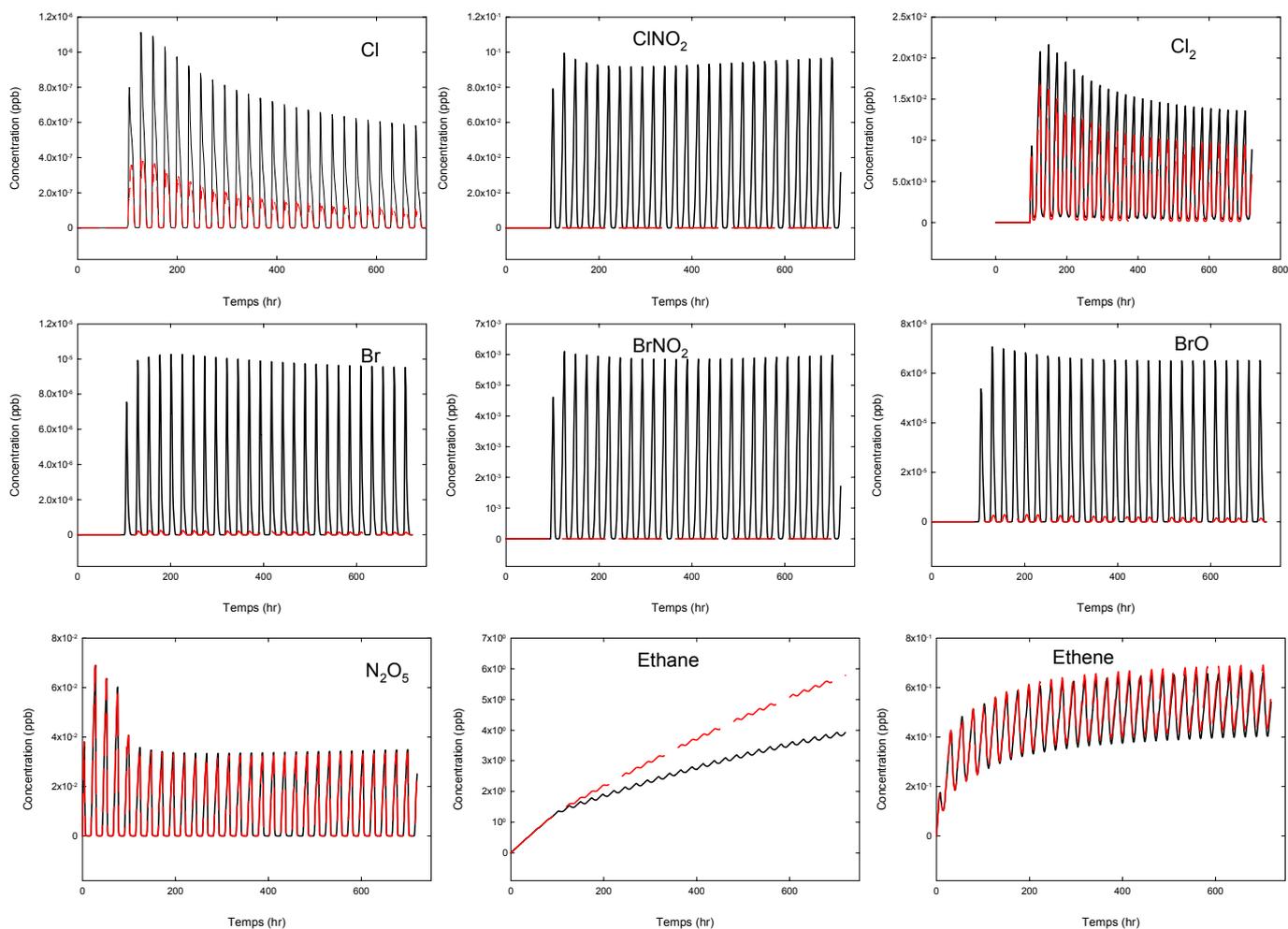
The yield in solutions representative of the real sea-salt aerosols (i.e. for chloride concentrations above 0.5M) is very close to unity i.e. the reactive uptake of  $\text{N}_2\text{O}_5$  proceeds mainly through reaction (11). The corresponding uptake coefficients have an average value of  $\gamma = 0.018 \pm 0.003$  between 262 and 278K [Schweitzer *et al.*, 1998b]. Other kinetic information for reactions (10) and (11) may be found in the work of Behnke *et al.* [Behnke *et al.*, 1997].

These were incorporated into our photochemical box model where the dynamics and microphysics are heavily parametrised i.e., the model is uniquely devoted to a better understanding of the chemistry. The height of the marine boundary layer was assumed to be 1km and constant over the simulated time. The aerosol itself was assumed to be represented by a single average radius of 1.66  $\mu\text{m}$  (with a particle concentration of 1.4  $\text{cm}^{-3}$ ) and refreshed within a characteristic time-scale of 48hr. The initial concentrations of the halide ions were taken from the work of Sander *et al.* [Sander and Crutzen, 1996] as 5.4M and  $8.1 \times 10^{-3}\text{M}$  for chloride and bromide respectively. In the particular simulations shown in Figure 6, an air mass was located for several days (as already said our goal was to test the chemistry schemes even in unrealistic conditions) over a polluted area, and was then allowed to interact with sea-salt aerosols.

Figures 6 present the simulated time evolution of the Cl and BrO radicals and their impact on the concentrations of some hydrocarbons for two distinct runs i.e., with the  $\text{NO}_y$  chemistry described above and with only the hydrolysis of  $\text{N}_2\text{O}_5$ . It clearly appears that halogen activation through dinitrogen pentoxide is an important pathway for polluted regions with potential impact on the hydrocarbon content. In fact, the concentrations of halogenated radicals simulated in the absence of formation of nitryl halides were much lower and with nearly no impact on the alkanes concentrations. It must be underlined that the simulated levels of Cl and BrO were never negligible.

In fact, in the absence of  $\text{N}_2\text{O}_5$  chemistry, other activation reactions may take place as for example the escape of HCl due to the acidification of the aerosol, or in the chain oxidation of S(IV) where electron transfer reactions are occurring through Caro's acid. Once some photochemical halogenated species are released from the condensed phase to the gas phase, cycling reactions take place through HOBr chemistry for example. Nevertheless, in a polluted area the nitryl halides appeared to be the main photochemical precursors of halogenated radicals.

The chloride and bromide concentrations in these runs were shown to drop very rapidly (within the first hours of heterogeneous reactions) from their initial concentrations due to their transformations into non-soluble gases which are escaping to the gas phase (i.e., the nitryl halides or other halogenated species as discussed above). The simulated deficiency in halogenides reached 90% or even more in agreement with field data obtained in polluted coastal regions [Martens *et al.*, 1973; Pszenny *et al.*, 1993].



**Figure 6:** time evolution of different species for a air mass staying over a polluted area over long times.

We also compared our chemical scheme to the one employed in MOCCA and found that the results were comparable. However, the new scheme with its explicit treatment of the chemistry of different families i.e., HOx, NOx, TMI, sulphur and C2 species can be employed in many different cases and is therefore "more universal".

The group at Strasbourg was also involved in the reduction of the scheme in order to obtain a code of reasonable size that can be implemented in a 1-D code such as the one done at Utrecht. In a highly collaborative manner between Leipzig-Leeds and ourselves we

achieved to reduced the size by about 50% without losing information on the major oxidation species.

### 3-4) References

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#### **4) Deviation from technical annex and reasons**

There is no deviation from the technical annex.

#### **5) Conclusions**

In regard to the number of studies made during the last year, the understanding of uptake kinetics but also of the underlying molecular processes has been significantly enhanced. Such knowledge in turn will lead to a better understanding and description of atmospheric chemistry. Nevertheless, more fundamental studies are required in order to correctly model the mass accommodation coefficients and estimate their values.

**Publication :**

F. Schweitzer, Ph. Mirabel et C. George

***1.1.3 Uptake of Hydrogen Halides by Water Droplets***

*Journal of Physical Chemistry*, 104, 72-76, 2000.

**Contractor 4:****Modelling of Cloud and Aerosol chemistry  
using a 1-D strato-cumulus model**

**Contractor:** Utrecht University, Institute for Marine and Atmospheric Research (IMAU)

**Leading Scientists:** J. Lelieveld and F.J. Dentener

**Scientific Staff:** C. Gonzalez, J.E. Williams, A.R. van den Berg

**1. Objectives for the reporting period**

During the MODAC project our group proposed to develop a 1-D column model which incorporates gas, aerosol and liquid phase chemistry components in conjunction with important meteorological processes. Using this model the aim was to integrate the MODAC reduced aqueous phase mechanism into the overall scheme and test for numerical stability. The overall effect of using this mechanism on predominant gas phase oxidants was then the main focus of the simulations. An additional task was to compile emission/deposition arrays for use by all project participants during the stage of mechanism reduction. As described below these objectives have been largely achieved during the reporting period.

**2. Main Results*****2.1 1-D model development***

An existing dynamical cloud model (Duynderke, 1987) was supplemented with a parameterization which describes the chemical change of aerosol particles, aerosol associated water, cloud droplets, aerosol-cloud interactions and interactions between the gas phase and clouds/aerosols. As a result this model involves a large number of chemical calculations on a 1-D 21 layer grid using a dynamical time step of 4 seconds over a typical simulation time of 3 days. To achieve this KPP software (Damian-Iordache, 1995) was utilised which generates a set of differential equations that were used in conjunction with the Rosenbrock sparse matrix solver (Verwer *et al.*, 1997). Initially the model was tested by using a modified CBM-4 gas phase mechanism (Houwling *et al.*, 1998) with a reduced version of the CAPRAM 2.3 aqueous phase mechanism (Herrmann *et al.*, 2000). This allowed the numerical stiffness of the model to be tested using an aqueous phase mechanism similar to that produced from the MODAC project. During this period a number of processes were identified as being influential to the stability of the model.

***2.2 Emission Scenarios***

For the MODAC project three sets of emission/deposition data were constructed from GEIA (<http://groundhog.sprl.umich.edu>) and EDGAR (Olivier *et al.*, 1997) inventories which were representative of urban, rural and marine conditions. The final tables were disseminated to all the participating groups for use within the 0-D box modelling studies.

***2.3 Simulations obtained***

All the simulations conducted during the reporting period were focused on the marine scenario due to the fact that stratocumulus clouds exist over the ocean for long periods of time. The gas phase chemistry was described using the RACM chemical mechanism (Stockwell *et al.*, 1997) and the wet aerosol/liquid chemistry using the MODAC reduced mechanism, as supplied by the other participants. Due to the large uncertainties associated with activity coefficients a value of 1 was used for all chemical species. Additional reaction sets were included to account for the effect of halogen activation which is thought to be an important sink for O<sub>3</sub> (Sander and Crutzen, 1996). Photolysis frequencies were modified using the approach of Ruggaber *et al.* (1994) for a latitude of 51°N with the simulations starting on the 21<sup>st</sup> June. Phase transfer was based on the method of Schwartz (1986) and the initial concentrations, along with emissions and depositions, were identical to those used by the box-modelling groups.

Typical results on the effects of the presence of cloud on some selected gas phase species are summarised in Table.1, where the first day of simulation was ignored so as to avoid any effects due to initialisation of the model. It can be clearly seen that in the cloud layer the concentrations of important free-radical oxidants such as OH and HO<sub>2</sub> are drastically reduced due to direct scavenging and removal in the liquid phase, whilst O<sub>3</sub> seems relatively unaffected. The most important finding to date is the large increase in gas phase HONO predicted by the model from the conversion of HNO<sub>4</sub>. However, in the region below the cloud the differences are much less marked and, in certain instances, the concentrations actually increase (most notably for HNO<sub>4</sub> and NO<sub>3</sub>). This is due to the increase in precursors such as NO<sub>x</sub>. Further effects are expected upon introducing the aerosol component into the overall model.

During a simulation the pH of the cloud reaches a value of between 3-4 with the predominant sources of H<sup>+</sup> being the scavenging of HNO<sub>3</sub> / HCl from the gas phase and the production of H<sub>2</sub>SO<sub>4</sub> via the oxidation of SO<sub>2</sub>. It is interesting to note that the majority of the S(IV) present in solution exists in the form of HMSA which could have important implications in terms of the rate of sulphate production as H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub> are thought to be unreactive towards this complex. The acidity of the droplets is also a crucial factor in determining the degree of dissociation of protonated species in solution and governs the uptake/release of species such as HONO, HO<sub>2</sub> and HCO<sub>2</sub>H.

Profiles obtained for OH, HO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, HONO and HCO<sub>2</sub>H over a 3 day simulation are shown in the figures 1-5 respectively, where the cloud layer is shown as a hashed region.

A limited set of sensitivity runs have been performed where certain reaction sets were switched off (e.g.) C<sub>2</sub> chemistry. A range of effects can be seen depending on which reaction set is chosen and these simulations are currently being used to highlight the predominant processes responsible for the observed reduction in the oxidising capacity of the free troposphere due to heterogeneous interactions.

### 3. Deviations from the work annex

The current portfolio of results obtained using the 1-D model is somewhat limited due to the final version of the reduced aqueous phase mechanism being delivered later than anticipated and the processor time needed for a 3 day simulation (~ 1 day). The individual contribution

due to the aerosol component is still being assessed due to instability associated with the aggregation of water to form deliquescent aerosol. The implementation of the condensed mechanism into global models is currently unrealistic due to the limitations associated with current processor power.

#### 4. Conclusions

A 1-D dynamical cloud model has been developed and used to test the MODAC reduced aqueous phase mechanism. The effects of incorporating this mechanism on important gas phase species has been investigated using conditions typical for a marine scenario. The results suggest that resident concentrations of certain radical precursors and free-radical oxidants can be dramatically altered due to uptake/release and removal in the aqueous phase.

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Species X	Overall Average	Below Cloud	In Cloud	Above Cloud
		300m	850m	1500m
O <sub>3</sub>	1.002	1.002	1.001	1.000
H <sub>2</sub> O <sub>2</sub>	0.745	0.831	0.479	0.999
OH	0.900	1.017	0.617	1.000
HO <sub>2</sub>	0.774	0.978	0.356	1.000
NO <sub>3</sub>	0.984	1.139	0.761	1.000
HONO	5.646	5.364	6.482	1.033
HNO <sub>4</sub>	1.005	1.249	0.469	1.001
HCO <sub>2</sub> H	5.441	7.157	5.935	1.005
ORA2	0.693	0.667	0.572	0.999
ACO <sub>3</sub>	0.784	0.854	0.601	1.000
ETHP	1.025	0.883	1.016	0.999
CH <sub>3</sub> O <sub>2</sub>	0.951	0.855	1.016	0.999

Table 1 : Effect of the presence of cloud on selected gas phase concentrations.

$$\text{Ratio} = \frac{[X]_{g+c}}{[X]_g}$$

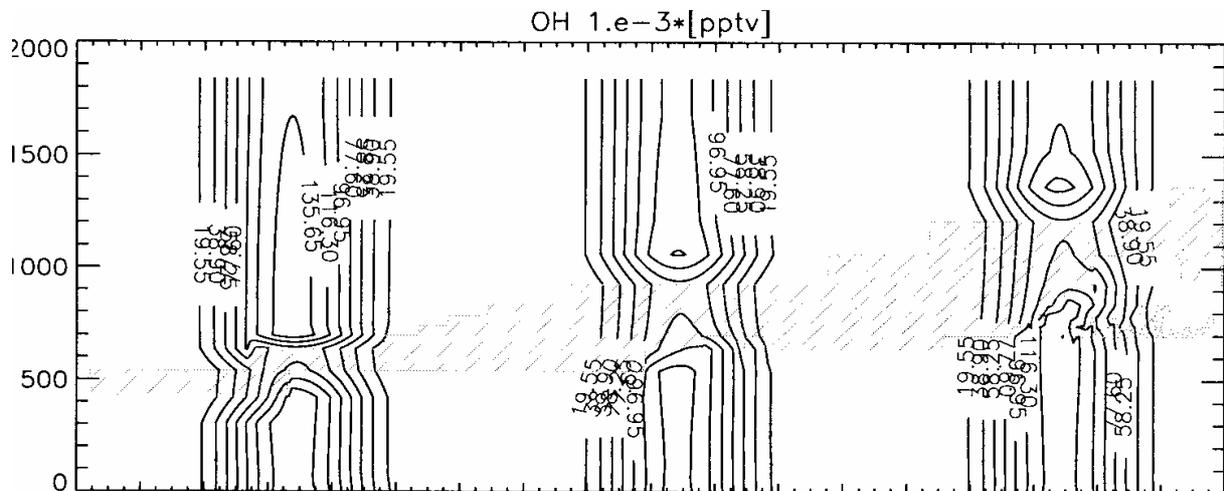


Figure 1 : Profile of the OH radical in the presence of cloud.



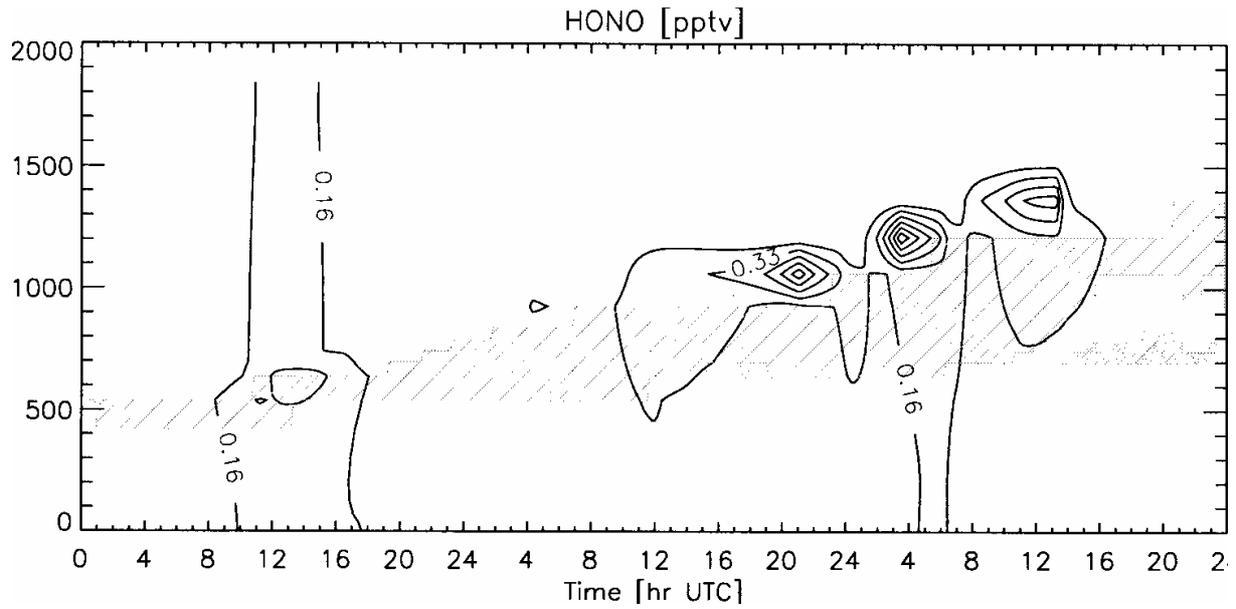


Figure 4 : Profile of HONO in the presence of cloud.

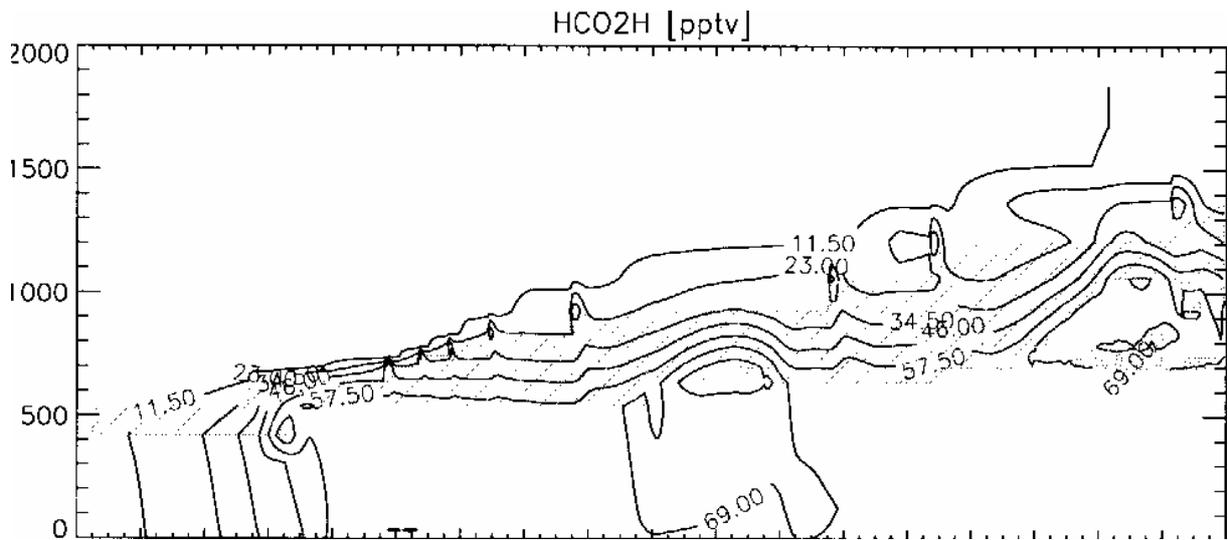


Figure 5 : Profile of HCO<sub>2</sub>H in the presence of cloud.

## **Annex: MODAC Project Meeting Reports**

### **Report of the MODAC-Meeting (13. Nov. 1997) in Essen**

The participants of this meeting were Dr. Ch. George (Strasbourg, F), Dr. A. Salmon (Leeds, UK), Dr. F. Dentener (Utrecht, NL), Dr. H. Herrmann (Essen/ Leipzig, FRG) and B. Ervens (Essen, FRG).

#### 1. Project Status Presentations

The Strasbourg and the Utrecht groups look for Ph. D. students, who take part at the project. In Leeds two persons, J. Roberts and J. Wang, began the experimental works. In future the groups should be inform each other about the status of the co-workers.

In Essen there is a Ph. D. student, B. Ervens, who takes care a part of the modelling calculations. Besides H. Herrmann is looking for a Ph. D. student in Leipzig for carry out further calculations.

F. Dentener described the model of his workgroup. The input parameters they use consist in the initial concentrations and emissions. In the model it is taken into consideration processes in aerosols and clouds. Also the marine sulfur cycle is treated. The heterogenous processes at the surfaces of clouds and aerosols are calculated. An accommodation coefficient of  $\gamma = 0,1$  is used. He assumes in his model only one drop size.

The model of the Leeds group were presented by A. Salmon. The model includes a lot of reactions of inorganic species. In the model the drop size distribution is disregarded, too. A more detailed report he will distribute to the other groups.

The model of the Essen group was presented by H. Herrmann. In future the model will describe the uptake processes better than until now. At present all heterogenous processes are described by Henry's Law coefficients. The uptake coefficients will be introduce firstly for eight species. It was proposed to use them for all species. Because this model includes a lot of organic reactions, it is planned to exchange the reactions with the Leeds group to create a whole mechanism. After assembling the mechanisms it is planned to reduce the system. All reactions they are neglectible will be delete in the mechanism.

The model of the group in Strasbourg was presented by Ch. George. Except cloud chemistry the model can calculate processes of nucleation in sulfuric acid aerosols (marine). The model is based on the publication of Sander and Crutzen. Besides it includes the marine chemistry of bromide and iodide ions. Ch. George has a collection of data of activity parameters, with

them ionic strength effects can be calculated. He can calculate processes in the cloud and aerosol chemistry with a drop size distribution.

All groups want to use the same gas phase reactions. The participants agreed on the Regional Atmospheric Chemistry Model (RACM) by W. R. Stockwell. In the next few weeks Ch. George will send the modelling program FACSIMILE and the paper, that contains RACM to the Essen group. Besides A. Salmon will send a graphic program to graph FACSIMILE files to the Essen group.

## 2. General Discussion

All groups have started the works for the MODAC project. The next meeting of the Leeds group and the Essen group is planned in February '98 for exchange the both mechanisms. This system of reactions will be send to Ch. George and F. Dentener, so that every group can do calculations with this system.

In May '98 the next meeting will take place with all participants of the project.

**MODAC-Meeting**  
**21.-23.10.98 in Leipzig**

Leipzig (DE): H. Herrmann, B. Ervens  
Leeds (UK): A. Salmon, J. Williams  
Strasbourg (FR): Ch. George  
Utrecht (NL): F. Dentener, A. van den Berg

### **1. Project Status Presentations**

Every group of the project presented the actual status of their work. The model of the Leipzig group were presented by B. Ervens. This model consists of three parts: the gas phase chemistry is described by RADM2 from Stockwell (158 reactions), a formulation of the uptake processes for 34 species with gas phase diffusion, mass accommodation and Henry's Law coefficients and CAPRAM2.3 (Chemical Aqueous Phase Radical Mechanism) with 236 reactions. Some concentration-time-profiles of radicals for three different environments and the most essential sink and source reactions for these species were presented. Additionally some results of comparisons calculated with and without liquid phase were shown.

The modelling results of the Leeds group were presented by A. Salmon. In this model the gas phase chemistry is treated with RACM, the phase transfers are described by Henry-Equilibria and for the aqueous phase chemistry an early version of CAPRAM (216 reactions) is used. Here the differences for example for OH between the cases calculated with and without liquid phase were nearly a factor 15 higher than in the comparisons of the Leipzig group. Additionally to the modelling studies the Leeds group have performed some kinetic investigations. J. Williams presented the reaction rates of the reactions between oxalate  $C_2O_4^{2-}$  and  $HC_2O_4^-$  with the sulfate radical anion  $SO_4^-$  and the reactions rate of  $HC_2O_4^-$  with  $SO_5^-$ . The reaction of  $C_2O_4^{2-}$  with  $SO_5^-$  will be investigated. These results are useful for implementing in the model because CAPRAM should be the first aqueous phase mechanism containing C1 and C2 chemistry.

Ch. George showed the results of the investigations for determine the uptake coefficients of HCl, HBr and HI. Further data can be estimated with a increment system developed in this group.

The model of the Utrecht group contains about 50 gas phase reactions and 100 aqueous phase reactions (incl. phase transfers) considering 21 layers. The results were represented as altitude/ time diagrams. Until now the model describes the marine boundary layer but it is

possible to extend it to continental stratocumulus clouds. This model is restricted to a chemistry part of about 200 reactions.

## **2. Further activities**

Firstly it is to clarify the differences between the different models used in the Leipzig and Leeds groups. Next the models of these groups should be adjusted. For this the gas phase chemistry of the Leipzig model will be changed in to RACM. Additionally CAPRAM was reviewed by the Leeds group, so that some changes will be made in CAPRAM2.3. The importance of the chemistry of the chlorine atom will be tested. Corresponding values are existing from the Leeds group. Then a complete mechanism can be developed. To this mechanism radical reactions of oxalate and glyoxal will be added. For this the data set of the reaction of oxalate have to be completed. Because at the moment a lot of temperature dependences are missing in CAPRAM it was thought over to estimate them.

The uptake coefficients used in the Leipzig model will be reviewed by Ch. George for implement them into the complete model.

It is planned to reduce this mechanism for to send it to the Utrecht group because its mechanism is limited to 200 reactions. This group will reduce RACM keeping reaction pathways of some C1 and C2 organic species. Furthermore, in this group a data set for emissions will be formulated for distribute it to all groups where this proposal will be discussed.

The next meeting will be take place in February '99 in Utrecht.

**MODAC Interim-Meeting, 21.04.99 in Utrecht**

Participants: H. Herrmann, B. Ervens (Leipzig, D)  
Ch. George (Strasbourg/ Lyon, F)  
J. Williams (Leeds, UK)  
F. Dentener, A. van den Berg (Utrecht, NL)

**Project Status Presentations**

Every group has presented its results of investigations relating to the project from the last half year.

The results from Utrecht were shown by F. Dentener. Indeed the solver for their TM3 model is expanded for treating in total a multiphase mechanism 500 reactions as a maximum. Besides the group has worked out a data set basing on a field campaign (''EDGAR'') from Dutch institutes including emission data for 23 organic species. Because it is planned that the modelling investigations within the project should be performed with emissions the Utrecht group will modify these emission data for use them in the gas phase mechanism RACM containing only 15 classes of organic species.

The results of the Leeds group were presented by J. Williams. The main subject of their work during the last half year was the critical review and extension of the mechanism CAPRAM. Most points of the update were discussed during the last months with the Leipzig group. A lot of suggestions were implemented, so that the mechanism of the group in its actual version includes 406 reactions in the aqueous phase (including 7 photolyses) and 30 uptake processes. Besides he showed some further reactions which could be implemented into the aqueous phase mechanism concerning mainly the chemistry of the chlorine atom. At moment the mechanism of the Leeds group is treating the uptake processes as Henry-equilibria; furthermore all photolyses are assumed as constant during the day.

After this presentation the latter studies of the Leipzig group were shown by B. Ervens. On the one hand some calculations with the original aqueous phase mechanism CAPRAM 2.3 coupled with the gas phase mechanism RADM2 were performed. Here before all it was attached importance to the effects to the concentration levels of important aqueous phase species (radicals) caused by variation of conditions such as the droplet diameter and the duration of the cloud period.

On the other hand the state of updating the mechanism CAPRAM was represented. Until now a lot of new reactions and more actual kinetic data suggested by the Leeds group were implemented, so that CAPRAM2.4 includes now 322 reactions in the aqueous phase. The

most important points of the extension were additional chemistry of the transition metal ions ( $\text{Fe}^{2+/3+/4+}$ ,  $\text{Mn}^{2+/3+/4+}$  and  $\text{Cu}^{+/2+}$ ) and the completion of the C2 organic chemistry including now reactions of glyoxal, glyoxylic acid, oxalic acid and oxalate with radicals.

The fourth presentation was made by Ch. George. He use at moment a box model describing before all marine aerosol chemistry including the initial concentrations of CAPRAM. The initial concentrations are concerned to runs with RACM by Stockwell. This aerosol model (high ionic strengths, high initial pH, particle diameter 1,66  $\mu\text{m}$ ) can be extended also to cloud chemistry. In the model depositions are considered. He pointed to the importance of the chemistry of  $\text{ClNO}_2$  and  $\text{BrNO}_2$  in coastal polluted regions considered in his model.

### **Next goals**

The data sets of emissions considering several scenarios will be hand out from the Utrecht group to all participants as basic conditions for comparison calculations including emission data.

The nearest goal of the Leipzig and Leeds groups will be a complete agreement to a common aqueous phase mechanism to perform comparison calculations under same conditions. For this a table with uncertain points will be sent by J. Williams to Leipzig for discuss them there. The final agreement should be got until the end of May. This mechanism will be distributed to all groups. The next point will be the reduction of the mechanism to a data set with less than 500 processes. In future discussions between all groups some certain important species in both phases will be selected, whose concentration levels are not allowed to differ very much after the reduction. These selection and the conditions under which the model should be investigated are also distributed to all groups. The reduction for the marine scenario will be performed in the Strasbourg group, that for the remote scenario by the Leeds group and the third (urban conditions) will be made by the Leipzig group. These condensed mechanisms will be sent to Utrecht to implement them into the 3D-model.

The results will be compared at the next meeting in July in Lyon.

**MODAC Interim-Meeting, 22.09.99 in Aachen**

Participants: H. Herrmann, B. Ervens, D. Weise, A. Walter (Leipzig, D)  
Ch. George (Strasbourg/ Lyon, F)  
J. Williams (Leeds, UK; Utrecht, NL)  
F. Dentener (Utrecht, NL)

**Project Status Presentations**

The main topic of this meeting was planning of the next steps of advance to find an agreement between the groups Leipzig, Leeds and Strasbourg/ Lyon in the results from the multiphase mechanism RACM/CAPRAM2.4.

All groups will use the same conditions in the model:

- droplet radius 10 $\mu$ m
- LWC = 3 $\cdot$ 10<sup>-7</sup> vol / vol
- day: 21.6.
- degree of latitude 51°
- no scattering light will be considered, i. e. the photolysis rates are assumed to be zero between 8:00 pm and 4:00 am

The comparisons will be made for the remote scenario. In the first step a permanent cloud will be considered for time period of four days. In the second step the same scenario will be tested for a period of six days but only at the third and fourth day the cloud is switched on between 2:00 and 6:00 p.m. If agreement is reached between the three groups the emissions will be implemented in this scenario. They are available from a data collection by the groups of Lyon/Strasbourg and Utrecht since the last meeting. Furthermore, the same calculations will be performed with the urban initial conditions.

Because the model from the Utrecht group is restricted to 500 reactions including the chemistry in both phases the mechanism has to be reduced. To test the methods of mechanism reduction of the different participants every of the three groups Leipzig, Leeds and Strasbourg/ Lyon will reduce the mechanism under consideration for urban initial conditions. After having the same condensed mechanism for urban conditions, CAPRAM2.4 will be condensed for the marine scenario by the Strasbourg/ Lyon group, the remote scenario by the Leeds group. The combination of the three resulting condensed mechanisms represents the final version of 'CAPRAM2.4-reduced'. This version can be implemented in the 1D-model in Utrecht.

### **Schedule**

The comparisons of RACM/CAPRAM2.4 and the reduction of the aqueous phase mechanism should be finished successfully until December, 15<sup>th</sup>. Then the participants from Utrecht will test and implement it in their model.

The final results will be available at the final meeting of the project, in March 2000.

**MODAC Final Meeting, 01.03-03.03.2000 in Lyon**

Participants: H. Herrmann, B. Ervens (Leipzig, D)  
Ch. George (Lyon, F), Ph. Mirabel (Strasbourg, F)  
A. Salmon (Leeds, UK)  
F. Dentener, J. Williams (Utrecht, NL)

**1. Project Status Presentations**

Every group presented results from model studies with the mechanism developed within the last months of the project (CAPRAM2.4 / CAPRAM2.4-reduced). Because different points of view (with/without emissions/depositions; complete/reduced; permanent/ temporary cloud) were emphasized in the groups performing the case studies (Leipzig, Leeds and Lyon) they agreed to make two different presentations of the most important reaction pathways of  $\text{OH}_{(\text{aq})}$ ,  $\text{NO}_{3(\text{aq})}$ ,  $\text{S(IV)}_{\text{aq}}$  and  $\text{O}_{3(\text{g})}$  (for the latter species only the effective loss processes excluding the photolysis and the loss by NO): On the one hand the instantaneous fluxes of the most important production and loss processes at  $t = 36$  h and  $t = 48$  h should be compared and on the other hand the integrated fluxes of these processes between the  $t = 4$  h, 2<sup>nd</sup> day until  $t = 4$ h, 3<sup>rd</sup> day should be depicted. The studies should be performed with the full mechanism and under consideration of a permanent cloud and with emissions/depositons. The results will be compared for all three scenarios.

Because from the side of the Utrecht group the reasonableness of the input parameter (initial concentrations and emissions/depositions) were doubted, it will suggest new input data in the next few days. These will be discussed and finally tested for the scenarios in the reduced and the full mechanism.

**2. Further activities**

With the final new input data the calculations will be repeated in the three groups to be clarify whether the reduced form of the mechanism can be applicated also for these data set. Furthermore the results from the sink/source studies described above will be compared in the three groups.

One goal of these activities will be joint publications of the results and evidences obtained from the model studies performed with CAPRAM2.4 in all its modifications. A main point will be the presentation of the influence of cloud chemistry to the gas phase concentration levels.