A1. The Reaction Between Methylglyoxal and OH Radical: OH Regeneration

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Methylglyoxal (CH_3COCHO, MGLY) is commonly present in urban and rural atmospheres [1, 2] which is mainly formed from secondary chemistry but it is also directly emitted by light-duty motor vehicles [3]. It is a common product formed in the oxidation of numerous hydrocarbons, including isoprene and aromatic [4, 5] and in the ozonolysis of numerous unsaturated hydrocarbons [6]. Therefore, to understand the atmospheric chemistry of MGLY is vital to understand the tropospheric degradation processes of terpenes and aromatics.

Previous studies [7, 8] have established that the tropospheric lifetime of MGLY will be at most a few hours, with two major gas-phase loss mechanisms likely: reaction with OH and direct photolysis. However, significant discrepancies and gaps exist in our quantitative understanding of both processes [9]. Because the two loss processes are expected to be competitive in the atmosphere and because different products may result, further studies of both processes are clearly warranted.

In this work, we report the results of a laboratory study of the mechanism involved in the OH oxidation of MGLY in the atmosphere. A flash photolysis system with LIF (Laser Induced Fluorescence) detection of OH/OD has been used to carry out these experiments.

The rate constants for OD/OH + MGLY is reported as a function of temperature (T = 298-233 K) and pressure (5-400 torr). We also characterized the dissociation processes of the primary product of this reaction: CH_3COCO that produce the OH regeneration in the presence of trace amounts of oxygen. Possible atmospheric implications in the understanding of tropospheric oxidation of terpenes are implied from this work.

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A2. Laboratory Investigations of OH Reactions in Aqueous Solution and Multiphase Mechanism Development: Capram 3.0

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The high reactivity and the ubiquity of OH radical make it one of the most important sink for volatile organic compounds both in the gas and aqueous tropospheric phases. A semi-direct method and kinetic competition method were used to the study the reactivity of OH radical towards oxygenated organic compounds in aqueous phase [1]. Spectroscopic and kinetic investigations were carried out using a laser flash photolysis long path laser absorption (LFP-LPA) setup (Figure 1). In aqueous solution, OH radicals were produced through the photolysis of H_2O_2 ($1 \cdot 10^{-4}$ M) at $\lambda = 248$ nm. The temperature dependence of second order rate constants for the reaction of OH radicals with 2-propanol, 1-butanol, 2-butanol, propionaldehyde, butyraldehyde isobutyraldehyde, acetone, methyl ethyl ketone, acetonylacetone, diacetyl, hydroxyacetone, D,L- malic acid, D,L-maleate dianion, glutaric acid, D,L-glutarate dianion, adipic acid, adipate dianion, pimelic acid, pimelate dianion, suberic acid and suberate dianion were measured between 278 and 318 K.

CAPRAM 3.0 [2] is the latest development of the CAPRAM (Chemical Aqueous Phase Radical Mechanism) series which is incorporating CAPRAM 2.4 [3] and a new extended reaction mechanism for atmospheric-relevant hydrocarbons containing more than two and up to six carbon atoms. The chemistry of organics containing three and four carbon atoms is now described in details. More than 300 new reactions are now implemented considering the chemistry of organic compounds containing different functional groups, i.e. alcohols, carbonyl compounds, mono- and dicarboxylic acids, polyfunctional compounds as well as some esters and heterocyclic compounds. The total number of aqueous phase reactions in CAPRAM 3.0 is 776.

The CAPRAM remote scenario which was chosen as standard scenario showed that the introduction of the higher organic chemistry has relevant influence on the standard subsystems. The diurnal peak concentration of OH radical in the droplets decreases with about 40% and the reactions of OH with hydrocarbons containing 3 or 4 carbon atoms account for about 10% out of the total sinks of OH in the droplets. A slightly stronger acidification of the aqueous phase in comparison to CAPRAM 2.4 is observed.

The formation and accumulation phase of substituted mono and dicarboxylic acids such as tartaric, mesoxalic and acetic acid in the aqueous is also observed.
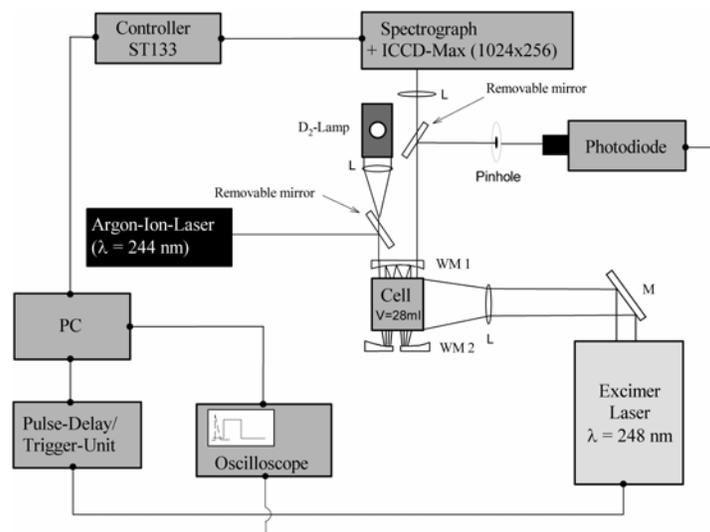
Figure 1: LFP-LPA set for semi-direct measurements of OH radical reactions in aqueous solutions.

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A3. Study of The Reactivity of Nitrate Radical Towards Substituted Phenols in Aqueous Solution

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Besides OH, NO_3 radical is an important key oxidant both in the atmospheric gas and aqueous phase. NO_3 radicals are mainly formed in the gas phase by the reaction of NO_2 with ozone. The main source of NO_3 radicals in the aqueous phase is the uptake from the gaseous phase. Substituted phenols may be emitted directly into the atmosphere or they are formed by the atmospheric oxidation of aromatic precursors (e.g. benzene, toluene). Phenols and its derivatives may affect human health, and the toxicity and phytotoxicity of many of these compounds are well-known. However, the knowledge about their chemistry in the atmosphere is still limited.

Within this work rate constants for the reactions of nitrate radicals with different substituted phenols in aqueous solutions have been investigated using a laser-photolysis-long-path-laser-absorption (LP-LPA) set-up. NO_3 radicals were generated under acidic conditions (pH = 0.5) by laser flash photolysis of nitrate anions.

$$NO_3^- + h\upsilon\ (\lambda = 248\ nm) + H^+ \rightarrow OH + NO_2$$

$$HNO_3 + OH \rightarrow NO_3 + H_2O$$
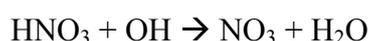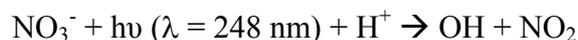
The time dependent decay of the nitrate radical was followed using a helium-neon laser (λ = 632.8 nm). All the kinetic measurements were carried out under conditions of pseudo first order [1,2].

The kinetic investigations comprised the measurement of rate constants at 298 K as well as their dependencies on temperature and ionic strength. The results obtained will be discussed and compared with available literature data. In the context of this work a linear free energy relationship between the measured rate constants ($k_{2nd,\ 298K}$) and the Hammett parameter (σ_p^+) was found (Figure 1). Such correlations are very useful, because they allow a prediction of unknown rates as well as a classification of the reactions to different reaction mechanisms (e.g electron transfer or H-abstraction).

Moreover, for the ionic strength dependencies a correlation between the dipole moment (μ) of the reactants and the kinetic salt coefficient (β) was found (Figure 2). The correlation shown in Figure 2 allows, for the first time, an estimation of the salt effect on neutral-neutral reactions. These correlations are also of importance for the modelling, since they allow a simple and fast access to kinetic data for a multiplicity of compounds. Furthermore, the kinetic data obtained will be used as input parameters for the multiphase tropospheric chemistry model CAPRAM (Chemical Aqueous Phase Radical Mechanism) [3].
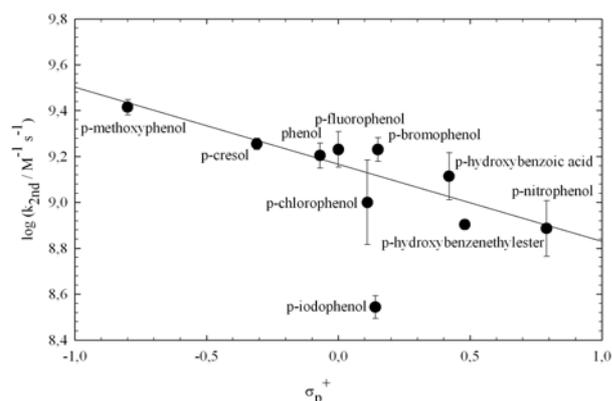
Figure 1: Plot of log (k_{2nd}) versus the Hammett parameter (σ_p^+) for electron transfer reactions of NO_3 with several substituted phenols
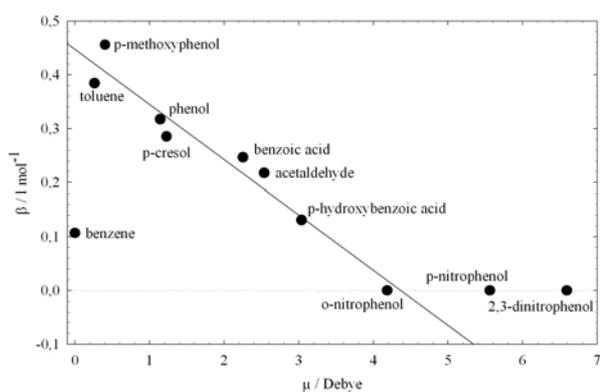
Figure 2: Plot of the dipole moment (μ) versus the kinetic salting coefficient (β)

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A4. Kinetics And Spectroscopy Of The Gas Phase Cs_2-Cl Adduct

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The adduct formed from the interaction of atomic chlorine with carbon disulfide is of interest in atmospheric chemistry [1-3] and as an agent for promoting selectivity in photochlorination reactions [4,5]. While the adduct absorption spectrum [4] and resonance Raman spectrum [6] have been observed in liquid CCl_4/CS_2 solutions, the gas phase adduct has not been directly observed, even though its existence is strongly suggested from kinetic observations [1-3] and electronic structure calculations [5-8]. The liquid phase absorption spectrum of CS_2-Cl consists of a strong band with $\lambda_{max} \sim 370$ nm and a weaker band with $\lambda_{max} \sim 490$ nm [4]. Comparison of the observed resonance Raman spectrum with theoretical vibrational frequencies suggests that the adduct responsible for the strong absorption band is the one formed via Cl addition to a sulfur atom [6]

We have coupled time-resolved UV-visible absorption spectroscopy with laser flash photolysis of $Cl_2CO/CS_2/N_2$ mixtures to make the first observations of the gas phase UV-visible absorption spectrum of CS_2-Cl. The spectrum is very similar to the liquid phase spectrum in CCl_4 solvent observed by Chateauneuf [4]; $CS_2-Cl(g)$ is found to possess a strong absorption band with $\lambda_{max} \sim 365$ nm and $\sigma_{max} \sim 2 \times 10^{-17}$ cm^2 as well as a weaker band with $\lambda_{max} \sim 480$ nm. The observed spectrum is found to be independent of temperature over the range $240 - 298$ K.

Using adduct absorption at 365 nm as the kinetic probe, rate coefficients have been measured for the gas phase reactions of CS_2-Cl with O_2, NO, and NO_2. At 298 K, no evidence for a $CS_2-Cl + O_2$ reaction is observed; our data suggest an upper limit rate coefficient $k_{O2} < 1 \times 10^{-17}$ cm^3 molec^{-1} s^{-1}, which is a factor of 25 slower than the lowest upper limit available in the literature [2]. Rate coefficients for CS_2-Cl reactions with NO and NO_2 at 30 Torr total pressure and T= 240 K are found to be $k_{NO} = 2.2 \times 10^{-11}$ cm^3 molec^{-1}s^{-1} and $k_{NO2} = 1.3 \times 10^{-11}$ cm^{3}molec^{-1}s^{-1}, respectively. The reactivity of $CS_2-Cl(g)$ with O_2, NO, and NO_2 is found to be very similar to that observed for reactions of DMS−Cl(g) [9] and DMSO−Cl(g) [10] with the same species (DMS ≡ dimethyl sulfide and DMSO ≡ dimethyl sulfoxide).

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A5. *Invited:* The Atmospheric Chemistry of Alkoxy Radicals: Recent Studies of Ether and Ester Oxidation

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Hydrocarbons are present in the earth's atmosphere as the result of emissions from natural and anthropogenic sources. Their oxidation in the atmosphere, initiated by such oxidants as OH, O_3, and NO_3, leads to potentially harmful secondary pollutants such as O_3, carbonyl species, organic acids and aerosols. These oxidations proceed via the formation of alkoxy radicals, whose complex chemistry controls the ultimate product distributions observed.[1] Alkoxy radicals can react with O_2, and can also undergo unimolecular dissociation and isomerization processes whose rates vary sharply with temperature. Furthermore, the alkoxy radical chemistry is often influenced by chemical activation - that is, alkoxy radicals generated from the exothermic reaction of the corresponding peroxy radical with NO often possess internal energy in excess of barrier heights for unimolecular processes, allowing "prompt" dissociation to occur. We have been carrying out hydrocarbon oxidation studies for a number of years now, using environmental chamber / FTIR absorption systems. A major focus of these studies has been on the product distributions obtained at low temperature. These studies not only provide data of relevance to the free/upper troposphere, but also allow for a more fundamental understanding of the alkoxy radical chemistry (eg., from the determination of the Arrhenius parameters for unimolecular processes, and the quantification of the extent of the involvement of chemical activation).

Following a brief overview of alkoxy radical chemistry, some recent studies on the oxidation mechanisms for diethyl ether (DEE) and a number of ester species will be presented. Atmospheric oxidation of diethyl ether leads to the formation of both ethyl formate and ethyl acetate: [2-4]

$$CH_3CH_2OCH_2CH_3 + OH \rightarrow CH_3CH\bullet OCH_2CH_3 + H_2O \tag{1}$$
$$CH_3CH\bullet OCH_2CH_3 + O_2 \rightarrow CH_3CH(OO\bullet)OCH_2CH_3 \tag{2}$$
$$CH_3CH(OO\bullet)OCH_2CH_3 + NO \rightarrow CH_3CH(O\bullet)OCH_2CH_3 + NO_2 \tag{3}$$
$$CH_3CH(O\bullet)OCH_2CH_3 \rightarrow HC(=O)OCH_2CH_3 + CH_3 \tag{4}$$
$$CH_3CH(O\bullet)OCH_2CH_3 + O_2 \rightarrow CH_3C(=O)OCH_2CH_3 + HO_2 \tag{5}$$

The product yield data, obtained over a range of temperature, O_2 partial pressures, and NO_x levels, show that thermal decomposition (R4) and reaction with O_2 (R5) are competing fates of the $CH_3CH(O\bullet)OCH_2CH_3$ radical, [4] and that the $CH_3CH(O\bullet)OCH_2CH_3$ radical is activated upon its formation via (R3). Prompt decomposition via both CH_3 (35% yield) and H-atom (10%) elimination occur.

Oxidation of the esters leads to the generation of alkoxy radicals of the general form RC(=O)OCH(O•)R. These radicals under a unique so-called "α-ester rearrangement", first discovered by Tuazon et al. [5], e.g.,
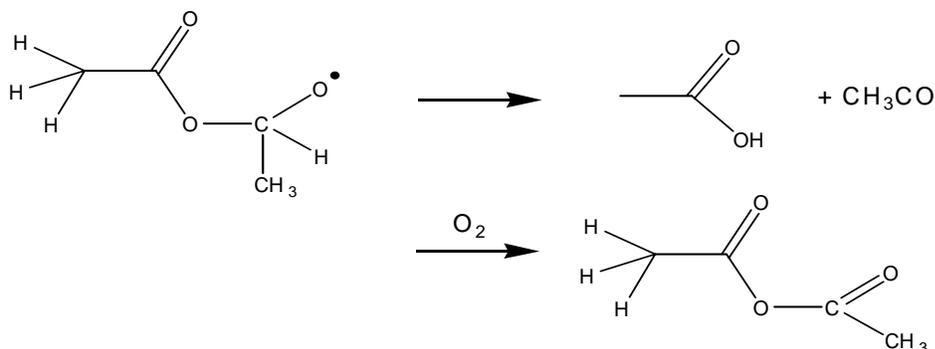
Competition between the α-ester rearrangement and reaction with O_2 has been studied for a number of systems (methyl acetate and formate, ethyl acetate and formate) over a range of conditions, allowing Arrhenius parameters for the rearrangements to be determined [6]. These data will be presented along with a discussion of the chemistry of some larger formates, time permitting.

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A6. Thermochemistry, Reaction Paths, Kinetics and Elementary Reaction Modeling the Atmospheric Reactions of the Benzene-OH Adduct with O_2

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The addition of OH radical to benzene and other aromatic species to form a cyclohexadienyl radical (***C•HD***-OH), is the first step for conversion of aromatic species in atmospheric chemistry. The reaction of this intermediate ***C•HD***-OH adduct, with oxygen forms a numbers of hydroxyl-cyclohexadienyl peroxy (***CHD***-OH-OO•) isomers, which further react to form aerosols.

Two para-***CHD***-OH-OO• diastereomers are: para- *cis*-(Z) ((Z)-p-***CHD***-OH-OO•) and para *trans*-(E) ((E)-p-***CHD***-OH-OO•), refer to the OO• group lying on the same (Z) or on the opposite (E) side of the ring with respect to the OH group. Four ortho-***CHD***-OH-OO• diastereomers are: ortho- *cis*-(Z) and ortho *trans*-(E) at pseudo-equatorial (e') and pseudo-axial (a') positions. The OH and OO groups on two adjacent carbons with:
(i) both in pseudo-axial positions ((E)-o-***CHD***-OH-OO•**I**),
(ii) both in pseudo-equatorial positions ((E)-o-***CHD***-OH-OO•**II**),
(iii) OH in pseudo-equatorial with OO in pseudo-axial position ((Z)-o-***CHD***-OH-OO•**I**), and
(iv) OH in pseudo-axial with OO in pseudo-equatorial positions ((Z)-o-***CHD***-OH-OO•**II**).

Thermochemistry, reaction paths, barriers, Arrhenius pre-exponential factors and thermodynamically consistent reverse rate constants of ***C•HD***-OH adduct with O_2 are important to oxidation of aromatics and aerosol formation in the atmosphere. Structures, intramolecular rotation barriers, and thermochemical properties of the hydroxyl-cyclohexadienyl peroxy isomers (***CHD***-OH-OO•), hydroperoxy-cyclohexadiene oxyl (***CHD***-O•-OOH) radicals, bicyclic-OH peroxy radicals, transition states, and products have been evaluated using ab initio, density functional and composite methods in computational chemistry. Reaction path analysis, reaction barrier, and pre-exponential factor of each elementary reaction step are evaluated. Kinetics for chemical activation reactions are analyzed using quantum Rice-Ramsperger-Kassel (QRRK) theory for $k(E)$ and master equation analysis for pressure falloff. The reaction energies (well depths, $\Delta H_{r, 298}$) of ***C•HD***-OH + O_2 ↔ ***CHD***-OH-OO• isomers were determined to be -10.63 ~ -13.67 kcal mol^{-1} with $\Delta S_{r, 298}$ of -32.07 ~ -35.08 cal mol^{-1} K^{-1} at G3(MP2)//B3LYP/6-31G(d,p) level.

The ***CHD***-OH-OO• isomers can stabilized, dissociate back to reactants, react via hydrogen transfer to hydroperoxy oxyl isomers, or cyclize to bicyclic-OH peroxy adducts. The [(E)-o-***CHD***-OH-OO•]* adduct also can dissociate to phenol + HO_2 via HO_2-molecular elimination. The hydrogen transfer path from hydroxy peroxyl to hydroperoxy oxyl does not occur in the reaction of [(E)-*p*-***CHD***-OH-OO•]* adduct. The cyclization from (Z)-*o*-***CHD***-OH-OO•**II** adduct to bicyclic peroxy radical **(E) BY-III** has the barrier of 15.21 kcal/mole (G3(MP2)//B3LYP/6-31G(d,p)). It is lower than isomerization (H-shift) to ***CHD***-O•-OOH adduct and other cyclization channels resulting from the resonance stabilization and two hydrogen bonds (Figure 1). All the product formation pathways of O_2 addition to ***C•HD***-OH radical involve barriers that are above the energy of the initial reactants (O_2 and ***C•HD***-OH radical).
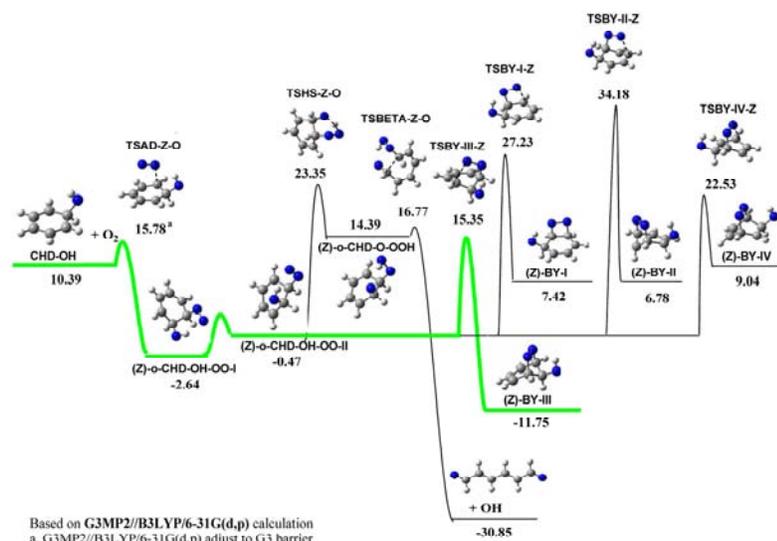
Figure 1

A detailed mechanism which includes microscopic reversibility for all the elementary reactions with reverse rate constants determined from the forward rate constant, the thermodynamic parameters, and microscopic reversibility is assembled. The reaction mechanism, which is based on the OH + benzene oxidation reaction system and consists of 126 species and 228 reactions, is utilized to analyze and understand the kinetic processes as a function of time, temperature and pressure and to compare the model against experimental results in the literature. The calculations for reactant decay of benzene, OH radical profile and phenol product formation from the mechanism are compared with experimental data on OH-initiated benzene oxidation. (Figure 2). The calculated rate constants of $C \cdot HD$-OH + $O_2 \rightarrow CHD$-OH-OO• are also in good agreement with experimental data (Figure 3).
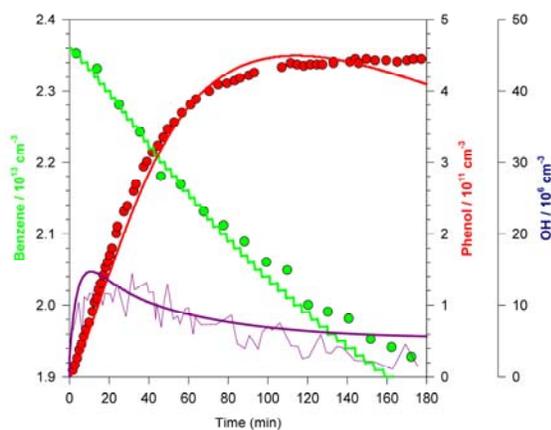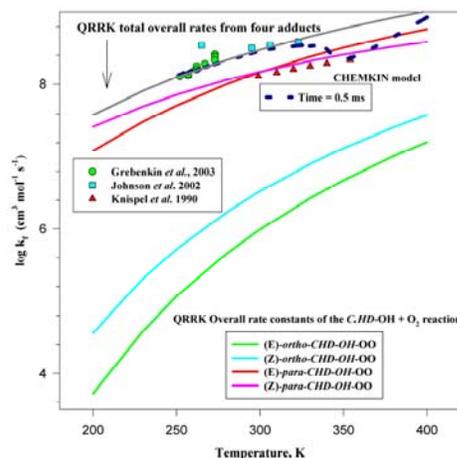

Figure 2

Figure 3

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A7. Rate Constants For OH(v) + O at 140-365 K

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The temperature dependence of the $OH + O \rightarrow H + O_2$ reaction was measured using a laser photolysis - laser induced fluorescence technique. A known excess of O atoms is prepared by complete 248 nm laser photolysis of a monitored ozone flow in nitrogen, with small amounts of added water or hydrogen to provide an OH source. A tunable frequency-doubled OPO laser fired at varying delay times excited OH (A-X) LIF in the center of the photolysis zone. We determined decay rate constants for v = 0-4 by exciting the (1,0), (2,1), (2,2), and (2,4) bands. The window-equipped flow cell is enclosed in a Dewar by which temperatures of 140K (LN_2), 235K (dry ice), and 365K (heated cell) were produced.

Modeled results for OH(0) + O under various conditions agree with the JPL panel recommendation at 298 K, independent of OH source, with a slightly larger temperature dependence (E = -0.40 kcal/mole). At 140 K, the rate constant has increased to $8.2 \times 10^{-11} cm^3/s$, 2.5 times the room temperature value.

Measured decays for OH(v=1,2, and 4) reflect reaction, and vibrational relaxation by O and by the $O_2(a^1\Delta)$ also created by the ozone photolysis. Results show an increase in rate with vibrational level, no evidence for vibrational relaxation for v≤2, a larger temperature dependence than seen for v=0, and a considerable increase in decay rate for v=4, perhaps due to vibrational relaxation processes. Interpreting the results from the perspective of an HO_2 intermediate and past theoretical efforts reveals some challenges.

Another set of experiments is described involving OH and O decay measurements in mixtures of O atoms from ozone, H_2, O_2, and Ar. These are sensitive to rate constant ratios involving OH + O (1), O + HO_2, (2) and OH + HO_2, (3) and suggest a small increase for k(2) and decrease for k(3).

Experiments were performed at 140 K for trace amounts of OH or O (<1 mtorr) in 40 torr O_2 or N_2 to search for evidence of the proposed weakly bound HO_3 atmospheric complex. Signal intensities and slow decays are identical, which provides an upper limit of 5 kcal/mole for the stability of this species.