

## **II. Atmospheric Modeling and Measurements: Reducing Uncertainties Through Improved Kinetics and Spectroscopic Data**

*Ross J. Salawitch*

Jet Propulsion Laboratory, 4800 Oak Grove Drive, M/S 183-601, Pasadena, CA 91109  
E-mail: [Ross.Salawitch@jpl.nasa.gov](mailto:Ross.Salawitch@jpl.nasa.gov)

This presentation will focus on outstanding issues in the areas of composition of the UT (upper troposphere) and LS (lower stratosphere) as well as the global carbon cycle that would benefit from improved knowledge of fundamental kinetics and spectroscopic data. The presentation will describe uncertainties in the rate constant of the ClO+HO<sub>2</sub> reaction and other rate limiting steps for the catalytic loss of ozone; the emerging importance of bromine radicals derived from the decomposition of very-short lived biogenic bromocarbon precursors for both the UT and LS and the need to define fundamental aspects of the photochemistry of the organic decomposition products as well as possible heterogeneous reactions and aerosol uptake of the final inorganic products; and, the state of knowledge regarding the OH/HO<sub>2</sub> and HNO<sub>3</sub>/NO<sub>2</sub> ratios in the UT/LS region and related kinetics uncertainties. Finally, I will briefly describe an upcoming mission that will map the global distribution of CO<sub>2</sub> from space and the spectroscopic needs that are associated with these measurements.

## I2. A Pulsed Laser Photolysis-Pulsed Laser Induced Fluorescence Kinetic Study of Gas-Phase OH Radical Reactions with Cl<sub>2</sub>, HCl, Br<sub>2</sub>, CH<sub>4</sub>, and C<sub>3</sub>H<sub>8</sub>

*Mikhail G. Bryukov,<sup>a</sup> Barry Dellinger,<sup>a</sup> Vadim D. Knyazev,<sup>b</sup> and Slawomir M. Lomnicki<sup>a</sup>*

<sup>a</sup> Chemistry Department, Louisiana State University, Baton Rouge, LA 70803

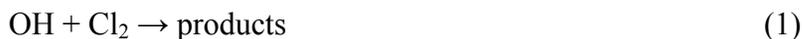
E-mail: [BarryD@LSU.edu](mailto:BarryD@LSU.edu)

<sup>b</sup> Department of Chemistry, The Catholic University of America, Washington, D.C. 20064

E-mail: [Knyazev@CUA.edu](mailto:Knyazev@CUA.edu)

Each year large quantities of toxic wastes containing halogenated-organics are generated by chemical and allied industries. A significant quantity of these chemicals are incinerated, flared, or are accidentally burned in fires. The understanding of the combustion chemistry is especially important in the case of brominated and chlorinated-organics, whose burning has the potential to generate toxic by-products (e.g., phosgene, molecular chlorine, polybrominated/chlorinated dibenzo-*p*-dioxins and dibenzofurans), which are more hazardous than the original chemical. This has stimulated the development of research directed at mechanistic and chemical kinetic modeling of combustion of bromo-chloro-organics. Accurate chemical kinetic modeling is essential for understanding the complicated chemistry of these processes. For example, combustion systems containing brominated and chlorinated species can undergo complex reaction sequences that govern the distribution of HCl, Cl<sub>2</sub>, HBr, and Br<sub>2</sub>. Since these species have varied halogenating ability, their relative concentrations can have significant impacts on the yields of brominated and chlorinated organic by-products. As in most combustion systems, the rates of reaction with OH have a major impact on the halogenated organic product distribution.

However, literature data on the reactions of OH with bromine and/or chlorine containing compounds are mostly confined to low temperatures, and high-temperature data relevant to combustion and thermal processes are sparse or controversial. In the current work, the absolute rate coefficients for the reactions of the hydroxyl radical with Cl<sub>2</sub>, HCl, Br<sub>2</sub>, CH<sub>4</sub>, and C<sub>3</sub>H<sub>8</sub>



have been determined as functions of temperature using a pulsed laser photolysis/pulsed laser induced fluorescence technique combined with heatable, slow-flow reactor. Reactions 4, 5 were studied in order to validate the experimental apparatus used here for the first time after its construction. The obtained bimolecular rate coefficients demonstrate no correlation with reaction pressure and their temperature dependences can be represented with the following expressions within corresponding temperature ranges (displayed in parentheses):

$$k_1 = 3.59 \times 10^{-16} T^{1.35} \exp(-745 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (297\text{--}826 \text{ K})$$

$$k_2 = 3.20 \times 10^{-15} T^{0.99} \exp(-62 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (298\text{--}1015 \text{ K})$$

$$k_3 = 1.85 \times 10^{-9} T^{-0.66} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (297\text{--}766 \text{ K})$$

$$k_4 = 3.82 \times 10^{-19} T^{2.38} \exp(-1136 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (298\text{--}1009 \text{ K})$$

$$k_5 = 6.64 \times 10^{-16} T^{1.46} \exp(-271 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (296\text{--}908 \text{ K})$$

To analyze the reaction mechanisms and to provide means for an extrapolation of the temperature dependences of the rate coefficients to temperatures outside the experimental ranges, theoretical models of reactions 1 and 2 were created. Potential energy surfaces of these reactions were studied using quantum chemical methods and bimolecular rate coefficients were calculated using transition state theory.

#### **Acknowledgment.**

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### **I3. The Reaction $\text{IO} + \text{NO}_2 \rightarrow \text{IONO}_2$ : The Bond Dissociation Energy in $\text{IONO}_2$**

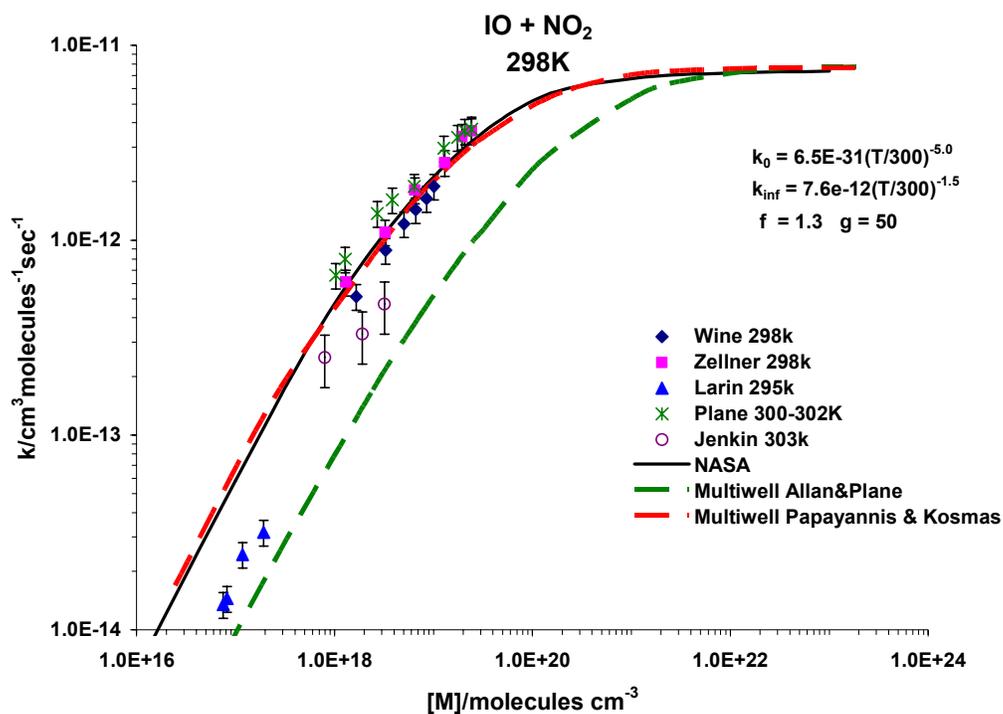
**David M. Golden**

Department of Mechanical Engineering  
Building 520, Stanford University, Stanford, CA 94305  
E-mail: [david.golden@stanford.edu](mailto:david.golden@stanford.edu)

The reaction between IO and  $\text{NO}_2$  presumably to form  $\text{INO}_3$  in some form, has been studied by several laboratories<sup>1-6</sup>. In addition the heat of formation of  $\text{IONO}_2$  and isomers ( $\text{IOONO}$  and  $\text{OINO}_2$  in various structures) has been calculated using various quantum methods.<sup>1,7,8</sup> We show in this work, by fitting the data with master equation/RRKM methods<sup>9</sup>, that only one of the calculated values fits the rate data. Interestingly, the difference shows up as a result of the centrifugal corrections to the energy (i.e the use of rotational energy to help in bond breaking and of course the reverse.)

Allen and Plane<sup>1</sup> use quantum calculations at the B3LYP/6-311+g(2d,p) level to compute a value for  $\Delta H_{f,0}^0(\text{IONO}_2) = 70 \pm 16$  kJ/mole. They fit their rate data with six parameters and indicate that the bond energy parameter is in reasonable agreement with their calculation. Papayannis and Kosmas<sup>7</sup> use MP2/LANL2DZpl and B3LYP/LANL2DZpl calculations for structure, frequencies and energetics. Single point calculations were carried out at the CCSD(T)/LANL2DZpl level. They suggest values for  $\Delta H_{f,0}^0(\text{IONO}_2)$  or either 36.1 or 42.4 kJ/mole depending on calculation of the bond energies IO- $\text{NO}_2$  or I- $\text{NO}_3$ .

The rate data for the reaction  $\text{IO} + \text{NO}_2 = \text{IONO}_2$  has been evaluated by the NASA/JPL Panel<sup>10</sup> and the data can be described by:  $k_0 = 6.5 \times 10^{-31} (\text{T}/300)^{-5.0}$ ;  $k_\infty = 7.6 \times 10^{-12} (\text{T}/300)^{-1.5}$ ;  $f = 1.3$ ;  $g = 50$  using the usual NASA expression of the Troe formula. In this work we used a restricted-Gorin model transition state that was fit to the NASA high pressure limit. Rational values, although surely uncertain, were used for the collisional energy terms. It was only possible to fit the data using the lower value for  $\Delta H_{f,0}^0(\text{IONO}_2)$ , that is a higher bond dissociation energy.



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## 14. Formation of HO<sub>2</sub> and OH in the Reaction of Methoxymethyl with Molecular Oxygen

*Kotaro Suzuki<sup>1</sup>, Kentaro Tsuchiya<sup>2</sup>, Mitsuo Koshi<sup>1</sup>, Atsumu Tezaki<sup>1</sup>*

<sup>1</sup>School of Engineering, The University of Tokyo, Hongo7-3-1, Bunkyo-ku, Tokyo, 113-8656, Japan

E-mail: Suzuki : [suzaki@comb.t.u-tokyo.ac.jp](mailto:suzaki@comb.t.u-tokyo.ac.jp), Koshi : [koshi@chemsys.t.u-tokyo.ac.jp](mailto:koshi@chemsys.t.u-tokyo.ac.jp),

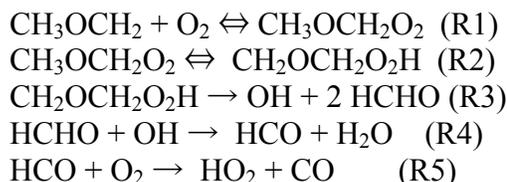
Tezaki : [tezaki@comb.t.u-tokyo.ac.jp](mailto:tezaki@comb.t.u-tokyo.ac.jp)

<sup>2</sup>National Institute of Advanced Industrial Science and Technology, Onogawa 16-1, Tsukuba, Ibaraki, 305-8595, Japan

E-mail: Tsuchiya : [k-tsuchiya@aist.go.jp](mailto:k-tsuchiya@aist.go.jp)

HO<sub>2</sub> and OH formation has been investigated in 355 nm photolysis of DME / Cl<sub>2</sub> / O<sub>2</sub> mixture between 296 K and 650 K. Frequency modulation spectroscopy with a Herriott type multi-path cell was applied to detect HO<sub>2</sub> at the first electronic transition and OH at the vibrational overtone in the region of 1.43 μm.

Figure 1 shows typical time profiles of (a) HO<sub>2</sub> and (b) OH. The HO<sub>2</sub> profile shows a gradual increase slower than the rate of CH<sub>3</sub>OCH<sub>2</sub> + O<sub>2</sub> like observed in small size alkanes [1, 2]. On the other hand, the OH profile shows a rapid rise with a peak yield larger than that of small size alkanes. According to a Curran et al. model of DME oxidation [3], an effective mechanism at 600 K is set as:



As shown in Fig.1, this model doesn't represent the HO<sub>2</sub> and OH profiles. To reproduce the rapid rise of OH, the direct forming pathway of OH is assumed; i.e.,



The reaction of OH with RO<sub>2</sub>, which is the main pathway of HO<sub>2</sub> formation in the case of neopentane [4], is also considered; i.e.,



Furthermore, the unimolecular decomposition of CH<sub>3</sub>OCH<sub>2</sub> was modified to suit the low-pressure experimental conditions. When the rate constants are assumed as  $k_3 = 1.25 \times 10^{13} \times \exp(-20100 \text{ cal/mol} / \text{RT}) \text{ s}^{-1}$ ,  $k_6 = 8.3 \times 10^{-12} \times \exp(-2100 \text{ cal/mol} / \text{RT}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , and  $k_7 = 1.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , both profiles are well reproduced as shown in Fig.1. Even at the rate of OH + CH<sub>3</sub>OCH<sub>2</sub>O<sub>2</sub> as high as the collision frequency, the OH +

HCHO pathway was found to be dominant for the HO<sub>2</sub> formation. Figure 2 shows potential energy diagrams of the CH<sub>3</sub>OCH<sub>2</sub> + O<sub>2</sub> reaction system. All calculations, including ours using G2M(CC1) // B3PW91/cc-pTVZ level of theory (MRMP2 // CASSCF/cc-pVTZ for TS<sub>4</sub>), favor the OH formation channel. We have found another pathway leading to HO<sub>2</sub> formation via



The HO<sub>2</sub> profiles are also reproduced when (R8) is included with a slight modification of k<sub>3</sub>.

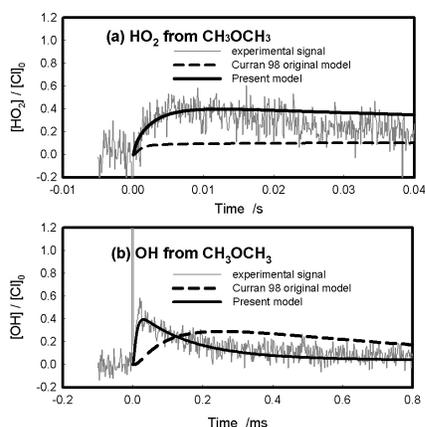


Fig.1 Time profiles of (a) HO<sub>2</sub> and (b) OH at 600 K.

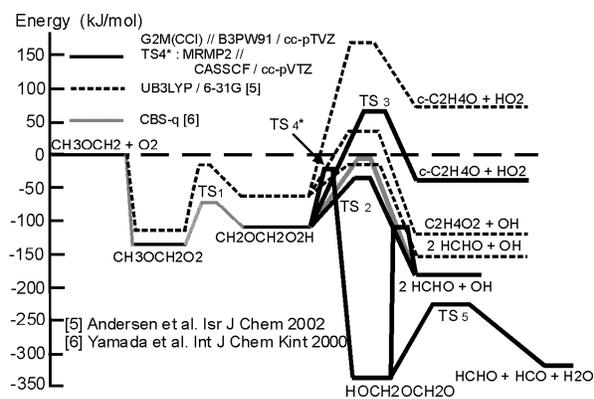


Fig.2 Potential energy diagrams of CH<sub>3</sub>OCH<sub>2</sub> + O<sub>2</sub> system

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## **I5. Halogenated Hydrocarbons: Accuracy of Photochemical Data for the Atmospheric Lifetime, Gwp, and Odp Estimations**

*Vladimir L. Orkin, Michael J. Kurylo*

Physical and Chemical Properties Division, National Institute of Standards and Technology  
Gaithersburg, Maryland 20899-8330

[vladimir.orkin@nist.gov](mailto:vladimir.orkin@nist.gov), [michael.j.kurylo@nasa.gov](mailto:michael.j.kurylo@nasa.gov)

The emissions of halogenated (Cl, Br, I containing) organics of both natural and anthropogenic origin contribute to the balance of and changes in the stratospheric ozone concentration. The associated chemical cycles are initiated by the photochemical decomposition of the portion of source gases that reaches the stratosphere. Reactions with hydroxyl radicals and photolysis are the main processes dictating the compound lifetime in the troposphere and release of active halogen in the stratosphere for a majority of halogen source gases. Halogenated compounds contribute to the radiative balance of the atmosphere as well. Therefore, the accuracy of photochemical data is of primary importance for the purpose of comprehensive atmospheric modeling and for simplified kinetic estimations of global impacts on the atmosphere, such as in ozone depletion (i.e., the Ozone Depletion Potential, ODP) and climate change (i.e., the Global Warming Potential, GWP).

The results of experimental kinetic investigations of a number of halogenated alkanes, alkenes, ethers, and alcohols over the temperature range of atmospheric interest will be presented to illustrate various complications in the accurate determination of OH reaction rate constants leading to uncertainties in the estimation of atmospheric lifetimes. The accuracy of present day laboratory measurements and the problems associated with the evaluation of kinetic data for use in atmospheric modeling will be discussed. Similarly, the accuracy of UV and IR absorption measurements will be highlighted to provide an improved basis for atmospheric modeling.

## 16. Kinetics, Mechanism, and Thermochemistry of the CH<sub>2</sub>CHO + O<sub>2</sub> Reaction

*E. Delbos<sup>a</sup>, C. Fittschen<sup>a</sup>, H. Hippler<sup>b</sup>, N. Krasteva<sup>b</sup>, M. Olzmann<sup>b</sup>, B. Viskolcz<sup>c</sup>*

<sup>a</sup> Physicochimie des Processus de Combustion et de l'Atmosphère UMR CNRS 8522, Cité Scientifique, Bât. C11, F-59655 Villeneuve d'Ascq, France

E-mail: Christa.Fittschen@univ-lille1.fr

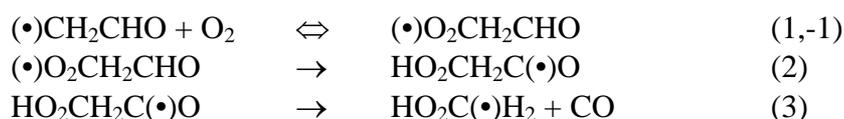
<sup>b</sup> Institut für Physikalische Chemie, Universität Karlsruhe, Kaiserstr. 12, D-76128 Karlsruhe, Germany

E-Mail: Matthias.Olzmann@chemie.uni-karlsruhe.de

<sup>c</sup> Department of Chemistry, J. Gy. Teacher's Training College, University of Szeged, H-6701 Szeged, P. O. Box 396, Hungary

E-Mail: Viskolcz@jgytf.u-szeged.hu

Vinoxy radicals, CH<sub>2</sub>CHO, occur as intermediates in combustion systems as well as in the atmospheric degradation of unsaturated hydrocarbons. The CH<sub>2</sub>CHO + O<sub>2</sub> reaction is an interesting example for an association reaction, which is comparatively slow but exhibits only a very weak temperature dependence. It is assumed to proceed via reversible complex formation with subsequent isomerization-dissociation steps:



In our paper we report on a combined experimental and theoretical study of this reaction sequence. The kinetics was investigated in the temperature range between 298 and 660 K and at pressures from 10<sup>-3</sup> to 50 bar (Helium). The experiments were conducted in a fast-flow reactor and in two different quasi-static reactors under pseudo-first order conditions with respect to O<sub>2</sub>. Vinoxy radicals were generated by the CH<sub>3</sub>CHO + F reaction and by laser-flash photolysis of CH<sub>2</sub>CHOC<sub>2</sub>H<sub>5</sub>, respectively. The progress of reaction was followed by laser-induced fluorescence of CH<sub>2</sub>CHO. At temperatures below 430 K we observed a monoexponential decay of [CH<sub>2</sub>CHO](t) attributable to reaction (1); between ca. 430 and 530 K a biexponential decay indicates that reactions (-1) and (2) become increasingly important, and at still higher temperatures, above 570 K, the decay is again monoexponential and essentially governed by reaction (2) with a fast pre-equilibration by reactions (1) and (-1). Rate coefficients k<sub>1</sub>, k<sub>-1</sub> and k<sub>2</sub> were determined and their temperature and pressure dependences were analyzed in terms of a master equation based on molecular and energetic parameters from ab initio calculations. Our results are compared with the limited data available from earlier works and a reasonable agreement is found. Activation and falloff parameters as well as thermochemical data for further use in atmospheric and combustion modeling are proposed.