2940 *J. Phys. Chem. A* **2006,** *110,* 2940−2943

Evaluating Data for Atmospheric Models, an Example: $IO + NO_2 = IONO_2$[†]

David M. Golden*

Department of Mechanical Engineering, Stanford University, Stanford, California 94305

Received: August 10, 2005

Data for the title reaction have been fit to the different formalisms used by the NASA and IUPAC data evaluation panels. The data are well represented by either formalism. Reported values for the bond dissociation energy at 0 K, $D_0(IO-NO_2)$ vary from about 95 to 135 kJ mol^{-1}, with uncertainty ranges of about 20 kJ mol^{-1}. Master equation/RRKM methods were employed in an attempt to reconcile these values with the data. This was possible within reasonable bounds and suggests a value in the neighborhood of 150 kJ mol^{-1}. As always, there are sufficient assumptions and unknowns in such an attempt, that this value is somewhat uncertain, but the true value is not expected to be too far from this result. Thus, it is possible to evaluate data of the type addressed here in a manner reasonably consistent with the basic understanding of pressure dependent rate coefficients for use in atmospheric or other models of "engineering" problems. There are, however, strict limits on our ability to know specific details. It is possible that true anharmonicity corrections that include stretch−bend interactions as well as effects due to averaging rotational contributions could combine to lower this value by as much as 10 kJ mol^{-1}. In addition collision and energy transfer parameters are somewhat uncertain.

Introduction

It has been the author's task for several years to evaluate data for association reactions and equilibrium constants for the NASA/JPL Evaluation.[1] By the nature of experimental limitations, data, when available, are restricted in scope. It is therefore very useful to compare extant data with theoretical understanding in an attempt to extrapolate to all values of pressure and temperature of interest. In this endeavor my attention was called to the title reaction. A comprehensive study by Allan and Plane [AP][2] delineates the reasons for atmospheric interest and complements and extends data of earlier workers as well as performing relevant quantum calculations. Papayannis and Kosmas [PK][3,4] have more recently performed theoretical calculations as well. Interestingly, there is significant disagreement between these two theoretical results. While the structure and vibrations for $IONO_2$ are essentially identical, the heats of formation are very different. AP compute at the B3LYP/6-311+G(2d,p) level. They report a bond dissociation energy at 0 K, $D_0(IO-NO_2)$/kJ mol^{-1} = 94.9 with uncertainty of the order of 20 kJ mol^{-1}. PK have carried out single-point coupled cluster calculations at the CCSD(T)/LANL2DZpl level on B3LYP/LANL2DZpl optimized geometries and compute $D_0(IO-NO_2)$/kJ mol^{-1} = 146.0, which they then convert to 137.6 or 131.7, depending on the value they use for the spin−orbit correction in IO. (In their more recent work[4] they seem to have settled on 131.4.) They also compute $D_0(I-ONO_2)$/kJ mol^{-1} = 157.3. They use the latter value to compute $\Delta H_{f,0}{}^0(IONO_2)$ /kJ mol^{-1} = 42.6, but they use $\Delta H_{f,0}{}^0(NO_3)$ /kJ mol^{-1} = 62.4, whereas the correct value[1] is 71.1, yielding $\Delta H_{f,0}{}^0(IONO_2)$ /kJ mol^{-1} = 51.3. Using the value[1] for $\Delta H_{f,0}{}^0(IO)$/kJ mol^{-1} = 121, one computes $D_0(IO-NO_2)$/kJ mol^{-1} = 105.6, revealing some uncertainty in the methods employed. These values are sufficiently different, and the rate data are close enough to the low-pressure regime, where the energy dependence of the density of states might allow one to distinguish between them. Herein is described treatment of the title reaction using a Master Equation/RRKM approach. (PK compute structures and energetics for several isomers of $IONO_2$. The stability of these isomers is so much less than that of $IONO_2$, that they are not expected to contribute to the association reaction of IO and NO_2.) An earlier theoretical calculation was performed by Rayez and Destriau[5] reported $D_0(IO-NO_2)$/kJ mol^{-1} = 134 ± 13. Chambers et al. [6] report an upper limit of the heat of formation of $IONO_2$ of 21 kJ mol^{-1}. However they used a value of the heat of formation of NO_3 in deducing this value that has been increased[1] by 9.3 kJ mol^{-1}, meaning that their upper limit becomes 29.3 kJ mol^{-1}.

Empirical Data Evaluation

For the NASA/JPL Evaluation,[1] data for the title reaction were taken from refs 7−11. (Data from a study by Blitz et al.[12] were presented as a poster at a meeting and agrees with data from ref 7.) Values of k_0, n, k_∞, and m were chosen to best describe the data according to

$$k(\mathrm{M},T) = \left(\frac{k_0(T)[\mathrm{M}]}{1 + (k_0(T)[\mathrm{M}]/k_\infty(T))}\right)0.6^{\{1+[\log(k_0(T)[\mathrm{M}]/k_\infty(T))]^2\}^{-1}}$$

with the rate constants represented as $k_0(T) = k_0(300\mathrm{K})(T/300)^{-n}$ and $k_\infty(T) = k_\infty(300\mathrm{K})(T/300)^{-m}$.

The IUPAC Evaluation[13] uses a somewhat different version of the equation and has also evaluated the same data.

$$k(\mathrm{M},T) = \left(\frac{k_0(T)[\mathrm{M}]}{1 + (k_0(T)[\mathrm{M}]/k_\infty(T))}\right)F_c{}^{\{1+[\log(k_0(T)[\mathrm{M}]/k_\infty(T))/(0.75-1.27\log(Fc))]^2\}^{-1}}$$

Both the evaluations describe the data adequately. The parameters from each evaluation are given in Table 1. (Most up to date results of both the NASA and IUPAC evaluations are found

---

[†] Part of the special issue "Jürgen Troe Festschrift".

* Corresponding author e-mail: david.golden@stanford.edu.

10.1021/jp058221k CCC: $33.50

TABLE 1: NASA and IUPAC Parameters Association Direction[a]

	k_0/cm^6 molecule^2 s^{-1}	k_∞/cm^3 molecule^{-1} s^{-1}	F_c	n	m
NASA	6.5E−31	7.6E−12	[0.6]	3.5	1.5
IUPAC	7.7E−31	1.6E−11	[0.4]	5	0
AP	1.3E−30	6.5E−12	.57	5	1.3

[a] Values in brackets were fixed. Rate constants represented as $k_0(T) = k_0(300\text{K})(T/300)^{-n}$ and $k_\infty(T) = k_\infty(300\text{K})(T/300)^{-1}$.

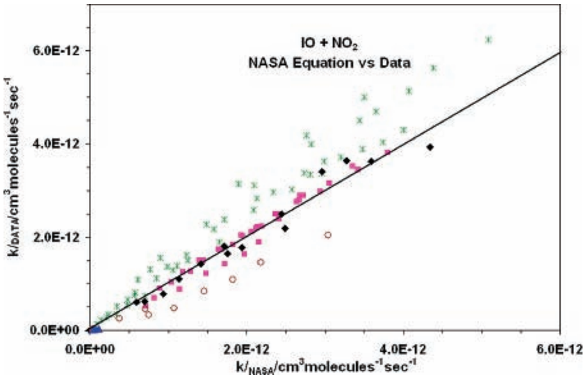

Figure 1. Measured rate constants vs values from NASA parameters (Table 1). The line is the 1:1 line—crosses: ref 2; squares: ref 8; diamonds: ref 7; open circles: ref 11; filled circles: ref 10; triangles: ref 9.

on their Web sites.) Figure 1 shows all the data compared with the predictions from the NASA equation. (A similar plot using the IUPAC parameters and equation looks similar.)

RRKM/Master Equation Analysis

The analysis proceeded in the following fashion:

1. Structure and frequencies for IONO$_2$ were taken from either ref 2 or 3. These are very similar. In this work values from PK were used. No conclusion reached herein is affected by these small differences.

2. Using the PK parameters, the moments of inertia shown in Table 2 are computed. The center of mass distance in the molecule is computed from the J moment. Using a Morse potential, computed using this center of mass coordinate, the position of the centrifugal maximum was obtained by adding the rotational energy at the maximum, assumed[14] to be kT and setting the derivative to zero. (Table 2 contains the constants used and the result of the maximization of the potential at 300 K. These values will change somewhat with values for the bond energy.) This value can then be used to replace the IO—NO$_2$ equilibrium bond length, and moments of inertia can be calculated for this new entity, the transition state. (Using a Varshni potential changes the value slightly. A Lennard-Jones potential gives a much larger value for the position of the centrifugal maximum and would require an even larger hindrance of the rotors in the transition state than we use. Moments of inertia may also be calculated by computing maxima at individual values of J and then using suggestions by Troe[15] to compute the centrifugal partition function, from which the moment of inertia may be computed. There is a very small difference in the value obtained using these methods.)

3. Frequencies and moments of inertia for the transition state were those of NO$_2$ used previously[16] and IO from the JANAF Tables.[17]

4. Energy transfer with the nitrogen bath gas was computed using the exponential down probability function, and the value of $\langle \Delta E \rangle_{\text{down}}$ could be adjusted in an attempt to reproduce the fitted curves. (Changing $\langle \Delta E \rangle_{\text{down}}$ within rational limits has only a small effect.) Lennard-Jones collision parameters and the value of $\langle \Delta E \rangle_{\text{down}}$ are given in Table 3.

TABLE 2: Calculation of Centrifugal Maximum

$V(r) = \text{De}[1-\exp(-\beta(r-re))]^2 + kT(\text{rmax}/r)^2$	
IONO$_{2(\text{PK}:\Delta H=150\text{ kJ/mol})}$	$T = 300$ K
IO- -NO$_2$ stretching frequency	$\omega = 627$ cm^{-1}
bond energy	$D_o = 12539$ cm^{-1}
change in zpe between IO+NO$_2$ and IONO$_2$	Δzpe = 1201 cm^{-1}
$D_o + \Delta$zpe	De = 13740 cm^{-1}
mass of IO	Ma = 142.9 amu
mass of NO$_2$	Mb = 46 amu
reduced mass	$\mu = 34.8$ amu
2D moment of inertia	$J = 398.9$ amu Å^2
IO- -NO$_2$ bond length	re = 1.434 Å
COM bond length = (J/m)$^{1/2}$	ree = 3.386 Å
$0.12177\omega(\mu/\text{De})^{1/2}$	$\beta = 3.842$ Å^{-1}
rmax (center of mass)	5.258 Å
rmax (bond distance) = rmax (center of mass) − (ree-re)	3.306 Å

5. Hindrance values were chosen to reproduce the high pressure rate constant from the NASA/JPL Evaluation, given a trial critical energy, at three separate temperatures (218, 277, and 298 K), and critical energies were chosen in the range of those suggested by either AP or PK. (Past experience suggests that changing the A-factor, for example to fit the IUPAC values, would change the hindrance values somewhat, but usually the data can still be accommodated.) Since the output of the Multiwell code[18] used for the calculations is the fraction of dissociation, $k_{\text{diss}}(P,T)/k_{\text{diss},\infty}(T)$, and since the output also yields $k_{\text{diss},\infty}(T)$, the equilibrium constant was calculated from the appropriate values of the enthalpy and the structure and frequencies of IONO$_2$, IO, and NO$_2$ using the "Thermo" code in the Multiwell suite, to compute the association rate constant, $k_{\text{assn}}(P,T)$. Table 3 shows values used in the calculations. (The same value results when the fraction, which may also be written as $k_{\text{assn}}(P,T)/k_{\text{assn},\infty}(T)$, is multiplied by the NASA/JPL high-pressure limit for association.) Values of the equilibrium constant using a critical energy of 150 kJ mol^{-1} are given in Table 4. (When other values of the critical energy were tried, the value of the equilibrium constant was recalculated.)

The "Hindered-Gorin" Transition State

Using the value of the centrifugal maximum calculated above, the collision rate between IO and NO$_2$ at 300 K is 3.7×10^{-10} cm^3 molecules^{-1} s^{-1}, and this would be an upper limit for the high-pressure limit of the association rate constant. Since both the NASA and IUPAC evaluations suggest an A-factor much smaller than this, the transition state must be tighter than the collision complex represented by the centrifugal maximum in the potential energy surface. As pointed out several times,[16] this tightening of the transition state can be modeled using the methods of variational transition state theory by changing frequencies of the transitional modes or by using a hindered-Gorin transition state which is tightened by restricting the rotations of the IO and NO$_2$ reactants to less than the 4π steradians that could be available to them. Over the temperature range addressed here, there may be no real difference, but over a large temperature range, the differences in heat capacity of the loosened transitional modes, which have the heat capacity of low-frequency vibrations (i.e. R), and the restricted rotations, which have energy spacing and thus heat capacity of a particle in a box (i.e. R/2), can become apparent. Past experience[19,20] with systems where the data were available over much larger temperature ranges leads toward use of the hindered-Gorin model.

TABLE 3: Parameters for Multiwell Calculations

$IONO_2$	
critical energy at 0 K/kJ mol^{-1}	150
vibrational frequencies[a]/cm^{-1}	1765,1336,837,769,627,371,188,737,*108*
hindered rotor:frequency/cm^{-1}; moment of inertia/AMU A^2; rotational symmetry (foldedness)	108; 13.12; 3
(J-rotor) adiabatic moments of inertia /AMU A^2	399
(K-rotor) active external rotor/AMU A^2	40.93
symmetry; electronic degeneracy; optical isomers	1; 1; 1
IO- - -NO_2 (Transition State) NASA Fit	
frequencies/cm^{-1}	1318,749.65,1617.8,649
(J-rotor) adiabatic moments of inertia /AMU A^2	848.7 @300 K; 854.8@277 K; 873.5@218 K
(K-rotor) active external rotor/AMU A^2	60.6 @300 K;60.7@277 K;61.1@218 K
moments of inertia active 2-D rotors/AMU A^2	52.6(IO); 9.34(NO_2)
hindrance: η(300K); η(277K); η(218K)	93%; 91%;87%
symmetry; electronic degeneracy; optical isomers	1; 1; 1
collisions: (σ/A^2; ϵ/K;) $IONO_2$	7.7; 1000
N_2	3.7; 82
$\langle \Delta E \rangle_{down}$/ cm^{-1}	400

[a] Frequency in italics replaced with hindered rotor with no important change in results, given the small temperature range considered.

TABLE 4: Equilibrium Constants

T (K)	K/cm^3 $molecule^{-1}$
200	1.98E+12
218	1.06E+09
277	1.94E+01
300	1.26E−01

for 200−300 K: $K = 5.04E28\exp(18233/T)$

Transition states were chosen to match the high-pressure parameters from fitting the NASA formula to the data[7−9,11,12] on association of IO with NO_2. The parameters are shown in Table 3. As is often found, to fit the observed negative activation energy for the high pressure limiting rate constant, the hindrances are somewhat larger at higher temperatures. This is consistent with the fact that the centrifugal barriers are at an increasingly shorter IO—NO_2 distance as the temperature increases.

Once the values that lead to the high-pressure parameters were fixed, the values for $\langle \Delta E \rangle_{down}$, the energy transfer parameter used in the exponential down model of energy transfer, and the Lennard-Jones collision diameters and well depths were chosen. The Lennard-Jones parameters for nitrogen were taken from the table of such values in the notes to the Multiwell[18] code, and the values for $IONO_2$ were estimated using the same table. (These latter values were chosen to produce the highest rational value for the Lennard-Jones collision frequency, thus ensuring that the value of the critical energy would be the lowest possible to fit the data.) As is shown in Table 3, the value for fitting the NASA expression is 400 cm^{-1} for the three temperatures we chose to fit. Changes in this parameter over a reasonable range can have a small effect on the value of the critical energy used. ($\langle \Delta E \rangle_{down}$ can be temperature dependent; this kind of variation was not required here. It is entirely conceivable that small changes in some of the other fitting parameters would accommodate a temperature dependence for $\langle \Delta E \rangle_{down}$.)

Discussion

In their paper AP[2] have also performed a master equation RRKM analysis. They fit their data using the inverse Laplace transformation (ILT) method.[14] They find the parameters that fit the data, including the collision parameters and their temperature dependence, by statistical methods. For the ILT method to be applicable the rate coefficient should be expressed in Arrhenius terms. (An exact argument can be made if the A-factor and activation energy are independent of temperature, although AP use a version[21] that allows for the form $k = A^\infty (T/300)^n \exp(-E^\infty/kT)$.) It seems that in using this ILT method AP set E^∞ to zero while incorporating any temperature dependence into the T^n type term. AP represent the high-pressure limit of the rate constant for the association of IO and NO_2 to form $IONO_2$, in the form $k^\infty = A^\infty(T/300)^n$, with $A^\infty = 6.46 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} and $n = -1.32$. If this is translated to the Arrhenius form, $k^\infty = A^\infty \exp(-(E^\infty/R)/T)$, over the temperature range of their study, the value becomes k^∞/cm^3 $molecule^{-1}$ $s^{-1} = 1.57 \times 10^{-12}$ $\exp(406.9/T)$. It is not clear what the effect of this change would be. (Plane[22] has reevaluated this procedure and finds that the data can be fit, using ILT methods, with $k^\infty = A^\infty(T/300)^n$, with $A^\infty = 1.6 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} and $n = -1.2$ or $6 \times 10^{-12}\exp(300/T)$.)

In addition, there are several other places in the AP analysis that cause some difficulty. Given the extent of falloff in all these experimental studies, the parameters for energy transfer become important. AP quote Lennard-Jones collision parameters as $\sigma = 5.7$ A and $\epsilon/k = 550$ K. These values are quite large. The usual way to compute the collision diameter σ for the $IONO_2/N_2$ pair would be to average the individual values for each molecule. Since the value given in the Multiwell[18] notes for N_2 is $\sigma = 3.74$ A, the value for $IONO_2$ required is 7.7 A, which is a bit large, but possible. As for the collision well depth, ϵ/k, the usual computation for a pair is the geometric mean of the individual values. The recommended value from the Multiwell notes for N_2 is 82 K, which requires a value of 3689 K for $IONO_2$. This is really big! AP used the exponential down probability function, with a value for $\langle \Delta E \rangle_{down}/cm^{-1} = 500(T/300)^{-1.15}$. This negative temperature dependence is a bit unusual. Using these values AP fit their data with a critical energy value of 105 kJ mol^{-1}. (Plane [22] now finds $\sigma = 4$ A and $\epsilon/k = 400$ K and $\langle \Delta E \rangle_{down}/cm^{-1} = 350(T/300)^{-1.2}$ and a critical energy of 128 kJ mol^{-1}.) In a full RRKM master equation calculation, using a hindered Gorin model for the transition state that fit the corrected A-factor and critical energy above and all other parameters from the recent communication,[22] I could not fit the data. Figure 2 shows the data near 298 K plotted together with the values from the NASA parameters as well the results using the parameters in Plane[22] (with the corrected A-factor fit by a hindered-Gorin transition state) and master equation results using the values in Table 3. It is apparent from Figure 2 that the Plane[22] parameters do not fit the data, while an enthalpy difference in the neighborhood of 150 kJ mol^{-1} does fit the data. (I was able to reconcile the newer values communicated

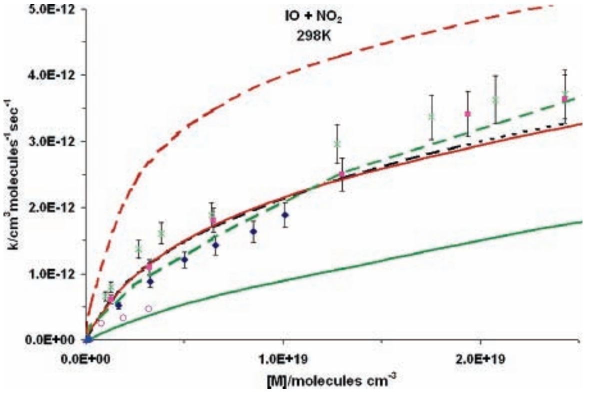

Figure 2. Measured rate constants at about 298 K (symbols as in Figure 1) compared with values from NASA parameters (black dotted line); master equation calculation with parameters from Table 3 (red solid line); master equation calculation with parameters from ref 22 (green solid line). Also shown are ILT calculations using the equivalent inputs, red and green dashed lines.

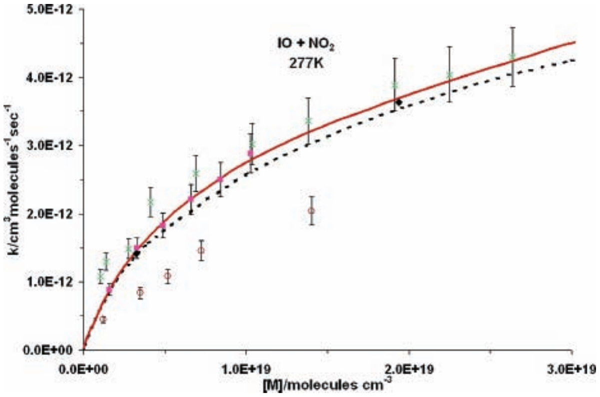

Figure 3. Measured rate constants at about 277 K compared with values from NASA parameters and master equation calculation with parameters from Table 3. Symbols are as in Figure 2.

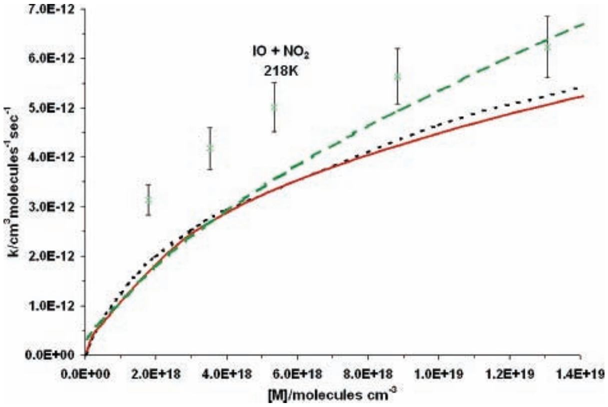

Figure 4. Measured rate constants at about 218 K compared with values from NASA parameters, master equation calculation with parameters from Table 3, and an ILT calculation using parameters from ref 22. Symbols are as in Figure 2.

by Plane[22] with the data, using the ILT method, but when I insert more acceptable collision parameters the fit to the data is destroyed. Note also that the ILT computations differ from the full RRKM values. Barker et al.[23] have discussed this issue.)

Figure 3 shows the Multiwell calculation and the data and empirical evaluations at 277 K.

AP do make an empirical fit of their data to the NASA equation. Their parameters are given in Table 1. Their equation, does indeed fit their data, but their data is on the high side of the extant values. This explains why at 218 K, where theirs is the only data, the evaluations and the master equation results of this report lie a bit below the AP data. See Figure 4.

Only the higher value of about 150 kJ mol^{-1} reproduces the data. The higher value of the bond dissociation energy means a higher value for the density of states of the reactant above the critical energy. This raises the *A*-factor for the low pressure limiting rate constant, and the higher activation energy is effectively canceled by the equilibrium constant when calculating the association rate constant. (It is possible that true anharmonicity corrections that include stretch−bend interactions as well as effects due to averaging rotational contributions could combine to lower this value by as much as 10 kJ mol^{-1}.)

My final point is that this, while a rational analysis, has so many approximations that attempts to analyze data of this type at a level more microscopic than used herein are an exercise in futility!

Acknowledgment. This work was supported through Grant # NNA04CC98 “Evaluation of Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling” from The NASA Upper Atmosphere Research Program. I take great delight in acknowledging Jürgen Troe for his contributions ranging from detailed fundamental chemical physics to the understanding that applications of this knowledge are vital. I had the pleasure of spending the academic year 1974−1975 with Troe and his colleagues, and it represented a scientific reeducation.

References and Notes

(1) Sander, S. P.; Finlayson-Pitts, B. J.; Friedl, R. R.; Golden, D. M.; Huie, R. E.; Kolb, C. E.; Kurylo, M. J.; Molina, M. J.; Moortgat, G. K.; Orkin, V. L.; Ravishankara, A. R. *Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation Number 14*; Jet Propulsion Laboratory, 2003.

(2) Allan, B. J.; Plane, J. M. C. *J. Phys. Chem. A* **2002**, *106*, 8634−8641.

(3) Papayannis, D.; Kosmas, A. *Chem. Phys. Lett.* **2004**, *398*, 75−81.

(4) Papayannis, D.; Kosmas, A. *Chem. Phys.* **2005**, *315*, 251−258.

(5) Rayez, M. T.; Destriau, M. *Chem. Phys. Lett.* **1993**, *206*, 278−284.

(6) Chambers, R. M.; H. A., Wayne, R. P. *J. Phys. Chem.* **1992**, *96*, 3321−3331.

(7) Daykin, E.; Wine, P. *J. Phys. Chem.* **1990**, *94*, 4528−4535.

(8) Hölscher, D.; Zellner, R. *Phys. Chem. Chem. Phys.* **2002**, *4*, 1839−1845.

(9) Larin, I. K.; Nevozhai, D. V.; Sapasskii, A. I.; Trofimova, E. M. *Kinet. Catal.* **1998**, *39*, 666−672.

(10) Maguin, F.; Laverdet, G.; La Bras, G.; Poulet, G. *J. Phys. Chem.* **1992**, *96*, 1775−1780.

(11) Jenkin, M. E.; Cox, R. A. *J. Phys. Chem.* **1985**, *89*, 192−199.

(12) Blitz, M.; Dillon, T.; Heard, D. Laser Induced Fluorescence Studies of the IO +NO_2 Reaction; 16th International Symposium on Gas Kinetics, 2000, Cambridge, U.K.

(13) Atkinson, R.; Baulch, D. L.; Cox, R. A.; R. F. Hampson, J.; Kerr, J. A.; Rossi, M. J.; Troe, J. *J. Phys. Chem. Ref. Data* **2000**, *29*, 167−266.

(14) Holbrook, K. A.; Pilling, M. J.; Robertson, S. H. *Unimolecular Reactions*, 2nd ed.; Wiley: Chichester, 1996.

(15) Troe, J. *Chem. Rev.* **2003**, *103*, 4565−4576.

(16) Golden, D. M.; Barker, J. R.; Lohr, L. L. *J. Phys. Chem.* **2003**, *107*, 11057−11071.

(17) Chase, M., Jr. *J. Phys. Chem. Ref. Data* **1998**, *Monograph No. 9*, 1404.

(18) Barker, J. R. *Int. J. Chem. Kinet.* **2001**, *33*, 232−245.

(19) Smith, G. P.; Manion, J. A.; Rossi, M. J.; Rodgers, A. S.; Golden, D. M. *Int. J. Chem. Kinet.* **1994**, *26*, 211−217.

(20) Stewart, P. H.; Smith, G. P.; Golden, D. M. *Int. J. Chem. Kinet.* **1989**, *21*, 923−945.

(21) De Avillez Pereira, R.; Baulch, D. L.; Pilling, M. J.; Robertson, S. H.; Zeng, G. *J. Phys. Chem. A* **1997**, *101*, 9681−9693.

(22) Plane, J. M. C. Personal communication.

(23) Barker, J. R.; Lohr, L. L.; Schroll, R. M.; Reading, S. *J. Phys. Chem. A* **2003**, *107*, 7434−7444.