Evaluation of Data for Atmospheric Models: Master Equation/RRKM Calculations on the Combination Reaction, $BrO + NO_2 \rightarrow BrONO_2$, a Conundrum

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Experimental data for the title reaction were modeled using master equation (ME)/RRKM methods based on the Multiwell suite of programs. The starting point for the exercise was the empirical fitting provided by the NASA (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 15*; Jet Propulsion Laboratory: Pasadena, California, 2006)[1] and IUPAC (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)[2] data evaluation panels, which represents the data in the experimental pressure ranges rather well. Despite the availability of quite reliable parameters for these calculations (molecular vibrational frequencies (Parthiban, S.; Lee, T. J. *J. Chem. Phys.* **2000**, *113*, 145)[3] and a value (Orlando, J. J.; Tyndall, G. S. *J. Phys. Chem.* **1996**, *100*, 19398)[4] of the bond dissociation energy, $D_{298}(BrO-NO_2) = 118$ kJ mol^{-1}, corresponding to $\Delta H_0{}^o = 114.3$ kJ mol^{-1} at 0 K) and the use of RRKM/ME methods, fitting calculations to the reported data or the empirical equations was anything but straightforward. Using these molecular parameters resulted in a discrepancy between the calculations and the database of rate constants of a factor of ca. 4 at, or close to, the low-pressure limit. Agreement between calculation and experiment could be achieved in two ways, either by increasing $\Delta H_0{}^o$ to an unrealistically high value (149.3 kJ mol^{-1}) or by increasing $\langle \Delta E_d \rangle$, the average energy transferred in a downward collision, to an unusually large value (>5000 cm^{-1}). The discrepancy could also be reduced by making all overall rotations fully active. The system was relatively insensitive to changing the moments of inertia in the transition state to increase the centrifugal effect. The possibility of involvement of BrOONO was tested and cannot account for the difficulties of fitting the data.

Introduction

The role of bromine in the chemistry of the stratosphere is by now well-established.[5−7] Although bromine compounds are present in much lower amounts than chlorine compounds, they nevertheless play a significant role. This is because a much larger fraction of bromine is partitioned into active forms (Br + BrO) rather than reservoir species as compared to chlorine. The most important bromine reservoir species in the lower stratosphere is bromine nitrate, which is formed via the BrO + NO_2 association reaction

$$BrO + NO_2 + M \rightarrow BrONO_2 + M \qquad (1)$$

Not surprisingly, the kinetics and equilibrium of reaction 1 have received the attention of researchers,[4,8−10] and quantum chemical (ab initio) calculations of the $BrO-NO_2$ bond strength also have been published.[4,8−11] The existing data recently have been evaluated by both NASA(JPL)[1] and IUPAC panels.[2] Under experimental (and atmospheric) conditions, this reaction is close to its low-pressure (third-order) region of pressure dependence. Using the well-established Troe and Gardiner-type formulations,[12] but with slightly different parameters, the pressure and temperature dependences are reasonably well-fitted. The main differences between NASA and IUPAC lie in the values for the high-pressure limiting (second-order) rate constants, $k_{1\infty}$ ($=k_{\infty,\mathrm{comb}}$), which have not been measured experimentally. It is perhaps slightly surprising that no RRKM or similar type of calculations have been carried out hitherto, in view of the importance of this reaction. Because of previous experience in this type of calculation and, in particular, in atmospherically relevant association reactions,[13] reaction 1 was an attractive target. Interest was heightened by recent discrepancies concerning the analogous IO + NO_2 reaction.[14,15]

The information required for RRKM-type calculations appears to be readily available and not controversial. Molecular vibrations and structural parameters for $BrONO_2$ are available from the theoretical study of Parthiban and Lee (PL).[3] A value of 118.0 ± 6.3 kJ mol^{-1} for the bond dissociation energy, $D_{298}(BrO-NO_2)$ (The enthalpy change at 298 K, $\Delta H_{298}{}^o$, for the reaction $BrONO_2 = BrO + NO_2$), was obtained by Orlando and Tyndall (OT)[4] by combining forward and reverse rate constants for bromine nitrate decomposition using both second- and third-law thermodynamic analyses. (If the reaction between BrO and NO_2 was to form isomers of bromine nitrate in any significant amounts, this analysis would not be valid.) Theoretical calculations of $D_{298}(BrO-NO_2)$ give values of 118 kJ mol^{-1}

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TABLE 1: NASA and IUPAC Rate Constant Parameters for BrO + NO$_2$ (+N$_2$)

	k_0 (cm^6 molecule^2 s^{-1})	k (cm^3 molecule^{-1} s^{-1})	F_c	n	m
NASA	5.2×10^{-31}	6.9×10^{-12}	0.6	3.2	2.9
IUPAC	4.7×10^{-31}	1.8×10^{-11}	0.4	3.1	0

(based on a calculated $\Delta H_{f,298}$(BrONO$_2$) value obtained from several isodesmic reactions[11]) and[16] 125 kJ mol^{-1}, in good agreement with experiment. An earlier theoretical calculation by Rayez and Destriau[17] reported D_{298}(BrO$-$NO$_2$) = 143 ± 8 kJ mol^{-1}. The potential complication of involvement of the BrOONO isomer would appear to be ruled out by the weakness of the O$-$O bond, for which values as low as 14 and not higher than 31 kJ mol^{-1} are implied by the calculations of Lesar et al.[18] However, calculations in the present study, allowing for both its formation and its isomerization to BrONO$_2$, showed that the master equation (ME) calculations were not sensitive to the existence of this weakly bound isomer.

Empirical Data Evaluation. Both the NASA[1] and the IUPAC[2] evaluations were based on kinetic data for the title reaction from Sander et al.,[9] Danis et al.,[8] and Thorn et al.[10] In the NASA evaluation, values of k_0, n, k_∞, and m were chosen to best describe the data according to

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

with the rate constants represented as $k_{0,T} = k_{0,300}(T/300\ \text{K})^{-n}$ and $k_{\infty,T} = k_{\infty,300}\ (T/300\ \text{K})^{-m}$.

The IUPAC evaluation[2] uses a somewhat different version of the equation

$$k(M,T) = \frac{k_0(T)[M]}{1 + k_0(T)[M]/k_\infty(T)} F_c^{\{1+[\log(k_0(T)[M]/k_\infty(T))/(0.75-1.27\log(F_c))]2\}^{-1}} \qquad (3)$$

with similar parametrization of the rate constants. The parameters from each evaluation are given in Table 1. (Most up-to-date results of both the NASA and the IUPAC evaluations are found on their websites: http://jpldataeval.jpl.nasa.gov/ and http://www.iupac-kinetic.ch.cam.ac.uk/.) Both the evaluations describe the data adequately as can be seen in Figure 2, although, clearly, the high-pressure limits are different.

RRKM/ME Analysis. The analysis proceeded in the following fashion: (1) The energetics of the two well calculations were based on (i) ΔH_0^o(BrO$-$NO$_2$) = 114.3 kJ mol^{-1} derived from the ΔH_{298}^o value of OT[4] (using the Thermo code in the Multiwell suite and the structure and frequencies of BrONO$_2$ from PL[3] and those of BrO and NO$_2$, as well as their heats of formation, from the JANAF compilation[19]) and (ii) ΔH_0^o(BrO$-$ONO) = 20.2 kJ mol^{-1} derived from the calculated energy difference between BrONO$_2$ and BrOONO of 94.1 kJ mol^{-1} (CCSD(T)/6-311G(d) level of theory) obtained by Lesar et al.[18] No values have been reported for the isomerization barrier between the two isomers, and this was arbitrarily set at 14.6 kJ mol^{-1} to allow the possibility of interconversion. These numbers are incorporated into the potential energy surface shown in Figure 1 for easy reference. (2) The structure and frequencies for BrONO$_2$ were taken from PL[3] and those for BrOONO from Lesar et al.[18] (3) Using the aforementioned geometries, the moments of inertia of BrONO$_2$ and BrOONO were computed. The two-dimensional (2-D) moment of inertia (shown in Table 2) is the root-mean-square of the two largest moments (J-moment). The center-of-mass distance in each molecule is calculated from the J-moment and the reduced mass of BrO and NO$_2$, treated as point masses (pseudo-diatomic approximation) by dividing by the reduced mass and taking the square root. Using a Morse potential, computed using this center-of-mass coordinate (which is greater for each molecule than the bond length of the breaking bond) and the known well depth, the position of the centrifugal maximum was obtained by adding the rotational energy at the maximum, assumed[20] to be kT, and setting the derivative to zero. (Table 2 contains the constants used and the results of the maximization of the potential at 300 K.) These values were then used to replace the BrO$-$NO$_2$ and BrO$-$ONO equilibrium bond lengths, and moments of inertia were calculated for these new entities, viz. the transition states. This was done at each temperature of interest, but in the limited temperature range of the data, 251$-$346 K, the values changed very little. A Lennard-Jones potential gave a larger value for the position of the centrifugal maximum and would have altered the moments of inertia somewhat. However, this could have been easily compensated for by the use of a larger hindrance of the rotors in the transition state, with very little effect on the

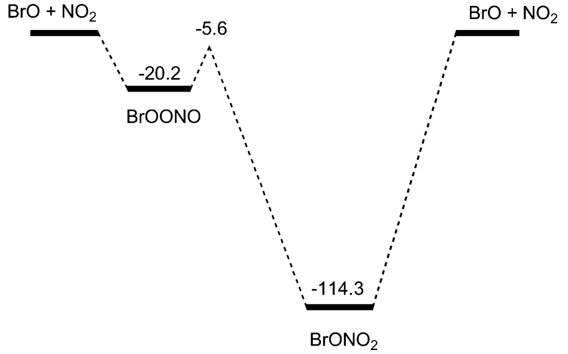

Figure 1. Energy surface for the BrO + NO$_2$ radical combination reaction. Energy values are in kilojoules per mole (0 K). See text for data sources.

TABLE 2: Centrifugal Maxima for BrO$-$NO$_2$ and BrO$-$ONO Dissociation

BrONO$_2$	
$V(r) = D_e[1 - \exp(-\beta(r - r_e))]^2 + kT(r_{max}/r)^2$	
temp (K)	300
BrO$-$NO$_2$ stretching wavenumber (ω, cm^{-1})	747
bond energy (ΔH_0^o) (D_o, cm^{-1})	9554.7
change in zpe between BrO + NO$_2$ and BrONO$_2$ (Δzpe, cm^{-1})	1117
$D_o + \Delta zpe$ (D_e, cm^{-1})	10671.7
mass of BrO (M_a, amu)	96.0
mass of NO$_2$ (M_b, amu)	46
reduced mass (μ, amu)	31.1
2-D moment of inertia (J, amu Å^2)	315.7
BrO$-$NO$_2$ bond length (r_e, Å)	1.486
center-of-mass bond length = $(J/\mu)^{1/2}$ (r_{ee}, Å)	3.186
$0.12177\omega\ (\mu/D_e)^{1/2}$ (β, Å^{-1})	4.91
r_{max} (center-of-mass) (Å)	4.623
r_{max} (bond distance) = r_{max} (center-of-mass) $-$ ($r_{ee} - r_e$) (Å)	2.923
BrOONO	
BrO$-$ONO stretching wavenumber (ω, cm^{-1})	980
bond energy (ΔH_0^o) (D_o, cm^{-1})	1688.6
change in zpe between BrO + NO$_2$ and BrOONO (Δzpe, cm^{-1})	500.7
$D_o + \Delta zpe$ (D_e, cm^{-1})	2189.3
2-D moment of inertia (J, amu Å^2)	312.4
BrO$-$ONO bond length (r_e, Å)	1.366
center-of-mass bond length = $(J/\mu)^{1/2}$ (r_{ee}, Å)	3.170
$0.12177\omega(\mu/D_e)^{1/2}$ (β, Å^{-1})	14.22
r_{max} (center-of-mass) (Å)	3.612
r_{max} (bond distance) = r_{max} (center-of-mass) $-$ ($r_{ee} - r_e$) (Å)	1.808

TABLE 3: Parameters for Multiwell Calculations for $BrONO_2$ Dissociation

$BrONO_2$ (Molecule)	
critical energy at 0 K (kJ mol^{-1}) (ΔH_0^o)	114.3
vibrational wavenumbers (cm^{-1})	1743, 1321, 818, 747, 744, 560, 393, 209
hindered internal rotors: wavenumber (cm^{-1}); moment of inertia (amu Å^2); rotational symmetry	112; 12.56; 2
(J-rotor) adiabatic moments of inertia (amu Å^2)	315.7
(K-rotor) active external rotor (amu Å^2)	41.5
symmetry; degeneracy; optical isomers	1; 1; 1
$BrO-NO_2$ (Dissociation Transition State)	
vibrational wavenumbers (cm^{-1})	1618, 1318, 750, 727
(J-rotor) adiabatic moments of inertia (amu Å^2)	675.7 (251 K); 671.7 (268 K); 664.8 (300 K); 656.0 (346 K)
(K-rotor) active external rotor (amu Å^2)	56.8 (251 K); 56.8 (268 K); 56.6 (300 K); 56.4 (346 K)
moments of inertia active 2-D rotors (amu Å^2)	39.3 (Br), 9.34 (NO_2)
hindrances (%)	83.7 (251 K); 86.9 (268 K); 91.0 (300 K); 94.3 (346 K)
symmetry; degeneracy; optical isomers	1; 1; 1
LJ collision parameters [σ (Å^2) and ϵ (K)]	5.2; 450 ($BrONO_2$), 3.74; 82 (N_2)
$\langle \Delta E_d \rangle$ (cm^{-1})	see text
BrOONO (Molecule)	
critical energy at 0 K (kJ mol^{-1}) (ΔH_0^o)	20.2
vibrational wavenumbers (cm^{-1})	1846, 980, 676, 560, 443, 307, 265
hindered internal rotors: wavenumber (cm^{-1}); moment of inertia (amu Å^2); rotational symmetry	210; 4.22; 1125; 42.8; 1
(J-rotor) adiabatic moments of inertia (amu Å^2)	312.4
(K-rotor) active external rotor (amu Å^2)	61.0
symmetry; degeneracy; optical isomers	1; 1; 2
BrO−ONO (Dissociation Transition State)	
vibrational wavenumbers (cm^{-1})	1618, 1318, 750, 727
(J-rotor) adiabatic moments of inertia (amu Å^2)	805.9
(K-rotor) active external rotor (amu Å^2)	2.19
moments of inertia active 2-D rotors (amu Å^2)	39.3 (Br), 9.34 (NO_2)
hindrance (%)	94.5
symmetry; degeneracy; optical isomers	1; 1; 1
LJ collision parameters [σ (Å^2) and ϵ (K)]	5.2; 450 (BrOONO), 3.74; 82 (N_2)
$\langle \Delta E_d \rangle$ (cm^{-1})	see text
BrOONO → $BrONO_2$ (Isomerization Transition State)	
critical energy at 0 K (kJ mol^{-1}) (ΔH_0^o)	14.6
vibrational wavenumbers (cm^{-1})	1800, 1500(2), 1000, 600, 500(3)
(J-rotor) adiabatic moments of inertia (amu Å^2)	739.3
(K-rotor) active external rotor (amu Å^2)	43.3
symmetry; degeneracy; optical isomers	1; 1; 2

outcome. (Moments of inertia also may be calculated by computing maxima at individual values of J and then using suggestions by Troe[21] to compute the centrifugal partition function. There is very little difference between the outcomes of these methods.) (4) Frequencies and moments of inertia for the transition states were taken to be those of NO_2, used previously,[22] and BrO, from the JANAF tables.[19] The frequencies for the transition state for isomerization between the nitrate and the peroxynitrous forms were based on reasonable estimates for a cyclic structure. This information is given in Table 3. (5) Energy transfer with the nitrogen bath gas was computed using the exponential down probability function, and the value of $\langle \Delta E_d \rangle$, the average energy transferred in a downward step, was set at 400 cm^{-1}, a reasonable value[15] for N_2. Normal uncertainties in this and the other collision parameters affected the fitting of the calculated curves to the results, but often, the data can be accommodated with only small changes in these quantities. As will become apparent next, one way that data could be fit for this BrO + NO_2 system was to make enormous changes in the $\langle \Delta E_d \rangle$ values. This will be discussed next. The parameter values also are given in Table 3. (6) The choice of the degrees of hindrance (which determine the high-pressure limiting A factor) is discussed in the next section. (7) Since the Multiwell code[23,24] used here, as for other RRKM codes, calculates the unimolecular rate constants for dissociation (i.e., for the reverse of reaction −1), it is necessary to know the equilibrium constants to compute the association rate constants. The equilibrium constants were calculated using the Thermo code within Multiwell, which employs the same input information (the enthalpy change and the structure and frequencies of $BrONO_2$, BrOONO, BrO, and NO_2) as for the RRKM calculation itself. The values for the computed thermodynamic parameters and equilibrium constants at the temperatures of interest are given in Table 4.

Hindered-Gorin Transition State. Using the value of the centrifugal maximum calculated previously, the collision rate constant between BrO and NO_2 at 300 K was 3.08×10^{-10} cm^3 molecule^{-1} s^{-1}, and this would be the maximum possible value for the high-pressure limit of the association rate constant. Since both the NASA and the IUPAC evaluations suggest that the A factor is much smaller than this, the transition state must be tighter than the collision complex represented by the centrifugal maximum on the potential energy surface. As pointed out several times previously,[13,22] this tightening of the transition state can be modeled using the methods of variational transition state theory either by changing the frequencies of the transitional modes or by using a hindered-Gorin transition state in which the rotations of the BrO and NO_2 reactant molecules are restricted to less than the 4π steradians that could be available to them. Over the small temperature range addressed here, there will be no real difference between these alternatives, but over a large temperature range, there can be a significant difference.

TABLE 4: Equilibrium Constants and Thermodynamic Quantities[a]

$BrO + NO_2 \leftrightarrow BrONO_2$

T (K)	K_c (cm^3 $molecule^{-1}$)	ΔS^o ($J\ K^{-1}\ mol^{-1}$)	ΔH^o ($kJ\ mol^{-1}$)
251	7.33×10^{-4}	−158.2	−118.1
268	2.16×10^{-5}	−158.4	−118.2
300	8.43×10^{-8}	−158.6	−118.2
336	5.88×10^{-10}	−158.6	−118.2
346	1.78×10^{-10}	−158.6	−118.2

$BrO + NO_2 \leftrightarrow BrOONO$

T (K)	K_c (cm^3 $molecule^{-1}$)	ΔS^o ($J\ K^{-1}\ mol^{-1}$)	ΔH^o ($kJ\ mol^{-1}$)
251	6.22×10^{-23}	−143.1	−22.3
268	3.33×10^{-23}	−142.7	−22.6
300	1.27×10^{-23}	−141.8	−22.3
336	5.49×10^{-24}	−140.9	−22.0
346	4.50×10^{-24}	−140.6	−22.0

[a] Standard state: 1 bar.

This is because the heat capacities of vibrators and rotors are different, causing temperature variation of pre-exponential terms to become apparent. Past experience[25,26] with systems where the data were available over much larger temperature ranges supports the use of the hindered-Gorin model.

Degrees of hindrance for the transition states were chosen (for the most part) to match the high-pressure rate constants obtained by the NASA formula, although some calculations also were carried out to explore the consequences of trying to fit the IUPAC equation instead.

Calculations and Results

Two well calculations were performed using the parameters in Table 3. Note that the 2-D rotations of $BrONO_2$ and $BrO-NO_2$ are assumed to be adiabatic. The wells correspond to $BrONO_2$ and BrOONO as shown in Figure 1. Each may be formed from the interaction of BrO and NO_2. In addition, it has been assumed that they may interconvert over the small arbitrarily set barrier via a cyclic transition state whose frequencies were estimated in this study. Two calculations must be made for each temperature: one starting with a chemical activation energy distribution for $BrONO_2$ formed from BrO and NO_2 and the other starting with a chemical activation energy distribution for BrOONO also formed from these species.

As a first approximation, it was assumed that the high-pressure rate constants for each path were equal and that the hindrances were chosen to reflect this assumption. Figure 2 shows the data, the NASA and IUPAC evaluations, and the results of the two well fit. The red line labeled Total in Figure 2 shows that the formation via chemically activated BrOONO only contributes at the highest pressures in the calculation, which are well above the experimental range. Most notable is the lack of fit to the data at low pressures, where the data are some 4 times higher than the calculations.

The red dashed line labeled Total I+ = 3000&2000 in Figure 2 was computed with the very unphysical assumption that the moments of inertia of the transition states for $BrONO_2$ and BrOONO were, respectively, increased to 3000 and 2000 amu $Å^2$. The fact that the results are insensitive to large changes in these moments of inertia shows that the difference between experiment and calculation is not due to errors in these moments. As to the source of the discrepancy between calculation and experiment, three further possibilities were considered, viz. the critical energy might be much higher than thought, or the energy transfer may be much more efficient than expected, or finally, all overall rotations could be assumed to be active. As regards the critical energy, the data can be fit by raising $\Delta H_0{}^o(BrO-NO_2)$ to a value of 149.3 kJ mol^{-1}; however, given the earlier discussion of the bond energy, it would seem that there is only a relatively small uncertainty in the value chosen and that this higher value is out of the range. With respect to energy transfer, the value of $\langle \Delta E_d \rangle$ was raised to the seemingly unphysical value of 5000 cm^{-1}. This comes close (within 50% at low pressures) to fitting the data as can be seen from the red dotted line in Figure 2. Presumably larger values for $\langle \Delta E_d \rangle$ would fit even better, but they do not seem realistic. If all rotations are taken as active, the red dashed−dotted line in Figure 2 results, showing again a significant improvement to the fit. This is the most that can be achieved with active rotations. One final small effect was found by lowering the isomerization barrier of BrOONO from 14.6 to 4.2 kJ mol^{-1}. This raised the rate constants by about 10%.

Calculations at the other reported temperatures show similar discrepancies with the data. Figures 3 and 4 show the differences at 251 and 346 K. The same considerations apply to these calculations as to those at 300 K. For instance, it seems clear that arbitrarily raising $\langle \Delta E_d \rangle$ also will accommodate these data.

A single channel calculation was carried out to try to match the dissociation rate constants of Orlando and Tyndall.[4] This is shown in Figure 5. Again, a strong discrepancy is apparent, even though the data in this case are in the intermediate region of pressure dependence. The lines labeled NASA and IUPAC have been computed by combining their rate constant values for the association reaction with the equilibrium constant values calculated here.

Although Figures 2−5 only show calculations matching the NASA/JPL high-pressure limiting rate constant values, other calculations (with different hindrance parameters) were carried out to match the IUPAC high-pressure limits. The calculated pressure dependence curves revealed exactly the same differences at the low-pressure region of the experimental data. Therefore, the previous analysis, and general discussion of the results, is independent of which data evaluation is employed.

Discussion

In the BrO + NO_2 system studied here, our calculations show that the inclusion of two wells (i.e., the incorporation of the hyponitrous isomer, BrOONO) makes very little difference to the calculated results. Our mechanistic model assumes the most favorable situation to assisting combination (i.e., one in which there is interconversion of BrOONO and $BrONO_2$). No attempt was made to include the additional complexities of possibly different behavior[27,28] of particular conformers of BrOONO. If the barrier to isomerization were higher (and this is still an issue of controversy for related systems[29,30]), it would have little effect on these calculations. Only if there was a serious error in the theoretical estimate of the overall isomerization energy and if BrOONO was substantially more stable than currently thought could its inclusion in these calculations have a more serious effect.

The methods described herein have been applied previously to several systems. Interestingly, the results of such calculations are in reasonable agreement with the data for the reactions of OH with NO_2[22] and for CH_4 dissociation along with CH_3 + H association.[31] However, problems similar to those found in this study also exist for the association[15] of IO with NO_2 and Cl with NO_2.[32]

A feature of these latter systems (as well as the present one) is that the values for $k_{\infty,comb}$, the high-pressure rate constants arising out of the fitting (although relatively far from the high-

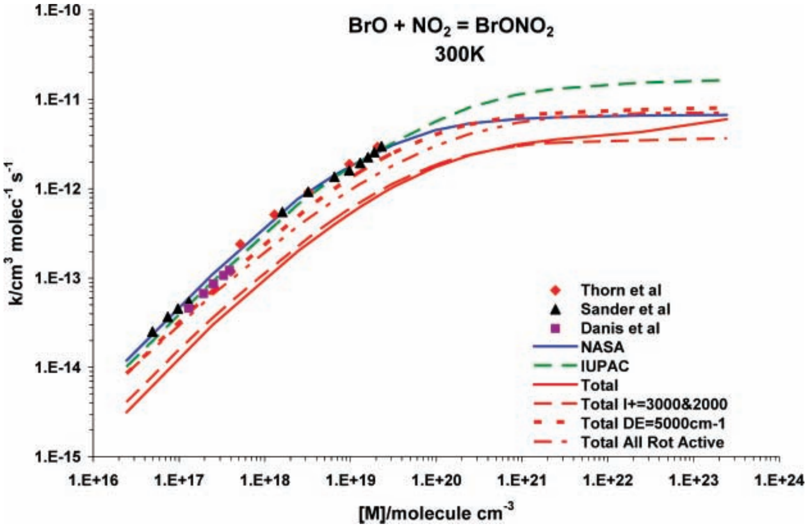

Figure 2. Comparison of data, empirical fits, and modeling for the title reaction at 300 K. The solid red line marked Total is for the total loss of reactants in the standard two well ($BrONO_2$ and BrOONO) computations using parameters from Table 3. The dashed red line marked Total I+ = 3000&2000 represents the effect of increasing the moments of inertia of the transition states leading to $BrONO_2$ and BrOONO to 3000 and 2000 amu Å^2, respectively. The dotted red line marked Total DE = 5000 cm^{-1} represents the results when the value of $\langle \Delta E_d \rangle$ is increased to 5000 cm^{-1}. The dashed−dotted line represents the results when all rotations are taken as active.

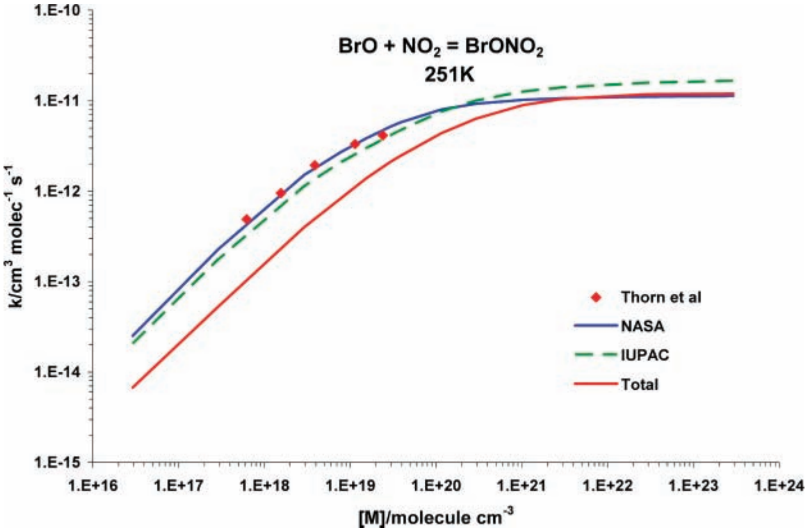

Figure 3. Comparison of data, empirical fits and modeling for the title reaction at 251K. Symbols are as in Figure 2.

pressure limit), are in agreement with those for simple alkyl radical combination. Although there are differences between the NASA[1] and the IUPAC[2] values, both are in the range for ethyl radical combination.[33] This implies tight transition states (which become even tighter when negative temperature dependences of $k_{\infty,\mathrm{comb}}$ are taken into account). These are not the relatively unencumbered transition states of alkyl radical combination with H-atoms.[31,34] The hindered-Gorin approach has no difficulty characterizing either type of transition state since the choice of hindrance parameter is purely empirical. However, despite recent studies,[27,28] there is clearly a need for further quantum chemical (ab initio) calculations of electronic energy surfaces to characterize better the bottleneck for $XO + NO_2$ combination. There is also a need for kinetic studies directed to obtaining $k_{\infty,\mathrm{comb}}$ for $XO + NO_2$ at higher pressures than those explored thus far.

On the other hand, the low-pressure limit presents a more difficult problem. The methods employed here involve the use of a 1-D ME, and given the relative insensitivity to the value of $I^{\ddagger}$, it is doubtful that a 2-D calculation would improve the situation much. Setting all the rotational energy as active, which is just a way of increasing the calculated density of states, still falls short of matching the data. (It has been suggested[35] that the anharmonicity above the reaction threshold is being underestimated.) The energy transfer process, a significant contributing factor to the magnitude of the low-pressure rate constant values, although heavily studied, is not well-understood. In all the calculations, the exponential down probability distribution was employed. There are others, and the Multiwell suite offers several. Perhaps different systems would be better described with different choices for this function. Or, perhaps those systems containing halogen atoms really do transfer energy with large step sizes.

A reviewer has suggested that bound triplet states might be involved, similar to suggestions[36] concerning $CH_3 + NO$. This reviewer also pointed out that the spin orbit splitting in BrO is higher than in NO but suggested that faster intersystem crossing could balance this out. If a triplet surface were to be involved, it would also affect the high-pressure limit, but this probably could be accommodated.

As far as $BrO + NO_2$ is concerned, both the NASA and the IUPAC evaluations described the data reasonably well in the

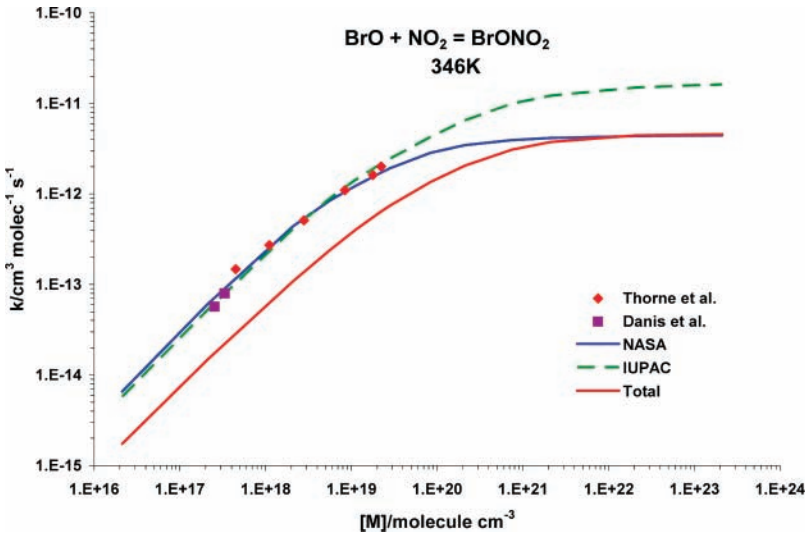

Figure 4. Comparison of data, empirical fits, and modeling for the title reaction at 346 K. Symbols are as in Figure 2.

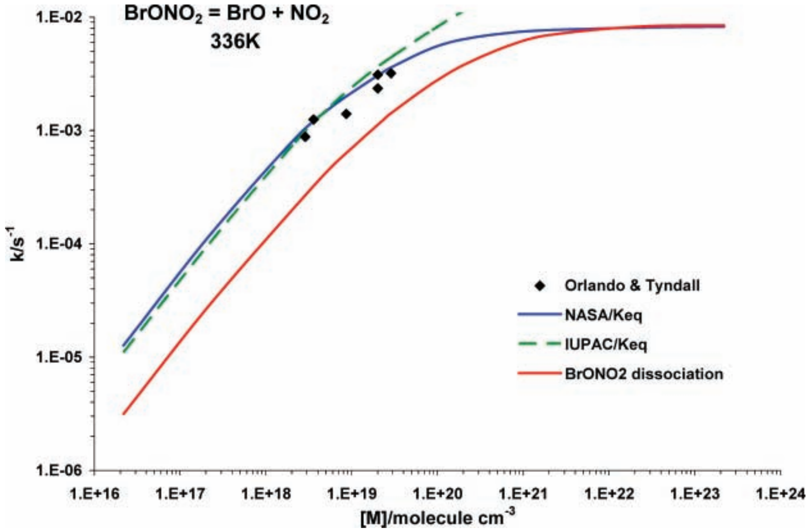

Figure 5. Comparison of data, empirical fits, and modeling for the dissociation of $BrONO_2$ at 336 K. NASA and IUPAC values were obtained via the equilibrium constant.

temperature and pressure regions of practical interest in atmospheric models. It remains a challenge to understand the low-pressure limit and, in particular, energy transfer in this system.

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