J. Phys. Chem. A **1998,** *102,* 31−34

Nonconservation of Spin in the Reaction of CN with O_2

Leon F. Phillips

Chemistry Department, University of Canterbury, Christchurch, New Zealand

Received: July 28, 1997; In Final Form: September 30, 1997[⊗]

Violation of spin conservation is likely to be a normal occurrence for reactions that satisfy the following criteria: (1) the reaction rate is limited by the rate of capture over a long-range centrifugal barrier in an attractive potential; (2) product formation is the result of fast rearrangement of a bound collision complex; and (3) attractive short-range potentials exist for more than one spin state of the complex. An analogy exists between the time evolution of the system during a reaction of this type and the optical phenomenon of quantum beats. Taking failure of spin-conservation into account removes some of the problems encountered in a previous calculation of the rate constant for reaction of CN with O_2 at very low temperatures. Problems encountered at very high temperatures suggest that this reaction system is too small for the decay of the NCOO* complex to be treated statistically.

1. Introduction

For references to the considerable body of previous work on this reaction the reader is referred to a critical review by Smith,[1] who concludes that there still remains considerable scope for further work on the topic, both experimental and theoretical. In a recent paper from this laboratory,[2] quasi-classical trajectory calculations were used to obtain the rate constant for formation of the NCOO* complex, as given by the rate of capture over the centrifugal barrier in a dipole−quadrupole + dipole−induced dipole + London + Morse potential. The results of quantum-chemical calculations of energies, moments of inertia, and vibration frequencies for the complex and for the transition state leading to the products OCN + O were then used, in combination with statistical reaction-rate theory, to calculate relative values of the first-order rate constants for decomposition of NCOO* to reactants and rearrangement to products over the temperature range 1−2000 K. The rate constant for the overall reaction was obtained as the product of the capture rate and the fraction of NCOO* complexes that rearranged to form OCN + O.

Probably the most notable feature of the work described in ref 2 was that, in contrast to earlier studies of this type,[3−5] the calculations were to a large extent unsuccessful, in that it was found to be impossible to reproduce the experimental values of the rate constant at temperatures below about 75 K. Because the calculated capture rates at low temperatures were too small, this difficulty was tentatively attributed to the use of a fixed spin-degeneracy factor of 1/3 to convert from the capture rate to the maximum possible reaction rate, which amounts to ignoring the possibility of the collision complex undergoing a nonadiabatic transition from the unreactive quartet potential surface to the reactive doublet surface when the centrifugal barrier occurs at long range, as originally proposed by Klippenstein and Kim.[6] The present paper uses a highly simplified model to rectify this omission, in a manner which allows the CN + O_2 reaction to be modeled more satisfactorily at low temperatures while revealing the existence of a different problem at high temperatures, and concludes that failure of spin-conservation and similar conservation rules is likely to be a normal occurrence for systems in which collision complexes in two or more different states correspond to attractive short-range potentials between the reactants.

At low temperatures the fraction of capture collisions leading to product formation is close to unity and the comparison of theory with experiment highlights any deficiencies in the capture-rate calculation. At very high temperatures the comparison highlights deficiencies in the statistical reaction-rate calculation. For CN + O_2 the calculated rate constants at high temperatures are again much too small. This proves to be a consequence of the fact that the calculated rate of decomposition of NCOO* back to the reactants CN + O_2 becomes so large as to be physically unreasonable, a result which implies that a statistical treatment is not realistic for a system as small as NCOO*.

2. Theory

Violation of spin-conservation has been demonstrated experimentally for several ion−molecule reactions involving N(^{4}S),[7] reactions for which the attractive ion−induced dipole interaction is insensitive to the resultant spin state of the system. Federer et al.[7] discussed their results in terms of the surface-hopping model which Zahr et al.[8] used to discuss quenching of O(^{1}D) by N_2. The essence of this model is that the efficiency of the nonadiabatic process is greatly enhanced by multiple crossings of a localized intersection between the potential surface of the long-lived collision complex and a potential surface which correlates with reaction products (Figure 1a). However, this kind of surface-hopping model does not apply very well to ion−molecule reactions, nor to radical−radical reactions such as CN + O_2, where the relevant potential surfaces are more likely to be of the form shown schematically in Figure 1b. These surfaces resemble the potential curves employed by Nikitin and co-workers[9] in their discussion of the large cross sections found for mixing of multiplet states of alkali metal atoms by collision with inert gases, which are such that nonadiabatic transitions may occur over relatively extended regions of the collision trajectory in the absence of a localized intersection of the diabatic surfaces. For the system of Figure 1b, neither the spin

---

[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1997.

S1089-5639(97)02489-4 CCC: $15.00

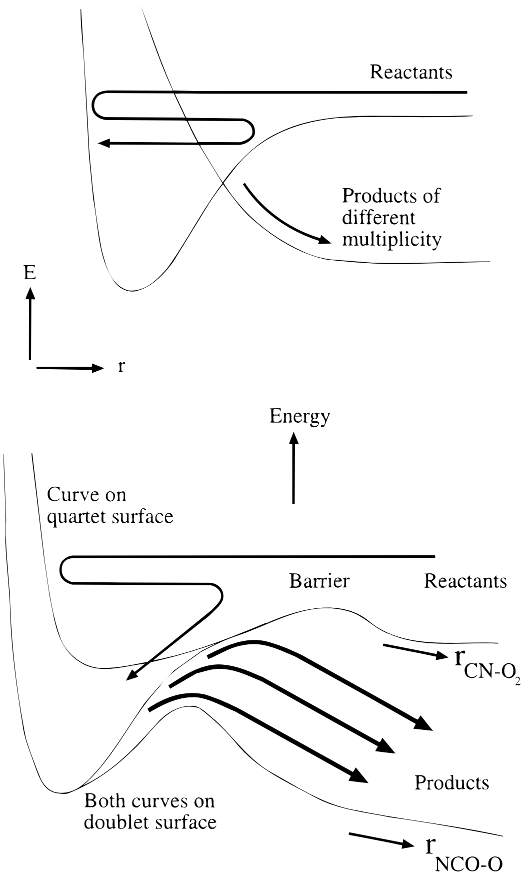

Figure 1. (a) Form of potential curves used by Zahr et al.[8] in their discussion of the $O(^1D) + N_2$ reaction. (b) Form of potential curves appropriate for reactions in which the states of differing multiplicity are degenerate at large reagent separations.

state nor the classical trajectory is well-defined during a collision, and the process that ensues is analogous to the optical phenomenon of quantum beats.[10,11] The common feature is that the system of interest exists in a state which is a coherent superposition of two eigenstates that have slightly different energies and widely differing decay rates. In the optical version, a population of atoms or molecules is excited coherently into a group of coupled states by a brief pulse of radiation, and the subsequent exponential decay of fluorescence shows superimposed oscillations that result from interference between the phase factors of the coupled states. In the chemical analogue a mixed state is prepared by the long-range collision, and the process corresponding to fluorescence decay is the passage of the system over a low potential barrier, amounting to an entropy bottleneck, on a trajectory that leads to products.

The chemical process can be described mathematically by an adaption of Bitto and Huber's description of quantum beat spectroscopy,[11] as follows. For two coupled energy eigenstates $|a\rangle$ and $|b\rangle$ the mixed state prepared at time zero, which might be taken, for example, as the time of crossing the potential barrier, is

$$|\Psi_0\rangle = c_a|a\rangle + c_b|b\rangle \tag{1}$$

where the squared modulus of a coefficient c_i is equal to the statistical weight w_i for populating state $|i\rangle$ during the collision. At time t the mixed state is

$$|\Psi_t\rangle = c_a|a\rangle \exp(-[i\omega_a+\gamma_a/2]t) + c_b|b\rangle \exp(-[i\omega_b+\gamma_b/2]t) \tag{2}$$

where $\omega_i = E_i/\hbar$ and the γ_i are decay constants which incorporate both the rate of nonadiabatic transition between $|a\rangle$ and $|b\rangle$ and the rate of transition to a final state $|f\rangle$, which here comprises the products OCN + O. In the case of state $|a\rangle$ the transition to the final state is likely to be dominant; in the case of state $|b\rangle$ the direct transition to the final state is assumed to be forbidden for dynamical reasons, so transition to $|f\rangle$ via state $|a\rangle$ predominates. For simplicity we ignore decay channels leading back to the original reactants. There is no way of distinguishing between products that derive directly from state $|a\rangle$ and those that derive from state $|b\rangle$ via a nonadiabatic transition to state $|a\rangle$, so interference effects are to be expected. The rate of formation of products is proportional to the square of the matrix element of some operator R_a between the state $|\Psi_t\rangle$ and the final state $|f\rangle$. Hence the rate of product formation at time t is proportional to

$$|\langle f|R_a|\Psi_t\rangle|^2 = w_a R_{fa}^{\,2}\, exp(-\gamma_a t) + w_b R_{fb}^{\,2} \exp(-\gamma_b t) + 2(w_a w_b)^{1/2} R_{fa} R_{fb} \exp(-[\gamma_a + \gamma_b]t/2) \cos(\omega_a - \omega_b)t \tag{3}$$

where the interference effects appear in the cosine factor. The breakdown of spin conservation is manifested as a nonzero value of the matrix element R_{fb}. In principle it should be possible to observe quantum beats in the reaction probability as a function of time by means of an experiment in which a collision complex of well-defined energy was prepared in a statistical mixture of the two coupled eigenstates. Because of divergence of potential surfaces of differing multiplicity at short range, the beat frequency observed in such an experiment would not remain constant during a trajectory, but would vary with the local energy difference between the eigenstates and might provide a sensitive probe of the energy difference. However, the variety of different possible relative orientations of CN and O_2 during collision would almost certainly cause any quantum beat effects to be averaged out in a simple beam experiment. Such effects might, however, be observable in an experiment in which the number of possible relative orientations was severely constrained, as for example in the polarized-laser photodissociation of the R−CN bond in an RCN−O_2 van der Waals complex.

In the situation where success or failure of a collision is determined mainly by crossing or failing to cross a centrifugal barrier at long range, potential surfaces of differing multiplicity remain quasi-degenerate until the intermolecular separation is within the range at which chemical effects begin to become important. This is also the range over which it is possible for one of the multiplet states to decay to products. Therefore, if violation of spin-conservation is to be significant, the nonreactive state should also be attractive over some or all of this range. For an ion−molecule reaction the strength of the ion−dipole or ion−induced dipole interaction ensures that this is often the case. For the CN + O_2 reaction the quartet surface is known to be weakly attractive.[2] For other radical−radical reactions the question of how long the multiplicity of states remain quasi-degenerate must be decided on an individual basis.

Conditions for violation of spin-conservation to be a likely occurrence can be summarized as (1) the reaction rate is limited by the rate of capture over a long-range centrifugal barrier in an attractive potential; (2) product formation is the result of fast rearrangement of a bound collision complex; and (3) attractive short-range potentials exist for more than one spin state of the complex. The second condition amounts to a statement that the rate of passage over the potential barrier to products should greatly exceed the rate of dissociation of a collision complex back to reactants. Both this and the require-

TABLE 1: Calculated $CN + O_2$ Capture Rate Constants (Units 10^{-10} cm^3 Molecule^{-1} s^{-1}) as a Function of Temperature, Morse Well Frequency ω_e, and Location of the Range (R_{switch}) at Which the Spin-Degeneracy Factor Changes from 1.0 (Long-Range) to 1/3 (Short-Range), Expressed as a Multiple of the Distance (R_{Morse}) at Which the Morse Potential Is Superseded by the Sum of the London, Dipole−Induced Dipole, and Dipole−Quadrupole Potentials

	$0.7R_{Morse}$, ω_ϵ =			$0.85R_{Morse}$, ω_ϵ =			$1.0R_{Morse}$, ω_ϵ =			infinity, ω_ϵ =		
T/K	350	500	650	350	500	650	350	500	650	350	500	650
1	0.860	0.753	0.763	0.860	0.753	0.763	0.564	0.707	0.763	0.287	0.251	0.254
2	1.07	0.852	0.854	1.07	0.852	0.854	0.568	0.712	0.845	0.357	0.284	0.285
5	1.54	1.03	0.972	1.54	1.03	0.972	0.652	0.686	0.893	0.513	0.342	0.324
10	2.06	1.22	1.05	2.05	1.22	1.05	0.787	0.666	0.833	0.688	0.406	0.351
20	2.70	1.53	1.19	2.54	1.53	1.19	0.968	0.697	0.749	0.899	0.510	0.396
30	3.12	1.79	1.33	2.74	1.79	1.33	1.10	0.750	0.727	1.04	0.598	0.442
50	3.69	2.20	1.59	2.85	2.19	1.59	1.28	0.851	0.746	1.23	0.733	0.529
75	4.19	2.57	1.86	2.89	2.51	1.86	1.44	0.952	0.794	1.40	0.856	0.619
100	4.54	2.85	2.08	2.89	2.72	2.07	1.57	1.03	0.844	1.53	0.951	0.692
150	5.00	3.29	2.42	2.90	2.93	2.39	1.76	1.16	0.930	1.73	1.10	0.807
200	5.19	3.61	2.69	2.91	3.05	2.59	1.91	1.26	1.00	1.89	1.20	0.900
250	5.31	3.87	2.90	2.94	3.07	2.74	2.03	1.35	1.07	2.01	1.29	0.974
300	5.37	4.08	3.09	2.96	3.07	2.84	2.13	1.42	1.13	2.12	1.37	1.05
350	5.40	4.26	3.26	2.98	3.07	2.92	2.22	1.48	1.20	2.21	1.44	1.12
400	5.40	4.40	3.40	3.01	3.07	2.98	2.31	1.54	1.27	2.29	1.50	1.19
500	5.39	4.62	3.66	3.07	3.07	3.10	2.44	1.65	1.41	2.43	1.61	1.35

ment of a long-range centrifugal barrier imply that nonconservation of spin is more likely to be important at low temperatures. The foregoing discussion has been in terms of states of differing spin multiplicity: more generally, other conservation laws might be violated provided there is a term in the Hamiltonian that mixes the states involved. This is relevant to the problem of calculating the fraction of capture collisions that lead to reaction in processes involving reactants in states with nonzero orbital angular momentum.[12]

In the present calculations for the reaction of CN with O_2 the transition from nonconservation to conservation of spin during a collision trajectory was modeled very crudely by switching the spin-degeneracy factor from 1 to 1/3 when the centrifugal barrier associated with a particular trajectory was located at distances shorter than some critical value. It would obviously be better to use realistic potential surfaces and to change the effective degeneracy factor gradually over a range of distances, but this is not possible at present in the absence of any information, theoretical or experimental, about the rate of change of curve-crossing probability with distance. Initially, the critical switching distance R_{switch} was chosen to be the distance (termed R_{Morse}) at which the short-range Morse potential became less attractive than the sum of the long-range dipole−quadrupole, dipole−induced dipole, and London potentials, but this proved unsatisfactory. Eventually the best value of R_{switch} was selected as 0.85 times R_{Morse}, as described in the next section. Apart from this modification of the capture-rate program, the present calculations were performed just as in ref 2.

3. Capture-Rate Calculations

Results of calculations for the temperature range 1−500 K are given in Table 1 for values of the vibration frequency ω_e of the short-range Morse potential equal to 650, 500, and 350 cm^{-1}. The 650 cm^{-1} value derives from the ab initio calculations of ref 2; the lower values were used to test the effect of increasing the width of the potential well near the dissociation limit, the Morse potential being well-known to approach the asymptote too rapidly at large distances. In practice the effect of varying ω_e from 650 to 350 cm^{-1} was found to be unimportant in comparison with the effect of varying the distance at which the spin degeneracy factor was switched from 1 to 1/3. Results are given in Table 1 for R_{switch} equal to 0.7, 0.85, and 1.0 times R_{Morse}, and also with the degeneracy factor fixed at 1/3, independent of distance. For R_{switch} equal to R_{Morse} the calculated capture rates at temperatures below 50 K are quite similar to the values obtained with the spin-degeneracy factor given a constant value of 1/3 and are smaller than the experimental rate constant by about a factor of 2 at temperatures near 20 K. For R_{switch} equal to 0.85 times R_{Morse} the capture-rate values near 10 K are reasonably close to the experimental rate constant for $\omega_e = 650$ and 500 cm^{-1} and are about a factor of 2 larger for $\omega_e = 350$ cm^{-1}. Further reduction of R_{switch} to 0.7 times R_{Morse} has little effect on the calculated capture rates in the low-temperature region and causes difficulties in the subsequent RRKM calculations by making the capture rates too large at moderate temperatures. The calculations of the overall rate constant have therefore used capture rates obtained with $R_{switch} = 0.85R_{Morse}$. For $\omega_e = 650$, 500, and 350 cm^{-1} the value of R_{Morse} was 5.82, 7.17, and 10.4 Å, respectively. Values of the mean radius of the centrifugal barrier are plotted in Figure 2 as a function of temperature for these three ω_e values. In calculating the mean values, each individual barrier radius was weighted in proportion to the contribution of the particular trajectory to the overall capture rate. Even at high temperatues, the calculated barrier radii all appear large enough to ensure that the first condition for nonconservation of spin is satisfied.

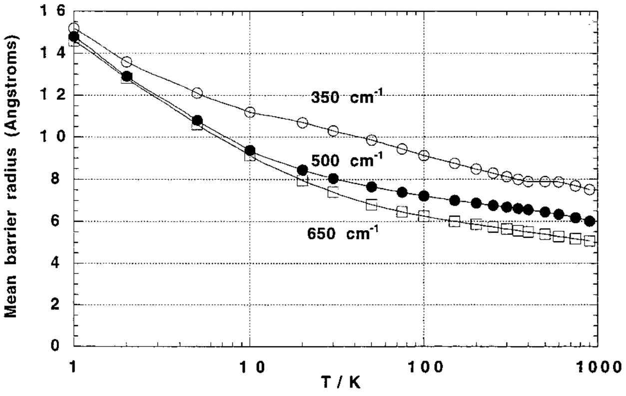

Figure 2. Variation with temperature of the mean radius of the centrifugal barrier for the $CN + O_2$ reaction, calculated with ω_e of the short-range Morse potential set at 350, 500, and 650 cm^{-1}.

4. Variational RRKM Calculations

These calculations were performed as in ref 2, with the difference that there was now less need to distort the fit to

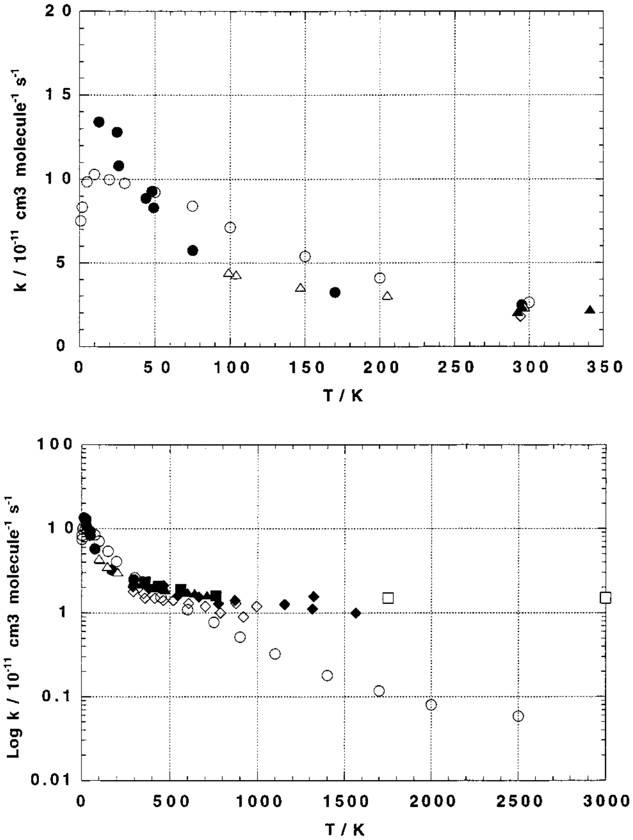

Figure 3. Temperature dependence of the calculated rate constant (unfilled circles) and experimental results of Sims et al.[13] (filled circles), Sims and Smith[14] (unfilled triangles), Durant and Tully[15] (unfilled diamonds), Sims and Smith[16] (filled triangles), Atakan et al.[17] (filled squares), Balla and Castleton[18] (filled diamonds), and Davidson et al.[19] (unfilled squares): (a) for temperatures below 350 K; (b) for temperatures up to 3000 K.

experimental data in the high-temperature range in order to obtain the largest possible rate constant values at low temperatures. As before, the transition state for the channel leading to redissociation of the CNOO* complex to reactants was located variationally for each pair of values of collision energy and angular momentum, and the number of states above the barrier at a given reactant separation was found by the use of calculated pendulum-mode frequencies in the dipole−quadrupole + dipole−induced dipole potential, with the distribution functions for total energy and angular momentum provided by the capture-rate program. Results for $\omega_e = 350$ cm^{-1}, with the complex well depth and final barrier height set at 180 and 118 kJ mol^{-1}, respectively, are shown in Figure 3, together with experimental rate constant values.[13−19] These well depth and barrier height values are not far from the values 176 and 106 kJ mol^{-1} found by ab initio calculation.[2] Other choices of ω_e lead to similar fits, with some adjustment of the well depth and barrier height and with the proviso that the final rate constants cannot exceed the capture rates in Table 1. In view of the crudity of the theoretical model, especially with regard to the use of a Morse potential at short range, the arbitrary nature of R_{switch}, and the abruptness of the transition from the Morse potential to the long-range potential, the agreement at temperatures below 350 K is probably to be regarded as satisfactory. The shape of the *k* versus *T* curve at temperatures below 300 K is not well predicted by the present model and might provide a useful test of future models. It is interesting to note that the capture-rate calculations still predict that the rate constant should fall off significantly at low temperatures, although the upper limit of the falloff region has now moved down to about 10 K. This is a point that needs to be tested by experiment.

The large difference between the observed and calculated rate constants at very high temperatures can be reduced but not eliminated by reducing the value of R_{switch}. This divergence might be due in part to the opening up of other reaction channels, such as that leading to the products CO + NO, a possibility that is not included in the present model. However, a more likely source of disagreement can be identified by noting that the calculated lifetime of the collision complex is significantly smaller than the calculated duration of a collision, regarded either as the time spent in the Morse well or the time between successive crossings of the potential barrier, over the entire temperature range, and is smaller than either measure of the collision duration by 3 orders of magnitude at 2500 K. The complex lifetimes calculated here depend on absolute values of rate constants for barrier crossing and so depend on the density of states of the NCOO* complex, as given by the Beyer−Swinehart algorithm[20,21] with no allowance for anharmonicity. This procedure is known to give state densities that are too small by about an order of magnitude for a four-atom system such as formaldehyde at energies near the dissociation limit.[22] The density of states cancels from the calculation of an overall reaction rate, and a discrepancy of 1 order of magnitude between the collision duration and the statistical lifetime might be tolerated, but a discrepancy of 3 orders of magnitude, with calculated statistical lifetimes in the subfemtosecond range, clearly points to a deficiency in the statistical treatment. Thus it appears that, at least at high temperatures, the behavior of the NCOO* system is controlled mainly by dynamics rather than statistics and that a proper theoretical treatment will require quite detailed knowledge of the relevant potential energy surfaces.

Acknowledgment. I am grateful to M. J. McEwan for helpful discussions. This work was supported by the Marsden Fund.

References and Notes

(1) Smith, I. W. M. In *The Chemical Dynamics and Kinetics of Small Radicals*; Liu, K., Wagner, A. F., Eds.; World Scientific: London, 1995.

(2) Vallance, C.; Maclagan, R. G. A. R.; Phillips, L. F. *Chem. Phys. Lett.* **1996**, *250*, 59.

(3) Phillips, L. F. *Chem. Phys. Lett.* **1987**, *135*, 269.

(4) Phillips, L. F. *Chem. Phys. Lett.* **1990**, *168*, 197.

(5) Meads, R. F.; Maclagan, R. G. A. R.; Phillips, L. F. *J. Phys. Chem.* **1993**, *97*, 3257.

(6) Klippenstein, S. J.; Klim, Y.-W. *J. Chem. Phys.* **1993**, *99*, 5790.

(7) Federer, W.; Villinger, H.; Lindinger, W.; Ferguson, E. E. *Chem. Phys. Lett.* **1986**, *123*, 12.

(8) Zahr, G. E.; Preston, R. K.; Miller, W. H. *J. Chem. Phys.*, **1975**, *62*, 1127.

(9) Nikitin, E. E. *Adv. Chem. Phys* **1975**, *28*, 317.

(10) Dodd, J. N.; Series, G. W. *Progress in Atomic Spectroscopy, Part A*; Hanle, W., Kleinpoppen, H., Eds.; Plenum: 1978; p 639.

(11) Bitto, H.; Huber, J. R. *Opt. Commun.* **1990**, *80*, 184.

(12) Phillips, L. F. *J. Phys. Chem.* **1990**, *94*, 7482.

(13) Sims, I. R.; Queffelec, J.-L.; Defrance, A.; Rebrion-Rowe, C.; Travers, D.; Rowe, B. R.; Smith, I. W. M. *J. Chem. Phys.* **1994**, *100*, 4229.

(14) Sims, I. R.; Smith, I. W. M. *Chem. Phys. Lett.* **1988**, *151*, 481.

(15) Durant, J. L.; Jr., Tully, F. P. *Chem. Phys. Lett.* **1989**, *154*, 568.

(16) Sims, I. R.; Smith, I. W. M. *J. Chem. Soc., Faraday Trans.* **1989**, *84*, 527.

(17) Atakan, B.; Jacobs, A.; Wahl, M.; Weller, R.; Wolfrum, J. *Chem. Phys. Lett.* **1989**, *154*, 449.

(18) Balla, R. J.; Castleton, K. H. *J. Phys. Chem.* **1991**, *95*, 2344.

(19) Davidson, D. F.; Dean, A. J.; Dirosa, M. D.; Hanson, R. K. *Int. J. Chem. Kinet.* **1991**, *23*, 1035.

(20) Stein, S. E.; Rabinowitch, B. S. *J. Chem. Phys.* **1973**, *58*, 2438.

(21) Gilbert, R. G.; Smith, S. C. *Theory of Unimolecular and Recombination Reactions*; Blackwell Scientific Publications: Oxford, 1990.

(22) Polik, W. F.; Guyer, D. R.; Moore, C. B. *J. Chem. Phys.* **1990**, *92*, 3453.