



**Understanding Reactivity at Very Low
Temperatures: The Reactions of Oxygen Atoms with
Alkenes**

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consider how to improve its activity. The DFT-calculated ΔG_H of the MoS₂ edge site is slightly positive at +0.08 eV, with calculations suggesting an H coverage of only one-quarter on the edge under operating conditions (8). Thus, only 1 in 4 edge atoms evolves molecular H₂ at a given time, unlike Pt(111) which operates at a H-coverage of ~1 ML (7, 26, 27). If all MoS₂ edge sites could be made to adsorb H, activity could be increased by a factor of 4. This might be accomplished by appropriately tuning the electronic structure of the edge to increase the bond strength of the adsorbed H (23). Such a modification could simultaneously improve the inherent turnover of each edge site, further improving the overall activity of the material toward that of Pt-group metals.

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- The cell, specifically designed for studies on UHV-transferred samples, is sealed upon the imaged (111) face of the sample with a viton o-ring, exposing ~0.10 cm² to the H₂SO₄ electrolyte (pH 0.24, 23°C), and cyclic voltammograms are recorded. This procedure ensures a one-to-one correlation between the imaged MoS₂ nanoparticles and the measured activity for hydrogen evolution.
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- We note that Au atoms along the particle edge also scale with the edge length; however, previous experimental

and computational studies have shown negligible interaction between the MoS₂ and the support (14, 15), leading us to conclude that such sites would be as inactive as those of the blank samples, prepared without MoS₂ deposition.

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Supporting Online Material

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Understanding Reactivity at Very Low Temperatures: The Reactions of Oxygen Atoms with Alkenes

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A remarkable number of reactions between neutral free radicals and neutral molecules have been shown to remain rapid down to temperatures as low as 20 kelvin. The rate coefficients generally increase as the temperature is lowered. We examined the reasons for this temperature dependence through a combined experimental and theoretical study of the reactions of O(³P) atoms with a range of alkenes. The factors that control the rate coefficients were shown to be rather subtle, but excellent agreement was obtained between the experimental results and microcanonical transition state theory calculations based on ab initio representations of the potential energy surfaces describing the interaction between the reactants.

Application of the CRESU technique (1) has shown that a surprising number of bimolecular reactions between neutral gas-phase species are rapid at very low temperatures. To date, rate coefficients for some 45 neutral-neutral reactions have been measured (2, 3), in

some cases at temperatures as low as 13 K (4). All have rate coefficients at 298 K [$k(298\text{ K})$] that are equal to or exceed $\sim 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$. Moreover, the general trend with temperature is for the rate coefficients to increase as the temperature is lowered.

These observations have led to a reevaluation of the chemistry that occurs in the cold cores (10 to 20 K) of dense, dark interstellar clouds (ISCs), where the majority of interstellar molecules have been identified. Although sequences of ion-molecule reactions initiated by the cosmic ray-induced ionization of H₂ clearly play a central role in this chemistry, neutral-neutral reactions are now expected to be more important than previously thought (5). Unfortunately, the kinetic database required for detailed astrochemical

modeling (6) is still far from complete. There are many reactions that may occur in ISCs, such as those between pairs of unstable species, for which low-temperature kinetic data neither exist nor are likely to be obtained in the foreseeable future. Theoretical or semi-empirical methods of estimating these rate coefficients are therefore desirable.

Several complementary theoretical treatments (7–9) have been advanced to explain the observed negative temperature dependences of rate coefficients for radical-radical reactions, principally on the basis of the notion of adiabatic capture of the reactants via long-range attractive forces. Although they differ in their details, these treatments all predict large rate coefficients at very low temperatures for radical-radical reactions, where there is generally no barrier on the minimum energy reaction path. In the case of radical-molecule reactions, a key issue is whether a potential energy barrier exists along the minimum energy path from reactants to products: either a real barrier (i.e., a maximum above the energy of the separated reactants) or a “submerged” barrier corresponding to a maximum along the minimum energy path between the shallow minimum associated with a prereaction complex and the products (see below). Further theoretical work, particularly by Georgievskii and Klippenstein (10, 11), has shown that a submerged barrier can serve as a second inner transition state (or bottleneck), because the internal states at this smaller interreactant separation are more widely spaced than at the outer, capture transition state. In these circumstances, the rate of reaction falls below that predicted by capture theories, and a version of microcanonical transi-

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tion state theory must be applied to make accurate predictions of the rate coefficients and their variation with temperature.

From the standpoint of modeling ISC chemistry, it would be useful to have semi-empirical methods to predict which reactions might remain fast at very low temperatures. In this spirit, Smith *et al.* (3) examined the data available for reactions between atomic and molecular free radicals and unsaturated hydrocarbons, seeking a framework to predict whether particular radical-molecule reactions would be rapid enough ($k > 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) to influence the abundances of chemical species in ISCs at temperatures $\leq 20 \text{ K}$. Their first method, based purely on an examination of the experimental data amassed to date, led them to propose that a radical-molecule reaction is likely to be rapid at 10 to 20 K if its room-temperature rate coefficient, $k(298 \text{ K})$, is greater than $\sim 5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and its activation energy, E_{act} , around 298 K is zero or

negative. Conversely, reactions with $k(298 \text{ K}) < 5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $E_{\text{act}} > 0$ are likely to be too slow at 10 to 20 K to be of importance in ISC chemistry.

Their second approach to the problem of predicting the presence of a real potential barrier to reaction rests on the notion that such barriers are often the product of an avoided curve crossing between two states: the reactant ground state, which correlates with a product ionic state, and an excited reactant ionic state, which correlates with the product ground state (12). The barrier that arises depends especially on the energy of the reactant ionic state, which depends in turn on the difference between the ionization energy (I.E.) of the molecule and the electron affinity (E.A.) of the radical, corresponding to virtual electron transfer between the molecule (the donor) and the radical (the acceptor). If (I.E. – E.A.) is small, in the presence of long-range attraction

this barrier can be submerged below the reactant energy.

After analyzing the rate coefficients and their temperature dependences for a large number of such reactions, most of which had been studied at very low temperatures, Smith *et al.* (3) proposed that, when (I.E. – E.A.) is greater than 8.75 eV, the reaction is likely to possess a true barrier and will therefore become negligibly slow at 20 K. On the other hand, reactions with (I.E. – E.A.) $< 8.75 \text{ eV}$ are likely to be characterized by, at most, inner barriers that are submerged below the asymptotic reactant energy. These latter reactions will be rapid at 20 K and of potential importance in ISC chemistry. Smith *et al.* further noted that the reactions between oxygen atoms in their ^3P electronic ground state and simple unsaturated hydrocarbons have values of (I.E. – E.A.) that bridge the critical value of 8.75 eV (see Table 1) and would therefore provide an important test of their hypothesis.

To test these ideas, we measured rate coefficients for the reactions between $\text{O}(^3\text{P})$ atoms and the alkenes listed in Table 1 in a continuous-flow CRESU apparatus (4). Experiments were performed at temperatures between 23 and 298 K with the use of different convergent-divergent Laval nozzles and carrier gases. Details of the experimental conditions are given in table S1.

For each kinetic experiment, in addition to the carrier gas (which was present in large excess), three gases were generally included in the supersonic flow: the alkene whose reaction was being studied; NO_2 , which was photolyzed at 355 nm by pulses from a frequency-tripled Nd:YAG laser to produce $\text{O}(^3\text{P})$ atoms; and NO . Chemiluminescence from excited NO_2 , formed in the association of $\text{O}(^3\text{P})$ with NO , served as a marker for the oxygen atom concentrations and decayed as the atoms were consumed in reaction with the alkene. Figure 1 shows two such decay traces, one recorded at 298 K and one at 39 K, both with a small concentration of *iso*-butene present in the gas mixture. Each trace was fitted to a single exponential curve to yield a pseudo-first-order rate coefficient ($k_{1\text{st}}$) for removal of $\text{O}(^3\text{P})$ atoms under the conditions of that particular experiment.

In each series of experiments, values of $k_{1\text{st}}$ were determined for several different concentrations of alkene and the second-order rate coefficient ($k_{2\text{nd}}$) for the reaction of that alkene with $\text{O}(^3\text{P})$ atoms at that particular temperature was derived, as shown in Fig. 1, from the gradient of a plot of $k_{1\text{st}}$ versus the concentration of the alkene. The results of these experiments are summarized in Fig. 2. Full quantitative details are given in table S1, and the errors in the experimental data are shown in fig. S1.

Figure 2 shows the existence of three distinct kinds of kinetic behavior for $\text{O}(^3\text{P}) + \text{alkene}$ reactions. *iso*-butene, *cis*-butene, and *trans*-butene have the lowest I.E.s of the alkenes used in our experiments, and (I.E. – E.A.) is less than 8 eV for the reactions of $\text{O}(^3\text{P})$ with these alkenes.

Table 1. In the first three lines, rate coefficients, $k(298 \text{ K})$, and activation energies, E_{act} , from Cvetanovic (13) are compared with (I.E. – E.A.) for the reactions of $\text{O}(^3\text{P})$ atoms with alkenes; the electron affinity of the $\text{O}(^3\text{P})$ atoms is 1.46 eV. The last two lines give CASPT2 energies on the minimum-energy path (all relative to the energy of the separated reactants in their ground state): E_{min} , electronic + zero-point energy at the minimum of the “pre-reaction complex”; E_{max} , electronic + zero-point energy at the inner transition state. Bracketed entries are for the excited-state potential; where there are upper and lower entries, the upper entries are for addition at a terminal site, lower entries for addition at a central site.

	Ethene	Propene	1-Butene	<i>cis</i> -Butene	<i>iso</i> -Butene	<i>trans</i> -Butene
$k(298) (10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$	0.073	0.40	0.42	1.8	1.7	2.2
$E_{\text{act}} (\text{kJ mol}^{-1})$	6.65	2.3	2.9	–1.2	–0.1	–0.1
(I.E. – E.A.) (eV)	9.05	8.27	8.09	7.65	7.76	7.64
$E_{\text{min}} (\text{kJ mol}^{-1})$	–1.3 (–0.9)	–4.7	–5.2	–5.7	–5.9	–6.3
$E_{\text{max}} (\text{kJ mol}^{-1})$	5.4 (11.8)	0.9 (5.9)	–0.5 (5.0)	–2.2 (3.3)	–2.5 (2.6)	–3.1 (2.3)
		1.5 (8.0)	0.1 (5.9)		–1.3 (6.4)	

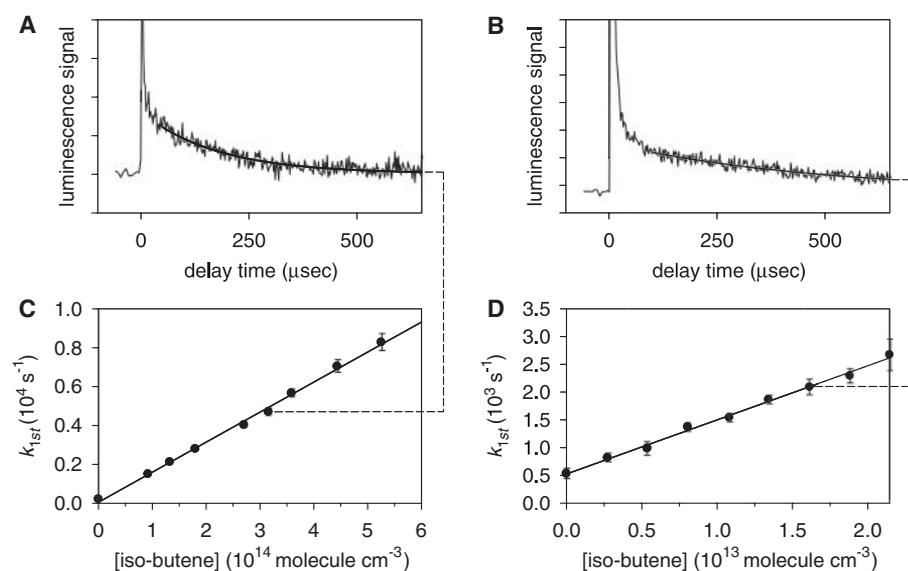


Fig. 1. (A and B) Fitted decays of the chemiluminescence from NO_2 observed in mixtures containing (A) $3.20 \times 10^{14} \text{ molecules cm}^{-3}$ *iso*-butene at 298 K and (B) $1.62 \times 10^{13} \text{ molecules cm}^{-3}$ *iso*-butene at 39 K. (C and D) Plots of the pseudo-first-order rate coefficients obtained from such experiments plotted against the concentration of *iso*-butene at (C) 298 K and (D) 39 K.

Moreover, the values of $k(298\text{ K})$ exceed $10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$, with the rate coefficients showing a zero or slightly negative dependence on temperature between 300 and 500 K. Below 298 K, as expected, the rate coefficients for these reactions show a monotonic increase as the temperature is lowered, reaching values of $\sim 10^{-10}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ at 23 K, the lowest temperature studied here.

The other limit of behavior is exhibited in the $\text{O}(^3\text{P}) + \text{C}_2\text{H}_4$ reaction. Our result of $k(298\text{ K}) = 7.4 \times 10^{-13}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ agrees very well with literature values (13), but only upper limits could be obtained at lower temperatures, $k(39\text{ K}) < 1.6 \times 10^{-13}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$. The appreciable activation energy for this reaction (13, 14) and its relatively large value of (I.E. – E.A.) both suggest

that this reaction should be very slow at the temperatures accessible in a CRESU apparatus (and present in dense ISCs). The existence of an appreciable real barrier on the potential for this reaction, as shown in Fig. 3, is also supported by previous ab initio calculations (15).

The reactions of $\text{O}(^3\text{P})$ atoms with 1-butene and propene provide the most demanding test of the hypotheses made by Smith *et al.* (3). The rate coefficients for both reactions at 298 K are close to the value of $k(298\text{ K}) = 5 \times 10^{-12}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$, which Smith *et al.* proposed might separate rapid from slow low-temperature reactions. Moreover, the rate coefficients exhibit small positive dependences on temperature, represented by the activation energies given in

Fig. 2. The points show the experimentally determined values of the rate coefficients for the reactions of $\text{O}(^3\text{P})$ atoms with alkenes at different temperatures, and the dashed lines show the results of the theoretical calculations. The solid lines to the right of the diagram represent the Arrhenius expressions recommended by Cvetanovic (13) to fit kinetic data between 300 and 500 K.

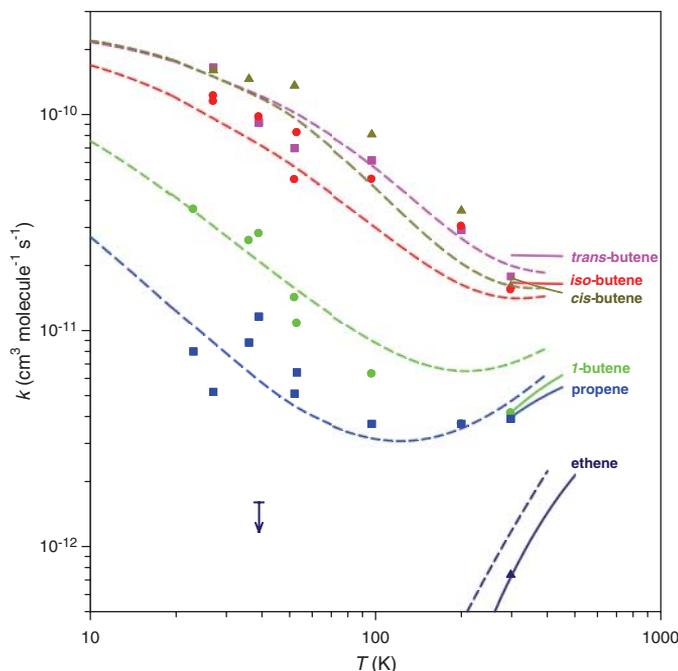


Fig. 3. Curves showing the variation of potential energy along the minimum energy paths for $\text{O}(^3\text{P}) + \text{ethene}$ (upper pair of curves) and $\text{O}(^3\text{P}) + \text{trans-butene}$ (lower pair of curves), calculated using the CASPT2 method. The ground and first excited electronic states are shown by the solid and dashed lines, respectively. All curves show minima associated with the prereaction complex and maxima associated with real or submerged barriers. The zero of energy is set at the energy of the separated reactants.

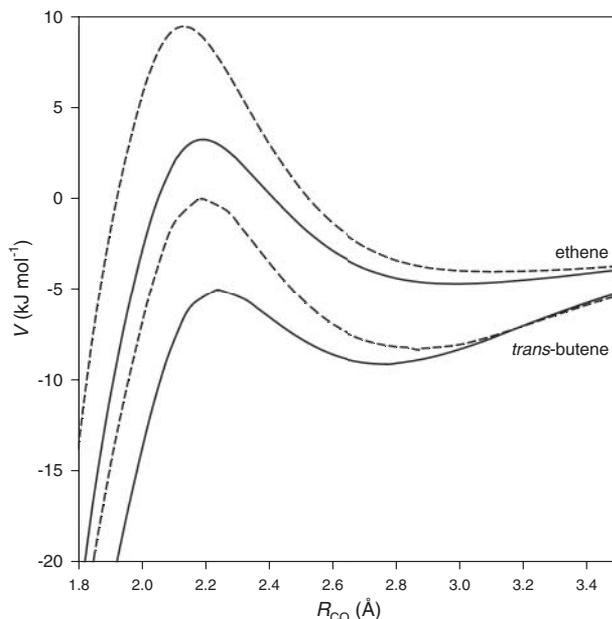


Table 1 and the curves in Fig. 2. On the other hand, their values of (I.E. – E.A.) are less than, although not much less than, 8.75 eV. The rate coefficients below 298 K measured in the present work increase as the temperature is lowered. The variation of the rate coefficients with temperature for both these reactions is similar to that found for the reaction of CN with C_2H_6 (16), which has recently been reproduced in microcanonical transition state theory calculations (11) that allow for the presence of both an outer and inner transition state.

To understand more deeply both the observed kinetic behavior of the reactions of $\text{O}(^3\text{P})$ atoms with alkenes and the origins of the partly successful correlations of the rate coefficients and the temperature dependence with (I.E. – E.A.), we carried out calculations similar to those on CN with C_2H_6 (11) and on OH with C_2H_4 (10). These calculations consider only the rate of formation of the strongly bound triplet addition complex between $\text{O}(^3\text{P})$ and an alkene. In general, this complex is either stabilized by collision with a third body or dissociates to exothermic reaction products (13), such as $\text{CH}_2\text{CHO} + \text{H}$ or $\text{CH}_3 + \text{HCO}$ when $\text{O}(^3\text{P})$ atoms react with C_2H_4 . The focus of the present calculations is the accurate treatment of both the inner and outer transition state regions on the basis of high-level ab initio studies of the potential energy surface. These properties were determined with second-order multireference perturbation theory (CASPT2) using the MOLPRO quantum chemistry package (17).

For the $\text{O}(^3\text{P}) + \text{alkene}$ reactions, there are multiple inner transition states correlating with different addition sites and with different electronic states. In particular, the $\text{O}(^3\text{P})$ atom can add to either carbon atom of the π bond, with the terminal addition (i.e., to the C atom of the $=\text{CH}_2$ group) generally being preferred. Also, two of the three orientations for the lone pair orbital on the oxygen atom correlate with strong bonding in the complex. However, the barrier for the first excited state is always above the energy of the reactants and thus has little effect at low temperatures.

The electronic dynamics are assumed to be adiabatic, and the ground and excited electronic states at the inner transition state are correlated with the long-range spin-orbit states (fig. S2). The inner, $N_{\text{inner},i}^\ddagger$, and outer, $N_{\text{outer},i}^\ddagger$, transition state number of states for a given electronic state i are related to an effective number of states, $N_{\text{eff},i}^\ddagger$, in Eq. 1 (10, 11, 18)

$$\frac{1}{N_{\text{eff},i}^\ddagger} = \frac{1}{N_{\text{inner},i}^\ddagger} + \frac{1}{N_{\text{outer},i}^\ddagger} \quad (1)$$

For each of the reactions studied here, a rate coefficient for long-range capture of ~ 4 to $5 \times 10^{-10}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ is predicted at 20 K, with a modest ($\sim T^{1/6}$) increase with temperature. The adiabatic electronic assumptions reduce the low-temperature rate coefficients by a factor of

3/5, to 2.5 to 3×10^{-10} $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 20 K, which is within a factor of 2 of the measured rate coefficients for *cis*- and *trans*-butene.

The CASPT2 predictions for the saddle point energies, given in Table 1, correlate with the expectations, discussed earlier, based on the different values of (I.E. – E.A.). For ethene, the positive barrier leads to a low reactivity at low temperature. Propene and 1-butene are near ideal intermediate cases, with barriers within 1 kJ mol^{-1} of the reactants. For propene, the inner transition state strongly affects the rate coefficient even at 20 K, but the barrier is just low enough that, with tunneling, the rate coefficient does not decay to small values at low temperatures. For 1-butene, the rate coefficient rises with decreasing temperature but is still an order of magnitude below the long-range capture value at 20 K. For the other butenes, the ground-state barriers are strongly submerged (i.e., by 2 to 3 kJ mol^{-1}) and the addition rates increase rapidly with decreasing temperature, exceeding $10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ by 20 K. The changing nature of the reaction with changing (I.E. – E.A.) is illustrated by the plots in Fig. 3 of the minimum energy path potentials as a function of the CO separation for the ground and first excited states in the $\text{O}(^3\text{P}) + \text{ethene}$ and $\text{O}(^3\text{P}) + \text{trans-butene}$ reactions.

The calculated rate coefficients for addition arising from the present two-transition state model are illustrated as dashed lines in Fig. 2. The calculations have been extended down to 1 K, and the results for the range from 10 to 1 K are given in fig. S1. For $\text{O}(^3\text{P}) + \text{propene}$, the predicted rate coefficients are highly sensitive to the energy of the inner saddle point with a factor of 2 variation at 100 K for a 0.7 kJ mol^{-1} change. The CASPT2 predicted barrier was adjusted downward by 0.6 kJ mol^{-1} to obtain optimum agreement with experiment. For consistency, this adjustment was applied to the other reactions as well. For the butene cases, this adjustment has an insignificant effect on the predictions.

The remarkably good agreement between the theoretical predictions and experimental observations strongly validates the present two-transition state model. The calculations show that both the inner and outer transition states have an effect on the reaction kinetics throughout the 20 to 400 K range. At low temperatures the outer transition state dominates, whereas at high temperatures the inner transition state dominates. The increasing importance of the inner transition state with increasing temperature causes the negative temperature dependence between 200 and 20 K. The $\text{O}(^3\text{P}) + \text{C}_2\text{H}_4$ reaction, where the positive barrier for the inner transition state dominates the kinetics at all temperatures, provides the only exception. The accurate treatment of both transition-state regions is a key prerequisite to understanding and predicting the kinetics of these reactions at low temperatures.

The agreement between experiment and theory found for the $\text{O}(^3\text{P}) + \text{alkene}$ reactions suggests two ways in which CASPT2 calculations of barrier heights might be used to estimate

the possible importance in ISCs of other reactions between radicals and unsaturated molecules, depending on whether experimental information is available for the kinetics of the reaction in question—for example, a measured value of the rate coefficient at room temperature. If so, uncertainty in the ab initio calculations of the inner barrier height, which experience suggests might amount to a few kJ mol^{-1} , could be reduced by comparing theoretical and experimental values of the room-temperature rate coefficient so as to tune the potential energy at the inner transition state, and thereby improve the theoretical estimate of the low-temperature rate coefficients. As described above, we adopted this method with the use of the data for $\text{O}(^3\text{P}) + \text{propene}$, although we found that the adjustment needed was quite small. In cases where no kinetic data exist, such as for the reactions of radicals with carbon chains (19), more reliance will have to be placed on the theory, guided by the success of the present calculations, or on the semi-empirical arguments concerning the value of (I.E. – E.A.). At the very least, these methods should provide guidance at the order-of-magnitude level, which is itself valuable at the present level of astrochemical modeling.

References and Notes

1. The acronym CRESU stands for Cinétique de Réaction en Ecoulement Supersonique Uniforme, or Reaction Kinetics in Uniform Supersonic Flow. The technique was originally developed by Rowe and his co-workers for the study of ion-molecule reactions (20).
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Supporting Online Material

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Long-Lived Giant Number Fluctuations in a Swarming Granular Nematic

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Coherently moving flocks of birds, beasts, or bacteria are examples of living matter with spontaneous orientational order. How do these systems differ from thermal equilibrium systems with such liquid crystalline order? Working with a fluidized monolayer of macroscopic rods in the nematic liquid crystalline phase, we find giant number fluctuations consistent with a standard deviation growing linearly with the mean, in contrast to any situation where the central limit theorem applies. These fluctuations are long-lived, decaying only as a logarithmic function of time. This shows that flocking, coherent motion, and large-scale inhomogeneity can appear in a system in which particles do not communicate except by contact.

Density is a property that one can measure with arbitrary accuracy for materials at thermal equilibrium simply by increasing the size of the volume observed. This is because a region of volume V , with N particles on average, ordinarily shows fluctuations with standard deviation ΔN proportional to \sqrt{N} , so that fluctuations in the number density go down as $1/\sqrt{V}$. Liquid crystalline phases of active or self-propelled particles (1–4) are different, with ΔN predicted (2–5) to grow faster than \sqrt{N} and as

fast as N in some cases (5), making density an ill-defined quantity even in the limit of a large system. These predictions show that flocking,

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