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ON THE STABILITY OF INTERSTELLAR CARBON CLUSTERS: THE RATE OF THE REACTION BETWEEN C_3 AND O

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ABSTRACT

New experimental results on the rates of selected neutral-neutral reactions involving either gas-phase atoms (C) or radicals (OH, CN) show that these reactions are much more rapid than previously believed. It is currently unclear, however, how general these results are. The results of chemical models of dense interstellar clouds are strongly affected by the inclusion of large numbers of rapid neutral-neutral gas-phase reactions, most of which have not yet been studied in the laboratory. Unstudied reactions involving atomic oxygen and carbon clusters are known to curtail the synthesis of complex molecules if they occur rapidly at low temperatures. In this paper, using quantum chemical and dynamical studies, we show that the prototype reaction between O and C_3 possesses a small activation energy barrier and does not occur rapidly at low temperatures, even when tunneling is considered.

Subject headings: ISM: abundances — ISM: clouds — molecular processes

1. INTRODUCTION

Recent experiments (Sims & Smith 1995) show that neutral-neutral reactions in which one reactant is either an atom or a radical may play an important role in the gas-phase chemistry of dense interstellar clouds. Such a role was not recognized in models published before these experiments were undertaken (Herbst & Leung 1989). Reactions between atomic carbon and a variety of hydrocarbons have been studied at room temperature (Clary et al. 1994) and were found to occur at rates near the capture limit (Clary et al. 1994; Liao & Herbst 1995), while reactions involving the radicals CN, CH, and OH and "stable" partners have been studied at temperatures as low as 13 K (Sims & Smith 1995). The radical reactions are rapid, and they show an inverse dependence on temperature, which is not duplicated by simple capture theories (Liao & Herbst 1995). The products of the recently measured neutral-neutral reactions are generally not known. Thus, there is still uncertainty regarding the new results and their interpretation.

Attempts to incorporate these recent experimental results into chemical models of dense interstellar clouds have been published (Herbst et al. 1994; Bettens, Lee, & Herbst 1995). These attempts do not limit the newly included reactions to those measured in the laboratory; rather they include larger but analogous classes of reactions. Herbst et al. (1994) found that the inclusion of the rapid neutral-neutral reactions has a detrimental effect on the synthesis of complex molecules. However, the more detailed study of Bettens et al. (1995) showed that the detrimental effect may or may not occur, depending on which classes of neutral-neutral reactions are rapid.

Among the most important but unstudied classes of reactions considered by Bettens et al. (1995) are those between atomic oxygen and bare carbon clusters C_n. If such reactions are rapid at low temperature, it is difficult, although not impossible, to produce observable amounts of complex molecules. Atomic oxygen is generally not reactive at room temperature, possessing activation energy barriers in reactions with stable neutral partners (Baulch et al. 1992), although it does react rapidly with radicals. It is difficult to use the laboratory evidence to argue whether or not reactions between O and bare carbon clusters are rapid because the clusters are not easily characterized as stable species or radicals—the latter term generally referring to species with an odd number of electrons. There seems to be no substitute for an actual detailed study of the reactive systems. In this paper, we present the results of a study of the reaction between O and the simplest polyatomic carbon cluster, C_3. Our study encompasses both a determination of the potential energy surface for reaction, using the methods of ab initio quantum chemistry, and a determination of the rate of reaction, using statistical approaches to the dynamics. A related ab initio quantum chemical study of the reaction between $C + C_2H_2$, a member of a family of reactions studied by Clary et al. (1994) that may enhance the interstellar synthesis of complex molecules, has been undertaken by Takahashi & Yamashita (1996).

2. POTENTIAL ENERGY SURFACE CALCULATIONS

The reaction between O and C_3 in their electronic ground states does not proceed directly to products (ground-state CO and $^3\Pi$ excited state C_2), but passes through the $^3\Pi$ excited state of C_3O. All of the stationary points along the lowest potential energy surface—between reactants and products that conserve the electronic spin of the reactants—are depicted in Figure 1, with energies (eV) relative to the energy of the reactants (excluding zero-point vibrational effects). Two potential energy barriers, or transition states (TS), separate the reactants and products from C_3O. The $O \cdots C_3$ TS is a key feature of this potential energy surface, and it dominates the reaction kinetics. The C_3O intermediate, which has a different electronic configuration from both the reactants and products, accounts for the distortions from linearity in both transition states.

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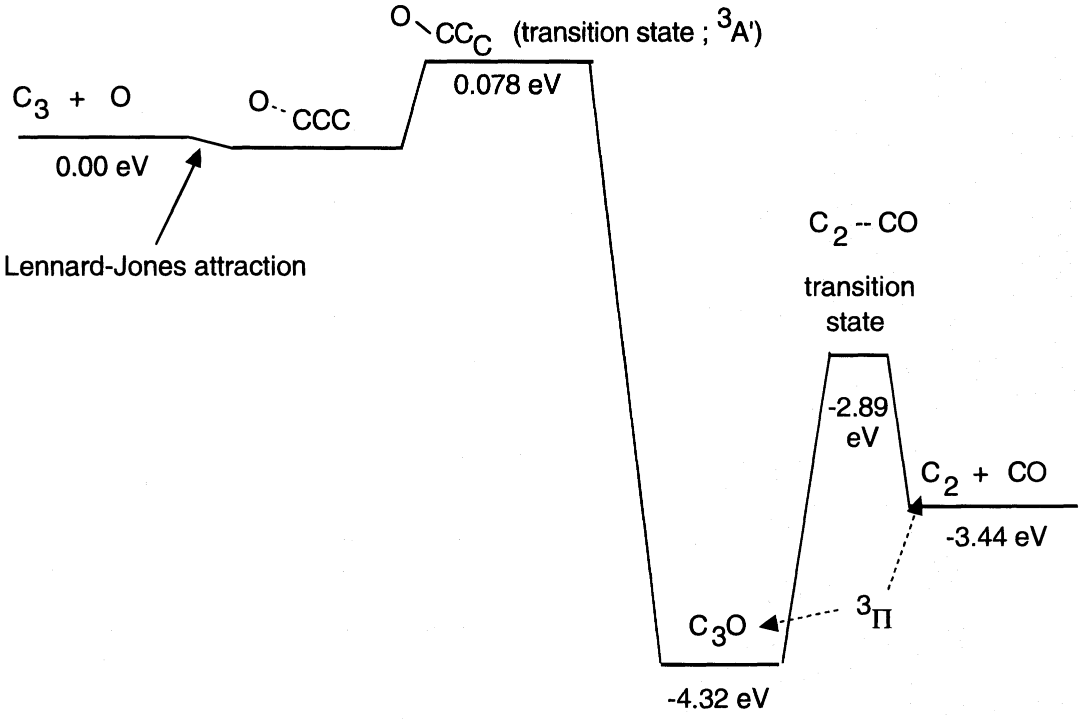

FIG. 1.—Minimum energy potential pathway from O + C_3 reactants to C_2 + CO products occurring on a potential surface of triplet spin multiplicity. Computed relative energies listed for the stationary points (reactants, transition states, C_3O, and products) are shown without zero-point energy corrections.

In the absence of any prior work, the ab initio investigation[1] of the O—C_3 surface began with a survey using a limited multiconfigurational self-consistent field (MCSCF) wave function (Werner & Knowles 1985) and cc-pVDZ sets from the suite of correlation consistent basis sets (Dunning 1989). Most of the critical points were then characterized more accurately at the correlated level with the restricted coupled cluster method RCCSD(T) (Deegan & Knowles 1994) and cc-pVTZ basis sets. The one exception to this was the $C_2 \cdots$ CO TS in the exit channel, which could not be treated with the single-reference RCCSD(T) method. Its position in the energy diagram in Figure 1 is based on limited internally contracted multireference configuration interaction (CMRCI) calculations (Werner & Knowles 1988). The geometries and total energies of the species in Figure 1 are given in Figure 2. The relative energetics in Figure 1 are based on these total energies. Harmonic frequencies for C_3, C_3O, and the two transition states were determined by numerical fits, using the SURVIBTM program (Harding & Ermler 1985), and were used to make zero-point energy corrections.

The ^3P (ninefold) electronic degeneracy of the reactants leads to three potential surfaces of triplet multiplicity; the upper two have not been followed in detail. The lowest energy triplet surface probably contains a small energy minimum as the reactants approach one another at long range. The energy structure corresponding to this

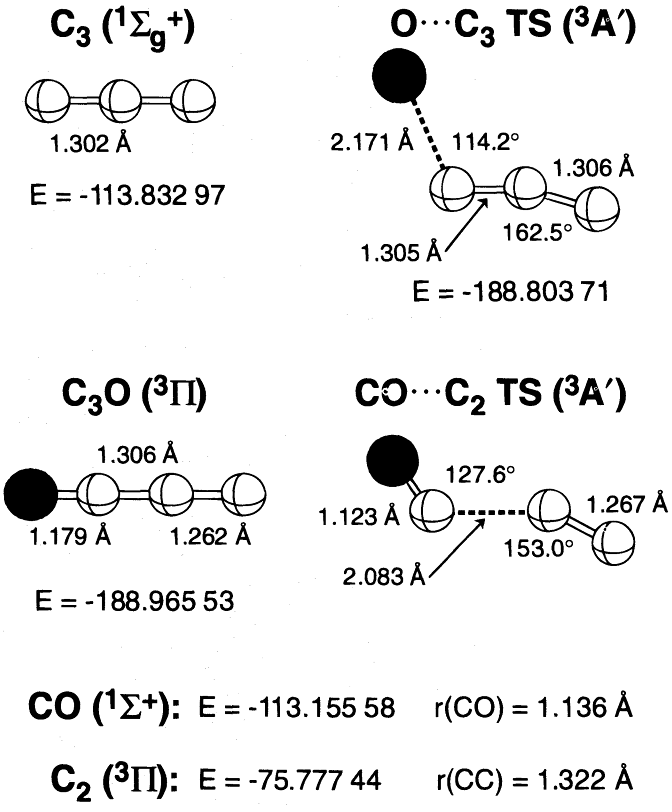

FIG. 2.—Geometries and total energies (in hartrees) of the species encountered along the O + $C_3 \rightarrow$ CO + C_2 reaction path. Oxygen is shaded, carbon unshaded. All structures and energies were computed at the RCCSD(T)/cc-pVTZ level except the $C_2 \cdots$ CO TS, which was done at the MCSCF/cc-pVTZ level.

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[1] All calculations were performed using the MOLPRO suite of ab initio programs written by H.-J. Werner and P. J. Knowles, with contributions by J. Almlöf, R. D. Amos, M. J. O. Deegan, S. T. Elbert, C. Hampel, W. Meyer, K. A. Peterson, R. M. Pitzer, A. J. Stone, and P. R. Taylor. Only valence electrons were correlated, and spherical contractions were used for *d* and *f* functions.

minimum, known as a van der Waals complex, has not been determined in this work. As the reactants approach more closely, they pass over the entrance channel TS, which is planar but not linear, with an electronic symmetry of $^3A'$ in the C_s symmetry group. The size of the barrier between the reactants and TS is relatively small compared with most neutral-neutral chemical systems, but its value (0.091 eV = 1060 K including zero-point energy effects) is large compared with interstellar cloud temperatures, and it prevents the reaction from occurring efficiently. After the entrance channel TS, the potential energy drops sharply to form the excited triplet state of the linear C_3O molecule. In the exit channel, the potential energy rises steeply from the C_3O minimum to the second TS, but this TS occurs at an energy well below that of the reactants, so the system passes over it easily. The potential energy surface then decreases smoothly to the C_2 and CO products. The reaction is very exothermic (−3.44 eV), even with the formation of the excited state C_2 product.

Since the ground electronic states of both C_3O and C_2 are singlet in character, it is clear that there is a potential energy surface of singlet multiplicity lying below the triplet surface calculated here for at least portions of the exit channel. We have not investigated this potential surface because coupling between it and the triplet surface is unlikely to be large.

3. CALCULATIONS OF THE REACTION DYNAMICS

The rate coefficient for a reaction with a TS in its potential energy surface can be estimated using the so-called activated complex theory (ACT; Weston & Schwarz 1972; Herbst 1996), in which the transition state structure is assumed to be in thermal equilibrium with the reactants. In this treatment, the rate coefficient $k(T)$ is given by the expression

$$k(T) = \frac{k_B T}{h} \frac{q_{AB^\dagger}}{q_A q_B} \exp\left(-\frac{E_0}{k_B T}\right) \tag{1}$$

for reactants A and B, where E_0 is the TS energy with respect to reactants including zero-point contributions, q represents the partition functions per unit volume, k_B is the Boltzmann constant, and the dagger † refers to the TS. This expression does not account for tunneling under the transition state barrier. A separable (multiplicative) tunneling correction, $\Gamma > 1$, to the rate coefficient is given by the expression

$$\Gamma \approx 1 - \frac{(h\nu_i)^2}{24(k_B T)^2} + \cdots , \tag{2}$$

where ν_i is the (imaginary) harmonic frequency at the TS. This tunneling correction is inadequate once it becomes significantly greater than unity, which, for the $O + C_3$ system, occurs at temperatures less than 100 K. Still, the dominant factor in the ACT expression for the rate coefficient is the Boltzmann factor, with E_0 often loosely referred to as the activation energy barrier. Given a barrier that is significantly greater than $k_B T$, the value for the rate coefficient will be significantly below the collisional value, since most collisions will not penetrate over or through the barrier.

For small activation energy barriers, tunneling corrections may well be important, especially at low temperatures, so that a more detailed treatment of the rate coefficient is necessary. The phase-space approach—a statistical theory in which angular momentum is conserved rigorously—is appropriate (Herbst 1996). The reactants, in specific rotational-vibrational states, collide at a specific collision energy to form a long-range complex, which may be weakly bound (as is the case here) under the influence of an attractive long-range potential. The complex subsequently redissociates into reactants or dissociates into products. There is also the possibility of complex stabilization (association) for complexes that are strongly bound. Our phase-space method, which has already been used for both ion-molecule (Herbst et al. 1991) and neutral-neutral (Herbst 1994) reactions, incorporates a tunneling algorithm first utilized by Miller (1979). Suitable averaging is needed to obtain a thermal (canonical) rate coefficient for reaction.

We have used both the ACT and phase-space approaches described above to calculate the rate coefficient for the $O + C_3 \rightarrow C_2 + CO$ system at temperatures between 10 and 300 K, utilizing the energies shown in Figure 1 and the parameters listed in Table 1, most of which have been calculated by the ab initio methods reported here. In the calculations, we have assumed that once the system crosses over or tunnels through the entrance channel TS (Fig. 1) it does not reverse direction and reform reactants, but rather passes rapidly over the exit channel TS to form products. The

TABLE 1

MOLECULAR PARAMETERS USED IN CALCULATIONS

Species	Rotation Constant (cm^{-1})	σ[a]	Vibrational Frequencies (cm^{-1})
Reactants:			
C_3 ($X\,^1\Sigma_g^+$)	0.4305	2	2097, 1196, 63.1(2)[b]
O (^3P)	...		
Entrance channel complex:			
O—CCC	0.2857	1	2082, 1226, 181, 108, 100,[c] 63
Transition state:			
O—CCC† ($^3A'$)	0.2857[d]	1	2082, 1226, 181, 108, 63, 244i

NOTE.—For the reactant O (^3P), $\epsilon = 50$ K and $a = 2.0$ Å. The dagger in row 3 refers to the transition state.

[a] The classical symmetry number. The electronic degeneracy of the O reactant is 3 times that of the transition state.

[b] Low-frequency bends and rotation constant from experimental compilation.

[c] Complex identical with transition state except for a real frequency of 100 cm^{-1} in place of the imaginary frequency.

[d] Geometric mean of three rotational constants used in spherical top approximation.

TABLE 2

CALCULATED RATE COEFFICIENT $k(T)$ ($\mathrm{cm}^3\ \mathrm{s}^{-1}$) FOR $C_3 + O$

T	ACT RESULTS		PHASE-SPACE RESULTS[a]	
(K)	Tunneling	No Tunneling	Tunneling	No Tunneling
10......	3.9(−56)	...	1.1(−22)	...
20......	...	...	1.5(−22)	...
30......	...	...	5.7(−22)	...
40......	...	...	5.0(−21)	...
50......	...	...	5.7(−20)	...
60......	3.5(−19)	1.5(−19)	7.7(−19)	1.4(−19)
70......	...	...	7.7(−18)	2.8(−18)
80......	...	...	5.3(−17)	2.6(−17)
90......	...	...	2.6(−16)	1.6(−16)
100......	2.5(−16)	1.6(−16)	9.5(−16)	6.6(−16)
100......	...	...	4.6(−16)[b]	...
300......	2.8(−13)	2.6(−13)	1.9(−12)	1.8(−12)

NOTE.—$a(-b)$ signifies $a \times 10^{-b}$.

[a] The phase-space calculations typically contain the assumption that only the lowest bending state of C_3 participates.

[b] Calculation includes the lowest five bending states of C_3.

long-range potential used in the phase-space calculation is a simple Lennard-Jones attraction of the form

$$V(R) = -4\epsilon(a/R)^6\ , \tag{3}$$

where the parameters ϵ and a are set to values that give a collision (capture) rate coefficient of $\approx 2\text{–}3 \times 10^{-10}\ \mathrm{cm}^3\ \mathrm{s}^{-1}$, which is a reasonable upper limit for neutral-neutral systems. The weakly bound (or van der Waals) complex formed from the reactants is assumed to have a binding energy (including zero-point energy) of 0.01 eV and vibrational frequencies identical to those calculated for the entrance channel TS, except for the addition of a low-frequency mode (100 cm^{-1}) to replace the imaginary frequency. The computed rate coefficients are not particularly sensitive to details of the van der Waals complex. Our results are listed in Table 2, while the phase-space results between 10 and 100 K are plotted in Figure 3.

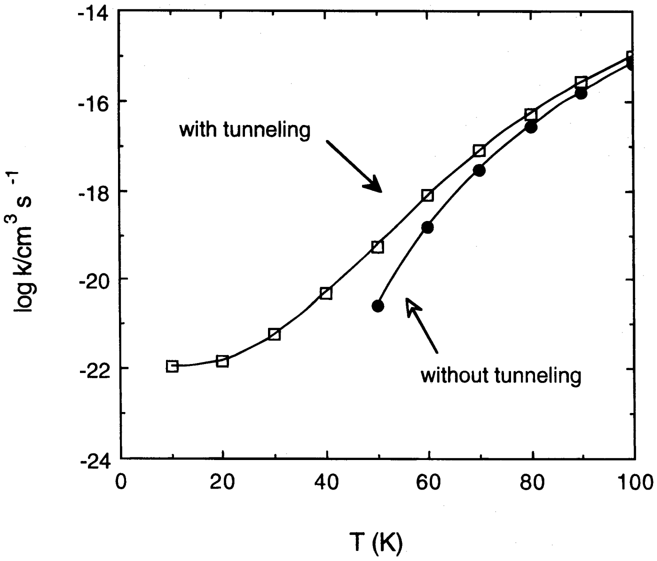

FIG. 3.—Rate coefficient for the reaction between O and C_3 is plotted versus temperature. The phase-space method is utilized with the assumption that only the lowest bending state of C_3 participates. Rates calculated without this simplifying assumption are smaller by factors of up to a few at temperatures near 100 K. Points labeled with open boxes include the tunneling correction.

4. DISCUSSION

The calculated rate coefficients between 10 and 300 K are all small compared with the collisional rate of 10^{-11}–$10^{-10}\ \mathrm{cm}^3\ \mathrm{s}^{-1}$ because of the activation energy barrier in the entrance channel. Table 2 shows that the ACT value for the rate coefficient at 300 K is $2.8 \times 10^{-13}\ \mathrm{cm}^3\ \mathrm{s}^{-1}$. This is more accurate than the listed phase-space value at this temperature of $1.9 \times 10^{-12}\ \mathrm{cm}^3\ \mathrm{s}^{-1}$ because the phase-space calculation only includes the lowest bending state of C_3. The rate coefficient decreases with decreasing temperature; by 100 K the ACT value has decreased to $2.5 \times 10^{-16}\ \mathrm{cm}^3\ \mathrm{s}^{-1}$. At this temperature, it is easier to estimate the effect of including excited bending states of C_3 on the phase-space rate coefficient; inclusion of the lowest five bending states leads to a rate coefficient that is less than a factor of 2 larger than the ACT value, whereas exclusion of the excited states leads to a rate coefficient that is 4 times higher.

In the 100–300 K temperature range, the effect of tunneling is not pronounced, increasing from a factor of nearly unity at 300 K to one of approximately 1.5 at 100 K in both treatments. But below 100 K, the tunneling effect increases and the ACT and phase-space treatments begin to diverge strongly. The rate coefficients in both treatments are the same at 60 K if tunneling is not considered because the effect of excited states of C_3 is no longer noticeable. But the rate coefficient with tunneling is larger in the phase-space treatment by more than factor of 2. By 10 K, the phase-space value exceeds the ACT value by more than 30 orders of magnitude. The very low temperature ACT result is inaccurate for two reasons: the separable thermal tunneling correction Γ must be replaced by a more detailed expression based on a microcanonical approach (Johnston 1966; Truong & Truhlar 1990), and the effect of the specific long-range attractive potential must be taken into account (Bates & Herbst 1988).

Figure 3 shows a plot of the rate coefficient calculated by the phase-space technique as a function of temperature in the range 10–100 K. With the inclusion of tunneling, the rate coefficient begins to level off toward the lowest temperatures. However, it does not increase with decreasing temperature in this range as was calculated and measured for the ion-molecule reaction between NH_3^+ and H_2 (Herbst et al. 1991) and as was calculated for the neutral-neutral reaction between C_2H and H_2 (Herbst 1994). In these latter systems, tunneling is more efficient than for the $C_3 + O$ system because of the lightness of the hydrogen reactant.

The phase-space value of $1.1 \times 10^{-22}\ \mathrm{cm}^3\ \mathrm{s}^{-1}$ for the $C_3 + O$ rate coefficient at 10 K is highly uncertain because it depends strongly on the values of the imaginary vibrational frequency and barrier height of the entrance channel TS. If one halves the barrier, the calculated rate coefficient increases to near $10^{-16}\ \mathrm{cm}^3\ \mathrm{s}^{-1}$. If one doubles the imaginary frequency, which has the effect of reducing the tunneling path, a similar increase in rate is achieved. Despite the fact that these large increases in rate are achieved with changes in the potential surface that we deem outside of the error limits in our ab initio computations, the computed rate coefficients are still far too small to contribute to the destruction of C_3 in chemical models of dense clouds. We can safely conclude that unless the ab initio calculations are grossly in error, the reaction between C_3 and O is of no importance in interstellar clouds.

Can our results be easily extended to reactions between atomic oxygen and other carbon clusters C_n? The question does not permit a facile answer because carbon clusters come in differing shapes (linear chains, rings) as well as ground states of differing spin multiplicities. The linear carbon clusters with an odd number of carbon atoms possess singlet ground states, and it is plausible to suggest that they too will not react rapidly with atomic oxygen. These linear species lie lower in energy than rings through ≈10 carbon atoms in size (Bettens & Herbst 1995). Ringed carbon clusters are, in general, less reactive than chains. The clusters with an even number of carbon atoms present a more complicated case; even for $n = 4$, the ground-state structure and multiplicity are not well established, although the linear clusters possess ground triplet states and may indeed be reactive with O. It appears that an analogous investigation of the reaction between atomic oxygen and linear triplet C_4 would be beneficial.

Bettens & Herbst (1995, 1996) have shown that, if the reactions between carbon clusters and atomic oxygen are all slow, the formation of fullerenes and even small dust particles through ion-molecule and neutral-neutral reactions may occur quite efficiently under interstellar conditions through a synthesis studied in the laboratory that proceeds through linear clusters, single rings, and tricyclic rings. The ≈100 interstellar molecules detected to date, through high-resolution observations, may then represent only a small portion of the chemical species synthesized in interstellar clouds.

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