IS INTERSTELLAR ACETONE PRODUCED BY ION-MOLECULE CHEMISTRY?

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ABSTRACT

The rate coefficient for the ion-molecule radiative association reaction $CH_3^+ + CH_3CHO \rightarrow (CH_3)_2CHO^+$ has been calculated in the range 10–300 K with the phase-space technique and the aid of a laboratory measurement of the analogous three-body association at room temperature. It has been suggested by Combes *et al.* that this reaction followed by dissociative recombination is responsible for the observed abundance of acetone (CH_3COCH_3) in Sgr B2. However, it is shown here that the radiative association reaction is probably too slow even at 10 K to lead to the observed abundance of acetone in this source. The question of how acetone is produced in Sgr B2 is thus still unanswered.

Subject headings: interstellar: molecules — molecular processes

I. INTRODUCTION

Several years ago Combes *et al.* (1987) obtained the first spectroscopic evidence for the presence of acetone (CH_3COCH_3) in the interstellar medium. These scientists detected eight rotational-torsional transitions of this species in Sgr B2 and inferred from their data an abundance ratio of $\approx 1/15$ between acetone and acetaldehyde (CH₃CHO), its presumed precursor. They also suggested that acetone was formed by the radiative association reaction

$$CH_3^+ + CH_3CHO \longrightarrow (CH_3)_2CHO^+ + hv$$
 (1)

followed by dissociative recombination

$$(CH_3)_2 CHO^+ + e \longrightarrow CH_3 COCH_3 + H$$
. (2)

Assuming that the intermediate ion $(CH_3)_2CHO^+$ is depleted principally by reaction with electrons and that the dissociative recombination proceeds mainly to form acetone, it is easily shown that

$$[CH_3COCH_3]/[CH_3CHO] = k_1[CH_3^+]/\Sigma_i k_i[l_i] \quad (3)$$

where [] represents fractional abundance with respect to H_2 , l_i is the *i*th ion that reacts with acetone to deplete it, and k_i is the rate coefficient for the reaction of the *i*th ion and acetone. Combes et al. (1987) first estimated the rate coefficient for reaction (1) using an empirical formula given by Bates (1983) to exceed 10^{-9} cm³ s⁻¹ at low temperatures. They then assumed that the principal ion depleting acetone was C^+ . Using the previous early-time model results of Herbst and Leung (1986) for the abundances of C^+ and CH_3^+ and assuming the reaction between C⁺ and acetone to proceed at the Langevin rate, they arrived at a value for the abundance ratio between acetone and acetaldehyde of 1/8-1/40, in reasonable agreement with the observed value. However, there are several points of their chemical analysis with which it is possible to take issue. The first is that C^+ is the only ion that will react with and deplete acetone, since other ions are also present. The second is that the reaction between C⁺ and acetone occurs at the Langevin rate since acetone is polar and at low temperatures probably reacts with ions at rate coefficients at least one order of magnitude larger than the Langevin rate. The third and possibly the most serious is that the rate coefficient for reaction (1) can be estimated by the approach of Bates (1983). Because this reaction competes with several exothermic channels, the approach of Bates is inapplicable (Bates and Herbst 1988). The proper estimation of the rate of reaction (1) via the phase-space technique (Herbst 1987) is a major purpose of this paper.

When normal exothermic channels compete with an association channel, the association rate is reduced, most often drastically. As shown by Bass et al. (1983) and Herbst (1985a, b, c; 1987), only an unusual type of potential surface, in which there is a barrier in the exit channel that slows down but does not completely eliminate the normal exothermic channel, can lead to a measurable association rate in the presence of competing exothermic channels. Such a competition has most recently been studied by theoretical and experimental methods for the reactions between CH3⁺ and CH3CN (Knight, Freeman, and McEwan 1986; McEwan et al. 1989; Herbst and McEwan 1990; Smith et al. 1990). In this system a radiative association channel has been detected at the lowest pressures of an ion cyclotron resonance (ICR) apparatus at room temperature, (McEwan et al. 1989). For CH_3^+ and CH_3CHO , on the other hand, a room temperature low-pressure ICR study (Anicich and Huntress 1986) indicates only a normal ion-molecule channel with products $CH_3CO^+ + CH_4$ and no evidence for radiative association. Even though ICR measurements are often thought to be suprathermal, a rather small upper limit for radiative association at room temperature can be deduced from this result. Thus, it seemed to us that the suggestion of Combes et al. (1987) that reaction (1) leads to interstellar acetone was probably incorrect. To test our tentative conclusion, we undertook measurements of the reactions between CH₃⁺ and CH₃CHO at room temperature in a high-pressure selected ion flow tube (SIFT) apparatus. Our results, which are in poor agreement with the earlier ICR study, show three normal exothermic channels and, surprisingly, a small (6%) association channel. At the gas densities of the SIFT apparatus, the association channel is three-body in nature but the very fact that association occurs shows that the potential surface for the reaction has at least a small barrier in the

output channel. In addition, the SIFT result allows us to estimate roughly the size of this barrier and other parameters needed to calculate the low-pressure radiative association rate coefficient as a function of temperature by the phase-space technique.

In this paper we report the results of our phase-space calculations of the rate coefficient of reaction (1) as a function of temperature in the range 10-300 K. We calculate that at 10 K the radiative association rate coefficient is $\approx 10^{-10}$ cm³ s⁻¹, which is an order of magnitude lower than the lower limit of the range of values suggested by Combes et al. (1987). Although this calculated rate coefficient is far larger than we originally had thought possible, it still appears that the abundance ratio [CH₃COCH₃]/[CH₃CHO] in interstellar clouds obtainable by the mechanism of Combes et al. (1987) is too low to explain the observation, especially if acetone is depleted via ion-molecule reactions with rapid rates due to its polarity $(\mu = 2.88D)$. If this and other ion-molecule mechanisms operating under normal interstellar conditions fail to explain the abundance of acetone, this molecule may be located in a region akin to the "compact ridge" source in Orion, in which oxygencontaining organic molecules have abundances higher than explained satisfactorily by current models (Blake et al. 1987; Herbst 1987).

The remainder of this paper is organized as follows. In § II we discuss the experimental and theoretical techniques used in obtaining k_1 . In § III the acetone/acetaldehyde abundance ratio is estimated and compared with observation. Finally, our conclusions are discussed in § IV.

II. EXPERIMENTAL AND THEORETICAL TECHNIQUES

The SIFT apparatus at the University of Birmingham, discussed in detail most recently by Smith and Adams (1989), has been used to study the reactions between CH_3^+ and CH_3CHO at room temperature and at a helium background gas number density of 1.8×10^{16} cm⁻³. Under these conditions, the following four channels are found:

$$CH_{3}^{+} + CH_{3}CHO + C_{2}H_{5}^{+} + H_{2}CO (55\%) + H_{3}CO^{+} + C_{2}H_{4} (36\%) + CH_{3}CO^{+} + CH_{4} (3\%) + (CH_{3})_{2}CHO^{+} (6\%) .$$
(4)

The branching ratios for each channel are listed above. The dominant normal channels here do not agree with that measured in the low-pressure ICR experiment (Anicich and Huntress 1986). This disagreement is not currently understood. The total rate coefficient obtained in the ICR work is 2.5×10^{-9} cm³ s⁻¹, whereas that obtained here is 5.5×10^{-9} cm³ s⁻¹. The association channel is a ternary one in which the background gas (helium) stabilizes the intermediate complex formed by the reactants. To relate the rate coefficient for the ternary association reported here to that for radiative association requires the use of theory.

The detection of an association channel, albeit a minor one, constrains the potential surface of the reaction to rise from a minimum, corresponding to the collision complex, through one or more maxima, known as transition states, before descending to the assorted energies of the product channels (see diagrams in Herbst 1985a, b, 1987). The calculation of the rate coefficient for an association channel on a potential surface of this type requires a more detailed theoretical treatment than the customary statistical approaches (Bates and Herbst 1988). Here we have chosen the phase-space approach with the additional simplifying assumption of a single transition state (Bass et al. 1983; Herbst 1985a, b, c; Herbst and McEwan 1990). To utilize this treatment, vibrational, structural, and thermodynamic information is needed concerning the reactants, complex, and transition state. The thermodynamic information for the reactants and complex can be found in the literature (Lias et al. 1988). Structural information for the reactants as well as the dipole moment and polarizability of acetaldehyde are also readily available. In addition, we have estimated the structure and vibrational frequencies of the complex based on the properties of similar (and better-studied) species. All relevant information is contained in Table 1.

The properties of the transition state—energy, structure, vibrational frequencies—are not known at all to the best of our knowledge and can be constrained only somewhat by normalizing the theoretical determination of the ternary association rate coefficient to agree with that measured on the SIFT. Another constraint is the lack of detection of an association channel in the room temperature ICR measurements. Finally, since the energy of the transition state must always exceed that of the least exothermic products ($C_2H_5^+ + H_2CO$) in order to produce a potential barrier in the output channel, a minimum

TABLE 1

	ROTATION			VIBRATIONAL DATA	
Species	(cm^{-1})	σ^{b}	$\Delta H^{\circ}_{f}(298 \text{ K})^{\circ}$ (kcal mol ⁻¹)	$E_z(eV)$	$\prod_i hv_i (eV^n)^d$
	مو بربر المالية م _و ي بربر المالية الارينيين	Reactar	nts		
СН,+	7.650	6	261.3		
СН ₃ СНО	0.5837	1	- 39.6	$\mu = 2.69D$	$\alpha = 4.59~\text{\AA}^3$
Ion	ic Complex (CO) a	nd Transitio	on State (TS) of (CH	₃) ₂ CHO ⁺	
со	0.2511	1	117.0	2.70	$1.30(-21)^{\circ}$
TS model 1	0.2511	1	191.9	2.62	$7.82(-21)^{\circ}$
TS model 2	0.2511	1	190.8	2.61	$7.82(-22)^{\circ}$
TS model 3	0.2511	1	190.1	2.61	$6.27(-23)^{\circ}$

MOLECULAR PARAMETERS USED IN CALCULATION

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

^a Geometric mean of three rotational constants is used in the spherical top approximation.

^b Symmetry number.

^c Lias et al. (1988) for all but the transition state models.

 $^{e}\beta = 1.23, 1.23, 1.33, 1.37$ for the complex and three transition states, respectively—see Forst 1973.

^d Units are eV raised to a power equal to the number of vibrational modes.

1990ApJ...358..468H

value for the transition state energy can be ascertained. In the recent studies of the association between CH_3^+ and CH_3CN in competition with normal exothermic channels, much more experimental information was available to constrain the transition state parameters.

In addition to the major uncertainties regarding the transition state, there is some uncertainty caused by our treatment of the stabilization of collision complexes by inelastic collisions with helium. Our previous approach (Herbst 1985a), in which the probability of one-step ("strong") collisional stabilization is a negative exponential function of the amount of energy needed to be removed from the system to achieve stabilization, was found to predict the pressure dependence of the threebody association rate coefficient inaccurately in several systems (Smith, McEwan, and Gilbert 1989a; Smith et al. 1990) and a more detailed master equation treatment in conjunction with RRKM theory has been proposed and utilized (Smith, McEwan, and Gilbert 1989a, b; Smith et al. 1990). The more detailed treatment is based on the assumption that stabilization proceeds stepwise. Since there is but little experimental information about the $CH_3^+ + CH_3CHO$ system we have not utilized the more detailed treatment but have chosen three widely varying collision stabilization models within the confines of our "strong" collision hypothesis-model 1, in which a modified version of our exponential treatment is utilized, and models 2 and 3, in which collisional deactivation occurs on a fixed percentage of collisions. (For low angular momentum partial waves, in which the energy of the system exceeds the effective potential of the transition state, this percentage is 0.1% and 1.0%, respectively. For high angular momentum collisions, in which the energy of the system is below the effective potential of the transition state, the efficiency is set at 30%, which is a standard collisional stabilization efficiency for helium atoms at room temperature [Bates and Herbst 1988].) With each of the three models, parameters involving the transition state (energy, vibrational frequencies) were varied to calculate a branching ratio for the association channel in agreement with the SIFT result. The sets of parameters utilized are listed in Table 1.

With the three different models, we have calculated the total rate coefficient for association $k = k_{ra} + k_{3b} n$ as a function of helium number density n at 300 K, where k_{ra} is the radiative association rate coefficient and k_{3b} the three-body association rate coefficient (Bates and Herbst 1988). The results are shown in Figure 1, in which the logarithm of k is plotted against the logarithm of helium number density. It can be seen that as the gas density is reduced, the association rate coefficient decreases until the low-pressure limit is reached, in which radiative association is dominant and the complex is stabilized only by the emission of photons. Depending on which model is chosen, the radiative association rate coefficient ranges from 1.2×10^{-12} cm³ s⁻¹ to 1.2×10^{-11} cm³ s⁻¹. These values have been obtained with a rate coefficient for complex stabilization by radiative (spontaneous) emission of 10^2 s^{-1} for collision complexes lying less than 2500 cm^{-1} in energy above the dissociation limit and 1 s^{-1} for complexes lying farther above this limit (Herbst 1985b). The dissociation limit is the energy below which the collision complex will not dissociate. The mechanism is presumed to be spontaneous emission from the quasi continuum of vibrational levels of the collision complex above the dissociation limit to the discrete levels below it. Although rates higher by one order of magnitude than those utilized here have been proposed, work on the CH₃⁺



FIG. 1.—The logarithms of the calculated effective two-body rate coefficients $k = k_{ra} + k_{3b} n \, (\text{cm}^3 \, \text{s}^{-1})$ at 300 K for the association of CH₃⁺ and CH₃CHO as functions of the logarithm of the helium number density, here labeled *n*. The results of three different models are shown. Models 1, 2, and 3 (Table 1) are depicted by open squares, filled-in diamonds, and filled-in squares, respectively. The results of all of these models reproduce the high-pressure SIFT data, taken at $n = 1.8 \times 10^{16} \, \text{cm}^{-3}$, but differ at other helium densities.

+ CH₃CN system showed the values used here to be more appropriate (Herbst and McEwan 1990), possibly due to the large size of the collision complex. If excited electronic states of the complex are accessible, radiative stabilization can be significantly more rapid (Herbst and Bates 1988). We take the absence of an observed association channel in the "room temperature" ICR experiment to imply that radiative association at room temperature cannot be more rapid than $\approx 10^{-11}$ cm³ s⁻¹ so that a faster radiative stabilization rate than used here is not appropriate.

Which of our three model results is the most accurate? This question cannot easily be answered, given the wide range of parameters consistent with the limited experimental information available. It should be mentioned that model 1 (the "exponential" model) overestimates the radiative association rate coefficient measured for $CH_3^+ + CH_3CN$ when fitted to the high-pressure SIFT data (E. Herbst, unpublished work). On the other hand, models 2 and 3 contain rather low vibrational frequencies for the transition state, making this a socalled "loose" structure which may be unphysical, especially for model 3. Although we cannot distinguish among the three models, we can assert more strongly that the value of the radiative association rate coefficient at 300 K is within the calculated range. Models with a somewhat larger value for k_{ra} than 10^{-11} cm³ s⁻¹ have been obtained upon variation in the parameters of the collision complex; however, the results of these are inconsistent with the negative results of the ICR experiment. Models in which a value of k_{ra} smaller than 10^{-12} $cm^3 s^{-1}$ is calculated appear to require an unphysical set of parameters for the transition state.

Using the three models discussed above, we have calculated the rate coefficient for radiative association as a function of temperature down to 10 K. The results, tabulated in Table 2, show a small inverse temperature dependence ($\approx T^{-1}$), unlike the case of association in the absence of competing exothermic channels, in which the inverse temperature dependence is much steeper (Bates and Herbst 1988). The largest rate coefficients are achieved at the lowest temperature studied—10 K—and are in the range 4 × 10⁻¹¹-2 × 10⁻¹⁰ cm³ s⁻¹. An earlier estiNo. 2, 1990

TABLE 2 CALCULATED RADIATIVE ASSOCIATION RATE COEFFICIENTS^a

Temperature (K)	Model 1	Model 2	Model 3
300 200	1.2(-11) 2.0(-11)	4.5(-12) 6.7(-12)	1.2(-12) 1.5(-12)
100 50 10	$\begin{array}{c} 4.3(-11) \\ 7.3(-11) \\ 2.1(-10) \end{array}$	$\begin{array}{c} 1.2(-11) \\ 1.9(-11) \\ 8.1(-11) \end{array}$	2.4(-12) 3.7(-12) 3.5(-11)

NOTE.—a(-b) signifies $a \times 10^{-b}$. a cm³ s⁻¹.

mate, with a more rapid spontaneous emission rate and the model in which association is most rapid (model 1), was 5.5×10^{-10} cm³ s⁻¹ at 10 K (Herbst and McEwan 1990). Given the negative ICR evidence at room temperature, this earlier approach, which results in a room temperature radiative association rate coefficient of 5.7×10^{-11} cm³ s⁻¹, can be ruled out. It is thus safe to conclude that, assuming the correctness of the theoretical approach, an upper limit of 2×10^{-10} cm³ s⁻¹ for the radiative association rate coefficient at 10 K pertains.

What about the possibility that the rotational state distribution of acetaldehyde in interstellar clouds is nonthermal but resides chiefly in the lowest rotational states? In this instance, the radiative association rate coefficient rises dramatically. Although Sgr B2 is a complex source, previous observations do not indicate large deviations of rotational populations from thermal equilibrium. For example, the observations of Combes et al. (1987) on acetone indicate that $T_{\rm rot} \approx 20$ K.

III. CALCULATED ABUNDANCE OF ACETONE

Equation (3) can be utilized to estimate the fractional abundance of acetone with respect to acetaldehyde. To obtain an upper limit for this ratio, we first assume k_1 (the rate coefficient for radiative association between CH₃⁺ and CH₃CHO) to be 2×10^{-10} cm³ s⁻¹, the largest value we were able to calculate. We then assume that only certain ions are able to deplete acetone via ion-molecule reactions. In particular, we exclude the reaction between acetone and the abundant protonated ion HCO^+ , because this reaction

$$HCO^+ + CH_3COCH_3 \longrightarrow (CH_3)_2CHO^+ + CO$$
 (5)

presumably produces only the protonated acetone ion and we have already assumed that this ion dissociatively recombines with electrons only to reform acetone. A more realistic assumption is that acetone is reformed on only $\frac{1}{2}$ of dissociative recombination reactions. We have investigated the more exothermic reaction between H₃⁺ and acetone on the SIFT and found that protonated acetone is not the only product; viz.,

$$H_{3}^{+} + CH_{3}COCH_{3} \longrightarrow (CH_{3})_{2}CHO^{+} + H_{2} (50\%)$$

$$\longrightarrow H_{3}CO^{+} + C_{2}H_{4} + H_{2} (35\%)$$

$$\longrightarrow C_{3}H_{5}^{+} + H_{2}O + H_{2} (10\%)$$

$$\longrightarrow CH_{3}CO^{+} + CH_{4} + H_{2} (5\%) ,$$
(6)

where the neutral products are not measured but deduced by mass balance. The measured overall rate coefficient for reaction (6) is 8.6×10^{-9} cm³ s⁻¹ at 300 K, reflecting the large

dipole moment of acetone and the lightness of the H_3^+ ion. Presumably what is occurring at least partially in reaction (6) is dissociative proton transfer; the large exothermicity of reaction permits the formation of an initial protonated acetone complex with sufficient energy to decompose into smaller products on 50% collisions. Since, however, the products of reaction (6) do not coincide with those of reaction (4), caution must be applied to this interpretation of reaction (6). Here we assume that destruction of interstellar acetone results on 50% of reactions with H_3^+ .

The major interstellar ions that deplete acetone are C^+ , H_3^+ , H^+ , and He^+ . With the trajectory scaling approach (Herbst and Leung 1986), the calculated rapid ion-polar rates at 10 K for reactions between acetone and these ions are 2.1×10^{-8} cm³ s⁻¹, 3.8×10^{-8} cm³ s⁻¹, 6.5×10^{-8} cm³ s⁻¹ and 3.3×10^{-8} cm³ s⁻¹ respectively (Herbst and Leung 1986). The estimated abundances of CH₃⁺, H₃⁺, C⁺, H⁺, and He⁺ can be taken from the "standard" early-time model of Herbst and Leung (1989, 1990) which reproduces accurately many molecular abundances in cold interstellar clouds distant from star-forming regions. With these abundances, we obtain a value for the abundance ratio [CH3COCH3]/[CH3CHO] of $\approx 1/2000$. This upper limit is too low by two orders of magnitude to explain the observations in Sgr B2. It should be noted that the early-time calculated abundance of acetaldehyde in the model of Herbst and Leung (1989) has been recently revised downward (Herbst and Leung 1990) due to a measurement of the synthetic reaction between H_3O^+ and C_2H_2 (Herbst et al. 1989) and is itself a factor of 5 below the observed value in Sgr B2. On an absolute scale, therefore, the calculated abundance of acetone is even worse.

IV. CONCLUSIONS

With the range of theoretical values obtained here for the rate coefficient of the radiative association reaction between CH_3^+ and CH_3CHO , it does not appear possible to account for the observed abundance of acetone in Sgr B2. Given uncertainties in model parameters and our theoretical approach, this conclusion cannot be regarded as definitive but only as suggestive.

What about other gas-phase ion-molecule synthetic reactions leading to acetone? Since we have presumed that a barrier in the exit channel of the $CH_3^+ + CH_3CHO$ reactions exists, it would appear that none of the exothermic products $(C_2H_5^+ + H_2CO, H_3CO^+ + C_2H_4, CH_3CO^+ + CH_4)$ can combine under low-temperature conditions to produce protonated acetone, the precursor to acetone. However, our hypothesis should be tested by suitable laboratory work. Another possibility is a reaction similar to the association reaction between $H_3O^+ + C_2H_2$ which may lead to a precursor to acetaldehyde (Herbst et al. 1989). In particular, we have searched in the laboratory for the association reaction

$$H_3O^+ + CH_3CCH \longrightarrow (CH_3)_2CHO^+$$
 (7a)

but have found only an exothermic proton transfer channel:

$$H_3O^+ + CH_3CCH \longrightarrow CH_3CCH_2^+ + H_2O$$
. (7b)

If none of these approaches is viable, then it is necessary to consider other possibilities, one of which is that acetone is being produced in a star-forming region of Sgr B2 in which normal ion-molecule chemistry is inapplicable. The chemistry of star-forming regions in the better studied Orion source has

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1990ApJ...358..468H 472

been discussed recently by a variety of authors (Blake et al. 1987; Brown, Charnley, and Millar 1988). In particular, certain oxygen-containing molecules appear to have very high abundances in the so-called "compact ridge" source (Blake et al. 1987) which cannot be accounted for on the basis of normal ion-molecule reactions (Herbst 1987). The chemistry of this region is not well understood although the suggestion has been advanced that high abundances of water flowing into the region from IRc2 initiate an unusual gas-phase chemistry (Blake et al. 1987). Alternatively, a nonreducing type of grain chemistry may be involved (Tielens and Allamandola 1987). Further observations concerning the acetone abundance in

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sources of differing physical conditions would help to constrain the possible chemical explanations.

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