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CAN GAS PHASE REACTIONS PRODUCE COMPLEX OXYGEN-CONTAINING MOLECULES IN DENSE INTERSTELLAR CLOUDS? A REVISION OF SOME IMPORTANT RADIATIVE ASSOCIATION RATE COEFFICIENTS

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ABSTRACT

In light of new laboratory measurements and theoretical techniques, previously suggested gas phase syntheses of dimethyl ether (CH_3OCH_3), ethyl alcohol (C_2H_5OH), and acetaldehyde (CH_3CHO) in dense interstellar clouds have been reexamined. Several radiative association rate coefficients leading to the precursor ions to these species are now calculated to be significantly smaller than previous estimates. On the other hand, a new and rapid synthesis of the precursor ion to acetaldehyde appears to be viable. The diminution in the values of selected radiative association rate coefficients raises the possibility that normal gas phase syntheses under ambient dense cloud conditions may not account fully for the observed abundances of ethyl alcohol and, especially, dimethyl ether.

Subject headings: interstellar: molecules — molecular processes

I. INTRODUCTION

The importance of ion-molecule radiative association processes in the gas phase syntheses of complex molecules in dense interstellar clouds has been discussed in detail in the literature (Smith and Adams 1978; Huntress and Mitchell 1979; Leung, Herbst, and Huebner 1984). In these processes, two atomic or molecular species, labeled A^+ and B, come together to form a compound molecule AB^+ via emission of a photon. Because it is difficult to study such processes in the laboratory, a variety of theoretical treatments have been advanced and utilized to calculate radiative association rate coefficients, especially at the low temperatures characteristic of dense interstellar clouds (Herbst 1980*a*, *b*; Bass *et al.* 1981; Bates 1983*a*, *b*; Herbst 1985*a*, *b*; Bates 1985). Although at least one radiative association reaction important to gas phase astrochemistry ($CH_3^+ + H_2 \rightarrow CH_5^+ + h\nu$) has been measured in the laboratory at 13 K (Barlow, Dunn, and Schauer 1984), the determination of radiative association rate coefficients is still predominantly a theoretical investigation.

Theories of radiative association can be partially confirmed by modifying them to treat the analogous case of three-body or ternary association, in which the compound molecule AB^+ is formed via collisional stabilization (Smith and Adams 1978; Bass, Chesnavich, and Bowers 1979; Bates 1979; Adams and Smith 1981; Herbst 1981). This process has been studied widely in the laboratory because at normal pressures it dominates the radiative mechanism. In general, although there are still some difficulties (Bass and Jennings 1984; Bates 1986), theoretical and laboratory determinations of ternary rate coefficients are in order-of-magnitude agreement when there is sufficient structural and thermodynamic information on reactants and products to permit a theoretical calculation.

Most previous calculations of association rate coefficients have been undertaken on systems in which association is the only possible reactive outcome. In these systems, the reactants collide to form a temporary "collision complex" which either stabilizes itself permanently via emission of a photon (radiative association) or via collisional deactivation (ternary association), or redissociates into reactants. However, many of the radiative association reactions thought to be important in the synthesis of complex molecules in dense interstellar clouds (Huntress and Mitchell 1979; Leung, Herbst, and Huebner 1984) involve reactants that can also undergo competitive normal exothermic ion-molecule reactions. Bates (1983*b*) has theorized that under such circumstances the association reaction rate coefficient is dramatically smaller than if no exothermic channel exists. However, there is a body of laboratory evidence that ternary association and normal exothermic channels can coexist and that the ternary rate coefficient can still be significant (Smith and Adams 1978). Recently, Herbst (1985*b*, *c*) has concluded that a mechanism exists whereby association and normal exothermic channels can indeed occur efficiently in each other's presence. This mechanism has also been utilized by Bass *et al.* (1983).

Herbst (1985*b*, *c*) performed calculations on the system

$$CH_3^+ + NH_3 \rightarrow H_4CN^+ + H_2 \qquad (1a)$$

$$\rightarrow NH_4^+ + CH_2 \qquad (1b)$$

$$\rightarrow H_6CN^+ \, . \qquad (1c)$$

He was able to reproduce the laboratory result of Smith and Adams (1978) that the ternary mechanism for reaction (1c) in the presence of helium is efficient; indeed, his calculated ternary rate coefficient is quite close to the experimental one. In addition, he was able to show that the radiative association to form H_6CN^+ at low temperatures is not greatly affected by the exothermic channels. The reason that Herbst (1985*b*, *c*) found the association channels to be efficient is the existence of a barrier in the dominant normal exothermic channel (1a). A view of this barrier and its place on the reaction potential surface is shown in Herbst (1985*b*, *c*); similar diagrams are discussed below. This barrier is not by itself sufficiently large to prevent the complex from exiting along this channel. However, the size of the barrier effectively increases as the relative angular momentum of the reaction partners increases. Eventually, the effective barrier becomes great enough to prohibit complex dissociation via the exothermic product channel. Thus, reaction partners with large amounts of relative angular momentum form a complex which can only be stabilized (via collisions or radiation) or redissociate to reactants. The existence of a permanent dipole moment on the neutral reactant is important to this mechanism because, according to a variety of treatments (see, for example, Bates 1982), it increases the range of relative angular momenta available in the process of complex formation. The calculated association rate coefficients, whether ternary or radiative, are strongly dependent on both the size of the barrier and the neutral reactant dipole moment. Thus, even if the existence of a barrier to a competitive exothermic channel is known, one cannot state categorically that the association channel rate coefficients are not greatly diminished as compared with the values obtained in the absence of competing channels.

The size of the barrier in the exit channel of process (1a) had been determined both theoretically (Nobes and Radom 1983) and experimentally (Bowers, Chesnavich, and Huntress 1973). Its existence had also been inferred by the experimental observation that H_4CN^+ and H_2 do not associate (Smith and Adams 1977). Unfortunately, the size and even the possible existence of exit channel barriers in most of the other association reactions of interstellar importance that must compete with normal exothermic channels (Huntress and Mitchell 1979; Leung, Herbst, and Huebner 1984) have not been determined. This situation has now been improved somewhat by a new paper on metastable and collision-induced dissociation studies from Jarrold *et al.* (1986).

In their paper, Jarrold *et al.* (1986) report studies on the various isomers with chemical formulae $C_2H_5O^+$, $C_2H_7O^+$, and $C_2H_8N^+$, the first two of which concern us here. In metastable dissociation studies, the assorted ions are formed from precursor neutrals with internal energies sufficient so that they dissociate slowly. Their dissociation is then monitored. From the translational energy spread of the dissociation products, the existence and size of a barrier to dissociation can be determined. Collision-induced dissociation studies are used to determine the structures of stable ions formed in ternary association reactions by comparing their collisional dissociation patterns with ions of known structures. The interested reader is referred to the paper of Jarrold *et al.* for a discussion of these techniques. What these experiments can determine in the context of association reactions are the size and existence of barriers in both the entrance channels and competitive exothermic channels, and the structures of the compound ions formed. Knowledge of structures is important because polyatomic ions often exist in several stable structures, and these structures may not be similar to the neutral species thought to be formed upon subsequent dissociative recombination in interstellar clouds. The existence of barriers in the entrance channels of proposed radiative association reactions tells us that these reactions cannot occur appreciably. The existence of barriers in competitive exit channels to association reactions tells us that the association reactions may be surprisingly efficient, as is the case for process (1c).

The particular ions of interest here, $C_2H_5O^+$ and $C_2H_7O^+$, each possess several structures among which are protonated precursors to acetaldehyde, dimethyl ether, and ethyl alcohol (Smith and Adams 1978; Huntress and Mitchell 1979; Leung, Herbst, and Huebner 1984). Interstellar acetaldehyde (CH_3CHO) is thought to be produced via dissociative recombination of CH_3CHOH^+, one of several stable isomers of $C_2H_5O^+$. Dimethyl ether (CH_3OCH_3) is thought to form via the precursor ion $(CH_3)_2OH^+$ and ethyl alcohol (C_2H_5OH) via the precursor ion $CH_3CH_2OH_2{}^+$, both ions of which have the structural formula $C_2H_7O^+$. In the detailed dense cloud model of Leung, Herbst, and Huebner (1984), all three of these ion precursors were assumed to form via radiative association. The particular reactions utilized are seemingly the most efficient of those considered by Huntress and Mitchell (1979). Protonated dimethyl ether is produced by

$$CH_3{}^+ + CH_3OH \rightarrow (CH_3)_2OH^+ + h\nu \tag{2}$$

and, to a lesser extent, by

$$H_3CO^+ + CH_4 \rightarrow (CH_3)_2OH^+ + h\nu \, . \tag{3}$$

Protonated ethyl alcohol is synthesized by

$$C_2H_5{}^+ + H_2O \rightarrow CH_3CH_2OH_2{}^+ + h\nu \tag{4}$$

and, to a lesser extent, by

$$H_3O^+ + C_2H_4 \rightarrow CH_3CH_2OH_2{}^+ + h\nu \, . \tag{5}$$

Finally, protonated acetaldehyde is produced via

$$CH_5{}^+ + CO \rightarrow CH_3CHOH^+ + h\nu \tag{6}$$

and, to a lesser extent, by

$$HCO^+ + CH_4 \rightarrow CH_3CHOH^+ + h\nu \, . \tag{7}$$

The results of Jarrold *et al.* (1986) affect the analysis of Leung, Herbst, and Huebner (1984) as amended by Herbst (1985*a*) in several ways, and it is the purpose of this paper to reexamine the interstellar syntheses of dimethyl ether, ethyl alcohol, and acetaldehyde utilizing this knowledge. First, Leung, Herbst, and Huebner (1984) and Herbst (1985*a*) did not consider competitive exothermic pathways in calculating the rate coefficients of reactions (2), (4), and (6). Now that the existence or lack of existence of barriers to these competitive pathways is known for (2) and (4) and a theoretical formalism exists to include the existence of exothermic channels in association rate coefficient calculations (Herbst 1985*b*, *c*), detailed calculations can be undertaken on these association reactions. The result, in general, is a diminution of these rate coefficients even in the case (reaction [2]) where a significant exit channel barrier exists. Secondly, reactions (3) and (7) (and probably [6]) are now known to possess energy barriers in their entrance channels, so that they do not occur appreciably under interstellar conditions. The net effect of these changes is a possibly serious diminution in the calculated formation rates of dimethyl ether, ethyl alcohol, and acetaldehyde in interstellar clouds. However, based on their experiments, Jarrold *et al.* (1986) suggested that protonated acetaldehyde could be formed efficiently via the association reaction

$$H_3O^+ + C_2H_2 \rightarrow CH_3CHOH^+ + h\nu \, , \tag{8}$$

and our detailed calculations, discussed below, support this contention. Therefore, it would seem that of the three oxygen-containing complex organic molecules discussed here, only two have gas phase syntheses that may well be inadequate.

The remainder of this paper is organized as follows. In § II, the theoretical formalism for the calculation of radiative association rate coefficients is reviewed with an emphasis on the treatment of systems in which normal exothermic reaction channels also exist. Our specific results for reactions (2)–(8) are discussed in § III, and their effects on detailed model predictions are considered in § IV. Finally, a brief summary is provided in § V.

II. THEORY

The particular approach to association rate coefficients utilized here is the so-called phase space theory, first utilized by Bowers and co-workers (see, e.g., Bass, Chesnavich, and Bowers 1979). This microcanonical approach, in which angular momentum and energy are conserved explicitly, is most appropriate for the case where exothermic products can exist (Herbst 1985*b*, *c*). Consider an ion A^+ and a neutral species B colliding with relative translational energy $E_{\rm coll}$ to form a collision complex AB^{+*}. The reactants are assumed to be in rotational states with rotational angular momentum quantum numbers $J_{\rm A}$ and $J_{\rm B}$ respectively and to be in their ground vibrational states. The complex possesses energy $E_{\rm total}$, which is the sum of the rotational energies of the reactants and $E_{\rm coll}$, and a range of angular momentum quantum numbers J, defined principally by the range of relative angular momentum quantum numbers L of the reactant partners and secondarily by the individual angular momenta of the reactants. Once the complex is formed, it can be stabilized by either emission of a photon (radiative association) or collision with a third body (ternary association), or it can dissociate, either back into reactants or into some set of products. The reactions can be depicted as

$$A^+ + B \rightleftarrows AB^{+*} \rightarrow C^+ + D\,, \tag{9a}$$

$$AB^{+*} \rightarrow AB^+ + h\nu\,, \tag{9b}$$

$$AB^{+*} + E \rightarrow AB^+ + E\,, \tag{9c}$$

where C^+ and D represent exothermic products and E (normally helium) a third body for ternary association.

If one makes the normal assumption that the concentration of the collision complex is at steady state (i.e., the time derivative of its concentration is zero), one can show that the rate law for the appearance of stable product AB^+ is given by the expression

$$d[AB^+]/dt = (k_{\rm ra} + k_{\rm 3b}[E])[A^+][B]\,, \tag{10}$$

where the symbol [ ] refers to concentration and $k_{\rm ra}$ and $k_{\rm 3b}$ are defined as the rate coefficients for radiative and ternary association respectively. The rate coefficient for radiative association is given by the expression

$$\begin{aligned} k_{\rm ra}(J_{\rm A}, J_{\rm B}, E_{\rm coll} \rightarrow J, E_{\rm total}) &= \{k_1(J_{\rm A}, J_{\rm B}, E_{\rm coll} \rightarrow J, E_{\rm total})k_{\rm rad}\}/ \\ &\quad \{k_{-1}(J, E_{\rm total}) + k_{-2}(J, E_{\rm total}) + k_{\rm rad} + k_{\rm coll}[E]\}\,, \end{aligned} \tag{11}$$

where k_1 is the rate coefficient for complex formation, k_{-1} and k_{-2} are the rate coefficients for complex dissociation back into reactants and into products respectively, $k_{\rm rad}$ is the rate coefficient for complex stabilization via photon emission, and $k_{\rm coll}$ is the rate coefficient for complex stabilization via collision. Note that at interstellar densities, the term $k_{\rm coll}[E]$ in the denominator of expression (11) is vanishingly small and $k_{\rm ra}$ is independent of density. An expression for the ternary association rate coefficient $k_{\rm 3b}$ can be obtained from relation (11) by changing the quantity $k_{\rm rad}$ in the numerator to $k_{\rm coll}$.

The rate coefficient k_1 for complex formation can be related to a cross section σ for this process via the relation

$$k_1(J_{\rm A}, J_{\rm B}, E_{\rm coll} \rightarrow J, E_{\rm total}) = v\sigma(J_{\rm A}, J_{\rm B}, E_{\rm coll} \rightarrow J, E_{\rm total}) \tag{12}$$

where v is the relative velocity between A^+ and B. The cross section σ can be written as (Light 1967; Herbst and Knudson 1981)

$$\sigma = (\pi\hbar^2 G/2\mu E_{\rm coll}) \sum_L (2L + 1)P(J_{\rm A}, J_{\rm B}, L \rightarrow J)\,, \tag{13}$$

where μ is the reduced mass of the reactants, L is the relative angular momentum quantum number of the reactants and runs between 0 and $L_{\rm max}$, P is the probability that a complex of angular momentum J will be formed, and $G\ (\leq 1)$ is the ratio of the electronic degeneracy of the complex to those of the reactants. In expression (13), it has been assumed that all collisions up to a certain $L_{\rm max}$ can form a complex. The range of L for which complex formation can occur is determined by the collision model utilized. If reactant B does not possess a permanent dipole moment, the Langevin model is applicable. In this model, $L_{\rm max}$ is given by the expression

$$L_{\rm max}(L_{\rm max} + 1) = [8(e\mu)^2 \alpha E_{\rm coll}]^{1/2}/\hbar^2\,, \tag{14}$$

where α is the polarizability of the neutral reactant and e is the electronic charge in esu. If reactant B possesses a permanent dipole moment, a different model must be used. We have chosen to utilize the approach of Bates (1982), in which $L_{\rm max}$ is also a function of $J_{\rm B}$. This dependence arises because as $J_{\rm B}$ increases, the neutral dipole rotates more rapidly and its net effect in attracting the ion A^+ diminishes. Bates (1982) has actually tabulated total rate coefficients for complex formation as a function of neutral rotational energy; we have utilized these numbers to determine $L_{\rm max}$ by first calculating an effective dipole for which the locked dipole expression of Moran and Hamill (1963) obtains the same rate coefficient and then utilizing the locked dipole expression for $L_{\rm max}$ in terms of this effective moment $D_{\rm eff}$:

$$L_{\rm max}(L_{\rm max} + 1) = (2\mu/\hbar^2)[eD_{\rm eff} + (2e^2\alpha E_{\rm coll})^{1/2}]\,. \tag{15}$$

The probability P that a complex of rotational angular momentum J is formed is given by the simple expression

$$\begin{aligned} P = \sum_{J_r} &\{(2J + 1)/[(2L + 1)(2J_r + 1)]\} \\ &\times \{(2J_r + 1)/[(2J_{\rm A} + 1)(2J_{\rm B} + 1)]\}\,, \end{aligned} \tag{16}$$

where $\mathbf{J}_r = \mathbf{J}_{\rm A} + \mathbf{J}_{\rm B}$ is the overall internal angular momentum for the reactants. The quantum number J_r ranges between $|J_{\rm A} - J_{\rm B}|$ and $J_{\rm A} + J_{\rm B}$.

Once k_1 is determined, the rate coefficient k_{-1} for redissociation of the complex into reactants is determined by microscopic reversibility. The derivation of k_{-1} is discussed in some detail in Herbst (1985*d*) and need not be repeated here. The calculation of the rate coefficient k_{-2} for dissociation of the complex into exothermic products depends critically on whether there is a potential barrier in the exit channel. If such a barrier exists, k_{-2} can be determined via RRKM theory (Forst 1973; Herbst 1985*b*, *c*) to be

$$\begin{aligned} k_{-2}(J, E_{\rm total}) = &\frac{\prod_{i=1}^{s} \nu_i^*}{\prod_{i=1}^{s-1} \nu_i^\#} \\ &\times \frac{\sigma^*[E_{\rm total} + D_0^\# + a^\# E_z^\# - E_{\rm rot}^\#]^{s-1}}{\sigma^\#[E_{\rm total} + D_0^* + a^* E_z^* - E_{\rm rot}^*]^{s-1}}\,, \end{aligned} \tag{17}$$

where all quantities designated by a * refer to the collision complex AB^{+*} and all quantities designated by a # refer to the maximum of the potential energy surface in the exothermic exit channel, commonly referred to as the transition state structure.

This well-known expression equates k_{-2} with the ratio of the number of available vibrational states of the transition state to the density of complex vibrational states. In equation (17), s represents the number of vibrational degrees of freedom of the complex; $s - 1$, the number of vibrational degrees of freedom of the transition state; ν_i, the vibrational frequencies of complex and transition state; E_z, the zero-point energies; D_0^*, the bond energy of the stabilized complex at 0 K with respect to reactants at 0 K; $D_0^\#$, the bond energy of the transition state at 0 K with respect to reactants at 0 K (in other words, the energy of the transition state below that of the reactants); a, the Whitten-Rabinovitch factor (Forst 1973); σ, the symmetry factors (utilized to treat, on the average, the reduction in the rotational densities of states due to nuclear spin considerations); and $E_{\rm rot}$, the rotational energies. In the spherical top approximation, used for all nonlinear molecules in this work, and for a linear molecule, the rotational energy $E_{\rm rot}$ is given by the expression

$$E_{\rm rot} = hcBJ(J + 1) , \tag{18}$$

where B(cm^{-1}) is the so-called rotational constant. As J increases, $E_{\rm rot}$ increases, and both the numerator and the denominator of the second factor on the right-hand side of equation (17) decrease. Because $D_0^* > D_0^\#$, the numerator decreases more rapidly and k_{-2} decreases as J increases. Once a certain maximum J is reached, the numerator is zero and the complex can no longer dissociate via the product channel. One can reframe equation (17) in terms of a centrifugal energy barrier (Herbst 1985*c*). In this formulation, the complex can no longer dissociate when the centrifugal energy barrier at the transition site is above the energy of the reactants.

If there is no barrier to dissociation of the complex along an exothermic exit channel, then the rate coefficient k_{-2} can be determined via microscopic reversibility and phase space theory in a manner analogous to the determination of k_{-1} (Herbst 1985*d*). Using this analysis, k_{-2} is given by the cumbersome equation

$$\begin{aligned} k_{-2}(J, E_{\rm total}) = {} & [h(2J + 1)\rho_v^*(E_{\rm total} + D_0^* - E_{\rm rot}^*)/\sigma^*]^{-1} \\ & \times \sum_{\rm vib} \sum_{\rm rot} g(J_{\rm C})g(J_{\rm D}) \\ & \times [(2J_{\rm C} + 1)(2J_{\rm D} + 1)\sigma_{\rm C}\sigma_{\rm D}]^{-1} \\ & \times \sum_{L} \sum_{J_r} 1 , \end{aligned} \tag{19}$$

where L is the relative angular momentum quantum number of the products; J_r is the total internal angular momentum quantum number of the products; g is the rotational degeneracy [taken to be $(2J_i + 1)^2$ for a non-linear molecule and $2J_i + 1$ for a linear one]; ρ_v^* is the vibrational density of states of the complex, which is a function of the vibrational energy of the complex $E_{\rm total} + D_0^* - E_{\rm rot}^*$; and the sums are first over all accessible values of L and J_r for a given set of $J_{\rm C}$ and $J_{\rm D}$, then over all accessible values of $J_{\rm C}$ and $J_{\rm D}$, and finally over all vibrational states of the products that are energetically accessible. A similar expression pertains for k_{-1} except that the indicies $\rm C^+$ and D should be replaced by $\rm A^+$ and B. Evaluation of k_{-1} and k_{-2} is made easier by the integral approach of Chesnavich and Bowers (1977), which is utilized here for a majority of the summations.

The remaining rate coefficients to be discussed are $k_{\rm rad}$ and $k_{\rm coll}$. Herbst (1985*a*) has estimated that $k_{\rm rad}$ is approximately 10^3 s^{-1} for ionic complexes of bond energies greater than or equal to several eV in situations where there are no competitive exothermic channels. The mechanism that results in this value for $k_{\rm rad}$ is single-photon infrared emission. A single infrared photon possesses an energy of $\sim$0.1–0.5 eV, which is more than sufficient energy for complex stabilization if there are no exothermic channels. If there are such channels, relaxation by this amount of energy need not necessarily result in a stabilized complex, and multiphoton emission via allowed transitions or single photon overtone or combination emission or both is necessary. This will result in a seriously diminished value of $k_{\rm rad}$, which we assume to be 1/100 the normal value or 10 s^{-1} whenever the energy needed to stabilize the complex exceeds 2500 cm^{-1} (0.31 eV).

Although the primary focus of our calculations here concerns radiative association rate coefficients at interstellar cloud temperatures, we are also interested in calculations of ternary association rate coefficients to check our theoretical approach for those reactants for which ternary association laboratory information (normally with helium as the third body) is available. In these calculations, we utilize the expression for $k_{\rm coll}$ detailed in Herbst (1985*c*) whenever there is a competitive exothermic channel with a barrier. For other types of systems, we utilize a value of 2.5×10^{-10} cm^{-3} s^{-1} or $\frac{1}{2}$ of the Langevin collision value unless there is a competitive barrierless exothermic channel with exothermicity greater than $\frac{1}{8}$ eV, in which case we utilize a value 1/100 this size, since only strongly inelastic collisions will stabilize the complex.

Once k_1, k_{-1}, k_{-2}, $k_{\rm rad}$, or $k_{\rm coll}$ are determined for a specific J, then equation (11) for $k_{\rm ra}$ (or an equivalent equation for $k_{\rm 3b}$) must be summed over all accessible values of J, the complex angular momentum quantum number. The range of J is from 0 to $J_{\rm max}$, where

$$J_{\rm max} = J_{\rm A} + J_{\rm B} + L_{\rm max}, \tag{20}$$

and $L_{\rm max}$ is obtained via equation (14) or (15). After this summation, one has obtained a value of $k_{\rm ra}$ (or $k_{\rm 3b}$) for reactants in specific quantum states colliding at a specific collision energy. One must then average this rate coefficient over a Maxwell-Boltzmann distribution to obtain the rate coefficient as a function of translational temperature. Finally, one can average the result over a suitable thermal or nonthermal distribution of internal (rotational) reactant quantum states. Indeed, one advantage of the microcanonical phase space approach is that complete thermalization of internal states is not required. Thus, one can calculate rate coefficients relevant to nonthermal distributions in interstellar clouds.

III. RESULTS

The specific systems initially studied in this work are reactions (2)–(8) in § I. (See § IV for an additional system.) In order to undertake phase space calculations on these systems, thermodynamic, structural, and vibrational information is needed. This information is contained in Table 1, in which molecular rotation constants, symmetry numbers, thermodynamic heats of formation, and vibrational frequencies (if needed) are listed. Some of the relevant thermodynamic information is also shown in the potential surfaces for the various reactions, seen in Figures 1–3. The rotation constants are geometric means of the two or three different rotation constants for nonlinear molecules. These are obtained from standard textbooks for the neutral reactants and products, from a recent paper for the ion $\rm H_3O^+$ (Liu and Oka 1985), and from theoretical work for the assorted other reactant and product ions. The rotational con-

TABLE 1

MOLECULAR PARAMETERS USED IN CALCULATIONS

Species	Rotation Constant[a] (cm^{-1})	σ[b]	$\Delta H_f{}^0$(298 K)[c] (kcal mol^{-1})	Vibrational Frequencies[d] (cm^{-1})
Ionic Reactants and Products				
$CH_3{}^+$	7.650	6	260[e]	...
H_3O^+	9.242	6	145[f]	...
$C_2H_5{}^+$	1.217	6	216	...
H_3CO^+	...	...	168	...
HCO^+	...	...	197	...
Neutral Reactants and Products				
H_2O	15.544	2	−58	...
C_2H_2	1.1766	2	+54	...
C_2H_4	1.587	4	+12	...
CH_3OH	1.410	1	−48	...
CH_4	...	...	−18	...
H_2CO	2.3997	2	−26	...
Ionic Complexes				
$(CH_3)_2OH^+$	0.500	2	130	3682, 2997, 2889(4), 2821, 1456, 1448, 1440(3), 1340(2), 1291(3), 1242, 1122, 1053, 929, 413, 270, 160
$CH_3CH_2OH_2{}^+$	0.449	1	121	3756, 3657, 3359, 2930(3), 1595, 1455(2), 1274(4), 1095, 1051(2), 883(2), 814(2), 700, 530, 433(2)
CH_3CHOH^+	0.584	1	139	3024, 3000, 2967, 2840, 2736, 1743, 1500(2), 1441, 1420, 1390, 1352, 1113, 919, 867, 764, 509, 140
$CH_3OCH_2{}^+$	0.505	1	158[g]	2997, 2889(3), 2821, 1456, 1448, 1440(2), 1291(2), 1242, 1122, 1053, 929, 413, 270, 160
Ionic Transition State Structures				
$(CH_3)_2OH^+\#$	0.500	1	187[h]	Same as $(CH_3)_2OH^+$ minus one 1340 mode
$CH_3OCH_2{}^+\#$	0.505	1	211[i]	Same as $CH_3OCH_2{}^+$ minus one 1440 mode

[a] Geometric mean for nonlinear species.

[b] See Hill 1960. Estimated effects of nonrigidity included here.

[c] Lias *et al.* 1984 unless otherwise noted.

[d] Typically estimates based on better studied but analogous species; parentheses enclose numbers of modes of the given frequency.

[e] Franklin *et al.* 1969.

[f] Bohme and Mackay 1981.

[g] Nobes *et al.* 1981.

[h] Jarrold *et al.* 1986.

[i] Value adjusted from that of Jarrold *et al.* 1986 to match experimental ternary association rate coefficient.

stants of the complexes and transition states are estimated as are the vibrational frequencies of these species, based on criteria such as the structure and frequencies of analogous but better studied species. The assorted heats of formation are mainly from a new standard reference work by Lias, Liebman, and Levin (1984) except for the transition states, where the recent work of Jarrold *et al.* (1986), as discussed above, has been crucial. Relevant dipole moments are listed in a paper by Adams, Smith, and Clary (1985), and polarizabilities are taken from standard sources. Since the rotational energy level patterns of reactants and products are simplified considerably, our results must be treated cautiously at 10 K where, typically, only a few rotational levels are populated. We have checked our results, where possible, with previous treatments in which the rotational level patterns were handled with more care (Herbst 1985*a*), but exothermic channels were not included and find good agreement (see below). The individual reactions are discussed separately.

TABLE 2

THREE-BODY ASSOCIATION RATE COEFFICIENTS

System	Temperature (K)	k^{expt} ($\mathrm{cm^6\ s^{-1}}$)	k^{theory} ($\mathrm{cm^6\ s^{-1}}$)
$CH_3^+ + CH_3OH + He$.........	300	4(−26)[a]	1.8(−26)[b]
$H_3O^+ + C_2H_4 + H_2$	300	1.8(−27)[c]	8.4(−28)[b]
$H_3O^+ + C_2H_2 + He$	325	Observed but not measured; product identified[d]	...
$CH_3^+ + H_2CO + He$..........	300	3.5(−26)[a]	1.9(−26)[b]

NOTE.—Parentheses enclose powers of factor 10.

[a] Smith and Adams 1978. Experiments are run at a number density of $\sim 1 \times 10^{16}\ \mathrm{cm^{-3}}$ and may not refer to the low-pressure limit.

[b] Calculation undertaken using the same density as the relevant experiment.

[c] Bohme and Mackay 1981.

[d] Jarrold *et al.* 1986.

a) $CH_3^+ + CH_3OH \rightarrow (CH_3)_2OH^+ + h\nu$

This reaction, important in the interstellar synthesis of the precursor to dimethyl ether, must compete with a normal exothermic channel leading to the production of $H_3CO^+ + CH_4$. The potential surface for this system is shown in Figure 1, where it can be seen that there is a significant barrier in the exit channel of the competitive exothermic reaction. Smith and Adams (1978) have measured the three-body rate coefficient for the association reaction at a gas density of $\sim 1 \times 10^{16}\ \mathrm{cm^{-3}}$ and a temperature of 300 K to be $4 \times 10^{-26}\ \mathrm{cm^{-6}\ s^{-1}}$. For these same conditions our phase space calculations yield $k_{3b} = 1.8 \times 10^{-26}\ \mathrm{cm^{-6}\ s^{-1}}$, which we consider to be excellent agreement and indicative of the accuracy of our radiative association calculations if our treatment of k_{rad} is correct. These and other three-body association results are contained in Table 2.

In our calculation of the radiative association reaction between CH_3^+ and CH_3OH under interstellar conditions, we have assumed that the reactants are thermalized at the cloud translational temperature. This is so for the methyl ion because it does not possess a permanent dipole moment and appears to be so for methanol, based on recent observational studies (see, e.g., Cummins, Linke, and Thaddeus 1986). The lowest allowed rotational level for the methyl ion has $J = 1$ due to the Pauli Principle.

The calculated results for this and all other radiative association rate coefficients are listed in Table 3 in the parameterized form $k_{\mathrm{ra}}(\mathrm{cm^3\ s^{-1}}) = a(T/300)^{-b}$ for the temperature range 10–50 K. Extrapolation of the parameterized rate coefficients outside this temperature range is not recommended. Also listed in Table 3 are the old values for the rate coefficients (Herbst 1985*a*), calculated without the results of Jarrold *et al.* (1986). It can be seen that the existence of the exit channel depresses the radiative association rate coefficient for $CH_3^+ + CH_3OH$ considerably. At 10 K, for example, our newly calculated value for k_{ra} is $3.3 \times 10^{-10}\ \mathrm{cm^3\ s^{-1}}$, which is 1/30 the old value. The old value of $1.0 \times 10^{-8}\ \mathrm{cm^3\ s^{-1}}$, obtained via a modified thermal calculation (Herbst 1985*a*), is in good agreement with our phase space value of $1.7 \times 10^{-8}\ \mathrm{cm^3\ s^{-1}}$, obtained by repressing the exothermic channel. The discrepancy between the values for k_{ra} calculated with and without the existence of the exothermic channel worsens with increasing temperature. Thus, although the existence of a potential energy barrier in the exit channel prevents a catastrophic decrease in the association rate coefficients and permits measurement of the ternary rate, the rate coefficients are still depressed by a considerable factor.

The existence of a barrier between the complex and the exothermic products $H_3CO^+ + CH_4$ tells us immediately that the association reaction of these species to form $(CH_3)_2OH^+$

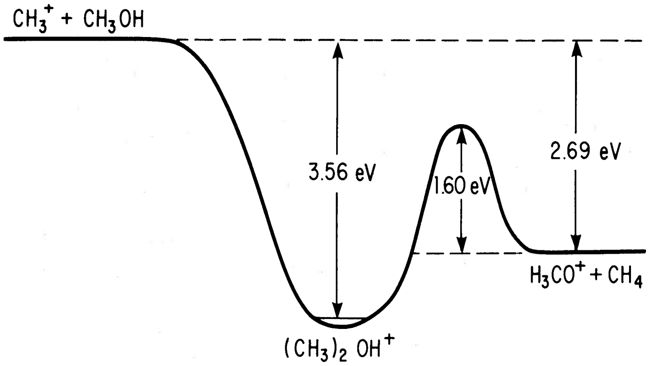

FIG. 1.—Potential energy surface for association reactions leading to protonated dimethyl ether.

TABLE 3

CALCULATED RADIATIVE ASSOCIATION RATE COEFFICIENTS IN THE 10–50 K RANGE

$[k_{\mathrm{ra}}(\mathrm{cm^3\ s^{-1}}) = a(T/300)^{-b}]$

	OLD COEFFICIENTS[a]		NEW COEFFICIENTS	
REACTANTS	*a*	*b*	*a*	*b*
	Protonated Ether Production			
$CH_3^+ + CH_3OH$	1.0(−08)	0.0	7.8(−12)	1.1
$H_3CO^+ + CH_4$	6.1(−16)	1.5	~0(barrier)	...
$CH_3^+ + H_2CO$[b]	...	...	3.4(−11)	1.0
	Protonated Ethyl Alcohol Production			
$C_2H_5^+ + H_2O$	9.5(−13)	2.5	4.1(−16)	2.4
$H_3O^+ + C_2H_4$	2.4(−13)	2.3	2.4(−14)	2.8
	Protonated Acetaldehyde Production			
$H_3O^+ + C_2H_2$	...	...	4.5(−12)	1.6
$HCO^+ + CH_4$	4.6(−14)	1.5	~0(barrier)	...
$CH_5^+ + CO$	7.2(−14)	2.3	~0(barrier?)	...

NOTE.—Parentheses enclose powers of factor 10.

[a] See Herbst 1985*a*.

[b] Reaction must be followed by radiative association with H_2; see text.

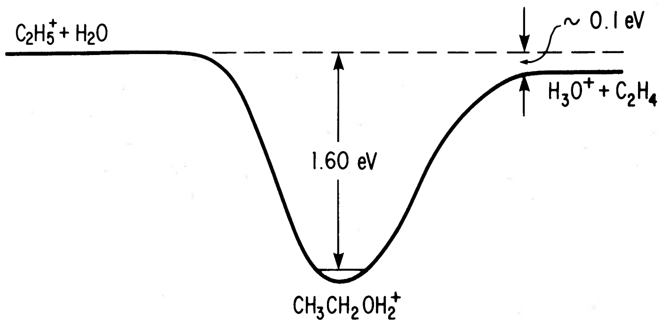

FIG. 2.—Potential energy surface for association reactions leading to protonated ethyl alcohol. Exothermic channel assumed to lie 0.061 eV below the reactants in the phase space calculations, see Bohme and Mackay (1981).

(reaction [3]), utilized in the model of Leung, Herbst, and Huebner (1984), cannot possibly occur.

b) $C_2H_5{}^+ + H_2O \rightarrow CH_3CH_2OH_2{}^+ + h\nu$

This association reaction, important in the interstellar synthesis of the precursor of ethyl alcohol, must contend with an exothermic channel leading to the products $H_3O^+ + C_2H_4$. In Figure 2, it can be seen that the potential surface leading to this exothermic channel possesses no barrier. We have performed calculations on this system using the phase space formulation for the dissociation of the complex via the product channel (see eq. [19]). In these calculations, we have assumed that the ethyl ion is thermalized at the kinetic temperature of the gas, whereas only two levels of water, corresponding to the ground and metastable level, are thermalized (Bates 1983*a*; Herbst 1985*a*). A glance at Table 3 shows that the addition of a barrierless exit channel depresses the radiative association rate coefficient significantly. At 10 K, for example, the newly calculated rate coefficient is 1.5×10^{-12} cm^3 s^{-1}, or more than three orders of magnitude smaller than the old value! The phase space calculation of the rate coefficient at 10 K in the absence of the exothermic channel yields a rate coefficient of 1.2×10^{-9} cm^3 s^{-1}, in reasonable agreement with the thermal model (Herbst 1985*a*) value of 4.7×10^{-9} cm^3 s^{-1}.

c) $H_3O^+ + C_2H_4 \rightarrow CH_3CH_2OH_2{}^+ + h\nu$

Since the reaction between $C_2H_5{}^+$ and H_2O is probably not an important source of interstellar protonated ethyl alcohol, we have reinvestigated the reaction between protonated water and ethylene. This reaction possesses no competitive exothermic channel, and the differences between our current calculated value, obtained via the phase space approach, and our previous value, obtained via the modified thermal approach (Herbst 1985*a*; Bates 1983*a*), are minimal. In the calculations reported here, we have assumed that the rotational levels belonging to the lower inversion doublet of H_3O^+ (Liu and Oka 1985) are fully thermalized. This is because the inversion splitting is so large that these rotational levels cannot relax efficiently via radiative dipole selection rules. The previous calculation contained the assumption that only the same levels known to be metastable in ammonia were appreciably populated. The ratio between our currently calculated and previous rate coefficients at 10 K is 0.6, and our current calculation shows a somewhat greater inverse temperature dependence.

Our phase space calculation can be partially confirmed by comparison with an experimental ternary association measurement at 300 K by Bohme and Mackay (1981). Based on their experimental data, we estimate that k_{3b} is $\sim 1.8 \times 10^{-27}$ cm^6 s^{-1} at a density of around 2×10^{16} cm^{-3}. Our theoretical value at this density is 8.4×10^{-28} cm^6 s^{-1}, which is only a factor of 2–3 low and is therefore in reasonable agreement with experiment.

d) $H_3O^+ + C_2H_2 \rightarrow CH_3CHOH^+ + h\nu$

The two radiative association reactions leading to protonated acetaldehyde in the dense cloud model of Leung, Herbst, and Huebner (1984)—reactions (6) and (7)—are now most unlikely pathways for this synthesis. Jarrold *et al.* (1986) have shown that the reaction between HCO^+ and CH_4 (reaction [7]) possesses a considerable entrance channel barrier toward formation of the protonated acetaldehyde complex. This is depicted in Figure 3. The reaction between $CH_5{}^+$ and CO (reaction [6]) probably possesses a barrier in the entrance channel as well, since these reactants are connected to HCO^+ and CH_4 by a simple proton transfer.

Jarrold *et al.* (1986) have suggested that the radiative association reaction between H_3O^+ and C_2H_2, previously unused in interstellar models, might be efficient in interstellar clouds in producing protonated acetaldehyde and have determined that the ternary association between these species does indeed produce CH_3CHOH^+. The reason that this association reaction occurs efficiently is shown in Figure 3, where it can be seen that although these reactants can theoretically undergo exothermic reactions to form products such as $HCO^+ + CH_4$ and $CH_5{}^+ + CO$, there is a barrier preventing the reaction to the former set of products and a probable barrier to the latter set as well.

In our calculation of the rate of the radiative association reaction between H_3O^+ and C_2H_2, we have therefore assumed no competitive exothermic pathways. We have assumed protonated water to have its lower inversion levels thermalized, as discussed above. Acetylene, with no dipole moment, is also assumed to be thermalized. Our result, shown in Table 3, is a large rate coefficient for this reaction.

IV. EFFECTS ON MODEL PREDICTIONS

How do these newly calculated results affect model predictions for the abundances of dimethyl ether, ethyl alcohol, and acetaldehyde in dense interstellar clouds? To determine the answer to this question, we have utilized the model results of Herbst and Leung (1986*a*, *b*). Herbst and Leung (1986*a*) updated the model of Leung, Herbst, and Huebner (1984), and Herbst and Leung (1986*b*) determined the modifications to

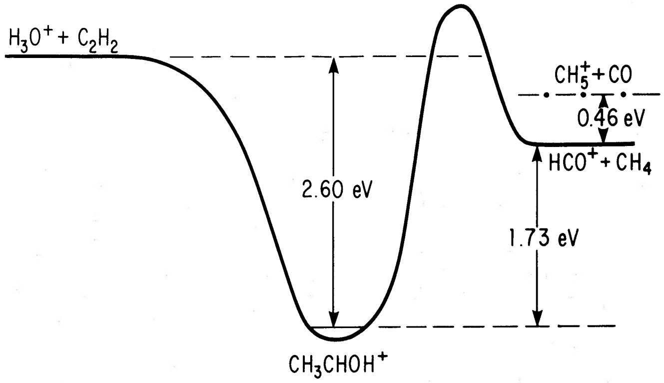

FIG. 3.—Potential energy source for association reactions leading to protonated acetaldehyde.

these new results when the large rate coefficients advocated by Adams, Smith, and Clary (1985) for ion-dipolar neutral exothermic reactions are utilized. As output from the program utilized in these studies, Herbst and Leung list the contribution of each reaction to the formation and depletion of each species as a function of time. Therefore, it is relatively easy to estimate the effect of a change in rate coefficient on production rate. For the case of acetaldehyde, where the protonated precursor is now formed via a totally different reaction from those considered by Herbst and Leung (1986*a*, *b*), the production rate of the new reaction was estimated by calculating the product of the radiative association rate coefficient and the concentrations of H_3O^+ and C_2H_2 as a function of time, utilizing the model results for these concentrations. Future detailed model calculations with these new rate coefficients are planned to corroborate our estimates here, since these estimates contain the tacit assumption that all other model results are unchanged.

The calculated results of Leung, Herbst, and Huebner (1984) and Herbst and Leung (1986*a*, *b*) show that the fractional abundances of complex organic molecules with respect to the molecular hydrogen abundance reach a peak at an "early time," well before steady state is achieved. In Table 4, we have listed these peak fractional abundances as calculated by Herbst and Leung (1986*a*, *b*) for dimethyl ether, ethyl alcohol, and acetaldehyde at temperatures of 10 K and 50 K and a total gas density $n = [\mathrm{H}] + 2[\mathrm{H}_2]$ of 2×10^4 cm^{-3}, the only density studied in these calculations. For both sets of calculations, the calculated abundances of the complex molecules are greater at the lower temperature because of the strong inverse temperature dependence of ion-molecule radiative association reactions. It can also be seen that use of the large (typically 10^{-7} to 10^{-8} cm^3 s^{-1}) ion-dipolar rate coefficients rather than the Langevin value of $\sim 10^{-9}$ cm^3 s^{-1} results in a diminution of the calculated fractional abundances by a factor of less than an order of magnitude. The reason for this decline is that the large ion-dipolar rate coefficients affect the depletion rates of large neutral molecules more strongly than the formation rates. Recent experimental evidence and a variety of theoretical treatments indicate that the rate coefficients of ion-dipolar neutral reactions are indeed larger than the Langevin value, especially at low interstellar temperatures. We therefore consider it probable that these large rate coefficients do pertain, although it is still not clear just how large the rate coefficients can become at temperatures under 50 K. (Herbst and Leung 1986*b* were forced to use some rather crude estimates.) In this work, we have estimated the change in the abundances calculated with the large ion-dipolar rates due to the new values for the radiative association reactions considered here.

In the last two columns of Table 4 are tabulated the newly estimated peak abundances of dimethyl ether, ethyl alcohol, and acetaldehyde. It can be seen that for ethyl alcohol and dimethyl ether, the new fractional abundances are significantly smaller than previously calculated, whereas for acetaldehyde there is no change at 10 K and an increase at 50 K. These calculated *maximum* fractional abundances are compared with observed fractional abundances for the clouds TMC-1, Sgr B2, and Orion (compact ridge) in Table 5. Although the density of the Herbst and Leung (1986*a*, *b*) calculations is probably below that of Sgr B2 and Orion, the density dependence of complex molecular fractional abundances is insufficient to affect the conclusions discussed below (Leung, Herbst, and Huebner 1984).

For TMC-1, estimated to have a kinetic temperature of 10 K, the calculated maximum fractional abundance of acetaldehyde exceeds the observed value. To the best of our knowledge, dimethyl ether and ethyl alcohol have not yet been detected in this source. For Sgr B2, the kinetic temperature of most of the source is probably between 10 K and 50 K. Our calculated maximum fractional abundances for acetaldehyde at 10 K and 50 K are once again higher than the observed value. For dimethyl ether and ethyl alcohol, our calculated results are rather low. Even at a temperature of 10 K, our calculated maximum abundances for these two species are one to two orders of magnitude below observed values. One cannot conclude from this discrepancy that ion-molecule reactions in the ambient environment cannot explain the observed abundances of dimethyl ether and ethyl alcohol in Sgr B2, because different detailed gas phase chemical models can yield abundances differing by up to several orders of magnitude. In particular, the calculation of Millar and Nejad (1985) obtains significantly higher abundances than the results of Herbst and Leung (1986*a*, *b*) for a wide variety of complex species, although the oxygen-containing species discussed here are not in their model. In addition, it is far from clear that we have considered all the possible major pathways for formation of these molecules (see below). Still, it is disturbing that our calculated maximum abundances at even the lower temperature are so low. Perhaps chemical syntheses other than standard ion-molecule schemes are dominant here.

For Orion, ethyl alcohol and acetaldehyde have not been detected, but dimethyl ether has been seen in the compact ridge source with a very large fractional abundance of $\sim 10^{-8}$. This

TABLE 4

CALCULATED MAXIMUM FRACTIONAL ABUNDANCES

	HL1[a]		HL2[b]		HL2 + NEW RATES (estimate)	
SPECIES	10 K	50 K	10 K	50 K	10 K	50 K
CH_3OCH_3	2.1(−09)	6.1(−11)	2.9(−10)	5.2(−11)	9.4(−12)[c]	2.9(−13)[c]
C_2H_5OH	8.7(−10)	6.4(−12)	1.0(−10)	2.6(−12)	9.7(−12)	1.5(−13)
CH_3CHO	5.1(−08)	5.3(−10)	9.5(−09)	2.6(−10)	9.5(−09)	1.5(−09)

NOTE.—Parentheses enclose powers of factor 10.

[a] Herbst and Leung 1986*a*.

[b] Herbst and Leung 1986*b*; 50 K results unpublished.

[c] These numbers increase to as high as 4.9×10^{-10} at 10 K and 7.7×10^{-11} at 50 K if reactions (21) and (22) in the text are included in the analysis.

TABLE 5

ESTIMATED MAXIMUM FRACTIONAL ABUNDANCES COMPARED WITH OBSERVATIONS

Species	Calculation (10 K)	TMC-1	Sgr B2	Calculation (50 K)	Orion (compact ridge)
CH_3CHO	1(−08)	6(−10)[a]	2(−10)[b]	2(−09)	<2(−10)[c]; <8(−10)[a]
CH_3OCH_3	9(−12)[d]	?	5(−10)[b]	3(−13)[d]	1(−08)[c, e]; 2(−08)[a]
C_2H_5OH	1(−11)	?	5(−10)[b]; 7.5(−10)[c]	2(−13)	<3(−10)[a]; <5(−10)[c]

NOTE.—Parentheses enclose powers of factor 10.

[a] Irvine *et al.* 1985.

[b] Cummins *et al.* 1986. $N(H_2) \approx 10^{24}$ cm^{-2}.

[c] Blake 1985.

[d] If reactions (21) and (22) are included, these numbers increase to as much as 4.9×10^{-10} and 7.7×10^{-11} at 10 K and 50 K respectively.

[e] Sutton *et al.* 1985.

compares with our calculated maximum value of 3×10^{-13} at 50 K, a minimum temperature for this source! Unless we have missed the dominant formation reactions for dimethyl ether, this dramatic discrepancy, far stronger than in Sgr B2, strongly suggests that normal ion-molecule reactions are *not* responsible for the bulk of the formation of dimethyl ether in Orion.

Huntress and Mitchell (1979) have considered several alternative pathways for the production of both dimethyl ether and ethyl alcohol, considered as less likely by Leung, Herbst, and Hueber (1984). Some pathways involve reactions of the ion CH_5^+ which would have to compete with the dominant proton transfer channel measured in most normal reactions of this ion. In our view, the least unlikely alternative pathway is one that leads to protonated dimethyl ether via two successive radiative association reactions:

$$CH_3^+ + H_2CO \rightarrow CH_3OCH_2^+ + h\nu \,, \tag{21}$$

followed by

$$CH_3OCH_2^+ + H_2 \rightarrow (CH_3)_2OH^+ + h\nu \,. \tag{22}$$

Even this process is somewhat suspect, because association reactions involving molecular hydrogen often possess activation energy barriers in their entrance channels and do not proceed at all (Herbst, Adams, and Smith 1983). Therefore, it is not very likely that reaction (22) occurs rapidly, although we would welcome a laboratory study at least of the analogous ternary association. The first association reaction is known to proceed efficiently as a ternary association at 300 K in the laboratory (Smith and Adams 1978) despite the existence of a competitive exothermic channel leading to HCO^+ and CH_4. Jarrold *et al.* (1986) have indeed measured the existence and size of a barrier in this exothermic channel. (Note that the ion produced in reaction [21] is a distinct isomer from protonated acetaldehyde.) We have utilized our theoretical treatment with the parameters given in Table 1 to calculate the rate of this association reaction. If we adopt the size of the barrier as given in Jarrold *et al.* (1986), our calculated value of the ternary association rate coefficient at 300 K is over one order of magnitude too low. Since the method used by Jarrold *et al.* (1986) to determine barrier heights can lead to low values, we have arbitrarily increased their barrier height by 0.5 eV and obtain the ternary rate coefficient shown in Table 2, in good agreement with experiment. With this value for the barrier height, we have calculated the radiative association rate coefficient for reaction (21) in the 10–50 K range with the assumption that the rotational temperature of H_2CO is a constant 10 K. As can be seen in Table 3, the rate coefficient is a large one. Assuming that reaction (22) proceeds efficiently ($k_{22} \geq 1 \times 10^{-13}$ cm^3 s^{-1}), we estimate that the synthesis of protonated ether and subsequently ether by reactions (21)–(22) is indeed more efficient than that via reaction (2) by a factor of as much as 270 at 50 K and leads to larger dimethyl ether maximum fractional abundances of 4.9×10^{-10} at 10 K and 7.7×10^{-11} at 50 K. These numbers are perhaps large enough to rationalize the observed abundance in Sgr B2 but are still short of the observed Orion abundance.

A recent and cogent suggestion by Blake (1985) addresses the formation of dimethyl ether in Orion. In Blake's view, the compact ridge source in Orion, in which dimethyl ether is centered, is formed from an interaction between the outflow from the plateau source and the quiescent cloud. This outflow is exceedingly oxygen-rich, and the enhancement in simple oxygen-containing species such as water results in enhanced abundances for species such as methanol and dimethyl ether via normal ion-molecule chemistry. The results of our analysis suggest that without this enhancement standard ion-molecule chemistry falls short of explaining the abundance of dimethyl ether in Orion, and that treatments such as that of Blake (1985) are highly desirable.

V. SUMMARY

Using new experimental results of Jarrold *et al.* (1986) and a new approach to the calculation of radiative association rate coefficients for those systems possessing competitive exothermic channels (Herbst 1985*b*, *c*), we have reinvestigated proposed gas phase ion-molecule synthesis of dimethyl ether, ethyl alcohol, and acetaldehyde under ambient dense interstellar cloud conditions. A new synthesis of acetaldehyde appears to account for the observed abundance of this species in TMC-1 and Sgr B2. The synthesis of ethyl alcohol results in a calculated fractional abundance that is low by more than an order of magnitude compared with the observed value in Sgr B2, even if a temperature of 10 K is assumed for this source. The synthesis of dimethyl ether might possibly explain the observed abundance of this species in Sgr B2 but falls significantly (more than two orders of magnitude) short of explaining its abundance in the compact ridge source of Orion, even if a question-able reaction pathway is invoked. It is at least arguable that, as suggested by Blake (1985), something in addition to normal ambient gas phase interstellar chemistry is occurring in this source.

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REFERENCES

Adams, N. G., and Smith, D. 1981, *Chem. Phys. Letters*, **79**, 563.
Adams, N. G., Smith, D., and Clary, D. C. 1985, *Ap. J.* (*Letters*), **296**, L31.
Barlow, S. E., Dunn, G. H., and Schauer, M. 1984, *Phys. Rev. Letters*, **52**, 902.
Bass, L. M., Cates, R. D., Jarrold, M. F., Kirchner, N. J., and Bowers, M. T. 1983, *J. Am. Chem. Soc.*, **105**, 7024.
Bass, L. M., Chesnavich, W. J., and Bowers, M. T. 1979, *J. Am. Chem. Soc.*, **101**, 5493.
Bass, L. M., and Jennings, K. R. 1984, *Internat. J. Mass Spectrom. Ion Proc.*, **58**, 307.
Bass, L. M., Kemper, P. R., Anicich, V. G., and Bowers, M. T. 1981, *J. Am. Chem. Soc.*, **103**, 5283.
Bates, D. R. 1979, *J. Phys.*, **B12**, 4135.
———. 1982, *Proc. Roy. Soc. London, A*, **384**, 289.
———. 1983*a*, *Ap. J.*, **270**, 564.
———. 1983*b*, *Ap. J.* (*Letters*), **267**, L121.
———. 1985, *Ap. J.*, **298**, 382.
———. 1986, *J. Chem. Phys.*, **84**, 6233.
Blake, G. A. 1985, Ph.D. thesis, California Institute of Technology.
Bohme, D. K., and Mackay, G. I. 1981, *J. Am. Chem. Soc.*, **103**, 2173.
Bowers, M. T., Chesnavich, W. J., and Huntress, Jr., W. T. 1973, *Internat. J. Mass Spectrom. Ion Phys.*, **12**, 357.
Chesnavich, W. J., and Bowers, M. T. 1977, *J. Chem. Phys.*, **66**, 2306.
Cummins, S. E., Linke, R. A., and Thaddeus, P. 1986, *Ap. J. Suppl.*, **60**, 819.
Forst, W. 1973, *Theory of Unimolecular Reactions* (New York: Academic).
Franklin, J. L., Dillard, J. G., Rosenstock, H. M., Herron, J. T., Draxl, K., and Field, F. H. 1969, *Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions* (NSRDS-NBS 26)
Herbst, E. 1980*a*, *Ap. J.*, **237**, 462.
———. 1980*b*, *Ap. J.*, **241**, 197.
———. 1981, *J. Chem. Phys.*, **75**, 4413.
Herbst, E. 1985*a*, *Ap. J.*, **291**, 226.
———. 1985*b*, *Ap. J.*, **292**, 484.
———. 1985*c*, *J. Chem. Phys.*, **82**, 4017.
———. 1985*d*, *Astr. Ap.*, **153**, 151.
Herbst, E., Adams, N. G., and Smith, D. 1983, *Ap. J.*, **269**, 329.
Herbst, E., and Knudson, S. 1981, *Chem. Phys.*, **55**, 293.
Herbst, E., and Leung, C. M. 1986*a*, *M.N.R.A.S.*, in press.
———. 1986*b*, *Ap. J.*, **310**, 378.
Hill, T. L. 1960, *An Introduction To Statistical Thermodynamics* (Reading, Mass: Addison-Wesley).
Huntress, W. T., Jr., and Mitchell, G. F. 1979, *Ap. J.*, **231**, 456.
Irvine, W. M., Schloerb, F. P., Hjalmarson, A., and Herbst, E. 1985, in *Protostars & Planets II*, ed. D. C. Black and M. S. Matthews (Tucson: University of Arizona Press), p. 579.
Jarrold, M. F., Kirchner, N. J., Liu, S., and Bowers, M. T. 1986, *J. Phys. Chem.*, **90**, 78.
Leung, C. M., Herbst, E., and Huebner, W. F. 1984, *Ap. J. Suppl.*, **56**, 231.
Lias, S., Liebman, J. F., and Levin, R. D. 1984, *J. Phys. Chem. Ref. Data*, **13**, 695.
Light, J. C. 1967, *Discussions Faraday Soc.*, **44**, 14.
Liu, D.-J., and Oka, T. 1985, *Phys. Rev. Letters*, **54**, 1787.
Millar, T. J., and Nejad, L. A. M. 1985, *M.N.R.A.S.*, **217**, 507.
Moran, T. F., and Hamill, W. H. 1963, *J. Chem. Phys.*, **39**, 1413.
Nobes, R. H., and Radom, L. 1983, *Chem. Phys.*, **74**, 163.
Nobes, R. H., Rodwell, W. R., Bouma, W. J., and Radom, L. 1981, *J. Am. Chem. Soc.*, **103**, 1913.
Smith, D., and Adams, N. G. 1977, *Ap. J.*, **217**, 741.
———. 1978, *Ap. J.* (*Letters*), **220**, L87.
Sutton, E. C., Blake, G. A., Masson, C. R., and Phillips, T. G. 1985, *Ap. J. Suppl.*, **58**, 341.

Note added in proof.—A new and possibly more efficient synthesis of the precursor ion to dimethyl ether has been proposed by G. A. Blake, E. C. Sutton, C. R. Masson, and T. G. Phillips (*Ap. J.*, **315**, in press [1987]) in which $(CH_3)_2OH^+$ is formed via the normal exothermic reaction

$$CH_3OH_2{}^+ + CH_3OH \rightarrow (CH_3)_2OH^+ + H_2O\ ,$$

which must, however, compete with an association reaction (Bass *et al.* 1983). Calculations or laboratory studies to measure its rate coefficient at temperatures under 100 K are needed to determine its viability.

Since this paper went to press, D. R. Bates (*Ap. J.*, **312**, 363 [1987]) has proposed that radiative association rate coefficients can often be enhanced by electronic rather than vibrational spontaneous emission leading to larger values of k_{rad}. Both Bates and I are working to quantify this effect; at present it certainly does not appear to be large enough to upset the major conclusions of this paper.

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