

THE RADIATIVE ASSOCIATION OF CH WITH H₂: A MECHANISM FOR FORMATION OF CH₃ IN INTERSTELLAR CLOUDS

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ABSTRACT

Estimates of the rate constants for the radiative association of methylenide radicals (CH) with molecular hydrogen (H₂), $\text{CH} + \text{H}_2 \rightarrow \text{CH}_3 + h\nu$, are reported for the temperature range (10–100 K) prevalent in dense interstellar clouds. These estimates are based on (1) new and extensive laboratory experiments on the *collisional* association of CH and H₂, $\text{CH} + \text{H}_2(+\text{M}) \rightarrow \text{CH}_3(+\text{M})$, including measurements of rate constants down to temperatures as low as 53 K; and (2) calculations of the rate constants for both radiative and collisional association based on methods originally proposed by Troe, modified to include the effects of quantum mechanical tunneling as proposed by Smith. The results suggest that radiative association of CH with H₂ may be a significant reaction in interstellar clouds because of the high abundance of H₂. Although the association of CH with H₂ seems likely to be only a minor route for the removal of CH radicals, the reaction does provide a pathway to the formation of CH₃, and subsequently simple hydrocarbons, which may be of comparable importance to other mechanisms based on ion-molecule chemistry. In addition, measured and estimated low temperature rate coefficients are reported for isotope exchange between CH, CD and H₂, HD, D₂ which may be relevant to isotopic fractionation in interstellar clouds.

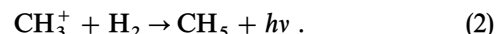
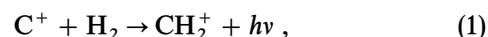
Subject headings: ISM: abundance — ISM: molecules — molecular processes

1. INTRODUCTION

Ever since chemical models of interstellar clouds were first proposed (Herbst & Klemperer 1973; Black & Dalgarno 1973) it has been recognized that radiative association reactions play an important part, especially in enabling polyatomic molecules to form in the low-density environment of even the densest molecular clouds. Association reactions frequently occur over potential energy surfaces which present no barrier to the formation of the initially created “collision complex” or “energized adduct”, so the low temperatures present in interstellar clouds do not prevent these reactions occurring at significant rates. On the other hand, the low total density in even the densest clouds means that stabilization of any collision complexes must occur by the emission of a photon, i.e., by radiative association, rather than by collisions involving a third body which provides the mechanism for stabilization under the conditions of most laboratory experiments.

Until recently, chemical models of interstellar clouds have been dominated by processes involving electrically charged particles, such as ion-molecule reactions and dissociative recombinations. This general statement is also true in regard to the inclusion in the models of radiative association reactions. These ion-molecule associations can be divided into two categories (Bates & Herbst 1988). In the first class, the neutral reagent is molecular hydrogen, which is, of course, overwhelmingly the most abundant molecular species in all dense interstellar clouds. Two very important reactions in this category, which have received extensive experimental (Luine & Dunn 1985; Barlow, Dunn, & Schauer 1984a, 1984b; Gerlich & Kaefer 1989; Gerlich & Horning 1992) and theoretical (Herbst 1981; 1982; Bates

& Herbst 1988; Smith 1989b) attention are

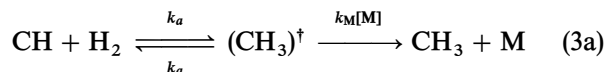


In the second type of ion-molecule association, the neutral reagent is a polyatomic molecule. If such reactions are to have significant rates, the much lower concentrations of the reagents in interstellar clouds must be compensated for by a much larger rate coefficient for radiative association, which is possible as the size of the collision complex, and hence its lifetime with respect to dissociation, grows.

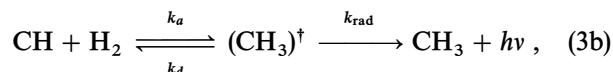
The general notion that the chemistry of interstellar clouds is dominated by processes involving ions is now being questioned (Herbst et al. 1994; Herbst 1995; Bettens, Lee, & Herbst 1995) following the finding that many neutral-neutral reactions occur rapidly at low temperatures. Among reactions between neutral species, those between pairs of free radicals often occur by association (Howard & Smith 1980), and rate coefficients for a number of radiative association reactions have been calculated (Smith 1989a; Barker 1992) by methods similar to those used to estimate the rates of ion-molecule associations. Clearly, any reaction of this type which is important in interstellar clouds must fall into the second of the categories identified by Bates & Herbst (1988) and is only likely to be fast enough to play a role in the chemistry of interstellar clouds if the collision complex is quite large and the rate approaches the binary collision rate.

However, facile association between neutral species is not confined to reactions between two radicals. Recently, in measurements on the reaction between CH, the methylenide radical, and H₂, between 53 to 784 K, it has been

found (Brownsword et al. 1997) that the dominant mechanism throughout most of this temperature range, and certainly at lower temperatures, is association to the methyl radical, CH_3 , and that this reaction becomes faster as the temperature is lowered. In the experiments association occurred, of course, via energized collision complexes, $(\text{CH}_3)^\dagger$, which are collisionally stabilized: i.e.,



However, the close connection between the rates of collisional association and of radiative association, in this instance,



has long been recognized (Bates & Herbst 1988). For radiative association, the rate coefficient can be expressed as

$$k_{\text{RA}} = k_{\text{rad}}(k_a/k_d), \quad (4)$$

where k_a and k_d are the rate coefficients, properly averaged over total energy (E) and angular momentum (J), for formation and dissociation of the energized collision complexes, and k_{rad} is the coefficient describing the rate at which energized complexes lose sufficient energy by photon emission to prevent them subsequently undergoing dissociation. The corresponding equation for collisional association is

$$k_M^0 = k_M[\text{M}](k_a/k_d), \quad (5)$$

where k_M is the coefficient describing the rate at which energized complexes are stabilized in binary collisions with the diluent gas M which is present in the experiments. In deriving equations (4) and (5), it is assumed that $k_d \gg k_{\text{rad}}$ and $k_d \gg k_M[\text{M}]$ and that any averaging over states of different E , J to find k_{rad} and k_M can be done separately from that done to estimate (k_a/k_d) . If quantum mechanical tunneling through the centrifugal barrier is ignored (see below), the evaluation of (k_a/k_d) is merely a problem in statistical mechanics since

$$(k_a/k_d) = Q_{\text{eff}}^\dagger/Q_A Q_B, \quad (6)$$

where Q_{eff}^\dagger , Q_A , and Q_B are the “per volume” partition functions for the energized complex, (AB^\dagger) , and the two reagents, A and B , respectively.

Troe (1977) has described a method for estimating values of (k_a/k_d) and hence of k_M^0 , i.e., what is usually referred to as the limiting low pressure rate constant, for radical-radical associations. This method takes proper, albeit approximate, account of the conservation of angular momentum. To apply this method with reasonable accuracy, it is necessary to have accurate thermochemical and spectroscopic data for all three of the species participating in the reaction. Such data are more likely to be available in the case of neutral-neutral, rather than ion-molecule, associations and when they are, as in the case of CH , H_2 , and CH_3 , it is reasonable to expect this method to reproduce the experimental results for collisional association at room temperature within a factor of about 2 (Troe 1977; Howard & Smith 1980). For the purposes of associations involving H atoms or H_2 at low temperatures, Smith (1989a, 1989b) has proposed a modification of the Troe (1977) method to allow for tunneling in processes (a) and (d) through the centrifugal barriers on the effective potential energy surfaces. In the cases of

reactions (1) and (2), this modification was shown to increase the values of k_{RA} at 10 K by a factor of about two.

In this paper we report briefly the results and analysis of our experiments on reaction (3b) and on the reaction of CH with D_2 and the removal of $\text{CH}(v=1)$ by H_2 and D_2 . Full details are given elsewhere (Brownsword et al. 1997). Then we present the results of theoretical calculations on collisional and radiative association of CH and H_2 obtained using Smith's modification of the Troe method. We argue that the best estimates of k_{RA} between 10 and 100 K are obtained by using our calculations to predict the temperature-dependence of the rate coefficient in this range and a comparison between the calculations for both radiative and collisional association and our experimental results at low temperature to obtain absolute values of the rate coefficients. Finally, we discuss the implications of our results for chemical models of interstellar clouds.

2. EXPERIMENTAL RESULTS

The rate coefficients for reaction between CH radicals and H_2 (and D_2) have been measured at temperatures between 53 and 784 K using pulsed laser photolysis (PLP) to generate CH radicals from the sequential multiphoton photolysis of CHBr_3 and laser-induced fluorescence (LIF) to observe the rate of their removal in subsequent chemical reactions (Brownsword et al. 1997). This general and powerful technique has been implemented in two different sets of experiments. Using heated or cryogenically cooled cells, rate coefficients have been determined between 784 and 88 K and over a range of total pressures, from 4 to 400 Torr at some temperatures, using argon as the diluent gas. To access even lower temperatures, experiments have been performed in a CRESU (Cinétique de Réaction en Ecoulement Supersonique Uniforme) apparatus (Sims et al. 1994; Sims & Smith 1995).

The second-order rate coefficients for reaction between $\text{CH}(v=0)$ and H_2 depend strongly on total pressure, and it is clear that, at room temperature and below, reaction proceeds entirely by association. (At higher temperatures, the endothermic bimolecular reaction producing $\text{CH}_2 + \text{H}$ starts to contribute to the overall rate of reaction.) However, the rate coefficients that have been measured do not vary linearly with total pressure and clearly therefore the kinetics are in the falloff regime (Smith 1980); i.e., the condition $k_d \gg k_M[\text{M}]$ that was assumed in deriving equation (5) was not satisfied in the experiments. To illustrate this behavior Figure 1 shows how the rate coefficients measured at 53 K in the CRESU apparatus vary with the total gas density in the range $0.52 < [\text{Ar}]/10^{17} \text{ molecule cm}^{-3} < 8.2$. To extract values of k_M^0 from the observed rate coefficient, the fall off behavior was analyzed using Troe's (1979) prescription and the assumption that the rate coefficients in both the low and high pressure limits can be expressed as $k(T) = k(298)(T/298)^n$. This “global” fitting procedure (Keiffer, Pilling, & Smith 1987) yielded the parameters for k_M^0 given in Table 1. Over the temperature range covered by the experiments, the reliability of this expression is quite high as the measured rate coefficients were obtained under conditions close to the low-pressure limit of the falloff region.

Rate coefficients have also been measured for the reaction between $\text{CH}(v=0)$ radicals and D_2 , and for the removal of $\text{CH}(v=1)$ by H_2 and D_2 (Brownsword et al. 1997). At all temperatures, these rates were independent of total pressure

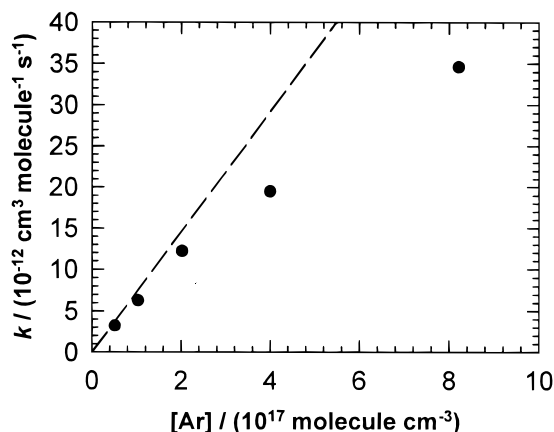


FIG. 1.—Second-order rate coefficients for the collisional association of CH with H₂ measured at 53 K in different pressures of argon. The dashed line represents the limiting low pressure rate coefficients, $k_A^0[\text{Ar}]$, derived from the global fit to all the experimental data (Brownsword et al. 1996).

and close to the collisionally determined limit. Expressions for the temperature dependence of these rate coefficients are given in Table 1. It is clear that the rates of all three of these processes are controlled by the facile formation of CH₃ or CHD₂ complexes (Brownsword et al. 1997). Below (see § 5) we discuss to what extent the isotope exchange reactions between isotopomers of CH and H₂ might play a role in the chemistry of interstellar clouds.

3. THEORETICAL METHOD

In treating radiative association and collisional association in the limit of low pressure, it is necessary to recognize that the rate coefficients for radiative stabilization (k_{rad}), for collisional stabilization (k_{M}) and most importantly of all for the formation (k_a) and dissociation (k_d) of the energized complex, (AB[†]), depend on the total energy (E) and total angular momentum (J) of the complex. Early attempts to calculate rate coefficients for radiative association for inclusion in chemical models of interstellar clouds failed to do this, resulting in estimates that were typically around 3 times too large (Bates & Herbst 1988). In this so-called thermal theory it was assumed that all internal states of the complex

were freely accessible. On the other hand, the “modified thermal theory,” which Bates (1979) was the first to use to treat radiative association, took account of the notion, which is built into the treatment of collision association recommended by Troe (1977), that the only accessible states of angular momentum in the complex are those which can be reached in collisions which surmount the centrifugal barrier on the long-range effective potential, but the modified thermal theory retained the assumption that k_{rad} was independent of J . Smith (1989a, 1989b) introduced a further refinement, in which it was recognized that states of the complex “behind the centrifugal barrier” could be reached (and could dissociate) as a result of quantum mechanical tunneling through the barrier. In addition, allowance was made for the dependence of k_{rad} on J because, for a given E , the higher J the smaller the vibrational energy in the complex and hence the lower the states of vibrational excitation which can be reached. Smith’s method has been used to calculate rate coefficients for radiative association of CH with H₂ in the present work. As the method has been described rather fully before (Smith 1989a, 1989b), only a fairly brief description will be given here.

In the situation where $k_{\text{M}}(E, J)[\text{M}] \ll k_{\text{rad}}(E, J)$ for all E, J (i.e., when stabilization of (AB[†]) occurs only by radiative emission) the equation for radiative association via states of specific E and J becomes

$$k_{\text{RA}}(E, J) = k_a(E, J)k_{\text{rad}}(E, J)/[k_{\text{rad}}(E, J) + k_d(E, J)]. \quad (7)$$

In both the thermal and modified thermal theories, it is assumed that this equation can be simplified by assuming that the E, J states of the complex are of two kinds: (1) those for which $E > E_0(J)$ and $k_d(E, J) \gg k_{\text{rad}}(E, J)$, and (2) those for which $E < E_0(J)$ and $k_d(E, J) \ll k_{\text{rad}}(E, J)$, so that

$$k_{\text{RA}}(E, J) = k_{\text{rad}}(E, J)[k_a(E, J)/k_d(E, J)] = k_{\text{rad}}(E, J)f(E, J), \quad (8)$$

and the value of k_{RA} at a given temperature was obtained by thermal averaging over E and J .

$$k_{\text{RA}} = \sum_J \int_{E_0(J)}^{\infty} dE k_{\text{rad}}(E, J)f(E, J) \quad (9)$$

The two treatments differ in their choice of the threshold energies $E_0(J)$. In the thermal theory, $E_0(J)$ is assumed to be

TABLE 1
RATE COEFFICIENTS^a FOR THE COLLISIONAL ASSOCIATION OF CH($v=0$) WITH H₂,
FOR THE REACTION OF CH($v=0$) WITH D₂, AND FOR THE REMOVAL OF
CH($v=1$) BY H₂ AND D₂

Reagents	$k_{\text{M}}^0(298)(\text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1})$ or $k(298)(\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$ n	Range of $(T/K)^b$
CH($v=0$) + H ₂	6.5×10^{-30} -1.4	53–744
CH($v=0$) + D ₂	$(0.94 \pm 0.08) \times 10^{-10}$ - (0.19 ± 0.04)	13–584
CH($v=1$) + H ₂	$(1.55 \pm 0.07) \times 10^{-10}$ - (0.07 ± 0.04)	23–584
CH($v=1$) + D ₂	$(1.29 \pm 0.08) \times 10^{-10}$ - (0.17 ± 0.04)	23–584

^a The rate coefficients are expressed as $k(T) = k(298)(T/298)^n$. For CH($v=0$) + H₂, the third-order rate constants are those for collisional association in the limit of low pressure; for CH($v=0$) + D₂, the second-order rate constants are for isotope exchange; for CH($v=1$) + H₂, D₂, the second-order rate constants are those for total removal from the $v=1$ level, largely by vibrational relaxation.

^b Range of temperatures covered in the experiments.

zero for all J ; i.e., there are no centrifugal barriers associated with the need to conserve angular momentum. In the modified thermal theory, $E_0(J)$ is taken to correspond to $V_{\max}(J)$, the energy of the centrifugal maximum on the assumed two-body curve of effective potential energy.

In Smith's (1989a, 1989b) extension of the modified thermal theory, it is recognized that there are, in reality, *three* kinds of E, J states: (1) the intrinsically unstable states, for which $E > V_{\max}(J)$ and $k_d(E, J) \gg k_{\text{rad}}(E, J)$, (2) the truly stable states for which $E < V_{\max}(J)$ and $k_d(E, J) \ll k_{\text{rad}}(E, J)$, and (3) the "metastable" states, for which $V_{\max}(J) > E > 0$. For this last group of states, $k_d(E, J)$ depends on the probability of quantum mechanical tunneling through the centrifugal barrier and $k_d(E, J)$ will show a wide range of values for states of given J as E increases from zero to $V_{\max}(J)$. The rate coefficients, $k_d(E, J)$, for dissociation from these metastable states can be equated to the product of a frequency, $\nu_d(E, J)$, with which the system approaches the barrier, and $\kappa(E, J)$, the probability of tunneling through the barrier. In the method proposed by Smith (1989a) and used to estimate rate coefficients for reactions (1) and (2) (Smith 1989b), calculations were performed to find the value of E for which, for a specified J ,

$$k_d(E, J) = \kappa(E, J)\nu_d(E, J) = k_{\text{rad}}(E, J). \quad (10)$$

This value of E was then taken to be $E_0(J)$, the threshold energy for that particular J and the lower limit for the integration over E in equation (10); i.e., states with $E > E_0(J)$ were taken to contribute fully to the value derived for $f(E, J)$, whereas those states with $E < E_0(J)$ made no contribution. Values of $\nu_d(E, J)$ were calculated (1989a, 1989b) via microcanonical transition state theory and of $\kappa(E, J)$ using the WKB approximation (Child 1974).

The method used to evaluate k_{RA} via equation (10) closely follows that developed by Troe (1977, 1979) to estimate rates of unimolecular dissociations (or the reverse collisional association reactions) in the limit of low pressure. According to this procedure, an initial estimate is made of k_{RA} for a nonrotating molecule, comprised of harmonic oscillators and containing an internal energy corresponding to the dissociation limit. Then this estimate is multiplied by a series of terms which allow for the initial neglect of various factors. Thus (Troe 1977; Smith 1989a, 1989b)

$$k_{\text{RA}} = k'_{\text{RA}} F_{\text{anh}} F_E F_{\text{rot}} F_{\text{int rot}}, \quad (11)$$

and the initial estimate of the rate constant is given by

$$k'_{\text{RA}} = \frac{k_{\text{rad}}[E_0(J=0)] Q_e^* \rho_{\text{vib},h}[E_0(J=0)] kT}{Q_{\text{trans}} Q_{\text{vib}} Q_e} \quad (12)$$

In these equations, $k_{\text{rad}}[E_0(J=0)]$ and $\rho_{\text{vib},h}[E_0(J=0)]$ are the rate coefficient for spontaneous emission and the density of harmonic oscillator states in the complex, respectively, in both cases at the dissociation limit which corresponds to the threshold energy for nonrotating (i.e., $J=0$) species. The Q are partition functions, and the F -factors are correction terms applied for initial neglect of anharmonicity (F_{anh}), energy spread (F_E), "external" rotations (F_{rot}) and any internal rotations ($F_{\text{int rot}}$).

In order to evaluate equations (11) and (12), information is required about the dissociation energy of the combined species and the vibrational frequencies, rotational constants, and electronic states of both (AB^\dagger) and the reagents. Densities of states are calculated using the formulae of

Whitten & Rabinovitch (1963), which, for a rotating molecule with total internal energy $D_0 + E_0(J)$ and adiabatic energy E_J , can be written as

$$\rho_{\text{vib},h}[E_0(J)] = \frac{[D_0 + E_0(J) - E_J + aE_z]^{s-1}}{(s-1)! \prod_{i=1}^s h\nu_i}, \quad (13)$$

which reduces for the nonrotating molecule to

$$\rho_{\text{vib},h}[E_0(J=0)] = \frac{(D_0 + aE_z)^{s-1}}{(s-1)! \prod_{i=1}^s h\nu_i}. \quad (14)$$

The method of estimating $k_{\text{rad}}[E_0(J=0)]$ has been described elsewhere (Smith 1989a, 1989b). It is similar to the procedure originally proposed by Herbst (1982) which in turn is based on a proposal originally made by Dunbar (1975). In essence, using the Whitten-Rabinovitch formulae, one estimates the probability $P_n^{(i)}$ that a molecule containing internal energy $E = D_0$ contains n_i quanta in its i th normal mode. The rate coefficient for radiative emission processes carrying molecules from states with n_i quanta to states with fewer quanta in the i th mode is assumed to be $n_i A_{1,0}$, where $A_{1,0}$ is the Einstein coefficient for spontaneous emission in the fundamental band $n_i = 1 \rightarrow n_i = 0$. The product of $P_n^{(i)}$ and $n_i A_{1,0}$ gives the contribution of these particular processes to the rate of spontaneous emission, and the overall rate coefficient is obtained by summing over all possible n_i and over all modes:

$$k_{\text{rad}}[E_0(J=0)] = \sum_i \sum_{n_i} P_n^{(i)}(E_{\text{vib}}) n_i A_{1,0}^{(i)}. \quad (15)$$

The full calculation of $k_{\text{rad}}(E)$ is only made once, for $E = E_0(J=0)$. The variation of $k_{\text{rad}}(E)$ with E is assumed to be linear (Herbst 1982; Smith 1989a, 1989b), and a correction factor for angular momentum states $J \neq 0$ is defined by

$$F_{\text{rad}}(J) = k_{\text{rad}}[E_0(J)]/k_{\text{rad}}[E_0(J=0)] \\ = [D_0 + E_0(J) - E_{\text{rot}}(J)]/D_0, \quad (16)$$

and incorporated into F_{rot} (see below, eq. [17]). The factors F_{anh} and F_E are assumed to be independent of J and can be evaluated using the formulae of Troe (1977, 1979). In the present case, $F_{\text{int rot}}$ equals 1.

F_{rot} is much the largest of the correction factors. It is defined (Smith 1989a 1989b) by

$$F_{\text{rot}} = \frac{1}{Q_{\text{rot}}} \sum_J \sum_{K=0}^{\min(J, K_{\text{max}})} g(J, K) \exp \left[\frac{-E_0(J)}{kT} \right] \\ \times \left\{ \frac{\rho_{\text{vib},h}[E_0(J)]}{\rho_{\text{vib},h}[E_0(J=0)]} \right\} \left[\frac{E_0(J) + D_0 - E_{\text{rot}}(J, K)}{D_0} \right]. \quad (17)$$

Here K , the quantum number associated with the third, active, rotational degree of freedom, is introduced explicitly, Q_{rot} is the product of rotational partition functions for the reagents which is evaluated by direct count, $g(J, K)$ is the degeneracy of the rotational states given by

$$g(J, K) = 2J + 1 \text{ for } K = 0, \\ g(J, K) = 2(2J + 1) \text{ for } K > 0, \quad (18)$$

and K_{max} is the largest K for which $E_{\text{rot}}(J, K) \leq E_0(J)$. In contrast to Troe's (1977) calculations (and apparently to those of Bates 1979) both the rotational partition functions and the remainder of the right-hand side of equation (17)

TABLE 2
 VIBRATIONAL PROPERTIES OF THE METHYL RADICAL

Mode	Symmetry (Degeneracy)	ν (cm ⁻¹)	$\frac{\mu}{D}$	A (s ⁻¹)	Reference
ν_1	$A'_1(1)$	3002	
ν_2	$A''_1(1)$	606	0.28 ± 0.049	4.9	Yamada & Hirota 1983
ν_3	$E(2)$	3161	0.029 ± 0.005	7.5	Tarrano et al. 1994
ν_4	$E(2)$	1396	...	1	Knowles 1996, private communication

are evaluated by direct summation, not by using the semi-classical formulae for partition functions and other approximations to evaluate the summations in equation (17). This is especially important because of the small moments of inertia and low temperatures which are of interest in the radiative association of CH with H₂. In addition, it is important to account correctly for nuclear spin effects.

The values of the threshold energies $E_0(J)$, which serve as the lower limit of the integration in equation (9), depend crucially on the form of the potential between the two combining species at long-range and strongly affects the magnitude of $F_{\text{rot}}(J)$ and hence of $\kappa(J)$ and k_{RA} . After careful consideration of a number of radical-radical systems, Troe (1977) concluded that it was reasonable to use a quasi-diatomic model with the effective potential represented by:

$$V_{\text{eff}}(x) = J(J+1)Bx^{-2} - 2D_0x^{-6}, \quad (19)$$

where $x = q/q_e$, the ratio of the instantaneous length of the bond being formed to its values in the stable molecule. The main justification for this expression (see below) is that calculations based on it satisfactorily reproduce experimental values for the rate of collisional association between radicals at low pressure. Standard operations (Smith 1980) yield formulae for the position and height of the centrifugal barrier.

4. RESULTS OF CALCULATIONS

The rotational and vibrational properties of the CH₃ radical are quite well-characterized. The molecule is an oblate symmetric top with rotational constants $A = 4.7$ cm⁻¹ and $B = 9.47$ cm⁻¹ (Amano et al. 1982). The properties of the vibrational modes are summarized in Table 2. The transition dipole moments for the fundamental bands associated with the singly degenerate (A'_2), out-of-plane bend ν_2 mode (Yamada & Hirota 1983), and for the doubly degenerate (E'), in-plane stretch, ν_3 mode (Tarrano et al. 1994; Bethardy & MacDonald 1995) have been measured and yield Einstein coefficients for spontaneous emission of 4.9 s⁻¹ and 7.5 s⁻¹, respectively. We have been unable to

find any similar experimental data for the doubly degenerate (E'), in-plane deformation, ν_4 mode. For this fundamental transition, we have assumed a value of the Einstein coefficient of 1 s⁻¹, based on approximate quantum calculations (Knowles 1996, private communication).

Based on the above data and using the methods described in the previous section, rate coefficients have been estimated for the collisional and radiative association of CH with H₂ to form CH₃. The rate coefficients for collisional association at different temperatures are listed in Table 3, calculated according to (1) the modified thermal theory, and (2) the modified thermal theory including tunneling. In each case, calculations have been performed using two values of the C_6^* coefficient expressing the long-range attractive potential ($V_{\text{att}} = -C_6^*r^{-6}$) between the reagents. Troe (1977) recommends setting $C_6^* = 2D_0r_e^{-6}$, where D_0 and r_e are respectively, the dissociation energy of the bond being formed and the equilibrium internuclear separation, on the basis that this choice seemed to yield estimates of k_M^0 that were in good agreement with experiment for a number of radical-radical associations. In our calculations, this choice for C_6^* yields the values of k_M^0 in the first two columns of Table 3. However, it seems likely that the value of $C_6^* = 2D_0r_e^{-6}$ is an overestimate of the value determined solely by the long-range dispersion and induction forces. As an alternative, C_6^* was estimated by assuming that the rate of removal of CH($\nu = 1$) by H₂ is determined solely by capture on the long-range isotropic potential between CH and H₂ (Brownsword et al. 1997). Therefore the relaxation rate coefficient (k_{inf}) was matched to the expression for two-body collisions subject to a $-C_6^*r^{-6}$ long-range potential (Smith 1980). This procedure yielded lower values of C_6^* and lower values of k_M^0 as shown in the third and fourth columns of Table 3.

It should be pointed out that, for collisional association, the procedure for incorporating tunneling into the calculations is less clearcut than in the case of radiative association because the tunneling rate has to be equated to a pressure-dependent deactivation rate (cf. eq. [10]) in order to

 TABLE 3
 RATE CONSTANTS FOR COLLISIONAL ASSOCIATION (cm⁶ molecule⁻² s⁻¹) CALCULATED ACCORDING TO DIFFERENT MODELS AND COMPARED WITH EXPERIMENTALLY DERIVED VALUES

$T(K)$	Modified Thermal (Troe C_6^*)	Modified Thermal + tunneling (Troe C_6^*)	Modified Thermal (C_6^* from k_{inf})	Modified Thermal + tunneling (C_6^* from k_{inf})	Expt.
740.....	6.6 (-31) ^a	7.6 (-31)	2.3 (-31)	2.7 (-31)	1.2 (-30)
580.....	1.1 (-30)	1.3 (-30)	3.5 (-31)	4.6 (-31)	1.8 (-30)
300.....	3.5 (-30)	4.2 (-30)	1.0 (-30)	1.4 (-30)	5.1 (-30)
160.....	8.0 (-30)	1.0 (-29)	2.3 (-30)	3.2 (-30)	1.4 (-29)
80.....	1.6 (-29)	2.1 (-29)	4.4 (-30)	6.7 (-30)	4.3 (-29)
40.....	3.0 (-29)	4.0 (-29)	7.8 (-30)	1.2 (-29)	1.3 (-28)

^a $6.6(-31) = 6.6 \times 10^{-31}$.

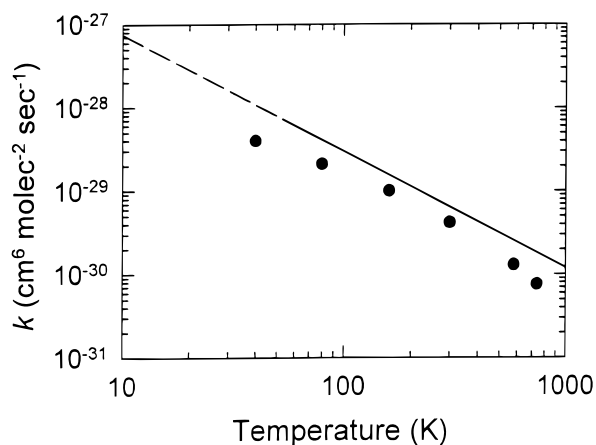


FIG. 2.—Comparison of the rate coefficients from the “modified thermal theory with tunneling” calculations, using Troe’s (1977) prescription for the long-range potential (third column of Table 3), with the experimentally derived expression for the rate coefficient in the limit of low pressure, $k_{\text{Ar}}^0(T)$, shown as a full line in the range covered by the experiments and a dashed line at lower temperatures.

find the thresholds $E_0(J)$. In our calculations, this latter rate constant was set at $k_{\text{M}}[\text{M}] = \beta_{\text{c}}(\text{Ar})Z^0(\text{CH}_3\text{-Ar})[\text{Ar}]$, where $Z^0(\text{CH}_3\text{-Ar})$ is the rate constant for all collisions between CH_3 and Ar and $\beta_{\text{c}}(\text{Ar})$ takes into account of the fact that not all collisions between energized CH_3 radicals and Ar atoms will remove sufficient energy to stabilize the radicals. In our calculations $[\text{Ar}]$ was chosen to be 10^{17} molecule cm^{-3} . In practice, the choice of $[\text{Ar}]$ was quite unimportant since the increase in k_{M}^0 brought about by the inclusion of tunneling is very slight for any reasonable choice of $[\text{Ar}]$. The values of the collisional efficiency, $\beta_{\text{c}}(\text{Ar})$, was set equal to 0.2 at room temperature, and values at other temperatures were estimated from the equation $\beta_{\text{c}}/(1 - \beta_{\text{c}}^{1/2}) = -\langle\Delta E\rangle/F_E kT$ (Troe 1977), assuming that $\langle\Delta E\rangle$, the mean value of the energy transferred, was independent of temperature.

Comparison of the calculated and experimental results for collisional association shows that the use of the Troe prescription for C_6^* gives the better agreement with experiment. In this case, the disagreement between theory and experiment is a factor of 1.5–2 between 580 and 80 K, whereas with the lower choice of C_6^* the disagreement widens to factors of between 4.6 and 6.1. In Figure 2, a comparison is made between the values of k_{Ar}^0 obtained from the calculations incorporating tunneling and using Troe’s formula for C_6^* and the experimentally derived expression for k_{Ar}^0 given earlier in Table 1.

The rate coefficients calculated for radiative association for the same two models and the same two choices of C_6^* as before are recorded in Table 4. With Troe’s choice of C_6^* , the rate coefficients between 80 and 10 K are increased by factors of between 2.4 and 4.9 by the inclusion of quantum mechanical tunneling. Over this range of temperature, k_{RA} increases by a factor of 3 as the temperature is lowered.

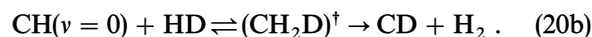
From the point-of-view of rate coefficients for astrochemical models, it seems best to “calibrate” the calculated results for radiative association using the experimental data on collisional association. Thus $k_{\text{M}}^0 \text{ expt(b)}/k_{\text{M}}^0 \text{ calc(b)} = 1.95$ at 80 K, and therefore we estimate that $k_{\text{RA}} \approx 1.95 \times k_{\text{RA}} \text{ calc(b)} = 6 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Likewise, at 40 K, we estimate $k_{\text{RA}} \approx 1.3 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Values of k_{RA} at lower temperatures are estimated by assuming that the increase over the value at 40 K corresponds to that given by the calculations. This assumption leads to values of values of k_{RA} of 1.8×10^{-16} and $2.5 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 20 and 10 K respectively.

5. DISCUSSION

The rate coefficients reported here for the reaction of CH with H_2 and D_2 are the first to be measured at the low temperatures of interstellar clouds. The reaction between $\text{CH}(v=0)$ and D_2 clearly proceeds via a CHD_2 energized adduct to produce $\text{CD} + \text{HD}$ (Brownsword et al. 1997):



The expression for the rate coefficient k_1 given in Table 1 yields values of 1.2×10^{-10} and $1.8 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 80 and 10 K, respectively. The equilibrium constant can be evaluated by careful use of statistical mechanics. The results are shown in Table 5, D_2 being assumed to be “normal,” i.e., a 2:1 mixture of ortho- and para-forms. From the rates of reaction (20a) it is possible to estimate the rates of reaction between $\text{CH}(v=0)$ and HD at low temperatures



To a good degree of approximation, two factors affect the relative values of the rate constants between pairs of isotopomers of CH and H_2 : first, the collisional rate and second, the relative temperature-dependent rates of fragmentation of the collision complex into different product channels (Brownsword et al. 1997). The rate coefficients estimated for (20b) are listed in Table 5, along with the equilibrium constants for this reaction.

TABLE 4
RATE CONSTANTS FOR RADIATIVE ASSOCIATION ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) CALCULATED
ACCORDING TO DIFFERENT MODELS

$T(\text{K})$	Modified Thermal (Troe C_6^*)	Modified Thermal + Tunneling (Troe C_6^*)	Modified Thermal (C_6^* from k_{inf})	Modified Thermal + Tunneling (C_6^* from k_{inf})
300.....	4.9 (–18) ^a	8.6 (–18)	1.5 (–18)	3.6 (–18)
160.....	8.3 (–18)	1.7 (–17)	2.3 (–18)	6.8 (–18)
80.....	1.2 (–17)	2.9 (–17)	3.3 (–18)	1.2 (–17)
40.....	1.6 (–17)	4.6 (–17)	4.1 (–18)	1.9 (–17)
20.....	1.8 (–17)	6.4 (–17)	4.6 (–18)	2.8 (–17)
10.....	1.8 (–17)	8.8 (–17)	4.6 (–18)	3.6 (–17)

^a 4.9 (–18) = 4.9×10^{-18} .

TABLE 5
RATE COEFFICIENTS k (cm³ molecule⁻¹ s⁻¹) AND EQUILIBRIUM CONSTANTS (K)
FOR THE REACTIONS:
CH($v=0$) + D₂ → CD + HD
CH($v=0$) + HD → CD + H₂

$T(K)$	CH($v=0$) + D ₂ → CD + HD k (cm ³ molecule ⁻¹ s ⁻¹) (K)	CH($v=0$) + HD → CD + H ₂ k (cm ³ molecule ⁻¹ s ⁻¹) (K)
80.....	1.2×10^{-10} 3.2	1.2×10^{-10} 1.95
40.....	1.4×10^{-10} 5.1	1.1×10^{-10} 1.46
20.....	1.6×10^{-10} 14.3	0.62×10^{-10} 0.48
10.....	1.8×10^{-10} 89	0.43×10^{-10} 0.27

The fractionation of H/D-containing isotopomers in dense interstellar clouds has been discussed, largely in terms of ion-molecule reactions, by Millar et al. (1989). In this paper, calculated ratios of deuterated-to-normal abundances are presented for several dense interstellar cloud models having temperatures in the range 10–70 K. In all cases, the CD/CH ratio was found to range within a few percent. This led to an abundance in the range $1\text{--}5 \times 10^{-10}$ for the deuterated methyldene radical. However, to our knowledge, CD has not yet been detected in the interstellar medium. Given the rate coefficients for reaction (20b) and its reverse at low temperatures, the concentrations of CH and CD are likely to come rapidly into equilibrium with one another and, at 10 K, [CD]/[CH] will be equal to 0.27 [HD]/[H₂]. Using the observed ratio of [HD]/[H₂] (about 10^{-6} ; Spitzer et al. 1973) and the observed abundance of [CH] $\approx 2 \times 10^{-8}$ (Friberg & Hjalmarsen 1990), the abundance of CD will be only 5×10^{-15} , far too low to play any significant role in the chemistry of interstellar clouds. This may also be the reason why CD is still unobserved. It would obviously be of particular interest to measure the rate coefficient of the reaction between CD and H₂ at low temperature. It is also worth noting that other deuterated species may be unobserved because of their ability to react with H₂. Clearly, the neutral chemistry of deuterated species deserves some attention at low temperature.

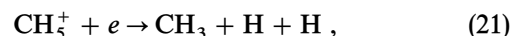
From the standpoint of astrochemistry, the principal results reported in this paper are the estimates of the rate coefficients for the radiative association of CH with H₂, a reaction which has not, up to now, been included in chemical models of interstellar clouds, as far as we are aware. In estimating its role in removing CH radicals, it is necessary to compare the first-order rate coefficient for removal by radiative association, i.e., $k_{\text{RA}}[\text{H}_2]$, with the same quantity for removal by reactions with other species.

In dense molecular clouds, the electron density and corresponding density of ions is relatively low (de Boisanger, Helmich, & van Dishoeck 1996) and CH is likely to be removed predominantly in reactions with other neutral species, especially H, N, O, and O₂. In “a compendium of recent model results,” Lee, Bettens, & Herbst (1996) present calculated fractional abundances for a large number of atomic and molecular species according to three different models. The models have been run for hydrogen densities (n_{H}) of 10^3 , 10^4 , and 10^5 cm⁻³ and for temperatures of both 10 and 50 K. For the new neutral-neutral model (Bettens et

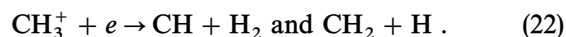
al. 1995) with $n_{\text{H}} = 10^4$ cm⁻³, the relative abundances of H, N, O, and O₂ at steady state are 2.3×10^{-4} (1.1×10^{-4}), 1.9×10^{-5} (6.5×10^{-6}), 1.5×10^{-4} (9.0×10^{-5}), and 3.0×10^{-5} (5.7×10^{-5}) at 10 K (50 K), respectively. The rate constant for reaction between CH and O₂ has recently been measured down to 13 K (Bocherel et al. 1996) and has a rate coefficient of ca. 1.5×10^{-10} cm³ molecule⁻¹ s⁻¹ between 10 and 50 K. Of the reactions involving neutral atoms, rate coefficients have been measured at low temperatures (down to 216 K) only for the reaction between N and CH (Brownsword et al. 1995). However, it is quite likely that all the reactions between CH and the radical atoms H, N, and O will have rate coefficients of the order of 10^{-10} cm³ molecule⁻¹ s⁻¹ (Messing et al. 1981; Smith 1995). On the basis of these figures, radiative association of CH with H₂ seems likely to provide only a minor pathway for CH removal in dense molecular clouds.

The situation is likely to be similar in diffuse clouds. Here the ionization fraction is much higher and reactions of CH with ions are likely to be important. In addition, much of the hydrogen will be present in atomic form so that the reaction of CH with H atoms is likely to be far faster in this environment than that with H₂.

Although the radiative association of CH with H₂ seems unlikely to be more than a minor channel for removal of CH radicals in interstellar clouds, it may provide a significant pathway to CH₃ and hence to the formation of simple hydrocarbon species. Here the uncertainties are larger than in the case of the destruction of CH. The UMIST database of rate coefficients for use in astrochemical modeling (Millar et al. 1997) lists almost 100 reactions which generate CH₃ radicals. At present, it seems that a major pathway is the dissociative recombination of CH₃⁺ with electrons, in which the yield of methyl radicals, via



is thought to be 20%–60% (Canosa 1991). However, the production of CH₃⁺ ions depends on the relatively slow radiative recombination of CH₃⁺ with H₂, i.e., reaction (2), and the successful competition of this reaction with the dissociative recombination of CH₃⁺ with electrons



The relative rates of reactions (2) and (22) will depend sensitively on the ionization fraction in dense clouds, a topic which has recently been discussed by de Boisanger et al. (1996).

To assess the importance of the production of CH_3 via $\text{CH} + \text{H}_2$ radiative association one can compare its rate, using observed or calculated abundances, with the rates of either reaction (2) or (21) estimated on a similar basis. Unfortunately the uncertainties are very large. Thus, using the electron density given by de Boisanger et al. (1996), the calculated abundances of CH and CH_5^+ according to the model of Lee et al. (1996) which gave the abundances of H , N , O , and O_2 cited above, and the rate coefficients for reaction (21) from the UMIST database (Millar et al. 1997) and for $\text{CH} + \text{H}_2$ estimated in the present work, then the rates of production of CH_3 by reaction (21) and by radiative association of CH and H_2 are of the same order of magnitude. On the other hand, if one compares the rates of radiative association of CH with H_2 and of CH_3^+ with H_2 (Gerlich & Horning 1992) using calculated abundances of CH and CH_3^+ (Lee et al. 1996) then it appears as if the former reaction will provide only a minor route to the formation of CH_3 .

In finally assessing the possible importance of the radiative association of CH with H_2 in interstellar environments, we stress again the uncertainties in the abundances of crucial species. For example, we note that the observed abundance of CH in TMC1 (Friberg & Hjalmarson 1990) is

about 2 orders of magnitude higher than the calculated value which we have used in making the comparisons referred to in the previous paragraph. Until such time that the error limits on these figures can be considerably reduced, it would seem to be wise to include the possibility of radiative association of CH with H_2 in models of dense interstellar clouds.

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