Deuterium Kinetic Isotope Effect and Temperature Dependence in the Reactions of CH[$^2\Pi$] with Methane and Acetylene

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Received: October 3, 1996; In Final Form: January 7, 1997[⊗]

The rate coefficients of the reactions of CH and CD with CH_4, CD_4, C_2H_2, and C_2D_2 have been measured in the temperature range $290 < T < 700$ K. All the rate constants show a slightly negative temperature dependence. They can be fitted in the observed temperature range by the following expressions: $k_{CH+CH_4} = (6.7 \pm 0.3)(T/293\ K)^{-(0.4\pm0.1)} \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}; $k_{CH+CD_4} = (4.2 \pm 0.2)(T/293\ K)^{-(0.3\pm0.1)} \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}; $k_{CD+CH_4} = (5.7 \pm 0.2)(T/293\ K)^{-(0.32\pm0.04)} \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}; $k_{CD+CD_4} = (3.6 \pm 0.1)(T/293\ K)^{-(0.27\pm0.08)} \times 10^{-11}$ cm^3 molecule^{-1} s$^{-1;}$ $k_{CH+C_2H_2} = (3.2 \pm 0.2)(T/293\ K)^{-(0.2\pm0.1)} \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}; $k_{CD+C_2H_2} = (2.8 \pm 0.1)(T/293\ K)^{-(0.13\pm0.06)} \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}; $k_{CH+C_2D_2} = (3.2 \pm 0.2)(T/293\ K)^{-(0.2\pm0.1)} \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}; and $k_{CD+C_2D_2} = (2.8 \pm 0.2)(T/293\ K)^{-(0.2\pm0.1)} \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, where all error estimates are $\pm 2\sigma$ and represent the precision of the fit. The observed temperature and pressure dependences are in accordance with a barrierless addition of the methylidyne radical to methane or acetylene with rapid decomposition of the adduct. The deuterium isotope effects on the reactions are not well-described by loose-transition state models and may reflect changes in the vibrational frequencies in the transition state for initial complex formation.

Introduction

The methylidyne radical, CH, is an extremely reactive radical species which plays an important role in hydrocarbon combustion[1−3] and in the chemistry of planetary atmospheres.[4] Because of its reactivity, CH is an excellent reaction zone marker for combustion imaging.[5] The kinetics of CH reactions have been the subject of a great deal of experimental and theoretical study,[6] and since the CH radical is relatively small, high-level calculations can be performed to characterize its reactions.[7,8] The reactions of CH with hydrocarbons form carbon-rich radicals which are thought to be important in soot formation.[9] These reactions in general have a highly exothermic metathesis pathway to produce a hydrogen atom and a larger hydrocarbon, and the CH + hydrocarbon reactions are fast.[10,11]

The reaction of CH with methane has been previously studied by Berman and Lin,[10] who described it as a barrierless insertion reaction to form a vibrationally excited ethyl radical (C_2H_5) which rapidly dissociates into H + C_2H_4. The reaction exhibits a negative temperature dependence, and the results are consistent with a capture-limited insertion reaction. Berman and Lin described the reaction using a loose transition state model with a modified Gorin treatment of the internal hindered rotor modes. While this treatment is in qualitative agreement with the experimental results, the details of the reaction mechanism have not yet been established.[12]

The reaction of CH with acetylene is also generally accepted to be a capture-limited reaction.[11] The Lin group measured a negative temperature dependence between 167 and 672 K, suggesting a barrierless addition to form C_3H_3 followed by rapid adduct decomposition. Recent calculations by Walch have characterized the stationary points on the CH + C_2H_2 surface and also indicate no barrier to initial adduct formation.[7]

The mechanism of many CH radical reactions has been postulated to involve insertion into chemical bonds. In the reactions of CH with saturated hydrocarbons, CH has been thought to insert into C−H bonds. Because the reactions are association-limited, the changes in chemical bonding which take place during the initial complex formation determine the overall reaction kinetics. The facility of these reactions has prompted the application of loose-transition state models, with transitional modes treated as hindered rotors or as low-frequency oscillators while the reactant vibrations are unchanged in the transition state. Such treatments, often modified to include variational effects, are reasonably successful in predicting the rate coefficients of reactions such as CH + CH_4. However, while the total rate coefficient is most sensitive to low-frequency vibrations, which contribute most to the partition functions, the kinetic isotope effect on the reaction will be sensitive to changes in the higher frequency vibrations in the transition state. The deuterium kinetic isotope effect in association-limited reactions may therefore reflect the nature of the incipient bonds in initial adduct formation. The kinetic isotope effect in the reaction of CH with O_2, for example, is inconsistent with a simple loose-transition state treatment.[13]

In the present work the rate coefficients for the reaction of CH and CD with CH_4, CD_4, C_2H_2, and C_2D_2 as a function of temperature between 290 and 700 K are reported. All of the reactions exhibit negative temperature dependences, consistent with capture-limited reactions. However, the kinetic isotope effects of the reaction with methane and acetylene are quite different; deuteration of the acetylene has a negligible effect on the rate coefficient while deuterated methane reacts 60% slower than CH_4. In both systems a small normal isotope effect is observed for deuterium substitution in the radical, $k_{CH+CH_4}k_{CD+CH_4} = 1.23 \pm 0.09$ and $k_{CH+C_2H_2}/k_{CD+C_2H_2} = 1.15 \pm 0.03$ at 293 K. The kinetic isotope effects are inadequately described by transition-state theory calculations using simple loose transition state models. Explicit consideration of the changes in vibrational frequencies during capture appears to be necessary to describe the experimental results. The difference in behavior between methane and acetylene presumably reflects

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[⊗] Abstract published in *Advance ACS Abstracts,* February 15, 1997.

S1089-5639(96)03033-2 CCC: $14.00

a difference in the nature of initial complex formation in the two reactions.

Experimental Section

In the present work, rate coefficients for CH and CD reactions are measured using the laser photolysis/CW laser-induced fluorescence (LP/cwLIF) method.[14] The experiments are performed in a quasi-static reactor; i.e., the gas flow is slow compared to the reaction time scale but high enough to prevent a buildup of reaction products in the observed volume. Since the experimental apparatus has previously been described in detail,[15,16] only a brief overview is given here.

The stainless steel reactor is resistively heated, and the temperature is measured by a retractable thermocouple directly above the photolysis volume. The pressure in the reactor is monitored with capacitance manometer gauges. All gas flows to the reactor are controlled by calibrated mass flow meters. The total gas flow is usually about 700−900 sccm. To achieve sufficiently low reactant and precursor gas flows, the bromoform and methane are premixed in helium (99.9999%) and stored in 12 l glass bulbs. The precursor concentration in the photolyte mixture is typically about 0.1% and the reactant mixture about 0.5%. Methane (99.99%), CD_4 (99 atom % D), and C_2D_2 (99 atom % D) are used without further purification. Acetylene (99.7%) is passed through an activated carbon filter to remove acetone, as confirmed by GC/MS analysis. The bromoform is purified by several freeze−pump−thaw cycles prior to use.

CH and CD radicals are formed by pulsed laser photolysis of $CHBr_3$ and $CDBr_3$, respectively, at 248 nm. The laser light is focused with a 300 mm lens in the reactor, the energy of a single shot is typically 10−25 mJ. The concentration of the methylidyne radicals is probed with a CW ring laser operating at 430 nm. The output of the probe laser is directed to the reactor cell via a fiber-optic link to ensure reproducible overlap and attenuated below 2 mW in order to remain in the weak probe limit. Under the conditions of these experiments the removal rate for vibrationally excited CH is always several orders of magnitude greater than the pumping rate of vibrationally excited CH by the probe laser via spontaneous emission.[17] Before coupling the probe laser light into the quartz fiber, the beam is passed through a chopper which is synchronized to the firing of the photolysis laser. The probe beam is expanded to approximately 10 mm diameter and collimated and crosses the excimer beam at a right angle. The fluorescence light is detected with a photomultiplier, operated in single photon counting mode and mounted perpendicular to both laser beams. To minimize the amount of scattered light, a narrow bandwidth filter is placed between the reactor and the photomultiplier.

The amplified signal is then transferred to a multichannel scaler, which samples the time-resolved fluorescence. The chopping of the probe laser is timed so that the probe laser is switched on and off for successive photolysis laser shots. The difference (probe on − probe off) is accumulated in the scaler. Because of the CW probing, the entire concentration vs time profile is obtained on every photolysis laser pulse. To achieve a reasonable signal-to-noise ratio, the signal is accumulated for 3000−5000 laser shots. The data are transferred to a personal computer for storage and analysis. A typical signal is shown in Figure 1; the rise time is presumably governed by collisional relaxation of electronically and vibrationally excited CH formed in the photolysis. Vibrational relaxation of CH(v=1) has been noted to be relatively slow (> 40 μs) at 30 Torr of Ar.[18] The rise time observed in Figure 1 (~20−30 μs) is consistent with a rate coefficient for relaxation by He on the order of 10^{-14} cm^3 $molecule^{-1}$ s^{-1}, which is not unreasonable for CH−rare gas collisions. However, no attempt was made to measure vibrationally excited CH. Metastable CH[$^4\Sigma$] is known to be formed from 193 nm multiphoton dissociation of $CHBr_3$ and is less reactive than the ground state,[19] but chemiluminescence measurements on the CH + O_2 reaction suggest negligible production at 248 nm under the conditions of these experiments.[13] If the excited state were considerably less reactive than the ground state and the relaxation rate coefficient were small, as perhaps for quartet CH, the decay could contain a component corresponding to disappearance of the excited state. However, the correspondence of the observed decay to a single exponential is excellent over more than four 1/e times, and such contributions have a negligible effect on the decay rate determinations in these experiments.

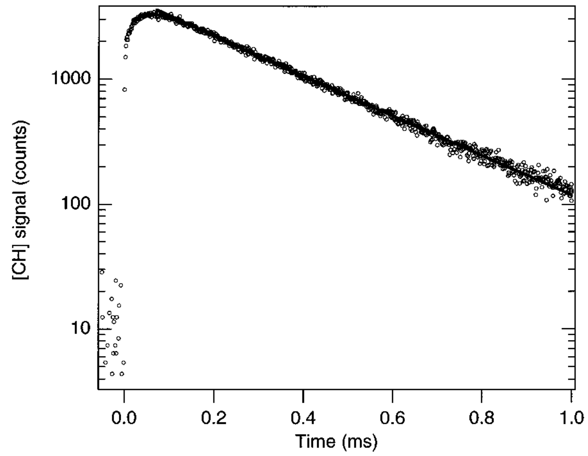

Figure 1. Typical time-resolved CH[X $^2\Pi$] LIF signal, from the reaction of CH with methane at 298 K, 100 Torr total pressure, with [$CHBr_3$] = 6 × 10^{12} molecules cm^{-3} and [CH_4] = 3.6 × 10^{13} molecules cm^{-3}. The rise time of the signal is due to the relaxation of electronically and vibrationally excited CH radicals produced in the photolysis. Fits to the decay (solid line) are carried out at longer times, after vibrational and electronic relaxation is complete.

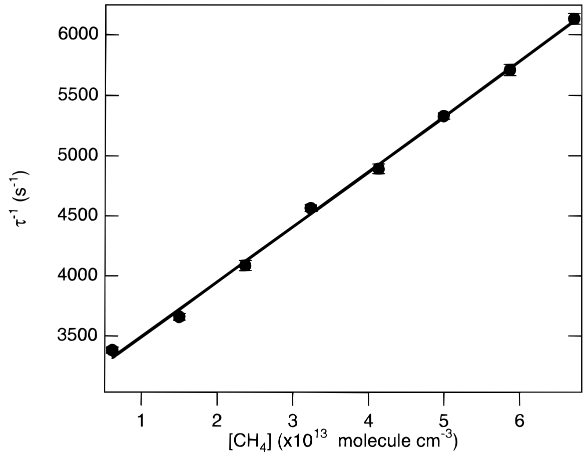

Figure 2. Plot of the pseudo-first-order rate coefficient vs reagent concentration for the reaction of CH with methane at 697 K. The intercept ([CH_4] = 0) is due to reactions with the bromoform precursor and with other photoproducts. Error bars are ±2σ and represent the precision of the exponential fit to the individual data traces.

Individual time traces are fit by exponential decays, and the time constants are plotted vs reactant concentration in the standard manner. A typical plot is shown in Figure 2. The second-order rate coefficient is extracted from the slope of a weighted fit to such a plot. The intercept reflects the reaction of CH with the photolyte and with other photolysis products. As has been noted previously, the value of the intercept would correspond to an unusually high rate coefficient for CH +

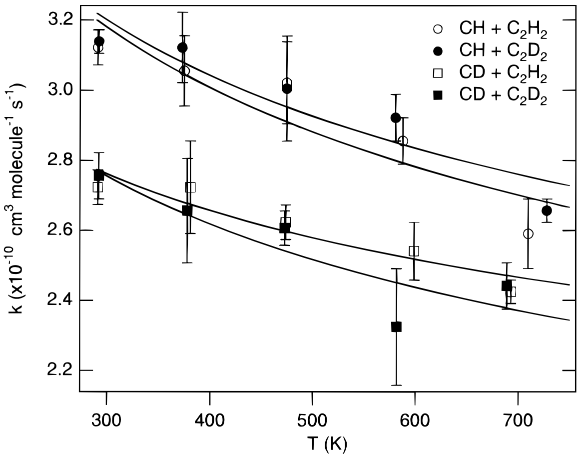

Figure 3. Rate coefficients as a function of temperature for the reactions of CH (circles) and CD (squares) with C_2H_2 (open symbols) and C_2D_2 (filled symbols) at 100 Torr total pressure. The lines are fits to a T^{-n} dependence. Error bars are ±2σ precision only.

TABLE 1: Reaction Rate Coefficients for CH + Acetylene and Isotopic Variants

reaction	T (K)	press. (Torr)	k (10^{-10} cm^3 $molecule^{-1}$ s^{-1})[a]
CH + C_2H_2	291	100	3.12 ± 0.05
	375	100	3.1 ± 0.1
	475	100	3.0 ± 0.1
	588	100	2.86 ± 0.07
	710	100	2.6 ± 0.1
	289	8	3.82 ± 0.08
	289	10	3.9 ± 0.1
	289	30	3.5 ± 0.1
	289	70	3.4 ± 0.1
	288	101	3.07 ± 0.06
	289	200	3.10 ± 0.05
	288	250	3.0 ± 0.1
	288	400	2.9 ± 0.2
CD + C_2H_2	291	100	2.72 ± 0.05
	381	100	2.7 ± 0.1
	474	100	2.62 ± 0.05
	599	100	2.54 ± 0.09
	693	100	2.42 ± 0.04
CH + C_2D_2	292	100	3.14 ± 0.04
	373	100	3.1 ± 0.1
	475	100	3.01 ± 0.03
	581	100	2.92 ± 0.07
	728	100	2.66 ± 0.04
CD + C_2D_2	292	100	2.76 ± 0.07
	378	100	2.7 ± 0.1
	473	100	2.61 ± 0.06
	582	100	2.3 ± 0.2
	689	100	2.4 ± 0.1

[a] Error estimates are ±2σ and reflect the precision of the fit.

$CHBr_3$ if it were due only to reactions with the photolyte, leading to postulates of reactions with ions or other radicals formed in the photolysis.[15] The bromoform concentration was kept as low as practical to minimize this contribution.

Results

CH + Acetylene. The reactions of CH and CD with acetylene and deuterated acetylene have been investigated between 290 and 720 K. The measured rate coefficients are shown in Figure 3 and are given in Table 1. All of the isotopic reactions exhibit a slight negative temperature dependence which can be fitted by a T^{-n} dependence, with $n \sim 0.2$. The reaction of CH with C_2H_2 has previously been measured as a function of temperature by Lin and co-workers.[11] Berman et al. reported a small negative temperature dependence between 171 and 657 K, which they fit to an Arrhenius form, yielding a negative activation energy of $E_a/R = 61 \pm 36$ K.[11] This is in excellent agreement with the temperature dependence observed in the present work, which gives $E_a/R = 79 \pm 56$ K. Previous determinations of the room temperature rate coefficient for this reaction have exhibited significant disagreement, with Bosnali and Perner reporting $(7.47 \pm 1.5) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K;[20] Butler et al., 2.2×10^{-10} cm^3 $molecule^{-1}$ s^{-1} at 298 K,[21] and Berman et al., $(3.49 \pm 0.42) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}.[11] The present value at 291 K, $(3.12 \pm 0.05) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}, is in good agreement with the most recent determination of Berman et al.

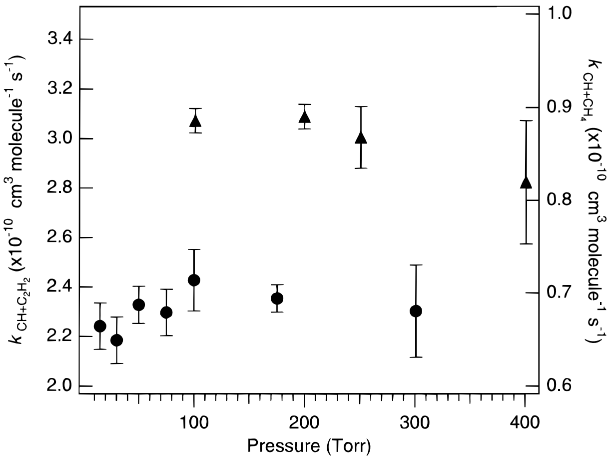

Figure 4. Observed rate coefficients for the reactions of CH with methane (circles) and acetylene (triangles) as a function of total pressure at 292 K. Error bars are ±2σ precision only. The rate coefficients for both reactions are independent of total pressure above 100 Torr. There is an apparent negative pressure dependence of the rate coefficient for CH + acetylene below 100 Torr (see Table 1), whose origin is unclear. We have assumed that it is an artifact of the preparation method, and the temperature dependence and isotope effects are measured in the pressure-independent region.

The observed rate coefficient is independent of pressure between 100 and 400 Torr (Figure 4); however, below 100 Torr the rate coefficient appears to increase with decreasing pressure. The reason for this unusual behavior is unclear. Possible errors due to secondary reactions of CH with reaction products, inaccuracies in flow measurements, and optical pumping of CH have been eliminated, and measurements of other CH reactions under the same conditions do not show the same behavior. Incomplete relaxation of the photolytically produced CH is unlikely to explain the results, since the LIF measurement probes the ground-state population and the decays are fit after the observed relaxation is complete. Nonetheless, in order to avoid contributions from unknown experimental artifacts, the reported temperature dependence and isotope effects are measured in the pressure-independent region.

A significant isotope effect is measured for CH vs CD reacting with acetylene and deuterated acetylene. The isotope effect at room temperature (291 K) is $k_{CH+C_2H_2}/k_{CD+C_2H_2} = 1.15 \pm 0.03$. A similar isotope effect (1.16 ± 0.06) has been observed for the reaction of CH with O_2, which is also thought to be an association-limited metathesis reaction.[13] The kinetic isotope effect for deuterium substitution on the acetylene is negligible and is well within experimental error over the entire temperature range of these experiments.

CH + Methane. The reaction of CH with methane is slower than that with acetylene and exhibits a stronger dependence on temperature. The rate coefficients for CH + CH_4 and isotopic variants are shown in Figure 5 and listed in Table 2. The room temperature (291 K) rate coefficient for CH + CH_4 is (7.1 ±

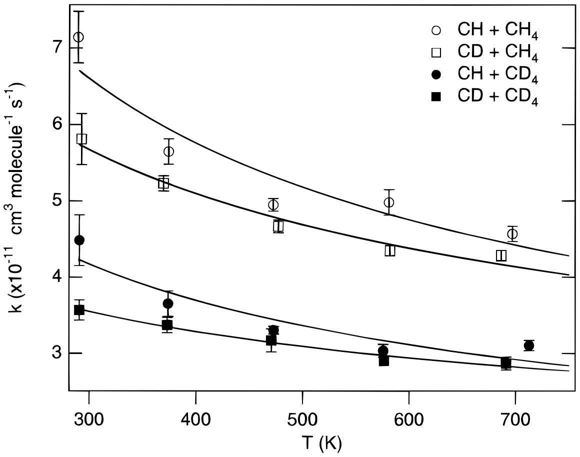

Figure 5. Rate coefficients as a function of temperature for the reactions of CH (circles) and CD (squares) with CH_4 (open symbols) and CD_4 (filled symbols) at 100 Torr total pressure. The lines are fits to a T^{-n} dependence. Error bars are ±2σ precision only.

TABLE 2: Reaction Rate Coefficients for CH + Methane and Isotopic Variants

reaction	T (K)	press. (Torr)	k (10^{-11} cm^3 molecule^{-1} s^{-1})[a]
$CH + CH_4$	290	100	7.1 ± 0.3
	374	100	5.6 ± 0.2
	473	100	4.95 ± 0.08
	581	100	5.0 ± 0.2
	697	100	4.6 ± 0.1
	290	15	6.6 ± 0.3
	290	30	6.5 ± 0.4
	290	50	6.9 ± 0.2
	290	75	6.9 ± 0.3
	290	175	6.9 ± 0.1
	290	301	6.8 ± 0.5
$CD + CH_4$	292.6	100	5.8 ± 0.3
	369.6	100	5.2 ± 0.1
	477.3	100	4.67 ± 0.08
	581.8	100	4.35 ± 0.06
	686.7	100	4.28 ± 0.06
$CH + CD_4$	290.6	100	4.5 ± 0.3
	373.9	100	3.7 ± 0.2
	472.8	100	3.30 ± 0.05
	575.7	100	3.04 ± 0.08
	712.8	100	3.11 ± 0.06
$CD + CD_4$	290.5	100	3.6 ± 0.1
	373.2	100	3.4 ± 0.1
	470.8	100	3.2 ± 0.2
	576.3	100	2.91 ± 0.05
	691.2	100	2.87 ± 0.08

[a] Error estimates are ±2σ and reflect the precision of the fit.

0.3) × 10^{-11} cm^3 molecule^{-1} s^{-1}. The rate coefficient is independent of pressure between 15 and 300 Torr, to within experimental error, as shown in Figure 4. Previous determinations of the room temperature rate coefficient for this reaction have ranged from 3.3 × 10^{-11} cm^3 molecule^{-1} s^{-1} by Bosnali and Perner[20] to (1.0 ± 0.3) × 10^{-10} by Butler et al.[21] Anderson et al. reported (5.4 ± 1.0) × 10^{-11} cm^3 molecule^{-1} s^{-1} using a flow apparatus at 290 K,[22] and Berman and Lin reported (1.02 ± 0.1) × 10^{-10} cm^3 molecule^{-1} s^{-1} at 297 K.[10] The temperature dependence of all isotopic variants of the CH + methane reaction is negative, with T^{-n} fits to the present data yielding $n \sim 0.4$. Berman and Lin measured the temperature dependence of this reaction between 167 and 652 K and reported a negative activation energy, $E_a/R = 200 \pm 31$ K.[10] An Arrhenius fit to the present data yields an activation energy of $E_a/R = 211 \pm 60$ K, in excellent agreement with the determination of Berman and Lin. During the preparation of this paper we became aware of recent measurements by Blitz et al., which give a somewhat steeper temperature dependence, with $E_a/R = 410 \pm 60$ K between 298 and 778 K.[23] Their measurements are in good agreement with the present values at high temperature but disagree near room temperature, where they report a rate coefficient of (9.79 ± 0.37) × 10^{-11} cm^3 molecule^{-1} s^{-1} at 298 K.

The kinetic isotope effect for deuterium substitution at the CH radical is measured to be slightly larger for the methane reaction than for the reaction with acetylene. At 292 K, $k_{CH+CH_4}/k_{CD+CH_4} = 1.23 \pm 0.09$. However, the kinetic isotope effect decreases significantly with increasing temperature, to $k_{CH+CH_4}/k_{CD+CH_4} = 1.07 \pm 0.03$ near 680 K. Similar effects are observed in the reaction of CH and CD with CD_4. The effect on the reaction rate of deuteration of the methane is considerably larger, with an isotope effect of $k_{CH+CH_4}/k_{CH+CD_4} = 1.60 \pm 0.13$ at 292 K. Blitz et al. also measured rates for the isotopic variants of $CH + CH_4$; their results are in good qualitative agreement with the present measurements, with a significantly larger kinetic isotope effect for deuteration of the methane than for deuteration of the CH radical.[23] However, the magnitude of the isotope effect is larger in the present study.

Discussion

The temperature dependence of the fast reactions of CH with most hydrocarbons are characteristic of a barrierless reaction, and these reactions have been rationalized using loose transition state models. However, the kinetic isotope effect offers additional information about the reaction which may not be adequately described by simple models. A general mechanism which has been successfully applied for many CH reactions, including CH + hydrocarbon reactions, is the initial formation of a vibrationally excited adduct followed by stabilization or decomposition to products. The general expression for the reaction rate will be the product of the adduct formation and the relative rates for collisional stabilization and dissociation of the adduct to products and to reactants. Isotope effects on the relative rate of dissociation to products or back to reactants could affect the measured total rate coefficient. Inverse isotope effects in systems such as CH (CD) + HCN (DCN) and HCO (DCO) + O_2 have been rationalized using similar explanations.[24,25] Langford and Moore have shown by RRKM calculations that isotope effects due to complex formation and redissociation can be compatible with a lack of pressure dependence.[25]

While it is possible that the normal isotope effects in the present systems could arise from a similar complex-mediated mechanism, the exothermicity of the product channels (~60 kcal mol^{-1} for $CH + CH_4 \rightarrow C_2H_4 + H$ and ~10 kcal mol^{-1} for $CH + C_2H_2 \rightarrow C_3H_2 + H$) seems to make dissociation back to reactants unlikely. However, it is not clear whether the kinetic isotope effects, especially that in the methane reaction, can be explained under the assumptions of an association-limited reaction.

If product formation is rapid, as may be expected for reactions such as CH + methane with highly exothermic metathesis pathways, the rate will be limited by the adduct formation rate. The reaction rate is then simply given by the high-pressure limiting transition-state theory expression,[26]

$$k_\infty = \frac{kT}{h}\frac{Q^\ddagger}{Q^{\text{react}}} \tag{1}$$

Here a double dagger is used to refer to the transition state. The partition functions of the reactants and the effective partition function of the transition state will change with temperature and upon isotopic substitution.

In the loose transition state limit, the vibrational frequencies of the reactant are considered to be unchanged in the transition state. As a result, the rate coefficient is governed by the transitional modes which correlate to the rotational motions of the reactants and by the rotational degrees of freedom in the transition state. There has been extensive theoretical work on treatment of these transitional modes; for loose transition states, several hindered-rotor treatments have been successfully applied.[27-30] In simple cases a hindered-rotor calculation reduces to the ratio of the pseudo-diatomic rotational partition function for rotation perpendicular to the reaction coordinate and the partition function for relative translation of the reactants, as shown by Aubanel et al.[27] The kinetic isotope effect is then the collision-frequency result, i.e., the square root of the ratio of the collision reduced masses (i.e., ~1.02 for CH (CD) + CH_4 or C_2H_2, ~1.05 for CH + CH_4 (CD_4), ~1.01 for CH + C_2H_2 (C_2D_2) reactions). The absolute rate coefficient is sensitive to the nature of the hindering potential and the treatment of the transitional modes, but when considering only the kinetic isotope effect, many of the parameters which depend on the potential are ratioed out. As a result, loose transition state models (i.e., those assuming no change in the frequencies of the conserved modes) generally predict small isotope effects.

The observed kinetic isotope effects in the CH + methane and the CH + acetylene system are too large to be described by a simplistic loose transition-state model. Treatment of the transitional modes in the collision complex as low-frequency oscillators can produce different isotopic behavior than a hindered rotor model, since the rotational partition functions no longer cancel from the transition state theory expression. The isotope effect is most sensitive to the high-frequency modes in the transition state,[31] so changes to the low-frequency transitional modes may have a limited effect. Since significant chemical forces occur at the transition state for adduct formation in neutral−neutral reactions,[32] it is not unreasonable to ask whether changes in the frequencies of the conserved modes could explain the kinetic isotope effects.

The reactions of CH with methane and acetylene have similar temperature behavior and occur on similar potential energy surfaces. Both systems have a deep attractive well corresponding to adduct formation and exothermic metathesis channels. Yet, the deuterium isotope effects on the reactions are markedly different. The effect of deuterating the CH radical is similar in both reactions and is also similar to that observed in the CH + O_2 reaction, which is also thought to proceed by adduct formation followed by rapid dissociation to products.[13] An isotope effect of this magnitude appears consistent with an association-limited reaction, although simple loose transition state calculations do not reproduce the experimental results. Isotope effects of this magnitude have been observed for additions with a tighter transition state, e.g., OH (OD) addition to ethylene.[33] It is possible that incipient bond formation may change the C−H bonding in the radical and change the frequency of the radical C−H stretch slightly in the transition state. However, since the rate coefficient is in general governed by a complicated average over open adiabatic channels, modest kinetic isotope effects such as these may very likely be explicable in a more exact treatment without changes in the conserved vibrational frequencies. A more detailed treatment of the conserved and transitional modes, perhaps including variational effects,[28-30] may be necessary to describe the CH/CD isotope effect.

A more suggestive result is the difference between deuteration of methane and deuteration of acetylene. The reaction of CH with acetylene is essentially insensitive to deuterium substitution of the acetylene. This suggests that the partition functions which are affected by the substitution are unchanged between reactants and transition state. The C−H bond in the acetylene, in particular, is presumably unaffected by the incipient complex formation, since a change in the high-frequency C−H vibration would be expected to produce a significant isotope effect. The potential energy surface for the CH + C_2H_2 reaction has recently been calculated by Walch.[7] According to the calculations, the reaction proceeds by barrierless addition of the CH to acetylene, with the CH approaching nearly parallel to the C−C triple bond. If at the transition state for association the CH radical interacts mainly with the π cloud of the acetylene, the C−H bonds in the acetylene may be expected to be unaffected by the approach of the CH, consistent with the observed negligible isotope effect.

The reaction with methane is considerably different. While a deep well exists corresponding to ethyl radical formation, no simple barrierless addition path exists. The reaction has been successfully modeled by Berman and Lin assuming an insertion mechanism.[10] Low-level calculations on the CH + CH_4 system by Yu et al. suggest that the insertion reaction may proceed via an "abstraction−addition" channel, where hydrogen transfer from the methane initiates the reactive encounter.[12] However, these calculations are somewhat crude and predict energetic barriers to reaction which are completely inconsistent with the experimental data. In any case, formation of an excited ethyl adduct from CH + methane clearly requires H atom motion. The experimental observations appear compatible with either a primary or a secondary effect; secondary kinetic isotope effects of a similar magnitude have been predicted by variational transition state calculations on the $CD_3H + H \leftrightarrow CD_3 + H_2$ reaction.[34] A reduction of methane C−H frequencies in the transition state is consistent with either reaction mechanism, which will produce a significant kinetic isotope effect favoring the fully hydrogenated species. The difference in kinetic isotope effect between the methane and acetylene reactions appears to be qualitatively related to differences in the mechanism of initial adduct formation. More detailed calculations which include changes in reactant vibrational frequencies in the transition state region and the possibilities of redissociation of the adduct back to reactants may be necessary to completely explain the present results.

Conclusions

The rate coefficients for CH and CD with CH_4, CD_4, C_2H_2, and C_2D_2 have been measured as a function of temperature between 290 and 700 K. The temperature dependences are compatible with the accepted picture of these reactions as barrierless association or insertion reactions followed by rapid dissociation of the adduct. There is a normal kinetic isotope effect for deuterium substitution of the CH radical for all the reactions, and the magnitude of the effect (~20%) is consistent with other association-limited CH reactions, such as CH + O_2. Deuterium substitution of methane has a large (60%) effect on the reaction with CH and CD, whereas deuterium substitution of acetylene has no measurable effect on the reactivity with CH or CD radicals. The measured kinetic isotope effects are not well-described by loose transition state models. The difference in isotopic behavior between methane and acetylene has a qualitative explanation in the different mechanisms of initial adduct formation in the two reactions.

Acknowledgment. This work is supported by the Chemical Sciences Division, Office of Basic Energy Sciences, U.S. Department of Energy. H.T. acknowledges the Deutsche Forschungsgemeinschaft (DFG) for a postdoctoral fellowship. J.M. is supported through the University College Galway's Committee on Inter-Institutional Relationship and thanks Dr. John Simmie and Dr. Joe Durant for organization of his visit.

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