

The reaction of methylidene (CH) with methanol isotopomers

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The reactions of the methylidene (CH) radical with a variety of methanol isotopomers has been studied using pulsed laser photolysis/laser induced fluorescence, as a function of temperature (298–753 K) and pressure (100–600 Torr helium). The rate coefficient was independent of total pressure and the following rate coefficients were determined:

$$k_{\text{CH}+\text{CH}_3\text{OH}} = (2.52 \pm 0.12)(T/298)^{-1.93 \pm 0.17} \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_{\text{CD}+\text{CH}_3\text{OD}} = (2.37 \pm 0.06)(T/298)^{-1.57 \pm 0.08} \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_{\text{CD}+\text{CH}_3\text{OD}}(298 \text{ K}) = (2.3 \pm 0.1) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_{\text{CH}+\text{CH}_3\text{OD}}(298 \text{ K}) = (2.22 \pm 0.07) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_{\text{CH}+\text{CD}_3\text{OH}}(298 \text{ K}) = (2.48 \pm 0.08) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_{\text{CD}+\text{CH}_3\text{OH}}(298 \text{ K}) = (2.20 \pm 0.06) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_{\text{CD}+\text{CD}_3\text{OH}}(298 \text{ K}) = (2.17 \pm 0.06) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

where the errors represent statistical uncertainties at the 1σ level. The reaction can either proceed *via* CH insertion into a C–H bond (as for the reaction with methane) or *via* an initial complex with subsequent insertion into either the O–H or C–O bonds (as for the reaction with water). The absence of any significant isotope effect indicates that the reaction proceeds *via* the latter mechanism, however, the room temperature rate coefficient is an order of magnitude greater than that for the reaction of CH with water. A correlation between the ionization potential of the substrate and rate coefficient is suggested to rationalise experimental observations. Above an ionization potential of approximately 11 eV, there is an inverse correlation between rate coefficient and ionization energy, below an ionization energy of 11 eV, the rate coefficient reaches a plateau of $\sim 3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

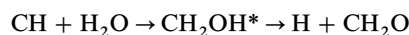
Introduction

Reactions of the CH (methylidene) radical have been the focus of many kinetic studies and an extensive database on the overall rate of removal of CH radicals by a variety of reagents exists.¹ Despite the number of kinetic studies and the importance of CH radicals in a range of chemical systems ranging from combustion to outer planetary atmospheres, much less is known about the mechanisms and products of CH radical reactions. Very few product studies have been undertaken;^{2–4} the extreme reactivity of the CH radical means that there are generally several exothermic channels, often generating other radical species, leading to complex reaction mixtures. A number of the more comprehensive kinetic studies, either using isotopomer^{5–8} or an extensive temperature range,^{9–11} have produced results indicating that CH reactions occur *via* mechanistically interesting and unusual pathways.

Earlier studies on the reaction of CH with methane both in this laboratory⁵ and by Taatjes *et al.*,⁷ raise some interesting questions. The reaction appears to be barrierless and is postulated to occur *via* the insertion of CH into a C–H bond forming an excited ethyl adduct. RRKM calculations show that the lifetime of the adduct is far too short to allow for stabilisation and rapid dissociation to form H + ethene occurs. Given the mechanism of the reaction, the observation from both studies of a significant isotope effect ($\sim 30\%$

reduction in rate coefficient) when changing from CH₄ to CD₄ is somewhat surprising. The absence of an activation barrier for the formation of the transition state renders conventional explanations of isotope effects invalid. Further analysis is hindered by a lack of knowledge of the transition state for such barrierless insertion reactions.

In contrast, the reaction of CH with water, which could take place *via* a similar insertion mechanism,



has no significant isotope effect although it too occurs without an activation barrier.⁶ The rationale that we suggested for this observation was that the rate determining initial step in the reaction was the formation of an intermediate complex with lone pairs of the oxygen atom, before insertion into the O–H bond. The idea of an initial complex is supported by theoretical calculations.¹²

The reaction of CH with methanol is an interesting extension of these studies as potentially both mechanisms could occur, with the CH radical either inserting directly into the C–H bonds of the methyl fragment or forming an initial complex with the lone pairs of the oxygen before inserting into either the O–H or C–O bond. In addition, the kinetics of the reaction of CH with methanol is of practical relevance. Methanol and other oxygenated compounds are finding increasing use as alternative fuels which have lower pollution

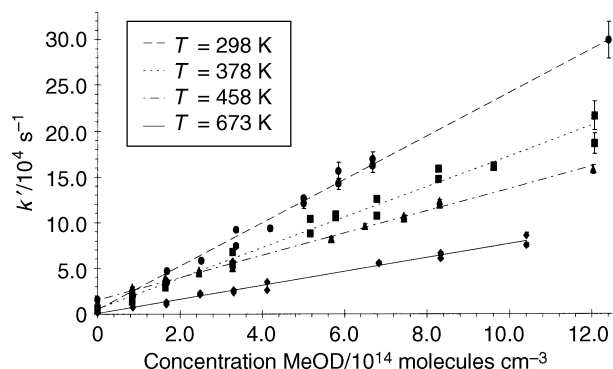


Fig. 2 Plot of the observed pseudo-first-order CD removal rate coefficient *vs.* [MeOD] at various temperatures. The lines represent linear least-squares fits. Total pressure of 100 Torr helium bath gas.

being the bimolecular rate coefficient for the target reaction. A typical example is shown in Fig. 2. Bimolecular rate coefficients were obtained for a variety of temperatures between 298 and 753 K and the results are shown in Table 1.

No significant isotope effects were observed for any of the CH/CD methanol combinations. Similar to the reaction of CH/D with water, the reaction of CH with methanol appears to be pressure independent over the range of experimental conditions tested (100–600 Torr at 298 K). Two extensive

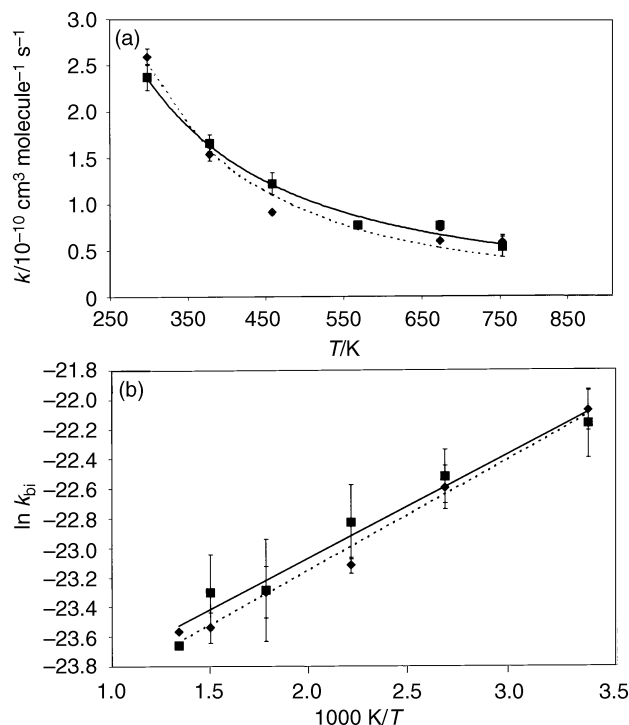


Fig. 3 Temperature dependence of the CH + MeOH (◆) and CD + MeOD (■) reactions (a) *k vs.* *T*. Lines represent AT^n fits to the data (b) the same data represented in Arrhenius format. In both cases the dashed lines refer to the CH + MeOH measurements and the solid line CD + MeOD.

temperature studies were performed on the reactions CH + CH₃OH and CD + CH₃OD. In both cases the rate coefficient decreases by ~80% over the temperature range 298–753 K. The temperature dependence of the bimolecular rate coefficient is displayed in Fig. 3a and in Arrhenius form in Fig. 3b. The parameters returned from the least squares fits are presented in Table 2.

The effect of vibrational excitation on the bimolecular rate coefficient was studied for both CH and CD (*v* = 1, 2) reactions at 298 K. Details of the conditions are presented in Table 1. The bimolecular rate coefficients for the reactions of vibrationally excited methylenes are, within experimental error, indistinguishable from the ground state values. Unlike the CH/D + water system, vibrational excitation of methylenes appears to have no effect on the observed bimolecular removal rate.

Discussion

Comparison with previous studies

There has only been one other study of the title reaction performed by Duncanson and Guillory.¹⁶ Their value is an indirect determination as a result of using infrared multiphoton dissociation of methanol to generate CH radicals for kinetic studies. A value for k_{298} was estimated from the intercept of Stern–Volmer plots. The resulting value $((1.02 \pm 0.06) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$ is of the same order as that determined in this study but the error limits of the two experiments do not overlap.

Comparison with other hydrides

Part of the rationale for this study was to investigate, *via* the measurement of overall kinetics, which mechanism (insertion into the C–H bond as for the reaction with methane, or initial complex formation, as for water) dominates in the reaction of methylenes with methanol. The lack of any significant isotope effect upon selective deuteration of methanol suggests that the reaction proceeds *via* initial complex formation, as is the case for water. The invariance of the rate coefficients for the various combinations indicates that, as might be expected for such fast, exothermic reactions, there are no exchange processes.

However, the observed magnitude of the rate coefficient for the reaction of methylene with methanol at room temperature is ~ a factor of 10 greater than the reaction with water. If one assumes that the availability of the lone pairs on the oxygen is related to the ease of complex formation, then the magnitude of the bimolecular rate coefficient should be inversely related to the ionisation potential. A number of other reactions that could also proceed *via* this mechanism have previously been studied,^{17–19} and their room temperature rate coefficients are plotted as a function of ionisation potential in Fig. 4a. For compounds with higher ionization potentials, there appears to be a correlation between rate coefficient and ionization potential, but these level off for the methylenes, an observation which might be

Table 2 Temperature dependence of the reactions of CH with CH₃OH and CD with CH₃OD at 100 Torr total pressure

Reaction	$k(T) = A(T/298)^n$		$k(T) = B \exp(-E_a/RT)$	
	$A/10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	<i>n</i>	$B/10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$E_a/\text{kJ mol}^{-1}$
CH + CH ₃ OH	2.52 ± 0.12	-1.93 ± 0.17	1.85 ± 0.19	-6.5 ± 0.3
CD + CH ₃ OD	2.37 ± 0.06	-1.57 ± 0.08	2.77 ± 0.40	-5.4 ± 0.4

^a Errors represent $\pm 1\sigma$.

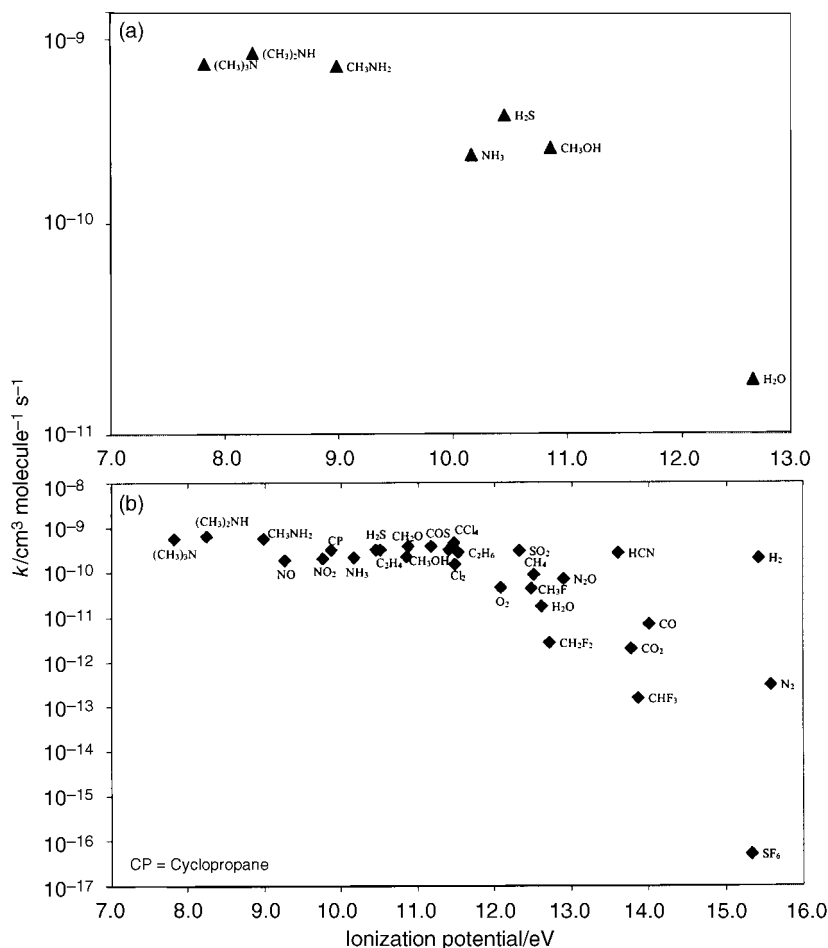


Fig. 4 (a) Correlation between the room temperature rate coefficient and ionization potential for the reactions of methyldene with simple hydrides and amines with lone pairs. (b) Correlation between the room temperature rate coefficient and ionization potential for the reactions of methyldene with a range of substrates. All data taken from the NIST kinetic database.¹ For termolecular reactions, the high pressure limiting value is shown. The value for SF_6 is an upper estimate.

expected given the proximity of these rate coefficients to the collision limit.

Yu *et al.*²⁰ have suggested that other reactions of methyldene also occur with complex formation. We have therefore plotted the room temperature rate coefficients of a number of CH reactions against ionization potential in Fig. 4b. The same general trend is observed with a correlation between the rate coefficient and ionization potential at high ionization energies, with the rate coefficients approaching the gas kinetic limit at a substrate ionization potential of ~ 11 eV. Above this ionization value there is generally a monotonic decrease of rate coefficient with ionization potential, although there are a number of out-lying species, most notably HCN and H_2 , which limit the predictive nature of such a plot. Such a simple analysis neglects a number of parameters of potential importance such as polarizability. We plan to address these issues in subsequent experimental and theoretical studies.

Vibrational excitation

In contrast to our earlier studies on the methyldene and water reaction,⁶ no significant enhancement of either the CH or CD systems was observed with vibrational excitation of the methyldene species, reflecting the fact that, unlike the analogous reaction with water, the $\text{CH}(v=0) + \text{CH}_3\text{OH}$ reaction is already close to a collision limiting value. Given that collisions already lead to reaction with virtually unit probability, there is little possibility of enhancing the overall $\text{CH}(v)$ loss rate by collisional relaxation. In complex forming reactions, the rate of vibrational relaxation can represent the process of

complex formation.²¹ Further studies will investigate the temperature dependence of vibrational relaxation to determine whether $\text{CH}(v)$ species are removed with unit efficiency at higher temperatures or whether the overall loss rate follows the trend of reactive $\text{CH}(v=0)$ collisions, suggesting that vibrational relaxation and reaction proceed *via* a common complex forming process.

Reaction products

The products of the methyldene methanol reaction will depend on the position of attack. Insertion into the C–H bond would be expected to lead to a hydroxyethyl intermediate, which would most likely yield OH and ethene as reaction products. An OH signal was observed but was found to be photolytic in origin rather than arising from the CH/methanol reaction confirming the conclusion of the isotopic studies that insertion into the C–H bond is not a significant channel in the title reaction. The sensitivity of the apparatus to OH limits the branching ratio to OH production to less than 1% of the total reaction.

Initial complex formation can subsequently proceed *via* two pathways: insertion into either the C–O or O–H bonds. Insertion into the O–H bond will form $\text{CH}_2\text{O}-\text{CH}_3$ from which the only realistic exothermic reaction products are formaldehyde and methyl radicals as shown in Fig. 5a. Insertion into the weaker C–O bond will give an initial $\text{HO}-\text{C}(\text{H})-\text{CH}_3$ intermediate. Four product pathways are thermodynamically accessible as shown in Fig. 5b. Stabilization of the hydroxy species is unlikely and considering the relatively low exother-

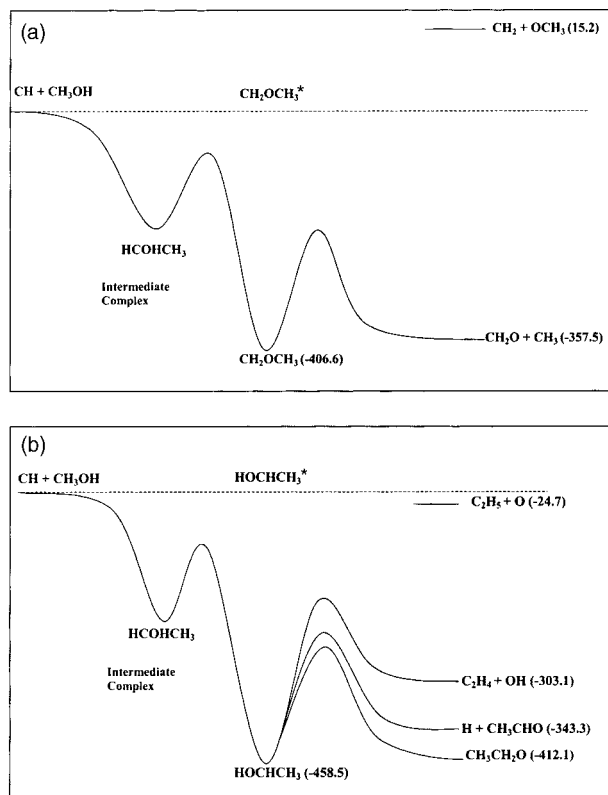


Fig. 5 Schematic potential energy surface showing the energies of the intermediates and reaction products (in kJ mol⁻¹) following the insertion of CH into either (a) the O-H bond or (b) the C-O bond. The diagrams are not to scale and values for the energies of the initial complex and saddle points are not known.

micity of the C₂H₅ + O products and the lack of any observed OH product, the dissociation channel to yield H + acetaldehyde seems the most likely result.

A series of product studies from CH reactions is currently being undertaken in this laboratory.⁴ Product studies on the methylenemethanol system will form part of this programme. Despite the negative temperature dependence of the reaction, methanol will still be an efficient sink for CH radicals during combustion. However, a full characterisation of

the reaction products is required before the effects of this reaction on the product spectrum of methanol combustion can be established.

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