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$^{12}\text{C}/^{13}\text{C}$ kinetic isotope effects in the reactions of CH_4 with OH and Cl

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Abstract. In qualitative agreement with previous MP2 level calculations of the $^{12}\text{C}/^{13}\text{C}$ kinetic isotope effects (KIEs) for H-abstraction of CH_4 by OH and Cl, higher level calculations yield KIEs at 300 K that differ from the corresponding experimental values, but in different directions. At QCISD(T)/6-311+G(2df,p), the theoretical KIE for $\text{CH}_4 + \text{Cl}$ is 32% less than the measured value, while for $\text{CH}_4 + \text{OH}$, the theoretical KIE is greater than the measured value, but only by 5%. Noticeable differences in atmospheric model simulation studies can occur if the measured KIEs are replaced by the analogous theoretical values. For example, the effect of carbon isotopic fractionation from the $\text{CH}_4 + \text{Cl}$ reaction on stratospheric $\delta^{13}\text{CH}_4$ will be significantly lower than that obtained by Bergamaschi *et al.* [1996]. It is suggested, for the $\text{CH}_4 + \text{OH}$ reaction and especially for the $\text{CH}_4 + \text{Cl}$ reaction, that additional KIE measurements are needed.

Introduction

Despite its relatively low average global tropospheric mixing ratio of 1.76 ppmv (1 ppmv = 10^{-6} v/v) [Blake and Rowland, unpublished results; Dlugokencky *et al.*, 1994], CH_4 has a significant impact on the radiative budget and the photochemistry of the atmosphere [Cicerone and Oremland, 1988; Lelieveld and Crutzen, 1992]. About 70% of the CH_4 budget is believed to be from anthropogenic sources and its yearly rate of increase has averaged about 1% over the past two decades. After CO_2 , CH_4 is the next most important anthropogenic greenhouse gas [Ramanathan *et al.*, 1985]. The removal of OH radicals is controlled in the southern hemisphere almost entirely by reaction with CH_4 and one of its oxidation products, CO. While there are other significant reactants for OH in the northern hemisphere, such as non-methane hydrocarbons and CO from direct emissions, the oxidizing capacity of the atmosphere is seriously affected by the increasing trend in CH_4 concentrations. The increasing atmospheric concentration of CH_4 also affects the concentrations of stratospheric trace gases such as CO, H_2 , H_2O , Cl, and O_3 . While the important sources and sinks of CH_4 have been identified, the magnitudes of the source strengths are still not narrowly constrained [IPCC, 1995].

For any atmospheric trace gas, measurements of its mixing ratios and isotopic composition in ambient air, along with analysis of its isotopic composition from flux measurements, serve to constrain its global budget. Moreover, with the aid of such isotopic measurements, the relative time-dependent contributions from various sources of a given trace gas to its

total source strength can be inferred. The value of stable isotopes (^{13}C , D) in such research has been described by Kaye [1987], while the radioactive isotopes (^{14}C , T) provide complementary information. Although the emission of some $^{14}\text{CH}_4$ and $^{12}\text{CH}_3\text{T}$ accompanies the use of artificial radioactivity, the biological origin of the majority of atmospheric methane has been established from the presence of cosmic-ray produced ^{14}C introduced through photosynthesis with $^{14}\text{CO}_2$.

The distribution of CH_4 in the earth's atmosphere is determined by the locations and strengths of its various surface sources in combination with atmospheric transport, and also by its loss processes from reactions with OH, Cl, and $\text{O}(^1\text{D})$ radicals and from surface soil microbes. Of these loss processes, reaction with OH radicals is believed to be the major sink in the troposphere, while reactions with Cl and $\text{O}(^1\text{D})$ become significant sinks in the stratosphere. Deducing the importance of the reactions of CH_4 and other hydrocarbons with Cl radicals in the marine boundary layer is currently an area of active research [Keene *et al.*, 1996].

The sources and sinks of atmospheric CH_4 have characteristic isotopic signatures. Indeed, for each of the above mentioned sinks, the $^{12}\text{C}/^{13}\text{C}$ kinetic isotope effect (*i.e.*, the ratio of the rate constant for reaction with $^{12}\text{CH}_4$ to that for reaction with $^{13}\text{CH}_4$) has been determined experimentally [Davidson *et al.*, 1987; Cantrell *et al.*, 1990; Tyler *et al.*, 1994; Saueressig *et al.*, 1995]. Of particular interest in this work are the $^{12}\text{C}/^{13}\text{C}$ kinetic isotope effects (KIEs) for the reactions of methane with Cl and OH radicals, which have also been theoretically evaluated using methods of electronic structure theory [Lasaga and Gibbs, 1991; Melissas and Truhlar, 1993; Tanaka *et al.*, 1996]. Unfortunately, the currently accepted experimental KIEs for these reactions are

Table 1. Comparison of $^{12}\text{C}/^{13}\text{C}$ Kinetic Isotope Effects* for the $\text{CH}_4 + \text{X}$ Reactions.

Type	KIE	Reference
X = OH		
Experimental	5.4 ± 0.9	Cantrell <i>et al.</i> [1990]
Calculated	7	Lasaga and Gibbs [1991]
Calculated	5	Melissas and Truhlar [1993]
Calculated	10	this work
X = Cl		
Experimental	66 ± 2	Saueressig <i>et al.</i> [1995]
Calculated	26	Tanaka <i>et al.</i> [1996]
Calculated	34	this work

*Values at 300 K given in parts per mil (‰).

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each from a single research group and thus far have not been confirmed by others. Worse, for the $\text{CH}_4 + \text{Cl}$ reaction, there is a significant discrepancy between the observed and previously calculated KIEs (Table 1), although for the $\text{CH}_4 + \text{OH}$ reaction, there is better agreement between the measured KIE and the previously reported theoretical KIEs. Note that we use the parts per mil basis ($\%o = 10^3[\text{KIE} - 1]$) to express numerical KIE values throughout this work.

Recent measurements have shown that the $^{13}\text{CH}_4/^{12}\text{CH}_4$ concentration ratio (or equivalently, $\delta^{13}\text{CH}_4$) in upper tropospheric and lower stratospheric air is greater than it is at the surface [Wahlen *et al.*, 1989; Brenninkmeijer *et al.*, 1995; Tyler, unpublished results]. However, modeling studies, based on the current understanding of the carbon isotopic fractionations in the sources and sinks of methane, show relatively small enrichment in stratospheric $\delta^{13}\text{CH}_4$ [Gupta *et al.*, 1996]. As will be discussed further, the model results are sensitive to the actual KIEs used.

In this study, we attempt to calculate converged KIEs for the $\text{CH}_4 + \text{OH}$ and $\text{CH}_4 + \text{Cl}$ reactions by systematically increasing the level of electronic structure theory used. Using these results, we then address the question of whether the previously calculated KIEs are stable with respect to changes in the theoretical methodology used, especially to the extent to which electron correlation [Raghavachari, 1991] is considered. Of ultimate interest is whether the apparent agreement and the apparent discrepancy (for the respective $\text{CH}_4 + \text{OH}$ and $\text{CH}_4 + \text{Cl}$ reactions) between the previously calculated and observed KIEs (Table 1) can be confirmed, since a significant discrepancy would strongly suggest the need for further measurements. Our conclusion is that ($\%o$) discrepancies of about a factor of two (in opposite directions) exist between our best calculations and experiment for these two H-abstraction reactions.

Theoretical Methods

Within the framework of conventional transition state theory (TST), and making use of the rigid rotor, harmonic oscillator approximation, the $^{12}\text{C}/^{13}\text{C}$ kinetic isotope effects for the $\text{CH}_4 + \text{X}$ reactions ($\text{X} = \text{OH}$ or Cl) can be expressed [Bigeleisen and Wolfsberg, 1958] as

$$\text{KIE} = \left[\prod_i^{3N^\ddagger-6} \frac{v_{1i}^\ddagger}{v_{2i}^\ddagger} \prod_i^{3N-6} \frac{v_{2i}}{v_{1i}} \right] \left[\prod_i^{3N^\ddagger-7} \frac{\sinh(u_{2i}^\ddagger/2)}{\sinh(u_{1i}^\ddagger/2)} \prod_i^{3N-6} \frac{\sinh(u_{1i}/2)}{\sinh(u_{2i}/2)} \right] \times \left[\frac{1 + |u_{1L}^\ddagger|^2/24}{1 + |u_{2L}^\ddagger|^2/24} \right] \quad (1)$$

where the subscripts 1 and 2 refer respectively to the lighter (^{12}C -containing) and heavier (^{13}C -containing) molecular species. The first bracketed term arises from the application of the Teller-Redlich product rule to the classical translational and rotational partition functions; the second bracketed term arises from the quantum mechanical harmonic oscillator partition functions; and the last bracketed term is the one-dimensional Wigner tunneling correction. The superscript \ddagger refers to quantities corresponding to the transition state structures CH_4X , while non-superscripted quantities refer to CH_4 . Also, N refers to the number of atoms, v_i refers to harmonic vibrational frequencies (one of which v_L^\ddagger for each transition state structure is imaginary), and $u_i = hv_i/kT$, where

h is Planck's constant, k is Boltzmann's constant, and T is absolute temperature.

As can be seen from equation (1), the basic inputs required are the sets of v_i for CH_4 and CH_4X . These were derived by diagonalizing the appropriately mass-weighted Cartesian force constant matrices of CH_4 and CH_4X , which were calculated at four levels of *ab initio* molecular orbital theory [Hehre *et al.*, 1986; Frisch *et al.*, 1995] that include the effects of electron correlation explicitly. In order of increasing sophistication (and if the basis set requirements are met, increasing accuracy), these levels are: MP2, MP4(SDQ), QCISD, and QCISD(T), where MP2 denotes Moller-Plesset perturbation theory truncated after 2nd order, MP4(SDQ) means truncation after 4th order within the space of single, double, and quadruple molecular orbital substitutions, QCISD denotes quadratic configuration interaction in the space of single and double substitutions, and QCISD(T) means a perturbational correction for triple substitutions is also included [Pople *et al.*, 1987; Raghavachari, 1991]. So that the effects of basis set size could be assessed, at each level of theory, two standard basis sets were employed: the medium-sized 6-311G(d,p) basis set and the extended 6-311+G(2df,p) basis set [Curtiss *et al.*, 1990].

Results and Discussion

Before calculating a given set of harmonic vibrational frequencies using one of the eight theoretical methods defined above, for CH_4 or for one of the transition state structures (CH_4OH or CH_4Cl), its equilibrium or saddle-point geometry was first fully (energy) optimized. The resulting geometries of the $\text{H}_3\text{C}\cdots\text{H}\cdots\text{Cl}$ transition state structures belong to the C_{3v} point group, whereas the geometries of the $\text{H}_3\text{C}\cdots\text{H}\cdots\text{OH}$ structures belong to the C_s (or C_1) point group, where a mirror plane containing an $\text{HC}\cdots\text{H}\cdots\text{OH}$ moiety exists (or nearly exists). It was verified at MP2 that slight displacements of a given transition state structure along its imaginary normal mode, in either direction along the reaction coordinate, leads to the desired reactants ($\text{CH}_4 + \text{X}$) or products ($\text{CH}_3 + \text{HX}$). As is evident from the H-abstraction bond lengths in the transition state structures, where the optimized $\text{H}_3\text{C}\cdots\text{H}\cdots\text{X}$ distances are about 0.2 Å longer for $\text{X}=\text{Cl}$ than for $\text{X}=\text{OH}$, the $\text{H}_3\text{C}\cdots\text{H}\cdots\text{Cl}$ transition state structure can be described as

Table 2. Calculated $^{12}\text{C}/^{13}\text{C}$ Kinetic Isotope Effects* for the $\text{CH}_4 + \text{X}$ Reactions.

Method \ Basis Set	6-311G(d,p)	6-311+G(2df,p)
X = OH		
MP2	7.9	6.2
MP4(SDQ)	10.2	10.7
QCISD	13.0	12.4
QCISD(T)	11.8	10.2
X = Cl		
MP2	29.0	29.3
MP4(SDQ)	26.3	27.9
QCISD	27.7	29.3
QCISD(T)	31.2	33.6

*Values at 300 K given in parts per mil ($\%o$).

occurring "later" along its reaction coordinate (*i.e.*, its structure is more "product-like") than the $\text{H}_3\text{C}\cdots\text{H}\cdots\text{O}\text{H}$ structure does along its H-abstraction reaction coordinate, which is in line with the fact that, while H-abstraction by OH is about 14 kcal/mol exothermic (300 K), the analogous $\text{CH}_4 + \text{Cl}$ reaction is endothermic by about 2 kcal/mol [Atkinson *et al.*, 1992]. Of more direct relevance to KIEs is that the longer $\text{H}_3\text{C}\cdots\text{HX}$ bond distance for $\text{X}=\text{Cl}$ results in significantly more movement by carbon in the imaginary normal mode, which leads to $\nu_{1L}^\ddagger - \nu_{2L}^\ddagger$ shifts of 8i-10i cm^{-1} (depending on which theoretical method is used), whereas the analogous shifts for $\text{X}=\text{OH}$ are in the 0-1i cm^{-1} range. Because the Wigner tunneling correction depends only on ν_{1L}^\ddagger , the tunneling factors in the KIEs for $\text{X}=\text{Cl}$ are about an order of magnitude larger (% basis) than are the analogous tunneling factors in the $\text{X}=\text{OH}$ KIEs; similar findings are made for the $\nu_{1L}^\ddagger/\nu_{2L}^\ddagger$ factors (in the first bracketed term in equation (1)).

As might be expected from the above comparisons, at 300 K the $^{12}\text{C}/^{13}\text{C}$ kinetic isotope effect for H-abstraction by Cl is consistently calculated to be at least two times larger (% basis) than the KIE for H-abstraction by OH (Table 2). According to our best (QCISD(T)/6-311+G(2df,p)) calculations, at 300 K the KIE for H-abstraction by OH is 10%, while that for Cl is 34%. As compared to the analogous experimentally derived KIEs, 5% and 66%, respectively, the theoretical values are different by factors of 2, higher for OH but lower for Cl. On an absolute scale the KIE(calc.)-KIE(obs.) difference is +5% for OH but -32% for Cl. The discrepancy for H-abstraction by Cl must be regarded as significant, and it is suggested that further experimental study of the $\text{CH}_4 + \text{Cl}$ KIE is warranted. While the +5% difference for H-abstraction by OH may also be indicative that further experimental study is needed, it must be remembered that our calculations have been carried out within the TST framework with the simple Wigner tunneling correction. Nevertheless, for H-abstraction by OH, Melissas and Truhlar [1993] have found that the differences between the KIEs calculated at MP-SAC2 (empirically scaled MP2)--using both TST/Wigner and interpolated variational transition state theory with a multidimensional small curvature tunneling correction (IVTST/SCT)--are nearly negligible over a wide (250-1000 K) temperature range. Their detailed factorization analyses show (where direct comparisons between TST/Wigner and IVTST/SCT can be made) that while some of the individual factors (*e.g.*, tunneling) contributing to the KIEs are noticeably different, taken together the various differences tend to counteract.

The KIEs given in Table 2 are only for 300 K, so the temperature dependencies (150-1000 K) of the KIEs at the four levels of theory employed are displayed in Figure 1 for the larger basis set. While the theoretical KIEs for $\text{CH}_4 + \text{Cl}$ increase monotonically with decreasing temperature, the KIE curves for $\text{CH}_4 + \text{OH}$ begin to level off at lower temperatures, their slopes eventually changing sign. In fact, at very low temperatures, the theoretical KIEs for H-abstraction by OH change from normal to inverted (*i.e.*, $^{13}\text{CH}_4 + \text{OH}$ is faster). This low temperature behavior can be attributed to the zero-point factors in the vibrational partition functions, whose contributions to the $\text{CH}_4 + \text{OH}$ KIEs become increasingly inverted (smaller) as the temperature decreases, which is opposite to their behavior in the $\text{CH}_4 + \text{Cl}$ KIEs. Compared to the KIE curves for $\text{CH}_4 + \text{OH}$, the KIE curves for $\text{CH}_4 + \text{Cl}$ rise relatively rapidly in the atmospheric temperature region (as the temperature decreases), which is in qualitative agreement

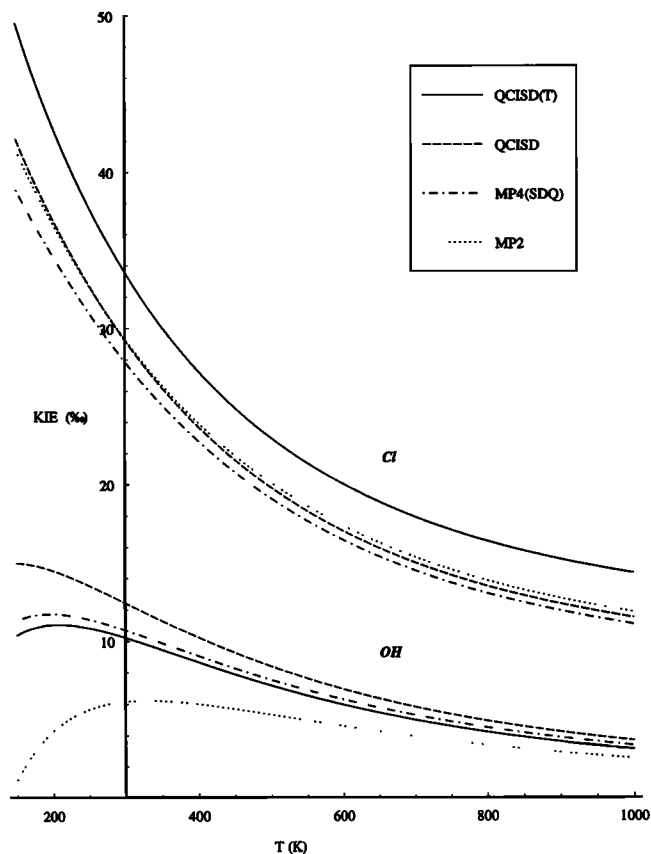


Figure 1. Temperature dependence of the KIEs for the $\text{CH}_4 + \text{OH}$ and $\text{CH}_4 + \text{Cl}$ reactions at four correlated levels of theory calculated using the 6-311+G(2df,p) basis set.

with the observed trends [Cantrell *et al.*, 1990; Saueressig *et al.*, 1995].

Results from two preliminary simulations performed using a two dimensional global tropospheric model [Gupta, 1996] show that the atmospheric distribution of $\delta^{13}\text{CH}_4$ is sensitive to the magnitudes of the KIEs used. For the first simulation, the measured KIEs of the $\text{CH}_4 + \text{OH}$ and $\text{CH}_4 + \text{Cl}$ reactions (Table 1) were used, and for the second simulation our calculated KIEs of 10% and 34%, respectively, were used. For both simulations, the temperature dependence of the $\text{CH}_4 + \text{Cl}$ KIE was included. With use of the latitudinal distributions of the total surface sources of CH_4 and $\delta^{13}\text{CH}_4$ [Gupta *et al.*, 1996], the calculated surface $\delta^{13}\text{CH}_4$ for January at 50°N was -47.5% in the first simulation, but -44.1% in the second. On the other hand, calculations of the relative enrichment of $\delta^{13}\text{CH}_4$ in the lower stratosphere with respect to the corresponding surface value were found to be rather insensitive to the KIEs used. For example, for March at 50°N , in the first simulation the relative enrichment in $\delta^{13}\text{CH}_4$ at 18 km with respect to the surface value was 1.10%, while in the second simulation it was 1.17%. In both simulations, the calculated relative enrichments in $\delta^{13}\text{CH}_4$ in the upper troposphere and lower stratosphere with respect to the corresponding surface values were seasonally dependent. For example, in the second simulation the relative enrichment in $\delta^{13}\text{CH}_4$ at 18 km for August at 50°N was 0.68%. Without including seasonal variations in the methane surface flux, the seasonal variation in the simulated relative enrichment of $\delta^{13}\text{CH}_4$ in the stratosphere results entirely from seasonal changes in the concentrations of OH and Cl radicals.

At present we are refining the simulations to model better the surface and stratospheric $\delta^{13}\text{C}$. We are also currently calculating the H/D kinetic isotope effects for the reactions of $^{12}\text{CH}_3\text{D}$ with OH and Cl because, in addition to isotopic information for $^{13}\text{CH}_4$, knowledge of the kinetic fractionation of $^{12}\text{CH}_3\text{D}$ (by far the most abundant form of deuterated atmospheric CH_4), further helps in constraining the global budget of atmospheric CH_4 . Inclusion of the reactions of $^{12}\text{CH}_3\text{D}$ in studying the global CH_4 cycle becomes especially valuable in situations where the $\delta^{13}\text{C}$ values of the various methane sources overlap one another. This work, as well as a more detailed description and analysis of our $^{12}\text{C}/^{13}\text{C}$ kinetic isotope effect calculations, will be reported elsewhere.

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