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Communication

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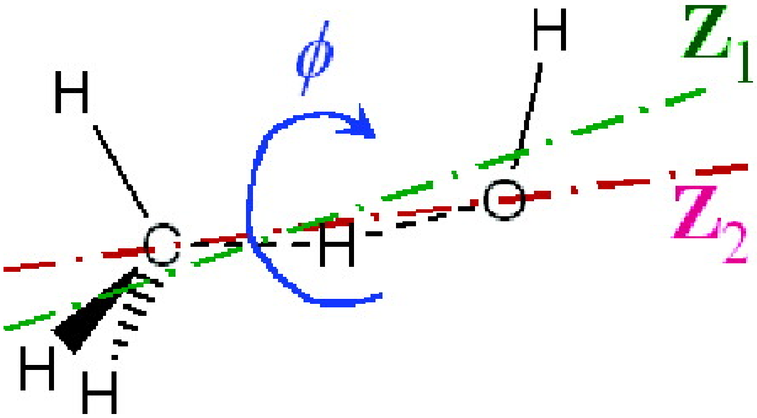

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# Temperature Dependence of Carbon-13 Kinetic Isotope Effects of Importance to Global Climate Change

Hai Lin, Yan Zhao, Benjamin A. Ellingson, Jingzhi Pu, and Donald G. Truhlar*

*Department of Chemistry and Supercomputer Institute, University of Minnesota,*
*Minneapolis, Minnesota 55455-0431*

Received November 1, 2004; E-mail: truhlar@umn.edu

The major atmospheric sink for the greenhouse gas methane is reaction with the OH radical. Computer simulations that use the $^{13}$C isotopic composition of atmospheric methane as a constraint have been performed to quantify the global distribution of methane sources and sinks; the output from these simulations is found[1] to be sensitive to the input $^{12}$C/$^{13}$C kinetic isotope effect (KIE) for the reaction OH + $CH_4 \rightarrow H_2O + CH_3$. Such a situation calls for accurate knowledge of the $^{12}$C/$^{13}$C KIE and its temperature dependence in the whole atmospherically important temperature range. Unfortunately the temperature dependence is smaller than the experimental error bars.[2,3]

Theoretical investigations[4−7] on the $^{12}$C/$^{13}$C KIE for have also been carried out, but the results show large variations in the magnitude of the KIE and even larger variations in its temperature dependence. For example, the calculations by Lasaga and Gibbs[4] and by Gupta et al.[6] were based on conventional transition state theory (TST) with one-dimensional tunneling corrections, and they both predicted very flat temperature dependence (see Figure 1). In this work, we address this problem by direct dynamics calculations based on variational transition state theory with multidimensional tunneling contributions (VTST/MT).[8−10] The potential energy surfaces (PESs) were generated at different levels of electronic structure theory, in particular, the hybrid density functional theory (HDFT) method MPW1K[11,12] using the MG3S[12] basis set and the recently developed doubly hybrid density functional theory[13] (DHDFT), in particular the MC3MPW and MC3BB models. Comparisons of our calculated KIEs with experimental data and theoretical values in the literature reveal the critical contributions of multidimensional tunneling and torsional anharmonicity.

The electronic structure calculations were performed by use of the *Gaussian*03[14] and MULTILEVEL[15] programs. Figure 2 shows the optimized saddle point. Dynamics calculations were carried out employing the GAUSSRATE[16] and MULTILEVELRATE[17] packages via direct dynamics calculations, i.e. the electronic structure calculations that define the PES were performed on the fly. To follow the minimum energy path (MEP) that connects the reactants to products in mass-scaled coordinates, which were scaled to a reduced mass $\mu$ of 1 amu, a step size of 0.005 $a_0$ was used for the gradient, and a new Hessian was calculated every 0.05 $a_0$ along the MEP. The reaction path was calculated out to 3.0 $a_0$ on the reactant side and to 1.5 to 3.0 $a_0$ on the product side to ensure convergence for the KIE. We included the electronic excited $^2\Pi_{1/2}$ states of OH with excitation energy of 140 cm$^{-1}$ in calculating the reactant partition functions. The generalized normal-mode analyses were carried out using the redundant internal coordinates as used in ref 18, and the harmonic approximation was employed for all modes except the internal rotational mode, which was handled by the hindered rotor RW[19,20] scheme. Multidimensional tunneling was included by the small curvature tunneling (SCT) method.[8,10]

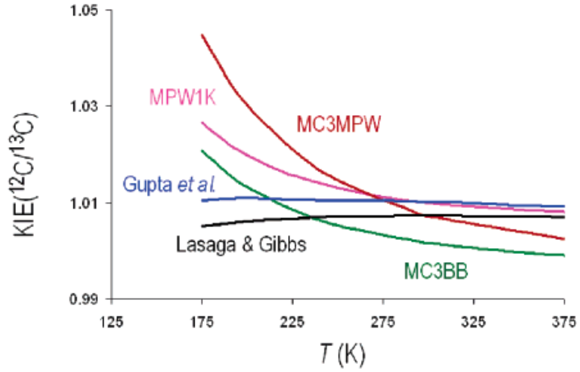
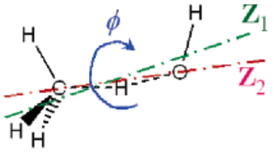


***Figure 1.*** Comparisons of $^{12}$C/$^{13}$C KIE and its temperature dependence for the reaction OH + $CH_4 \rightarrow CH_3 + H_2O$ computed in this work and in the literature.



| | $R_{CH}$ | $R_{HO}$ | $\theta_{CHO}$ | $V^\ddagger$ | $\Delta E$ |
|---|---|---|---|---|---|
| MPW1K | 1.22 | 1.28 | 173 | 7.3 | -10.2 |
| MC3MPW | 1.19 | 1.33 | 173 | 6.2 | -12.6 |
| MC3BB | 1.19 | 1.32 | 173 | 6.1 | -11.8 |

***Figure 2.*** Saddle point optimized at the MPW1K, MC3MPW, and MC3BB levels of theory. The bond distances (Å) and angle (deg) involving the H atom that is being transferred are given, as well as the zero-point-exclusive barrier height and reaction energy in kcal/mol. For the torsional mode, the RW scheme determines the internal rotational axis to be the line $\mathbf{Z}_1$ through the center of mass of the whole system. Also shown is the line $\mathbf{Z}_2$ connecting the C and O atoms, which does not necessarily pass through the center of mass of the whole system. Note that $\mathbf{Z}_1$ depends on isotopic masses and PES but $\mathbf{Z}_2$ does not.

The $\mathbf{Z}_1$ axis used in the RW scheme for the hindered rotation is illustrated in Figure 2. This axis, which is determined by orthogonality to the other normal modes and to translation and rotation,[19] does not pass through the C atom, and therefore, the hindered rotation contributes to the $^{12}$C/$^{13}$C KIE. Such contributions are not possible if one chooses the $\mathbf{Z}_2$ axis passing through the C and O atoms, which is the conventional[21] choice.

The KIEs calculated in this work are plotted in Figure 1. Although the different PESs yield different KIEs, the temperature dependences that we obtained are similar [ranging −6 to −13 part per thousand (ppt), as defined in the footnote *a* of Table 1], and they are qualitatively different from those in refs 4 and 6. Table 1 compares the final calculations (denoted Anharm), additional calculations using the harmonic approximation for all modes (denoted Harm), and the experimental results.

Several conclusions emerge from the results in Table 1. First, let us focus on the MC3BB calculations. Looking at the harmonic results, one finds that although the TST KIE is close to the experimental values, the temperature dependence is +1 ppt, i.e., the KIE decreases as temperature decreases. The inclusion of the

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**Table 1.** $^{12}C/^{13}C$ KIE and Its Temperature Dependence[a]

| | | KIE(296 K) | | temperature dependence | |
|---|---|---|---|---|---|
| exp (ref 2) | | 1.004 | | not available | |
| exp (ref 3) | | 1.005 | | not available | |
| Cal | | Harm | Anharm | Harm | Anharm |
| MC3BB | TST | 1.006 | 0.986 | +1 | +1 |
| | TST/W | 1.006 | 0.986 | +1 | +1 |
| | CVT | 1.026 | 0.994 | −1 | −2 |
| | CVT/MT | 1.036 | 1.002 | −6 | −7 |
| MC3MPW | CVT/MT | 1.042 | 1.008 | −13 | −13 |
| MPW1K | CVT/MT | 1.036 | 1.010 | −6 | −6 |

[a] Temperature dependence is defined by [1 − KIE(225 K)/KIE(296 K)] × 1000. TST stands for conventional transition state theory, W for one-dimensional Wigner tunneling, CVT for canonical variational transition state theory, and MT for multidimensional tunneling. Harm denotes that all vibrational modes were treated harmonically in curvilinear coordinates, and Anharm denotes the use of the hindered rotor treatment for the torsional mode.

Wigner[22] one-dimensional tunneling correction does not change the situation. These findings are similar to those of Gupta et al.[6] in their earlier study using different levels of electronic structure calculations. Thus, although the values of temperature dependence are quantitatively sensitive to the shapes of the PES, as computed from different levels of electronic structure theory, the qualitative trend does not seem to be sensitive to the PES.

Improvements in dynamical theory are more important. The improved dynamics calculations, employing VTST, do change the sign of the temperature dependence from unusual (+1 ppt) to normal (−1 ppt); the trend is further significantly enhanced (−6 ppt) by inclusion of multidimensional tunneling contributions[8−10] that consider the effects of reaction path curvature that couple the motion along reaction coordinates to motions of the transverse normal mode vibrations. Such couplings are responsible for corner-cutting paths for tunneling.[9,23]

The harmonic KIE value is larger than the experimental results. The reason is that a very anharmonic vibration, the torsion (see Figure 2), has been treated by the harmonic approximation when computing the vibrational partition functions. The barrier height for this torsional mode is very low, ranging from 8 to 33 $cm^{-1}$ (depending on the PES) at the saddle point and does not change much along the MEP. Since $k_BT$ (where $k_B$ is Boltzmann's constant and $T$ is temperature) is near 140 $cm^{-1}$ at 200 K and is even larger at higher temperature, the situation here is expected to be closer to the free rotor limit than to the harmonic oscillator limit. Using the harmonic approximation, the contribution from the torsional mode to the KIE is negligibly small ($<0.01\%$). The inclusion of anharmonicity has a large effect on the magnitude of the KIE, as can be seen in Table 1; the KIE is now much closer to experimental data, although the agreement is not yet perfect. The improvement is also obtained in MC3MPW and MPW1K calculations. Moreover, there is no qualitative change in the temperature dependence, again confirming our conclusion that the temperature dependence is qualitatively insensitive to the PES, provided the PES is qualitatively correct.

Finally, we can now understand where two earlier studies that were also based on VTST/MT calculations went wrong. The deficiency in the work by Melissas and Truhlar[5] is that the frequencies along the reaction path were obtained by interpolation from very limited electronic structure data, and this resulted in a spurious difference of the high-frequency-mode contribution at the variational transition state from that at the saddle point, and this error canceled the temperature dependence due to tunneling. Thus, although the resulting KIE is close to experimental values, the temperature dependence is almost negligible in the temperature range considered here. The more recent work by Espinosa-García and Corchado[7] used an analytic potential energy surface (APES) and treated the internal torsion using the RO[19,20] hindered rotor scheme. Although their temperature dependence is similar to ours, their KIE values are much larger, and we found that this is the case even if the RW scheme is used. We found two notable differences: (1) less contribution by the torsion, e.g. the torsion contribution to the TST KIE at 296 K is 0.991 using the APES and is 0.981 using MPW1K and (2) more contribution by tunneling, e.g. the SCT tunneling contributes 1.011 (APES) and 1.005 (MPW1K) to the CVT/SCT KIE at 296 K. Thus, their larger KIEs are due to the different shape of their PES.

We have studied the $^{12}C/^{13}C$ KIE and its $T$ dependence for the reaction of methane with OH radical. We found that: (1) an advanced level of dynamical theory, VTST/MT, is necessary for quantitative prediction of the $T$ dependence, and (2) the inclusion of torsion anharmonicity is critical even for qualitative prediction of the KIE magnitude. There is a large error in the calculated $^{12}C/^{13}C$ KIE if one assumes that the axis for an internal rotation lies on the bond axis. Our finding of a significant $T$ dependence of this important KIE is a result that should be incorporated into future atmospheric models.

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**Supporting Information Available:** Calculated rate constants and KIEs. This material is available free of charge via the Internet at http://pubs.acs.org.

## References

(1) McCarthy, M. C.; Boering, K. A.; Rice, A. L.; Tyler, S. C.; Connell, P.; Atlas, E. *J. Geophys. Res.* **2003**, *108*, 4461.
(2) Cantrell, C. A.; Shetter, R. E.; McDaniel, A. H.; Calvert, J. G.; Davidson, J. A.; Loew, D. C.; Tyler, S. C.; Cicerone, R. J.; Greenberg, J. P. *J. Geophys. Res.* **1990**, *95*, 22456.
(3) Saueressig, G.; Crowley, J. N.; Bergamaschi, P.; Brühl, C.; Brenninkmeijer, C. A. M.; Fischer, H. *J. Geophys. Res.* **2001**, *106*, 23127.
(4) Lasaga, A. C.; Gibbs, G. V. *Geophys. Res. Lett.* **1991**, *18*, 1217.
(5) Melissas, V. S.; Truhlar, D. G. *Journal of Chemical Physics* **1993**, *99*, 3542.
(6) Gupta, M. L.; McGrath, M. P.; Cicerone, R. J.; Rowland, F. S.; Wolfsberg, M. *Geophys. Res. Lett.* **1997**, *24*, 2761.
(7) Espinosa-García, J.; Corchado, J. C. *J. Chem. Phys.* **2000**, *112*, 5731.
(8) Truhlar, D. G.; Gordon, M. S. *Science* **1990**, *249*, 491.
(9) Liu, Y. P.; Lynch, G. C.; Truong, T. N.; Lu, D. H.; Truhlar, D. G.; Garrett, B. C. *J. Am. Chem. Soc.* **1993**, *115*, 2408.
(10) Truhlar, D. G.; Garrett, B. C.; Klippenstein, S. J. *J. Phys. Chem.* **1996**, *100*, 12771.
(11) Lynch, B. J.; Fast, P. L.; Harris, M.; Truhlar, D. G. *J. Phys. Chem. A* **2000**, *104*, 4811.
(12) Lynch, B. J.; Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2003**, *107*, 1384.
(13) Zhao, Y.; Lynch, B. J.; Truhlar, D. G. *J. Phys. Chem. A* **2004**, *108*, 4786.
(14) Frisch, M. J. et al. *Gaussian03*; Gaussian, Inc.: Pittsburgh, PA, 2003.
(15) Zhao, Y.; Rodgers, J. M.; Lynch, B. J.; Fast, P. J.; Chuang, Y.-Y.; Pu, J.; Truhlar, D. G. MULTILEVEL; Version 4.0/G03. University of Minnesota: Minneapolis, 2003.
(16) Corchado, J. C.; Chuang, Y.-Y.; Coitiño, E. L.; Truhlar, D. G. GAUSSRATE; Version 9.1. University of Minnesota: Minneapolis, 2003.
(17) Pu, J.; Corchado, J. C.; Lynch, B. J.; Fast, P. L.; Truhlar, D. G. MULTILEVELRATE; Version 9.3. University of Minnesota: Minneapolis, 2004.
(18) Albu, T. V.; Corchado, J. C.; Truhlar, D. G. *J. Phys. Chem. A* **2001**, *105*, 8465.
(19) Truhlar, D. G. *J. Comput. Chem.* **1991**, *12*, 266.
(20) Chuang, Y.-Y.; Truhlar, D. G. *J. Chem. Phys.* **2000**, *112*, 1221.
(21) Wilson, E. B.; Decius, J. C.; Cross, P. C. *Molecular Vibrations*; McGraw-Hill: New York, 1955.
(22) Wigner, E. *Z. Phys. Chem. B* **1932**, *19*, 203.
(23) Skodje, R. T.; Truhlar, D. G.; Garrett, B. C. *J. Chem. Phys.* **1982**, *77*, 5955.

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