

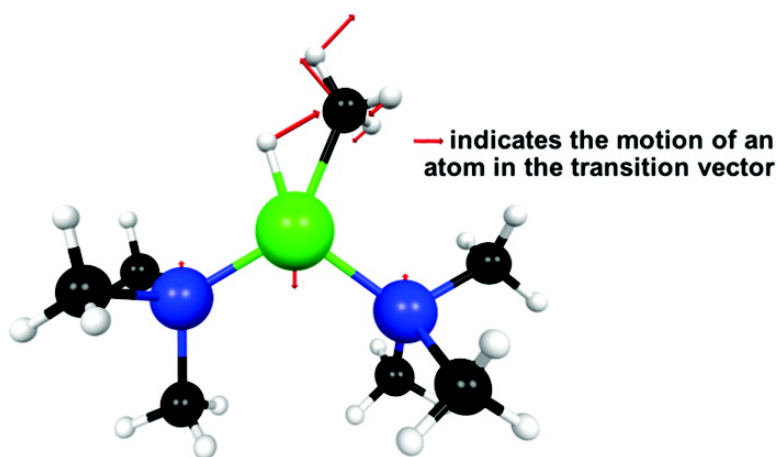
Communication

Calculations Find That Tunneling Plays a Major Role in the Reductive Elimination of Methane from Hydridomethylbis(trimethylphosphine)platinum: How to Confirm This Computational Prediction Experimentally

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Calculations Find That Tunneling Plays a Major Role in the Reductive Elimination of Methane from Hydridomethylbis(trimethylphosphine)platinum: How to Confirm This Computational Prediction Experimentally

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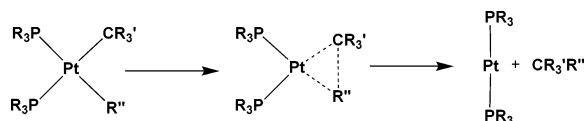
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Activation of methane, by oxidative addition of a C–H bond to a transition metal complex, and the reverse process, reductive elimination of methane, are organometallic reactions of fundamental importance¹ and great current interest.² Kinetic and equilibrium H/D isotope effects have been measured for a number of these reactions.³ Although calculations that include tunneling corrections have been reported on a model oxidative addition reaction,⁴ to the best of our knowledge, there has been no consideration of how quantum mechanical tunneling might affect the kinetic isotope effects (KIEs) for these reactions.

In this Communication, we report the results of our calculations on the reductive elimination of methane from hydridomethylbis(trimethylphosphine)platinum (**1d**). We chose this reaction because of its mechanistic simplicity. Through rate studies on **1a** and **1b**, Halpern has shown that the reaction proceeds in one step, without prior phosphine ligand dissociation.⁵ Previous calculations on **1c**^{6a} and **1d**^{6b} have confirmed that direct reductive elimination to form a weak complex between (R₃P)₂Pt and methane is strongly endothermic and favored by a significant margin over a mechanism involving phosphine dissociation.

Halpern measured a primary H/D KIE of $k(\mathbf{1a})/k(\mathbf{1b}) = 3.3 \pm 0.3$ for reductive elimination from **1a** at 248 K in toluene.⁵ Despite the modest size of this KIE, the calculations reported in this Communication find that tunneling has a significant effect on not only the rate of reductive elimination of methane from **1d** but also the primary and secondary H/D KIEs for this reaction. The results of our calculations lead us to propose a purely experimental test of our computational conclusion, that tunneling plays an important role in the reductive elimination of methane from **1d**.



- 1a, R = Ph, R' = R'' = H
 b, R = Ph, R' = H, R'' = D
 c, R = R' = R'' = H
 d, R = CH₃, R' = R'' = H
 e, R = CH₃, R' = D, R'' = H
 f, R = CH₃, R' = H, R'' = D
 g, R = CH₃, R' = R'' = D

- 2a, R = Ph, R' = R'' = H
 b, R = Ph, R' = H, R'' = D
 c, R = R' = R'' = H
 d, R = CH₃, R' = R'' = H
 e, R = CH₃, R' = D, R'' = H
 f, R = CH₃, R' = H, R'' = D
 g, R = CH₃, R' = R'' = D

As in our previous studies,⁶ calculations were performed using the B3LYP version of DFT, which is comprised of Becke's hybrid three-parameter functional⁷ and the correlation functional of Lee, Yang, and Parr.⁸ The relativistic, compact, effective core potential and valence basis set of Stevens, Basch, Krauss, and Jasien⁹ were used for platinum. The polarized, Dunning/Huzinaga, double- ζ , D95** basis set¹⁰ was used for all of the other atoms, except for the phosphine methyl hydrogens, for which the 2p polarization functions were omitted. Transition structures were located using

canonical variational transition state theory (CVT).¹¹ Quantum effects on the reaction dynamics were computed, using the small-curvature tunneling (SCT) approximation.¹² Direct dynamics calculations were carried out with GAUSSRATE¹³ as the interface between Gaussian 03¹⁴ and POLYRATE.¹⁵

Without inclusion of tunneling, the CVT rate constant for reductive elimination of methane from **1d** at 248 K was computed to be $k = 1.27 \times 10^{-4} \text{ s}^{-1}$. However, inclusion of small-curvature tunneling was found to give a CVT + SCT rate constant of $k(\mathbf{1d}) = 5.11 \times 10^{-4} \text{ s}^{-1}$, which is about a factor of 4 larger than the CVT rate constant. The CVT + SCT rate constant is in better agreement than the CVT rate constant with Halpern's experimental value of $k(\mathbf{1a}) = (4.5 \pm 0.5) \times 10^{-4} \text{ s}^{-1}$ for reductive elimination of methane from **1a** at 248 K.⁵

At 248 K, 86.0% of the reductive elimination of methane from **1d** is computed to involve tunneling.¹⁶ Tunneling makes the CVT + SCT values of both $E_a = 18.1 \text{ kcal/mol}$ and $\log A = 12.5$ at 248 K smaller than the CVT values of $E_a = 19.8 \text{ kcal/mol}$ and $\log A = 13.4$ at this temperature. Thus, at 248 K, thermally activated tunneling through the reaction barrier lowers the calculated E_a by 1.7 kcal/mol but at the expense of reducing the A factor for reaction by nearly an order of magnitude.

The amount of energy that is available for thermally activated tunneling depends on the temperature. Therefore, the CVT + SCT activation parameters for reductive elimination of methane from **1d** are temperature-dependent. They decrease from $E_a = 18.6 \text{ kcal/mol}$ and $\log A = 13.0$ at 300 K to $E_a = 17.4 \text{ kcal/mol}$ and $\log A = 11.8$ at 200 K. The temperature dependence of E_a and A can be seen in the change in the slope and intercept of the Arrhenius plot of the CVT + SCT rate constants in Figure 1 of the Supporting Information.

A curved Arrhenius plot is one signature of a reaction that involves tunneling,¹⁷ but the importance of tunneling in a reaction is more frequently inferred from the H/D KIEs.¹⁸ For reductive elimination of methane from **1d**, without inclusion of tunneling, the primary KIE at 248 K is computed to be only $k(\mathbf{1d})/k(\mathbf{1f}) = 2.26$ by CVT calculations. However, because deuterium tunnels less effectively than protium,^{17,18} our CVT + SCT calculations give a primary KIE of $k(\mathbf{1d})/k(\mathbf{1f}) = 4.12$ at 248 K.

The measured, primary H/D KIE of $k(\mathbf{1a})/k(\mathbf{1b}) = 3.3 \pm 0.3$ at 248 K⁵ is about midway between the calculated CVT and CVT + SCT values for $k(\mathbf{1d})/k(\mathbf{1f})$. Consequently, comparison with experiment does not provide convincing evidence that the higher H/D KIE, computed for $k(\mathbf{1d})/k(\mathbf{1f})$ when tunneling is included, actually is correct.

Is there a purely experimental way of verifying the importance of tunneling in the reductive elimination of methane from **1**, without having to rely on comparisons between calculated and observed rate constants or KIEs? For example, we have recently pointed out¹⁹ that $k_H/k_D = 0.1 \exp(2.5 \text{ kcal mol}^{-1}/RT)$ for the measured

temperature dependence of the primary H/D KIE on the rearrangement of 5-methyl-1,3-cyclopentadiene²⁰ provides prima facie evidence for the importance of tunneling in this reaction. The small ratio of A_H/A_D and the large value of $E_a(D) - E_a(H)$ are both indicative of tunneling.^{19,21}

Unfortunately, the CVT + SCT expression for the calculated temperature dependence of the primary H/D KIE on the reductive elimination of methane from **1d** is $k(\mathbf{1d}/\mathbf{1f}) = 0.7 \exp(0.9 \text{ kcal mol}^{-1}/RT)$. The closeness of the computed ratio of A_H/A_D to 1.0 and the relatively small difference between the calculated values of $E_a(D)$ and $E_a(H)$ do not hold out much promise that actual measurement of the temperature dependence of the primary H/D KIE for reductive elimination of methane from **1d** would provide evidence for the importance of tunneling in this reaction.

However, our calculations do predict that measuring $k(\mathbf{1d})/k(\mathbf{1e})$, the secondary KIE on the reaction of **1d**, and comparing it with $k(\mathbf{1f})/k(\mathbf{1g})$, the measured value of the secondary KIE on the reaction of **1f**, should provide a convenient and convincing demonstration that tunneling does, in fact, play an important role in the reductive elimination of methane from **1d**. Without tunneling, the rule of the geometric mean predicts that these two secondary KIEs should be the same; but, with tunneling, these KIEs can, at least in principle, be different.^{21,22}

In fact, as predicted by the rule of the geometric mean, our CVT calculations do find $k(\mathbf{1d})/k(\mathbf{1e}) = 0.99$ and $k(\mathbf{1f})/k(\mathbf{1g}) = 1.00$ to be nearly identical. However, our CVT + SCT calculations, which include tunneling, find that the two secondary KIEs are $k(\mathbf{1d})/k(\mathbf{1e}) = 1.35$ and $k(\mathbf{1f})/k(\mathbf{1g}) = 1.06$. Thus, our calculations predict that these two secondary KIEs will differ by enough for their experimental measurement to show unequivocally that tunneling does play an important role in the reductive elimination of methane from **1d**.

Why is the secondary KIE, $k(\mathbf{1d})/k(\mathbf{1e}) = 1.35$, computed with inclusion of tunneling, so much larger than the value of $k(\mathbf{1d})/k(\mathbf{1e}) = 0.99$, computed without tunneling? An animation of the transition vector (the vibration with an imaginary frequency in the transition structure) for the reductive elimination of methane from **1d**²³ shows that there is motion of the three methyl hydrogens, as the fourth hydrogen is transferred from platinum to carbon. Consequently, replacement of CH_3 in **1d** by CD_3 in **1e** increases the effective mass that moves along the reaction coordinate in the reductive elimination reaction of CHCD_3 from **1e**. Since the rate of tunneling decreases with increasing mass,¹⁷ the rate of reaction of **1e** is significantly slower than that of **1d**, and this is why our SCT + CVT calculations predict a rather large, secondary KIE of $k(\mathbf{1d})/k(\mathbf{1e}) = 1.35$ at 248 K.

Tunneling is not only the cause of the large CVT + SCT value of the secondary H/D KIE for reductive elimination from **1d**, but tunneling is also the reason that the secondary H/D KIE for reductive elimination is predicted to be much smaller for **1f** than for **1d**. Consider the limit in which the effect of replacing H in **1d** with D in **1f** is so large that, in contrast to **1d**, **1f** reacts exclusively by passage over the top of the barrier. If tunneling did not contribute to the rate of the reductive elimination of methane- d_1 from **1f**, the CVT + SCT secondary KIE would be the same as the CVT value of $k(\mathbf{1f})/k(\mathbf{1g}) = 1.00$, rather than the slightly larger value of $k(\mathbf{1f})/k(\mathbf{1g}) = 1.06$ that is actually computed.

In fact, at 248 K, replacement of the Pt–H bond in **1d** by the Pt–D bond in **1f** only reduces the percentage of the reaction that is calculated to occur by tunneling from 86.0% in **1d** to 80.6% in **1f**. Nevertheless, the representative tunneling energies²⁴ at this temperature show that tunneling occurs 0.6 kcal/mol closer to the top of the barrier in the reaction of **1f** than in the reaction of **1d**.

Since tunneling occurs 0.6 kcal/mol closer to the top of the barrier in **1f** than in **1d**, the effect of a CD_3 group on the tunneling rate is much smaller in **1f** than in **1d**.

In summary, our CVT + SCT calculations predict that tunneling should result in a strong violation of the rule of the geometric mean, so that at 248 K the secondary KIE on the rate of reductive elimination of methane from **1d** [$k(\mathbf{1d})/k(\mathbf{1e}) = 1.35$] should be much larger than the secondary KIE for reaction of **1f** [$k(\mathbf{1f})/k(\mathbf{1g}) = 1.06$]. Experimental verification of the large predicted difference between the secondary KIEs for the reductive elimination of methane from **1d** and of methane- d_1 from **1f** would provide purely experimental evidence of the importance of tunneling in the former reaction.

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Supporting Information Available: Optimized geometries, energies, thermal corrections, and harmonic frequencies for **1d**, **2d**, and the transition structure connecting them, CVT and CVT + SCT rate constants for **1d–g** from 100 to 500 K, an Arrhenius plot of the CVT + SCT rate constants for **1d**, and the complete lists of authors for refs 14 and 15. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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