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Computational Investigations into Hydrogen-Atom Abstraction from Rhodium Hydride Complexes by Methyl Radicals in Aqueous Solution

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The controversy in the reported kinetics for the hydrogen-atom abstraction reaction by methyl radicals for *cis*- and *trans*-$[(\mathrm{Cyclam})\mathrm{Rh}^{III}\mathrm{HCl}]^+$ and *trans*-$[(\mathrm{Cyclam})(\mathrm{H_2O})\mathrm{Rh}^{III}\mathrm{H}]^{2+}$ has been resolved by studying several feasible mechanistic pathways with density functional theory. The only low-energy reaction mechanism predicted by these calculations involves a single-step radical-propagation mechanism in which the methyl radical simply abstracts the Rh bound H atom from the complex to form methane and the reduced Rh product. Previous experimental work on the chloride and aquo complexes suggested contradictory kinetic isotope effect (KIE) values of 0.66 ± 0.30 and 1.42 ± 0.07 as well as rate constants for the reaction differing by four orders of magnitude. The calculated mechanism predicts a KIE value of 1.08 and a high reaction rate. The alternative mechanisms are described briefly.

Introduction

Reactions of the type M–R + R′ → M + RR′ have long been known to play an important role in biologically relevant processes such as the Coenzyme B12 system.[1] In an effort to understand the kinetics and subsequent mechanism of these types of reactions, Shaham et al. examined the reaction of $[(\mathrm{NH_3})_5\mathrm{Co}^{III}(\mathrm{CH_3})]^{2+}$ with $^{\cdot}\mathrm{CH_3}$ formed in situ by pulse radiolysis and concluded that the reaction proceeds through a one-step radical-propagation process affording C_2H_6 and $[(\mathrm{NH_3})_5\mathrm{Co}^{II}(\mathrm{OH_2})]^{2+}$.[2] The authors propose two mechanistic routes: (1) Radical attack of the $^{\cdot}\mathrm{CH_3}$ on the carbon atom bound to the metal center; (2) Ligand substitution to form $[(\mathrm{NH_3})_4\mathrm{Co}^{IV}(\mathrm{CH_3})_2]^{2+}$ followed by reductive elimination. While both mechanisms are consistent with the observed concentration dependence of the reaction, the authors noted that the overall rate of the reaction is significantly faster than that of a typical ligand exchange reaction for similar systems and therefore suggested that the route is a direct radical attack (1).

In an effort to test the generality of this mechanism for reactions of M–R with $^{\cdot}\mathrm{CH_3}$, Kats et al. recently examined the reaction between *cis*- and *trans*-$[(\mathrm{Cyclam})\mathrm{Rh}^{III}\mathrm{HCl}]^+$ (Cyclam = 1,4,8,11-tetraazacylclotetradecane) complexes (Figure 1) and $^{\cdot}\mathrm{CH_3}$ (derived in situ from DMSO by radiolysis) to form CH_4.[3] The authors demonstrated that the formation of methane increased with increased complex concentration and that no CH_3Cl was formed during the reaction. Initially, the authors hypothesized that the observed reaction was simply an $^{\cdot}\mathrm{H}$ abstraction to form CH_4 and $[(\mathrm{L})\mathrm{Rh}^{II}\mathrm{Cl}(\mathrm{OH_2})]^+$. In order to confirm that the hydrogen-atom abstraction occurred at the metal center (and not on the ligand) the authors performed a deuterium labeling study, in which the aforementioned reactions were performed with Rh–D complexes. Because $^{\cdot}\mathrm{H}$ abstraction from C–H groups involves a sizeable normal kinetic isotope effect (KIE),[4] the authors expected this experiment to result in a measureable normal KIE. The results of this experiment, however, were more complex and unexpected, as the reaction appears to have an inverse KIE of 0.66 ± 0.30 and an overall rate constant of $2.8 \times 10^5\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$. While these results are intriguing this rate constant is significantly different from that reported by Bakac in 1998 in which the *trans*-$[(\mathrm{Cyclam})(\mathrm{H_2O})\mathrm{Rh}^{III}\mathrm{H}]^{2+}$ complex was observed to react with $^{\cdot}\mathrm{CH_3}$ at a rate of $1 \times 10^9\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$.[5] In an effort to

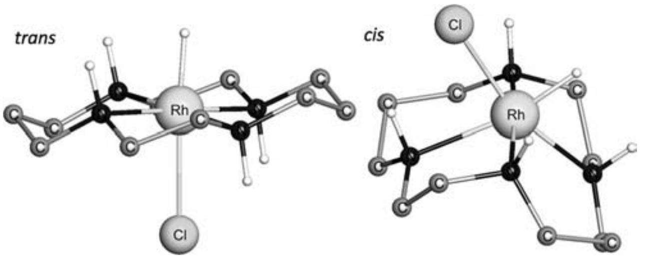

Figure 1. The lowest energy isomers of *trans*- (top) and *cis*-$[(\mathrm{Cyclam})\mathrm{Rh}^{III}\mathrm{HCl}]^+$ (bottom).

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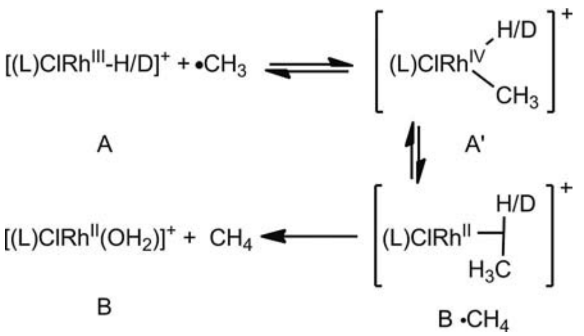
resolve this apparent discrepancy, Pestovsky et al. recently examined the reaction of this $(OH_2)Rh–H$ complex with benzyl and methyl radicals and they report rates of the order of 10^8–10^9 $M^{-1} s^{-1}$ and normal KIE values of 1.4–1.5.[6]

To rationalize the apparent inverse KIE, Kats et al. proposed a reaction mechanism that proceeds through an equilibrium between the octahedral complex and a seven coordinate Rh^{IV} methyl intermediate followed by C–H reductive coupling to form a Rh^{II}–methane complex and subsequent loss of methane, Scheme 1.[3] This reaction mechanism could be at work and could potentially result in the apparent inverse KIE because of the equilibrium step (**A′** → **B·CH₄**) that precedes the rate determining loss of methane.[7]



Scheme 1.

To further complicate the issue, Bakac and coworkers reported that in water *trans*-$[(Cyclam)Rh^{III}HCl]^+$ is converted to *trans*-$[(Cyclam)(H_2O)Rh^{III}H]^{2+}$, as the position *trans* to the hydride is known to be labile (Scheme 2). Therefore while Kats et al. reported a reaction between the chloride complex and methyl radical, they may actually be observing the reaction of the aquo complex with the methyl radical.[6,7]

$$[(L)Rh^{III}HCl]^+ + H_2O \rightleftharpoons [(L)(H_2O)Rh^{III}H]^{2+} + Cl^-$$

Scheme 2.

Here, computational chemistry, namely density functional theory (DFT), provides further insight into these contradictory results and offers a possible reaction mechanism, which leads to a re-examination of some of the experimental results and the conclusions drawn.

Results and Discussion

Beginning with *trans* Rh–HCl, species **A** (Figure 2), the least complicated pathway to the products and the first to be considered is simply the abstraction of $^{\cdot}H$ from Rh–H by $^{\cdot}CH_3$ to form CH_4 in one step (**A** → **B**, Figure 2). The calculated ΔG_{sol} for conversion of **A** to **B** is –42.1 kcal mol⁻¹ (Figure 2). Examination of the potential energy surface (PES) around species **A** and **B** shows a stable van der Waals complex, **A·CH₃** (not shown), in which the $^{\cdot}CH_3$ is still planar and lies above one of the protonated nitrogens of the ligand. Although ΔG_{sol} for species **A·CH₃** is 6.5 kcal mol⁻¹, ΔH_{sol} is actually –1.3 kcal mol⁻¹ demonstrating that the complex is bound, but the unfavorable entropy effects cause the equilibrium to lie toward **A**. A transition state, **TS(AB)** (Figure 3), was found for the H atom abstraction with $\Delta G^{\ddagger}_{sol}$ = 7.1 kcal mol⁻¹, which is again dominated by the entropy ($\Delta H^{\ddagger}_{gas}$ = –1.3 kcal mol⁻¹ with respect to **A**) with $k \approx 3.9 \times 10^7$ $M^{-1} s^{-1}$ using $(k_B T/h)$ $(e^{[-\Delta G^{\ddagger}/RT]})$. The potential energy surface around **TS(AB)** was examined in an attempt to find a stable intermediate with the methyl associated with the hydride, but all structures lead to either species **A·CH₃** or the products CH_4 and **B**, which possibly coordinates a water in its sixth coordination site.

While examining the KIE for this reaction mechanism it is important to point out that despite the commonly held belief reported in a statement by Kats et al. that inverse KIEs cannot arise from elementary reaction steps, this is not the case.[3] In fact, since the H/D splitting (the difference in zero-point energy, ZPE) for $H_3C–H/D$ (2.07 kcal mol⁻¹) is larger than that for Rh–H/D (1.62 kcal mol⁻¹), this single step could result in an inverse KIE if the transition state were significantly product-like, i.e. the Rh–H bond is broken and the C–H bond formed.[8]

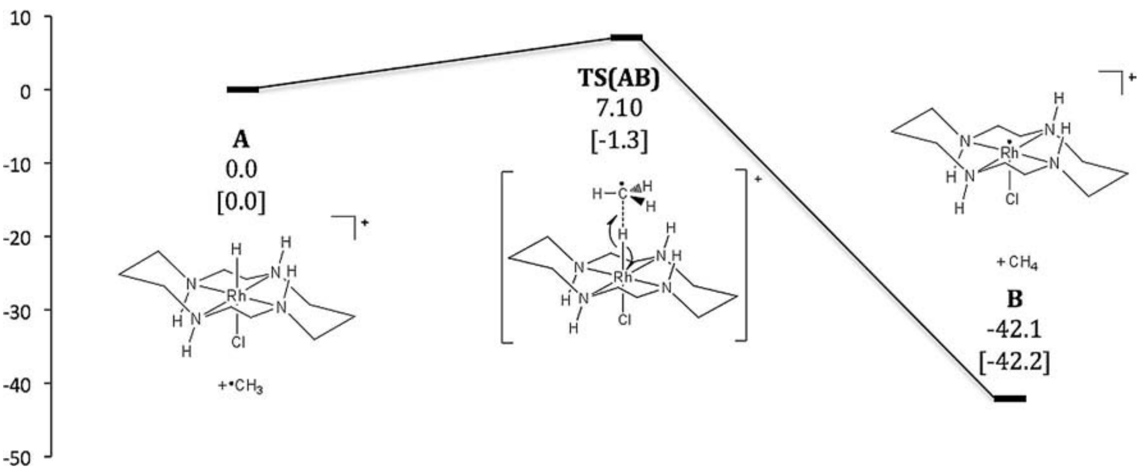


Figure 2. Energy surface for a one-step radical-propagation-type reaction of Rh–H with $^{\cdot}CH_3$. Energies are ΔG_{sol} [ΔH_{sol}] (kcal mol⁻¹).

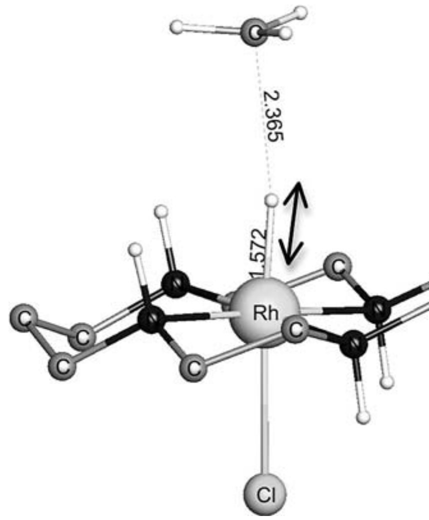


Figure 3. Detailed structure of **TS(AB)**. The double arrow indicates the Rh–H stretch, which corresponds to the imaginary frequency associated with this transition state (–57.74 cm^{-1}).

However, in accordance with the Hammond postulate, this exothermic reaction should have a reactant-like transition state not a product-like one. A comparison of the transition-state energies for the H and D surfaces leads to an H/D splitting of 1.58 $kcal\,mol^{-1}$ and a very small approximate KIE of 1.08. This very small normal KIE is consistent with the reactant-like transition-state geometry, in which the Rh–H bond has stretched only slightly (from 1.566 to 1.571 Å) indicating that the bond is still intact, that the C–H bond is long (2.365 Å compared to 1.09 Å calculated for CH_4), and that the CH_3 moiety is still planar. This normal KIE is again consistent with the work of Pestovsky et al.[6]

While these initial results suggest that the reaction could proceed rapidly through this simple one-step pathway resulting in a small normal KIE, they do not consider what might happen to the Rh complex in solution prior to reaction with $^{\cdot}CH_3$ nor more complex pathways such as the proposed formation of a seven-coordinate methyl complex. Thus, examination of a number of other possibilities were undertaken: (1) the loss of Cl^- or $^{\cdot}Cl$, (2) formation of various six- and seven-coordinate methyl species, (3) formation of a complex with solvent or one of the other molecules present in the reaction (e.g. OH_2, DMSO, etc.), and (4) reduction of the Rh^{III} complex to Rh^{II} by one of the hydrated electrons known to be produced in the radiolysis procedure. The other possibilities are described briefly below and additional details are presented in the Supplementary Information.

Because of the complete absence of CH_3Cl in the reaction the loss of $^{\cdot}Cl$ from **A** was not considered further, but the possible loss of Cl^- is a source of ongoing debate with regard to the resting state of this complex in water. To examine this further all four local extrema on the potential energy surface (**A**, **TS(AB)**, **B**, and **A·CH₃**) were examined with a water molecule and a vacancy *trans* to the hydride (Table 1). While the loss of Cl^- to form a five-coordinate 16-electron Rh^{III} dianion is energetically unfavorable by only 2.6 $kcal\,mol^{-1}$ the formation of the corresponding *trans* aquo complex is calculated to be uphill by 7.3 $kcal\,mol^{-1}$. This is not unexpected as the data from Bakac and coworkers suggests $\Delta G° \approx 4.5$ $kcal\,mol^{-1}$.[9] Thus, *trans*-$[(Cyclam)Rh^{III}HCl]^+$ is indeed predicted to be lower in energy but because of very low concentrations of complex and the abundance of solvent water the expected predominant species under the experimental conditions is the *trans*-$[(Cyclam)(H_2O)Rh^{III}Cl]^{2+}$.[10] Furthermore, the reaction profiles of these species with $^{\cdot}CH_3$ to form a Rh^{II} complex and CH_4 is seemingly independent of the *trans* ligand in that the reaction is highly exothermic and the local potential energy surface shows a monotonic decrease in energy and a primarily entropic barrier for the reaction. This suggests that a fast reaction would be expected regardless of the resting state (*trans* ligand) of the complex.

Table 1. Effects of the *trans* ligand on energies for **A**, **TS(AB)**, and **B** (ΔG_{sol} [ΔH_{gas}], $kcal\,mol^{-1}$).

trans Ligand	A	TS(AB)	B	A·CH3
Cl^-	0.0 [0.0]	7.1 [–1.3]	–42.1 [–42.2]	6.5 [–1.3]
H_2O	7.3 [7.4]	15.8 [5.8]	–36.8 [–36.7]	14.6 [6.1]
Vacancy	2.6 [13.4]	9.1 [11.4]	–44.0 [–33.8]	9.8 [12.0]

Further investigation was unable to locate any stable 19-electron species {such as $[LRh^{IV}H(Cl)(CH_3)]^+$, **A′**, and $[LRh^{II}(Cl)(CH_4)]^+$, **B·CH₄**, from Scheme 1} as all computational attempts resulted in the loss of methane to form species **B**. Thus, an equilibrium step involving such species prior to the rate-determining reductive elimination must be eliminated from further considerations, as these 19-electron species are too unstable to be formed.

Additional negative results were found when examining reactions of complexes with other possible species in solution such as solvent shells, where explicit H_2O molecules were included both as a H-atom transfer mediator between Rh–H/D and $^{\cdot}CH_3$ and as a hydrogen-bound impediment preventing $^{\cdot}CH_3$ from direct reaction with the Rh–H/D. No intermediates were found to exist in which a water molecule formed a hydrogen bond (often referred to as a dihydrogen bond) to the metal hydride. Examination of the charge distribution indicates that the Rh–H/D bond is nonpolar with little charge localized on either the Rh or the H/D (Mulliken charges of 0.25 and 0.29 electrons on Rh and H/D, respectively). In cases with one or two explicit water molecules, the water molecules simply form hydrogen bonds with the protonated amines while in cases with more water molecules they simply form clusters of water molecules. At first it may seem that water molecules bound to the protonated amines (the same place that the methyl radical is located in species **A·CH₃**) would prevent complexation with the methyl radical, but we find that in these cases the methyl radical forms a van der Waals complex with the associated water molecules. In fact the lowest energy pathway with explicit water molecules is exactly the same [$\mathbf{A(OH_2)_2} \rightarrow \mathbf{TS(AB)(OH_2)_2} \rightarrow \mathbf{B(OH_2)_2}$] and the additional water molecules do not affect the energy profile or the calculated KIE. In cases with clusters of water molecules (three or more

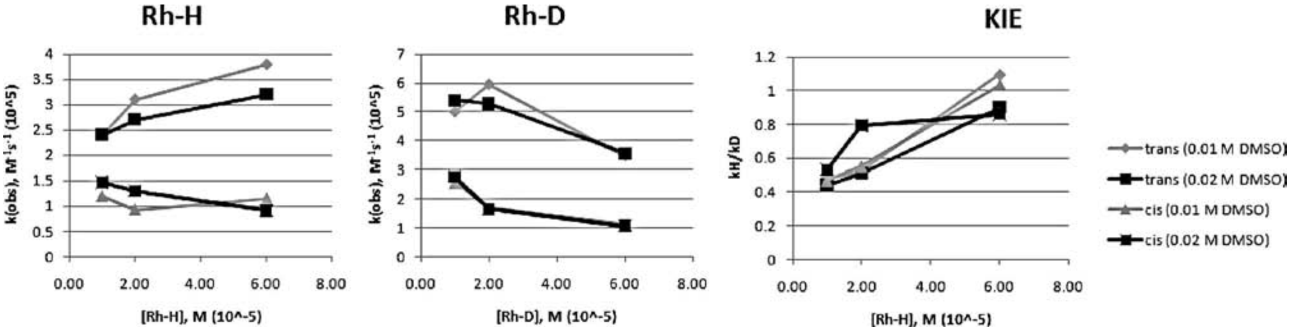


Figure 4. Observed rate constant [k(obs)] for the formation reaction of CH_4 from reactions of $^{\cdot}CH_3$ with Rh–H (left) and Rh–D (middle) and the corresponding KIEs (right).

explicit waters) we still find that the water molecules have no affinity for the hydride, do not impede the approach of the methyl radical, and do not change the lowest energy pathway. However, in these aquo complexes, we do find that we can proceed through a new water assisted mechanism, in which one hydrogen atom is passed from the Rh to the associated water while a second hydrogen atom is transferred from that water to the methyl radical. However, this process is higher in energy and once again leads to a small positive KIE.

While the production of methyl radicals is understood to arise from reactions of $^{\cdot}OH$ with DMSO prior to reaction with the Rh complex, Rh species complexed by DMSO and reacted directly with $^{\cdot}OH$ were still examined. Like the water molecules, the DMSO molecule had no affinity for the metal hydride and no Rh–H/DMSO complex was found in which a reaction with $^{\cdot}OH$ would produce $^{\cdot}CH_3$ in the vicinity of the Rh–H group.

As mentioned above the radiolysis procedure employed in these experiments is known to produce hydrated electrons. These reactions are performed in saturated N_2O solutions and while it is generally understood that all of the hydrated electrons produced in the radiolysis experiment react with N_2O, the fact that this anionic complex is a suitable candidate for a one-electron reduction through the addition of an electron could not be ignored. In fact, the 1e⁻ cell potential calculated[11] for the conversion of **A** to [(L)-$Rh^{II}HCl]^-$, **A^e**, is –3.19 V with respect to ferrocene. From species **A^e** we can imagine a set of pathways corresponding to all of the pathways mentioned above, but again the lowest energy pathway is simply the abstraction of an H atom by $^{\cdot}CH_3$ to form a Rh^I species, which immediately loses Cl^- (see SI). Thus, this route would also result in a KIE value near 1.

Because no viable mechanism could be found that would produce an inverse KIE, we re-examined the experimental results from Kats et al. (Figure 4).[3] Note that their observed KIE of 0.66 ± 0.30 does not exclude a KIE ≈ 1.0 as determined by the calculations. Upon closer examination of the data (Figure 4, right) it is clear that the observed behavior is complex, as the relative rates observed for H and D vary from D being almost three times as fast (KIE ≈ 0.4) at lower concentrations of the Rh complex to the two rates being virtually indistinguishable (KIE ≈ 1.0) at higher concentrations of the Rh complex. The trend of the KIE toward 1 with increasing concentration is unexpected, as the KIE should be independent of concentration. If, however, there is some other reaction contributing to the methane production, then the KIE at large complex concentrations should asymptotically approach the actual KIE as the reaction of the methyl radical with the complex begins to dominate.

Conclusions

In an effort to understand the complex kinetics observed for reactions of *cis*- and *trans*-$[(Cyclam)Rh^{III}HCl]^+$ with $^{\cdot}CH_3$ by Kats et al.[3] and to resolve the contradiction between that work and the work of Bakac and coworkers[5,6] on the aquo analogue, we have performed a thorough examination of feasible mechanistic pathways with density functional theory. We find that the reaction mechanism involved is simply a single-step radical-propagation-type mechanism in which the methyl radical abstracts the Rh-bound H atom from the complex resulting in the formation of methane and Rh^{II}. Calculations of the KIE for this reaction gave us a value of 1.08 for the *trans* species. While this value only agrees with the upper range of the experimental KIE of 0.66 ± 0.30 from Kats et al.,[3] it is in excellent agreement with their experimental KIEs of 1.10 for the *trans* complex and 1.04 for the *cis* complex at high complex concentration and low methyl radical concentration and it is in good agreement with the somewhat larger normal KIEs reported by Bakac and coworkers.[6] The small value predicted by the DFT calculations is a result of a transition state that is very reactant-like so that there is very little bond breaking or bond making in the transition state. Thus, the Rh–H(D) stretching frequency contributes equally to both reactant and TS for both isotopes. Therefore our calculations clearly demonstrate that this system has a small normal KIE.

Computational Methodology

Preliminary calculations were performed with the hybrid DFT functional B3LYP as implemented by the Gaussian 09 programming package.[12] This functional utilizes the Becke 3-parameter exchange functional (B3)[13] combined with the correlation functional of Lee, Yang, and Par (LYP)[14] and is known to produce good descriptions of reaction profiles for transition-metal containing compounds.[15,16] Rh atoms were described using the LANL2DZ effective core potential (ecp) and basis set of Hay and Wadt[17] with the 5p orbitals replaced by the split valence functions from Couty and Hall.[18] All other atoms (C, H, N, and Cl) were modeled using a Pople-style[19] double-ζ 6-31G(d′,p′) basis set with polarization functions optimized for heavy atoms.[20]

All geometries were fully optimized and evaluated for the correct number of imaginary frequencies through calculation of the vibrational frequencies using the analytical Hessian. Zero imaginary frequencies corresponding to an intermediate or local minimum whereas one designates a transition state or saddle point. From the analytical Hessian, zero-point energies as well as enthalpy and entropy corrections were calculated for 298.15 K, consistent with the ambient temperatures of the experiment. These corrections were added to the total electronic energy to obtain a total free energy, ΔG[298.15].

Implicit solvent effects were incorporated using the polarizable continuum model[21] with water as the solvent using the parameter $\varepsilon = 75.3553$. For this method we chose to employ the radii and non-electrostatic terms from the SMD solvation model of Truhlar and coworkers.[22] The solvent effects were calculated for geometries calculated in the gas phase. The resulting solvation free energy correction was added to the total free energy from above to obtain the total free energy.

Kinetic isotope effects (KIE) were examined through calculation of the analytical Hessian upon substitution of deuterium for hydrogen. The new zero-point energies and enthalpy and entropy terms for the deuterated species were thus determined and used to obtain the corresponding free energies. The approximated KIEs were then calculated from $k_H/k_D = e^{(\Delta G_D - \Delta G_H/RT)}$ where the difference in free energies ($\Delta G_D - \Delta G_H$) is essentially the difference in ZPE for the deuterated and undeuterated species.

Standard-state corrections were added to all species to convert concentrations from 1 atm to 1 M. This was accomplished by the equation $\Delta G^{\circ\prime} = \Delta G^\circ + RT\ln(Q^{\circ\prime}/Q^\circ)$, where the initial concentration Q° = 1 atm (1/24.5 M for an ideal gas) and the final concentration $Q^{\circ\prime}$ = 1 M.[23] Thus, a value of about –1.894 kcal mol⁻¹ was added to the total free energy for each species. The overall effect of this correction is the addition of $(M - N)\times 1.894$ kcal mol^{-1} for the conversion of M molecules to N molecules. This approximation is added in order to better model the changes in solvent-phase translational entropy when there are changes in the number of molecules present.

Supporting Information (see footnote on the first page of this article): Additional discussion of the non-productive pathways as well as Cartesian coordinates for all species discussed.

Acknowledgments

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[9] Data from ref.[6] demonstrates about 90% conversion of the chloride complex (3.6 mM initial concentration) to the aquo complex. $K_{eq} = [(H_2O)RhH^{++}]\times[Cl^-]/([RhHCl^+]\times[H_2O]) = 0.00324^2/(0.00036\times 55.5) = 5.25\times 10^{-4}$, and therefore $\Delta G^\circ = -RT\ln(K_{eq}) \approx 4.5$ kcal mol^{-1}.

[10] Assuming $K_{eq} = 5.25\times 10^{-4}$ (ref.[9]) and the initial concentration of the chloride complex is less than 6×10^{-4} M from ref.[3], >95% conversion of the chloride complex to aquo would be predicted.

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