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Hydrogen Electrooxidation in Ionic Liquids Catalyzed by the NTf₂ Radical

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Abstract

Hydrogen electrooxidation via a “hydrogen abstraction” mechanism in an aprotic ionic liquid 1-butyl-1-methylpyrrolidinium bis-(trifluoromethylsulfonyl) [Bmpy][NTf₂] under anaerobic conditions was investigated using cyclic voltammetry and density functional theory (DFT). It is found that a platinum bound NTf₂ radical (NTf₂[•]) formed by the oxidation of NTf₂⁻ at anodic potential can catalyze the oxidation of hydrogen and enhance its reaction rate. Both experimental and theoretical studies (DFT) have supported a mechanism involving a NTf₂[•] radical intermediate that catalyzes the hydrogen redox processes.

Graphical Abstract

INTRODUCTION

The increase in global energy demand has prompted a growing interest in developing alternatives to fossil fuels. Proton exchange membrane hydrogen fuel cells (PEM-HFCs) are

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ASSOCIATED CONTENT

Supporting Information

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Additional scan rate experiments (peak current versus scan rate, CV cycles) and computational optimized geometries of radicals (PDF)

The authors declare no competing financial interest.

among the most attractive source of alternative energy due to their high output power density.^{1,2} As the anodic reaction of PEM-HFCs, the hydrogen oxidation reactions (HOR) have been studied over a century due to their fundamental and applied significance.³ In addition, HOR was shown to be central in the development of fundamental electrocatalysis theories. The vast literature of HOR studies are performed in various aqueous electrolytes on platinum electrodes, due to its appropriate adsorption energy which enables Pt as the best catalyst of HOR.⁴ It is well-known that in aqueous solvent, hydrogen oxidation involves two oxidation steps, the first step is the formation of hydrogen adsorbate on platinum (Pt-H_{ad}) also known as the Tafel step, and the second step is dissociative oxidation step (typically referred as Heyrovsky and Volmer step).⁵ However, it is also found that electrolytes can play a significant role in altering the reaction pathway of HOR.^{6,7} For example, ionic liquids (ILs) composed of organic cations or anions are widely employed as nonaqueous electrolytes in various chemical and electrochemical applications including fuel cells and batteries.^{8,9} Our previous investigation shows that the oxidation of hydrogen in ILs at an aerobic condition utilizes a different reaction pathway that involves the coupling reaction with oxygen.¹⁰ Walsh et al. also found an inhibition effect of HOR in protic ionic liquids due to the formation of adsorbed oxide layer on platinum surface.¹¹ In addition, the kinetics of the reaction of HOR are also affected by the water contents of the IL electrolytes.¹² Although various reaction pathways have been proposed for explaining the observed phenomena in different electrolytes for HOR, this study in ILs is needed to obtain new insights and validate the possible mechanism of HOR for further application (e.g., improving the efficiency in PEM-HFCs).

Previously, we demonstrated that NTf_2 in IL can be oxidized at anodic potentials to form $\text{NTf}_2^\bullet$ radicals that are found to increase the rate and reduce the potential of oxidation of methanol.¹³ The $\text{NTf}_2^\bullet$ radicals catalyze oxidation by abstraction of hydrogen atoms from methanol. In addition, the $\text{NTf}_2^\bullet$ radicals were further shown to catalyze the electro-oxidation of methane.¹⁴ Thus, we hypothesized that these catalytic effects of NTf_2 radicals would extend to hydrogen and could promote the direct oxidation of hydrogen. Our hypothesis is supported by the study by Silvester et al. in which they characterized the hydrogen oxidation in ten different ILs with NTf_2^- , OTf^- , BF_4^- , PF_6^- , Cl^- , and FAP^- anions.¹⁵ They observed an increase of the oxidation peak current of hydrogen in NTf_2^- and TfO^- anion-based ILs when a preanodized (“activated”) potential more positive than the oxidation peak potential of hydrogen was applied in the cyclic voltammetry (CV) experiments. Preanodization is a process where the electrode is generally equilibrated at a higher positive potential, where oxide layers can be formed and during subsequent reduction processes oxide layers may be desorbed.^{16–18} The CV results of HOR with the applied preanodization activation are also electrochemically more reversible than those without activation.^{15,16} However, Silvester’s work did not explain the reason for the peak current increase in their preanodized condition for the HOR. In this work, the hydrogen oxidation processes were studied with and without preanodized activation at the Pt electrode using both constant potential and CV methods in $[\text{Bmpy}][\text{NTf}_2]$. Our results confirmed that the *in situ* generation of $\text{NTf}_2^\bullet$ radicals on the platinum electrode (via preanodization at 2 V) enhance the rate of the electrooxidation of hydrogen. This work thus provides an additional

example for using NTf₂ based ILs to generate radical catalysts in hydrogen abstraction reactions.

EXPERIMENTAL SECTION

Chemicals and Reagents

1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([Bmpy][NTf₂], 99%) was purchased from IOLITEC Inc. The IL was dried before use in the electrochemical experiments in a vacuum oven at 70 °C for overnight until no visible signs of water peak in the IR spectrum. High purity gases (nitrogen 99.99%, hydrogen 99.99%, air) were obtained from Airgas Great Lakes (Independence, OH).

Electrochemical Studies

A backflow electrochemical gas cell (Clark-type) similar to our previous investigation¹⁹ was used in this study. A platinum gauze (Sigma-Aldrich) was used as a polycrystalline platinum working electrode and directly assembled on top of a gas permeable porous Teflon membrane. The electrochemical active surface area (5.96 cm²) was calculated on the basis of the charge of hydrogen adsorption/desorption (210 μC cm⁻²) experiments on a platinum electrode in 0.1 M HClO₄. The counter and reference electrode are 0.5 mm diameter platinum wires. An amount of 150 μL IL was added into the electrochemical cell as the electrolyte. All of the potential reported was referenced versus Fc⁺/Fc reference unless specifically noted. The hydrogen gas (H₂) was purged through the gas inlet and diffused directly through the Pt working electrode. The total gas flow rate was maintained at 200 sccm by digital mass-flow controllers (MKS Instruments, Inc.) and the volume ratio (v/v)% of hydrogen to nitrogen (N₂) was adjusted by two mass-flow controllers, in which one was used to control the background gas (N₂) flow and the other was used to control the analyte gas (H₂) flow. All electrochemical measurements were performed on a VersaStat MC potentiostat (Princeton Applied Research, Oak Ridge, TN, U.S.A).

Computational Study

We employ the B3LYP density functional method implemented in the Gaussian 09²⁰ suite of programs to compute the energetics and equilibrium thermodynamics of reactions including the effect of the IL environment ($\epsilon = 11.7$) by use of the integral equation formalism of the polarized continuum model (IEF-PCM) of Tomasi et al.¹⁷ The structure of NTf₂ (radical and anion states), a platinum cluster constituting of four Pt atoms (Pt₄), and NTf₂ (radical and anion) interacting with Pt₄ and single Pt atom are fully optimized using the 6-311++G** basis set for all nonmetal atoms whereas the LANL2DZ effective core pseudopotential was used for the Pt atom. The applied DFT methodology was herein designated as B3LYP-PCM/6-311++G**.

The performance of the B3LYP functional for the calculation of heat of formations was compared to experiment as well as to a highly accurate G3 data set by Curtiss et al. for a total of over 200 heats of formation.^{21,22} The mean absolute deviation (MAD) was found to be 4.81 kcal/mol. Zhao and Truhlar assessed the performance of the various DFT methods and for B3LYP the mean unsigned error for thermochemistry was reported to be 1.5–5 kcal/

mol.²³ On the basis of these reports, our calculated Gibbs energies (ΔG) reported in Table 1 should have an estimated error of ca. 5 kcal/mol. Energies found for most reactions are far larger than these estimates of errors.

RESULTS AND DISCUSSION

Electrochemical Studies

A potential of 2 V was selected as the preanodization potential to oxidize NTf₂[−] on the basis of our early studies.^{13,24} Figure 1 shows multiple cyclic voltammograms of 1% (v/v) hydrogen in [Bmpy][NTf₂] with (Figure 1b) and without (Figure 1a) a constant potential preanodization step (5 min at 2 V). In Figure 1a, the CV in the pure IL background shows only the charging current and the presence of hydrogen leads to an oxidation peak at 0.4 V and a reduction peak 0.3 V. The peak current I_{pa}/I_{pc} ratio obtained for these oxidation and reduction peaks is at the value of unity, which indicates a reversible redox reaction of hydrogen in [Bmpy][NTf₂]. The mechanism of hydrogen oxidation at Pt without the preanodization step should be similar to that in aqueous electrolytes,²⁵ as described in eq 1 below:

The properties of ILs are very different from those traditional aqueous and nonaqueous electrolytes. ILs contain pure cations and anions that will result in a unique IL–electrode interface. ILs are more viscous than water so that the redox species will have different diffusion coefficients in the ILs than that of aqueous electrolytes. Although the NTf₂[−] anion is widely used as an IL forming anion, which has a notable electrochemical stability, by applying an anodic potential at platinum electrode, NTf₂[−] anions can be oxidized to NTf₂[•], which can adsorb at a platinum electrode and show redox behavior.²⁶ The oxidation of anion required high anodic potential; thus, the electrode was preanodization at 2 V to satisfy this requirement. Figure 1b shows the multiple CV cycles in [Bmpy][NTf₂] without the presence of hydrogen but with an applied preanodization potential (2.0 V) for 5 min. At this potential, the anions of the IL will be oxidized. An oxidation peak appeared at 0.3 V, but there is a negligible reduction peak. Because there is no hydrogen in this experiment, the oxidation peak at 0.3 V is attributed to a Pt–NTf₂[•] intermediate formed in the NTf₂[−] oxidation processes. During multiple CV cycles, the redox peak gradually increases to a constant value at which the saturated coverage of Pt–NTf₂[•] at Pt electrode has been reached.

Figure 1b also shows the multiple CV cycles of 1% hydrogen in [Bmpy][NTf₂] with 2 V preanodization step. With the preanodizing process, the peak current density of hydrogen oxidation is three times higher. A slightly negative potential shift (200 mV) was also observed for the oxidation peak of hydrogen. This result supports the catalytic activity of the Pt–NTf₂[•] radical for the oxidation of hydrogen compare to that of without the presence of this catalyst. Taking together our prior findings of Pt–NTf₂[•] radical in methane and methanol oxidation processes,¹³ the reaction mechanism for the catalytic hydrogen oxidation in NTf₂ based IL is proposed as shown in eqs 2–5.

The negative shift of hydrogen oxidation potential observed in Figure 1b with the preanodization condition should be directly related to the hydrogen adsorption and radical formation process in eq 4, in which highly active surface adsorbates ($\text{Pt-NTf}_2^\bullet$) promote the oxidation process of hydrogen that decrease the potential needed for oxidation of hydrogen.

Figure 2a summarizes the results of different scan rates of CV experiments of 1% (v/v) hydrogen in $[\text{Bmpy}][\text{NTf}_2]$ without preanodization condition. The anodic or cathodic redox peak current density has a linear relationship with the scan rates (Figure S1). The linear relationship of peak currents vs scan rates validates the surface adsorption during the hydrogen oxidation process in the IL, which is also consistent with the high catalytic properties of the platinum electrode for surface proton redox reactions.⁷ Figure 2b shows that $I_{\text{pa}}/I_{\text{pc}}$ decreases from a value bigger than unity to reach a value close to unity with increasing cycle numbers, the initial higher than unity value of $I_{\text{pa}}/I_{\text{pc}}$ may be related to the association of proton with NTf_2^- anion to form HNTf_2 , which decreased the reduction current of proton in cyclic voltammetry. It takes more cycle numbers in the CV experiments to reach the equilibrium of plateau value of $I_{\text{pa}}/I_{\text{pc}}$ at a high scan rate (e.g., 500 mV/s) vs a low scan rate (e.g., 25 mV/s). This result further supports the conclusion that the hydrogen mass transport rate is slow and is the rate-determining step in the high viscosity IL compared to the facile electrode oxidation of hydrogen on platinum.

We also carried out the preanodization step by cyclic voltammetry to study the catalytic hydrogen oxidation processes. Our earlier work showed that a positive potential larger than 1.4 V is required to oxidize the NTf_2^- anion to $\text{NTf}_2^\bullet$ radicals in CV experiments,¹³ as shown in eq 2. Thus, the CV at a wider potential (0–1.8 V) window was performed for generating the $\text{NTf}_2^\bullet$ radical that mimics a preanodization condition. Figure 3a shows the multiple cyclic voltammograms at a potential window (0–1.8 V) in $[\text{Bmpy}][\text{NTf}_2]$. When these were compared to the CV in Figure 1a, an oxidation peak starting at 1.4 V was observed, which validates the oxidation of the NTf_2^- anion corresponding to the reaction in eq 2. The oxidation peak at 0.4 V related to the formation of surface adsorbate $\text{Pt-NTf}_2^\bullet$ radicals, which is consistent with the peak observed in the experiments with an applied preanodization potential in Figure 1b and support the proposed mechanism in eq 3. A

smaller oxidation current (20%) of the Pt-NTf₂[•] radical formed during CV experiments than that of electrolysis at fixed preanodization potential (2.0 V) in Figure 1b. The dynamic CV scanning results in less accumulation of NTf₂[•] radicals on an electrode surface because some of the NTf₂[•] radicals formed can be reduced back to NTf₂⁻. As shown in the Figure 3b, the introduction of hydrogen increases the oxidation current and causes a negative shift of the oxidation peak from 0.4 to 0.2 V, which relates to the formation of H-Pt-NTf₂ from the interaction between Pt-NTf₂[•] radicals and H₂ in eq 4. These results are consistent with the observation in the preanodization potential experiments shown in Figure 1b. In addition, the hydrogen oxidation with the coupling with the NTf₂[•] radical reactions in the multiple CV experiments show a different trend of the I_{pa}/I_{pc} value vs CV cycling numbers. In Figure 2b, without the preanodization step (narrow potential window), the I_{pa}/I_{pc} values at initial CV cycles are larger than unity due to the formation of HNTf₂, which reduced the number of free protons but reached a constant value about one after cycle number six. As shown in Figure 3c, however, when NTf₂[•] radicals were involved in the oxidation process of hydrogen in the wider potential window CV experiments, the I_{pa}/I_{pc} values for hydrogen oxidation were smaller than that at the initial CV cycle numbers and then increased from cycle number one to cycle number ten and then decreased from cycle number ten to cycle number 50. These characteristics of I_{pa}/I_{pc} vs cycle numbers in the CV experiments support an irreversible process which accounts for the decrease at high cycle number and the modification of reversible mechanism in eq 4.

We further verified the NTf₂[•] radical catalytic mechanism using potential step methods to apply a preanodization potential at 2 V for 5 min. Figure 4a shows the currents vs scan rates for 1% hydrogen oxidation with the preanodization condition. The data of I_{pa}/I_{pc} value vs cycle number in preanodization condition are shown in Figure S2 which is similar to those observed in Figure 2b. A linear relationship for peak current vs scan rate also demonstrates the surface adsorption process of hydrogen oxidation with preanodization step (Figure S3). Figure 4b compared the I_{pa}/I_{pc} vs scan rates value with and without the preanodization step. At the preanodization condition, the I_{pa}/I_{pc} ratio of the oxidation and reduction peak current vs scan rates increases from a value at 0.45 to reach a constant value close to unity. This verifies the higher reversibility of hydrogen redox process in [Bmpy][NTf₂] at high scan rates compared to that at low scan rates. According to Nicholson and Shain's theory derived from the results at stationary electrode polarography,²⁷ the peak current ratio vs scan rate can serve as an indicator for electrochemical mechanisms that involve coupled reactions, as shown in Figure 4b. At fast scan rate (500 mV/s) the hydrogen redox process is an E_rC_r mechanism with a reversible electron transfer E_r followed by a reversible chemical reaction C_r (eq 1), demonstrated by their near unity value of current vs scan rate curves with and without per-anodization step in Figure 4b. At slow scan rates, the reaction mechanism is changed to a reversible electron transfer E_r followed by an irreversible chemical reaction C_{ir} reaction, corresponding to the formation of Pt-NTf₂[•] radical and further protonation with hydrogen (eq 4), which is consistent with the results obtained in Figure 4b with the existence of preanodization step at slow scan rate that larger deviation value of I_{pa}/I_{pc} (<1) was presented. However, the general trend of I_{pa}/I_{pc} vs scan rate is consistent with a previous wide potential windows investigation (Figure 2b), which confirms the reaction mechanism is changed from a reversible electron transfer E_r followed by a reversible chemical reaction C_r

(E_rC_r mechanism, eq 1) to a reversible electron transfer followed by an irreversible chemical reaction (E_rC_i mechanism, eq 4) that corresponds to formation of $Pt-NTf_2^\bullet$ radical and further protonation with hydrogen. Theoretical calculation is employed in the following to further verify the reaction mechanisms and the feasibility of $NTf_2^\bullet$ radical reaction in catalyzing hydrogen oxidation.

Theoretical Calculations

With the B3LYP/6-311++G** method and including the ionic liquid environment ($\epsilon = 11.7$) the abstraction reaction of $NTf_2^\bullet$ with molecular hydrogen (H_2) was found to be slightly exergonic by $G = -7.4$ kJ, eq 6. The recombination reaction of the H atom and $NTf_2^\bullet$ is quite favorable with $G = -415.1$ kJ (eq 7). The sum of eqs 6 and 7 yields the overall eq 8, which is also very favorable ($G = -422.5$ kJ). Because the expected errors for calculations at this level are ca. 5 kcal/mol, the overall reaction energy is well predicted.²³

Overall

The presence of the platinum surface would also be a major factor and likely creates an even more favorable overall reaction (eqs 9–11). To test reactions 6–8 occurring on a model platinum surface, we studied the adsorption of $NTf_2^\bullet$, NTf_2^- , and H atom on a single Pt atom and on four Pt atoms (Pt_4). This provides an estimate of the effect of Pt on the chemistry. The B3LYP-PCM/6-311++G** (with LANL2DZ effective core pseudopotential for Pt) optimized geometries taking part in the reaction are presented in Figures S4–S6 in the Supporting Information. The optimized structures of $NTf_2^\bullet$ bound to Pt and Pt_4 are shown in Figure 4. The binding Gibbs energy (G) of $NTf_2^\bullet$ with Pt and Pt_4 are -391.8 kJ/mol and -376.0 kJ/mol, respectively; see reaction R2 in Table 1. The high binding energies explain why $NTf_2^\bullet$ efficiently absorbs on the platinum surface. In our calculation, the absorption of $NTf_2^\bullet$ on Pt_4 is considered in two different conformations (i) N of NTf_2 directly interacting with the Pt atom of Pt_4 and (ii) oxygens of NTf_2 interacting with the Pt atoms of Pt_4 ; see Figure S5 in the Supporting Information. In the present calculation, we considered only the former conformation (Figure 5b) because this was found to be more stable than the later conformation (Figure S5b) by 46.0 kJ/mol.

The H_2 absorption (binding) Gibbs energy (G) of H_2 with $NTf_2^\bullet-Pt$ (NTf_2-Pt-H) is calculated as -141.8 kJ whereas the absorption (binding) Gibbs energy (G) of H_2 on $NTf_2^\bullet-Pt_4$ (NTf_2-Pt_4-H) depends on the site of H attachment with Pt in $NTf_2^\bullet-Pt_4$ with the

site shown in Figure 6b has a binding energy of -1.3 kJ. The optimized structures are presented in Figure 6 and in Figures S5b and S6 in the Supporting Information. The complete reaction of absorption of $\text{NTf}_2^\bullet$ and H_2 on Pt_4 (with the H atom attached to the same Pt atom as the NTf_2 adduct (Figure 6b) along with calculated reaction free energies (ΔG) are given in reactions 9–11. The reaction Gibbs energy (ΔG) of the similar reaction with single Pt atom is given in Table 1 (reactions R2–R4). The overall reaction 11 is calculated to be highly exergonic (-753.2 kJ) in nature.

In addition, we considered the energy needed to oxidize the H absorbed on the Pt_4 with and without the $\text{NTf}_2^\bullet$ attached. NTf_2^- anion is also present but only to capture the proton after oxidation. The Gibbs energy of oxidation of H in $\text{NTf}_2 - \text{Pt}_n - \text{H}$ ($n = 1$ and 4) are 481.2 and 551.5 kJ, respectively (see reactions 12 and 13 and results in Table 1 for $n = 1$). These are compared to the Gibbs energies of oxidation of H without NTf_2 radical attached to platinum in $\text{Pt}_n - \text{H}$ (for $n = 1$ and 4). These values are larger: 520.2 and 671.1 kJ, respectively (see reactions 12 and 13 and results for R5, R6 in Table 1 for $n = 1$). Thus, the Gibbs energy of reaction for the oxidation of the $\text{NTf}_2 - \text{Pt}_n - \text{H}$ (for $n = 1$ and 4) is reduced significantly for both $n = 1$ and 4 (120 and 39 kJ, respectively); see reactions 12 and 13 below.

Oxidative potential for

As can be seen, both models at $n = 1$ and $n = 4$ show a catalytic effect but $n = 1$ is far larger with nearly 120 kJ lowering of Gibbs energy (reactions R5 and R6 in Table 1). Two other Pt_4 structures with the hydrogens attached ortho and para to the NTf_2 adduct site gave results that would be noncatalytic (see Table 1 and Figures S6b and S6c in the Supporting

Information). These might be equivalent to hydrogens in second layers in a Pt surface and show the location of the hydrogen atom is critical to the catalytic effect.

In this paper, we present a new mechanism for hydrogen oxidation in a NTf₂ based IL in which an in situ generated NTf₂ radical catalyzes the hydrogen oxidation process. This mechanism is supported by cyclic voltammetry and computational studies. The formation of NTf₂[•] radicals changes the conventional E_rC_r hydrogen oxidation mechanism to a E_rC_i mechanism owing to the coupling reaction between hydrogen and NTf₂[•] radical on platinum surface. In addition, theoretical calculations show high binding energies of NTf₂[•] radical to platinum enable their efficiently adsorption. DFT calculations predict exergonic coupling reactions between NTf₂[•] radical and H₂ on Pt surface as well as a lowering of the oxidative potential which is consistent with experimental observation of the catalytic process involving the NTf₂[•] radical.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1.

Multiple cyclic voltammetry cycles of 1% (v/v) hydrogen in $[\text{Bmpy}][\text{NTf}_2]$ ionic liquid (a) without and (b) with a 5 min preanodization potential (2 V) before the CV experiment (dashed line without hydrogen, solid line with 1% hydrogen). Scan rate: 100 mV/s.

Figure 2.

(a) Multiple cyclic voltammetry cycles in 1% v/v hydrogen in [Bmpy][NTf₂] in potential window 0–1.0 V and (b) I_{pa}/I_{pc} versus the cycle number value from (a).

Figure 3.

Multiple cyclic voltammetry cycles (a) of pure [Bmpy][NTf₂] and (b) with the presence of 1% (v/v) hydrogen in a wide potential window (0–1.8 V), scan rate 100 mV/s; (c) I_{pa}/I_{pc} for the hydrogen oxidation vs the cycle numbers in (b).

Figure 4.

(a) Multiple cycles CV with a 5 min 2.0 V preanodization step for 1% hydrogen in [Bmpy][NTf₂]. (b) I_{pa}/I_{pc} value vs scan rate with and without a preanodization step at last CV cycle.

Figure 5.
B3LYP-PCM/6311++G** optimized structures of (a) NTf₂^{*}-Pt and (b) NTf₂^{*}-Pt₄.

Figure 6. B3LYP-PCM/6-311++G** optimized geometries of (a) H bonded to NTf₂[•]-Pt ((NTf₂-Pt-H) and NTf₂[•]-Pt₄ (NTf₂-Pt₄-H) and (b) H near the N atom of NTf₂.

Table 1

Reaction Gibbs Energies (G) of H_2 , NTf_2^* , and NTf_2^- Absorption on Pt_4 and Pt Calculated^a in an Ionic Liquid Environment ($\epsilon = 11.7$) (Energy Given in kJ)

reaction	Gibbs energy (G) with Pt_4 ($n = 4$)	Gibbs energy (G) with Pt ($n = 1$)
(R1) $2Pt_n + H_2 \rightleftharpoons 2Pt_n-H$	-79.3	-381.1 ^a
(R2) $2NTf_2^* + 2Pt_n \rightleftharpoons 2NTf_2^*-Pt_n$	-751.9	-783.6 ^a
(R3) $2NTf_2^*-Pt_n + H_2 \rightleftharpoons 2NTf_2-Pt_n-H$	-1.3 ^{a,b}	-141.8 ^a
	-110.2 ^{a,c}	
	-113.2 ^{a,d}	
(R4) $2NTf_2^* + 2Pt_n + H_2 \rightleftharpoons 2NTf_2-Pt_n-H$	-753.2 ^{a,b}	-925.4 ^a
	-862.1 ^{a,c}	
	-865.1 ^{a,d}	
(R5) $NTf_2^- + NTf_2-Pt_n-H \rightleftharpoons NTf_2^*-Pt_n + NTf_2-H + e^-$	481.2 ^{a,b}	551.5 ^a
	535.7 ^{a,c}	
	537.2 ^{a,d}	
(R6) $NTf_2^- + Pt_n-H \rightleftharpoons Pt_n + NTf_2-H + e^-$	520.2 ^a	671.1 ^a

^aB3LYP-PCM/6-311++G** for all atoms except LANL2DZ effective core pseudopotential for Pt. Estimates of errors from previous work are ca. 5 kcal/mol.²³

^bSee Figure 6b or S6a for structure.

^cSee Figure S6b for structure.

^dSee Figure S6c for structure.