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Switchover of the Mechanism between Electron Transfer and Hydrogen-Atom Transfer for a Protonated Manganese(IV)–Oxo Complex by Changing Only the Reaction Temperature

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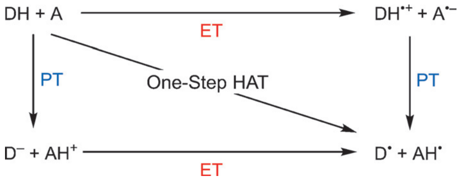
Abstract: *Hydroxylation of mesitylene by a nonheme manganese(IV)–oxo complex, $[(N4Py)Mn^{IV}(O)]^{2+}$ (**1**), proceeds via one-step hydrogen-atom transfer (HAT) with a large deuterium kinetic isotope effect (KIE) of 3.2(3) at 293 K. In contrast, the same reaction with a triflic acid-bound manganese(IV)-oxo complex, $[(N4Py)Mn^{IV}(O)]^{2+}$-$(HOTf)_2$ (**2**), proceeds via electron transfer (ET) with no KIE at 293 K. Interestingly, when the reaction temperature is lowered to less than 263 K in the reaction of **2**, however, the mechanism changes again from ET to HAT with a large KIE of 2.9(3). Such a switchover of the reaction mechanism from ET to HAT is shown to occur by changing only temperature in the boundary region between ET and HAT pathways when the driving force of ET from toluene derivatives to **2** is around −0.5 eV. The present results provide a valuable and general guide to predict a switchover of the reaction mechanism from ET to the others, including HAT.*

Hydrogen-atom transfer from hydrogen donors (RH) to hydrogen acceptors is one of the most important and fundamental reactions that have attracted much attention not only in organic chemistry but also in inorganic chemistry.[1–7] There are three reaction mechanisms proposed in hydrogen transfer, such as electron transfer (ET) followed by proton transfer (PT), one-step hydrogen-atom transfer (HAT), and PT followed by ET (Scheme 1).[1a,8–12] The one-step HAT mechanism implies that the hydrogen-atom transfer reaction occurs without a transient intermediate when an electron and a proton are transferred at the same time. In contrast, the sequential pathway involves mechanistically distinct ET and PT steps. In particular, there has been a long-standing ambiguity as to the mechanistic borderline where a HAT pathway is changed to a rate-determining ET pathway followed by a PT pathway or vice versa.[10–13] A more general question is whether the rate-determining ET and the other pathways are distinguishable and competing reactions, or whether the mechanism is continuously changed between the two extremes.[14–19] Such a general question has never been clarified previously.



Scheme 1. Possible reaction mechanisms in hydrogen-atom transfer reaction.

In ET reactions, the $\Delta S^{\neq}$ value is generally close to zero owing to the structureless transition state.[20–22] In contrast, HAT affords a largely negative $\Delta S^{\neq}$ value because of the highly structured transition state.[1] Large differences in the $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values between ET and HAT reactions may result in the change of the reaction mechanism depending on temperature, particularly in the borderline region between the two pathways. However, there has been no report on the switchover of the mechanism between ET and HAT reactions by changing only reaction temperature.

We herein report for the first time that the reaction mechanism in the hydroxylation of 1,3,5-trimethylbenzene (mesitylene) by a triflic acid-bound manganese(IV)–oxo complex, $[(N4Py)Mn^{IV}(O)]^{2+}$-$(HOTf)_2$ (N4Py = *N*,*N*-bis(2-pyridylmethyl)-*N*-bis(2-pyridyl)methylamine),[23,24] changes from a sequential rate-determining ET pathway (followed by an PT pathway) to an HAT pathway, both of which are clearly distinguishable, only by lowering temperature. Such a switchover of the mechanism has been confirmed by a drastic change of the deuterium kinetic isotope effect (KIE) from 1.0(1) at 293 K to 2.9(3) at temperatures lower than 263 K when mesitylene and $[D_{12}]$mesitylene were used as substrates. The ET driving force dependence of the rate constants in the hydroxylation of toluene derivatives by $[(N4Py)Mn^{IV}(O)]^{2+}$-$(HOTf)_2$ was examined to reveal the conditions, where switchover of the mechanism between ET and HAT can occur only by varying reaction temperature.

The manganese(IV)–oxo complexes, $[(N4Py)Mn^{IV}(O)]^{2+}$ (**1**) and $[(N4Py)Mn^{IV}(O)]^{2+}$-$(HOTf)_2$ (**2**), were generated and characterized spectroscopically as reported previously.[23,24] Mesitylene was hydroxylated by **1** in CF_3CH_2OH/CH_3CN ($v/v = 1{:}1$) to yield 3,5-dimethylbenzyl alcohol and $[(N4Py)Mn^{III}]^{3+}$ [Eq. (1)].

The yield of 3,5-dimethylbenzyl alcohol was determined to be 42(4)% with a small amount of 3,5-dimethylbenzaldehyde (3.9(8)%; Supporting Information, Table S1). It was

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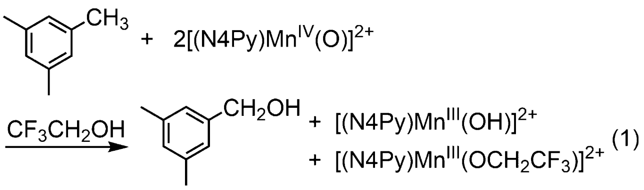
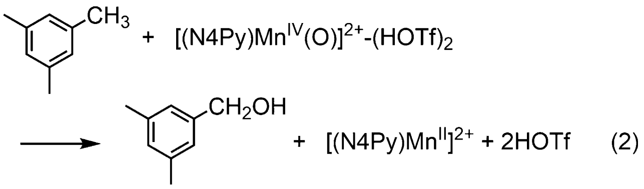


confirmed that the decayed product of **1** was not $[(\mathrm{N4Py})\mathrm{Mn}^{\mathrm{II}}]^{2+}$ but $[(\mathrm{N4Py})\mathrm{Mn}^{\mathrm{III}}]^{3+}$ species, which was EPR silent (Supporting Information, Figure S1a).

In the hydroxylation of mesitylene by **2**, 3,5-dimethylbenzyl alcohol was obtained in 94(5) % yield as the major product with a negligible amount of 3,5-dimethylbenzaldehyde [Eq. (2)].



In this case, the decayed product of **2** was $[(\mathrm{N4Py})\mathrm{Mn}^{\mathrm{II}}]^{2+}$, not $[(\mathrm{N4Py})\mathrm{Mn}^{\mathrm{III}}]^{3+}$, which is different from the reaction of **1** and mesitylene (Supporting Information, Figure S1b). Similar results were obtained in the hydroxylation of hexamethylbenzene (HMB) by **1** and **2** (Supporting Information, Figure S2).

Rates of the hydroxylation of mesitylene and other toluene derivatives by **1** and **2** were monitored by the decay of the absorption band at 940 nm for **1** and the absorption band at 550 nm for **2** at 273 K (Figure 1). The decay of **1** obeyed pseudo first-order kinetics (Supporting Information, Figures S3 and S4), and the pseudo-first-order rate constants (k_1) were proportional to concentrations of toluene derivatives (Supporting Information, Figures S5 and S6). The second-order rate constant (k_{obs}) increased with an increase in the number of methyl group of benzene ring (Table 1).

Table 1: One-electron oxidation potentials (E_{ox}) of toluene derivatives and second-order rate constants of hydroxylation of toluene derivatives by $[(\mathrm{N4Py})\mathrm{Mn}^{\mathrm{IV}}(\mathrm{O})]^{2+}$ in the absence and presence of HOTf (30 mM) at 273 K.

Toluene derivative	E_{ox}[a] [V vs. SCE]	k_{obs} [$\mathrm{M}^{-1}\,\mathrm{s}^{-1}$]	
		without HOTf	with HOTf
HMB	1.57	2.1×10^{-2}	6.7×10^{2}
pentamethylbenzene (PMB)	1.69	4.5×10^{-3}	8.7×10
1,2,4,5-tetramethylbenzene	1.74	2.1×10^{-3}	3.5
mesitylene	2.02	1.7×10^{-3}	1.8×10^{-3}

[a] The one-electron oxidation potentials of substrates were determined by cyclic voltammetry in $\mathrm{CF_3CH_2OH/CH_3CN}$ ($v/v=1{:}1$) containing 0.10 M n-$\mathrm{Bu_4NPF_6}$ as a supporting electrolyte at 298 K.

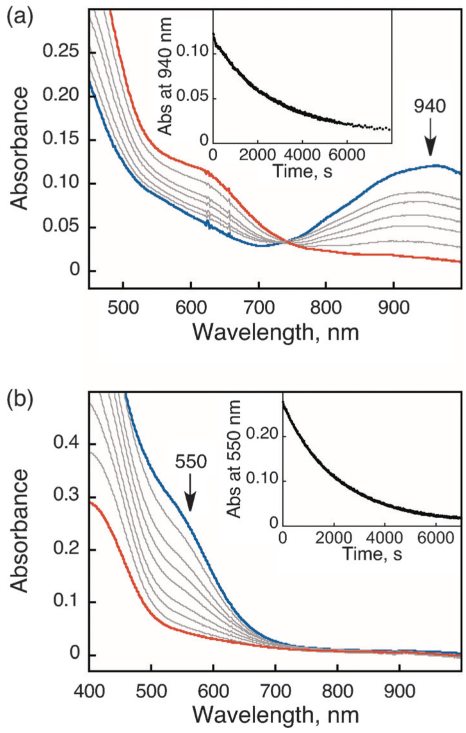


Figure 1. a) Visible spectral changes observed in the reaction of **1** (0.50 mM) with mesitylene (300 mM) in $\mathrm{CF_3CH_2OH/CH_3CN}$ ($v/v=1{:}1$) at 273 K. Inset: time course of the absorbance change monitored at 940 nm for the decay of **1**. b) Visible spectral changes observed in the reaction of **2** (0.50 mM) with mesitylene (300 mM) in the presence of HOTf (30 mM) in $\mathrm{CF_3CH_2OH/CH_3CN}$ ($v/v=1{:}1$) at 273 K. Inset: time course of the absorbance change monitored at 550 nm for the decay of **2**.

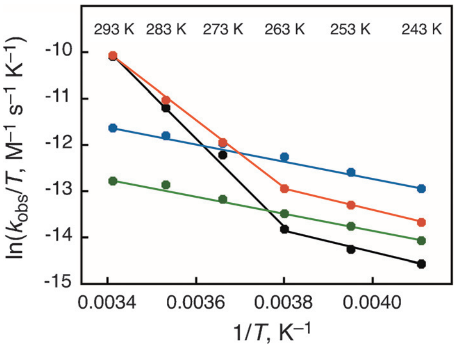


Figure 2. Eyring plots of $\ln(k_{\mathrm{obs}}/T)$ against $1/T$ obtained in the reactions of **1** with mesitylene (blue circles) and [D$_{12}$]mesitylene (green circles) and **2** with mesitylene (red circles) and [D$_{12}$]mesitylene (black circles) at various temperatures (243–293 K).

The temperature dependence of the second-order rate constant (k_{obs}) in the oxidation of mesitylene by **1** and **2** was examined to obtain the Eyring plots (Figure 2, blue and red circles, respectively). A linear correlation was obtained for **1**, whereas two different slopes were observed for **2**. At temperatures higher than 273 K, the k_{obs} values of **2** are larger than those of **1**. At temperatures lower than 273 K, the k_{obs} values of **2** are smaller than those of **1**. At 273 K, the k_{obs} values of **1** and **2** are about the same (see also Figure 1 a and b for **1** and **2**, respectively).

When mesitylene was replaced by [D$_{12}$]mesitylene, no deuterium kinetic isotope effect (KIE) was observed for **2** at

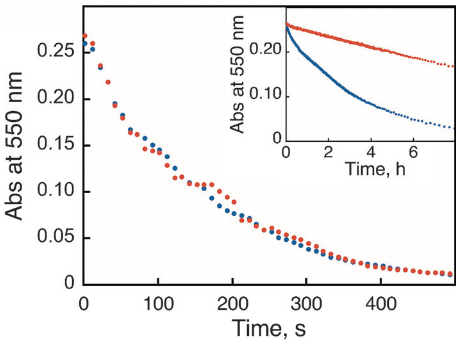


Figure 3. Absorbance changes monitored at 550 nm for the reactions of **2** (0.50 mM) with mesitylene (blue, 300 mM) and [D$_{12}$]mesitylene (red, 300 mM) at 293 K. Inset shows the time profiles observed under the identical reaction conditions at 253 K.

293 K (Figure 3), indicating that the hydroxylation of mesitylene by **2** proceeds via ET from mesitylene to **2**. At temperatures lower than 263 K, however, a KIE value of 2.9(3) was obtained for the reaction of **2** (Figure 3, inset), indicating that the hydroxylation of mesitylene by **2** proceeds via HAT rather than ET. In the case of **1**, the KIE remains large (KIE = 3.2(3)) in the temperature range of 243–293 K (Supporting Information, Figure S7). The activation parameters of the oxidation of mesitylene by **1** and **2** are listed in Table 2. The $\Delta H^{\neq}$ value of **2** is larger than that of **1**, whereas the absolute $\Delta S^{\neq}$ value of **2** is much smaller than that of **1**. The $\Delta S^{\neq}$ value of ET is close to zero or negative, being much less negative than that of HAT; the transition state of which is more ordered to afford the largely negative $\Delta S^{\neq}$ value. In such a case, ET is energetically more favored at higher temperatures. This is the reason why the mechanism changes from ET at 293 K with no KIE to HAT at temperatures lower than 263 K with a large KIE of 2.9(3). At temperatures lower than 263 K, the k_{obs} value of **2** is smaller than that of **1**, which is probably due to the steric effect of HOTf, which is bound to the oxo group of $[(N4Py)Mn^{IV}(O)]^{2+}$.[24] The observation of the different mechanisms by changing only temperature indicates that the two mechanisms are distinguishable and competing without the continuous change of the mechanism and that either ET or HAT pathway becomes dominant by changing only reaction temperature. It should be noted that this is the first time to show that two mechanisms are competing and one or the other is dominant by changing only reaction temperature.

Table 2: Activation parameters determined in the hydroxylation of mesitylene and hexamethylbenzene (HMB) by **1** and **2**.

Toluene derivative	$\Delta H^{\neq}$ [kcal mol^{-1}]		$\Delta S^{\neq}$ [cal mol^{-1} K^{-1}]	
	1	**2**	**1**	**2**
mesitylene	3.8 ± 0.3	15 ± 1[a] 4.8 ± 0.3[b]	−57 ± 4	−16 ± 1[a] −54 ± 4[b]
HMB	11 ± 1	13 ± 1	−28 ± 2	1.9 ± 0.2

[a] from 243 K to 263 K. [b] from 263 K to 283 K.

In the case of hexamethylbenzene (HMB), the k_{obs} values of **2** are always much larger than those of **1** in the temperature range of 263–293 K (Supporting Information, Figure S8). In this case again, the $\Delta H^{\neq}$ value of **2** is larger than that of **1**, whereas the absolute $\Delta S^{\neq}$ value of **2** is much smaller than that of **1**, being close to zero. The KIE values of 1.0(1) was obtained in the oxidation of HMB by **2** at both 263 and 293 K, whereas KIEs larger than 1.0 (1.7(1)) were observed in the oxidation of HMB by **1** (Supporting Information, Figures S9 and S10).[25] Thus, the oxidation of HMB by **2** proceeds via ET, whereas the oxidation by **1** proceeds via HAT in the temperature range of 263–293 K. In this case, no switchover of the mechanism was observed.

Figure 4 shows the dependence of $\log k_{et}$ on driving force of ET from electron donors to **2** at 273 K. The rate constants (k_{et}) of ET from one-electron reductants to **2** (black circles in Figure 4; see also Table 1) are well fitted in the light of the Marcus theory of adiabatic outer-sphere electron transfer [Eq. (3)]:[20]

$$k_{et} = Z\exp[-(\lambda/4)(1+\Delta G_{et}/\lambda)^2/k_B T] \qquad (3)$$

where Z is the collision frequency, taken as $1\times10^{11}\,M^{-1}\,s^{-1}$, λ is the reorganization energy of electron transfer, k_B is the Boltzmann constant, and T is the absolute temperature. From the fitting of the ET rate constants (black line in Figure 4), the λ value of ET from one-electron reductants to **2** was determined to be 2.20(2) eV.[24] The k_{obs} values of the hydroxylation of toluene derivatives by **2** fit well into the Marcus line (red circles in Figure 4), whereas those by **1** are much larger than those expected from the ET line (blue circles in Figure 4). The borderline between ET and HAT is located at $-\Delta G_{et} \approx -0.5$ eV, as reported previously.[9b,12a] The $-\Delta G_{et}$ value of the hydroxylation of mesitylene by **2** is located close to the borderline. This is the reason why the mechanism of the hydroxylation of mesitylene by **2** is changed from ET to HAT only by lowering temperature.

In conclusion, hydroxylation of toluene derivatives by a nonheme manganese(IV)–oxo complex, $[(N4Py)Mn^{IV}$-

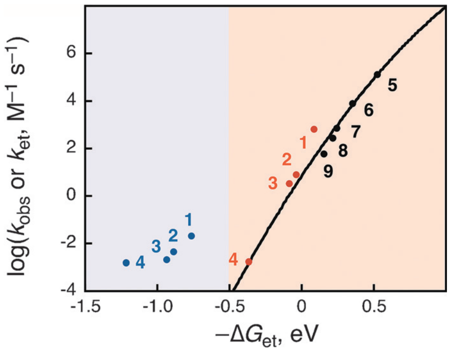


Figure 4. Plots of $\log k_{obs}$ for the hydroxylation of toluene derivatives (**1** HMB, **2** PMB, **3** 1,2,4,5-tetramethylbenzene, and **4** mesitylene) by **1** (blue circles) and **2** (red circles) at 273 K. The black circles show the driving force dependence of the rate constants ($\log k_{et}$) of ET from one-electron reductants (**5** $[Ru^{II}(Me_2bpy)_3](PF_6)_2$, **6** $[Ru^{II}(bpy)_3](PF_6)_2$, **7** $[Ru^{II}(5\text{-}Clphen)_3](PF_6)_2$, **8** $[Ru^{II}(5\text{-}Brbpy)_3](PF_6)_2$, and **9** $[Ru^{II}(5\text{-}NO_2phen)_3](PF_6)_2$] to **2** in the presence of HOTf (30 mM) at 273 K.[24]

$(\mathrm{O})]^{2+}$ (**1**), proceeds via HAT irrespective of reaction temperatures. In contrast, hydroxylation of toluene derivatives by a triflic acid-bound manganese(IV)–oxo complex, $[(\mathrm{N4Py})\mathrm{Mn}^{\mathrm{IV}}(\mathrm{O})]^{2+}$-$(\mathrm{HOTf})_2$ (**2**), proceeds via ET with a KIE value of 1.0 at 293 K. In the case of hydroxylation of mesitylene by **2**, however, the reaction pathway is changed from ET with a KIE value of 1.0 to HAT with a KIE value of 2.9(3) at temperatures lower than 263 K. The ET driving force dependence of the k_{obs} values of hydroxylation of toluene derivatives by **2**, in comparison with that of the k_{et} values of ET from one-electron reductants to **2**, reveals that switchover of the mechanism from ET to HAT by lowering temperature occurs for substrates which are in borderline between ET and HAT pathways at $-\Delta G_{\mathrm{et}} \approx -0.5$ eV. This study provides the first quantitative basis to predict switchover of the mechanism between ET and HAT in C–H bond activation reactions without the continuous change between ET and HAT. The long-standing ambiguity as to the mechanistic borderline between ET and HAT has been clarified for the first time in this study.

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