

Carbon-Carbon Bond Activation of TEMPO by a Rh^{II} Metallo-Radical:

A Combined Experimental and Theoretical Study

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Supporting Information

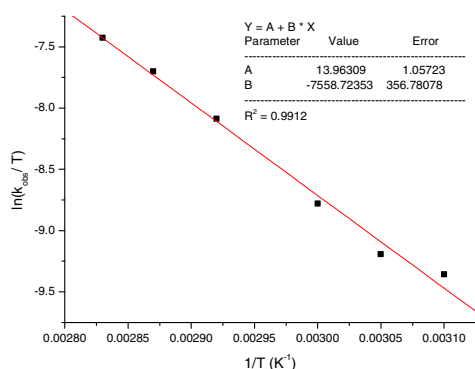


Figure S1 Eyring plot of the reaction of Rh(tmp) with TEMPO.

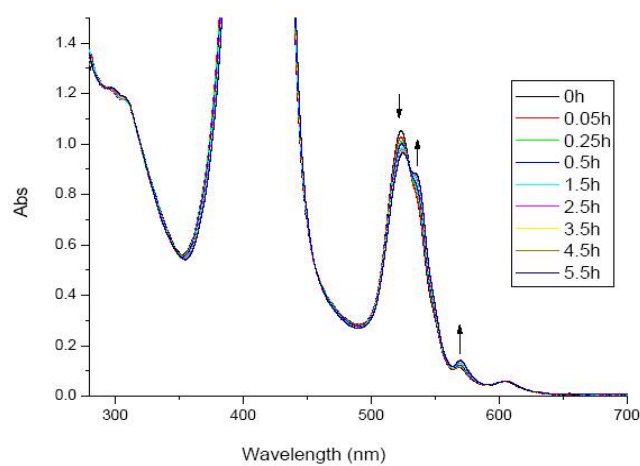


Figure S2 Wavelength scan of the reaction between Rh(tmp) and TEM

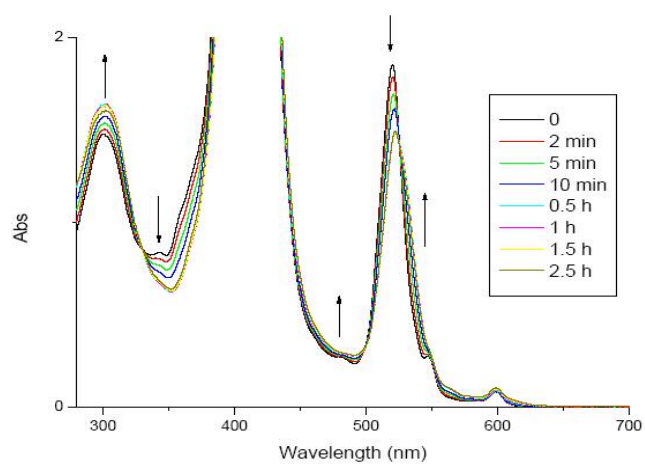
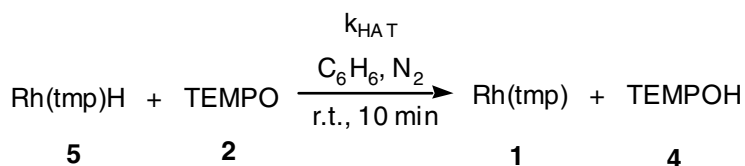
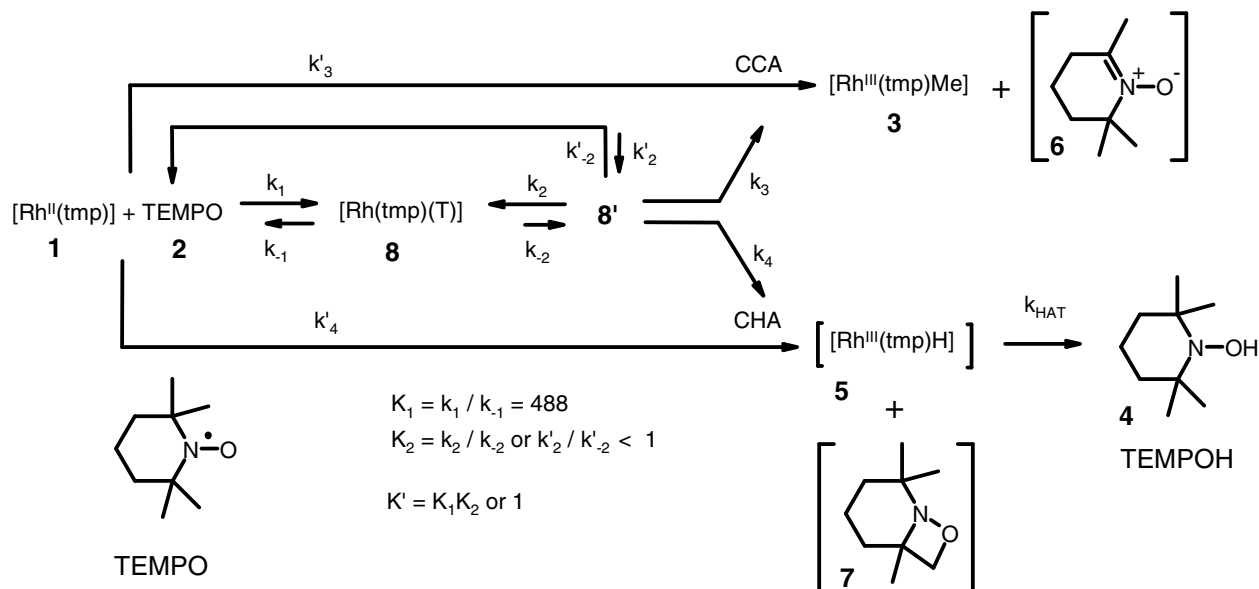


Figure S3 Wavelength scan of the reaction between Rh(tmp)H and TEMPO.

Derivation of Rate Laws

Scheme 1. Kinetic pathways for CCA and CHA of TEMPO by $[\text{Rh}^{\text{II}}(\text{tmp})]$ Consistent with the Experimental Data.



According to Scheme 1:

$$d[3]/dt = k_3[8'] \quad (1)$$

$$= k_3 K_1 K_2 [1] [2] \quad (2)$$

$$d[4]/dt = k_{\text{HAT}} [5] [2] \quad (3)$$

$$d[5]/dt = k_4 [8'] - k_{\text{HAT}} [5] [2] \quad (4)$$

$$= k_4 K_1 K_2 [1] [2] - k_{\text{HAT}} [5] [2] \quad (5)$$

With $[2] \gg 10 [1]$, $[2] \sim \text{constant}$.

From experiments it is clear that the reaction of 5 with 2 to give 1 and 4 is faster than that of 8' to 3 and 4. Thus applying steady-state approximation to 5, then eq 5 becomes:

$$d[5]/dt = 0 \quad (6)$$

$$k_4 K_1 K_2 [1] [2] - k_{\text{HAT}} [5] [2] = 0 \quad (7)$$

$$k_{\text{HAT}} = k_4 K_1 K_2 [1] / [5] \quad (8)$$

Substituting it into eq 3

$$d[4]/dt = k_{\text{HAT}} [5] [2] = k_4 K_1 K_2 [1] [2] \quad (9)$$

$$\text{Rate of reaction} = (k_3 + k_4) [8'] \quad (10)$$

$$= (k_3 + k_4) K_1 K_2 [2] [1] \quad (11)$$

$$= \{ (k_3 + k_4) K_1 K_2 [2] [1]_0 \} / \{ 1 + K_1 K_2 [2] \} \quad (12)$$

$$\text{where } [1]_0 = [1] + [8] + [8'] \quad (13)$$

Assuming $1 \gg K_1 K_2 [2]$ (see argumentation in the main manuscript), eq 12 becomes

$$\text{Rate} = (k_3 + k_4) K_1 K_2 [2] [1]_0 \quad (14)$$

Equation 14 conforms to the experimentally observed rate law with $[\text{Rh}(\text{tmp})]_0$ and $[\text{TEMPO}]$ both first order.

Case 1:

If 8' reacts with another TEMPO molecule to give Rh(tmp)Me and Rh(tmp)H

Equation 12 becomes for condition: $1 \gg K_1 K_2 [2]$

$$\begin{aligned} -d[\text{Rh}(\text{tmp})]/dt &= \{ (k_3 + k_4) K_1 K_2 [2] [1]_0 \} / \{ 1 + K_1 K_2 [2] \} [2] \quad (15) \\ &= (k_3 + k_4) K_1 K_2 [2]^2 [1]_0 \end{aligned}$$

This is not consistent with the experimentally observed rate order. Therefore, we rule out this mechanism.

Case 2:

If 8, but not 8', react with another TEMPO molecule to give Rh(tmp)Me and Rh(tmp)H

the rate law will become:

$$-d[\text{Rh}(\text{tmp})]/dt = \{ (k_3 + k_4) K_1 [2] [1]_0 \} [1] / \{ 1 + K_1 [2] \} \quad (16)$$

$$\text{At } 70^\circ\text{C}, K_1 [2] = 488 \text{ M}^{-1} \times 3.313 \times 10^{-3} \text{ M} = 1.61 \quad (17)$$

Equation 16 cannot be further simplified and is unlikely to be first order in $[2]$ in the fairly large range of concentrations of 2 studied ($8.282 - 49.7 \times 10^{-4} \text{ M}$). Therefore, we rule out this mechanism.

General:

Both $1 + 2$ and $8' + 2$ react to give $3 + 7$.

$$\text{Rate} = (k_3 K_1 K_2 + k'_3 + k_4 K_1 K_2 + k'_4) [2] [1]_0$$

This is a general rate equation for the Scheme 1. This is consistent with the experimental data, which do not allow us to discriminate between the concurrent k_3 and k'_3 steps. If pre-coordination of TEMPO is required for the CCA pathway, the equation simplifies to:

$$\text{Rate} = (k_3 K_1 K_2 + k_4 K_1 K_2 + k'_4) [2] [1]_0$$

Table S1. Free energies and negative eigenvalues of the DFT optimized geometries and transition states described in the main text.^[a]

| | Free energies | | negative eigenvalues |
|--------------------------------|---------------|----------|--------------------------|
| | a.u. | kcal/mol | |
| 353 K | | | |
| TEMPO | -483.3505001 | | - |
| [Rh ^{II} (por)] | -1098.456204 | | - |
| I | -1581.806704 | -18.2211 | - |
| II | -1581.777666 | 0 | - |
| III | -1581.759418 | 11.45063 | - |
| IV | -1581.81534 | -23.6405 | - |
| TS1 | -1581.759053 | 11.67988 | -760.38 cm ⁻¹ |
| TS2 | -1581.750659 | 16.94683 | -558.04 cm ⁻¹ |
| | | | |
| TEMPO | -483.3505001 | 0 | - |
| Methyl radical | -39.81776068 | | - |
| Dmpo-like product | -443.5065627 | | - |
| Dmpo-like product + Me radical | -483.3243233 | 16.42591 | - |
| TS | -483.2889635 | 38.61423 | -230.17 cm ⁻¹ |
| | | | |
| | Free energies | | negative eigenvalues |
| | a.u. | kcal/mol | |
| 298 K | | | |
| TEMPO | -483.3414701 | | - |
| [Rh ^{II} (por)] | -1098.445054 | | - |
| I | -1581.786524 | -16.6398 | - |
| II | -1581.760006 | 0 | - |
| III | -1581.741508 | 11.6075 | - |
| IV | -1581.796 | -22.5863 | - |
| TS1 | -1581.741393 | 11.67988 | -760.38 cm ⁻¹ |
| TS2 | -1581.732349 | 17.35471 | -558.04 cm ⁻¹ |
| | | | |
| TEMPO | -483.3414701 | 0 | - |
| Methyl radical | -39.81376068 | | - |
| Dmpo-like product | -443.4976227 | | - |
| Dmpo-like product + Me radical | -483.3113833 | 18.87944 | - |
| TS | -483.2795635 | 38.8464 | -230.17 cm ⁻¹ |

^[a] Turbomole (b3-lyp, TZVP), cosmo solvent corrections (with $\epsilon = 2.28$), corrected for ZPE and thermal effects (enthalpy and entropy).

Complete ref. 25a:

Ahlrichs, R.; Bär, M.; Baron, H.-P.; Bauernschmitt, R.; Böcker, S.; Ehrig, M.; Eichkorn, K.; Elliott, S.; Furche, F.; Haase, F.; Häser, M.; Hättig, C.; Horn, H.; Huber, C.; Huniar, U.; Kattannek, M.; Köhn, A.; Kölmel, C.; Kollwitz, M.; May, K.; Ochsenfeld, C.; Öhm, H.; Schäfer, A.; Schneider, U.; Treutler, O.; Tsereteli, K.; Unterreiner, B.; von Arnim, M.; Weigend, F.; Weis, P.; Weiss, H. Turbomole Version 5, January **2002**. Theoretical Chemistry Group, University of Karlsruhe.