

Supporting Information Available

Kinetics of hydrogen abstraction by the active metal hydroxo and oxo intermediates: revealing their unexpected similarities in the transition state

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Chemicals and instruments Acetone was purchased from Baker; Sodium hydride and ammonium hexafluorophosphate were from Alfa Aesar; DMSO- d_6 was from Cambridge Isotope Laboratories; 9,10-dihydroanthracene was from Aldrich; Ethanol, hydrogen peroxide, sodium hydroxide and HCl were from Sinopharm Chemical Reagent; deuterated 9,10-dihydroanthracene was synthesized according to the literature,¹ and then further sublimated before use. Kinetic data were collected on analytikjena, specord 205; GC-MS analysis was performed on Agilent 7890A/5975C; and NMR analysis was performed on Bruker AV400.

Reference:

1. C. R. Goldsmith, R. T. Jonas, T. D. P. Stack, *J. Am. Chem. Soc.* **2002**, 124, 83.

Activation parameter measurements To measure the kinetic parameters for hydrogen abstraction with the Mn^{IV} -OH moiety in $Mn^{IV}(Me_2EBC)(OH)_2^{2+}$, and the $Mn^{IV}=O$ in $Mn^{IV}(Me_2EBC)(O)_2$, 9,10-dihydroanthracene (DHA- h_4 , 0.04 M) or deuterated 9,10-dihydroanthracene (DHA- d_4 , 0.04 M) was chosen as substrate in different runs, and kinetic reactions were performed with the freshly synthesized manganese(IV) complexes (4 mM) in acetone/water (ratio 4:1) under the selected initial pH values and temperature range. The pH values were adjusted by NaOH or HCl as needed. For the Mn^{IV} -OH moiety in $Mn^{IV}(Me_2EBC)(OH)_2^{2+}$ at pH 4.0, due to the sluggish hydrogen abstraction from deuterated 9,10-dihydroanthracene by the Mn^{IV} -OH moiety and the relatively low boiling point of acetone solvent (56 °C), the reaction was carried out in the temperature range of 298-318 K. For the $Mn^{IV}=O$ in $Mn^{IV}(Me_2EBC)(O)_2$ at pH 13.4, due to the fast hydrogen abstraction from 9,10-dihydroanthracene by the $Mn^{IV}=O$ moiety, the reaction was carried out in the temperature range of 283-308 K. The disappearance of the manganese(IV) species was monitored by UV-visible spectrophotometry and the pseudo first order rate constant was calculated. Since the manganese(IV) complex was not very stable in solution, the control experiment

without substrate was conducted in parallel for each of the oxygenation reactions, and the correction from the control experiment has been applied in the calculation of the pseudo first order rate constant.

Calculations

The tunneling model developed by Bell^{1,2} was applied to calculate the barrier height E and width of $2a$. The detailed calculations of the tunneling correction (Q_t) were performed by following the method in Newcomb's work³, and the related equations are shown as follows:

$$(1) \quad k = Q(T) \times A \times \exp(-E/RT)$$

$$(2) \quad Q_t = ((e)/(\beta - \alpha))(\beta e^{-\alpha} - \alpha e^{-\beta})$$

$$(3) \quad \alpha = E/k_B T$$

$$(4) \quad \beta = 2\pi^2 a (2mE)^{1/2} / h$$

Here, h is Planck constant ($6.626 \times 10^{-34} \text{ J} \cdot \text{s}$), k_B is Boltzmann constant ($1.381 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$), m is the mass, and T is absolute temperature in degrees Kelvin (K).

References

1. R. P. Bell, Ed., *The Tunnel Effect in Chemistry*, Chapman and Hall, London, 1980.
2. R. P. Bell, F.R.S., J. A. Fendley, J. R. Hulett, *Proc. Roy. Soc.*, 1956, **A235**, 453.
3. Z. Pan, J. H. Horner, M. Newcomb, *J. Am. Chem. Soc.*, 2008, **130**, 7776.

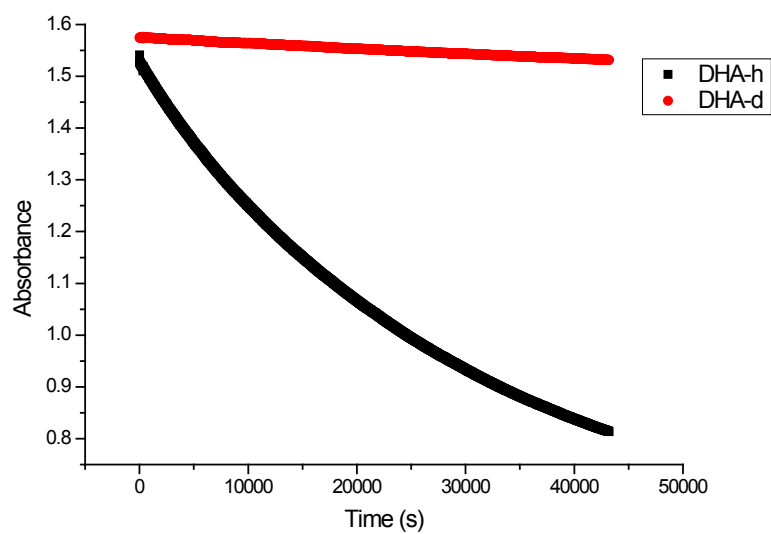


Fig. S1 Kinetics of hydrogen abstraction from 9,10-dihydroanthracene (40 mM) by manganese(IV) complex (4 mM) in acetone/water (4:1) at pH 4.0, 298 K, $k_{\text{obs}}(\text{DHA-h}_4) = 3.51 \times 10^{-5} \text{ s}^{-1}$, $k_{\text{obs}}(\text{DHA-d}_4) = 7.35 \times 10^{-6} \text{ s}^{-1}$.

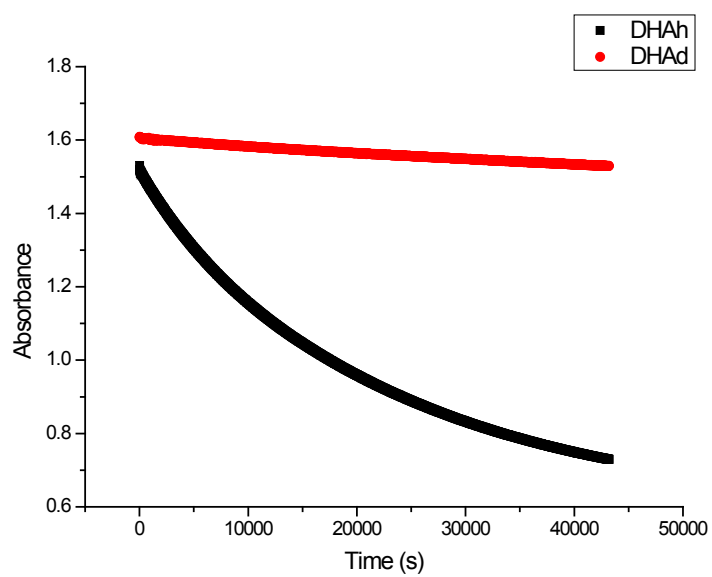


Fig. S2 Kinetics of hydrogen abstraction from 9,10-dihydroanthracene (40 mM) by manganese(IV) complex (4 mM) in acetone/water (4:1) at pH 4.0, 303 K, $k_{\text{obs}}(\text{DHA-h}_4) = 4.95 \times 10^{-5} \text{ s}^{-1}$, $k_{\text{obs}}(\text{DHA-d}_4) = 1.38 \times 10^{-5} \text{ s}^{-1}$.

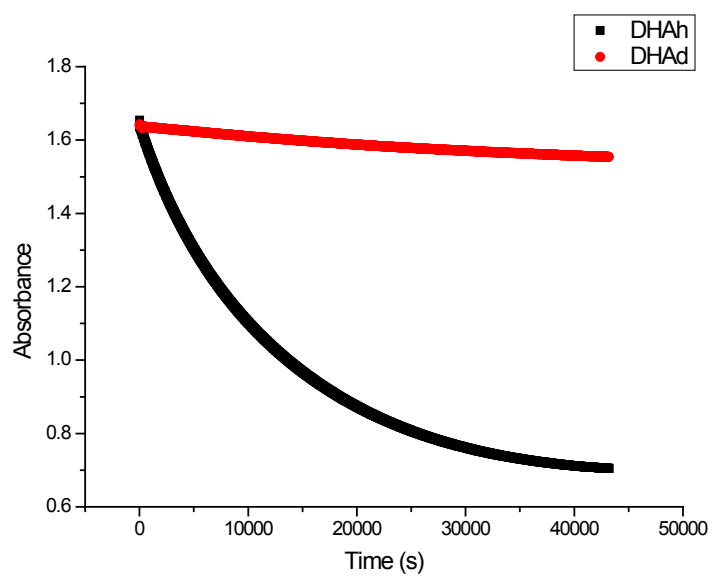


Fig. S3 Kinetics of hydrogen abstraction from 9,10-dihydroanthracene (40 mM) by manganese(IV) complex (4 mM) in acetone/water (4:1) at pH 4.0, 308 K, $k_{\text{obs}}(\text{DHA-h}_4) = 7.83 \times 10^{-5} \text{ s}^{-1}$, $k_{\text{obs}}(\text{DHA-d}_4) = 2.58 \times 10^{-5} \text{ s}^{-1}$.

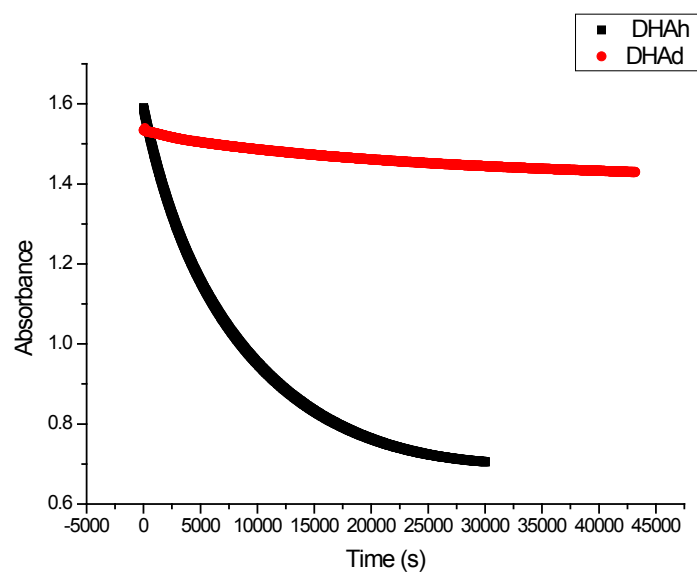


Fig. S4 Kinetics of hydrogen abstraction from 9,10-dihydroanthracene (40 mM) by manganese(IV) complex (4 mM) in acetone/water (4:1) at pH 4.0, 313 K, $k_{\text{obs}}(\text{DHA-h}_4) = 1.2 \times 10^{-4} \text{ s}^{-1}$, $k_{\text{obs}}(\text{DHA-d}_4) = 4.59 \times 10^{-5} \text{ s}^{-1}$.

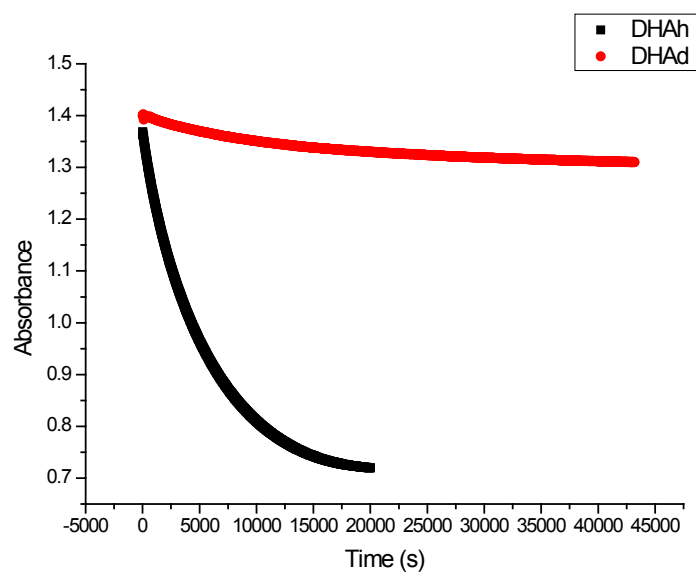


Fig. S5 Kinetics of hydrogen abstraction from 9,10-dihydroanthracene (40 mM) by manganese(IV) complex (4 mM) in acetone/water (4:1) at pH 4.0, 318 K, $k_{\text{obs}}(\text{DHA-h}_4) = 1.79 \times 10^{-4} \text{ s}^{-1}$, $k_{\text{obs}}(\text{DHA-d}_4) = 7.19 \times 10^{-5} \text{ s}^{-1}$.

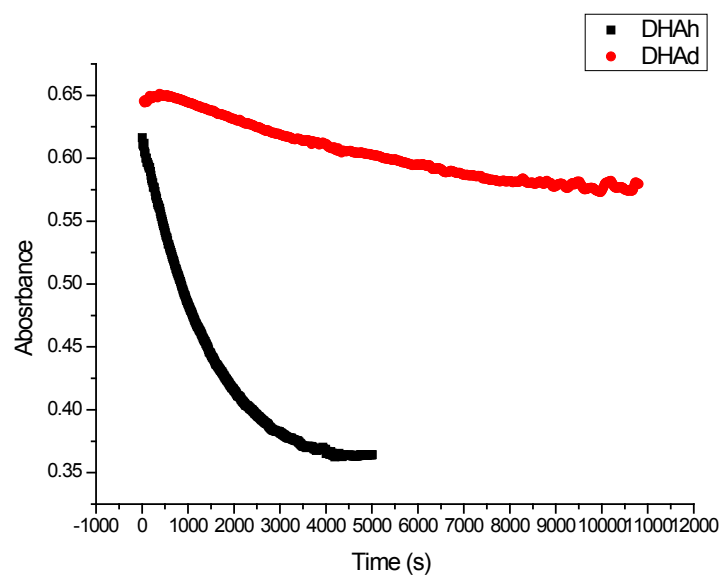


Fig. S6 Kinetics of hydrogen abstraction from 9,10-dihydroanthracene (40 mM) by manganese(IV) complex (4 mM) in acetone/water (4:1) at pH 13.4, 283 K, $k_{\text{obs}}(\text{DHA-h}_4) = 7.19 \times 10^{-4} \text{ s}^{-1}$, $k_{\text{obs}}(\text{DHA-d}_4) = 1.51 \times 10^{-4} \text{ s}^{-1}$.

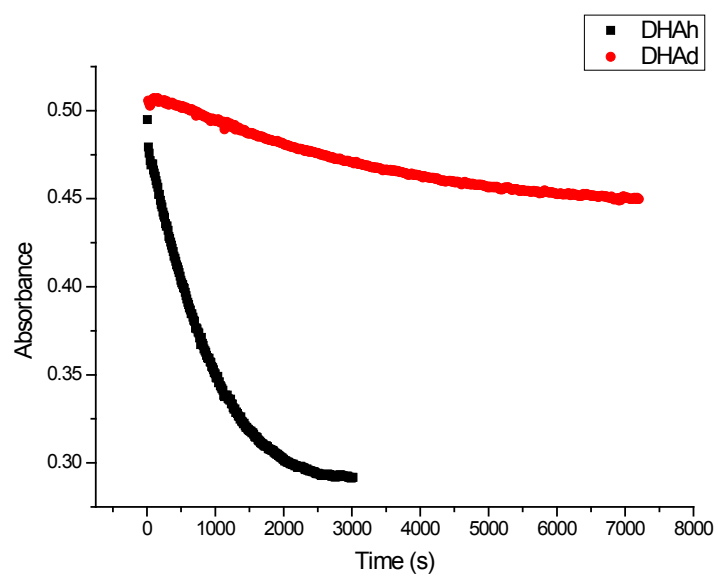


Fig. S7 Kinetics of hydrogen abstraction from 9,10-dihydroanthracene (40 mM) by manganese(IV) complex (4 mM) in acetone/water (4:1) at pH 13.4, 288 K, $k_{\text{obs}}(\text{DHA-h}_4) = 1.1 \times 10^{-3} \text{ s}^{-1}$, $k_{\text{obs}}(\text{DHA-d}_4) = 2.63 \times 10^{-4} \text{ s}^{-1}$.

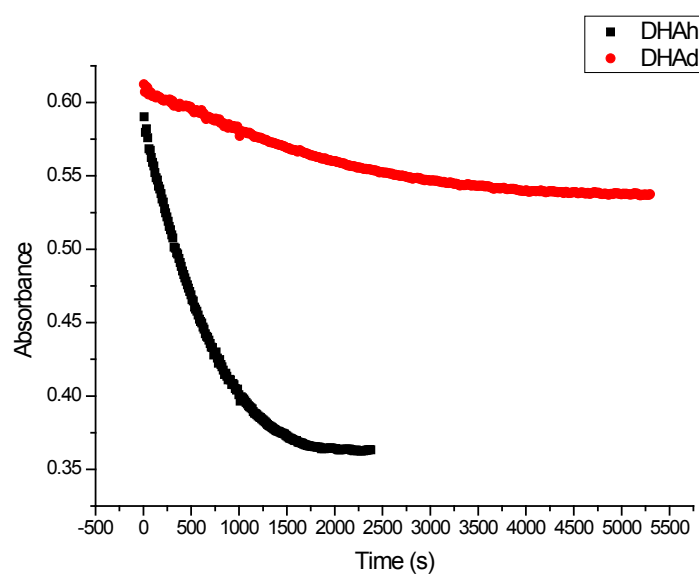


Fig. S8 Kinetics of hydrogen abstraction from 9,10-dihydroanthracene (40 mM) by manganese(IV) complex (4 mM) in acetone/water (4:1) at pH 13.4, 293 K, $k_{\text{obs}}(\text{DHA-h}_4) = 1.55 \times 10^{-3} \text{ s}^{-1}$, $k_{\text{obs}}(\text{DHA-d}_4) = 4.99 \times 10^{-4} \text{ s}^{-1}$.

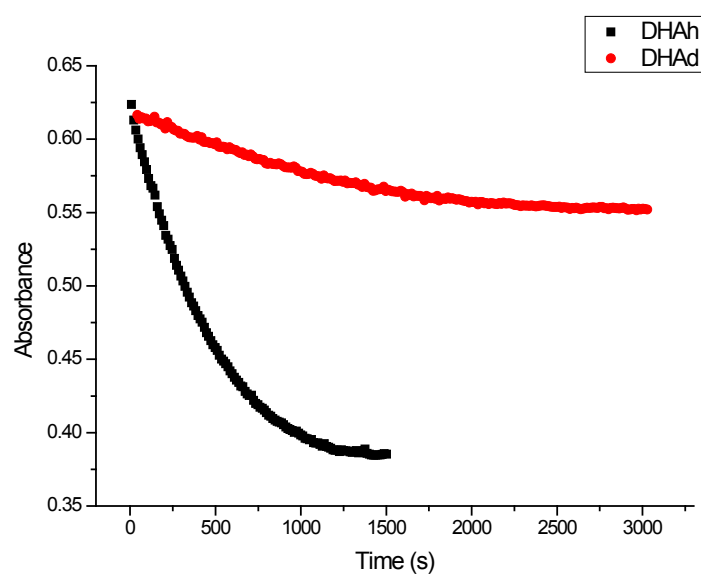


Fig. S9 Kinetics of hydrogen abstraction from 9,10-dihydroanthracene (40 mM) by manganese(IV) complex (4 mM) in acetone/water (4:1) at pH 13.4, 298 K, $k_{\text{obs}}(\text{DHA-h}_4) = 2.21 \times 10^{-3} \text{ s}^{-1}$, $k_{\text{obs}}(\text{DHA-d}_4) = 8.53 \times 10^{-4} \text{ s}^{-1}$.

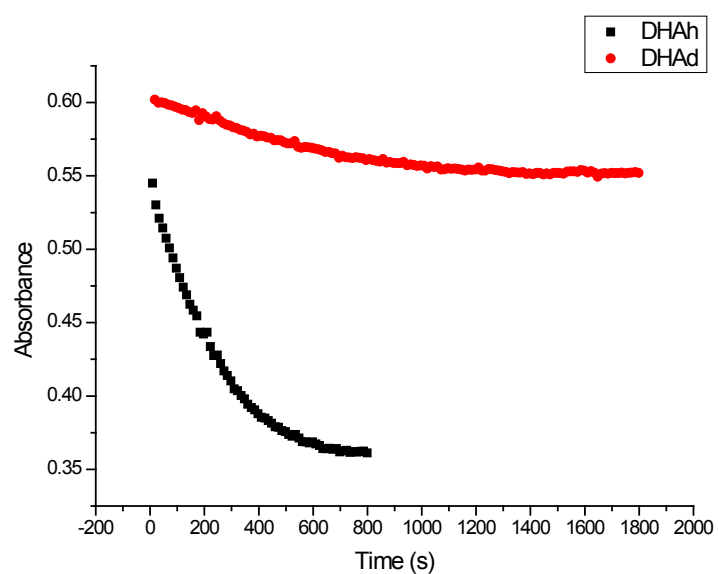


Fig. S10 Kinetics of hydrogen abstraction from 9,10-dihydroanthracene (40 mM) by manganese(IV) complex (4 mM) in acetone/water (4:1) at pH 13.4, 303 K, $k_{\text{obs}}(\text{DHA-h}_4) = 4.06 \times 10^{-3} \text{ s}^{-1}$, $k_{\text{obs}}(\text{DHA-d}_4) = 1.77 \times 10^{-3} \text{ s}^{-1}$.

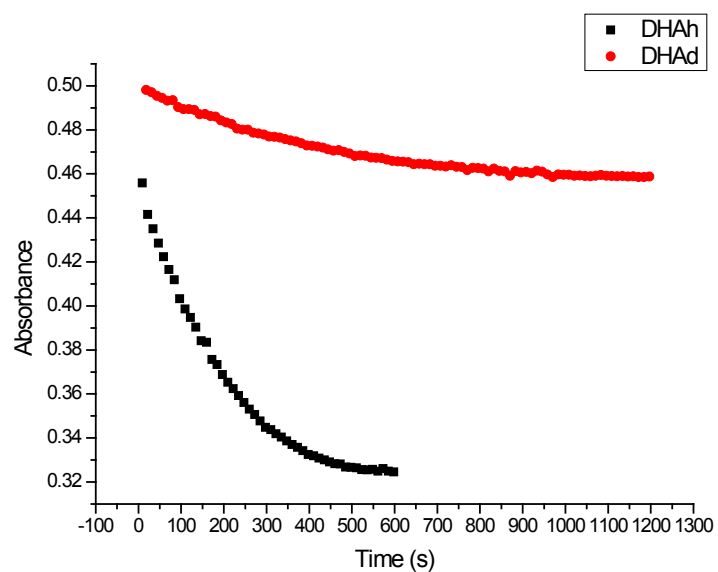


Fig. S11 Kinetics of hydrogen abstraction from 9,10-dihydroanthracene (40 mM) by manganese(IV) complex (4 mM) in acetone/water (4:1) at pH 13.4, 308 K, $k_{\text{obs}}(\text{DHA-h}_4) = 5.15 \times 10^{-3} \text{ s}^{-1}$, $k_{\text{obs}}(\text{DHA-d}_4) = 2.38 \times 10^{-3} \text{ s}^{-1}$.