JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Subscriber access provided by American Chemical Society

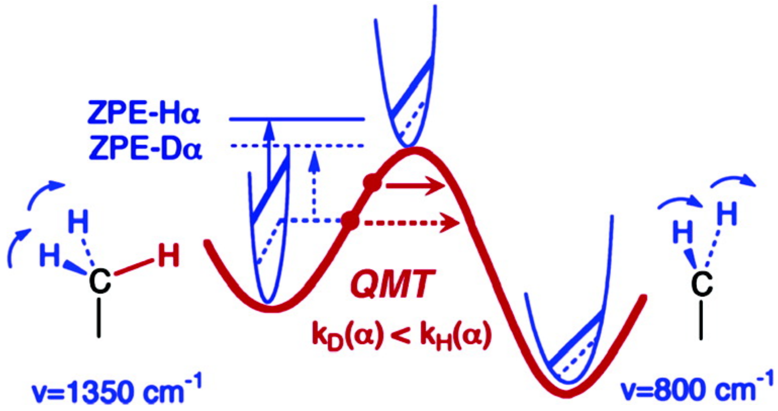
Communication

# Secondary Alpha Isotope Effects on Deuterium Tunneling in Triplet *o*-Methylanthrones: Extraordinary Sensitivity to Barrier Width

Luis M. Campos, Manoj V. Warrier, Krisztina Peterfy, K. N. Houk, and Miguel A. Garcia-Garibay

*J. Am. Chem. Soc.*, **2005**, 127 (29), 10178-10179• DOI: 10.1021/ja052487n • Publication Date (Web): 02 July 2005

**Downloaded from http://pubs.acs.org on March 25, 2009**



**More About This Article**

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 1 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML

ACS Publications
High quality. High impact.

Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
COMMUNICATIONS

Published on Web 07/02/2005

# Secondary Alpha Isotope Effects on Deuterium Tunneling in Triplet *o*-Methylanthrones: Extraordinary Sensitivity to Barrier Width

Luis M. Campos, Manoj V. Warrier, Krisztina Peterfy, K. N. Houk,* and Miguel A. Garcia-Garibay*

*Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90095-1569*

Received April 27, 2005; E-mail: mgg@chem.ucla.edu

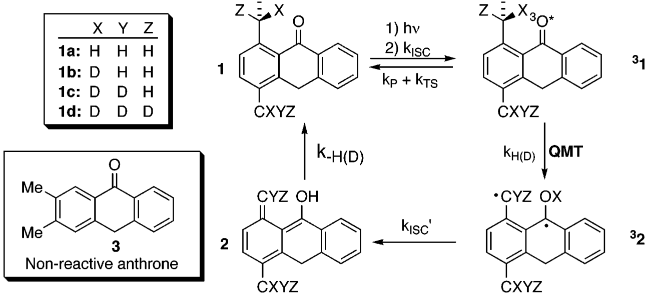
Quantum mechanical tunneling (QMT) has been invoked in reactions that occur under cryogenic conditions,[1,2] enzymatic processes involving proton and hydride transfer,[3] hydrogen-bonded networks,[4] gas phase,[5] and interstellar chemistry.[6] In the past few years, we have analyzed the structural and electronic factors that affect the rate of photoinduced H-atom tunneling in *ortho*-methyl ketones prepared with natural abundance (**1a**) and trideuterated methyl groups (**1d**, Scheme 1).[7,8] The reaction[9,10] starts by electronic excitation and rapid intersystem crossing to $^3$**1** ($k_{ISC} \sim 10^{12}$ s$^{-1}$), followed by a hydrogen atom transfer to form the triplet biradical $^3$**2**. Excited-state hydrogen transfer ($k_{H(D)}$) to form $^3$**2** competes with thermal and radiative decay back to the ground state ($k_{TS} + k_P$). Once $^3$**2** decays to the singlet state, the enol **2** reverts to **1** by a proton tunneling mechanism.[11]

To measure the rate constant for H(D) transfer ($k_{H(D)}$), the rate of disappearance of the triplet ketone ($k_{dec}$) has been determined by phosphorescence between 4 and 100 K.[7] We consider the rate of triplet decay ($k_{dec}$) to be the sum of thermal and radiative rates ($k_{TS} + k_P$), plus the rate of H(D) transfer ($k_{H(D)}$, eq 1).[12]

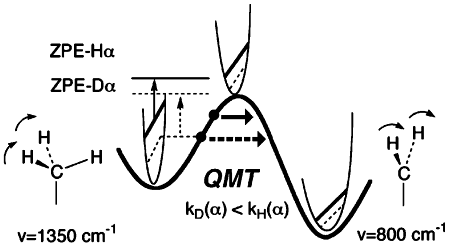
$$k_{dec} = k_{TS} + k_P + k_{H(D)} \tag{1}$$

To obtain $k_{H(D)}$, we assume that $k_{TS}$ and $k_P$ are isotope-independent and may be obtained from a nonreactive compound with a similar chromophore, such as **3** ($k_{TS} + k_p = 5 \times 10^{-2}$ s$^{-1}$).[7,12] Notably, the rate of H-transfer in **1a** is much greater (ca. $k_H > 10^6$ s$^{-1}$) than $k_{TS} + k_P$, and no emission is observed. In contrast, rate measurements for D-transfer in **1d** can be carried out easily due to a much slower reaction. Thus, a QMT mechanism was deduced by a large tunneling isotope effect (TIE) with a lower limit of ca. $k_H/k_D > 10^3$ and confirmed by a curved Arrhenius plot of **1d**, where the rate of D-transfer becomes temperature-independent below 30 K, as expected for reactions that occur along zero-point energy (ZPE) levels.[7] Recognizing that the TIEs for **1a** and **1d** result from a combination of primary and secondary effects, we decided to analyze the latter with isotopologues **1b**−**1d**. Assuming a semi-classical approximation, secondary alpha isotope effects of reactions that change hybridization from sp$^3$ to sp$^2$ are small and positive.[13] The orthogonal vibration that couples more strongly to the reaction coordinate is a C−H bending mode that changes from ca. 1350 cm$^{-1}$ in the reactant to ca. 800 cm$^{-1}$ in the product.[13] The ZPE contribution of the C−H bending mode of the alpha hydrogens on a vibrationally adiabatic surface and a qualitative depiction of its effects on the barrier height and width are illustrated in Scheme 2. From an experimental perspective, alpha secondary TIEs offer an opportunity to probe the sensitivity of QMT to very subtle changes in the width and height of the barrier.[3]

***Scheme 1***



***Scheme 2***



Phosphorescence intensities and lifetime measurements of **1b**−**1d** were carried out as described previously between 100 and 4 K in methylcyclohexane glasses.[7] The phosphorescence spectra of **1b**−**1d** measured between 77 and 5 K confirmed recent solid-state $^2$H NMR measurements, suggesting that methyl rotation is slow within the time scale of the QMT reaction.[14] As illustrated in Figure 1, samples of **1b** had no detectable emission, and samples of **1c** and **1d** had relative intensities with values **1c**:**1d** ≈ 1:5. We interpret these differences in terms of a statistical effect related to the conformation of the methyl group, which has one C−H bond opposite and two on the side of the carbonyl group and the corresponding fraction of conformers predisposed for H- and D-transfer. Thus, while all three methyl rotamers of **1b** have a hydrogen atom that can be transferred and can deactivate the triplet state, **1c** has only one rotamer with two D-atoms facing the carbonyl. The emission of **1c** is closer to a statistical 33% as compared to **1d**. Arrhenius plots constructed with rates of D-transfer for **1c** and **1d** (Figure 1B) show the curvature and plateau

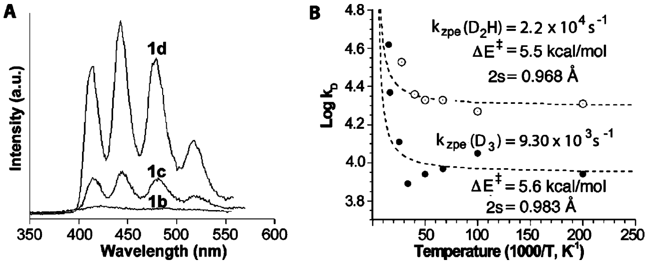


***Figure 1.*** (A) Emission spectra of compounds **1b**−**d** measured in methylcyclohexane glasses at 10 K. (B) Arrhenius plot of the D-transfer reactions of **1c** and **1d**. The rate of reaction from zero-point energy levels ($k_{ZPE}$), the calculated barrier height ($\Delta E^{‡}$), and width (2s) are indicated (the dotted lines are only qualitative).

10.1021/ja052487n CCC: $30.25 © 2005 American Chemical Society

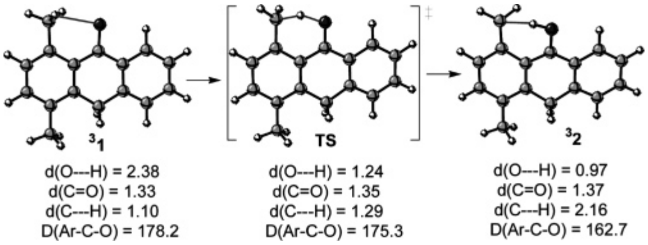


***Figure 2.*** Optimized reactant $^3$**1**, transition structure **TS**, and enol $^3$**2** (parameters listed, d = distance, D = dihedral angle).

***Table 1.*** Energetics for D-Abstraction in the Triplet State: $\Delta E^‡$ is the ZPE-Inclusive Barrier Height, $\Delta E_o$ is the Zero-Point Inclusive Energy of Reaction, $\nu^‡$ is the Imaginary Frequency of the Transition State, and ZPE is the Scaled ZPE of the Reactant[18]

| triplet ketone | $\Delta E^‡$ (kcal/mol) | $\Delta E_o$ (kcal/mol) | $\nu^‡$ (cm$^{-1}$) | ZPE (kcal/mol) |
|---|---|---|---|---|
| $^3$**1a** | 4.5 | −4.0 | 1477i | 154.3 |
| $^3$**1b** | 5.4 | −4.2 | 1088i | 150.3 |
| $^3$**1c** | 5.5 | −4.1 | 1086i | 146.4 |
| $^3$**1d** | 5.6 | −4.0 | 1077i | 142.4 |

characteristic of reactions that occur from ZPE levels.[1,15] Tunneling rates of $k_{ZPE}(D_2H) = 2.2 \times 10^4$ s$^{-1}$ and $k_{ZPE}(D_3) = 9.3 \times 10^3$ s$^{-1}$ reveal a positive and relatively large secondary α-TIE of 2.4.

Density functional theory (DFT, B3LYP/6-31G*)[16,17] was used to obtain structure and energetic information along the triplet state reaction coordinate. The optimized structures for the triplet state H-transfer reaction are shown in Figure 2 and the ZPE-inclusive[18] energetics in Table 1.

Calculations show that the reaction proceeds with minimal heavy atom motion. The dihedral angle between the aromatic and C═O groups (D[Ar−C−O]) change from 178.2 in $^3$**1** to 175.3 in the **TS** and acquire a slight twist in $^3$**2** (D[Ar−C−O] = 162.7). The transferring H(D) atom is only 2.38 Å from the carbonyl oxygen in $^3$**1**, which is less than the sum of their van der Waals radii (2.72 Å).[19] An O−H distance of 1.24 Å in the **TS** structure is close to that in the triplet enol $^3$**2** (d[O−H] = 0.97 Å). These results are in good agreement with a recent literature report.[20]

The ZPE-inclusive barrier height, $\Delta E^‡$, increases with deuterium substitution due to differences in ZPE values in $^3$**1** and **TS**. The results in Table 1 indicate that H/D abstraction is exothermic by ~4 kcal/mol ($\Delta E_o$) and that barrier height differences for a primary isotope effect (**1a** vs **1b**) and a secondary α-isotope effect (e.g., **1c** vs **1d**) are about an order of magnitude different (0.9 and 0.1 kcal/mol, respectively). In search of qualitative insight into the temperature-independent tunneling reaction, we calculated the rate of tunneling from zero-point energy levels ($k_{ZPE}$) using the approach described by Truhlar et al.[15] Their model considers a parabolic barrier with an imaginary frequency $\nu^‡$, and an adiabatic barrier height, $V_o$, without the ZPE contribution of the C−D stretching mode involved along the reaction coordinate. The tunneling rate is given by eq 2, where $P^G(E_{ZPE})$ is the quantum mechanical permeability defined in eq 3.

$$k_{ZPE} = c\nu_{C-D}P^G(E_{ZPE}) \tag{2}$$

$$P^G(E_{ZPE}) = 1/(1 + \exp\{[2\pi/(hc\,|\nu^‡|)]\,(\Delta E^‡)\}) \tag{3}$$

Secondary alpha isotopes cause variations in the height of the barrier ($\Delta E^‡$) from 5.5 kcal/mol for **1c** to 5.6 kcal/mol in **1d**. Changes in the width of the barrier (2s) are estimated from the assumed parabola, which can be described by the values of $\nu^‡$, $V_o$, and the scaling reduced mass $\mu$ (eq 4, $\mu$ = 1 amu). Imaginary frequency values of −1086 and −1077 cm$^{-1}$ in **1c**$^‡$ and **1d**$^‡$ result in barrier widths of 0.968 and 0.983 Å, respectively.

$$s = \sqrt{\frac{2V_o}{\mu(2\pi c|\nu^‡|)^2}} \tag{4}$$

Finally, the calculated $k_{ZPE}$ values obtained with eq 2 taking a frequency factor, $c\nu_{C-D} \approx 6.5 \times 10^{13}$ s$^{-1}$ [$k_{ZPE}(D_2H)_{calcd} = 1.8 \times 10^6$ s$^{-1}$ and $k_{ZPE}(D_3)_{calcd} = 1.2 \times 10^6$ s$^{-1}$] are 2 orders of magnitude larger than those determined experimentally ($k_{ZPE}(D_2H)_{exp} = 2.2 \times 10^4$ s$^{-1}$ and $k_{ZPE}(D_3)_{exp} = 9.3 \times 10^3$ s$^{-1}$). While a calculation error of ca. 2.3 kcal/mol in the height of the barrier could explain this discrepancy, an excellent agreement is obtained with known pre-exponential factors[9] of ~5 × 10$^{11}$ s$^{-1}$ for the H-transfer reaction. A small disagreement between experimental (2.4) and calculated (1.5) tunneling isotope effects suggests that the one-dimensional treatment of tunneling accounts only partially for the experimental observations. However, a simple model based on the effect of isotopes on ZPE and the shape of the barrier accounts for the measured results and suggests that a difference of only 0.015 Å in barrier width leads to 2-fold differences in tunneling rates at very low temperatures. Studies with higher level calculations and direct dynamics methods will be reported in due course.

**Acknowledgment.** This work was supported by NSF Grant CHE0242270. L.M.C. thanks the NSF, Paul & Daisy Soros Fellowship, and NSF IGERT: MCTP, Grant: DGE-0114443). We thank Prof. D. Truhlar for valuable comments and advice.

**Supporting Information Available:** Synthesis of isotopically labeled anthrones **1b**−**1d** and Cartesian coordinates of the stationary points. This material is available free of charge via the Internet at http://pubs.acs.org.

## References

(1) Zuev, P. S.; Sheridan, R. S.; Albu, T. V.; Truhlar, D. G.; Hrovat, D. A.; Borden, W. T. *Science* **2003**, *299*, 867.
(2) Bell, R. P. *The Tunnel Effect in Chemistry*; Chapman & Hall: London, 1980.
(3) (a) Kohen, A.; Klinman, J. P. *Acc. Chem. Res.* **1998**, *31*, 397. (b) Doll, K. M.; Bender, B. R.; Finke, R. G. *J. Am. Chem. Soc.* **2003**, *125*, 10877. (c) Alhambra, C.; Sanchez, M. L.; Corchado, J. C.; Gao, Y.; Truhlar, D. G. *Chem. Phys. Lett.* **2002**, *347*, 512.
(4) Horsewill, A. J.; Jones, N. H.; Caciuffo, R. *Science* **2001**, *291*, 100.
(5) Garrett, B. C.; Truhlar, D. G.; Bowman, J. M.; Wagner, A. F.; Robie, D.; Arepalli, S.; Presser, N.; Gordon, R. J. *J. Am. Chem. Soc.* **1986**, *108*, 3515.
(6) Hiraoka, K.; Sato, T.; Takayama, T. *Science* **2001**, *292*, 869.
(7) Garcia-Garibay, M. A.; Gamarnik, A.; Bise, R.; Jenks, W. S. *J. Am. Chem. Soc.* **1995**, *117*, 10264.
(8) (a) Al-Soufi, W.; Eychmuller, A.; Grellmann, K. H. *J. Phys. Chem.* **1991**, *95*, 2022−2026. (b) Smedarchina, Z.; Enchev, V.; Lavtchieva, L. *J. Phys. Chem.* **1994**, *98*, 4218.
(9) Wagner, P. J.; Park, B.-S. *Org. Photochem.* **1991**, *11*, 227−366.
(10) (a) Wagner, P. J.; Chen, C.-P. *J. Am. Chem. Soc.* **1976**, *98*, 239. (b) Scaiano, J. C. *Chem. Phys. Lett.* **1980**, *73*, 319.
(11) Grellmann, K.-H.; Weller, H.; Tauer, E. *Chem. Phys. Lett.* **1983**, *95*, 195−199.
(12) (a) Johnson, B. A.; Kleinman, M. H.; Turro, N. J.; Garcia-Garibay, M. A. *J. Org. Chem.* **2002**, *67*, 6944. (b) Johnson, B. A.; Hu, Y.; Houk, K. N.; Garcia-Garibay, M. A. *J. Am. Chem. Soc.* **2001**, *123*, 6941.
(13) Streitwieser, A., Jr.; Jagow, R. H.; Fahey, R. C.; Suzuki, S. *J. Am. Chem. Soc.* **1958**, *80*, 2326.
(14) Cizmeciyan, D.; Yonutas, H.; Karlen, S. D.; Garcia-Garibay, M. A. *Solid State Nucl. Magn. Res.* **2005**, *28*, 1−8. The UB3LYP/6-31G* ZPE-inclusive barrier for the methyl rotation in $^3$**1** is 1.0 kcal/mol.
(15) Wanchoba, S. E.; Hu, W.-P.; Truhlar, D. G. *Phys. Rev. B* **1995**, *51*, 9985.
(16) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652. (b) Head-Gordon, M.; Pople, J. A. *Chem. Phys. Lett.* **1988**, *153*, 503.
(17) Calculations were performed using the Gaussian 98 suite of programs.
(18) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502.
(19) Ihmels, H.; Scheffer, J. R. *Tetrahedron* **1999**, *55*, 885.
(20) Casadesus, R.; Moreno, M.; Lluch, J. M. *J. Phys. Chem. A* **2004**, *108*, 4536.

JA052487N