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Rate Acceleration below 20 K in the H-Atom Tunneling of Triplet *ortho*-Methyltetralones

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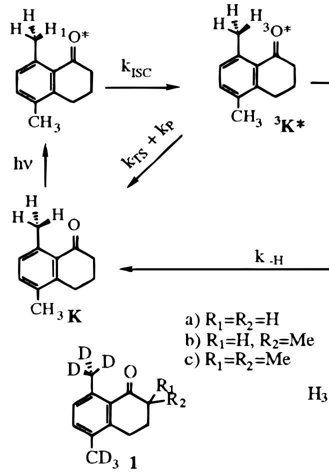
Our interest in reactions that occur under highly restricted molecular motion in crystalline[1] and amorphous solids[2] has led us to analyze transformations that occur at extremely low temperatures. Recent examples include the photoenolization of conformationally restricted *ortho*-methyl aryl ketones, which are illustrated in Scheme 1 with 5,8-dimethyltetralone (**1a**).[3] The reaction transforms an *ortho*-methyl aryl ketone (**K**) into an *ortho*-quinodimethane (**E**)[4] in a process that occurs at ultralow temperatures by quantum mechanical tunneling (QMT) in the triplet excited state.[2,3,5]

While it is well known that QMT depends on the height and width of the activation barrier and how the reaction trajectory couples to the vibrational dynamics of reactants and products at energies that are below that of the transition state,[6,7] it is not clear how these will relate to the structure of the reactant. To probe the sensitivity of QMT to subtle structural changes, we have analyzed several *ortho*-alkyl benzocycloalkanones with various substitution patterns.[8] In this communication, we report results with deuterated *ortho*-methyltetralones **1b** and **1c** which differ from **1a** only by having one or two methyl groups next to the carbonyl carbon. We found that small differences caused by the α-methyl groups on the vibrational structure of the reactant do not change significantly the results previously obtained for **1a**. However, with measurements extended to 4 K, we discovered a remarkable rate acceleration that we interpret in terms of triplet-state polarization, slowed equilibrium between triplet sublevels, and distinct triplet sublevel QMT rates.

Experimentally, deuterium-transfer rates can be obtained by considering that the rates of triplet decay (k_{dec}) are the sum of thermal and radiative rates ($k_{TS} + k_P$) plus the rate of deuterium transfer (k_D, eq 1),[2] and by assuming that the first two rates ($k_{TS} + k_P$) may be obtained from model compounds with similar chromophores but with no reaction possible (e.g., **2a**−**c**).

$$k_{dec} = k_{TS} + k_P + k_D \qquad (1)$$

Scheme 1



As expected from their different decay options, the triplet decays of *ortho*-methyl ketones **1a**−**c** are faster and have a greater temperature dependence than those of (unreactive) ketones **2a**−**c**. Because of a large primary isotope effect (ca. $k_H/k_D > 10^3$), no emission was detected from protio compounds **1a**−**c** ($k_H > 10^7$ s^{-1}).[5] The contribution of reaction to triplet decay was confirmed by accumulation and spectroscopic detection of *ortho*-quinodimethanes (**E**) in ethanol, even under conditions where the rate of triplet decay of deuterated **1a**−**c** is slowest. All triplet decays were relatively complex but could be fit reasonably to a double exponential, with rates k_1 and k_2 and preexponential factors I_1 and I_2. Although solvation effects, slightly different conformations, and mixing of nearby π,π^* states may contribute to the observed nonexponentiality,[2,9] the greatest deviations were observed at the lowest temperatures. Given the complexity of the experimental data, to carry out a qualitative but insightful analysis of deuterium transfer using eq 1, the average decay rates of **1a**−**c** and **2a**−**c** were calculated according to eq 2, with the contribution of each component obtained from the ratios I_1/k_1 and I_2/k_2.[2d]

$$k_{dec} = (I_1/k_1 + I_2/k_2)/(I_1/k_1^2 + I_2/k_2^2) \qquad (2)$$

Arrhenius plots were constructed with the average D-transfer rates (k_D) obtained by subtracting the average decay rates of **2a**−**c** from those of **1a**−**c**. As shown in Figure 1, the temperature dependence of the average deuterium transfer rate constants between 120 and 4 K has a very complex behavior. The temperature dependence in Figure 1 was not paralleled by the nonreactive ketones **2a**−**c**. In the region labeled A in Figure 1, between ca. 40−120 K, the average decay rates of **1a**−**c** undergo a ca. 16-fold change that is assigned to the starting contributions from a thermally activated deuterium transfer reaction. Due to extensive QMT, the activation energy and preexponential factors estimated from the slopes in region A ($E_a \approx 0.1−0.2$ kcal/mol, log $A \approx 4−5$) are much smaller than those expected for purely activated processes.[6a,7] As previously observed for **1a**, the average decay rates of **1b,c** remained essentially constant between ca. 40−20 K (region B), suggesting that QMT occurs from vibrational states approaching zero-point energy levels of the reactant. However, an unexpected rate increase below 20 K (region C) indicates a thermally dependent process involving molecular or environmental states with energy differences consistent with phonon dynamics and/or electron spin effects.

To explore the origin of these observations, we take a closer look at the rate changes giving rise to the data shown in Figure 2. A semilogarithmic superposition of decays obtained with **1b**

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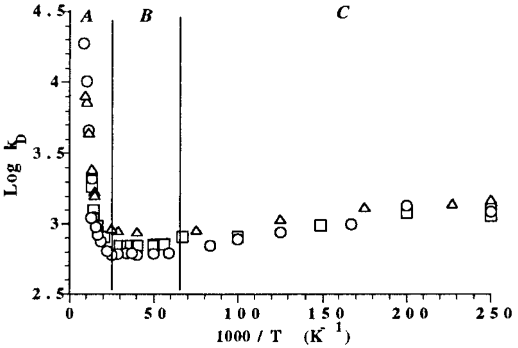


Figure 1. Arrhenius plot of the average decay rates of **2a** (△), **2b** (□), and **2c** (○) between 4 and 100 K.

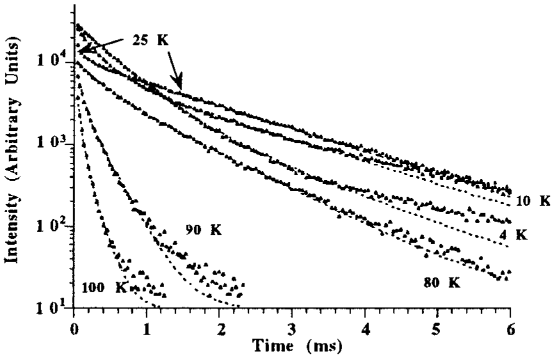


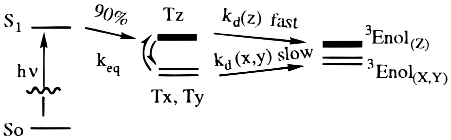
Figure 2. Decay of phosphorescence intensity for **1b** at 80, 25, 10, and 4 K in MCH glasses. The dotted lines indicate the corresponding double-exponential fit.

at 100, 90, 80, 25, 10, and 4 K during a 6-ms window and a 40-μs delay after the pulse reveals a kinetic heterogeneity that affects the lifetimes and contributions of fast and slow components, k_1 and k_2 (eq 2).

Deviations from a double exponential near the end of the decay are clear for all the plots, but we made no attempts to fit the data to more complex models. Decay traces at 80 K and higher temperatures are the least complex with relatively similar slow and fast components: at 100 K, values of $k_1 = 5.6 \times 10^3$ and $k_2 = 2 \times 10^4$ s^{-1} give an average decay rate of $k_{\mathrm{dec}} = 1.0 \times 10^4$ s^{-1}. The complexity of the decay data above ca. 25 K is assigned primarily to the structural heterogeneity of the glassy media. Remarkably, differences in values and relative contributions from the two components increase at lower temperatures. The first 200 μs of the data collected at 25 K shows a very fast component (ca. 1.2×10^4 s^{-1}) which has a relatively small contribution (4% of all the photons emitted) to the average rate of 0.61×10^3 s^{-1}. The average decay rate at 25 K is about 16 times smaller than that at 100 K. At 10 K, the data can also be approximated in terms of fast and slow components. The fast component at 10 K is not as fast as that at 25 K (3.7×10^3 s^{-1}), but a greater contribution to the average decay rate (30%) results in a greater average value. Finally, the data collected at 4 K show the greatest kinetic heterogeneity and the most severe deviations from a double exponential. Continuing with the trend, the fast component at 4 K is slower than those at 25 and 10 K, but its contribution to the average decay is the greatest (2.4×10^3 s^{-1}, 50%). These complex changes account for the 2-fold increase between ca. 25 and 4 K calculated for the average rates in Figure 1.

With measurements carried out in different glassy matrixes and in crystals, we are able to rule out explanations based on environmental factors for the changes in Figures 1 and 2.[8] Results with other benzocycloalkanones confirm that this is a general phenomenon in aryl ketone chromophores. Although the average decay rates of nonreactive **2a**−**c** displayed a much smaller temperature dependence, a reorganization of fast and slow components was also observed below 20 K (not shown). Based on information from magnetic resonance studies of triplet ketones, we propose that the rate increase and kinetic heterogeneity below ca. 25 K reflect the interplay of three elementary processes:[10,11] (a) spin polarization of triplet sublevels by intersystem crossing selection rules, (b) slowing of triplet sublevel equilibrium with decreasing temperatures (e.g., by a spin−lattice mechanism), and (c) distinct photophysics and photochemistry of the triplet sublevels (Scheme 2).[12]

Scheme 2



It is known that selection rules for intersystem crossing in aromatic ketones preferentially populate one of the triplet sublevels (T_z),[11a] and it has also been shown that T_Z decays significantly faster than the other two sublevels (T_x and T_y).[10−12] Zero-field-splitting parameters for similar tetralones indicate that T_z is higher in energy by 0.245 cm^{-1} relative to T_x and T_y, which are separated from one another by only ca. 0.010 cm^{-1}.[13]

The temperature dependence of the decay data between 25 and 4 K was qualitatively reproduced with a kinetic model that considers preferential population of T_z (90%), distinct hydrogen-transfer rates from each triplet sublevel, and a temperature-dependent spin-state equilibration (Scheme 2).[11−13] Rather than fitting the data to three starting populations, distinct triplet sublevel decay rates, and different rates of interconversion between spin sublevels, we used a simple model with two experimentally distinguishable states (i.e., T_z and T_x,T_y), two temperature-independent elementary rates of decay [e.g., $k_{\mathrm{dec}}(Z) = 2 \times 10^3$ s^{-1} and $k_{\mathrm{dec}}(X,Y) = 2 \times 10^2$ s^{-1}], and two temperature-dependent equilibration rates between spin subleves (Scheme 2). Although there is a high uncertainty from using four adjustable parameters, a good qualitative fit of the experimental data was obtained with equilibrium rates ranging from 10^6 to 10^2 s^{-1} as the temperature changed from 30 to 4 K. The model implies that triplet sublevel equilibrium (k_{eq}) is faster than decay above ca. 20 K, of similar magnitude below 10 K, and not much slower at 4 K. Thus, while deuterium tunneling above ca. 30 K occurs with rates weighed by equilibrium populations of all three triplet sublevels, the rate of tunneling becomes highly heterogeneous as the rate of equilibrium between triplet sublevels becomes comparable to the elementary rates from each sublevel at the lowest temperatures. As measured by this model, the equilibrium between triplet sublevels slows to the millisecond regime at about 10 K but is not completely frozen within the time scale of reaction and radiative decay at 4 K. It is interesting that differences in tunneling rates between different triplets confirm[13] state-specific surfaces proposed from time-resolved EPR experiments. Finally, it is also noteworthy that subtle structural modifications near the reaction center in **1a**−**c** do not appear to affect the vibrational dynamics that are relevant to their zero-point-energy triplet tunneling trajectories.

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Supporting Information Available: Derivation of eq 2 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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