Electronic Supplemental Information for

Contrasting the excited state reaction pathways of phenol and *para*-methylthiophenol in the gas and liquid phases

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FT-IR Measurements for Determining the Monomer Fraction

The absorption in the IR range ($1000 < \nu < 4000$ cm^{-1}) of phenol in cyclohexane solution was determined by a Vertex 80v FT-IR spectrometer (Bruker). The spectra for various phenol concentrations (5.0, 9.7, 20, 49, 66, 96 mM) were taken in a standard IR cell with 1 mm path length and BaF_2 windows (International Crystal Laboratories). The instrument resolution was 1 cm^{-1} and the spectra were averaged over 16 scans. Both the optical bench and the sample compartment were evacuated to < 300 Pa in order to avoid absorption from carbon dioxide and water vapor. The absorption of the BaF_2 and solvent cyclohexane were measured under the same experimental parameters and subsequently subtracted from the spectra of the above phenol solutions.

Much literature has discussed the origin of the three O-H stretch bands, and the consensus is that, in analogy to aliphatic alcohols in non-polar organic solvents,[1-4] the sharp peak at the highest frequency (3617 cm^{-1}) is originated from free O-H stretch, the relatively broader band centered at ~3500 cm^{-1} is due to the O-H stretch from the phenol being a proton donor in a H-bonded complex, and the very broad structured centered at 3340 cm^{-1} is caused by the OH group being simultaneously proton donor and acceptor, which is usually seen in the H-bonded polymeric long chain (see fig. 1).[5-8] Although there are some debate on distinguishing the free O-H stretch of the monomer from the dimer, and the structure of the phenol dimer (see fig. 6 in main text),[5,6] the appearance of the dimeric and polymeric bands provides direct evidence of self association, and the fraction of free OH group at different concentrations can be deduced from the absorption strength of the 3617 cm^{-1} band.[9]

Fig. 1 (a) and (b) show the O-H stretch region on an expanded scale, from which we can see that at very dilute phenol concentration, *i.e.*, 5 and 10 mM, the dimeric and polymeric bands are not yet developed (the negative absorption is due to the imperfect subtraction of the cyclohexane background signal), indicating that the phenol molecules do not self-associate at this concentration regime. The dimeric band at ~3500 cm^{-1} becomes more pronounced at 20 mM solution but no polymeric band is visible. For higher phenol concentrations (49, 66, 96 mM), all three bands are visible, which indicates the coexistence of free molecule, dimer and polymeric long chain.

To quantify the fraction of free OH in cyclohexane solution, the extinction coefficient of the free O-H stretch is estimated to 270 M^{-1} cm^{-1}, which is calculated from the optical density of the 5 and 10 mM solution (average of the two). Note that this number is five times higher than that estimated from HOD [10] and ten times higher than water in n-octane (although in this case there are both symmetric and asymmetric stretch),[11,12] but it is very close to the extinction coefficient of O-H stretch measured from 4-chlorophenol in carbon tetrachloride solution (220 M^{-1} cm^{-1}).[13] Figure 1 (c) and (d) present the deviation of O-H stretch optical density from the “expected value” calculated from the extinction coefficient. Figure (c) shows the strongest feature in the IR spectrum, the ring deformation mode, has optical density which scales linearly as the phenol concentration (blue circle and solid line). This shows the upper limit of the dynamic range of the instrument is at least O. D. 2.6 and thus firmly establishes that the deviation from linearity of the O-H modes is solely due to the H-bonded complex formation. It is also shown that the O-H bent mode at 1174.6 cm^{-1} exhibits similar behavior as O-H stretch at 3617.3 cm^{-1}. Figure (d) presents the calculated monomer fraction at our concentration range (blue solid line). Our estimate is fully in accordance with the ultraviolet absorption[14] and other IR experiments[15] in carbon tetrachloride. At the highest concentration employed in the TA experiments (90 mM), it is estimated there are 70% of monomer in the system.

Geminate Recombination Fitting

We have previously used the radical-radical recombination model to fit the *p*-MePhS radical kinetics in ethanol solution,[16] and we use the same method to model the recombination in cyclohexane solution in this work. Briefly, in the spherically symmetric limit and under fieldfree diffusion of the radicals,[17,18] the survival probability of the radical, represented by its *normalized* transient absorption signal, can be described by the following equation.

$$\mathrm{TA}(t) = \mathrm{erfc}\left(\frac{r_{xn}}{\sqrt{4D' t_{\mathrm{g}}}}\right) + \frac{r_{xn} \exp\left[-r_{xn}^{2}/4D'(t+t_{\mathrm{g}})\right]}{\sqrt{\pi D'(t+t_{\mathrm{g}})}}\left[\mathrm{erfc}\left(\sqrt{\frac{r_{xn}^{2} t}{4D' t_{0}(t+t_{\mathrm{g}})}}\right)\right] \qquad (1)$$

where r_{xn} is the reaction radius – the distance between geminate partners where recombination is assumed to occur instantaneously. D' is the sum of the diffusion coefficient D_{H} and $D_{radical}$ as described in the main text. Assuming a Gaussian distribution of the initial radical-radical separation distance (ejection length), the average distance is related to the width of Gaussian function t_g:

$$\langle r_0 \rangle = (8\pi)^{1/2} \sqrt{2D' t_g} \qquad (2)$$

For fitting the data in Figure 3, we attempted to use a smaller r_{xn} (2.7 Å), which is the $\mathrm{R}_{\text{S-H}}$ value at kT below the p-MePhS($\tilde{\mathrm{X}}$) + H asymptote,[19] to model the decay kinetics of the radical. This value, however, assumed that the geminate partners recombined at the S atom to reproduce the parent p-MePhSH molecule, and neglected another possible recombination site at the ring position. The latter pathway is supported by our TA spectra, which showed a slow rising feature at ~380 nm assignable to p-MePh(H)S. In light of this, both r_{xn} and t_g were allowed to float in order to obtain the best fit of the experimental data. The same protocol (floating r_{xn} and t_g) was followed for PhO + H recombination.

References and Notes

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9 There is a subtle effect of relating the number of free O-H to the number of monomers in the solution. As discussed above, The O-H stretch from the terminal of the open chain dimer and polymer may not be distinguishable from the O-H stretch from the true monomer. Therefore, the IR spectra give information on the number of free OH groups, which is the upper limit of phenol monomer. However, the fact that they have similar spectroscopic properties means that they have similar electronic structures and thus are likely to exhibit similar photochemical behaviors.

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Figure 1.

(a) IR absorption spectra of phenol in cyclohexane, expanded to the O-H stretch region. Inset: expanded to show the H-bonded O-H stretch. (b) Spectra normalized to the 3617 cm^{-1} peak to emphasize the change in the shape of spectra as a function of concentration. (c) absorption peak intensities as a function of phenol concentration: ring deformation (blue), O-H stretch (black), O-H bend (red). (d) monomer fraction estimated from the free O-H stretch extinction coefficient (calculated from the 5 and 10 mM solution, assuming all phenol molecules exist in monomer form).