Photooxidation of the Phenolate Anion is Accelerated at the Water/Air Interface

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ABSTRACT: Molecular photodynamics can be dramatically affected at the water/air interface. Probing such dynamics is challenging, with product formation often probed indirectly through its interaction with interfacial water molecules using time-resolved and phase-sensitive vibrational sum-frequency generation (SFG). Here, the photoproduction formation of the phenolate anion at the water/air interface is probed directly using time-resolved electronic SFG and compared to transient absorption spectra in bulk water. The mechanisms are broadly similar, but 2 to 4 times faster at the surface. An additional decay is observed at the surface which can be assigned to either diffusion of hydrated electrons from the surface into the bulk or due to increased geminate recombination at the surface. These overall results are in stark contrast to phenol, where dynamics were observed to be 10^4 times faster and for which the hydrated electron was also a photoprodut. Our attempt to probe phenol showed no electron signal at the interface.
The transient SFG data in comparison show a faster initial rise but subsequently has broadly similar kinetics, suggesting that a similar overall model may apply to the interface. However, rather than reaching a long-term offset, the SFG signal continues to decay on a longer time scale. Thus, there are also clear differences and these must be associated with the differing solvation environments. In the first instance, we attempted to fit the kinetics with the same model. However, from Figure 1, \( k_d \) is clearly much larger than \( k_n \) and \( k_d \) so that the bulk kinetic model can be simplified to

\[
N(t) = \frac{k_d}{k_d + k_n} + \frac{k_n}{k_d + k_n} e^{-(k_d+k_n)t}
\]

The fit of the SFG data to this model is shown in Figure 3 and shows some clear deviations that the model cannot account for: overshooting the data at early times, then undershooting, and overshooting again at long time. A plot of \( \ln[N(t)] \) confirms that the signal is not a simple monoexponential decay (see Supporting Information). Other than the initial rise (associated with \( k_p \)), the long-time decay observed is the most obvious difference between the surface and bulk. Bradforth and co-workers accounted for a longer-time (100s ps) decay of \( e^-_{(aq)} \) following CTTS of bulk iodide by including the diffusion of the free \( e^-_{(aq)} \) and \( I^-_{(aq)} \) which can then recombine to form the contact pair \([1:e^-(aq)]\) and undergo the subsequent competing kinetics in the model.\(^5\) In the context of phenolate, this would correspond to recombination of \( e^-_{(aq)} \) and Ph\(^+\) to reform \([\text{Ph:e}^-]_{(aq)}\). On the surface, diffusion can take a different form: diffusion away from the surface would lead to a depletion in the observable SFG signal, and diffusion in two dimensions may have very different kinetics to recombine \([\text{Ph:e}^-]_{(surf)}\). Both would increase the rate of electron loss at long times. Given the potential complexity, we have accounted for these processes by adding a single exponential decay, noting that diffusion is not necessarily a simple first-order process. The migration of the surface electron to the bulk is shown schematically in Figure 2. The surface electron loss is quantified by the rate coefficient \( k_p \). The overall concentration of electrons at the surface, \( N_{surf}(t) \), then becomes (assuming that \( k_p \gg k_n \) and \( k_d \) that the absorption spectrum, or more precisely the \( \chi^{(3)} \) spectrum, of \([\text{Ph:e}^-]_{(surf)}\) and \( e^-_{(surf)} \) are indistinguishable):

\[
N_{surf}(t) = \frac{k_d}{k_b - (k_d + k_n)} e^{-(k_d+k_n)t} - e^{-k_p t} + e^{-(k_d+k_n)t}
\]
Figure 3 shows the fit of the SFG data to this extended model, which appears significantly improved and captures much of the previous shortcomings. The lifetimes associated with the three processes are given in Table 1. We conclude that the processes taking place at the interface are broadly similar to those in the bulk, but with different rates and with the additional electron loss component at longer times. All processes ($k_p$, $k_d$, and $k_o$) are faster at the interface. There are several factors that can impact the observed increase in rates. The lower density will affect polarization, electrostatic interactions, hydrogen bonding, and anisotropy of the interactions. Intuitively, the increase in $k_d$ could be rationalized as the lower density of water molecules would be expected to enable the contact pair [Ph: e$^-$ (surf)] to dissociate more readily (i.e., larger $k_d$), because it would be easier to break the solvation cage surrounding both species. The faster non-adiabatic recombination ($k_o$) could be justified as the free-energy surfaces are altered leading to changes in charge-transfer rate in a Marcus picture. Similar arguments were made to explain the moderate increase in rates observed for aqueous iodide at the interface (increase by a factor of 1.3 in $k_d$ and 1.4 in $k_o$).  

$\text{In phenolate, there is no } \pi\sigma^*$ state and the } \pi\pi*$ state could be formed. Regardless, there are clearly very interesting dynamics taking place at the water/air interface with pertinence in many areas of science. We hope our work here will encourage more experiments that probe the products directly.

* ASSOCIATED CONTENT

† Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.2c04935.

Details of the experimental arrangement of both transient absorption and SFG experiments; description of the fluorescence removal; signal processing; and full transient absorption spectra; error analysis; phenol SFG data and consideration of sensitivity. (PDF)

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Notes

The authors declare no competing financial interest.

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