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Correlating solvent dynamics and chemical reaction rates using binary solvent mixtures and two-dimensional infrared spectroscopy

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Two-dimensional infrared (2D-IR) spectroscopy was performed on Vaska’s complex (VC) and its oxygen adduct (VC-O₂) in binary solvent mixtures of chloroform or benzyl alcohol in d₆-benzene. The second order rate constants for oxygenation were also measured in these solvent mixtures. The rate constant in chloroform mixtures is linear with mole fraction within the error of the measurements but changes nonlinearly in benzyl alcohol mixtures, displaying a preference for the alcohol over benzene. The rate constants were compared with FTIR spectra of the carbonyl ligand and the frequency-frequency correlation function of this mode determined by 2D-IR. The line shape broadening mechanisms of the linear spectra of the CO bound to VC and VC-O₂ are similar to those previously reported for VC-I₂. There is a particularly strong correlation between rate constants and homogeneous linewidths of the carbonyl vibration on the VC-O₂ product state. Concurrently, the FTIR spectra and spectral diffusion observed by 2D-IR corroborate an increase in solvent heterogeneity around the product. We interpret these results in the context of the potential role of solvent dynamics in facilitating chemical reactivity. © 2015 AIP Publishing LLC.

I. INTRODUCTION

Bis(triphenylphosphine)iridium(I)carbonyl chloride, or Vaska’s complex (VC), has been extensively studied for its catalytic ability and its willingness to oxidatively bind small molecules.¹⁻¹⁵ The kinetics and mechanism of O₂ addition to form the VC-O₂ adduct (Scheme 1) have been the focus of many previous studies.²⁻⁸,¹² The reversible side-on binding of O₂ to VC provides a small molecule mimic of biological oxygen transport systems,¹⁻¹⁵ and is also a simple model of the first mechanistic step in a catalytic cycle wherein the substrate is bound to the active site of a catalyst. As is true for most chemical reactions, the rate of O₂ addition to VC is sensitive to the nature of the solvent.²⁻⁸,¹²,¹⁷ The entropy of this process was found to be negative and the rate constant increased with increasing solvent polarity, suggesting the presence of a polar transition state, similar to a Menshutkin reaction.² This interpretation was disputed by early studies analyzing electronic ligand effects,¹⁸⁻²⁰ and more recently, it has been shown by Wilson and coworkers that ligand properties can dictate relative rates for this and analogous compounds.²¹ Thus, for the same reactant in different solvents, the mere increase in rate with polarity does not in and of itself give enough information to determine whether a polar transition state was present. A further computational study modeled the mechanism and calculated transition states for the reaction of O₂ with the trimethylphosphine analogue of VC.²² This study showed that the mechanism begins with an end-on triplet O₂ approach, proceeds via a pincer motion of the CO and Cl ligands through a side-on O₂ position (as surmised by Ugo).²⁰ passes through another end-on state, and then undergoes intersystem crossing to the side-on singlet product.²² The largest energy cost (the transition state) comes at the pinching step, which was calculated to be structurally similar to the VC-O₂ product and still fairly nonpolar.²² In this light, the role of the solvent in dictating the reaction kinetics is not immediately clear.

An alternate explanation is that the dynamics of the molecules in the immediate solvation shell around the solute impact the rate of barrier crossing. The generalized Langevin equation provides a reasonable model for motion in the case of a reaction with a barrier and describes the solvent effect as a time dependent frictional force.²³ This force is represented as a correlation function of solvent fluctuations exerted in the direction of the reaction coordinate.²¹ Though transition state theory predicts that only the energies of the reactants and transition state will matter to the final rate, it is important to note that, for our system, the product gives more information relevant to the reaction coordinate; the CO frequency in VC-O₂ is uniquely attuned to the environment around the O₂ ligand.²⁴,²⁵ It has also been shown in accordance with Onsager’s linear regression hypothesis that the molecular motions that comprise solvation dynamics (the movement of solvent molecules in response to a change in the solute) are not distinct from the solvent dynamics (the movement of solvent molecules around a solute).²⁶ With this understanding, it seems reasonable to hypothesize that the dynamics that might be measured experimentally could at least partly capture the same dynamics that facilitate chemical reactivity, as long as the observable has the appropriate sensitivity.

With this in mind, we previously used two-dimensional infrared (2D-IR) spectroscopy to characterize the solvent dynamics experienced by the carbonyl ligand on VC and

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VC-O₂ in pure solvents that had different oxidative addition kinetics.²⁵ While we were able to extract time scales and amplitudes of some solvent shell rearrangements for the reactant and product species, extrapolating these results to explain the reactivity trends was speculative. However, building on the approaches of others,²⁷⁻⁻³⁰,³⁹ we found that binary solvent mixtures were extremely useful in identifying which solvent shell properties were correlated.³⁷,³⁸

Binary solvents provide a common coordinate along which to map many observables, both static and dynamic. In a mixture of two solvents, it is generally true that the composition of the first shell of solvent molecules around a solute is different than that of the bulk solvent. This is due to the relative interaction strength of each solvent with the solute and neighboring solvent molecules, and the dynamics of solvent exchange into and out of the solvation shell.²⁷⁻⁻³⁰,³⁹ If an observable varies linearly with the mole fraction of the second solvent in a binary mixture, then this indicates that the composition of the solvation shell in the regions that influence that variable matches the bulk values. For example, the vibrational lifetimes of the metal-bound carbonyl on VC-O₂ and the iodine adduct (VC-I₂) in binary solvent mixtures of δ₀-benzene with chloroform (CHCl₃) or benzyl alcohol (BA) showed a linear variation with mole fraction of either CHCl₃ or BA.³⁷ As a counter example, the center frequency of the carbonyl vibrational on VC-O₂ varies in a highly nonlinear fashion in δ₀-benzene/BA mixtures, with a small mole fraction of BA causing most of the frequency shift.²⁵,³⁷ This shows that there is preferential solvation of VC-O₂ by BA in ways that perturb the frequency of the metal-bound CO, but not its vibrational lifetime. These two examples illustrate that for the same solute in the same binary solvent mixtures, two different observables can report the absence and presence of preferential solvation. The solvatochromic frequency shift is achieved through electrophilic interactions with the O₂ ligand, which has π bonds that interact with the back-bonding orbitals on the iridium,²⁴,²⁵,⁴⁰ whereas vibrational relaxation primarily occurs via solute-to-solvent energy transfer in the vicinity of the CO ligand.³⁷ It also highlights the possibility of drawing connections between quantities that might otherwise be difficult to correlate, such as solvent dynamics and reaction kinetics, when distinct nonlinear patterns are observed across the binary solvent coordinate.

In the following work, we have carried out a comprehensive binary solvent study of Vaska’s complex and its oxygen adduct. The second order rate constants for O₂ addition were measured in binary solvent mixtures of δ₀-benzene with CHCl₃ or BA to identify any preferential kinetic behaviors. Then, numerous FTIR and 2D-IR spectroscopic observables were analyzed across the same solvent mixtures to identify correlations between steady-state and dynamic quantities with the reaction kinetics.

II. EXPERIMENTAL METHODS

Bis(triphenylphosphine)iridium(1)carbonyl chloride (Vaska’s complex, 99.99%, Sigma Aldrich, Strem Chemicals), chloroform (CHCl₃, 99.8%, Sigma Aldrich), benzyl alcohol (BA, ≥99%, Sigma Aldrich; puriss. Sigma Aldrich), and perdeuterated δ₀-benzene (99.5% D, Cambridge Isotope Laboratories, Inc.) were used as received without further purification for laser studies. (We found that the majority of commercially available ≥99% BA lots contained impurities that react with VC. Those who reproduce this work are advised to use only puriss. BA or to purify the solvent before use. The ≥99% lot used for all previous and part of this work was unusually pure, as found by GC-MS; the impurity was most problematic for the dilute solutions used in the kinetics experiments, causing loss of the CO stretch in the FTIR and the MLCT peaks present in the UV-vis spectrum.) All solutions were filtered prior to data collection. For solutions of VC, the solvents were degassed by sparging with nitrogen prior to mixing, and all subsequent steps of solution preparation were performed under nitrogen. For solutions of VC-O₂, mixing and dissolution were carried out under ambient conditions. The solutions were capped and covered with parafilm and stored until completion of the oxygenation reaction (24-48 h). All measured samples were ~4 mM in VC or VC-O₂.

Infrared spectra were collected on a Nicolet 6700 FTIR spectrometer (Thermo Scientific) with at least 16 scans and a typical resolution of 1 cm⁻¹. Path lengths of both 150 μm and 25 μm were used for FTIR measurements.

Kinetics data were measured by UV-visible spectroscopy (Perkin-Elmer Lambda 12). Disappearance of the VC absorbance at 387 nm (ε = 4040 M⁻¹·cm⁻¹) was monitored over up to 33 hours under pseudo-first order conditions (ambient O₂, 0.1 and 0.05 mM VC). The solubilities of O₂ in pure benzene and CHCl₃ were determined from their Henry’s law constants (benzene = 9.24 × 10⁻¹ M/atm,⁴² CHCl₃ = 9.225 × 10⁻³ M/atm⁴³). The Henry’s law constant for BA was not available, but we used the value for toluene as has been reported by others⁴² (toluene = 1.914 × 10⁻¹ M/atm⁴²). The Henry’s law constants for binary mixtures were determined as described by Krichevsky.⁴⁵,⁴⁶ An ambient O₂ partial pressure of 0.21 atm was used as the concentration of O₂ in each solution. Under these conditions, the lowest concentration of O₂ for any solutions was 1.8 mM, which was at least an order of magnitude larger than the concentration of VC or VC-O₂ to ensure pseudo-first-order kinetics. The resulting decays were fit well by a single exponential decay. Second order rate constants were determined using the method described by Corbett.⁴⁷ Representative UV-visible kinetics data are provided in the supplementary material.⁴⁷

The 2D-IR setup has been described in detail previously.²⁵ Briefly, a beam of tunable IR pulses (1 kHz, ~90 fs duration full width at half maximum (FWHM), ~200 cm⁻¹ bandwidth FWHM, and 3 μJ/pulse) centered around 1950 cm⁻¹ for the VC and 2000 cm⁻¹ for the VC-O₂ experiments was
split into three beams of ∼33% power and a fourth weaker beam (local oscillator) of 1%. The three intense beams combined at the sample with controlled arrival times. The echo signal, emitted in the phase-matched direction, was combined with the local oscillator at a MCT array detector to enable the recovery of phase information. The data acquisition (chopped at 500 Hz) took the echo + local oscillator signal, subtracted the local oscillator signal and divided the local oscillator signal to compensate for the excitation pulse spectral shape. A Fourier transform followed by phase correction was applied to the resulting data, which were then added to obtain the purely absorptive spectrum. Since the pump-probe projection theorem was used in the phase correction process, and since in our setup the probe beam passes through the sample while the local oscillator does not, the FTIR transmission spectrum was used as an absorption correction prior to phasing. The frequency-frequency correlation function (FFCF) was obtained using the centerline slope (CLS)/FTIR fitting method described in the literature.

III. RESULTS AND DISCUSSION

The second order rate constants for oxidative addition of O$_2$ to VC (Scheme 1) in binary solvent mixtures of d$_6$-benzene with CHCl$_3$, or BA are shown in Figure 1 (numerical values are provided in Table S1 in the supplementary material). To our knowledge, this is the first work to examine this reaction in mixed solvents. The rate constants in neat solvents follow the trends previously observed by Steiger and Chock, increasing with solvent polarity index (benzene < CHCl$_3$ < BA) as 1.9, 2.4, and 12.5 M$^{-1}$ min$^{-1}$. They also follow the expected trend of anticorrelating with the solubility of Vaska’s complex. The rate constant in BA is considerably greater than in pure CHCl$_3$ or d$_6$-benzene. Although the Henry’s law constant used here could affect this value, the toluene constant is generally considered a good surrogate for BA, and even if the solubility of O$_2$ in BA was twice that of toluene, the calculated rate constant would still be a factor of 3 higher than that of CHCl$_3$.

Examining the shapes of the kinetics data in mixed solvents, neither shows a fully linear trend with mole fraction. This is highlighted by the black line connecting the first and last data points. Positive deviation, or deviation above the black line, generally indicates that the higher endpoint solvent has a stronger effect on the observable, whereas for negative deviation, the opposite is true. Considering the error bars, CHCl$_3$ mixtures only show significant deviations from linearity for 0.7 and 0.9 mole fraction (notably in opposite directions), whereas BA mixtures show a sharp increase in $k_2$ with just a small increase in mole fraction but then continue to increase more linearly as the BA concentration is increased. Even at a mole fraction of only 0.05 BA, the $k_2$ is already considerably faster than in pure CHCl$_3$.

It is useful to define a preference parameter following the approach of Rosés and coworkers. In the simplest case, an observable, $y$, displays a preference for one solvent over the other that is constant over the entire range of solvent mole fractions, allowing the data to be modeled with a single preference parameter, $f_{2/1}$,

$$y = y_1 + f_{2/1}(y_2 - y_1)X_2$$

where $y_1$ and $y_2$ are the values of the observable in pure solvents 1 and 2, respectively, and $X_2$ is the mole fraction of solvent 2 in solvent 1 in the bulk solution. For this study, we consider solvent 1 to be d$_6$-benzene and solvent 2 is either CHCl$_3$ or BA. Since the solvation shell influences the stability of molecular configurations, it is possible that the preference parameter is not constant over the entire mole fraction range but undergoes a crossover between two molecular configurations having different solvent preferences. For this more complex case, we can define a crossover mole fraction, $X_C$, and then modify Eq. (1) using preference parameters below ($f_{2/1}^{below}$) and above ($f_{2/1}^{above}$) this point,

$$y = y_1 + f_{2/1}^{below}X_C(y_2 - y_1)X_2 (1 - X_2) + f_{2/1}^{above}X_2 (1 - X_2)$$

As expected, Eq. (1) is recovered when the crossover mole fraction is set to unity. This equation can be used to quantify the preference of a given observable for solvent 2 (CHCl$_3$ or BA) versus solvent 1 (d$_6$-benzene). For the simple single preference case, the data can be fitted by floating only a single preference parameter, $f_{2/1}$, while three adjustable parameters are needed when a crossover is included ($f_{2/1}^{below}$, $f_{2/1}^{above}$, and $X_C$).

Returning to the kinetics data in Figure 1, the overlaid dashed lines show fits to Eq. (2) for each solvent mixture. The data in CHCl$_3$ mixtures (Figure 1(a)) were modeled by a single $f_{2/1}$ of ∼2 (all preference parameters are tabulated...
in the supplementary material). For such a value, the rate of addition of O$_2$ to VC increases in going from pure d$_6$-benzene to pure CHCl$_3$, but something about the properties of the solvation shell enables this to occur about twice as fast as would be expected from the bulk solvent composition. However, in light of the error bars on these data points, it is difficult to conclude that the rate constant increase is not linear in mole fraction. Though the function with an $f_{2/1}$ of 2 is the best fit, and although the majority of deviations from linearity occur above the line between the endpoints, within the standard deviation the majority of the points do not deviate significantly from that line.

The kinetics in d$_6$-benzene/BA mixtures in Figure 1(b) are not modeled well by a single preference parameter. The addition of small amounts of BA increases $k_2$ with a preference for BA over d$_6$-benzene by more than 13:1, followed by a more gradual rise to the pure BA value. This shows that small quantities of BA preferentially modify the composition and/or dynamics of the solvation shell in ways that favor O$_2$ addition to VC. Beyond a crossover point of about 0.2 mole fraction BA, the solvation shell composition and/or dynamics continue to be modified in ways that have a smaller impact on the reactivity of the solute, exhibiting almost no solvent preference.

The nonlinearity of the BA kinetics could be because of preferential solvation, where the composition of the solvent shell is different than that of the bulk solvent. Alternatively, the composition of the solvation shell may match that of the bulk solution but be heterogeneously distributed about the solute in ways that preferentially impact the reactivity of VC to O$_2$. Another possibility, which is not exclusive of the previous two, is that the dynamic behavior of the solvent shell and/or solute contributes to the addition reaction, and that these time dependent fluctuations are modified in a nonlinear fashion by the added mole fraction of BA.

Figure 2 shows the trends for the FTIR peak centers for the carbonyl stretching frequencies, $\nu_{\text{CO}}$, on VC (top) and VC-O$_2$ (bottom) in mixed solvents. The vibrational spectra have been previously reported for VC in pure solvents but not in binary solvent mixtures. Numerical values of $\nu_{\text{CO}}$ are provided in Table S1 in the supplementary material. Beginning with VC in Figure 2(a), we see that although this mode is less solvatochromic than when it is bound to VC-O$_2$ (Fig. 2(b)), its frequency does shift nonlinearly with the mole fraction of the solvent system. The most unusual behavior is observed for VC in CHCl$_3$ mixtures, in which the beginning and ending frequencies are nearly identical but in the intermediate mole fractions the center blue-shifts by about 1 cm$^{-1}$. This clear, though small, increase in frequency occurs only when both solvents are present. Equation (2) cannot model a change in observable that is outside of the range of the pure solvents. The $\nu_{\text{CO}}$ for VC in BA mixtures, however, provides a case that can be analyzed. We find that the positive deviation from linearity for the $\nu_{\text{CO}}$ indicates $f_{2/1}$ of 2.1 preferring BA over d$_6$-benzene for the characteristics of the solvation shell that influence the carbonyl frequency.

Figure 2(b) shows that VC-O$_2$ exhibits larger solvatochromic carbonyl frequency changes than VC due to changes in iridium bonding caused by electron density changes at the O$_2$ ligand. The FTIR spectra for VC-O$_2$ have been published and discussed previously for these neat solvents and binary solvent mixtures but were reanalyzed here with improved solvent subtraction. The trends with mole fraction are readily fit by Eq. (2) using $f_{2/1}$ values of 2 and 9 for CHCl$_3$ and BA, respectively. The positive deviation from linearity is notably greater for BA, which provides some support for the polar transition state hypothesis since the geometry of VC-O$_2$ is believed to be similar to the transition state. The center frequency always has a greater influence from the more polar solvent (positive deviation), but to differing degrees depending on the adduct.

The FWHMs in Figure 3 increase with increasing mole fraction of either CHCl$_3$ or BA. This could be due to an increased number of environments around the carbonyl ligand with a more polar solvent; however, it is impossible to distinguish inhomogeneous broadening from an increase in width due to homogeneous broadening (faster dephasing or relaxation). VC shows only a slight preference ($f_{2/1} = 1.3$) for CHCl$_3$ over d$_6$-benzene and VC-O$_2$ is effectively linear. Clearly whatever produces nonlinearity in the frequency does not have as strong of an influence on the peak widths for these mixtures.

In BA mixtures, VC shows a similar preference to the center frequency ($f_{2/1} = 2$), but VC-O$_2$ shows a strong bimodal preference as described above with $f_{2/1}^{\text{below}} = 76$ and $f_{2/1}^{\text{above}} = 0.11$ and a crossover of 0.7 mole fraction. This is a considerably greater preference at low mole fractions than $\nu_{\text{CO}}$ shows in Figure 2(b). The VC-O$_2$ carbonyl FWHM values in BA mixtures all have very similar widths, which is considerably wider than the value in pure d$_6$-benzene but narrower than that in pure BA. This indicates a strong interaction with BA that is inhibited by even small amounts of benzene. The carbonyl widths of VC and VC-O$_2$ are similar in value; VC-O$_2$ is always slightly larger than VC in BA mixtures and the reverse is true in CHCl$_3$ mixtures. Neither
FIG. 3. FTIR FWHMs for the carbonyl vibration on (a) VC and (b) VC-O₂ as a function of the mole fraction of CHCl₃ (red circles) or BA (blue squares) added to d₆-benzene. Black lines are aids to the eye connecting the first and last points. Red and blue dashed lines are the best fits to the data calculated by VC-I₀.

VC nor VC-O₂ shows the dramatic width changes exhibited by VC-I₂ collo. Surprisingly, considering the more open square planar configuration, the VC FTIRs show less preferential solvation in both width and frequency than those of VC-O₂. This is a reflection of the preferential solvation of the dioxyn ligand, communicated via changes in electron density of the iridium.

These trends in the carbonyl FTIR parameters can be compared to those observed in the kinetics traces. First, the νCO for VC in either solvent system in Figure 2(a) shows no qualitative resemblance of the χ₂ changes with solvent mole fraction, so we can conclude that the factors that increase the rate constants in Figure 1 are likely unrelated to those that impact the center frequency of the reactant species. Next, we note that although the linewidth on VC is responsive to a change in solvent composition (Figure 3(a)), it exhibits no particular behavior that would correlate it with the kinetic trends. On the other hand, the νCO for VC-O₂ shows a mild preference for CHCl₃ and a strong preference for BA (Figure 2(b)), which at least matches the kinetics data qualitatively. The FWHM perhaps shows the stronger relationship (Figure 3(b)) with a mostly linear trend in CHCl₃ mixtures, a fast rise at low mole fractions of BA, and a crossover point at higher concentrations.

Based on these correlations, one could hypothesize that the changes in the solvation shell of VC-O₂ that perturb the νCO and FWHM when small amounts of BA are added to benzene are also important to facilitating the addition of O₂. As noted in the introduction, calculations by Yu and coworkers indicated that the VC-O₂ structure is a better surrogate for the transition state structure and therefore might be influenced by the solvent composition in similar ways.

The vibrational lifetimes (T₁) of the CO stretch were also measured and are recorded in Table S1 in the supplementary material. Those for VC-O₂ have been published previously, but the T₁ values for VC have not been measured in these mixtures before. In keeping with previous observations, all of the carbonyl lifetimes are significantly shorter for VC than those of VC-O₂ or VC-I₂ due to the lower frequency of the vibration. The range over which the lifetimes change in the same mixtures is also considerably smaller than either of the octahedral adducts. Curiously, the lifetime decreases slightly in the CHCl₃ mixtures, rather than increasing. This may indicate a more intramolecular mechanism than was suggested for VC-O₂ and VC-I₂. For the current study, we are most interested in dynamic parameters that vary nonlinearly with mole fraction so that distinct correlations might be found with kinetic data. The trends in T₁ for VC are linear with mole fraction and will not be discussed further here.

Figure 4 shows representative 2D-IR plots for VC at short (Tₚ = 0.3 ps, top row) and long (Tₚ = 30 ps, bottom row) waiting times. In each 2D-IR spectrum, the positive peak (red) arises from the vibrational coherence between the ground and first excited states for the metal-bound carbonyl, and the negative peak (blue) arises from the coherence between the first and second excited states. The horizontal axis is the excitation frequency and the vertical axis is the vibrational echo emission frequency. Starting with the neat d₆-benzene spectra (center column, (e) and (f)), it is clear that increasing the Tₚ causes both peaks to evolve from diagonally elongated to symmetric and round. At Tₚ = 0.3 ps, the vibrational oscillators are correlated with their starting frequencies, but by Tₚ = 30 ps, they have diffused spectrally and sampled nearly the entire FTIR linewidth. These dynamics that are normally obscured by the inhomogeneous FTIR line shape can be characterized by analyzing the CLS from each 2D-IR spectrum as a function of Tₚ, which has been shown in many cases to be proportional to the FFCF.

To the left from the center column in Figure 4, the 2D-IR spectra are shown for 0.5 mole fraction and pure CHCl₃. To the right from the center are 0.5 mole fraction and pure BA. The increase in FTIR linewidth in Figure 3(a) is manifested in the increase of the diagonal widths with addition of either CHCl₃ or BA in Figure 4. Comparing the diagonal widths in Figures 4(a)–4(i) shows that the dynamical contributions to the line shape are different for these two solvents. The narrowing along the diagonal direction for BA mixtures indicates that the homogeneous linewidth is growing narrower, a trend seen previously for VC-I₂. The anti-diagonal broadening for CHCl₃ mixtures cannot immediately be attributed to a homogeneous linewidth change since the diagonal width is also increasing; however, this will be determined below in the quantitative analysis of the CLS plots. It is also apparent that spectral diffusion dynamics are different for these solvents since the long Tₚ data in Figures 4(b) and 4(j) show the CHCl₃ spectrum to be symmetric and round while the BA spectrum is still diagonally elongated. We can predict that some of the spectral dynamics will exhibit preferential behavior since the 0.5 mole fractions of both solvents (Figures 4(c), 4(d), 4(g), and 4(h)) look quite similar to the neat solvent spectra. Hence, whatever dynamics result in frequency fluctuations of the carbonyl ligand, they appear to have been mostly developed by this mole fraction.

The same 2D-IR plots for the VC-O₂ adduct are shown in Figure S1 in the supplementary material. In both solvent
mixtures, the same qualitative trends hold as were described for VC. In total, for VC and VC-O\textsubscript{2} in all solvent mixtures studied at all $T_w$ values, more than 600 2D-IR spectra were collected and analyzed. All spectra are provided in the supplementary material.\textsuperscript{57} The CLS treatment was applied to the 0-1 carbonyl transition in every spectrum to distill this enormous dataset into a tractable form.

Figure 5 shows the CLS decays as a function of $T_w$ for each of the mixture series and adducts. A first observation is that the addition of CHCl\textsubscript{3} (Figures 5(a) and 5(b)) has a notably smaller effect on the dynamics than addition of BA. In general, CHCl\textsubscript{3} mixtures look more similar to pure d\textsubscript{6}-benzene than BA mixtures, with any deviations appearing at longer $T_w$ values. Spectral diffusion in BA (Figures 5(c) and 5(d)) is considerably slower than in d\textsubscript{6}-benzene or CHCl\textsubscript{3}. The overall spectral diffusion for VC-O\textsubscript{2} in BA shows the same trends as the FTIR FWHM; the endpoints are distinct while the mixtures are very similar. Also the y-intercept of the CLS, which in some situations is related to the homogeneous linewidth, is higher for BA mixtures than for CHCl\textsubscript{3}. It is also generally higher in VC mixtures than in VC-O\textsubscript{2}, so the homogeneous linewidth is likely larger for VC-O\textsubscript{2}. Looking at Figure 5 as a whole, aside from differences in the y-intercepts, the dynamical data extracted from the 2D-IR spectra look fairly similar for VC and VC-O\textsubscript{2} in a given solvent system. This supports the notion that the carbonyl vibrational mode mostly reports on the dynamics of the proximal solvation shell rather than the intramolecular dynamics of the molecule to which it is bound, which was also recently concluded for a family of rhenium catalysts.\textsuperscript{54}

The full FFCFs were found by fitting to the FTIR spectra as well as the CLS decays.\textsuperscript{50,51} With only a few exceptions, the data in Figure 5 and their corresponding FTIR spectra were well fit by a double exponential function (Eq. (3)), including a motionally narrowed term (for the homogeneous line shape) as shown in

$$FFCF(t) = \frac{\delta(t)}{T_2} + A_1^e e^{-t/\tau_1} + A_2^e e^{-t/\tau_2} + A_0^e.$$  \hspace{1cm} (3)
through S35 in the supplementary material present each of the FFCF parameters graphically, followed by some discussion of parameter correlations and uniqueness. In order to minimize the possibility of such errors influencing our correlation, we focus the following discussion on the homogeneous linewidth, $\Gamma$, and the inhomogeneous amplitude, $\Omega$, as defined in

$$
\Omega = \sum_{n=0}^{2} \Delta_{n}^{2}, \tag{4}
$$

$$
\Gamma = \frac{1}{\pi T_{2}} = \frac{1}{2\pi T_{1}} + \frac{1}{2\pi T_{2}} + \frac{1}{3\pi T_{or}}. \tag{5}
$$

In these equations, $T_{2}$ is the pure dephasing time and $T_{or}$ is the orientational relaxation time. Generally, $T_{or}$ is on the order of hundreds of picoseconds for molecules of this size and so does not contribute significantly to $\Gamma$.

Figure 6 shows the values for $\Gamma$ calculated from the CLS analysis of the 2D-IR spectra for VC and VC-O$_{2}$ in CHCl$_{3}$ (red circles) and BA (blue squares) mixtures. The general trends are very similar to those previously observed for VC-I$_{2}$, where the homogeneous linewidth changes very little in CHCl$_{3}$ (red circles) and decreases in BA (blue squares) mixtures. In spite of the differences in y-intercepts for the CLS decays noted above, the homogeneous linewidths are not very different for the two solutes. In the CHCl$_{3}$ mixtures at low mole fraction, VC-O$_{2}$ is broader, but the distinction disappears after 0.7 mole fraction, when the linewidth of VC rises slightly. The broadening noticed in the FTIR for VC with increasing amount of CHCl$_{3}$ could be partly coming from this increase in the homogeneous linewidth; however, it does not show the same preference for CHCl$_{3}$. The notable outlier in this figure is the $\Gamma$ for VC-O$_{2}$ in BA mixtures (blue squares, Figure 6(b)). The homogeneous linewidth variations for this adduct and this solvent mixture are clearly nonlinear, displaying a quick decrease with the addition of a small amount of BA to d$_{6}$-benzene. Since the $T_{1}$ values for this adduct range from 56 to 92 ps (see Table SI), the vibrational lifetime contribution to $\Gamma$ is minor (<0.1 cm$^{-1}$), but more importantly, its variation is highly linear. Removing the $T_{1}$ contributions to $\Gamma$ in Figure 6(b) results in a nearly identical curve that is within the negative error bars of the full gamma. Hence, the nonlinear trend in $\Gamma$ is specifically a nonlinear change in the pure dephasing time scale. Fitting the data to Eq. (2) reveals a preference for BA in the solvation shell of about 16:1, which is the same within error as the preference observed for the rate constant for O$_{2}$ addition. There is a clear correlation between the homogeneous linewidth of the product complex and the reaction rate constant.

Figure 7 shows that a complementary trend exists between the homogeneous linewidth and the inhomogeneous amplitude, $\Omega$. The CHCl$_{3}$ mixtures vary linearly with mole fraction added, but the VC-O$_{2}$ values in Figure 7(b) show that $\Omega$ quickly increases with small additions of BA. Comparing Figure 7 to Figure 3, it is quite clear that the changes in the FTIR linewidth with mole fraction track remarkably well with the changes in the inhomogeneous amplitude in the FFCF. This shows that linear and nonlinear behaviors of the steady state line shape differences in different mole fractions of either solvent system are the result of increases in the inhomogeneity of chemical environments around the solute. The abrupt increase

![FIG. 6. Homogeneous linewidth, $\Gamma$, for (a) VC and (b) VC-O$_{2}$ as a function of the mole fraction of CHCl$_{3}$ (red circles) or BA (blue squares) added to d$_{6}$-benzene. Black lines are aids to the eye connecting the first and last points. Red and blue dashed lines are the best fits to the data calculated from Eq. (2) for CHCl$_{3}$ and BA mixtures, respectively.](image-url)
The kinetics for mixtures of CHCl₃ and d₆-benzene showed a linear trend with solvent mole fraction, precluding any distinct correlations with steady-state and dynamic parameters. However, binary mixtures of BA and d₆-benzene provided a case in which the rate constant varied nonlinearily with a rapid change upon addition of small quantities of BA. This preferential kinetic behavior was closely mirrored by increases in the FTIR linewidth of the metal-bound carbonyl ligand. Extraction of the FFCF from 2D-IR spectra revealed that beneath the linear line shape, the homogeneous linewidth for VC-O₂ in BA mixtures was anticorrelated with the preferential kinetics, meaning that the fast dephasing dynamics slow down as the inhomogeneity of the solvation shell increases. An exciting hypothesis that can be drawn from these results is that the nonlinearity in the rate constant is in fact driven or facilitated by changes in the ultrafast solvation dynamics around the product, which in this case happens to closely resemble the transition state. A greater variety of solvation environments may increase accessibility to favorable configurations, and slowing of the microscopic motions that lead to pure dephasing of the carbonyl could decrease the solvent friction around the transition state. Correlation does not guarantee causality, and we cannot rule out the possibility that the kinetic and spectroscopic observables are simply slaved to a common source. Nonetheless, it is remarkable, and potentially important, that such a particular correlation exists otherwise unseen without the benefit of multidimensional spectroscopy.

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in k₂ with small quantities of BA is accompanied by a corresponding increase in the spectral inhomogeneity around the product species (VC-O₂). At the same time, beneath the inhomogeneous line shape, Figure 6 shows that the fast pure dephasing events that dominate the homogeneous line shape slow down. Returning to the view that VC-O₂ reflects the transition state structure, the preferential behavior of the kinetics in BA/d₆-benzene mixtures is mirrored by a general increase in chemical heterogeneity in the solvation shell and a slowing of fast solvent dynamics. It is curious that these very fast motions around the product should be correlated with the nonlinearity when those occurring around the reactant do not. This confirms that the product-like transition state calculated by Yu and coworkers is an accurate picture of the actual reaction mechanism. If these fast motions around the product carbonyl behave in the same fashion around the activated complex, then it may be that they somehow assist the pincer motion and enable reactivity. Identifying the molecular origins of these dynamics is an important next step that would be facilitated by molecular dynamics simulations. Molecular dynamics simulations of the solute and its solvation shell during oxidative addition would enable one to confirm this hypothesis. It could also be useful to determine whether these correlations exist for other additions to VC, such as the addition of I₂, which is considerably faster as well as being irreversible.

IV. CONCLUSIONS

We performed an extensive spectroscopic and kinetic study on the oxidative addition of O₂ to Vaska’s complex. We measured the solvent dynamics around both product and reactant species at equilibrium. This work is a departure from the majority of 2D-IR/kinetics studies, as the reaction is not in the low-friction limit of solvent-solute interactions, and it thus provides an opportunity to examine a reaction that is squarely in the range where transition state theory works well.
57. See supplementary material at http://dx.doi.org/10.1063/1.4920953 for representative UV-visible kinetics data, tabulated kinetic rate constants, FTIR parameters, vibrational lifetimes (T1), tabulated preference parameters, tabulated FFCF parameters, 2D-IR spectra equivalent of Fig. 4 for VC-O2, all 2D-IR spectra for both VC and VC-O2 in CHCl3 and BA mixtures, and graphical presentation of FFCF parameters with discussion.