Dynamics of Chemical and Photochemical Reactions in Solution

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Introduction

Molecules in a liquid solution are subjected to continual interactions with the surrounding solvent that influence their chemical reactivity. These intermolecular interactions fluctuate on timescales on the order of 100 fs and affect the flow of energy within transient reactive intermediates and control equilibration with the solvent bath. Our experimental and computational studies contrast the ultrafast dynamics of unimolecular and bimolecular reactions in solution with the corresponding processes in the gas phase to explore how solvents modify chemical mechanisms. Ultrafast transient absorption spectroscopy using the ULTRA Facility monitors the evolution of reaction intermediates to products with sub-picosecond time resolution. The transient spectra obtained with ULTRA for reactions in solution are complemented by gas-phase studies in our laboratory at the University of Bristol using techniques such as velocity map imaging. Interpretation of the experimental results draws heavily on computed potential energy surfaces (PESs) and simulations of the chemical dynamics that incorporate explicit treatment of the solvent bath.

Our work to date has demonstrated that many features of the prompt dynamics occurring in solution in organic solvents such as hexane/cyclohexane, dichloromethane or acetonitrile are similar to those for isolated conditions in the gas phase [1,2]. However, processes specific to the solvent environment do influence the chemical dynamics in observable ways. Examples include solvent caging, complexation of radicals with solvent molecules, geminate recombination and isomerization pathways, and vibrational coupling to solvent modes. Transient infra-red, visible and ultraviolet absorption spectroscopy offers many insights into these various solvent-induced effects.

Bimolecular Reaction Dynamics

Exothermic reactions involving transfer of a hydrogen (or deuterium) atom from an organic molecule to a labile radical (e.g. CN, F or Cl) serve as model systems for our studies of collision-induced chemistry in solution [1,3]. Time-resolved infra-red (TRIR) absorption spectroscopy has revealed the formation of vibrationally excited products and subsequent equilibration by energy transfer to the solvent. The reactions are initiated by UV excitation of a precursor that liberates a reactive radical, and we have carefully characterized these photo-initiation processes. For example, UV photolysis of CCl_4 releases a Cl atom that can be observed using a transient charge-transfer band centred at 330 nm. However, geminate recombination of the Cl and CCl_3 photoproducts can also produce the Cl-Cl-CCl_2 isomer which exhibits a strong absorption band in the visible region [4]. We have demonstrated that XeF_2 photodissociation at 266 nm in acetonitrile releases an F atom on a sub-picosecond timescale, but that confinement of F and XeF within a solvent cage strongly perturbs the UV absorption spectrum of the XeF fragment [5]. Figure 1 illustrates the decay of a broad shoulder to the 345-nm XeF (*B*–*X*) absorption band with a time constant of 4 ps as F atoms react with solvent molecules. This spectroscopic signature of the loss of F atoms is confirmed by TRIR measurements of the growth of bands assigned to DF (for experiments in CD_3CN) or HF (in CH_3CN).

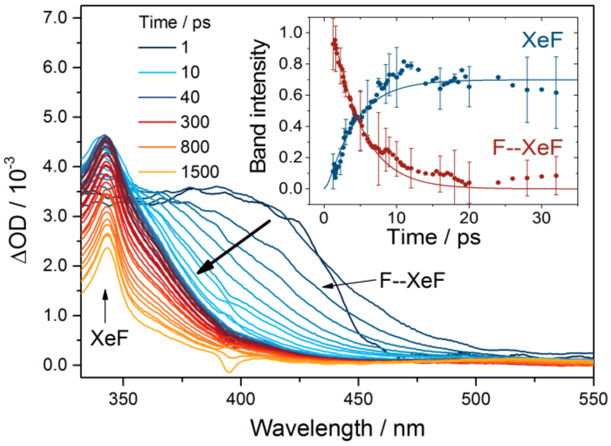


Figure 1: Transient UV/visible absorption spectra of XeF and solvent-caged F--XeF following the photolysis of XeF_2 in CD_3CN. The heavy arrow indicates the change in the spectral feature assigned to the F--XeF complex with time; the decline, with time constant of 4 ps, is attributed to reactive removal. The inset shows the variations of the spectral band intensities with time delay between photolysis and probe lasers.

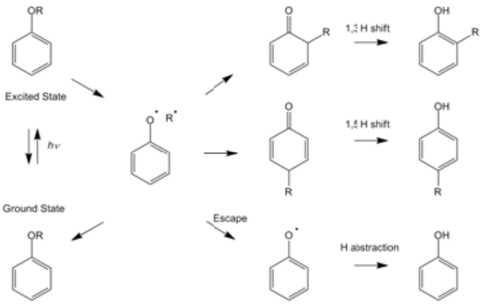
Reaction of Cl atoms with 2,3-dimethylbut-2-ene produced HCl by direct abstraction despite the presence of a deep well on the PES corresponding to addition of the Cl atom across the central C=C bond [6]. The "roaming" dynamics we identified in the gas phase, in which the addition complex eliminates HCl via a loose transition state, appear to be suppressed in solution by steric constraints imposed by the solvent shell, and by rapid collisional stabilization of the adduct.

F-atom reactions with organic compounds are exothermic by ~150 kJ mol^{-1}, and in the gas phase much of the available energy is channeled into vibrational excitation of the HF (or DF) products. Our TRIR studies of HF and DF formation from, respectively, F + acetonitrile and F + d_3-acetonitrile reactions indicate lower excitation of product vibrational motion, suggesting solvent-induced modification of the reaction dynamics. Computer simulations of the reaction with d_3-acetonitrile reproduce the key experimental observations and show that incipient hydrogen bonding of the newly formed DF with the solvent, although requiring molecular reorientation, occurs in <1 ps. However, the experimental measurements reveal a slower (~10 ps) shift in the IR absorption bands that appears to correspond to further restructuring of the solvent to accommodate the reaction products.

Photodissociation Dynamics

Recent work by the Bristol group (and others) has served to highlight the pivotal role of πσ* excited states in photoinduced bond fission processes. For example, our previous report detailed UV pump - TRIR probe studies of thiophenols and thioanisoles in cyclohexane or acetonitrile solution, designed to complement recent studies of the same photolyses under isolated molecule conditions in the gas phase. Analysis of TRIR absorption spectra obtained following 267 nm photoexcitation of thiophenol confirms S–H bond fission on the $^1\pi\sigma^*$ PES (as in the gas phase) but also allows detailed mechanistic and kinetic study of additional processes unique to the condensed phase. These include vibrational cooling (via collision with solvent molecules) of the thiophenoxyl radicals formed in the primary bond fission and two geminate recombinations: S–H bond reformation, yielding ground (S_0) state parent molecules, and H addition to the ring, yielding a thioquinone-like structure [2]. In all cases thus far, insights gained from studying the equivalent photolysis in the gas phase provide an excellent starting point for describing the solution phase dynamics.

Such ideas have been advanced in two ways. The photo-Claisen and photo-Fries reactions are widely used to convert aryl phenyl ethers or phenyl esters into 2- or 4-substituted phenol products.



The above reaction scheme highlights the parallels between such reactions and the foregoing studies of thiophenol and thioanisole photochemistry. TRIR absorption studies following 267 nm photoexcitation of allyl phenyl ether in cyclohexane solution results in population of the corresponding $^1\pi\sigma^*$ excited state of the ether, RO–allyl bond fission (on a ~90 ps timescale), and determination of the kinetics and quantum yields of the subsequent radical recombination reactions yielding the ground state parent molecule or, more productively, an allyl substituted cyclohexadienone. Complementary transient UV/visible absorption measurements allowed similarly detailed investigation of the radical escape channel, but the rates of the H atom shift and/or abstraction reactions involved in the final product forming step are much too slow to be monitored with the current pump-probe spectroscopy set-up [7].

There is no reason why πσ* states should only mediate the fission of pendant bonds like S–H, S–Me or O–R. πσ* states should be equally relevant in enabling the photo-induced ring-opening of heterocyclic molecules, for example. Indeed, ring cleavage has been proposed as an ultrafast radiationless deactivation pathway in several cyclic heteroatom containing systems (*e.g.* furan, thiophene, various substituted spiropyrans) but direct experimental evidence of such ring-opening processes has traditionally been hard to find. One reason for this paucity is simply the challenge of studying such processes in the gas phase. The reactant and product molecules are structural isomers, so many classic gas phase experiments that rely upon mass-specific detection are incapable of distinguishing reactant from product. In addition, the ring-opened products will usually be formed highly vibrationally excited (a result of the large geometry changes that accompany ring-opening), complicating their study by any IR or electronic spectroscopy based method.

Studying photoinduced ring-opening processes in the condensed phase alleviates many of these problems. The presence of solvent allows efficient relaxation of the excess vibrational energy, and enables reactants and products to be distinguished through their IR spectra. The photoinduced ring-opening of heterocyclic α-carbonyl systems (*e.g.* furanone, thiophenone or N-methyl-2-pyridone (NMP)) is particularly well suited for detailed mechanistic study in this way, since both reactant and product can be tracked by TRIR spectroscopy (via their carbonyl (~1650 cm^{-1}) and ketene (~2100 cm^{-1}) stretch modes, respectively). By way of illustration, fig. 2 shows TRIR data following 267 nm of NMP in CH_3CN. Several parent bleach signals (including the C=O stretch at 1665 cm^{-1}) are evident in fig. 2(a), which (largely) recover with increasing pump-probe time delay. Measurements at higher wavenumber reveal a feature that is formed vibrationally hot and cools (blue shifts) at later times (fig. 2(b)). This is the signature of a ketene product; its presence confirms photo-induced ring opening.

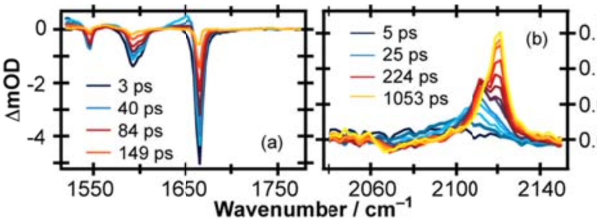


Figure 2: TRIR absorption spectra of NMP in CH_3CN, showing (a) 1520-1775 cm^{-1}, and (b) 2040-2160 cm^{-1} probe regions.

Data analysis is ongoing, but several conclusions are already apparent. Ultrafast pump-probe spectroscopy in the condensed phase provides a powerful route to studying photo-induced ring opening processes. Such reactions appear common place, and are mediated by a ring-centred πσ* PES that forms conical intersections with the S_0 PES (amongst others). As such, excited state ring-opening provides an efficient route for population transfer back to the S_0 PES, whereupon it has a choice – to reform the parent heterocycle (*i.e.* ring opening / closing constitutes an internal conversion route) or to undergo further rearrangement (usually an H atom shift) to form a stable ring opened product. Our studies to date show this branching to be very molecule dependent; understanding the factors that influence such choice remains an ongoing challenge.

Conclusions

Ultrafast broadband transient absorption spectroscopy in the IR and UV/visible regions of the spectrum allows us to follow the dynamics of collision or photoinduced reactions in solution and to characterize the reactive pathways. Spectroscopic signatures of transient intermediates reveal the time constants for their formation and loss, whether by chemical transformation or by loss of excess internal energy to the solvent bath. Benchmarking the observed behaviour in solution against gas-phase mechanisms reveals how the presence of a solvent modifies the dynamics and introduces new, competing chemical pathways.

Acknowledgements

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References

1. S.J. Greaves *et al*., Science **331**, 1423 (2011).
2. S.J. Harris *et al.*, PCCP **15**, 6567 (2013).
3. A.J. Orr-Ewing, J. Chem. Phys. **140**, 090901 (2014).
4. F. Abou-Chahine *et al*., J. Phys. Chem. A **117**, 13388 (2013).
5. G.T. Dunning *et al*., PCCP in press (2014).
6. F. Abou-Chahine *et al*., Chem. Sci. **4**, 226 (2013).
7. S.J. Harris *et al.*, Chem. Sci. **5**, 707 (2014).