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Radiation Physics and Chemistry 72 (2005) 159–167
Radiation Physics and Chemistry
www.elsevier.com/locate/radphyschem

Solvent effects on geminate recombination dynamics after photodetachment

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Received 13 January 2004; accepted 8 June 2004

Abstract

The time-dependent survival probability for photoelectrons produced following resonant excitation of I^- in its first charge-transfer-to-solvent (CTTS) band is determined by femtosecond pump–probe spectroscopy. The solvent effect on localization and recombination dynamics of the detached solvated electrons in various hydroxylic solvents (H_2O, CH_3OH, C_2H_5OH, C_3H_7OH, C_4H_9OH) is studied. The data are consistent with a caged geminate pair being formed in the CTTS photodetachment step. In all solvents, the geminate recombination of the detached electron can be modeled as competition between diffusive escape from an attractive short-range potential ($\sim 3k_BT$) and reverse electron transfer to reform ground state iodide.

Keywords: Photodetachment; Solvated electron; Geminate recombination

1. Introduction

Much renewed attention has been recently given to the photodetachment mechanism of inorganic anions in solution when excited into their charge-transfer-to-solvent (CTTS) states. Photoexcitation into such a transient excited state results in the ejection of a photoelectron into solution and the formation of a radical. The aqueous iodide system has long provided the benchmark for such behavior (Franck and Scheibe, 1928; Platzman and Franck, 1954; Jortner et al., 1963). A rather detailed picture has now emerged for photodetachment of this ion based on femtosecond spectroscopy (Kloepfer et al., 2002a), mixed quantum/classical simulations (Sheu and Rossky, 1996) and gas phase cluster spectroscopy (Serxner et al., 1996; Lehr et al., 1999). In addition to detailed studies of iodide photodetachment in bulk water from our group (Kloepfer et al., 2000, 2002b; Vilchiz et al., 2001), a temperature-dependent electron yield study has recently been reported in ethylene glycol (Chandrasekhar and Krebs, 2000) as well as a time-resolved study in acetonitrile (Xia et al., 2002). Parallel studies on alkali metal anions in low polarity ethers provide complementary insights into the key role of solvent motions in dictating the detachment and subsequent electron dynamics (Barthel et al., 2001, 2003; Martini et al., 2001; Wang et al., 2003). Atomic anion systems lack intramolecular modes and hence all reorganization on electron transfer must be in the solvent degrees of freedom. Thus, atomic CTTS reactions serve as a prototype for developing a

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doi:10.1016/j.radphyschem.2004.06.013

microscopic understanding of electron transfer. In this report, we systematically vary the solvent environment while observing the changing electron localization and geminate recombination dynamics. Iodide once again provides an ideal test case as it possesses no other electronically excited states and yields close to 100% initial quantum yield for electrons after excitation into the lowest CTTS state (Kloepfer et al., 2002b).

Our picture for photoejection from aqueous iodide is as follows. Upon CTTS excitation, the water molecules in the first solvation shell surrounding the halide ion start undergoing rearrangement to accommodate the diffuse electron cloud of the electronically excited state (Bradforth and Jungwirth, 2002). This rearrangement reshapes the electron cloud and causes the electron to fully detach from the iodine atom. Because the initial wavefunction extends only into the neighboring solvent sphere, the detached electron on average resides in a caged pair with the newly formed iodine radical (Sheu and Rossky, 1993a–c; Staib and Borgis, 1996). The water molecules must rearrange once again to accommodate the caged pair, $(\mathrm{I}:\mathrm{e}^-)_{\mathrm{solv}}$, in the solvent cavity (Vilchiz et al., 2001). Once the electron is solvated, it can react with its geminate partner and reform ground state iodide or it can diffuse away. Since experimental results show rather slow recombination dynamics (Kloepfer et al., 2000), our model includes a (non-instantaneous) first-order back reaction rate for on-contact reverse electron transfer (ET). This slow reaction rate could be due to a large solvent barrier to electron return or a requirement on the spin of the electron before recombination on the singlet surface (Ichino and Fessenden, 2003). One would expect that if the geminate pair does not quickly recombine, then the electron would rapidly diffuse away; this is true if there is no barrier to diffusive escape. However, the electron induces a dipole in the polarizable atom leading to an attractive interaction. The electron must overcome this induced-dipole potential before leaving the contact-pair cage. In addition, solvent rearrangement is necessary for the electron to leave the cage. Once the electron has left the solvent cage and diffused some distance away, there still remains a possibility, following random walk, for it to return to the vicinity of the geminate radical and make subsequent attempts at recombination (Kloepfer et al., 2002b). Therefore, the main factors determining the solvated electron escape yield are the rate of reverse ET on contact, the ejection distance, the magnitude of the pair attraction and how well this interaction potential is screened by the solvent (i.e., the potential of mean force (Staib and Borgis, 1996; Gaigeot et al., 2000)).

Since the potential well is caused, at least in part, by the electrostatic interaction between the electron and its geminate radical partner, when the radical is changed the depth of the well changes. This effect has been tested for photodetachment from a range of halides, pseudohalides and hydroxide (Crowell et al., 2004; Vilchiz et al., 2004). However, in the experiments presented here, the ion to be photodetached is kept constant so any changes in the attractive potential are due to the difference imposed by the solvent environment through, for example, enhanced screening. To zero order, one might expect that if detachment leads to a contact-pair in all solvents, the variation in the magnitude of the potential interaction is likely to be small. This hypothesis can be tested as well as the conjecture that detachment in a general polar solvent leads to contact pair formation. In addition, the contact rate for the reverse ET reaction may be compared in different solvents.

2. Experimental

Time-resolved transient absorption data were collected with a 200 kHz amplified ultrafast laser system and UV pump–visible probe spectrometer that has been described previously (Kloepfer et al., 2000; Vilchiz et al., 2001). Briefly, the sample, potassium iodide dissolved in a variety of polar solvents, is delivered either via a free-flowing jet ~200 μm thick or, to improve signal-to-noise ratio, via a 1 mm path length $\mathrm{CaF_2}$ flow cell. The iodide anions are excited into their CTTS state at 225 nm and the resultant solvated electron product is tracked with a visible wavelength probe pulse. The 225 nm pulses (energy ~5 nJ) are generated by sum frequency mixing in a 90 μm Type I BBO crystal the signal output of a 400 nm pumped optical parametric amplifier with residual 400 nm. The probe pulses are obtained from a white-light continuum with the use of a 22.5 nm bandpass interference filters centered at 500 or 700 nm, or from the amplifier fundamental itself at 800 nm. The use of two probe colors allows us to determine and isolate the thermalization dynamics from the geminate recombination (Kloepfer et al., 2000). In methanol, propanol and butanol, 700 nm is to the red of the peak absorption wavelength for the solvated electron while 500 nm is to the blue. For ethanol, 800 nm provides a probe wavelength to the red of the equilibrated electron peak while 500 nm again is to the blue. The instrument response function is ~165 and ~700 fs in the jet and cell, respectively; the 225 nm pulses ultimately determine the instrument response for the jet sample but temporal walkoff limits the time resolution in the long path cell. The sample solutions are prepared so that the solution's optical density at 225 nm is ~0.2 OD. For aqueous iodide, this corresponds to a concentration of ~1 mM. Potassium iodide (Mallinckrodt) was dissolved in the following solvents that were all used as received: deionized water (Sparklets), ethanol (AAPER Alcohol, 200 proof), methanol (Mallinckrodt, reagent grade), *n*-propanol (Sigma-Aldrich, ACS grade) and *n*-butanol (Mallinckrodt, reagent grade). The pump intensity at the