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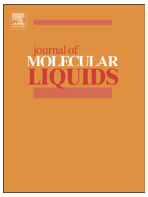

Effect of *N* butyl pyridinium bis(trifluoromethyl sulfonyl)imide on the photoinduced electron transfer between duroquinone and amines

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ABSTRACT

The photoinduced electron transfer (PET) reactions have been characterized using laser flash photolysis, wherein a photoexcited acceptor, the excitation triplet state of duroquinone (^{3}DQ*), abstracts an electron from a ground state donor, aniline or diphenylamine. After adding the ionic liquid (IL) *N* butyl pyridinium bis(trifluoromethyl sulfonyl)imide ([BPy][NTf$_2$]) to acetonitrile (MeCN) solution, the decay of ^{3}DQ* became slower and the efficiency of electron transfer also decreased, while the lifetimes of radicals which generated from PET turned longer. In addition, the reaction rate in the IL/MeCN mixed system was lower than that in MeCN, which is not consistent with the previous report that [BPy][NTf$_2$] facilitated the PET reactions. It could be found that the PET reaction was very weak under oxygen condition, which indicates that oxygen quenching reaction plays a primary role in the mixed IL/MeCN solution. It was also found that the measured rate constants were all lower than the estimated diffusion rate constants in either pure acetonitrile solution or in IL-co-solvent mixture. This finding suggests that the viscosity and the diffusion rate have great impacts on the PET process.

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1. Introduction

Photoinduced electron transfer is an important reaction in the photochemical process and is widely existed in the biological and chemical systems, which has received extensive attention for its many potential applications in molecular photonics, light triggering and solar energy conversion [1–5]. There are a lot of researches on PET in traditional solvents [6–8]. However, some properties of traditional solvents, such as volatility and toxicity, could not fully meet the requirements of some researches. Therefore, it is necessary to find new solvents for further research. As a new type of green solvent, ionic liquids have been known for their high viscosity, strong polarity, less volatility and several other interesting features [9–13]. In recent years, many researchers have studied the process of PET in IL, and discovered many new phenomena [14–18].

For example, the electron transfer rate of *N,N* Dimethylaniline (DMA) and 7 amino coumarin dyes in ionic liquid *N,N* dimethyl ethanol ammonium formate was lower than that in acetonitrile [14]. Yuan and co-workers studied the PET of different kinds of dye molecules and DMA in imidazolium-based ionic liquids. It was found that the efficiency of the fluorescence quenching of coumarin 152 by DMA could increase with the increasing of the alkyl chain length of IL, but the coumarin 102, 151, 153 are not consistent with this law [15]. The radiolysis behaviors of neat pyridinium ionic liquids and their aqueous solutions were investigated using nanosecond pulse radiolysis techniques [17]. The experimental results showed that the electron-transfer rate constants in [BPy][BF$_4$] were lower than those measured in water but were significantly higher than the diffusion-controlled rate constants estimated based on viscosity.

As one type of biological molecule, duroquinone (DQ) plays an important role in the energy transferring of photosynthesis and some other physiological processes [19–21]. As typical aromatic quinone, the reactivity of DQ triplet state has been extensively investigated [22]. The PET between ^{3}DQ* and other electron donors has been widely reported where DQ as a common photosensitizer [23–26]. Grätzel et al. studied the PET process and the reaction mechanism of DQ and diphenylamine (DPA) in a microemulsion system by laser flash photolysis [25]. They found that ^{3}DQ* could abstract an electron from DPA. Behar et al. studied the reaction process of several oxidation reactions in pyridinium ionic liquids and other organic solvents by pulsed radiolysis. It was found that pyridinium cations could combine with solvated electrons to form pyridinium neutral radicals which then would undergo electron transfer with DQ to form pyridinium cation radicals and duroquinone anion radicals (DQ•$^-$) [27]. In our previous work about the PET between *N,N,N′,N′* tetramethyl *p* phenylenediamine (TMPD) and ^{3}DQ*, it was found that the apparent decay rate constants (K_{obs}) of ^{3}DQ* exhibit a special variation with the ratio of IL/MeCN. Moreover, with the increase of IL concentration, the electron transfer between ^{3}DQ* and TMPD could be inhibited [24].

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Because of the strong reduction ability, amine is usually used as electron donor [28–29]. Ghosh [30] and Barman [31–32] et al. studied the PET process where aniline as an electron donor in the traditional solvent. In 2008, Vieira and Falvey studied solvent-mediated PET process in the pyridinium ionic liquid *N* butyl pyridinium bis(trifluoromethyl sulfonyl)imide ([BPy][NTf_2]) and found that [BPy][NTf_2] could actively facilitate PET reactions by providing a solvent-mediated pathway for electron transfer [16]. Since that time, few articles reported the electron transfer reaction in [BPy][NTf_2]. Recently, we have done some related work on [BPy][BF_4] and found that the reaction rate decreased in this ionic liquid [23,24]. Will PET reactions certainly be facilitated in [BPy][NTf_2]? In this work, we investigated the PET in the pure MeCN and [BPy][NTf_2]/MeCN mixed system by laser flash photolysis where DQ as the photosensitizer and Aniline or diphenylamine as the electron donor. All the chemical structures are presented in Fig. 1.

2. Experimental

2.1. Materials

Aniline (AN), diphenylamine (DPA) and acetonitrile were purchased from J&K Company. Duroquinone was purchased from ACROS. Ionic liquid (declaring >99%) was purchased from Green Chemistry and Catalysis, LICP, CAS, China. It was dried in a vacuum oven for 24 h to remove the water and volatile organic compounds before use.

2.2. Equipment and experimental condition

Laser photolysis experiments were carried out using a Nd: YAG laser that provided 355 nm laser pulse with a duration of 6 ns and a maximum energy of 20 mJ per pulse. The probe light source was a 300 W xenon lamp. The brightness of xenon lamp can instantly enlarge 100 times after the trigger. The laser and analyzing light passed perpendicularly through a quartz cell. Then the analyzing light passed through the monochromator and was detected by a photomultiplier tube whose effective detection range is 280–750 nm. The signals were collected by a transient recorder and processed with the home-made dynamics software. All samples were bubbled with high purity nitrogen or oxygen (99.99%) for 20 min. Viscosities of samples were tested by a rotary viscometer (Model NDJ-1, Shanghai). UV–Vis spectra were measured with a UV-3900 spectrophotometer (Hitachi, Japan). All the experiments were performed at room temperature.

To illustrate the above choice for material and conditions is appropriate, we measure the steady-state absorption spectra [33,34] before beginning of the formal experiment. As shown in Fig. 2, the absorption peak of DQ is near 350 nm, and [BPy][NTf_2] hardly absorbs light near 350 nm. Therefore, it is appropriate for us to study photochemical reactions by using [BPy][NTf_2] as a solvent. Otherwise, AN and DPA have strong absorption near 280 nm, but hardly absorb at 355 nm, which are inserted in Fig. S1 in Supplementary data.

3. Results and discussions

3.1. Photolysis of DQ in [BPy][NTf_2]/MeCN

The flash photolysis of DQ in N_2-saturated acetonitrile solution has been studied in our previous work [23]. There is a strong absorption band around 480 nm after photolysis, which is the characteristic absorption band of the triplet $^3DQ^*$ [25]. The decay of $^3DQ^*$ is mainly achieved by non-radiative transitions such as intersystem crossing (ISC) and collisions under nitrogen atmosphere [24]. $^3DQ^*$ also could be rapidly quenched by oxygen, the reaction paths are as Scheme 1:

Keeping the same concentration of DQ and increasing the proportion of [BPy][NTf_2] gradually, it was found that the position and intensity of the characteristic absorption band of $^3DQ^*$ were almost the same, except that the position of the maximum absorption peak was a little blue shift (Fig. 3), which implies that $^3DQ^*$ did not react with [BPy][NTf_2]. By fitting the time profiles of $^3DQ^*$ at 480 nm, it was found that the decay of time profiles accorded with pseudo-first order kinetics in either pure MeCN or [BPy][NTf_2]/MeCN mixed solution. On the other hand, with the increase of IL proportion, the decay of $^3DQ^*$ became slower, as shown in the inset of Fig. 3.

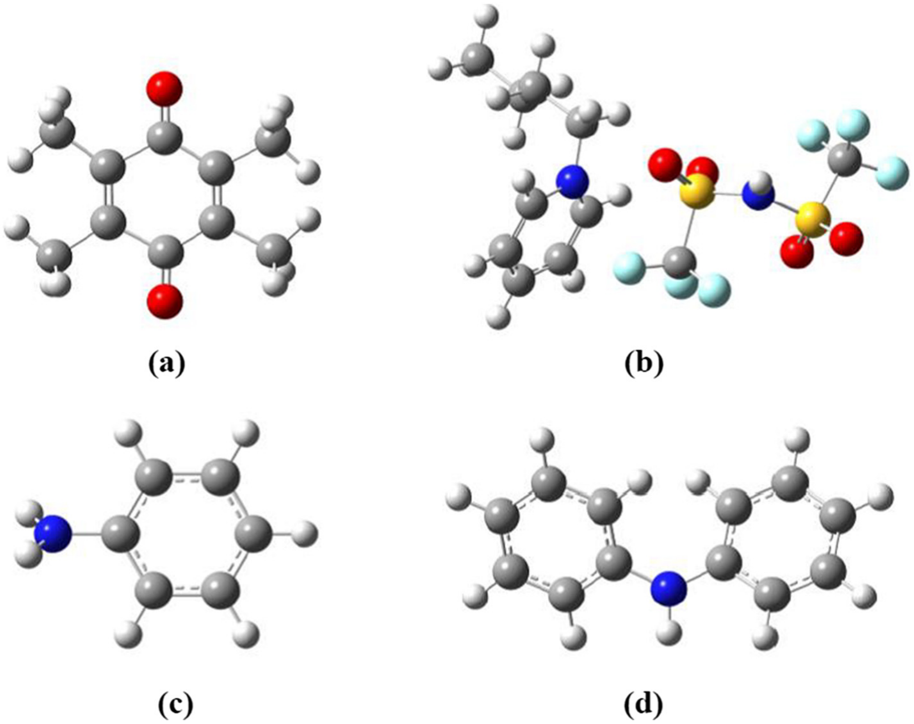

Fig. 1. Chemical structures of different molecules: (a) duroquinone, (b) [BPy][NTf_2], (c) aniline, (d) diphenylamine.

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