

Does Photoisomerization Proceed in an Ionic Liquid?

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Photoisomerization of *trans*-stilbene has been investigated in an ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate([bmim]PF₆). It has been found that the photo-isomerization indeed proceeds in this ionic liquid with a rate much larger than that expected from its polarity and shear viscosity.

Liquids that are composed solely of ions are called ionic liquids. Ionic liquids are expected to afford a unique environment for chemical reactions. They are considered as one of the most promising new solvents in the “green chemistry”. Although a number of synthetic and electrochemical studies have already been reported,¹ there are only few that are concerned with the physicochemical properties of ionic liquids.

In the present paper, we investigate photoisomerization of *trans*-stilbene in 1-butyl-3-methylimidazolium hexafluorophosphate([bmim]PF₆), which is a well studied ionic liquid that is air and moisture stable. Photoisomerization of *trans*-stilbene is known to be strongly influenced by the solvent polarity and viscosity.² Therefore this system is suitable for studying the properties of ionic liquids as solvents. Since [bmim]PF₆ is an extremely viscous solvent (312 cP at 303 K)³ that may well hinder the internal rotation, primary interest here is to elucidate whether or not the photoisomerization of *trans*-stilbene proceed efficiently in [bmim]PF₆.

[bmim]PF₆ was synthesized as described in the literature.⁴ *trans*-Stilbene was recrystallized from ethanol before use. Picosecond time-resolved fluorescence spectra were obtained with the use of the third harmonic of a titanium-sapphire laser (c.a. 266 nm, 5–10 mW, 1kHz) as an excitation source and a streak camera (Hamamatsu C2909) for detection. A polarizer was placed at magic angle to eliminate the effect of rotational diffusion. Typical time resolution of the system was 15 ps. Sample concentration was 3×10^{-3} mol dm⁻³.

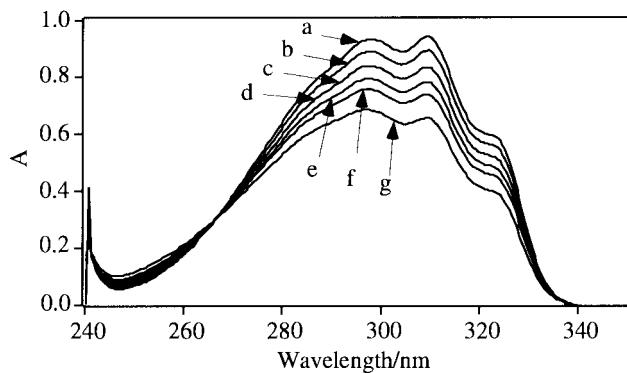


Figure 1. Change of UV absorption spectra of *trans*-stilbene in [bmim]PF₆. Each spectrum corresponds to (a) 0 min, (b) 2 min, (c) 4 min, (d) 6 min, (e) 8 min, (f) 10 min and (g) 14 min irradiation.

In order to evaluate the polarity of [bmim]PF₆, we first examined the $E_T(30)$ value, which is equal to the transition energy of the charge transfer absorption band of N-phenoxide betaine dye. $E_T(30)$ is commonly used as an empirical indicator of solvent polarity.⁵ We obtained 54 kcal/mol for [bmim]PF₆. This value is comparable to those of highly polar solvents such as alcohols; $E_T(30)$ is 55.5 kcal/mol for methanol and 47.6 kcal/mol for decanol.

We then observed steady-state absorption change of *trans*-stilbene in [bmim]PF₆ with irradiation by a Xe flash lamp with a filter cutting below 300 nm. The result is shown in Figure 1. The absorption band of *trans*-stilbene at 300 nm decreases and the band of *cis*-stilbene at 250 nm increases as the irradiation time increases. A clear isosbestic point appears at 266 nm, indicating that there is no other side-reactions in the *trans*-*cis* photoisomerization process. Therefore, we exclude the possibility that the stilbene reacts with [bmim]PF₆. However, from a separate experiment, we find that the [bmim]PF₆ itself generates photoproducts when irradiated with a wavelength shorter than 300 nm.

The time profile of the observed fluorescence at 320–420 nm is shown in Figure 2. The decay curve is fitted well by a double exponential function. The fast component has a lifetime 138 ps and the slow component has a lifetime as long as a few nanoseconds. The intensity ratio is about 10:1 with the fast component stronger than the slow. From the fluorescence spectral shape, the fast component of the decay is ascribed to the fluorescence of *trans*-stilbene. The slow component is ascribed to the fluorescence from unknown photoproduct of [bmim]PF₆, which is generated by the laser excitation at around 266 nm. As a result, the S₁ state lifetime of *trans*-stilbene is obtained as $\tau = 138$ ps in [bmim]PF₆. In the case of S₁ *trans*-stilbene, the isomerization is considered to be the only non-radiative decay process both in non-polar⁶ and polar⁷ solvents. Though we can not rule out the possibility that a new non-radiative decay channel opens in an ionic liquid, we assume here that the isomeriza-

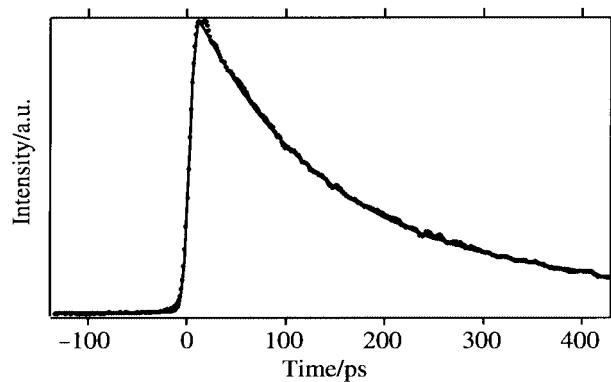


Figure 2. Fluorescence decay profile of *trans*-stilbene in [bmim]PF₆. Best fitted curve is also shown in solid line.

tion is the only non-radiative decay channel. Then the isomerization rate $k_{\text{iso}} = 6.6 \times 10^9 \text{ s}^{-1}$ is obtained using the relationship $k_{\text{iso}} = 1/\tau - k_r$, where k_r is a radiative rate ($k_r = 6 \times 10^8 \text{ s}^{-1}$).

The photoisomerization rates of *trans*-stilbene in various solvents including [bmim]PF₆ are compared in Figure 3. The viscosity and the polarity dependence of the rate are clearly seen in the figure. For the same viscosity, polar solvents give longer photoisomerization rates. Since the $E_T(30)$ value of [bmim]PF₆ is close to those of alcohols, we compare the isomerization rate in [bmim]PF₆ with those in alcohols. When we

extrapolate the isomerization rates in alcohols to the value of [bmim]PF₆ (312 cP at 303 K)³ by using a power-law relation, $k_{\text{iso}} \propto \eta^\alpha$ ($\alpha = 0.6$ for alcohols²), we obtain a very small value ($9.7 \times 10^8 \text{ s}^{-1}$) as indicated in the Figure 3. However the observed rate is much larger ($6.6 \times 10^9 \text{ s}^{-1}$) than the rate thus expected from alcohols.

It is concluded that photoisomerization of *trans*-stilbene does proceed efficiently in spite of its large viscosity in an ionic liquid [bmim]PF₆. This result clearly indicates the intriguing nature of ionic liquids, which can not be described in the conventional framework using polarity and shear viscosity. Further studies are being planned from the viewpoint of microscopic solvent dynamics.

References and Notes

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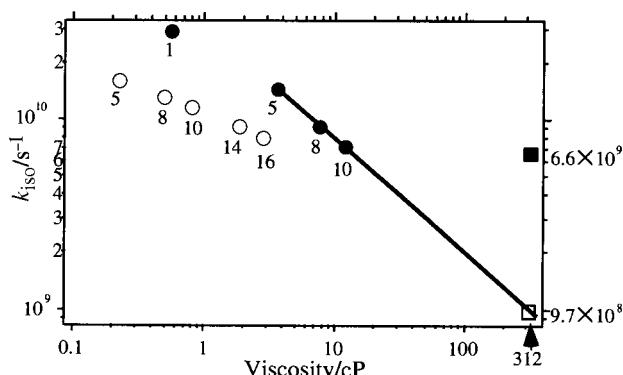


Figure 3. Isomerization rate in many solvents. ○; in alkanes, ●; in alcohols (with number of carbon atoms), □; extrapolated value, ■; in [bmim]PF₆. Solid line; empirical fit extended from alcohols. Data in alkanes and alcohols are extracted from ref 8.