On the Branching Ratio of Photoisomerization of 4-Aminoazobenzene

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Introduction] Study of the reaction path ways and the relaxation processes of photoexcited molecules are fundamental part of investigation for any photoinduced reaction and such information yields an opportunity to control the photochemical reactions.   For that purpose, photoisomerization reaction in azobenezne (AB) and its derivatives has been well studied in which trans-to-cis isomerization reaction is initiated by the irradiation of UV-visible light.[1] On the other hand, cis-to-trans thermal isomerization spontaneously takes place in the dark owing to the thermodynamic stability of the trans isomer[1], and our recent study on 4-aminoazobenzene (AAB) has revealed that the mechanism and the kinetics of thermal isomerization of AAB strongly depends on the polarity of the medium and is independent of the viscosity of the medium.[2]

In this study, as a part of our investigation on the photoreaction network of AAB, we focused on the branching ratio of photoisomerization, namely the production ratio between cis-isomer and trans-isomer from photoexcited state of trans-isomer.   The most significant aspect of the study is that the method for estimating the branching ratio does not require the ultrafast time resolved measurement but a simplistic approach has been employed.   Briefly, the population at photostationary state (cis isomer) is measured as function of pumping rate, and the observed results are discussed quantitatively based on the three-level model (described below) which provide some insight on the mechanism of photoisomerization in viscous medium.

Experimental and Analysis]   AAB obtained from Wako Pure Chemical Industries, Ltd., Japan (99% pure), was used as such.   All the solvents used were of spectroscopic grades**.**   The experimental setup is shown in Fig. 1.   A cw laser (405 nm, ~200 mW, purchased from World Co. Ltd) was used as an excitation source and an electric lamp (MINI MAGLITE 2AA) was used as source for probe beam.   Decrease in the absorbance of AAB caused by the excitation was measured under the photostationary condition as a function of intensity of 405 nm laser light.   Further details of the setup are in ref. 2.
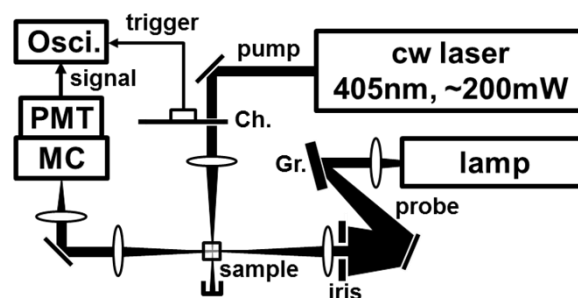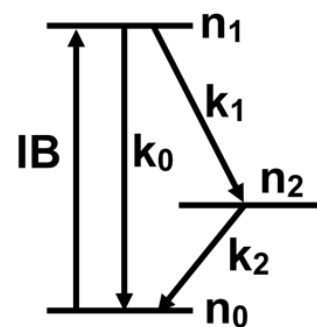

Fig. 1 Experimental setup

In general, for understanding the photoisomerization in azobenzene family schematically, a five level energy diagram (scheme 1) is considered.   In our case, photoexcitation of cis-AAB is negligible due to very low absorption cross-section for pump 405 nm.   Therefore, the effect of excited state of cis-isomer can be neglected and the five level system can be modified to four level system as indicated by red broken line in the scheme 1.   Furthermore, under the definition of branching ratio as described above, the four level system can be simplified to three level system as shown in scheme 2.   In scheme 2, n_0 corresponds to the population of trans-form in the ground state under photostationary state, n_1 represents the sum of the population of trans-form in the excited state and population in the intermediate state. The population of cis produced by photoisomerization of trans is denoted by n_2. The rate constants, k_0 and k_1, represent the decay rate of those molecules which do not undergo for
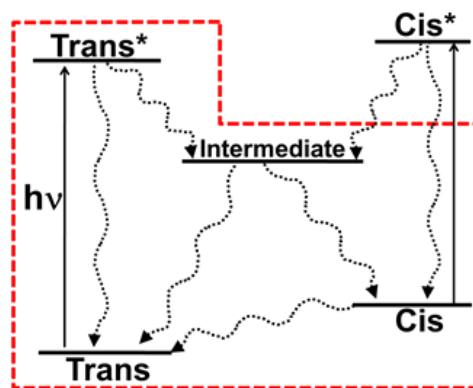
Scheme 1

photoisomerization and the decay rate of those molecules which relax after photoisomerization, respectively. Rate of thermal cis-to-trans isomerization is shown by k_2. In our recent study the order of the k_2 in MeOH and EG has been determined[2] as in the order of one. However the rate constant for k_0 and k_1 has also been determined which is much higher[3] (in the order of 10^{12} to 10^{14} s^{-1}) than k_2. Thus the total population (N) of the three level system which is sum of n_0, n_1, and n_2, i.e., $N = n_0 + n_1 + n_2$, can be expressed as $N \sim n_0 + n_2$.

Using three level system and above approximation, the branching ratio (r) defined as above is equivalent to ratio of k_0 to k_1. Namely, the branching ratio can be expressed as $r = k_0/k_1$. For estimation of branching ratio, the population under photostationary state as function of pumping rate (IB) is calculated by monitoring the bleaching at absorption peak for methanol (MeOH) and ethylene glycol (EG). In the analysis, under steady state condition, it is assumed that number of bleached molecules in level-0 are equal to the number of molecules present at level 2 (scheme 2). The ratio of N/n_0 versus IB is plotted and fitted to the equation as follows;

$$\frac{N}{n_0} = 1 + m \times IB \qquad \text{where} \quad m = \frac{1}{(r+1)\,k_2} \quad \text{and} \quad r = \frac{k_0}{k_1} \qquad (1)$$

Eq.(1) is derived from the solution of differential equation for scheme 2 under steady state condition. For calculating IB, at first, decrease in pump power before and after the sample is noticed and divided by per photon energy (i.e., 5×10^{-19} J for 405 nm) which is the measure of bleached /excited molecules or absorbed photon per second. Further, by dividing to number of photon absorbed per second by active sample volume, the value of IBn_0 can be obtained. Once the IBn_0 is known and by measuring the n_0, IB can be estimated.

Results and discussion] The plot of N/n_0 versus IB is fitted to Eq. 1 gives a slope (m) as shown in Fig. 2 and hence branching ratio (r) can be estimated based on the value of k_2 reported in our previous report[2]. It is observed that branching ratio is significant different between MeOH and EG. Calculated value of the branching ratio (k_0/k_1) for MeOH and EG is 0.9 (± 0.06) and 0.3 (± 0.02), respectively. Here it should be mentioned that MeOH and EG have similar polarity but quite different viscosity. Therefore, it seems that in contrast to thermal isomerization, mechanism for photoisomerization for 4-AAB is sensitive to viscosity and photoisomerization mechanism may be different in EG than MeOH. Alternatively, this situation can be better probed by ultrafast transient experiments which are under course of investigation.
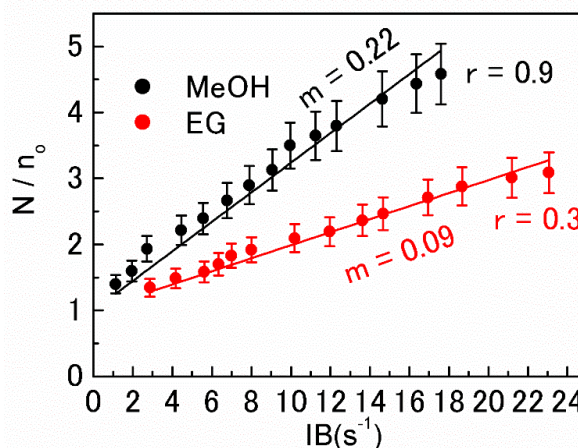

Fig. 2 Plot of N/n_0 versus pumping rate (IB). Straight line indicates fitting of the data to eq. 1. m is the slope of the fitted line and r is the branching ratio.

References

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