Reply to Comment on "Supercritical Fluid Tuning of Reaction Rates: The Cis−Trans Isomerization of 4-4'-Disubstituted Azobenzenes"

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We appreciate the interest of Professor Asuni and his co-workers in this paper. We respond with two types of clarification−semantic and conceptual.

First, we have never said that transition state theory (TST) does not apply to this reaction, and we cannot agree with these authors' interpretation of our work in this regard. We certainly believe that there is in fact a transition state, in equilibrium with the substrate, which decomposes to product at a given frequency. It is only the solvent shell reorganization which is in question. Even here we have not claimed to have determined a mechanism. We acknowledge that inversion and rotation are competing mechanisms, but we feel that the large rate increases from protic cosolvents suggest the possibility of a more polar transition state, which would correspond to some rotation character. What we have done is to suggest a mechanism, consistent with published results of others, that is consistent with the data. In fact, some data exist for an S_N2 reaction which also suggest that solvent reorganization of the type we suggest may play a role.

There are many reports of rate constants for solvents that are of low dielectric constants that unequivocally fall in the "inversion" regime (e.g., Schanze et al. *J. Org. Chem.* **1983**; Marcandalli et al. *J. Chem. Soc., Perkin. Trans.* **1984**). In all cases, the rate increases with increased dielectric constant with no deviations from Kirkwood or Hammet plots for dielectric constants less than 10. This is in opposition to the idea that there should be a decrease in the rate at increasing SCF density due to solvent effects. The dielectric increases slightly; therefore, according to all other data we should see a slight increase in the rate constant if there were not a density dependence (solvent rearrangement). Asano et al. attribute a slight positive activation volume for the inversion mechanism to a reduced polarity of the transition state. If this were the case, rates would decrease with increasing polarity in the "inversion" regime where there is no significant contribution from the "rotation" mechanism. (We have shown this by decoupling the hydrogen bonding and dielectric effects.) Also, as we have reported in our paper, others have seen the same density effects on the isomerization of stilbenes in SCF CO_2.

Our mechanism is consistent with all experimental data. Certainly we have not proven the mechanism and other mechanisms would be possible. It does seem, however, that there are issues in the comments of Asano et al. which may be at odds with the literature and the data.

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