COMMENTS

Comment on “Supercritical Fluid Tuning of Reactions Rates: the Cis−Trans Isomerization of 4-4′-Disubstituted Azobenzenes”

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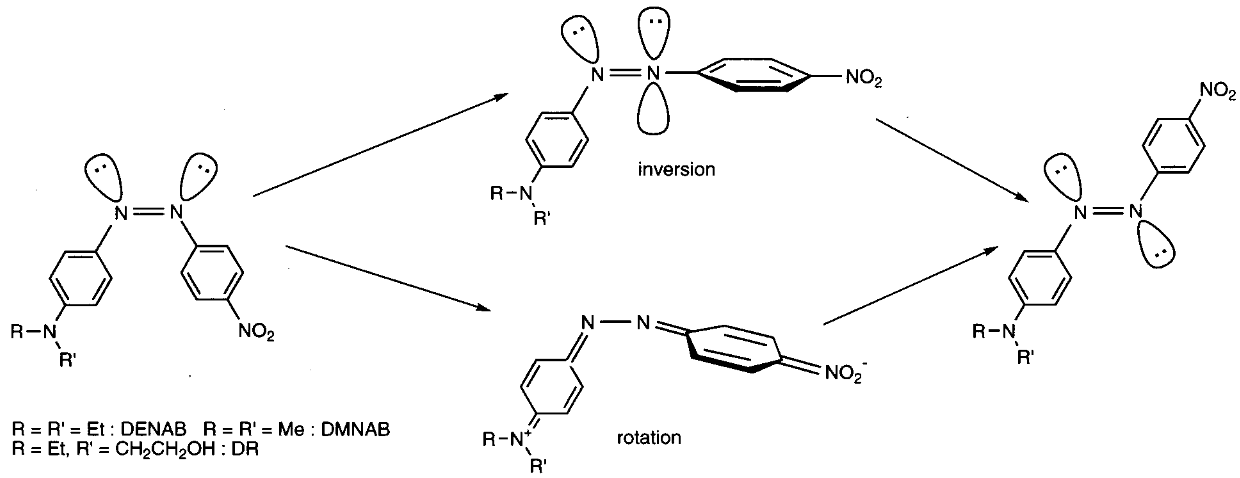
In a recent paper in this journal, Eckert and co-workers[1] reported the thermal geometrical isomerization rate of push−pull substituted azobenzenes in supercritical carbon dioxide and ethane in the presence and absence of organic cosolvent. The azobenzenes they used were DENAB and DR shown in Scheme 1. Their observations can be summarized as follows: (1) The reaction was retarded by an increase in the concentration of the supercritical fluid. (2) The presence of relatively low concentration of an organic cosolvent (0.02−0.13 mol dm^{-3}) accelerates the reaction. (3) The acceleration by a protic cosolvent (methanol or 1,1,1,3,3,3-hexafluoro-2-propanol) was larger than that by an aprotic one (acetone or *N*,*N*-dimethylacetamide). The results in pure carbon dioxide with DENAB are in agreement with the ones reported by Sigman and Leffler some 10 years ago.[2] We also made similar observations with DMNAB in supercritical CO_2.[3] However, to rationalize their results, Eckert assumed that the thermal movements of the supercritical fluids may not be fast enough to validate the transition state theory (TST). The purpose of this comment is to show that their results can be fully rationalized within the framework of TST.

SCHEME 1



According to Kramers,[4] TST fails both at the low and high density/viscosity region of the medium. In the low density region, the energy transfer from the medium to the reactant regulates the reaction. In this region, the rate constant is expected to increase with increasing medium density. Since the reaction rate decreased with an increase in the density, the Eckert’s experiments were not performed in this region. At the high viscosity end, the reaction is controlled by slow thermal fluctuations of the medium molecules and the rate is expected to decrease with increasing medium viscosity. Experiments by Asano and co-workers[5,6] unequivocallydemonstrated that viscosities higher than 10 Pa s were necessary to bring the isomerization into this region. Therefore, it is almost certain that TST is valid in the conditions used by Eckert. In other words, the solvent thermal fluctuations are fast enough to maintain thermal equilibrium between the initial and the transition state. This view is also in accordance with the characteristics of supercritical fluids, i.e., a higher density than in gaseous state and faster translational and rotational movements of molecules than in liquid state. Under such conditions, it is unreasonable to assume that the reaction proceeds through an intermediate state M, as assumed by Eckert, where the reactant is already converted to the *E*-isomer in the initial state solvation shell. The energy required for such structural changes must be definitely larger than that for a normal route via the activated complex with an optimum solvation shell. A contribution of a route through M cannot be significant. Their results can be easily rationalized on the basis of the two-route reaction mechanism in Scheme 1. In pure ethane and carbon dioxide, the reaction proceeds almost exclusively through the inversion transition state as in liquid hydrocarbons.[7−9] The slight decrease in the polarity during the activation[7−10] makes this reaction faster in less dense fluids. The presence of a polar cosolvent opens the rotation route and it competes with inversion as in liquid carbon tetrachloride and benzene.[8,9] Since the “local” dielectric constant range (ca. 1.5−4.5) estimated by considering local composition enhancement exceeds the values for these organic solvents, it is likely that rotation and inversion compete to each other in the presence of polar molecules. Retardations by an increase in the density of a supercritical fluid in the presence

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of a cosolvent at a constant concentration must be a result of a suppression of the inversion route.

In summary, the observations made by Eckert and co-workers can be explained satisfactorily on the basis of TST and Scheme 1. It is not necessary to assume that isomerization to the *E*-isomer precedes the solvent rearrangement in the solvation shell.

References and Notes

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