

## Highly efficient triplet chain isomerization of Dewar benzenes: Adiabatic rate constants from cage kinetics

Quantum yields as high as 120 were achieved for triplet-sensitized photoisomerizations of several Dewar benzene reactants, R, to the corresponding benzene products, P. Considerable chain amplification is maintained even at high conversion. All relevant rate constants of this triplet chain reaction were extracted from laser flash photolysis plus steady-state photolysis experiments. The crucial rate constant  $k(a)$  for adiabatic isomerization of the triplet reactant to triplet product ( $R^* \rightarrow P^*$ ) cannot be directly measured because it is so large relative to the bimolecular rate of  $R^*$  formation via sensitization. However,  $k(a)$  was obtained indirectly using a cage/encounter complex model to analyze the competition between the dissociation of encounter pairs with the sensitizer, e.g.,  $S/R^* \rightarrow S + R^*$ , and the in-cage processes,  $S/R^* \rightarrow S/P^* \rightarrow S^*/P$ , in nonviscous and viscous solvents. These measurements yielded  $k(a)$  values of (similar to  $4\text{--}9 \times 10^9 \text{ s}^{-1}$ ), which suggests that only a small (similar to 3 kcal/mol) energy barrier exists along the potential energy surface from  $R^*$  to  $P^*$ . Steady-state data indicated that the chain-terminating rate constant  $R^* \rightarrow R$  is negligibly small, an ideal condition for chain amplification. Triplet energy transfer from a series of sensitizers to the Dewar benzene derivatives shows a nonclassical falloff in rate constants with decreasing sensitizer triplet energy, suggesting energy transfer to thermally distorted configurations having lower singlet-triplet energy gaps. As a result of distorted geometries of  $R^*$  and  $P^*$ , the chain-propagating energy transfer from  $P^*$  to R proceeds with a rate constant of only similar to  $2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ , despite strong exothermicity. The isomerization reaction can release over 100 kcal/kcal of absorbed photons due to the high-energy content of the reactant together with the large chain length.