## PHOTOOXYGENATION OF STILBENES IN ZEOLITE BY EXCITATION OF THE CONTACT CHARGE TRASFER COMPLEXES WITH OXYGEN

## Masanobu Kojima

<sup>††</sup>Department of Bioscience and Biotechnology, Faculty of Agriculture, Shinshu University 3-1-1 Asahi, Matsumoto, Nagano 390-8621, Japan

Recently, metal ion exchanged zeolites have aroused interest as unique photochemical reaction vessels, in which stabilization of photoexcited specie, enhancement of intersystem crossing by the metal ions, and increase in intermolecular interaction between adsorbed guest molecules have been observed, in addition to the steric effect and regioselectivity due to the restricted spaces in zeolites [1-5]. With respect to our studies of the photoinduced electron transfer (PET) reaction of contact charge transfer (CCT) complexes in solution between aromatic olefins like styrenes and oxygen molecules [6], it is particularly significant that aliphatic olefins like alkyl substituted ethylenes form strong charge transfer complexes with oxygen in zeolite supercages [7]. Therefore, it is probable that, compared to solvents, the zeolite cavities also promote greater stabilization of the CCT complexes for aromatic olefins and the ionic intermediates generated by selective excitation of the CCT bands. that CCT complexes of cis- and trans-stilbenes with oxygen molecules were formed in zeolite Excitation of the CCT bands by a 313-nm wavelength light produced the corresponding benzaldehydes through an electron transfer reaction to generate stilbene cation Irradiation of the CCT complexes by a 254-nm radicals and superoxide anion. wavelength light, in contrast, gave rise to isomerization and formation of phenanthrene without yielding any oxygenation products, as in the photoreaction under oxygen in solution.

$$hv | hv' \text{ or } \triangle$$

$$c\text{-St} \xrightarrow{O_2/M^+Y} \left( c\text{-St}^{\delta+} - O_2^{\delta-} \right) \xrightarrow{hv_{cct}} c\text{-St}^{+\bullet} + O_2^{-\bullet}$$

$$hv | CCT \text{ complex}$$

$$t\text{-St} \xrightarrow{O_2/M^+Y} \left( t\text{-St}^{\delta+} - O_2^{\delta-} \right) \xrightarrow{hv_{cct}} t\text{-St}^{+\bullet} + O_2^{-\bullet}$$

$$CCT \text{ complex}$$

$$CCT \text{ complex}$$

Scheme. Formation of benzaldehyde via CCT excitation:  $M^+ = Na^+$ ,  $K^+$ ,  $Cs^+$ .

- [1] V. Ramamurthy, and N. J. Turro, J. Inclusion Phenom. Mol. Recognit. Chem., 21, 239-282 (1995).
- [2] M. Kojima, H. Takeya, Y. Kuriyama, and S. Oishi, Chem. Lett., 1997, 997-998.
- [3] Y. Kurivama, H. Takeya, S. Oishi, and M. Kojima, Chem. Lett., 1998, 843-844.
- [4] H. Takeya, Y. Kuriyama, and M. Kojima; Tetrahedron Lett., 39, 5967-5970 (1998).
- [5] C. Matsubara and M. Kojima, Tetrahedron Lett., in press.
- [6] M. Kojima M. H. Sakuragi, and K. Tokumaru, Bull. Chem. Soc. Jpn., 60, 3331-3336 (1987); b) M. Kojima, H. Sakuragi, and K. Tokumaru, Bull. Chem. Soc. Jpn., 62, 3863-3868 (1989); M. Kojima, A. Ishida, and S. Takamuku, Bull. Chem. Soc. Jpn., 71, 2211-2220 (1998).
- [7] a) F. Blatter and H. Frei, J. Am. Chem. Soc., 115, 7501-7502 (1993); b) H. Sun, F. Blatter, and H. Frei, J. Am. Chem. Soc., 118, 6873-6879 (1996).