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Photooxygenation of Stilbenes in Zeolite by Excitation of Their Contact Charge Transfer Complexes with Oxygen

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Abstract: Contact charge transfer (CCT) complexes of *trans*-stilbenes with oxygen molecules were formed in zeolite NaY. Excitation of the CCT bands by a 313-nm wavelength light produced the corresponding benzaldehydes through an electron transfer reaction to generate stilbene cation radicals and superoxide anion radical. Irradiation of the CCT complexes by a 254-nm wavelength light, by contrast, gave rise to isomerization and formation of phenanthrene without yielding any oxygenation products, as in the photoreaction under oxygen in solution.

Keywords: Electron transfer; Oxygenation; Photochemistry; Zeolites

Recently, metal ion exchanged zeolites have aroused interest as unique photochemical reaction vessels, in which stabilization of photoexcited species [1], enhancement of intersystem crossing by the metal ions [2], and increase in intermolecular interaction between adsorbed guest molecules [3] have been observed, in addition to the steric effect [4, 5] and regioselectivity [6] due to the restricted spaces in zeolites. 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 [7-9], it is particularly significant that aliphatic olefins like alkyl substituted ethylenes form strong charge transfer complexes with oxygen in zeolite supercages [10, 11]. 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. We report here on the photoreactivities of stilbenes under oxygen adsorbed in

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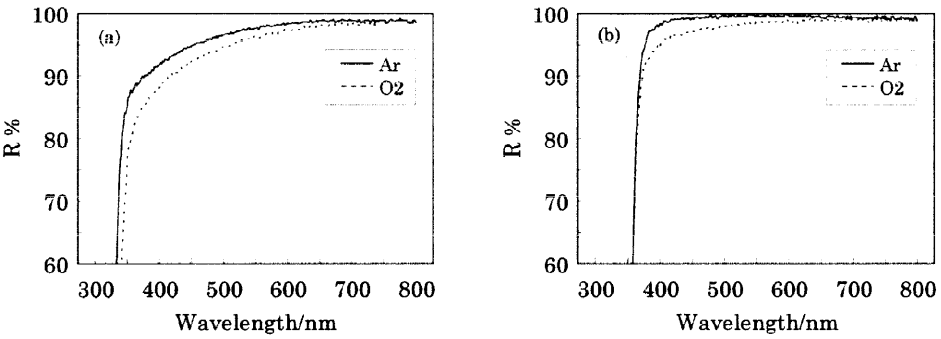


Figure 1. Diffuse reflectance spectra of stilbenes adsorbed in NaY: (a) *t*-St; (b) *t*-DMSt.

the zeolite supercages of NaY, KY, and CsY, in which benzaldehyde was produced on excitation of the CCT complexes and phenanthrene on direct excitation of the stilbenes.

The zeolite samples containing *cis*- and *trans*-stilbenes (*c*-St and *t*-St, respectively) and *trans*-4,4'-dimethoxystilbene (*t*-DMSt) were prepared as previously reported [12] and dried under vacuum before use. The formation of the CCT complexes between stilbenes and oxygen in solution has not been reported. However, as shown in Figure 1, it was clearly observed that the CCT absorption bands for *t*-St and *t*-DMSt completely disappeared under argon; by contrast, the band for *c*-St was not observed. Irradiation of the samples (200 mg) was carried out without solvent under oxygen in a quartz cell (length x width x thickness = 350 x 300 x 4/mm) using a 100-W high-pressure mercury lamp through a Pyrex glass filter (effective at 313 nm) and through a Hoya UV-36 glass filter (effective at 366 nm) and also using a 160-W low-pressure mercury lamp (effective at 254 nm). The reaction products were extracted from the zeolite samples using dichloromethane and analyzed by gas chromatography (Table 1). The total yields of starting olefins and photoproducts were between 12 % for *c*-St/KY and 87 % for *c*-St/NaY; therefore, the polymeric and bulky products, which could not be extracted, were probably formed inside the zeolites on irradiation.

It is well-known that the excited singlet *c*-St (^1c-St*) undergoes [2 + 4] cycloaddition to yield dihydrophenanthrene, which is readily oxidized under oxygen to give phenanthrene, as confirmed by the results we obtained with cyclohexane (Table 1). However, irradiation of the cyclohexane slurry of the stilbene/NaY samples under oxygen using a 313-nm wavelength light only caused isomerization and did not yield phenanthrene. It is significant that benzaldehyde was produced together with *c*- and *t*-St and phenanthrene when the stilbene/NaY samples were irradiated without solvent using 313 and 366-nm wavelength lights. The isomerization and [2 + 4] cycloaddition of stilbenes adsorbed in NaY supercages must have occurred through direct excitation of the stilbenes, while the photooxygenation probably proceeded through the PET reaction of the CCT complex composed of *t*-St and oxygen to generate the stilbene cation radical (t-St$^{\cdot+}$) and superoxide anion radical ($O_2^{\cdot-}$), followed by cycloaddition of the ion radical pairs to give the corresponding 1,2-dioxetane, which thermally decomposed to

Table 1

Product Distribution Obtained by Irradiation of Stilbenes under Oxygen in Zeolites and Solution[a]

Condition	Olefin	EW/nm[b]	Yield/%[c]	Product Distribution/%[d]			
				cis	*trans*	Phenanthrene	ArCHO
C_6H_{12}[e]	*c*-St	313	98	0	0	100	0
C_6H_{12}[e]	*t*-St	313	98	0	0	100	0
NaY/C_6H_{12}[f]	*c*-St	313	82	83	17	trace	0
NaY/C_6H_{12}[f]	*t*-St	313	86	24	76	trace	0
NaY	*c*-St	313	24	74	11	5	10
NaY	*t*-St	313	43	56	30	7	7
NaY	*c*-St	254[g]	87	83	12	5	0
NaY	*t*-St	254[g]	84	19	72	9	0
NaY	*c*-St	366	84	81	19	3	3
NaY	*t*-St	366	43	65	19	3	13
NaY	*t*-DMSt	313	46	46	38	0	16
KY	*c*-St	313	12	19	7	30	65
KY	*t*-St	313	30	20	6	16	58
CsY	*c*-St	313	60	44	40	1	15
CsY	*t*-St	313	61	46	38	1	15

[a] Irradiation time, 4 h.

[b] Effective excitation wavelength.

[c] Total yield of a starting olefin and products.

[d] Products extracted by CH_2Cl_2.

[e] Irradiated in cyclohexane.

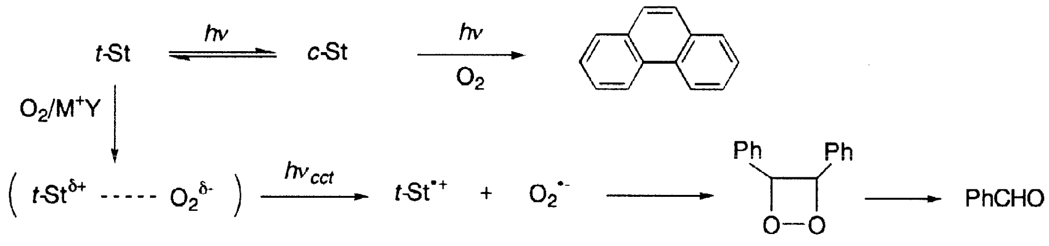
[f] Irradiated as cyclohexane slurry.

[g] Irradiation time, 3h.

benzaldehyde [13], as shown in Scheme 1.

The mechanism proposed above is supported by the following results. First of all, irradiation of the stilbene/NaY samples using a 254-nm wavelength light produced no benzaldehyde because stilbenes absorb the light to suppress the PET reaction. Secondly, irradiation of the CCT absorption band composed of *t*-DMSt and oxygen selectively formed 4-methoxybenzaldehyde at the expense of the corresponding phenanthrene. This is because in the wavelength region above 340 nm, the absorption band of *t*-DMSt itself sharply decreases, as seen in Figure 1b and the CCT complex between *t*-DMSt and oxygen was excited more selectively compared to the case of *t*-St. Thirdly, the photooxygenation was not affected at all by the presence of 2,3-dimethyl-2-butene, employed as a singlet oxygen trap. Therefore, it is clear that benzaldehydes were produced by the PET reaction of the CCT complexes.

For KY and CsY, as in the case of NaY, benzaldehyde was also produced. However, it should be noted that considerably less phenanthrene was produced for CsY. This is probably because the intersystem crossing of ^{1}c-St* to the excited triplet state of *c*-St accelerated due to the heavy atom effect of the metal ion [2].



Scheme 1. Formation of benzaldehyde via CCT excitation: M^+= Na^+, K^+, Cs^+.

In a related investigation, the dye sensitized photooxygenation of *t*-St and *t*-DMSt adsorbed in zeolites has been studied in cyclohexane slurry, in which benzaldehydes were produced through the PET reaction between the exited dye and the stilbenes [14]. However, it was pointed out that photooxygenation did not occur in the absence of dye. Therefore, it is probable that the solvent molecules impede the interaction between the stilbenes and oxygen that forms the CCT complexes; in fact, we have observed oxygenation products of solvents such as cyclohexanone and cyclohexanol by GC analysis when the stilbene/NaY cyclohexane slurry was irradiated by wavelengths of more than 290 nm.

The present findings clearly show that CCT complexes between aromatic olefins and oxygen formed in zeolite supercages are more stable than those in solution, probably due to the strong electrostatic field [10, 11] and also to the condensation effect of the zeolite supercages. Therefore, there is a probability that the organic guest molecules in zeolite nanospaces become more photoreactive on the formation of the CCT complexes.

We are now conducting further studies into the reactivities of the CCT complexes using other aromatic olefins.

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