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Stereoselectivity control of [2 + 2] photocycloaddition by changing site distances of hydrotalcite interlayers

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Stereoselectivity of photocyclodimers of unsaturated carboxylates is shown to be controlled by changing the site distances of clay interlayers.

Clay compounds intercalate electrostatically various ionic molecular species in their interlayers.[1] The intercalated ionic species have been assumed to be regularly packed as randomly antiparallel oriented aggregates on the basis of the fact that stilbazolium ions in montmorrilonite resulted in the selective photocyclodimerization to give *syn*-head-to-tail dimers.[1,2] In our previous paper, we reported that photoreactions of unsaturated carboxylates in the presence of hydrotalcite clay gave rise to two cyclodimers, *syn*-HH (head-to-head) and *syn*-HT (head-to-tail), and the stereoselectivities are controlled by the position of double bond.[3] Now our interest turned to the correlation between the structure of clay compounds and the stereoselectivity of photocycloaddition. In the present study, we report on the interesting effect of site distances of hydrotalcite on the efficiency and stereoselectivity of photocycloaddition.

Hydrotalcite clays were synthesized according to the known procedures.[5] Because the anion exchange sites are produced by substituting trivalent Al^{3+} for divalent Mg^{2+}, the site distances are controlled by changing *n*, the fraction of Al^{3+}, of $[Mg_{1-n}Al_n(OH)_2]^{n+}$. Four kinds of hydrotalcites with *n* value from 0.15 to 0.30 were synthesized and employed as the test layer compounds, on considering that stable layered structures are known to be formed with the Al^{3+} fractions.[5,6] Fig. 1 shows idealized distributions of anion exchange sites on hydrotalcite layer with changing *n* value. Their layered structures and compositions of metal ions were confirmed by X-ray diffraction analysis and chelatometric titrations, respectively.[6]

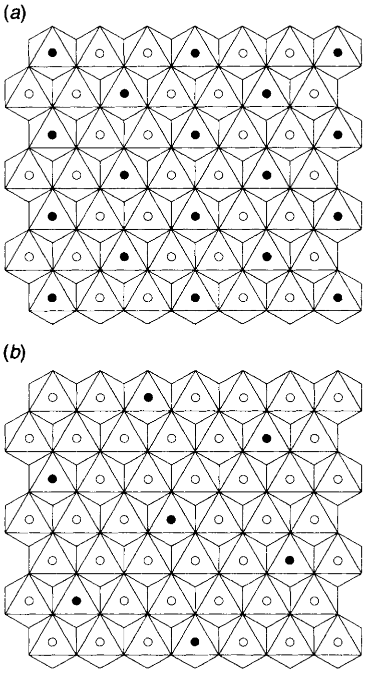

Fig. 1 Idealized site distributions of isomorphously replaced Al^{3+} ions in the $Mg(OH)_2$ octahedral lattice of hydrotalcite clays, $[Mg_{1-n}Al_n(OH)_2]^{n+}$, (*a*) *n* = 0.30, (*b*) *n* = 0.15; Mg^{2+} (○), Al^{3+} (●)

Intercalations of carboxylates **1** were carried out as previously described.[3] An aqueous suspension of clay-intercalated **1** was irradiated with a 300 W medium-pressure mercury lamp through a Pyrex vessel under an Ar atmosphere. Products from **1a**, **b** were characterized on the basis of spectroscopic data (1H NMR and mass).[3]

Table 1 shows results of the photoirradiations using clays of various *n* values. The intercalation of 4-(2-phenylethenyl-)bezoate **1a** was quantitative and the irradiation resulted in the efficient formation of photodimers, *syn*-HH (**2a**), *anti*-HH (**3a**) and *syn*-HT (**4a**). In contrast, the intercalation degrees of cinnamate **1b** were relatively low and two photodimers, *syn*-HH (**2b**) and *anti*-HH (**3b**), and significant amount of *cis* isomer were produced. The most striking effect of the site distance was found in the formation of *syn*-HH **2** and *anti*-HH dimers **3**. Upon decreasing the *n* value, *i.e.* increasing the site distance, ratios of **2**:**3** decreased remarkably. This result is caused by the suppression of *syn*-HH formation and by the promoting of formation of *anti*-HH on account of increase of site distance. This can be rationalized by the coincidence between the site distance and the anion site distance of photodimers; the shorter site distance of *ca*. 5 Å is close to the X···X distance of *syn*-HH **2**, while the longer one (8 Å) is close to those of *anti*-HH **3**.

In addition to the effect on the HH dimer distributions as mentioned above, the formation of *syn*-HT dimer (**4a**) from **1a** was also affected by changing *n*. It is apparent that the *syn*-HT **4a** is produced from a pair of antiparallel packed molecules, one of which is adsorbed on the upper surface but the other on the lower one. Such a HT pairing is possible within 5 Å even in the case of the smallest *n* value (*n* = 0.15), since one exchange site on one layer is located in the middle position of three exchange sites (forming a regular triangle as shown in Fig. 1) on a neighbouring layer. Therefore the dimerization of HT pairing can not be affected by changing the site distances on one surface. The more favourable formation of **4a** with the clay of lower *n* value is rationalized by the compensation of the *syn*-HH dimer formation. In the case of **1b**, no HT dimer was produced because of vertical deviation of the two double bonds of the carboxylate units adsorbed on the upper and lower surfaces.[3] Therefore, increase of the site distance results in the increase of *cis–trans* isomerization, suppressing photodimerization.

The site distance of 8.2 Å for the clay with *n* = 0.15 is larger than the critical distance of 4–5 Å for [2 + 2] photocycloaddition of the molecules.[7] According to the idealized site distribution of Fig. 1, no HH dimer can be produced with the clay of lowest *n* value. The fact that the formation of *syn*-HH was not completely inhibited in the clay of lowest Al^{3+} content, (mean site distance = 8.2 Å), seems to indicate a somewhat irregular scattering of Al^{3+} ions and the presence of layers of shorter site distance.

In conclusion, the present results suggest that photodimerizations of clay-intercalated unsaturated carboxylates can be controlled by changing the site distance in the clay interlayers.

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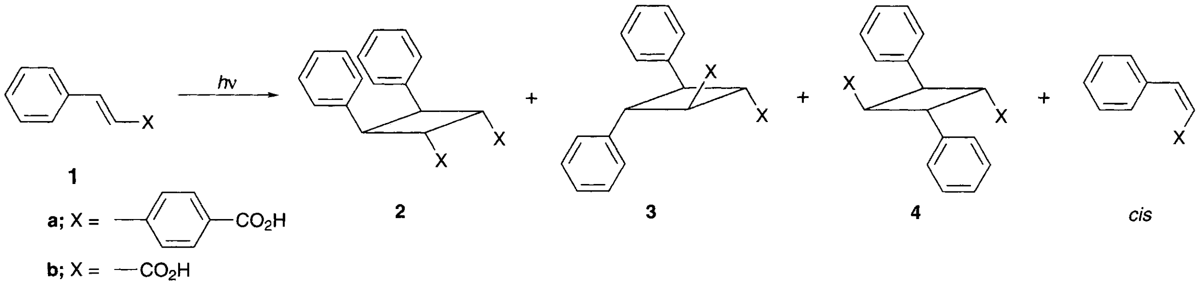
Table 1 Effect of aluminium ion content in hydrotalcite on the photodimerization of unsaturated carboxylates (**1a**, **b**) in clay inter-layers[a]



Compound	n^b	Site distance[c]	Adsorption degree (%)	Conv. (%)[d]	Selectivity (%)[e]				2/3
					2	**3**	**4**	*cis*	
1a	0.30	5.4	>99	100	67	0.8	30	0.8	84
	0.25	6.2	>99	100	59	4.9	34	1.6	12
	0.20		>99	99	50	8.9	38	2.2	5.6
	0.15	8.2	>99	100	42	11	42	3.6	3.8
1b	0.30	5.4	36	96	66	1.6	0	32	41
	0.25	6.2	33	95	39	2.9	0	58	13
	0.20		34	91	19	10	0	71	1.9
	0.15	8.2	34	80	14	18	0	68	0.8

[a] *Conditions*: [**1a**/**b**] = 5.0 mmol dm^{-3} in aqueous clay suspension; [clay] = 5.5 mmol dm^{-3}. Irradiation for 4 h through a Pyrex filter. [b] Aluminium ion content of $[\mathrm{Mg}_{1-n}\mathrm{Al}_n(\mathrm{OH})_2]^{n+}$. [c] Calculated distance (Å) between adjacent aluminium ions. [d] Conversion of unsaturated carboxylate. [e] The selectivities of products are based on the intercalated material.

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