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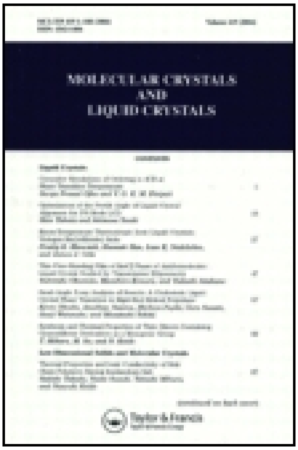

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Photocyclodimeiuzation of Olefins on Clay Minerals

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PHOTOCYCLODIMERIZATION OF OLEFINS ON CLAY MINERALS

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Abstract Ionically charged olefins intercalated in the interlayers of clay minerals are subject to photocyclodimerization with quite high efficiencies and regioselectivities. These product selctivities can be used to study molecular aggregate structure in an assistance with their fluorescence properties.

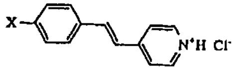
INTRODUCTION

Clay minerals tend to adsorb cationic or anionic organic substances by substituting with exchangeable counter ions in their interlayers. These intercalated organic materials are confined in an organized two dimensional space in the layer, forming a molecular aggregate. A long alkyl chain ammonium ion is known to form a bilayer in the interlayers like a Langmuir-Blodgett film. A [2+2] photocyclodimerization may be useful for studying the structure of the aggregate.

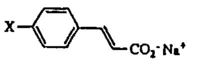
In this paper, the authors have disclosed a photocyclodimerization of clay-intercalated ionic olefins(1-4) and clarified a correlation between stereochemistry of the products and the starting olefin packing in clay minerals in an assistance of their fluorescence spectra.

EXPERIMENTAL

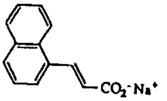
Clays employed here are Sumectone SA kindly given by Kunimine Kogyo K. K.:$[(Si_{7.20}Al_{0.50})\text{-}(Mg_{5.97}Al_{0.03})O_{20}(OH)_4]^{-0.77}(Na_{0.49}Mg_{0.14})^{+0.77}$; CEC 99.8 meq/100g, and Hydrotalcite (KW-2200) also kindly gifted by Kyowa Chemicals K. K.:$[Mg_{4.5}Al_2(OH)_{13}](OH)_2\ mH_2O$ m=3-3.5; AEC 380 meq/100g. Stilbazolium ions(1), cinnamate ion(2), α-naphthylacrylate ion(3), and stilbene carboxylate ion(4) were used as ionic adsorbates for the photocyclodimerization.



1a, X=H
b, X=CH$_3$
c, X=Cl
d, X=CN



2a, X=H
b, X=Ph



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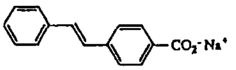

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Intercalation in clay interlayers was carried out in the following procedures. An aqueous solution of the above ionic olefins was dropwisely added in an aqueous equimolar solution of an appropriate clay colloid based on the ionic exchange capacity (CEC or AEC), and stirred with an ultrasound sonicator. Some of intercalated clays form a precipitate depending on the concentration and the adsorption degree of guest molecules. The resulting solutions including a precipitate were irradiated by a 300W mercury arc lamp through a Pyrex filter under nitrogen atmosphere. After irradiation, the reaction mixtures were treated with conc. HCl followed by CH_2Cl_2 extraction. Product analysis was done by a HPLC or a GC technique, and by NMR, IR, and UV spectroscopically after chromatographic separation.

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RESULTS AND DISCUSSION

INTERCALATION ON CLAY INTERLAYERS

Intercalation of the olefins in the clay interlayers was quantitative, except for in the case of **2a** and **3**. Adsorption degrees of **1**-**4** were shown in Table 1. Intercalation on the clay interlayers is based on hydrophobic interaction of adsorbates as well as electrostatic interaction of adsorbates with ionically charged sites on the layers. Equilibrium constant (K) of adsorption of ionic organic materials exceeds over unity; K value of **1** was cestimated around 400 under conditions below CEC. X-ray analysis of the clay-intercalated olefin indicates a lengthened space distance between the layers, which is also added in Table 1. In case of **1a**, the basal space in saponite(Sumecton SA) is elongated from 6.2A to 9.2A by the intercalation, which is comparable with the molecular length of **1a**, 10.4A. In addition, the basal space of Hydrotalcite is similarly elongated from 18.2A to 23A on adsorption of **2b**. Accordingly, these olefin molecules at least form monolayer in the interlayers, although typical surfactant molecules, e.g., cetyltrimethylammonium bromide, are known to form a bilayer.

Table 1 Photocyclodimerization of Clay-intercalated Olefins

Olefin	Clay	Adsorptiondegree (%)	α-Dimer: β-Dimer	Layerspacing (A)
1a	Sumecton SA	>97	79 : 6	9.2
1b		>97	76 : <1	9.5
1c		>97	93 : <1	-
1d		>97	35 : 32	8.6-9.8
2a	Hydrotalcite	35	<3 : >97	8.5
2b		96	<1 : >99	-
3		40	<1 : >99	-
4		99	30 : 61	22.3

PHOTOCYCLODIMERIZATION

UV irradiation of the clay-intercalated olefins resulted in the efficient photocyclodimerization among four cyclodimers, syn head-to-tail (syn HT)(α), syn head-to-head (syn HH)(β), anti head-to-head (anti HH)(δ), and anti head-to-tail dimers (anti HT)(ε). Table 1 shows the product distribution of the above ionic olefins.

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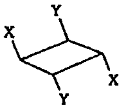
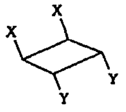
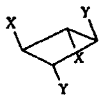


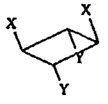
syn - HT
(α)



syn - HH
(β)



anti - HH
(δ)



anti - HT
(ε)

Regiochemistry of photocyclodimers is exclusively syn HT in case of stilbazolium cation(**1**), but preferentially syn HH in case of cinnamate ions(**2** and **3**) and stilbenecarboxylate ion(**4**). Here, it is noted that an organized reaction media control the alignment of adsorbate aggregates and plays an role of a template to yield photoproduct reflecting their mutual disposition. Hence, **1**'s arrange in anti-parallel with each other and **2**-**4** orient in a parallel fashion but they are all almost perpendicular to the layers.

ADSORPTION DEGREE AND AGGREGATED FORM

The intercalated olefin molecules may be oriented almost perpendicular against the interlayer planes. This is because parallel orientation makes their quantitative adsorption difficult on account of an interference of adjacent adsorption sites. Moreover, they form a monolayer assembly judging from the interlayer spacings. One of the crutial factors determining the alignment would be a layer structure of clay and the ionic exchange capacity. Sumectone SA is a 2:1 layered sheet structure with anionic exchanging sites on upper and lower layers, but Hydrotalcite is a single sheet with cationic exchanging sites much higher density than Sumecton SA. Now, molecular alignment is pictured as shown in Scheme 1(A) and (B) for stilbazolium ions and cinnamate ions, respectively. Fluorescence spectra provide an evidence for the molecular aggregation. Thus, stilbazolium ions (**1**) exhibit a strong excimer fluorescence in the interlayers,which is not observed at all in homogeneous solutions (Figure 1).

Furthermore, interesting is a clusterization of the aggregates, especially in a quite short coverage of olefin molecules. As shown in Figure 2, no essential decrease of the excimer fluorescence intensities was observed with a decreased coverage of **1** from 100% to only 1.25%. At the same time, no monomer fluorescence was appeared until the coverage is shorter than 0.1%. Figure 3 shows that cyclodimer formation is also little affected by the decreased coverage.

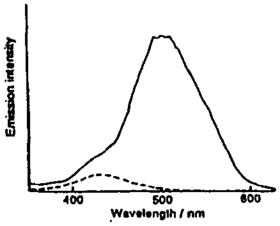


Figure 1 Excimer and Monomer Fluorescence of 1

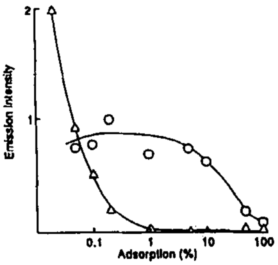


Figure 2 Coverage Effect on Excimer Intensity

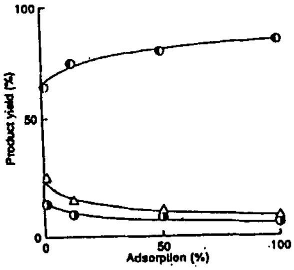


Figure 3 Coverage Effect on Dimer Formation

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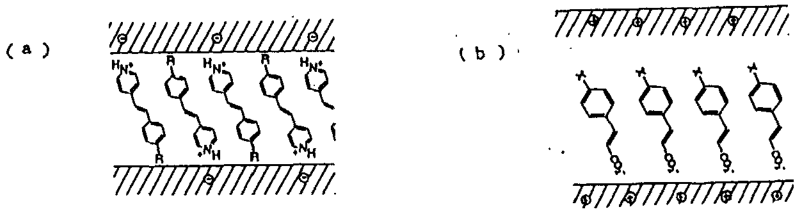
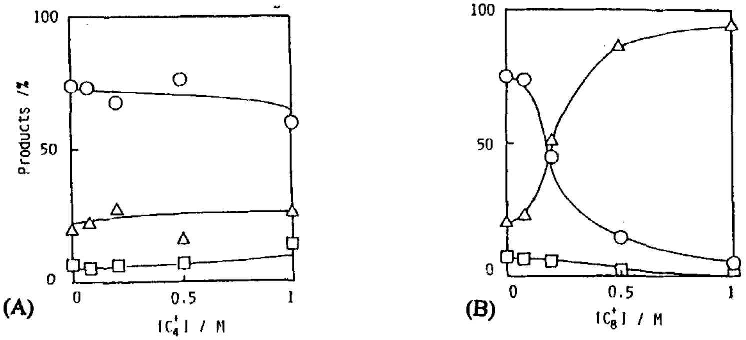


Scheme 1 A Picture of Molecular Alignment in Clay Interlayers

EFFECT OF ALKYLAMMONIUM IONS ON AGGREGATION OF 1

Effect of alkylammonium ions(C_n^+) on the photochemical behaviors of the intercalated 1 was studied in order to examine the formation and dissociation of the aggregates in the interlayers. The photocyclodimerization of 1 was remarkably affected by certain kinds of C_n^+. As shown in Figure 4, octylammonium ion (C_8^+) heavily retarded the dimerization, but butyl homolog(C_4^+) was practically no effect.



(A) (B)

Figure 4 Effect of alkylammonium ions,C_4^+(A) and C_8^+(B) on photocyclodimerization

Two possibilities are conceivable as an origin for the inefficient cyclodimerization in the presence of longer chain ammonium ions. One is such that stilbazolium ions in the clay layers are substituted by ammonium ions and extracted into the bulk solution. The other one is that coadsorbed C_n^+ ions may cause a significant change in the packing mode of 1 favorable for the cyclodimerization. By studying in details an effect of coadsorbate on the excimer fluorescence of the clay-intercalated 1, coadsorbing long alkyl chain ammonium ions is effective on an assumption that the molecular cluster of 1 was dissociated by C_8^+, but not C_4^+, and that the two adsorbates of 1 and C_8^+ were homogeneously mixed on the layers.

CONCLUSION

The present study reveals that product distribution in the photocyclodimerization may reflect the orientation of the starting olefin molecules intercalated in the layers of clay minerals. Their assumed alignments are in good accordance with their emissive properties. In addition, the photochemistry clarifies clusterization of the adsorbates in the interlayers.