Intercalation of Aliphatic Carboxylates in Hydrotalcite Interlayers: Selective Photochemical Hydrogen Abstraction by Benzophenonecarboxylate

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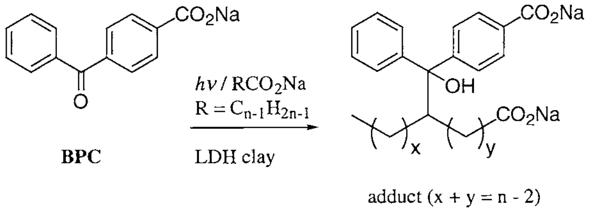
The photochemical hydrogen abstraction of *p*-benzoylbenzoate ions (**BPC**) from aliphatic carboxylate ions in LDH (hydrotalcite) interlayers yielded a series of their 1:1 adducts. The product distributions were rather selective as well as distinctive from those of sodium salts and methyl esters in homogeneous solutions without LDH. These results have been discussed on the basis of their mutual disposition on the layer surfaces of the LDH.

Layered double hydroxide (LDH), a lamellar metal hydroxide, is able to intercalate various organic anions by means of electrostatic interactions with the cationic sites on the layer surfaces.[1, 2] There is a tendency for intercalated guest molecules to be oriented as organized aggregates of anisotropic nature. For example, Dutta has reported on the formation of mono- and bilayer films of surfactant aliphatic carboxylate ions on the interlayer surfaces of LDHs.[3, 4] Such a unique organic-inorganic composite possessing two-dimensional structure has been studied as photonic devices.[5-7] Among the various kinds of nanoporous inorganic materials,[8, 9] we have studied the intercalation behavior of photoactive compounds electrostatically incorporated in the interlayers of LDH and clay minerals as a means to investigate photochemical probe reactions.[10, 11]

In the present article, we will disclose our findings on the selective hydrogen abstraction between an excited triplet *p*-benzoylbenzoate (**BPC**) and a series of aliphatic carboxylate anions, both of which are intercalated in the same interlayers of Mg-Al LDH (layered double hydroxide) clays. The LDH employed in the present work is Kyowaad 2200, the anion-exchange capacity (AEC) of which is 705 meq/100 g.[12]

An aqueous suspension of a mixture of 5 mM of sodium **BPC** and 25 mM of sodium caprylate (n = 7), caprate (n = 9) or laurate (n = 11) was kept at 70 °C for 12 h with 33 mM of Kyowaad 2200 on the basis of its AEC. The intercalation degrees of these aliphatic carboxylates as well as **BPC** were measured to be almost quantitative (more than 90%) and the clearance spaces of the intercalated LDHs were more or less comparable with the molecular lengths of the guest molecules. The resulting aqueous LDH suspension was irradiated with a medium pressure 300 W Hg lamp through a pyrex filter (>280 nm) under Ar atmosphere. After irradiation for 8 h, about 80% of the starting **BPC** was consumed. The GPC[13] of the mixture after treatment with CH_2N_2 gave rise to a series of isomeric 1:1 adducts in isolated overall yields of 34% based on the consumed **BPC**. However, the corresponding benzhydrols and/or benzpinacols from **BPC** could not be observed under the present conditions. A control experiment showed that their formation was substantial at molar ratios of more than 1/3 of **BPC** against the aliphatic carboxylate. The ^{13}C-nmr spectra of the isomeric 1:1 adducts showed six aromatic peaks at around 130 ppm and complex aliphatic peaks at 15-50 ppm, among which at least three peaks at 40.5, 43.0, and 44.0 ppm were each assigned to the corresponding tertiary carbons of the isomeric adducts by means of DEPT techniques.[14] The electron bombardment of the isolated products in all runs of n = 8 - 12 exhibited fragment ions of m/e 241, the **BPC** ketyl ions. The IR spectrum shows the tertiary alcohol group at 1200 cm^{-1}. Analyses of these spectral data suggest that the photoproducts consist of isomeric 1:1 adducts, as shown in Scheme 1.



Scheme 1.

Thus obtained 1:1 adducts were definitely characterized by their transformation into the corresponding thioacetals of methyl ketocarboxylates. The sequences were carried out according to previously reported, though somewhat revised, procedures.[15, 16] Table 1 shows the general trend of the isomeric distributions of the resulting methyl ketocarboxylates in which, characteristically, none of the 1-, 2-, and 3-ketocarboxylates was formed in the LDH (e.g., note the cases of n = 7 - 11 in Table 1). The photolysis of a mixture of 5 mM of **BPC** and 25 mM of caprate without LDH in water clearly shows that, in contrast to the LDH systems, the 3-keto isomer was significantly formed.

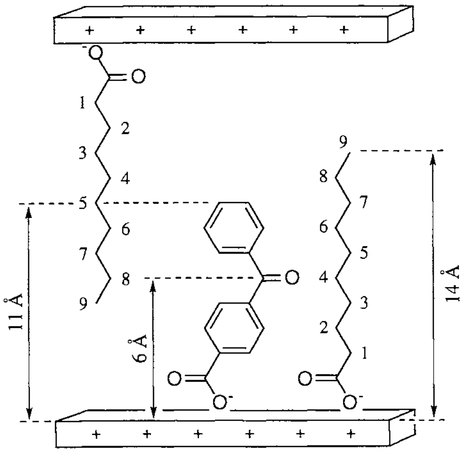
Since no micelles were formed under the present conditions (cmc of sodium caprate = ca. 0.1 M),[17] these results suggest the negligible formation of isomers which reacted with the carbons near the carboxylate group (C-1 and C-2), presumably because of the electrostatic repulsion between the two carboxylate groups of caprate and **BPC**. In extreme cases using methyl caprate, all of the caprate methylene protons except for the terminal methyl were abstracted at random. In the LDH system, product selectivity somewhat decreased with the increase in the alkyl chain length of the carboxylates, but a rather rigorous inhibition for hydrogen

Table 1. Isomeric product distribution in the photolysis of **BPC** and a series of sodium aliphatic linear carboxylates

$C_nH_{2n+1}CO_2Na$	Isomeric ketocarboxylate/% location of hydrogen abstraction										
n	1	2	3	4	5	6	7	8	9	10	11
(A) intercalated in LDH:											
7[a]	0	0	0	19	31	50	0	–	–	–	–
9[a]	0	0	0	3	17	18	23	40	0	–	–
11[a]	0	0	0	12	9	13	17	17	13	20	0
(B) in homogeneous solution without LDH:											
9[b]	0	0	24	16	11	16	16	17	0	–	–
9[c]	28	1	6	14	8	12	13	17	0	–	–

[a] In water. [b] Acetonitrile : water = 1 : 3. [c] In acetonitrile.

abstraction at C-1, -2, and -3 could still be observed in the aliphatic carboxylates series. A general trend toward more favorable positions of hydrogen abstraction could be seen at C-6, -8, and -10 in the case of caprylate (n = 7), caprate (n = 9) or laurate (n = 11), and **BPC**, respectively, though the selectivities were not so high.



Scheme 2. A simplified cross-section drawing of LDH including **BPC** and caprate ions in the same layers: parallel and antiparallel packing of caprate ions and **BPC**.

It has been demonstrated that both the aliphatic carboxylates and **BPC** were efficiently intercalated in the interlayers of LDH. Powder X-ray analysis revealed that a 2.9 Å to 16-23 Å opening in the layer distance could be seen on the basis of the length of the aliphatic carboxylates. This implies the formation of a single layered and, at the same time, anti-parallel packed orientation, as depicted in Scheme 2. The **BPC** was found to be mixed and coadsorbed with aliphatic carboxylate ions with molar ratios of 1 : 5 on the interlayer surfaces. A decrease in the molar ratios resulted in the increased formation of the corresponding pinacol of **BPC** which could be detected by HPLC, while at a ratio of 1, the pinacol was formed to be approximately equal to the 1:1 adducts. At the present molar ratio of 5, trace amounts of the pinacol could be detected. The apparent clearance space of the intercalated LDH seems to be determined by the aliphatic carboxylates, but not by **BPC** which is much shorter than the carboxylates (16-23 Å). Under these layer circumstances, either head-to-tail (HT) or head-to-head pairings (HH) are feasible: HT leads to hydrogen abstraction preferably at C-6, C-8, and C-10 of the caprylate, caprate, and laurate, respectively. In contrast, the HH pairing leads to the reaction of all these carboxylates at C-4. Table 1 shows that hydrogen abstraction does indeed occur from the molecular packing as proposed in Scheme 2, except for the case of caprate. In summary, LDH intercalated aliphatic carboxylates were found to be essentially perpendicularly oriented and form anti-parallel monolayer packing. In such circumstances, methylene carbons in the neighborhood of the anchored carboxylate group are packed tightly so as not to be attacked by the excited carbonyl group, but the terminal methylene groups are so flexible and loosely packed that they can randomly be attacked.

The present results were comparable with those for various kinds of surfactant-forming micelles and multicomponent aggregates including cationically charged benzophenone.[15] In such cases, the dodecyl and hexadecyl chains of the surfactants are hydrogen abstracted by excited benzophenone with considerably lower selectivities. It has been proposed that these alkyl chains may be coiled or folded within the micelles. Although no reactions at C-1 to C-3 were generally observed for both systems, a much higher selective hydrogen abstraction was realized for the present LDH interlayers.

Further studies with the **BPC** of longer alkyl chains similar to the aliphatic carboxylates are now underway.

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