

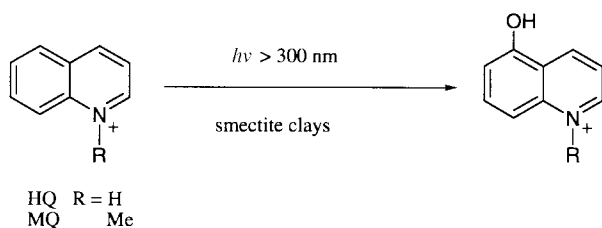
Regioselective Photohydroxylation of Quinolinium Ions in Smectite Clay Interlayers

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Quinolinium and *N*-methylquinolinium intercalated in smectite clays were irradiated with ultraviolet light longer than 300 nm under air atmosphere. 5-Hydroxyquinolinium was primarily obtained in both systems.

Clay minerals and their synthetic derivatives have been focused as photochemical reaction field because the interlayer space of clays with high polarity can control their arrangement having nanoscale regularity in the interlayer gallery.¹ The molecular arrangement can promote stereoselective photo-cyclodimerization² and photosensitized isomerization.³ The high polarity of the interlayers also promotes photoelectron-transfer⁴ and reversible photocyclization of spiropyranes.⁵ In this paper, a regioselective photohydroxylation of quinoliniums is reported as a novel photoreaction promoted by clay layers under air atmosphere.



Quinolinium ions can be readily intercalated in clay layers. An aqueous solution of quinoline protonated with hydrochloric acid (HQ) was mixed with a colloidal aqueous solution of saponite clay for one hour. A gelatinous fine precipitate obtained was filtered off with a membrane filter. Amount of intercalated HQ was evaluated from the attenuation of absorption spectra of the filtrate. Figure 1a shows that plots of the amount of intercalated HQ vs added HQ seem to bend at 50% vs the cation exchange capacity (CEC). The trend suggests that the

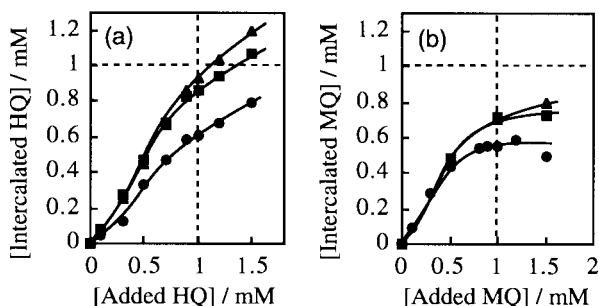


Figure 1. Intercalation of quinolinium ions in clay. (a) HQ, (b) MQ. [clay] = 1 mM aq in both systems. (1 M = 1 mol dm⁻³). -●- saponite, -■- montmorillonite (Tsukinuno), -▲- montmorillonite (Wyoming). Broken lines represent the equivalent concentration vs CEC.

intercalation of HQ into saponite clay is not quantitative especially in the case that the amount of intercalation exceeds 50% of the CEC. Intercalation of *N*-methylquinolinium (MQ) in saponite clay was obviously saturated at a half of the CEC as shown in Figure 1b. The intercalation in montmorillonite is also saturated at about 70% of the CEC. These intercalation behavior are in contrast with a quantitative intercalation of long *n*-alkylammonium ions.⁶ Consideration of the bulky structure of MQ and charge density of the clay surface suggests that an MQ molecule occupies about two ion-exchange site in the clay interlayer. On the other hand, some of the HQ can be intercalated as neutral free base because HQ is under the equilibrium of the free base form and the protonated form. Therefore, it can be explained that the neutral free base of HQ feels much less electrostatic interaction from the anionic site in clay, allowing their rearrangement for much dense packing.

The UV-vis spectra of these quinoliniums intercalated in smectite clays were the same as those in aqueous homogeneous solutions. These results indicate that intercalated quinoliniums interact very weakly with the clay layers and the adjacent molecules at the ground state. The quinoliniums intercalated in saponite clay were irradiated by a 150 W Xe lamp with UV30 optical filter ($\lambda > 300$ nm). Absorption of the clays themselves was negligible in the region above 300 nm, except small scattering under the experimental condition. As shown in Figure 2a, the absorption maximum of HQ at 317 nm has decreased over irradiation time, accompanying growth of a new absorption band close to 275 nm. The isosbestic points were observed at 288 nm and 347 nm. Therefore, this reaction is apparently a simple reaction in which products mainly of one type are obtained. Similar spectral change on irradiation was also observed for MQ/saponite clay system, as shown in Figure 2b. In Wyoming montmorillonite, however, the spectral change was so quick that absorption maximum at 317 nm was disappeared in 15 min. No isosbestic

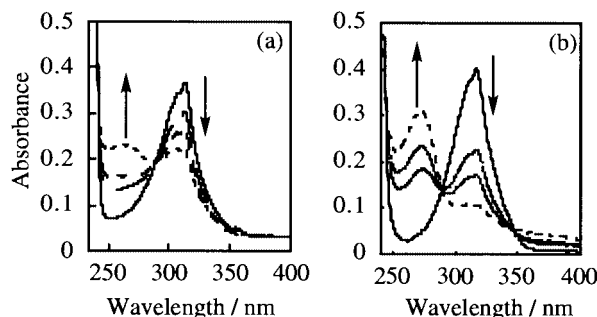


Figure 2. Change in absorption spectra on irradiation in saponite clay. (a) [HQ] = 50 μM; (b) [MQ] = 50 μM. In both systems, [saponite] = 100 μM. (1 M = 1 mol dm⁻³) Irradiation were carried out for 0, 30, 60, 120, 180 min using 150 W Xe-lamp with UV30 filter.

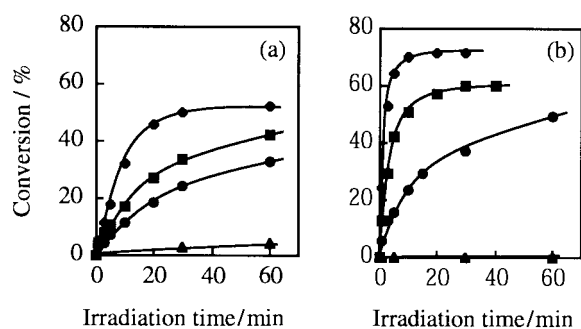


Figure 3. Time-conversion curves. (a) [HQ] = 50 μM , (b) [MQ] = 50 μM . (1 M = 1 mol dm^{-3}) - \blacklozenge -, montmorillonite (Wyoming); - \blacksquare -, montmorillonite (Tsukinuno); - \bullet -, saponite (JCSS-3501); - \blacktriangle -, control without clay. Concentration of clay was 100 μM in the clay containing system. Irradiation: 150 W Xe lamp with UV30 filter.

point was observed, indicating that a few complex reactions took place competitively. The irradiation in Wyoming montmorillonite system was scaled up and the reaction mixture in clay layers was extracted and recrystallized from aqueous ethanol. According to its ^1H and ^{13}C NMR spectra,⁷ the main product for the photoreaction of HQ and MQ was identified as 5-hydroxyquinolinium (HQ-OH) and *N*-methyl-5-hydroxyquinolinium (MQ-OH), respectively. Each hydroxyquinolinium has an absorption maximum at around 260 nm and small shoulder at around 380 nm. Spectral change in Figure 2 shows that selectivity of MQ-OH was about 60%, however no additional growth in the spectra was observed. A breakthrough in the extracting procedure is required to identify other minor products remained in the clay interlayers.

Figure 3 shows time-conversion curves traced from the changes in the UV absorption spectra. A conversion of 52% was obtained under irradiation of HQ for 30 min in Wyoming montmorillonite. The reactivity was decreased in the order of montmorillonite (Wyoming), montmorillonite (Tsukinuno), saponite (JCSS-3501) and an aqueous homogeneous solution without clay. Irradiation of MQ showed similar trend, but the reactivity increased 5 times as fast as that of HQ. For example, a conversion of 70% and the selectivity of MQ-OH about 65% was obtained under irradiation for about 15 min in montmorillonite (Wyoming). Considering the intercalation degree in Figure 1 and the reactivity in Figure 3, it can be demonstrated that only the intercalated quinoliniums are effectively hydroxylated at the specific carbon.

What are the factors that promote the photohydroxylation in clays? Main features of clay interlayer as photochemical reaction fields include high polarity and control of molecular arrangement. However, in homogeneous water, ethanol, or acetonitrile that contained no clay, only a decomposition of several percent has occurred and hydroxylation did not proceed. Catalytic effect of silica, alumina and magnesium oxide, major inorganic oxides constituting the clays, was also studied. Individual powders of those oxides or their mixtures were dispersed in an aqueous solution of MQ and irradiated, but MQ-OH was not obtained. The above results made it clear that the reaction cannot be explained by simple polarity of solvent and the surface of those oxides.

Table 1. Basal spacings of quinolinium–intercalated clays

Clays ^a	Basal spacing ^b /nm		
	Na/clay	HQ/clay	MQ/clay
Saponite	1.26	1.32	1.33
Montmorillonite (Tsukinuno)	1.25	1.48	1.39
Montmorillonite (Wyoming)	1.25	1.30	1.32

^aDried in air at 60 °C for 6 h, then ground in mortar. ^bEstimated by XRD (Cu K_{α}).

Molecular arrangements of HQ and MQ in clay interlayer were estimated by X-ray diffraction analyses. Table 1 shows that the basal spacing estimated from the 001 diffraction peaks ranges 1.30–1.48 nm, indicating slight increases from a basal spacing of 1.26 nm of the original clay. Since a monomolecular layer of adsorbed water is usually present on both surface of clay layer, the practical thickness of the clay layer becomes 0.96 nm.¹ Therefore, a clearance space of about 0.36–0.52 nm can be calculated by subtracting this value from the basal spacing obtained. This value of the clearance space and the molecular size of quinoliniums suggest that quinoliniums had an arrangement in which the aromatic ring was generally parallel to the clay layer. Such orientation is known for the molecules having conjugated aromatic rings.⁸ The parallel molecular arrangement can promote the photohydroxylation. However, it cannot clearly explain the difference in the reactivity in the montmorillonites and the saponite at the present stage.

Photohydroxylation of a quinolinium to 5-hydroxyquinolinium was reported as a novel example of photoreaction promoted in smectite clay minerals. Studies on selectivity, active species, and reaction mechanism are in progress.

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