

Direct Evidence of Clay-Mediated Charge Transfer

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The charge transfer (CT) from montmorillonite K10 (iron-containing clay) was studied by monitoring the reaction of halides (Cl^- , Br^- , and I^-) with the intercalated photosensitizer, 10-methylacridinium (AcH^+). The electrodes, which were fabricated by the AcH^+ -intercalated clays (denoted clay/ AcH^+), showed no current responses to bromide and chloride. However, there was a significant current response corresponding to the reduction of iodine and this response was enhanced by light irradiation. These differences in the electrochemical behavior suggested the electron transfer on the clay/ AcH^+ surface was regulated by the electrochemically active iron species in the clay. The lifetime of AcH^+ is ca. 36 ns, whereas for $\text{AcH}^+_{(\text{clay})}$, it is as fast as the instrumental response (<10 ns), indicating the clay can efficiently quench the excited acridinium, AcH^{+*} . Moreover, a long-lived species, attributed to I_2^{*-} , was recorded in KI solutions (pH 4) containing either AcH^+ or clay/ AcH^+ . In contrast, the transient species, presumed to be Br_2^{*-} , was only observed in the solutions containing free AcH^+ . Both electrochemical and laser spectroscopic results indicated that the electron transfer between AcH^{+*} and I^- is mediated by the iron species in montmorillonite K10.

Introduction

Since the work pioneered by van Damme¹ and Bard,² clays and clay-modified electrodes (CME) have attracted increased attention from chemists which has resulted in a vast body of research on their electrochemistry and photoelectrochemistry.³ In the past decade, photocatalysis reactions involving clays have shown that these clays are able to spatially compartmentalize electron donors and acceptors and can separate photo products. Nevertheless, in these systems, as in many other heterogeneous photocatalytic systems such as zeolites,⁴ layered phosphates,⁵ and γ -alumina and silica gels,⁶ the solid phase merely provides microenvironments for the photoreactions. They do not actively participate in or mediate the charge transfer reactions. Probably due to this reason, quantum yields in these systems are generally low. In this work we report a photocatalytic system which was fabricated by montmorillonite K10 and 10-methylacridinium,⁷ in which the electron transfer was mediated by the host clay and high yields of a long-lived photoinduced charge separation state were created.

Experimental Section

General Procedure. Montmorillonite K10 and hydrogen peroxide were supplied by Aldrich. NaCl (99.999%), AgNO_3 (99.9%), and LiClO_4 (anhydrous) were supplied by Alfa Products. 10-methylacridinium hexafluorophosphate (AcHPF_6) was synthesized according to a method in the literature,⁶ which was slightly modified by using CH_3I as solvent and NH_4PF_6 for anion exchange.

Apparatus. Scanning electron micrographs (SEM) were recorded with a scanning electron microscope (Cambridge Model S 360). UV–Vis absorption spectra were recorded with a JASCO M7850 UV/VIS spectrophotometer. Powder X-ray diffractograms were measured with a Siemens model D-500 X-ray diffraction spectrophotometer. Illumination was provided by a high-pressure mercury lamp (1000 W, Oriel) with a 10 cm long water filter to remove the unnecessary IR radiation.

Clay Preparations. Typically 1.0 g of clay was first heated with 200 mL of H_2O_2 (34%, 60 °C) for 2 h to remove organic

contaminants and then suspended in 500 mL of NaCl (1 M) for 6 h. The latter process was repeated eight times to ensure that the ion exchange sites on the clay are in the Na form. Subsequently, the slurry was thoroughly washed with deionized water until no chloride was detected with silver nitrate. The resulting slurry was resuspended in water. The slurry was left for 30 min to sediment and then the upper part of suspension was collected, centrifuged (Fischer Scientific, Marathon M 21KR, 10K rpm), and treated with 50 mL of H_2SO_4 (1 mM, 60 min) to remove any soluble iron species. The resulting slurry was rinsed thoroughly with deionized water, air-dried, and stored under nitrogen.

Clay/ AcH^+ particles were prepared by reacting clay (0.5 g) with AcHPF_6 (10 mM, 50 mL in CH_3CN) for 2 days and this was followed by extensive wash with CH_3CN . XRD spectra showed about 30% of the (001) reflection (in terms of peak intensity) was expanded from 9.99 Å ($2\theta \approx 8.8^\circ$) to 14.02 Å ($2\theta \approx 5.7^\circ$) after AcH^+ exchange. The amount of unexchanged AcH^+ was quantized by UV/Vis absorption spectrophotometry monitored at 357 nm ($\epsilon = 43000 \text{ M}^{-1} \text{ cm}^{-1}$). The loading of AcH^+ in clay was therefore estimated to be ca. 10^{-5} mol/g .

Electrode Modification. Clay-modified electrodes were fabricated on conductive SnO_2 glass (indium-doped, 0.7 mm thick, $20 \Omega/\text{cm}^2$; Delta Technology). The glass sheets (ca. 0.25 cm^2) were first ultrasonically treated sequentially with chloroform, 1 M H_2SO_4 and deionized water. A portion of the clay slurry ($30 \mu\text{L}/\text{cm}^2$, 100 mg/100 mL of water) was cast onto the glass sheets and the slurry film was dried at room temperature. The electrodes were then reinforced with polystyrene (PS, M_w 13000, Aldrich, $30 \mu\text{L}/\text{cm}^2$, 10 mg/mL in 1:1 (v/v) ethyl acetate/toluene). The thickness of the clay film was estimated to be ca. $10 \mu\text{m}$ by SEM. The modified glass squares were then mechanically mounted on glass rods using epoxy patch (Huntington Lab.) as electrodes. Ohmic contact was made with a silver paint (Alfa Products).

Electrochemical Experiments. All electrochemical experiments were carried out under nitrogen in a one-compartment cell using a standard three-electrode configuration with a Pt counter electrode and a saturated calomel (SCE) reference electrode. Potentiostats (PAR 273, EG&G Princeton Applied

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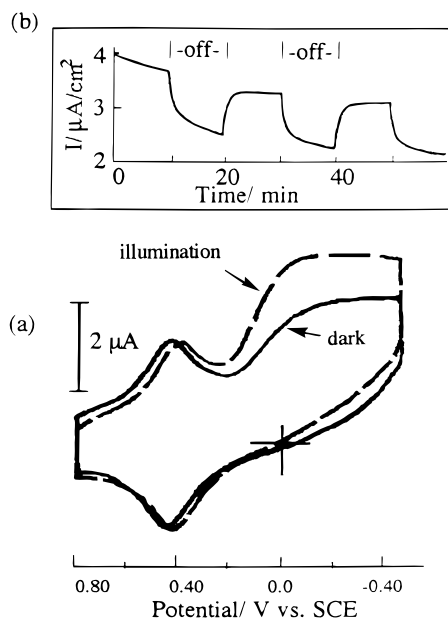


Figure 1. (a) CV curves for clay/AcH⁺ electrodes in a solution containing 0.1 M LiClO₄ and 1 mM of KI (curve a); scan rate 50 mV/s. Solvent system: 1:1 (v/v) CH₃CN/acetate buffer (pH 4, μ = 0.1 M). (b) i-t curves recorded at -0.1 V vs SCE.

Research, and CV-50, Bioanalytical System Inc.) were used to obtain i-V curves and for electrolysis experiments. Electrical signals were recorded with an xy recorder (Kipp & Zonen model BD 91) or analyzed with a microcomputer. Before electrochemical tests, the electrodes were allowed to equilibrate in the desired electrolyte (open circuit) until stable CV curves were obtained. Unless otherwise stated, the potential scan was set from +0.8 to -0.4 V.

Laser Spectroscopy. All samples (0.33 g/L) were prepared in sodium acetate buffer (pH 4) and degassed prior to laser experiments. Laser experiments were performed at the Beckman Institute Laser Resource Center at Caltech. The third harmonic of a Q-switched Nd:YAG laser, 355 nm (fwhm = 10 ns, 2 mJ per pulse), was used as the excitation source. A pulsed Xe-Arc lamp was used as the probe light source for transient absorption experiments. Luminescence decay kinetics were deconvoluted from the instrumental response function to give the single exponential decays.

Results and Discussion

Recently we⁸ and others⁹ have reported several montmorillonite clays containing electrochemically active iron species which show potential for UV-light recognition and chemical sensing. In this work, we prepared the acridinium-exchanged montmorillonite K10 particles (denoted clay/AcH⁺) and investigated the photoinduced electron transfer between the intercalated photosensitizer and solution phase halides (Cl⁻,¹⁰ Br⁻, and I⁻).

The typical i-V curves for the clay/AcH⁺ electrodes in the presence of iodide are shown in Figure 1a, in which a cathodic wave is recorded at about 0.1 V vs SCE (solid lines) after the reduction peak of Fe^{III} ($E_p \approx 0.4$ V). The clay/AcH⁺ electrodes are highly photosensitive, which is reflected in the enhancement of the cathodic current on exposure to white light (broken lines). The limiting values of the cathodic currents at 0.1 V (dark and light) increase with the increasing concentration of KI. We attribute this cathodic current to the reduction of I₃⁻ (i.e., I₂ + I⁻) produced at the clay surface. In contrast, the clay/AcH⁺ electrodes gave an indifferent response to bromide when KBr

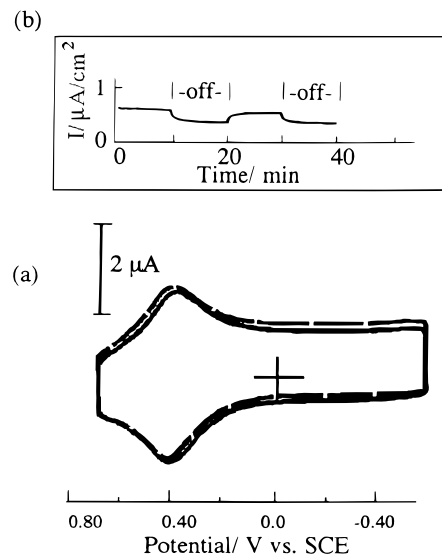
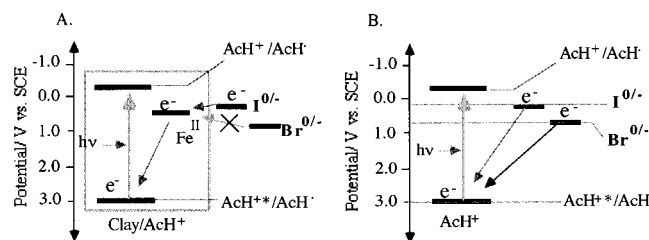
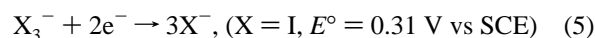
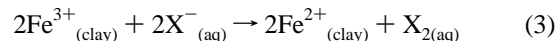
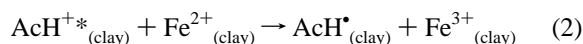


Figure 2. (a) CV curves for clay/AcH⁺ electrodes in a solution containing 0.1 M LiClO₄ and 1 mM of KBr (curve a); scan rate 50 mV/s. Solvent system: 1:1 (v/v) CH₃CN/acetate buffer (pH 4, μ = 0.1 M). (b) i-t curves recorded at -0.1 V vs SCE.

SCHEME 1: Schematic Illustrations for the Electron Transfer between Halides and AcH⁺_(clay) (A) and AcH⁺_(aq) (B)



was added instead of KI (Figure 2), and the bare clay electrodes produce almost no photocurrents in the solutions containing KI or KBr. These experiments strongly suggest that the photoeffects recorded with the clay/AcH⁺ electrodes are caused by the photocatalysis of the acridinium ion, which is summarized in Scheme 1 A and described as follows:



According to the proposed mechanism, the dark current shown in Figure 1 is contributed by reactions 3–5, and the photocurrent comes from reactions 1–5. Scheme 1A indicates that the reaction between Fe^{3+/2+}_(clay) ($E^\circ = 0.39$ V)^{8a} and Br^{0/-} ($E^\circ = 0.84$ V vs SCE) is thermodynamically unfavorable and the oxidation of bromide, reaction 3, cannot occur in the dark or under irradiation, and leads to no cathodic current for bromine. In fact, AcH⁺* is a powerful oxidant ($E^\circ_{\text{AcH}^{+*}/\text{AcH}} \approx 2.32$ V vs SCE) which can oxidize various reductants including naphthalene, halides, NO₂⁻, and many transition metals.¹¹ If halides migrate into the clay and react with AcH⁺* directly, the reactions will follow the pathways in Scheme 1B, where both bromide and iodide can be oxidized by AcH⁺*. Control

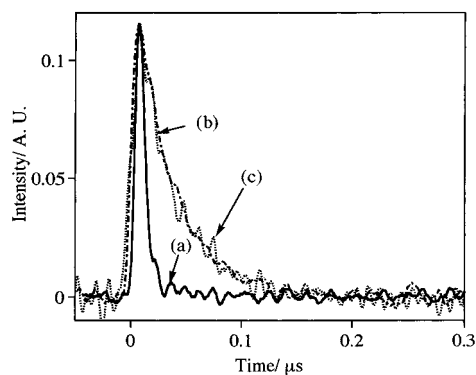
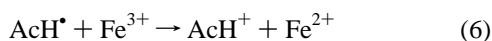


Figure 3. Time-resolved laser spectroscopy (pH 4, acetate, $\mu \approx 0.1$ M, $\lambda_{\text{em}} = 500$ nm) for clay/AcH⁺ (a) and free AcH⁺ (b). Trace (c): control experiment with the AcH⁺ adsorbed at the synthetic smectite (containing no iron).

experiments show that acridinium exists a large overvoltage at bare SnO₂ electrodes ($E'_{\text{AcH}^{+0}} \approx -0.43$ V vs SCE^{11,12}). The ill-defined cathodic wave merges with the charging current in the potential range of 0.8 to -0.6 V, causing an insignificant photoeffect to the system regardless of the presence of KI or KBr. However, control experiments also show that if a small amount of Fe³⁺ is added into the system, the photoeffect becomes significant and results in an enhancement of the cathodic current near -0.55 V. Such results reveal a great similarity to those performed with the clay/AcH⁺ electrodes, suggesting that the electron transfer occurring at clay/AcH⁺ is mediated by Fe^{2+/3+}_(clay) as described in eqs 2 and 3. The growth and decay of the photocurrent ($E_{\text{appl.}} = -0.1$ V) shown in Figure 1b is very slow (in the order of 10 min). We believe the slow growth of the current is due to the slow diffusion of I₃[−] across the clay/electrolyte interface, and the slow decay is caused by slow charge recombination, i.e., a long-lived charge separation state at the clay/AcH⁺ surface during photo irradiation. Time-resolved laser spectroscopy fully supports these hypotheses.

As shown in Figure 3, the lifetime of AcH⁺_(aq) (trace b) is 36 ns whereas the decay for AcH⁺_(clay) (trace a) occurs in the same time scale as the instrumental response ($\ll 10$ ns, cannot be resolved by any excited-decay behavior). Control experiments with the synthetic smectite^{9b} which contains no iron show that the lifetime of the intercalated AcH⁺ is 35 ns (trace c), not significantly different from that of the free AcH⁺. This result provides a strong evidence showing that the iron species in montmorillonite K10 should be active quenchers for AcH⁺_(clay), agreeing well with the reductive quenching mechanism as depicted in eq 2. In addition, the decay of AcH⁺_(clay) shows no residual of any slow kinetics, suggesting the AcH⁺_(clay) species are strongly adsorbed onto montmorillonite K10 and that the leaching of AcH⁺ is negligible. Transient absorption signals recorded at 400 nm with free AcH⁺ and AcH⁺_(clay) only exhibit a ground-state bleach and recovery, and the rate of recovery is identical with the luminescence decay rate. No long-lived species are observed in these experiments. The lack of an electron-transfer product from AcH⁺ in the clay is believed to be due to the fast reaction of AcH[•] with the Fe³⁺ species in the clay.



When KI (0.18 M) is introduced to the solutions containing free AcH⁺ or clay/AcH⁺, a long-lived positive signal, which is attributed to the formation of I₂^{•−} (i.e., I[•] + I[−]),¹³ is recorded in both solutions and persists for seconds. According to Figure 4a,b, the quantum yields for the formation of I₂^{•−} in both solutions are nearly identical,¹⁴ indicating that the electron-transfer process

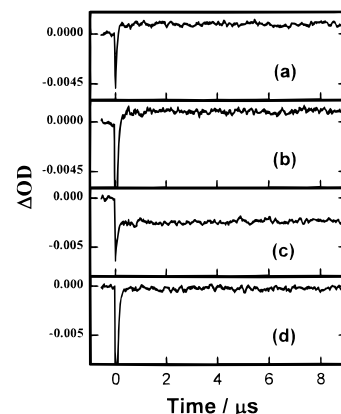
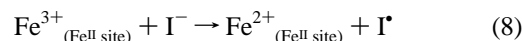
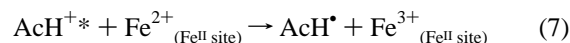


Figure 4. Transient absorption spectra (pH 4, acetate, $\mu \approx 0.1$ M, $\lambda_{\text{abs}} = 400$ nm) for (a) AcH⁺ with 0.18 M KI; (b) clay/AcH⁺ with 0.18 M KI; (c) AcH⁺ with 0.18 M KBr; (d) clay/AcH⁺ with 0.18 M KBr. The larger spikes seen in spectra (b) and (d) compared to (a) and (c) were attributed to light scattering by the clay.

is not inhibited by the clay. When KBr is added instead of KI, the results are quite different. As seen in Figure 4d, no long-lived transient signals were observed in the clay/AcH⁺ solutions, unlike the results recorded in the solutions containing free AcH⁺ (Figure 4c). These results suggest the electron transfer from AcH⁺ to halides follows the reaction pathways proposed in Scheme 1A, in agreement with the observations by electrochemical techniques.

In view of the fast decay of AcH⁺_(clay) to the ground state when iodide is initially absent, the oxidation of iodide must be competitive with this process, reaction 6. However, it is difficult for negatively charged ions diffuse into the negatively charged framework of clay, and therefore, it is less likely that I[−] can react with AcH⁺ within 10 ns (presumably I[−] and AcH⁺ are separated by the clay). Based on these results, the oxidation of I[−] by AcH⁺ must be through an indirect processes, such as those proposed in eqs 7 and 8.



If the reverse reaction of 7 is faster than reaction 8, the concentration of I₂^{•−} must be low and the associated lifetime must be extremely short. In fact, Figure 4b shows a high yield and long lifetime for I₂^{•−}; therefore, the reverse reaction of 7 must be a slow process. The decay of AcH[•]_(clay), reaction 6, is a fast process (no signal of AcH[•] was detected in a time scale of 10 ns), and therefore we believe that the quench of AcH[•] in the clay cannot be solely attributed to Fe³⁺_(Fe^{II} site) via the reverse reaction of 7. In other words, the quench of AcH[•] must be aided by another Fe³⁺ species in the clay, e.g.,



Many authors¹⁵ have pointed out that clays may exist different sites for the intercalated photosensitizers in terms of emission-quench and that Fe³⁺ is one of the active quenchers.^{15a} In our previous study, we also reported that montmorillonite K10 contain Fe²⁺ and Fe³⁺ species at different sites.^{8a} Once AcH⁺_(clay) is excited, Fe²⁺_(Fe^{II} site) quenches AcH⁺ to yield AcH[•], which reacts quickly with the nearby Fe³⁺ in the Fe^{III} sites and returns to the ground state (AcH⁺). Subsequently the resulting Fe³⁺ in the Fe^{II} sites reacts with iodide at the clay surface over a longer time scale, presumably via a charge-transfer reaction (e.g., hopping) from the Fe^{II} sites to the outer surface of the

clay. Since the yield in the conversion of I^- to I_2 at the clay/ AcH^+ surface is high (Figure 4b), we believe the electronic coupling between $Fe^{2+}_{(Fe^{II} \text{ site})}$ and $Fe^{3+}_{(Fe^{III} \text{ site})}$ is poor (or the reorganization energy is very large). Our previous study on montmorillonite K10 had reached a similar conclusion, in which the mutual communication between $Fe^{2+}_{(Fe^{II} \text{ site})}$ and $Fe^{3+}_{(Fe^{III} \text{ site})}$, reflected in the associated exchange current, is poor ($i_o \ll 10^{-9}$ A/cm²).^{8a} Besides, time-resolved laser spectroscopy (λ_{em} 500 nm) reveals that the lifetime of $AcH^{+*}_{(clay)}$ shows no explicit dependence on the intensity of the excitation light (λ_{ex} 355 nm, 5–450 mW) (e.g., it is still in the same time scale as the instrumental response ($\ll 10$ ns)). According to Ghosh's study,^{15b} by varying the intensity of the excitation light and monitoring the change in the emission property of the intercalated photosensitizers, one might be able to probe the quenching sites for the photosensitizers if the relative amount of the photosensitizer to the quencher is appropriate. In this regard, we tentatively ascribe the insignificant change in the lifetime of $AcH^{+*}_{(clay)}$ with the variation in the excitation power to a relatively smaller amount of AcH^+ to Fe in montmorillonite K10; as a result, no detectable change in either the emission intensity or lifetime of $AcH^{+*}_{(clay)}$ is observed.

In summary, we have provided evidence showing that montmorillonite K 10 can mediate the electron transfer via the contained electrochemically active iron species. Because of this action, a high yield, long-lived photoinduced charge separation state is observed at the clay/ AcH^+ surface when iodide is used as the probe but not when bromide is used, and this leads to different photoelectrochemical behavior between iodide and bromide.

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