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Efficient triplet–triplet energy transfer using clay-bound ionic sensitizers

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Abstract—Both cationic and anionic clays, with sensitizers anchored onto their interlayer by ionic linkage, are found to be useful 'microreactors' to achieve triplet state reactivity of myrcene in an experimentally simple, inexpensive and clean reaction. These clay-bound sensitizers are characterized by X-ray and their advantages are highlighted. © 2002 Elsevier Science Ltd. All rights reserved.

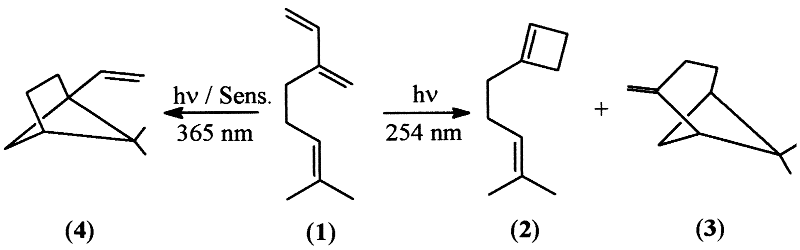
The singlet–triplet chemistry of olefins and β,γ-unsaturated ketones has been widely studied.[1,2] Direct irradiation of acyclic dienes gives cyclobutene and bicyclobutane.[3] The reactivity of these dienes, however, is different from their triplet state.[4] For example, the direct irradiation of myrcene (**1**) in solution at 254 nm gives two major products (singlet products (**2**) and (**3**)).[5] The sensitized irradiation of myrcene at 365 nm with a variety of triplet sensitizers gives a single product (5,5-dimethyl-1-vinylbicyclo[2.1.1]hexane (**4**)) which is also obtained in small amounts in the case of direct irradiation (Scheme 1).

A survey of recent literature[6] shows few instances of efficient utilisation of clays as organised assemblies for photochemical reactions and photophysical studies. The photooxidation of tryptophan, sensitized by methylene blue anchored onto a variety of clays has been investigated.[7] Clay-bound methylene blue[8] efficiently sensitizes the photooxidation of sulfides. The spatially controlled photocycloaddition of stilbazolium cations inside a saponite clay has been reported.[9] In devising strategies for the generation of excited triplet states of organic guests inside zeolite 'microreactors' to achieve their photochemistry, elegant and novel approaches are reported.[10] Triplet reactivity is increased by heavy cations and also by a second sensitizer guest molecule within the zeolite cage. The increased efficiency by including both the sensitizer and the guest molecule inside the zeolite cages in the singlet–triplet chemistry of 11-substituted-9,10-dihydro-9,10-ethenoanthracene has also been reported.[11] The regioselectivity imposed by zeolites in the photochemical dimerisation of enones has been demonstrated by Turro and co-workers.[12]

These interesting findings, coupled with our interest in utilising layered aluminosilicates, namely clays as media for achieving selective transformations in thermal[13,14] and photochemical reactions,[8] have prompted us to undertake the present investigation, in which triplet–triplet energy transfer is achieved in the photolysis of myrcene using clay-bound ionic sensitizers.

1. Results and discussion

In the present study, both cationic (bentonite) and anionic (hydrotalcite) clays were employed and the sensitizers, after



Scheme 1. Direct and sensitized irradiation products of myrcene (**1**).

Keywords: clay-bound sensitizers; energy transfer; myrcene; hydrotalcites; bentonites.

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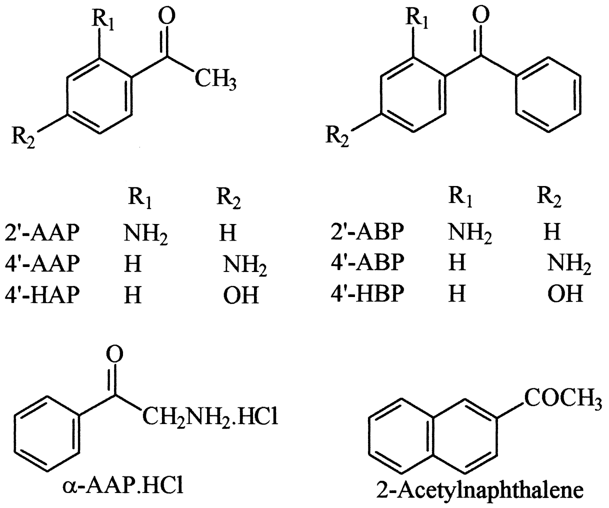

Scheme 2. Sensitizers employed in the present study.

ionization, were immobilized onto their surface by interaction with clay acidity/basicity. In Scheme 2, the various sensitizers used in this work are presented.

In the direct irradiation of myrcene (in diethyl ether) only two major products (**2**) and (**3**), along with a small amount of the product of the sensitized irradiation (**4**) were identified, in accordance with earlier reports.[1a,5] Irradiation in the presence of heavier cation-exchanged clays were also carried out and both cationic (Na$^+$ form of bentonite) and anionic (hydrotalcite) clays were employed. Direct irradiation of myrcene using low-pressure as well as medium pressure mercury vapor lamps in Cs$^+$ and Tl$^+$-exchanged bentonites and also I$^-$-exchanged hydrotalcites resulted in the same product composition as that of the solution irradiation (Table 1). This indicates the absence of any significant heavy atom effect in the present study. This is in contrast to the heavy atom response of dibenzobarrelene[10,11] and benzobarrelene,[10] and also the oxa-di-Π-methane behaviour of bicyclic enones[15] wherein 100% triplet behaviour is observed in Tl$^+$ and Cs$^+$-exchanged zeolites. Thus, it is likely that in clays (as in zeolites) the degree of heavy atom effect on mixing the states of different multiplicity depends on the electronic configuration[10] (n, Π^* and Π, Π^*) and is in accordance with 'El Sayed's rule'.[16]

The results presented in this work amply demonstrate the efficiency of clay media as a tool for triplet–triplet energy transfer. The product distribution of photosensitized internal addition of myrcene in the presence of various sensitizers anchored onto acidic as well as basic clays are presented in Table 1. Irradiation in the presence of various sensitizers (2-acetylnaphthalene, acetophenone, benzophenone, $4'$-hydroxyacetophenone and $4'$-hydroxybenzophenone) yields only the triplet product and among the various sensitizers, 2-acetylnaphthalene is found to be the most efficient, consistent with literature reports.[1a,5] The reaction was found to proceed conveniently in presence of $2'$ and $4'$-aminoacetophenones and benzophenones anchored onto the clay surface by ionic bonds (after initial protonation of amino groups by Bronsted acidic sites in clays).

Table 1. Products distribution in direct and sensitized photolysis of myrcene (**1**) in clay microenvironment

Medium	% Conversion of (**1**)	Products distribution (%)[a]			
		(**2**)	(**3**)	(**4**)	X[b]
(i) Direct irradiation[c]					
Diethyl ether	64 (–)[d]	70 (52)[d]	13 (22)[d]	11 (12)[d]	6 (14)[d]
Na$^+$-bentonite	29	73	22	5	–
Cs$^+$-bentonite	32	73	21	6	–
Tl$^+$-bentonite	32	74	19	6	1
Hydrotalcite	51	76	19	5	–
I$^-$-hydrotalcite	61	72	19	9	–
(ii) Sensitized irradiation[e]					
2-Acetylnaphthalene	38 (–)	–	–	100 (100)	–
Acetophenone	12	–	–	100	–
$4'$-AAP-bentonite[f]	15	–	–	100	–
$4'$-AAP-bentonite[g]	14	–	–	100	–
$2'$-AAP-bentonite	Nil	–	–	–	–
α-AAP-bentonite	Nil	–	–	–	–
$4'$-HAP-hydrotalcite	16	–	–	100	–
$4'$-HAP-hydrotalcite[g]	15	–	–	100	–
Benzophenone	8	–	–	100	–
$4'$-ABP-bentonite	21	–	–	100	–
$4'$-ABP-bentonite[g]	19	–	–	100	–
$2'$-ABP-bentonite	Nil	–	–	–	–
$4'$-HBP-hydrotalcite	12	–	–	100	–
$4'$-HBP-hydrotalcite[g]	12	–	–	100	–

Irradiation as slurry in dry ether for 20 h with stirring.

[a] Analysed by GC; error limit ±5%.

[b] Unidentified products.

[c] Irradiated in a 254 nm multilamp reactor.

[d] The values in parentheses correspond to the literature data.[1]

[e] Irradiated in a 365 nm multilamp reactor.

[f] For structures of the sensitizers, refer Scheme 2.

[g] Sensitizer used for the second time.

The presence of only triplet product and the absence of any singlet-derived products under these conditions ruled out any reaction in the liquid phase of these clay slurries. Among the substituted acetophenone and benzophenone sensitizers used, the 4′-substituted sensitizers were found to be more effective than 2′-substituted sensitizers in the reaction. This is in accordance with their efficiency in solution indicating that the 2′ and 4′-isomers behave differently in their sensitization efficiency.

Similarly, anchoring through the other side of the sensitizer, as in α-aminoacetophenone hydrochloride also resulted in inefficient energy transfer. Anionic hydrotalcites clays were also used as microreactors. 4′-Hydroxyacetophenone and 4′-hydroxybenzophenone anchored onto anionic hydrotalcites by ionic exchange were also found to be efficient sensitizers to myrcene. Though the overall conversion was only around 20% with these clay-bound sensitizers, this disadvantage was offset by their other advantages such as reusability, simpler work-up, etc. When they were used for the second time (after a simple filtration, washing and drying), there was only a marginal decrease in the percentage conversion (Table 1).

Using these clay-bound sensitizers, an improved yield of triplet product was observed compared to the corresponding (Table 1) free sensitizer in solution. This is ascribed to decreased two-dimensional mobility within the clay layers and consequent increase in energy transfer between the immoblised sensitizer and the substrate. Another interesting observation which would also have contributed to the increase in energy transfer is, when these sensitizers are converted to their ionic forms, the consequent shift in their λ_{max} brings them closer to that of 2-acetylnaphthalene (λ_{max} 281 nm), the sensitizer with a triplet energy (59.5 kcal mol^{-1}) which is the most efficient for myrcene. For example, the λ_{max} values of the free 4′-aminoacetophenone (314 nm) and 4′-aminobenzophenone (332 nm) have decreased to 278 and 293 nm upon treatment with an equimolar quantity of hydrochloric acid. Thus, it is likely that ionization and consequent anchoring of the sensitizer onto clay interlayer decreases the energy difference between the triplet states of the sensitizer and myrcene and had ensured efficient energy transfer. Attempts to identify the nature of the interaction of the sensitizer with clay by recording the UV diffuse reflectance spectrum was not successful, as we were unable to record a good clean spectrum. This may be due to the low amount of sensitizer and also the poor sensitivity of UV absorption to diffuse reflectance measurements.

Thus the present approach provides an useful route to achieve triplet state chemistry of organic substrates within the layered clay microenvironment. Besides acting as a constrained microreactor, they also help in anchoring the sensitizer of choice, thus opening up the possibility of extension of this approach to other more complex and difficult systems. Unlike zeolites[10,11] (where only nonpolar solvents are used to confine the substrates inside the cages), in the present study a wide range of solvent systems may be employed (more polar solvents can also used) and size restrictions[8] on the substrate are no longer the constraints or limiting factor. The other advantages of using clay-bound sensitizers are their reusability with only a marginal decrease in their efficiency and the easier removal of the sensitizer from the reaction medium. This approach of ionizing and then anchoring the sensitizer onto the clay surface, removes restrictions on the choice of the sensitizers and those sensitizers which are not soluble in the reaction medium can also be used. The results are thus significant, since clean triplet–triplet energy transfer is demonstrated for the first time in a photochemical reaction in the layered clay microenvironment, materials which in spite of their huge natural abundance are of less interest to photochemists so far and studies in them are restricted mainly to photophysical events.

2. Experimental

Bentonite clay obtained from Aldrich, was used after repeated exchange with sodium chloride. Mg–Al-HTlc was prepared as per reported procedure.[17] A typical example for 5:1 HTlc is described below: $Al(NO_3)_3{\cdot}9H_2O$ (0.01 mol) and $Mg(NO_3)_2{\cdot}6H_2O$ (0.05 mol) were dissolved in deionised water (100 mL), and a second solution (60 mL) of Na_2CO_3 (0.03 mol) and NaOH (0.07 mol) was prepared. After the first solution was slowly added to the second one, the resulting mixture was heated at 65°C for 18 h with vigorous stirring. The white slurry was then cooled to room temperature, filtered, washed well with deionised water and dried overnight at 110°C.

The sensitizer anchored clays were prepared by stirring 1 g of Na^+-exchanged bentonite/hydrotalcite with 50 mg of sensitizer in 10 mL of AR acetone for 6 h. Evaporation of the solvent at reduced pressure gave a powder, which was washed repeatedly with diethyl ether, to remove any surface adsorbed sensitizer. The clay sensitizer matrices were characterized by X-ray powder diffraction patterns. A comparison of the data for Na^+-bentonite (A) with that of 4′-aminoacetophenone-bentonite (B), 2′-aminoacetophenone-bentonite (C), α-aminoacetophenone-bentonite (D), 4′-aminobenzophenone-bentonite (E) and 2′-aminobenzophenone-bentonite (F) revealed substantial differences. The ratio of the major peaks (at *d* values of 2.7631 and 1.9729 Å) in Na^+-bentonite at 2.03 had changed to 1.82, 1.80, 1.80, 1.77 and 1.87, respectively, in (B)–(F). A prominent new peak at ~10–12 Å was observed in all sensitizer-anchored clays, which was absent in Na^+-bentonite. In addition the three peaks at 3.0–3.2 Å in (A) now had altered intensities. For example, the peak at *d*~3.3 Å in (A) now had increased intensity in (B)–(F). In the case of (B), new peaks were observed at d values of 6.8099, 6.6075 and 6.4168 Å. These observations indicate that the sensitizers are indeed all anchored onto clay surface. Myrcene was purified by distillation under vacuum and stored under cooling in a refrigerator.

In a typical photolysis experiment, 0.1 mL (0.588 mmol) of myrcene and 200 mg of sensitizer anchored clay were irradiated for the specified time as a slurry in dry ether under a nitrogen atmosphere. All the sensitized irradiations were carried out at 365 nm and the direct irradiation reactions at 254 nm for 20 h with stirring. After irradiation, clay samples were filtered, extracted with chloroform and the solvents were evaporated. The reaction mixtures were analysed by capillary gas chromatography (SHIMADZU—17A, FID detector, SE-30 10% capillary column, high purity nitrogen as the carrier gas, with a column temperature programming (80°C–4°C min^{-1}—140°C–2 min) while the injection port and the detector were maintained at 120°C. The products were identified by comparison of their retention times with products obtained as reported earlier.[1a,5]

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