Photochemical hydrogen abstraction by aromatic carbonyl compounds in zeolite slurries

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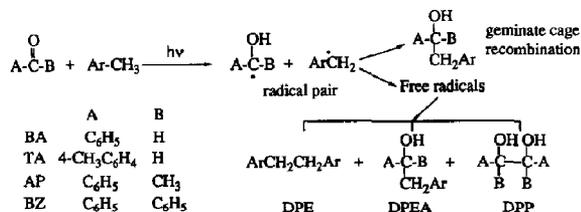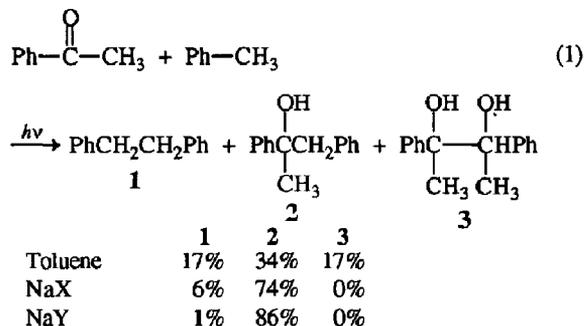*Chemistry Department, Columbia University, New York, NY 10027, (USA)*

Abstract

Irradiation of solutions of aromatic aldehydes or ketones generally results in photoinduced hydrogen abstraction and yields mixtures of both asymmetric and symmetric coupling products of the radicals resulting from hydrogen abstraction. In contrast, irradiation of hydrocarbon–faujasite zeolite slurries of aromatic aldehydes or ketones results in production of radical pairs by intermolecular hydrogen abstraction, which is followed by the formation of good yields of the asymmetric geminate coupling products. The mechanistic basis of this difference in chemoselectivity is proposed to result from a combination of strong preferential adsorption of the carbonyl compounds to the internal surface of the zeolite and inhibition of the diffusional motion of the geminate radical pair produced by photolysis by the "spectator" hydrocarbon molecules that occupy the internal surface but which do not participate chemically in the reactions.

1. Introduction

The intermolecular hydrogen abstraction reaction of photoexcited carbonyl compounds is one of the most investigated and best understood reactions in all of molecular organic photochemistry [1]. A simplified version of the conventional working paradigm for intermolecular hydrogen abstraction is shown in Scheme 1 with a methyl-containing aromatic hydrocarbon as hydrogen donor. The paradigm states that since the hydrogen abstraction step is generally a relatively slow process compared with intersystem crossing in excited singlet carbonyl compounds, it is expected to occur from the triplet excited state and to produce a triplet geminate radical pair. Because of the efficient and rapid separation of the primary geminate pair to form free radicals, chemoselective formation of the gem-

inate asymmetric coupling products of the triplet geminate pair is expected to occur with very low probability. It is therefore expected that non-chemoselective coupling of free radicals to form both symmetric and asymmetric coupling products or scavenging of free radicals will occur instead [2]. For example, the photolysis of acetophenone in toluene results (eqn. (1)) in formation of coupling products expected from statistical coupling of the radicals produced by the hydrogen abstraction step, *i.e.* the coupling products **1**, **2** and **3** are formed in the ratio 1:2:1.

$$Ph-\overset{O}{\overset{\|}{C}}-CH_3 + Ph-CH_3 \qquad (1)$$

$$\xrightarrow{h\nu} PhCH_2CH_2Ph + Ph\overset{OH}{\underset{CH_3}{\overset{|}{C}}}CH_2Ph + Ph\overset{OH}{\underset{CH_3}{\overset{|}{C}}}\overset{OH}{\underset{CH_3}{\overset{|}{-}}}CHPh$$

	1	**2**	**3**
Toluene	17%	34%	17%
NaX	6%	74%	0%
NaY	1%	86%	0%

The paradigm of Scheme 1 reveals a possible strategy for obtaining high chemoselectivity for the asymmetric coupling product produced by coupling of the geminate pair only: to find conditions for which escape of the pair from the geminate state is slow relative to geminate combination of the

Scheme 1.

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pair. Such a strategy has been effectively exploited to enhance greatly geminate reactions of triplet radical pairs produced by photochemical α-cleavage of ketones constrained in the restricted reaction spaces of micelles [2, 3], cyclodextrins [4], and zeolites [5]. However, micelles and cyclodextrins are not good candidates for enhancing the geminate pair reaction of pairs produced by the relatively slow process of intermolecular hydrogen abstraction, because the excited triplet states can also react by hydrogen abstraction from the micelle surfactant chain [4, 6] or from the carbohydrate framework of the cyclodextrin molecule [7]. In contrast, the internal surface of zeolites, consisting of SiOSi and SiOAl units, is resistant to reaction with triplet ketones and may therefore serve as an unreactive restricted space which enhances geminate combination reactions, if the geminate pair can be prevented from separating to form free radicals.

The internal void space of the supercages of the faujasite zeolites (the X and Y family) consists of roughly spherical cavities of *ca.* 13 Å diameter. Each supercage is connected through a tetrahedral network to four other supercages through 8 Å windows (Fig. 1) [8]. Diffusion within and between supercages is possible, but can be strongly inhibited by the addition of "spectator" molecules, which simply occupy space within the supercages and prevent molecules within a given supercage from passing through the windows into an adjacent supercage. Thus, the presence of inert guest molecules can modify the chemistry of geminate pairs produced by photochemistry in the supercages of faujasites.

With the lessons of the two paradigms in mind, we decided to explore the following strategy to improve the yield of geminate coupling products produced by the hydrogen abstraction of ketones. The internal cages of the faujasite zeolites (*e.g.* NaX) can simultaneously contain a molecule of carbonyl compound, such as benzaldehyde or acetophenone, and a molecule of hydrogen donor
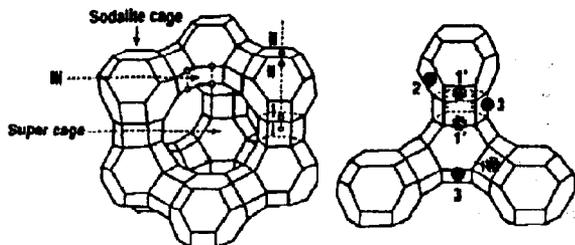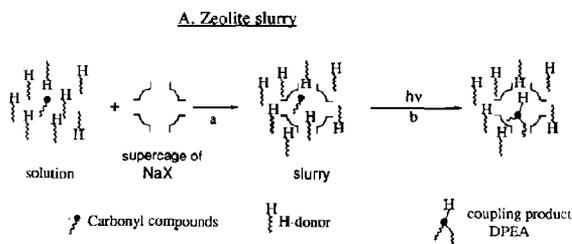

Fig. 1. Supercage structure of the X and Y zeolites. I, II and III in the figure on the left refer to the location of cations.

a. The polar zeolite selectively adsorbs the carbonyl compound molecules from solution into its internal surface. The remaining space is filled by hydrogen donor molecules.
b. During irradiation, the ketyl-benzyl radical pair generated by hydrogen abstraction is forced to form diphenylethanol.

B. Homogeneous solution:

The product distribution follows a statistical distribution

Scheme 2.

such as toluene [9]. Furthermore, since the more polar carbonyl molecules are more strongly bound to the zeolite cage than the hydrocarbon molecules, even at low percentage mole fraction in a carbonyl–hydrocarbon slurry, the carbonyl compound is selectively adsorbed onto the internal surface of the zeolite. For example, when NaX (or NaY) was added to a toluene solution of acetophenone (toluene:zeolite:acetophenone = 1   ml:100   mg:4   mg), no acetophenone was detected in the supernatant after 1 h. An appropriate loading guarantees that each zeolite cavity will contain a carbonyl-containing molecule and a molecule of a hydrocarbon. Excess hydrocarbon molecules will fill the void space in the zeolite that is not occupied by the carbonyl compounds. These hydrocarbon molecules are expected to serve as blockers which inhibit diffusion of geminate radical pairs produced by hydrogen abstraction and therefore inhibit free radical formation. Thus, the strategy (shown schematically in Scheme 2) is to generate triplet geminate pairs selectively by intermolecular hydrogen abstraction in a zeolite cage and to encourage geminate combination over free radical formation by employing the excess hydrogen donor as inhibitors of escape of the geminate pair from the zeolite cage in which it is formed.

2. Experimental section

A typical photoreaction and work-up were performed as follows. A slurry composed of the carbonyl compound (*ca.* 1 mg), zeolite (*ca.* 25 mg), and aromatic hydrocarbon (*ca.* 0.25 ml) in a quartz cell were degassed by three freeze–pump–thaw

cycles. The resulting sample was irradiated with a 450 W medium pressure mercury lamp through a Pyrex filter under continuous stirring. On completion of irradiation (ca. 15–30 min with a conversion of ca. 50%), p-methoxyacetophenone was added as an external standard, the zeolite was dissolved in 1 N hydrochloric acid and then neutralized with 1 N sodium hydroxide. After this treatment no noticeable quantity of dehydration products (e.g. stilbene) was detected. The upper organic layer was separated, dried with anhydrous magnesium chloride, and analyzed by gas chromatography–mass spectrometry (GC–MS).

The main products listed in Table 1 (symmetric free radical products, 1,2-diphenylethanes (DPE) and 1,2-diphenylpinacols (DPP); asymmetric geminate coupling product, 1,2-diphenylethyl alcohols (DPEA)) were identified by comparison with authentic samples or, in the case of DPEA, by synthesis. (The DPEA were identified by both GC–MS and nuclear magnetic resonance (NMR), e.g. for 1,2-di(p-methylphenyl)ethanol, GC–M results (m/z) were 121, 106, 91, 77; ^{1}H NMR results were δ(300 MHz, TMS) = 7.14–7.29 (dd, 4H), 7.1 (s, 4H), 4.84 (m, 1H), 2.85–3.06 (m, 2H), 2.35 (s, 3H), 2.33 (s, 3H), 1.6 (s, 1H).) Other products include benzyl alcohols (usually less than 5% formed in slurries, 15%–40% in homogeneous solution), and small amounts of deoxybenzoins

which were also identified by GC–MS and are not listed in Table 1.

3. Results

Table 1 summarizes the results of the photolysis of slurries of toluenes or xylenes and p-tolualdehyde (TA), benzaldehyde (BA), acetophenone (AP), and benzophenone (BZ).

With toluene as a hydrogen donor and solvent, the yields of the asymmetric coupling products are 36%, 35% and 54% for triplets of BA, AP and BZ as hydrogen abstractors respectively. The yields of the asymmetric (now nearly exclusively the geminate) coupling product are increased to 83%, 74% and 77% respectively when the photolyses are conducted in toluene–NaX slurries. In most cases, even higher yields of DPEAs were formed in NaY slurries (e.g. in eqn. (1), the percentage yields of 2,3-diphenyl-2,3-butadiol formed in photolysis of acetophenone in toluene–NaX and NaY slurries are 74% and 86% respectively). The higher yields of geminate product may result from a stronger binding of the carbonyl compounds to the internal surface of NaY. From both the synthetic and the mechanistic standpoint, it is interesting to note that the yields of free radical products (DPE and DPP) are drastically reduced when the photolyses are conducted in the zeolite slurries.

With xylene as a hydrogen donor, a similar enhancement of the geminate coupling product is observed when the photolysis is conducted in a xylene–NaX slurry. It is of mechanistic interest to note that for slurries of NaA, which possesses 4 Å pores which are too small to adsorb either the carbonyl compound or the hydrocarbon into the internal surface, the product distribution is similar to that for homogeneous solution, i.e. a relatively high yield of free radical coupling products is formed. This result is consistent with the expected requirement that the free diffusion of the pair in the liquid phase of the slurry should occur (100% of p-tolualdehyde was detected in the supernatant after mixing NaA, p-xylene, and p-tolualdehyde for 4 h).

The greater than theoretical stoichiometric yield of coupling product in the TA–p-xylene system (based on the TA consumed) requires some explanation and reflects on the yield of the coupling products in the other examples. It appears that this peculiar observation is the result of some oxidation of the p-xylene during the photolysis to produce TA. If this were to occur, of course, the

TABLE 1. Product distribution in the photolysis of carbonyl compounds in zeolite–aromatic slurries

Carbonyl[a] compound	H donor	Zeolite	Yield[b] (%)		
			DPE[c]	DPEA[d]	DPP[e]
TA	p-xylene	4A	29	55	8
	p-xylene		28	46	0
	p-xylene	NaX	1	114[f]	0
	o-xylene		23	49	0
	o-xylene	NaX	1	94	0
	m-xylene		28	55	0
	m-xylene	NaX	3	80	0
BA	Toluene		13	36	1
	Toluene	NaX	1	83	0
AP	Toluene		17	35	17
	Toluene	NaX	6	74	0
BZ	Toluene		20	54	0
	Toluene	NaX	3	77	0

[a]TA, p-tolualdehyde; BA, benzaldehyde; AP, acetophenone; BZ, benzophenone.
[b]The experimental errors are usually within 5%.
[c]Diphenylethanes.
[d]1,2-diphenylethyl alcohols.
[e]1,2-diphenylpinacols.
[f]The high yield reflects a certain degree of oxidation of the xylene during photolysis to produce the molecules of TA. See text for discussion.

initial amount of TA would be more than the theoretical amount available for reaction. To test for the occurrence of this possibility, a p-xylene–NaX slurry in the absence of TA but in the presence of air or oxygen was irradiated. Indeed, both TA and the coupling product were produced under these conditions. For example, the irradiation of both degassed and aerated p-xylene–NaX slurry resulted in the formation of 8% and 50% respectively of the oxygenated product DPEA and TA. (This provides a method for one-step synthesis of symmetrical 1,2-diphenylethanols. For example, irradiation of p-xylene–NaX slurry in the presence of air and oxygen both gave 50% of 1,2-di(p-methyl)phenylethanol (corresponding to a 0.4% sample) together with tolualdehyde). This observation is interesting in its own right since it highlights the ability of molecular oxygen to diffuse readily through the zeolite framework, even in the presence of a high loading of hydrocarbon. In recent oxygen scavenging experiments of radicals generated by photolysis of deutero dibenzyl ketone in zeolites, we found that scavenging may occur at all stages of radical formation and the scavenged products (acids and aldehydes) formed at low oxygen pressure (below 10^{-2} Torr) are independent of the loading of the ketone [10]. The latter has been attributed to chemisorbed oxygen.

4. Conclusion

Intermolecular photoreactions in zeolites are still relatively rare [11]. The results presented here demonstrate that geminate coupling products can be produced in good yields and that free radical reactions can be strongly suppressed under the conditions of photolysis of appropriate systems such as zeolite-containing slurries. There is great potential in the investigations of such systems from both the synthetic and the mechanistic standpoints.

The cage effect, selective binding of a reagent and the combined role of a substrate as both a reagent and a modulator of diffusional motion offer a novel set of parameters on which to design strategies for controlling syntheses. An obvious and intriguing extension of these ideas is the possibility of employing substrates that can serve to induce chirality in the coupling products of radicals produced by intermolecular (or intramolecular) photoreactions.

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