

Evidence for an acid-catalysed reaction subordinated to the occurrence of a previous electron transfer in the incorporation of an electron-rich alkene within NaY zeolite

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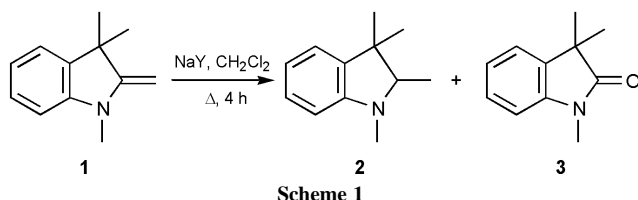
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The first observation of an acid-catalysed reaction subordinated to the occurrence of an electron transfer upon the incorporation of an electron-rich alkene in NaY zeolite is reported; the key point is the generation in the electron transfer process of suitable hydride donor species that react with the carbocation generated in the acid catalysed mechanism.

It is well documented that acid zeolites can behave either as solid acids or as electron acceptors.^{1–8} In the former case the resulting reaction mechanism generally involves carbocations while in the latter case the key reaction intermediates are radical cations. Studies showing the concurrent occurrence of both type of processes are rare. Herein by using an electron-rich alkene, 1,3,3-trimethyl-2-methyleneindoline **1** (Scheme 1), we provide



evidence that: (i) the products of both mechanisms (proton or electron transfer) are different and characteristic of each type of reaction intermediate and (ii) formation of the acid-catalysed product does not occur unless the electron-transfer product is formed previously (subordination).

A highly reactive, electron-rich alkene **1** was selected for the present study.[†] Upon stirring a dichloromethane solution of this indoline in the presence of thermally dehydrated NaY zeolite at reflux temperature under aerated conditions the progressive disappearance of the starting material, accompanied by the formation of 1,2,3,3-tetramethylindoline **2** (40%) and 1,3,3-trimethyl-2-indolinone **3** (60%) was observed (Scheme 1). This product distribution is not unprecedented and it parallels those found in the reaction of 1,1-diphenylethene over CaY zeolite wherein 1,1-diphenylethane and benzophenone were formed.^{9–11}

Addition of a small amount of pyridine (10 mg g⁻¹) totally quenches the reaction and neither of the two products was formed. This can be taken as evidence that the reaction involves the weak acid sites present in commercial batches of NaY. Precedents for acid-catalyzed reactions promoted by NaY have been reported previously for vinylanisole and anethole dimerisation¹² and spectroscopic titration of NaY acid sites has also been reported.¹³ We have found that this product distribution is not specific to NaY but that liquid acids such as trifluoroacetic or methanesulfonic acids behave analogously.

It is obvious that the formation of indolinone **3** should involve as reagent either molecular oxygen or water, or both. In an attempt to clarify this point, the reaction of indoline was carried out under argon atmosphere. However, when indoline **1** was

refluxed in the presence of thermally activated NaY under Ar atmosphere, not only the formation of indolinone **3** but also the formation of 1,2,3,3-tetramethylindoline **2**, which does not incorporate any oxygen atoms in its molecular formula, is quenched. Clearly, the formation of both products is inhibited by adding a base or in the absence of molecular oxygen.

Raman spectra of indoline **1** adsorbed into NaY zeolite under Ar atmosphere indicates that under conditions in which no products are observed in the liquid phase, indoline **1** is stable upon incorporation within NaY.

Fig. 1 shows the diffuse reflectance UV–VIS spectra of the corresponding NaY sample obtained after incorporation of indoline **1** under argon atmosphere (a) and under aerated conditions (b). In the latter case, the extra band at 440 nm matches the absorption band of indolinone **3** in dichloromethane solution, thus providing spectroscopic evidence that this product is formed rapidly upon incorporation of **1** within NaY in the presence of air.

To disclose the reaction mechanism of formation for both products, indoline **1** was submitted to photochemical oxidation under typical electron transfer conditions. It is known that 1,4-dimethoxybenzene (DMB, $E = 1.34$ V, vs. SCE) in the presence of oxygen is a selective electron transfer photosensitizer that does not generate singlet oxygen.¹⁴ Photosensitized irradiation of indoline **1** ($E = 0.76$ V, vs. SCE) in acetonitrile (0.5 wt% water content) containing DMB gives rise to the formation of indolinone **3** with almost complete selectivity at 98% of indoline conversion (Scheme 2). Thus, based on the known ability of zeolites to promote single electron transfer reactions¹⁵ and on the results of the photoinduced electron transfer that shows that the radical cation of compound **1** leads exclusively to indolinone, we propose that the most reasonable reaction mechanism to explain the formation of indolinone involves the indoline radical cation (Scheme 3).

Concerning the formation of tetramethylindoline **2**, it has been reported that treatment of 1,1-diphenylethene and benzonorbornadiene with CaY leads to the corresponding saturated 1,1-diphenylethane and benzonorbornane through the

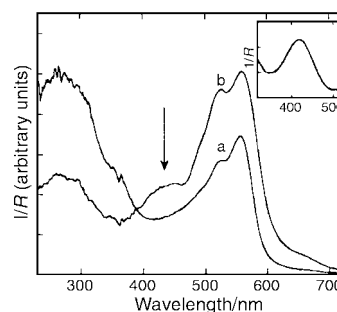
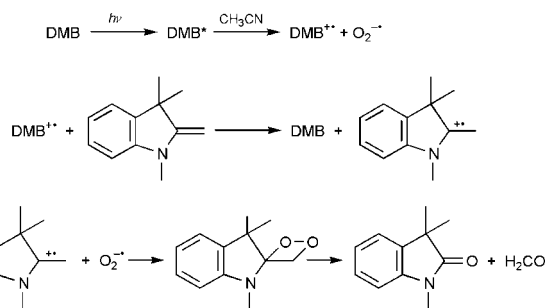
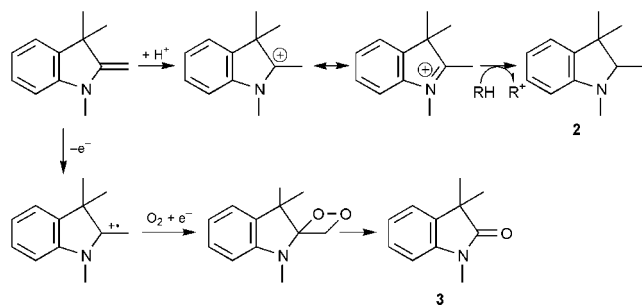


Fig. 1 Diffuse reflectance UV–VIS spectra of indoline **1** adsorbed onto NaY in the presence of air (a) and under Ar atmosphere (b). The insert shows the UV–VIS spectra of a dichloromethane solution of indolinone **2**.

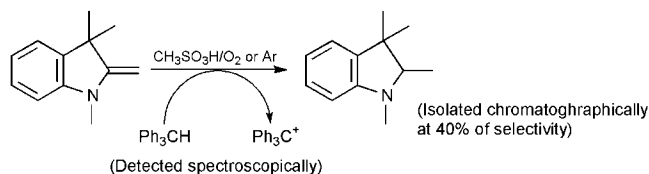


Scheme 2



Scheme 3

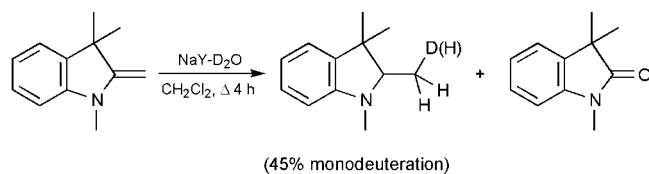
corresponding radical cation.¹⁶ Other reports have invoked a radical cation intermediate to affect the C=C double bond hydrogenation.¹⁷ However, the fact that the photoinduced DMB electron transfer reaction does not give detectable amounts of compound **2**, seems to rule out this possibility. An alternative explanation for the formation of **2** would be acid-catalyzed protonation to generate a carbocation followed by hydride abstraction. To support this reaction mechanism, a reactive hydride donor such as triphenylmethane (TPM) was added to a solution of indoline **1** in methanesulfonic acid (Scheme 4).



Scheme 4

Under these conditions, both in the presence or absence of oxygen, 1,2,3,3-tetramethylindoline was formed in 40% selectivity at 90% indoline conversion.[‡] Concurrently the triphenylmethyl cation characterized by 405 and 425 nm bands in the UV-VIS spectrum of the acid solution was observed.

To further support the mechanism shown in Scheme 4, the NaY zeolite was submitted to deuteration by two consecutive cycles consisting in soaking the NaY solid with D₂O and subsequent drying at 110 °C. The resulting deuterated zeolite was used for the reaction with **1**. The corresponding GC-MS of the reaction mixture showed the presence of 2-deuteromethyl-1,3,3-trimethylindoline at a level of 45% of the total amount of **2** (Scheme 5). This result supports that formation of **2** occurs



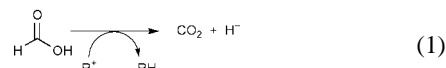
Scheme 5

through proton transfer from the zeolite framework to the 2-methylene substituent in a Markovnikov manner. The in-

complete deuteration can be explained by the incomplete deuteration of the zeolite OH or by back H/D exchange.

The absence of oxygen should exclusively inhibit formation of compound **3** the only product containing oxygen. To explain why the absence of oxygen also inhibits formation of **2**, we speculated on the possibility that the hydride donor required in the formation of **2** arises from the formation of **3**. In this context, it should be noted that formation of **2** according to the conditions of Scheme 3 should occur equally well both in the presence or absence of oxygen.

Thus, we suggest that formaldehyde, formic acid or any product derived thereof could act as hydride donors in the formation of **2**. Since these species are formed concomitantly with **3** this would explain why **2** is not formed under conditions in which **3** is inhibited. In this regard, it is well documented that formic acid can be an effective reducing agent and also can act as a hydride donor according to eqn. (1).¹⁸



In summary, incorporation of an electron rich alkene 1,3,3-trimethyl-2-methyleneindoline within the voids of NaY zeolite gives rise to a product distribution characteristic of the concurrent operation of two different reaction mechanisms involving electron transfer and acid catalysis. In the latter case, formation of the corresponding product requires a hydride donor species that arises in the electron transfer pathway. Our report constitutes the first example establishing a connection between the products of these two different mechanisms.

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Notes and references

† Adsorption of indoline (Aldrich) within NaY (P.Q. Industries), was accomplished by heating at reflux temperature under magnetic stirring a suspension of NaY zeolite (1 g) previously dehydrated (500 °C, 5 h) in a solution of indoline **1** (100 mg) in CH₂Cl₂ (25 ml) for 4 h. At the end of the reaction the solid was filtered off, and Soxhlet extracted with CH₂Cl₂. The combined CH₂Cl₂ supernatant and extraction liquor was analysed by GC and GC-MS.

‡ Residual amounts of water interact with the formed cation decreasing the process selectivity.

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