Generation of stable and persistent carbocations from 4-vinylanisole within zeolites

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Stable and ultrastable carbocations from 4-vinylanisole are spontaneously generated within zeolites; these reactive intermediates are stable for several weeks within the confined environments of zeolites.

Spontaneous generation of long-lived organic cation radicals on the surfaces of zeolites has been known for over three decades.[1] However, only during the last few years has this phenomenon been widely recognized and the technique has been developed into a routine laboratory tool to generate stable cation radicals.[2,3] Simultaneous formation of carbocations may occasionally complicate the characterization of organic cation radicals within zeolites. This discrepancy prompted the present investigation. Our efforts to characterize stable reactive intermediates generated by inclusion of 4-vinylanisole within a number of zeolites are presented here. The behavior of 4-vinylanisole is typical of the many styrenes we have investigated. Persistent carbocations are formed more readily than cation radicals in all these cases.

Inclusion of 4-vinylanisole into activated Na ZSM-5 (Si/Al ≈ 15, the PQ Corporation-CBV 3010; Si/Al $\approx$ 25, Chemie Utikon) turned the zeolite blue–purple, as reported by Pollak *et al.*[4] The diffuse reflectance spectrum of the purple solid displayed in Fig. 1 consists of three maxima (*ca.* 280, 580 and *ca.* 640 nm). Of these the short-wavelength absorption is due to 4-vinylanisole. The appearance of an intense red–violet color and a visible absorption (*ca.* 580 nm) were general within a number of zeolites (Ca Y, H Y, Na omega-5, Na ZSM-11 and Na-beta). Of the zeolites examined, only Na X was totally inert. The appearance of a maximum at 640 nm was unique to ZSM zeolites. In no other zeolites was this peak recorded. The absorption spectrum of the 4-vinylanisole radical cation in solution consists of two maxima, one in the UV and the other in the visible region.[5] Close examination of the spectrum recorded for zeolite samples revealed that the absorption in the UV range (340–380 nm) in solution, was absent. To be sure that the zeolites do not influence the electronic transitions, the diffuse reflectance of the 4-vinylanisole radical cation included within Na Y was recorded by generating such a species by photoionization. The spectrum of such a generated 4-vinylanisole radical cation within Na Y was similar to that in solution. This indicated to us that no stable radical cation of 4-vinylanisole is generated under our conditions.

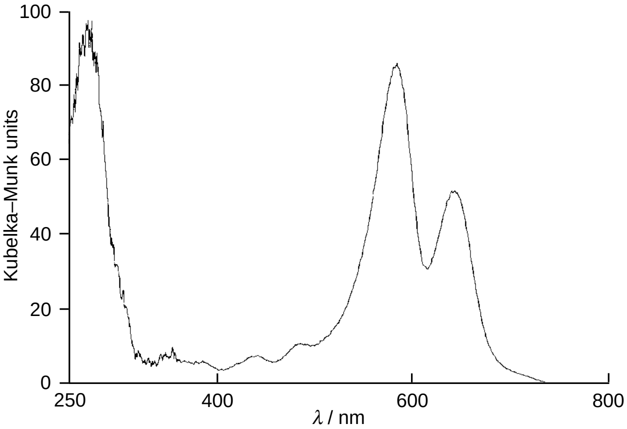


Fig. 1 Diffuse reflectance spectrum of 4-vinylanisole upon inclusion in Na ZSM-5 (Si/Al ≈ 25)

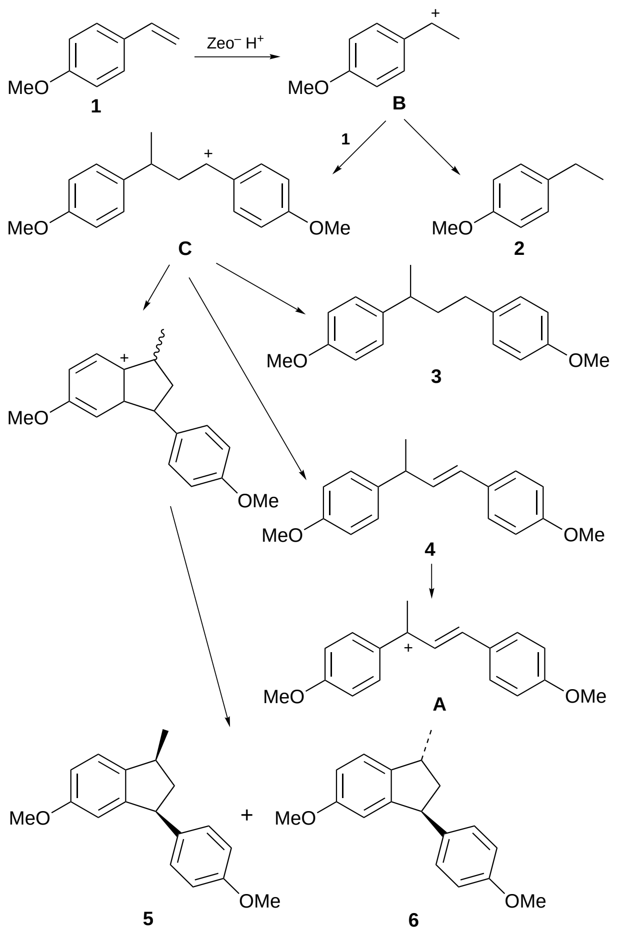
Extraction of the red–violet zeolite with either CH_2Cl_2 or tetrahydrofuran–H_2O gave several products. The yields of products in various zeolites are summarized in Table 1. Since the total isolated yields of the products and the reactant after extraction amounted to *ca.* 90%, the species responsible for the red–violet color must be present only in small amounts within a zeolite. The formation of products **2**–**6** can be mechanistically rationalized on the basis of a primary step involving a proton transfer from the zeolite to 4-vinylanisole (Scheme 1). We believe that the acid sites, generated upon calcination, are directly involved in the formation of products **2**–**6**.[6]

Support for the involvement of the postulated reactive intermediates in Scheme 1 was obtained by recording the diffuse reflectance absorption spectrum of the colored zeolites. For example, activated Ca Y when dropped into a solution of 4-vinylanisole in hexane, developed a vibrant red–violet color. The diffuse reflectance spectrum of the solid zeolite sample presented in Fig. 2 consists of two broad absorption centered at 340 and 580 nm (note the absence of the transition at 640 nm). Of the two absorptions, the one at 580 nm was found to be permanent; the zeolite retained the red color and the absorption at 580 nm remained under all conditions including refluxing in HCl or NaOH solutions. The diffuse reflectance spectrum of the zeolite that has been extracted with a polar solvent did not show the absorption at 340 nm (Fig. 2). This leads us to suggest that an intermediate absorbing at 340 nm is responsible for the formation of products **2**–**6**. We attribute the absorption at *ca.* 340 nm to the carbocation(s) **B** and/or **C**. The absorption spectrum for the 4-methoxy phenylethyl cation has been reported in solution and that remarkably coincides with the

Table 1 Product distribution (%) upon inclusion of vinylanisole within zeolites

	Compound				
Conditions[a,b]	**2**	**3**	**4**	**5 + 6**	Conversion
Ca, Y, oven, 500 °C	22	36	37	6	> 80%
Ca Y, vac. line, 400 °C	10	78	6	6	> 90%
H Y, oven 500 °C	12	—	76	12	> 90%
ZSM-5, oven, 500 °C	4	—	5	65	> 90%
Na Y, oven, 500 °C	5	—	63	32	< 20%
Na X, oven, 500 °C	—	—	—	—	—

[a] Ca Y and H Y were prepared from Na Y obtained from Aldrich & Co; Na X was an Aldrich sample; Na Y received from Aldrich showed the most thermal reaction. Samples obtained from Zeolyst International (CBV-100) showed the least thermal reaction. [b] ZSM-5 samples were obtained from PQ Corporation and Chemie Utikon. Both samples showed similar behavior.



Scheme 1 Mechanism of proton-transfer mediated reactions within zeolites

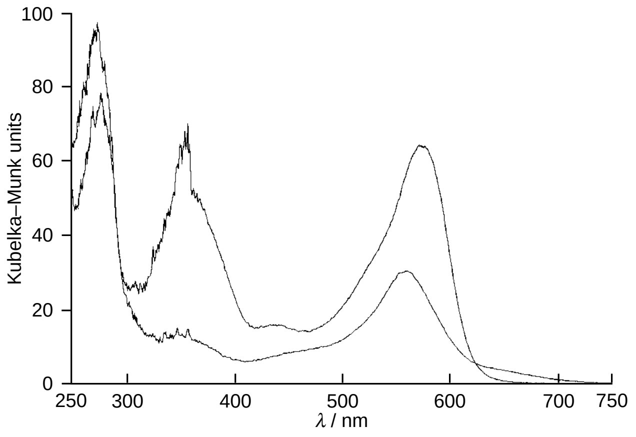
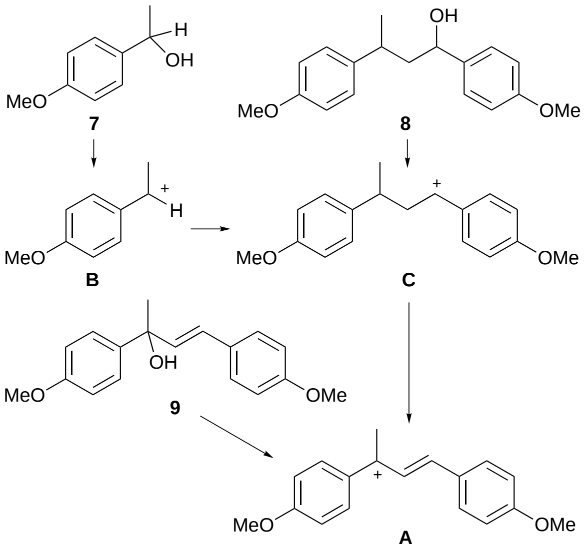


Fig. 2 Diffuse reflectance spectrum of 4-vinylanisole upon inclusion into Ca Y. The spectrum with two maxima is before washing and that with one maximum is after washing.

absorption maximum observed in zeolite.[7] We propose that the absorption at *ca.* 580 nm is due to the persistent carbocation **A** shown in Scheme 1. This suggestion is consistent with the expected absorption for the 1,3-diphenyl propenyl cation.[8]



Scheme 2 Generation of carbocations from the corresponding carbinols

Support for the above assignment was obtained by generating the same carbocations from an independent source, from carbinols **7**, **8** and **9** (Scheme 2). Addition of activated Ca Y, H Y and Na ZSM-5 to hexane solutions of **7**, **8** and **9** resulted in an immediate development of a bright red–pink color. The diffuse reflectance spectrum, independent of the carbinol, possessed absorptions at 580 nm, identical to the one obtained when 4-vinylanisole was included into these zeolites. This suggested to us that independent of the source, within a zeolite, the cations **B** and **C** readily transform themselves into the persistent carbocation **A**.

It is clear from the above presentation that zeolites, when properly prepared, can generate and stabilize 'reactive' intermediates from neutral molecules. On the basis of the behavior of 1,2-diarylethylenes which yield stable cation radicals, we had expected the formation of cation radicals from these systems as well.[3] It is surprising to note that 1-arylethylenes yield persistent carbocations.[9] At this stage the origin of such a difference is not obvious.

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Footnote and References

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