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Carbenium Ions Generated upon Adsorption of 4-Methoxystyrenes onto Acid Zeolites. A Kinetic Study

Vicente Fornés, Hermenegildo García,* Vicente Martí, Lorenzo Fernández

Instituto de Tecnología Química CSIC-UPV, Universidad Politécnica de Valencia, Apartado 22012, 46071-Valencia, Spain; e-mail address: hgarcia@vega.cc.upv.es

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Abstract. Adsorption of vinylanisole and *trans*-(4-methoxyphenyl)-1-propene into HY, Hß and HZSM-5 allows us to detect the corresponding substituted 1,3-bis(4-methoxyphenyl)-1-propylium (**2**), 1-(4-methoxyphenyl)-6-methoxy-1-indanylium (**5**) and 1,3-bis(4-methoxyphenyl)-2-propen-1-ylium (**8**) cations as reactive intermediates. The kinetics can be followed by conventional spectrophotometers. Cation **2** appears as the shorter lived species, decaying in hours for the HY sample and within days when embedded in HZSM-5 zeolite. Cyclic indanyl cation **5** shows a lifetime much longer than **2**. A growth of **8** concomitantly with the decay of **2** has been also observed. This has been taken as a proof of a hydride transfer from neutral 1,3-bis(4-methoxyphenyl)-1-propenes (the corresponding acyclic dimers observed as products) as donors to cations **2** as acceptors leading to **8**.

INTRODUCTION

Carbenium ions are among the most important reaction intermediates in Organic Chemistry and their study under a variety of conditions and media constitutes a topic of continuous interest.[1] Zeolites are a large family of natural and synthetic crystalline, microporous aluminosilicates.[2,3] Their internal voids formed by channels and cavities of molecular dimensions contain a variable number of charge-balancing cations to compensate the negative charge borne by the lattice. These microporous solids have been found to be a very convenient medium to generate, embed and stabilise positively charged organic species. We have been recently studying the species generated upon incorporation of vinylanisole (**1a**) into acid zeolites.[4] By a combination of diffuse reflectance spectroscopy (DR) and product studies we have been able to characterize the formation of 1,3-bis(4-methoxyphenyl)-1-butylium (**2a**), 1-(4-methoxyphenyl)-6-methoxy-3-methylindan-1-ylium (**5a**) and 1,3-bis(4-methoxyphenyl)-2-buten-1-ylium (**8a**) cations. This is in contradistinction with a related precedent assigning the color developed after adsorption of **1a** on acid zeolites to $(\mathbf{1a})^{\bullet +}$ radical cation.[5] Furthermore, the carbenium ion or radical cation nature of the intermediates generated upon adsorption of arylolefins onto acid zeolites is a matter of much current interest.[6,7]

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Herein we report on the kinetics and transformation among the cations **2**, **5** and **8** determined by conventional diffuse reflectance spectroscopy. In previous reports, we have been able to characterise by spectroscopic means the formation of xanthylium,[8-10] pyrylium,[11] tritylium[12] and α,ω-diphenyl substituted allyl[13] cations as persistent, indefinetely stable species within the zeolite micropores. For other much less stable cations we have established their generation and disappearance on the submillisecond time scale by means of time resolved techniques.[14,15] In the present case, we have observed that the decay of the species derived from 4-methoxystyrenes **1a,b** takes place in hours or days and, therefore, they can be conveniently followed by using a conventional spectrophotometer.

RESULTS AND DISCUSSION

For the present study, we used three different zeolites in their H^+-form, namely, HY (Si/Al 17), Hß (Si/Al 13) and HZSM-5 (Si/Al 27). Adsorption was carried out by stirring, at 80 °C, isooctane solutions of 4-methoxystyrenes **1** in the presence of thermally dehydrated samples (500 °C, overnight). The resulting highly colored solids were outgassed at room temperature under 10^{-1} Torr for 1 h. The samples placed in a cell were stored by the open air, while diffuse reflectance (DR) spectra were periodically recorded. The spectra, plotted as the inverse of the reflectance (1/R), recorded upon adsorption of **1a** in HY at different times after preparation are presented in Figure 1A.

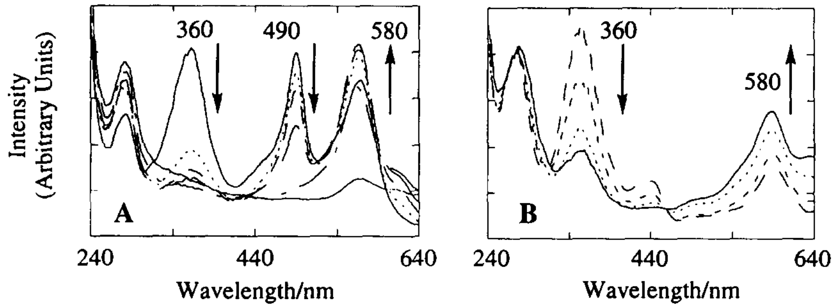
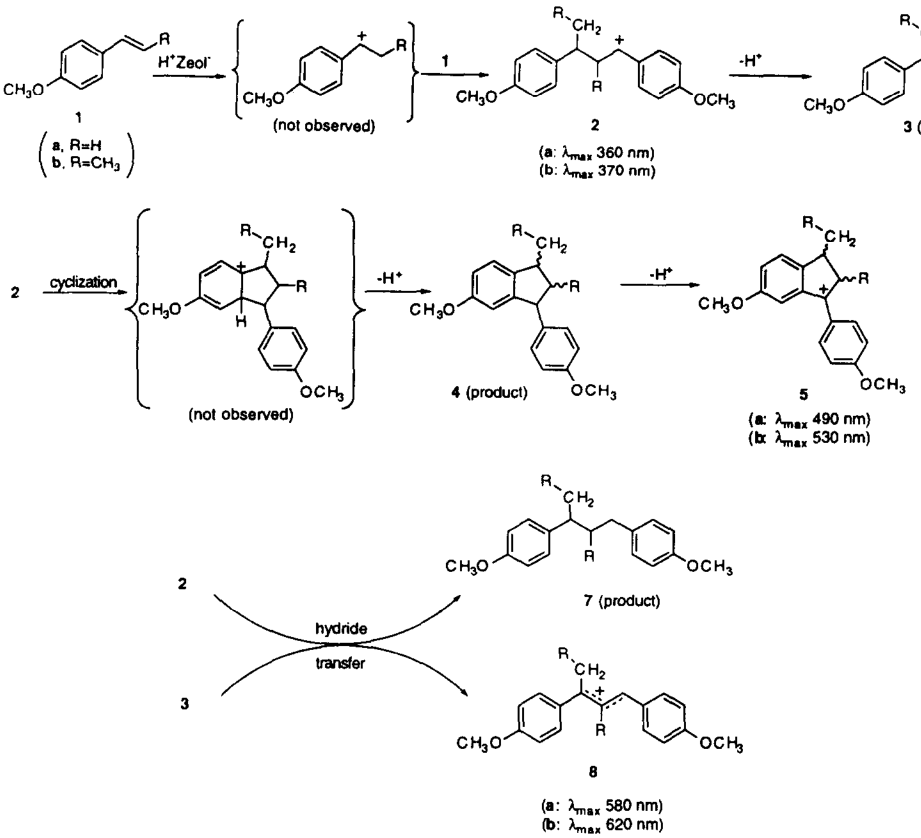


Figure 1. DR spectra (taken every hour) of **1a** adsorbed onto **A**) HY zeolite and **B**) HZSM-5, showing the kinetic of disappearance and growing of the different intermediate species. For assignment see Scheme 1.

The spectra show three characteristic absorption bands at 360-nm, 490-nm and 580-nm corresponding to the benzylic **2a**, indanyl **5a** and allylic **8a** cations, respectively.[4] The most remarkable fact is the rapid decay of the band corresponding to **2a**, which completely vanishes in HY 90 min after the initial scan. This decay is accompanied by an increase in the intensity of the absorption corresponding to the allyl cation **8a**. This behaviour lends support to the proposed reaction mechanism outlined in Scheme 1. According to it, **8a** would be derived from the open dimer **3a** by a hydride transfer to cation **2a**. The higher stability of the resulting allylic cation **8a** compared to **2a** would be the driving force for this process. It has to be remarked that open and cyclic dimers (**3a**+**4a**) along with appreciable amounts of 1,3-dianisylbutane (**7a**) have been previously observed as the final reaction products upon incorporation of **1a** into acid zeolites.[4]

However, inspection of the kinetics shows that the decay of **2a** is faster than the growth of **8a**. This data indicates that other processes besides the formation of **8a** are taking place after the disappearance of **2a**. Among other possibilities, cyclization to the indanic cation and capture of **2a** by water from the ambient moisture (not shown in Scheme 1) would justify that the decay of **2a** does not fit with the growth of **8a**.

Worth noting is the influence of the void dimensions of the zeolite in the lifetime of cation **2a** (Figure 1B). We observed that while in the large spherical cages of HY zeolite (1.3 nm of diameter) **2a** disappears within hours, the kinetics of disappearance of **2a** is remarkably much slower for the ZSM-5 zeolite (channels of 0.54 nm). This reflects the more severe geometric restrictions imposed by the pentasil framework that hinders the decay of **2a**.



Scheme 1.

As it is inferred from the previous Figure, it is clear that the ratio between the involved reaction intermediates changes during the time elapsed from the preparation. But the ratio between intermediates **2a**, **5a** and **8a** at the starting time also depends on the zeolite and particularly on the incorporation protocol. By increasing up to 12 h the adsorption time of **1a** in HY at reflux of hexane, spectra shown in Figure 2A were recorded. Under these conditions, the cyclic dimer **4a** is the major product in the organic phase, while the zeolite exhibits as the most intense band that corresponding to carbenium ion **5a**. This allowed us to follow conveniently the disappearance kinetics of **5a** and compare them to that of **2a** (Figure 2B).

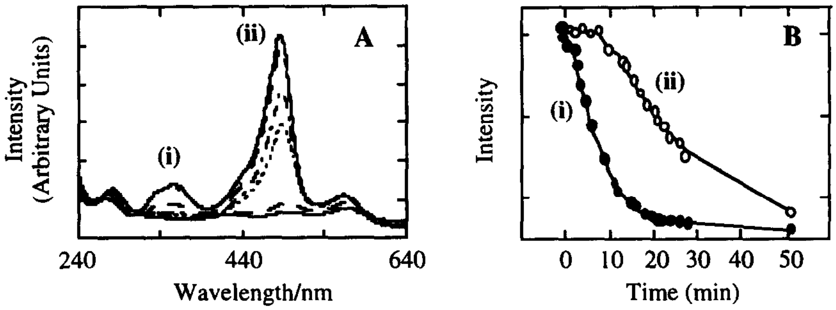


Figure 2. A) DR (1/R) of **1a** adsorbed onto HY zeolite at reflux of hexane. B) Normalized decay profiles of bands (i) and (ii) of Figure 2A.

In agreement with the proposed Scheme, no growth of **8a** was observed during the decay of **5a**. This has to be due to the absence of the acyclic unsaturated dimer **3a** which is the precursor of **8a**. Cyclization of the open dimer **3a** to the indanic dimer **4a** in the presence of HY zeolites has been established for related styrene derivatives.[16,17]

This study was extended to *trans*-(4-methoxyphenyl)-1-propene **1b**. As expected, the reactivity of **1b** upon adsorption on acid zeolites followed the same reactive pattern outlined in Scheme 1. In spite of the lower redox potential of **1b** (E^{ox} =1.3 V vs SCE) compared to **1a** (E^{ox} =1.4 V vs SCE)[18] and a previous report of the generation of $(\mathbf{1b})^{+\cdot}$ on HY based on the observation of the coloration of the zeolite,[5] no evidences for radical cation generation could be obtained by DR. The only products observed after extraction of the solids were the corresponding dimers **3b** and **4b**, whose structures are indicative of an acid-catalyzed reaction involving carbenium ions intermediates as those proposed in Scheme 1. The stereochemistry of **4b** was found to be *trans, trans* based on the coupling constants. DR spectra of the zeolites after incorporation of **1b** exhibit peaks at 370, 530 and 620-nm attributables to carbenium ions **2b**, **5b** and **8b**, respectively. Some selected examples are shown in Figure 3. Notably, the decay of **2b** in ZSM-5 was slower than that of **2a** and the exchange between

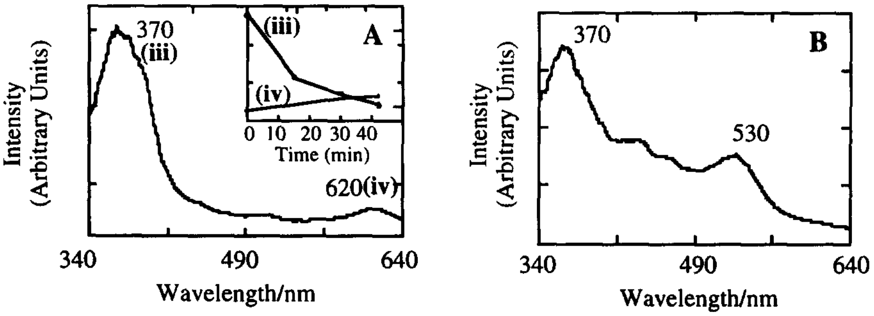


Figure 3. A) DR (1/R) of **1b** adsorbed onto HZSM-5 zeolite at reflux of isooctane (The inset shows the decay and growth profiles of bands **iii** and **iv**). B) DR (1/R) of **1b** adsorbed onto HY zeolite at reflux of isooctane.

cation **2b** (decaying) and **8b** (growing) occurred in a lesser extent than for the intermediates derived from **1a**. We rationalize these facts as reflecting the somewhat bigger dimensions of the intermediates derived from anethole as compared to those of *trans*-(4-methoxyphenyl)-1-propene, that would hinder bimolecular processes as those proposed in Scheme 1.

Comparing the decays of intermediates **2** and **5**, it has been measured that **5** decays much more slowly than **2** under identical conditions. The higher stability of five membered ring cations have also been experimentally established. In fact, in related work dealing with styrene dimerization into acid zeolites by ^{13}C-NMR using ^{13}C-labelled compounds, cations analogous to **5** were the only species detected.[19]

On the other hand, a comparison of the decay of **5** and **8** in HY establishes that they are consecutive. As Figure 1A shows, no decay of **8a** occurs until **5a** has completely disappeared. This fact can be rationalized assuming that both intermediates are decaying by reaction with ambient moisture. The quenching rate constant for the reaction of **5** with H_2O must be much higher than that for the reaction with **8a**.

In conclusion, kinetics of cations **2**, **5** and **8** generated upon adsorption of 4-methoxystyrenes **1a,b** into acid zeolites can be conveniently followed by routine DR spectroscopy. Carbenium ions rather than radical cations are detected in this case as reaction intermediates. The lifetime of these species increases from benzylic cation **2** to indanyl **5**, being the allyl cation **8** the longest lived of the series. A hydride transfer from the open dimer **3** to cation **2** has been established as the most likely mechanism for the generation of **8**. The present report shows the potential of zeolites as solid matrices to gain insight on the chemical reactivity of organic carbocations.

EXPERIMENTAL

HY was obtained by steam dealumination at 300°C of the previously NH_4^+-exchanged NaY zeolite (Union Carbide SK-40, Si/Al 2.6); the Si/Al ratio measured by chemical analysis was 15.[6] Hβ was prepared by thermal decomposition (500°C, N_2 stream, 2 h) of an as-synthesized sample containing tetraethylammonium template according to reported procedures.[6] ZSM-5 was synthesized following the patent literature and calcined at 550 °C under N_2 to decompose the tetrapropylammonium template, forming the protonic ZSM-5 zeolite.[6]

Adsorption of 4-methoxystyrenes (40 mg) was carried out by stirring at room temperature an isooctane solution (50 ml) in the presence of dehydrated (500 °C, overnight) zeolites (1.00 g) for 2 h. DR spectra were recorded in a Shimadzu UV-2101 PC scanning spectrophotometer using an integrating sphere. For product studies, the solids were submitted to continuous solid-liquid extraction in a micro-Soxhlet equipment using CH_2Cl_2 as solvent. The liquid phase was analyzed by GC (Hewlett-Packard 5890 provided with a 25 m capillary column of 5 % phenylmethylsilicone), GC-MS (Varian spectrometer with the same column and conditions as GC) and GC-IR (Hewlett-Packard 5988A same column and conditions as GC with an 5965 A infrared detector). Isolation of pure dimers was accomplished by column chromatography using silica gel (Merck, 60 mesh) and a mixture as hexanes-dichloromethane (5:1) as solvent. ^{1}H and ^{13}C-NMR were recorded in $CDCl_3$ using a 300 MHz Varian Geminis spectrometer with a SAM work station. Chemical shifts are reported as δ values (ppm) using TMS as internal standard. Mass spectra were indicated as m/z ratios and relative abundances (percentages, in brackets) are given only for the main peaks. Compounds **3a** and **4a** have been previously reported.[4,20]

Spectroscopic data of the new compounds: **1,3-Bis(4-methoxyphenyl)-2-methyl-1-pentene (3b)**: HRMS calculated for $C_{20}H_{24}O_2$ (M^+) 296.17763, found 296.17770; MS (m/z): 296 (60), 267 (15), 189 (30), 121 (100); ^{1}H-nmr ($CDCl_3$): 0.84 (t, J=7.4Hz, 3H), 1.57 (d, J=0.9Hz, 3H), 1.7 (m, 2H), 3.1 (t, J=7.5Hz, 1H), 3.73 (s, 6H), 6.35 (m, 1H), 6.8 (m, 4H), 7.1 (m, 4H); ir (cm^{-1}): 3005 (w), 2941 (w), 2882 (w), 1606 (w), 1509 (s), 1247 (s), 1174 (s), 1040 (w).

***Trans,trans*-3-ethyl-6-methoxy-1-(4-methoxyphenyl)-2-methylindane** (**4b**, single peak by GC): HRMS calculated for $C_{20}H_{24}O_2$ (M^+) 296.17763, found 296.17900; MS: 296 (100), 267 (25), 109 (60), 121 (70); ^{1}H-nmr ($CDCl_3$): 0.99 (t, J=7.6Hz, 3H), 1.15 (d, J=6.6Hz, 3H), 1.84 (m, 2H), 2.02 (m, 1H), 2.62 (dt, 1H, J_1=5.4 Hz, J_2=9.3), 3.67 (d, 1H, J=9.9Hz), 3.69 (s, 3H), 3.83 (s, 3H), 6.89 (m, 3H), 7.11 (m, 4H). ir (cm^{-1}): 3071 (w), 2963 (s), 2844 (w), 1608 (w), 1510 (s), 1490 (s), 1240 (s), 1247 (s), 1177 (w), 1037 (w).

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