ORGANIC
LETTERS

1999
Vol. 1, No. 3
531−534

Absolute Rate Constants for S_N1-like Ionization Reactions in Zeolites: Determination of Zeolite Ionizing Power

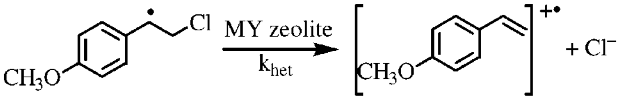
Wendy Ortiz, Frances L. Cozens,* and Norman P. Schepp

Department of Chemistry, Dalhousie University, Nova Scotia, Canada, B3H 4J3

fcozens@is.dal.ca

Received June 10, 1999

ABSTRACT



A *kinetic* probe molecule has been developed to investigate the absolute ionizing power of cation-exchanged (LiY, NaY, KY, RbY, and CsY) Y-zeolites. The probe, the 2-chloro-1-(4-methoxyphenyl)ethyl radical, was generated within the supercages of MY upon laser photolysis of 2-chloro-1-(4-methoxyphenyl)ethyl acetate under both dry and hydrated conditions. The ionizing power of the cation-exchanged Y-zeolites depends on the nature of the counterion and increases upon going from CsY to LiY. In addition, the ionizing powers of the dry zeolites are weaker than that of neat water and are more similar to water/methanol mixtures containing from 30% to 70% water. A significant reduction in the absolute ionizing ability of the zeolite was found when the zeolite was hydrated by the coadsorption of water.

Zeolites are microporous crystalline aluminosilicate materials made up of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra where every aluminum present in the framework carries a net negative charge that must be balanced with a charge-balancing cation.[1,2] The tetrahedra are arranged to give zeolites an open framework structure consisting of cavities and pores that readily accept organic compounds. The internal properties of zeolites and their effect on the chemistry of incorporated guest molecules have been the subject of extensive studies.[3−8] One well-documented property of their internal voids is the ability to support and promote charge separation reactions such as, for example, oxidation of alkenes to radical cations[9−11] and bond heterolysis of alkyl halides to carbocations.[12,13] To fully understand these reactions taking place within zeolites, it would be useful to have quantitative information concerning the ionizing ability of various zeolites, especially in comparison to that of common solvents such as water or alcohols. For example, with respect to bond heterolysis reactions, knowing where the ionizing power of zeolites ranks on scales that are commonly used to represent the ionizing power of solvents and solvent mixtures, such as the Y scale,[14,15] would be useful in the further development of zeolites as host materials for organic reactions.[16]

In the present work, we focus on determining the ionizing power of various alkali metal cation exchanged Y-zeolites

---

(1) van Bekkum, H.; Flanigen, E. M.; Jansen, J. C. *Introduction to Zeolite Science and Practice*; Elsevier: Amsterdam, 1991.

(2) Breck, D. W. *Zeolite Molecular Sieves*; John Wiley and Sons: New York, 1974.

(3) Ward, J. W. *J. Catal.* **1968**, *10*, 34−46.

(4) Corma, A. *Chem. Rev.* **1995**, *95*, 559−614.

(5) Rao, V. J.; Perlstein, D. L.; Robbins, R. J.; Lakshminarasimhan, H. M.; Kao, H. M.; Grey, C. P.; Ramamurthy, V. *Chem. Commun.* **1998**, 269−270.

(6) Hattori, H. *Chem. Rev.* **1995**, *95*, 537−558.

(7) Lavelley, J. C.; Lamotte, J.; Travert, A.; Czyzniewska, J.; Ziolek, M. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 331−335.

(8) Ramamurthy, V. *Photochemistry in Organized and Constrained Media*; VCH: New York, 1991.

(9) Pitchumani, K.; Corbin, D. R.; Ramamurthy, V. *J. Am. Chem. Soc.* **1996**, *118*, 8152−8153.

(10) Cozens, F. L.; Bogdanova, R.; Régimbald, M.; García, H.; Martí, V.; Scaiano, J. C. *J. Phys. Chem.* **1997**, *101*, 6927−6928.

(11) Yoon, K. B. *Chem. Rev.* **1993**, *93*, 321−339.

(12) Murray, D. K.; Chang, J. W.; Haw, J. F. *J. Am. Chem. Soc.* **1993**, *115*, 4732−4741.

(13) Murray, D. K.; Howard, T.; Goguen, P. W.; Krawietz, T. R.; Haw, J. F. *J. Am. Chem. Soc.* **1994**, *116*, 6354−6360.

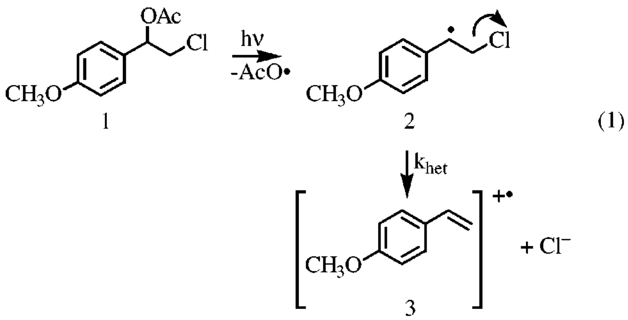
(14) Bentley, T. W.; Llewellyn, G. *Y_x Scales of Solvent Ionizing Power*; Taft, R. W., Ed.; J. Wiley & Sons: New York, 1990; Vol. 12, pp 121−158.

(15) Fainberg, A. H.; Winstein, S. *J. Am. Chem. Soc.* **1956**, *78*, 2770−2777.

(16) (a) Conceptually similar attempts have been made to place the acid strength of zeolites on scales such as the Hammett acidity function, H_o. (b) Haw, J. F.; Nicholas, J. B.; Xu, T.; Beck, L. W.; Ferguson, D. B. *Acc. Chem. Res.* **1995**, *29*, 259−267.

10.1021/ol990728o CCC: $18.00

by using nanosecond diffuse reflectance laser photolysis to measure quantitatively the absolute rate constants for the heterolytic cleavage of a carbon−leaving group bond, a reaction that is analogous to the rate-determining step of fundamental S_N1 reactions. Our approach involved the development of a *kinetic* probe that is specifically designed to undergo a rapid S_N1-like ionization reaction with a rate constant that is sensitive to its environment. The organic probe, the 2-chloro-1-(4-methoxyphenyl)ethyl radical **2**, eq 1, has several properties that make it ideal for examining the ionizing power of zeolites. The radical is readily generated photochemically from a precursor, 2-chloro-1-(4-methoxyphenyl)ethyl acetate **1**, which is thermally stable within zeolites.[17] In addition, the product formed upon ionization of the carbon−chlorine (C−Cl) bond is the 4-methoxystyrene radical cation **3**, which has distinctive absorption bands at 365 and 610 nm,[18] and is relatively long-lived within zeolites.[10] As a result, the ionization reaction is easily monitored using time-resolved diffuse reflectance spectroscopy. Furthermore, the reactivity of **2** in solution has recently been studied,[19] and these results can be applied to determine the ionizing power of zeolites relative to common solvents such as water and 2,2,2-trifluoroethanol (TFE). Finally, the size and shape of the probe molecule is similar to that of many classes of aromatic compounds that are currently being investigated within the cavities of zeolites.



Transient diffuse reflectance spectra generated upon 266-nm laser irradiation[20] of 2-chloro-1-(4-methoxyphenyl)ethyl acetate **1** under vacuum (10^{-3} Torr) conditions in dry and slightly hydrated[21] (5 ± 1 wt %) alkali metal cation exchanged zeolites[22] (LiY, NaY, KY, RbY, and CsY)[23] are in each case dominated by strong absorption bands at 365 and 610 nm. Figure 1 shows the spectra obtained after 266-nm laser excitation of **1** in slightly hydrated RbY as a representative example. The bands at 365 and 610 nm are identical to those for the 4-methoxystyrene radical cation generated previously in solution[18] and in zeolites,[10] and can therefore be confidently assigned to the 4-methoxystyrene radical cation **3**. The spectrum also shows the presence of a transient species at 310 nm, which is similar to that of radical **2** generated upon laser photolysis of **1** in solution.[19] The transient is completely quenched by oxygen, confirming its identity as radical **2**. In the absence of oxygen, the radical decays with a first-order rate constant of $6 \times 10^5\ s^{-1}$ which matches the growth of the absorption bands at 365 and 610 nm due to the formation of radical cation **3**. This indicates that the radical cation is generated by unimolecular heterolysis[24] of the C−Cl bond (eq 1). Support for this conclusion comes from the observation that purging the zeolite sample

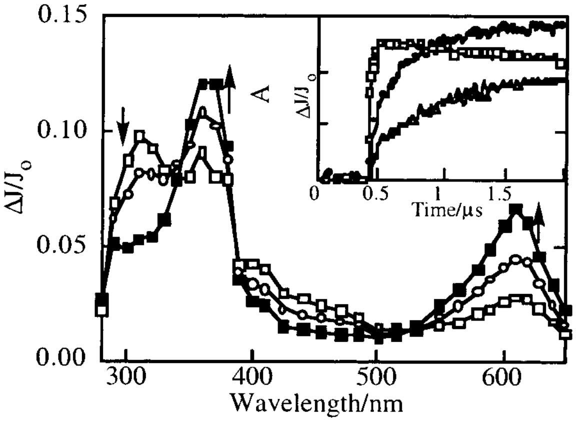


Figure 1. Diffuse reflectance spectra obtained after 266-nm laser photolysis of **1** in hydrated RbY under vacuum (10^{-3} Torr) conditions. Spectra were obtained 520 ns (□), 1.80 μs (○), and 12.9 μs (■) after the laser pulse. The inset shows the change in reflectance at 610 nm as a function of time upon 266-nm laser photolysis of **1** in dry NaY(□), RbY(●), and CsY(△) at 22 ± 1 °C.

---

[17] Continuous extraction of zeolites after incorporation of **1** using hexane as the solvent resulted in complete recovery of **1**.

[18] Schepp, N. P.; Johnston, L. J. *J. Am. Chem. Soc.* **1993**, *115*, 6564−6571.

[19] Cozens, F. L.; O'Neill, M.; Bogdanova, R.; Schepp, N. P. *J. Am. Chem. Soc.* **1997**, *119*, 10652−10659.

[20] Continuum Nd:YAG laser 266 nm, <8 mJ/pulse, <8 ns/pulse.

[21] Water was introduced by cooling the activated zeolites under atmospheric conditions for a specific time period (∼1 min) prior to sample incorporation.

[22] The Y-zeolites were activated at 400 °C for 24 h, except LiY which was activated at 500 °C. Substrate **1** was incorporated by stirring ∼3.5 mg of **1** dissolved in 20 mL of hexane with ∼350 mg of activated zeolite for 1 h. The suspension was centrifuged, and the isolated zeolite was washed with hexane and dried under vacuum for at least 12 h. The dried samples were then transferred into laser cells in a nitrogen glovebag to ensure that no water was coabsorbed during the transfer. The samples were then placed back on the vacuum line for at least 5 h and sealed under vacuum (10^{-3} Torr). The loading level was kept constant at one molecule of substrate for every 10 zeolite cavities.

[23] (a) The exchanged zeolites were prepared by stirring NaY with 1 M aqueous solutions of the corresponding chlorides (LiCl, KCl, RbCl, CsCl) at 80 °C for 1 h. The zeolites were then washed until no chlorides appeared in the washing water and dried under vacuum. This procedure was repeated three times and the zeolite was calcinated between washings. NaY has three types of exchangeable cations. The number of cations per unit cell of zeolite Y are 16 site I cations, 32 site II cations, and 8 site III cations. It is well established that only site II and III cations are accessible to guest molecules.[23b] The percent exchange was found to be 47% for LiY, 97% for KY, 44% for RbY, and 47% for CsY. It is known that for the larger cations such as Rb^+ and Cs^+ only the accessible Na^+ which occupy type II and type III sites can be readily exchanged.[1] Thus, the maximum cation exchange is ∼70%. Values of ∼50% exchange indicate that a small percentage of type II cations are not completely exchanged. The low percent exchange for the LiY sample used in this study is because hydrated Li^+ also does not readily exchange the type III cations. (b) Ramamurthy, V.; Turro, N. J. *J. Inclusion Phenom. Mol. Recogognit. Chem.* **1995**, *21*, 239−282.

[24] Direct detection of the formation of the radical cation from the initially generated radical unambiguously confirms that the ionization reaction is unimolecular and is not assisted by the zeolite framework through nucleophilic assistance.

with oxygen completely inhibits the formation of the radical cation. As the 4-methoxystyrene radical cation is largely unreactive toward oxygen,[18,25] the nonappearance of radical cation **3** under oxygen conditions[26] is best explained by a process in which the radical is trapped by oxygen more rapidly than ionization of the leaving group.

Kinetic traces for the C−Cl bond heterolysis as monitored by the formation of the radical cation at 365 or 610 nm were obtained in each of the different cation-exchanged Y-zeolites under dry and slightly hydrated conditions, and representative results are shown in Figure 1. In each case, the growths fit well to a first-order expression, giving the rate constants summarized in Table 1.[27]

Table 1. Rate Constants for the Heterolysis of Chloride from the 2-Chloro-1-(4-methoxyphenyl)ethyl Radical (22 ± 1 °C) in Dry and Hydrated Alkali Metal Cation Exchanged Y-Zeolites

M	k_{het},[a] s^{-1} dry	k_{het},[a] s^{-1} hydrated	field[b] V $Å^{-1}$	Y values (dry)[c]
Li^+	$>50 \times 10^6$	$>50 \times 10^6$	2.1	>4.7 (7.3)[d]
Na^+	$(39 \pm 2) \times 10^6$	$(12 \pm 3) \times 10^6$	1.3	4.5
K^+	$(9.9 \pm 0.5) \times 10^6$	$(1.8 \pm 0.5) \times 10^6$	1.0	3.3
Rb^+	$(4.0 \pm 0.6) \times 10^6$	$(0.6 \pm 0.1) \times 10^6$	0.8	2.5
Cs^+	$(1.8 \pm 0.3) \times 10^6$	$(0.6 \pm 0.1) \times 10^6$	0.6	1.8

[a] Average of 2−4 rate constants from time-dependent diffuse reflectance changes at 365 and 610 nm. [b] Electrostatic field strength in dry zeolites taken from ref 3. [c] Y values calculated from k_{het} (dry) values as explained in the text. [d] The Y value of 7.3 for dry LiY is estimated using the extrapolated value, $k_{het} = 1 \times 10^9$ s^{-1} (ref 27).

These rate constants provide interesting insights into the ionizing power of zeolites felt by the probe molecule. First, the rate constants for heterolysis are all quite large and illustrate very clearly that the environment within the zeolites is well-suited to support reactions involving transition states with significant charge-separation characteristics. In addition, the rate constants increase considerably as the size of the counterion decreases. This trend follows the increasing electrostatic field strength within zeolites as the size of the counterion decreases[28] (Table 1) and shows that electrostatic field strength is an important parameter in determining zeolite ionizing power. Our results also show that the rate constants are highly sensitive toward the hydration state of the zeolite. In particular, the ionization reaction in the slightly hydrated zeolites is consistently slower than in the corresponding dry zeolites. Presumably, the water molecules associate with the cations and attenuate the electrostatic field,[29] reducing the ionizing power and causing a decrease in the rate constant.

It is especially interesting to compare the results in the present work to the rate constants for the same heterolysis reaction measured previously[19] in solution. As shown in Figure 2, the rate constants in the dry zeolites range from 1.8×10^6 s^{-1} to 3.9×10^7 s^{-1} and are considerably smaller than the rate constant of $>1 \times 10^8$ s^{-1} for the same reaction in the highly ionizing solvents, water and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP). Thus, while these alkali metal cation exchanged Y-zeolites clearly support bond heterolysis reactions, their ionizing powers are at least 1 to 2 orders of magnitude *weaker* than those of strongly ionizing solvents. On the other hand, the zeolites possess an ionizing power 1 to 2 orders of magnitude *stronger* than that of neat methanol in which the heterolysis reaction of **2** is too slow ($<10^5$ s^{-1}) to observe. The ionizing power of NaY is also somewhat stronger than that of TFE, another common solvent that enhances solvolysis reactions, while KY has an ionizing power that is virtually identical to that of TFE.

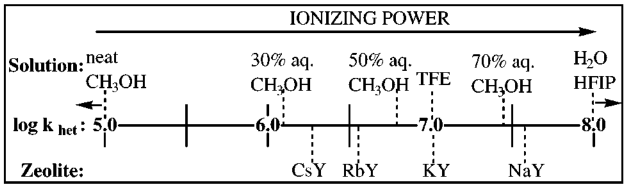


Figure 2. Schematic representation of the ionizing power of dry alkali metal cation exchanged Y-zeolites relative to the ionizing power of common solvents.

Estimates of Y values for the alkali metal cation exchanged zeolites can be made by placing the rate constants measured in the present work on the correlation line defined by the relationship between rate constants for heterolysis of **2** in methanol/water mixtures[19] and the corresponding Y_{AdCl} values.[14] The Y values range from 1.8 for CsY to 4.5 for NaY under dry conditions (Table 1), indicating that CsY has an ionizing power similar to that of 30% aqueous methanol, while the ionizing power of NaY is similar to that of 70% aqueous methanol.

Just as Y values in solution are not absolute and depend on a variety of factors, including the nature of the leaving group, the ionizing powers measured in the present work may not be universally applied to all substrates. Nonetheless, the fact that the structural features of the probe molecule which include an aromatic ring and chloride ion as the leaving group are common in organic systems indicates that our results should be relevant to a wide range of organic substrates. In addition, the close similarity between our

---

(25) It is well-documented that cationic species typically do not react with oxygen.

(26) The sample was purged with dry oxygen for 30 min prior to photolysis.

(27) Strong, long-lived ($\tau = 20$ ns) fluorescence at 365 nm was observed in LiY, making it impossible to monitor the real growth of the radical cation. However, at 610 nm, the growth was essentially complete within the laser pulse, which leads to a lower limit estimate of 50×10^6 s^{-1} for the heterolysis of the C−Cl bond of radical **2** in LiY. A much larger rate constant of 1×10^9 s^{-1} is predicted by extrapolation of the linear relationship between the log of the rate constants in dry CsY, RbY, KY, and NaY and electrostatic field strength.

(28) (a) Other factors could contribute to the observed reactivity trend such as enhanced electrophilic catalysis by the smaller alkali metal cations. However, while electrophilic catalysis by some metal cations such as Ag^+ and Hg^{2+} has been observed in solution for the ionization of chloride from alkyl chlorides, alkali metal cations show no such activity. (b) Clacke, G. A.; Taft, R. W. *J. Am. Chem. Soc.* **1962**, *84*, 2295−2303.

(29) Imanaka, T.; Okamoto, Y.; Takahata, K.; Teranishi, S. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 366−372.

observation that the internal cavities of zeolites possess an ionizing power that is analogous to solvents such as aqueous methanol and TFE, and conclusions from previous work using aromatic probes that zeolites are quite polar[30,31] with intracavity micropolarities close that of 50% aqueous methanol[32] and Taft α values similar to TFE[33] lends support to the generality of our results.

In conclusion, the novel kinetic probe developed in the present work allows a direct comparison to be made between rate constants for a fundamental S_N1-like reaction in zeolites and rate constants for the same reaction in solution. The results illustrate that the internal ionizing power of the alkali metal cation exchanged zeolites depends strongly on the nature of the counterion and the presence of water, and that zeolites possess a strong ionizing ability that is similar to solvents such as TFE and methanol/water mixtures. Further studies into the ionizing power of zeolites are currently in progress, especially with regard to the effect of probe structure and the nature of the leaving group.

Acknowledgment. This work was supported by the Natural Sciences and Engineering Research Council of Canada (NSERC) and Dalhousie University. We thank NSERC for a PGS (W.O.) and a WFA (F.L.C.).

OL990728O

---

(30) Liu, X. S.; Iu, K. K.; Thomas, J. K. *J. Phys. Chem.* **1989**, *93*, 4120−4128.

(31) Ramamurthy, V.; Sanderson, D. R.; Eaton, D. F. *Photochem. Photobiol.* **1992**, *56*, 297−303.

(32) Sarkar, N.; Das, K.; Nath, D. N.; Bhattacharyya, K. *Langmuir* **1994**, *10*, 326−329.

(33) Dutta, P. K.; Turbeville, W. *J. Phys. Chem.* **1991**, *95*, 4087−4092.