

Comparison of Activation Parameters for Ionization Reactions within Zeolites and in Aqueous Solution

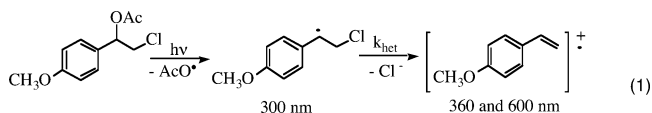
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Zeolites are microporous aluminosilicate materials made up of $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ tetrahedra arranged in a defined manner to give the material an open framework structure of cavities and pores. Each aluminum in the framework carries a net negative charge that must be balanced with a charge-balancing cation,¹ and the presence of these charged components produces a highly polar environment within the cavities of zeolites.^{2–6} As a result, these materials have a well-documented ability to promote charge separation reactions of guest molecules incorporated within the cavities,^{7,8} including heterolysis reactions of carbon–halide bonds that lead to the formation of carbocations.^{9,10}

This ability to support chemical reactions that produce charged intermediates is similar to the well-known ability of polar, ionizing solvents to support the same kinds of reactions.¹¹ However, given the considerable differences between the rigid structure of zeolites and the fluid, dynamic nature of liquid media, the factors responsible for rapid formation of charged intermediates in zeolites and those responsible for the same phenomena in polar solvents may be quite different. In an effort to probe these differences, we have carried out a study in which the activation parameters for the S_N1 -like ionization reaction of 2-chloro-1-(4-methoxyphenyl)ethyl radical to the 4-methoxystyrene radical cation, eq 1, are measured in both Y zeolites and in solution. The results presented here represent the first direct comparison of activation parameters for the same reaction measured in these two distinct reaction media.



We chose to study the ionization of 2-chloro-1-(4-methoxyphenyl)ethyl radical because accurate kinetics for the reaction, k_{het} , can be readily obtained using nanosecond laser photolysis both in zeolites¹² and in solution.¹³ Furthermore, the absolute rate constants for this reaction in both environments are very similar; thus the free energies of activation are also very similar, and attention can be focused on the differences in the entropies and enthalpies of activation.

The 2-chloro-1-(4-methoxyphenyl)ethyl radical was generated by photohomolysis of 2-chloro-1-(4-methoxyphenyl)ethyl acetate,^{12,13} eq 1, both in zeolites and in aqueous methanol at various temperatures. Rate constants for ionization of chloride ion were then determined by monitoring the time-resolved growth at 360 and 600 nm due to the formation of the 4-methoxystyrene radical cation, eq 1.

Several observations are consistent with the formation of the 4-methoxystyrene radical cation by ionization of chloride. Under all conditions, a band at 300 nm which is produced promptly within the laser pulse can be assigned to the 2-chloro-1-(4-methoxyphenyl)ethyl radical.^{12,13} This band decays with the same first-order rate

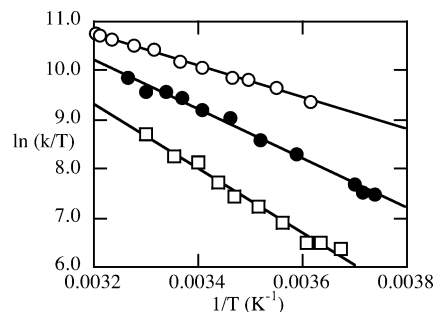


Figure 1. Temperature dependence of the ionization of chloride from the 2-chloro-1-(4-methoxyphenyl)ethyl radical in (●) dry KY, (□) hydrated KY, and (○) 50% aqueous methanol.

constant as the formation of the 4-methoxystyrene radical cation, which is consistent with the radical cation being generated from the radical. Furthermore, addition of oxygen completely suppresses the presence of the 300 nm band of the radical as well as the 360 and 600 nm bands of the radical cation. Because the 4-methoxystyrene radical cation is known to be relatively inert to oxygen,¹⁴ its absence from the spectrum under oxygen purged conditions is consistent with a mechanism for the formation of the 4-methoxystyrene radical cation upon photolysis of 2-chloro-1-(4-methoxyphenyl)ethyl acetate that involves rapid β -heterolysis of the photogenerated β -substituted arylethyl radical.^{12,13}

Figure 1 shows the temperature dependence of the rate constants for ionization in dry KY, hydrated KY, and in 50% aqueous methanol. A good linear relationship exists between the rate constant and the inverse of the temperature, and linear least-squares analysis leads to values for the entropy and enthalpy of activation, which were used to calculate the free energy of activation for the ionization reaction. The temperature dependence of the rate constants in other alkali-metal cation exchanged zeolites under dry vacuum and hydrated conditions, and in other methanol–water mixtures, were also analyzed in the same manner. All of the activation parameters obtained, as well as rate constants for ionization, are summarized in Table 1.

The data in Table 1 show that the reaction in aqueous methanol mixtures (entries 5–8) is characterized by low enthalpies of activation. These activation enthalpies are sufficiently low to overcome the unfavorable activation entropies, which in every case for the reaction in solution are fairly large and negative due to solvation. Thus, the rapid rate of ionization in solution is largely driven by favorable enthalpic factors, with the polarizing and solvating abilities of the aqueous methanol media providing the environment required for the reaction to proceed with low enthalpic barriers.

The values for the activation parameters (entries 1–4) measured in the dry zeolites lead to a somewhat different conclusion. In the zeolites, the activation enthalpies are still quite low, but considerably larger than those measured in solution. For example, ΔH^\ddagger in NaY

Table 1. Observed Rate Constants and Enthalpies, Entropies, and Free Energies (at 25 °C) of Activation for the β -Heterolysis Reaction of 2-Chloro-1-(4-methoxyphenyl)ethyl Radical in Dry and Hydrated Cation Exchanged Y Zeolites, and in Aqueous Methanol Mixtures^a

	conditions	k_{het} (s ⁻¹)	ΔH^\ddagger (kJ/mol)	ΔS^\ddagger (J/mol·K)	ΔG^\ddagger (kJ/mol)
1	dry NaY	2.1×10^7	39	22	32
2	dry KY	3.8×10^6	42	23	35
3	dry RbY	2.3×10^6	41	14	36
4	dry CsY	5.0×10^5	52	40	40
5	70% aq. CH ₃ OH	2.0×10^7	18	-45	31
6	60% aq. CH ₃ OH	1.4×10^7	25	-26	32
7	50% aq. CH ₃ OH	8.0×10^6	27	-21	33
8	30% aq. CH ₃ OH	2.2×10^6	28	-32	35
9	hydrated NaY	1.4×10^7	43	35	32
10	hydrated KY	1.1×10^6	50	42	37
11	hydrated RbY	3.2×10^5	58	53	42
12	hydrated CsY	2.6×10^5	64	73	42

^a Activation plots consisted of 8–10 rate constant measurements made over a 30–40 °C temperature range (ca. -5 to 35 °C). In each media, one of those rate constant measurements was obtained at a temperature between 22 and 26 °C, and that observed rate constant (k_{het}) is shown in the table. Errors (95% confidence limit) in activation parameters are ≤ 3 kJ/mol for ΔH^\ddagger , ≤ 3 J/mol·K for ΔS^\ddagger , and ≤ 4 kJ/mol for ΔG^\ddagger .

is 2-fold (or 21 kJ/mol) greater than that in 70% aqueous methanol, despite the rate constants for ionization in both cases being virtually identical. If unaccompanied by a favorable change in activation entropy, such a large increase in ΔH^\ddagger would cause a significant reduction in the rate constant for ionization. However, the magnitudes of the rate constants remain the same, primarily due to a reversal in the sign of the activation entropies. Thus, while values for ΔH^\ddagger in zeolites are still quite low, it is the large increase in ΔS^\ddagger values that provides the necessary driving force for the rate constants to maintain their large value.

The larger ΔH^\ddagger values measured in the zeolites seem contrary to a large body of data indicating that the polarity within zeolites is greater than that of 50% aqueous methanol.^{5,15,16} Thus, factors other than polarity may be responsible for the larger ΔH^\ddagger values measured in this work for ionization within the zeolites. In particular, unlike the situation in solution where the solvent molecules can readily adopt new orientations to accommodate the charges formed as the reaction progresses to the transition state, the rigid framework of the zeolites does not possess a dynamic “solvating” ability. This would ultimately lead to larger values for the enthalpy of activation. At the same time, the reduced ability to solvate negates the unfavorable entropy effects observed in solution; as a result, within the zeolites, the activation entropies favor ionization and nicely compensate for the less favorable enthalpy term.

The data in Table 1 also show that activation parameters are influenced by the composition of the zeolite. One clear trend is that the values for ΔH^\ddagger increase as the size of the metal cation increases from Na⁺ to Cs⁺ (entries 1–4). This trend is consistent with previous results showing that the electrostatic field strength

increases in the same direction¹⁷ and thus nicely illustrates the importance of the electrostatic field strength on determining ΔH^\ddagger . The larger ΔH^\ddagger values in hydrated zeolites (entries 9–12) as compared to dry zeolites also show that the strength of the electrostatic field is important; under hydrated conditions, water molecules bind strongly to the metal cations, thus reducing the strength of the electrostatic field.⁶

A potentially more dynamic environment might be present in the hydrated zeolites which could lead to a considerable decrease in the values for ΔS^\ddagger upon going from the dry to the hydrated zeolites. Instead, the values for ΔS^\ddagger tend to increase under hydrated conditions. This trend is consistent with the notion that water molecules are organized around the metal cations within the zeolite cavities.⁶ As the reaction progresses, the water-cation structure is disrupted by the presence of the charged transition state, resulting in an overall increase in disorder.

The results described in the present work highlight that both zeolites and aqueous media are fully capable of promoting charge separation reactions. However, the activation parameters reveal that the fundamental factors allowing for such rapid reactions are not the same in the two distinct media. In zeolites, the reaction takes advantage of the ability of the zeolite to provide favorable enthalpic and entropic conditions, while the reaction in aqueous methanol solutions relies entirely on charge stabilization factors.

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Supporting Information Available: Tables of rate constants as a function of temperature in the dry and hydrated alkali-metal cation exchanged zeolites, and in aqueous methanol (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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