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Transformations of Toluene Radical Cation in ZSM-5 and Silicalite*

M. V. Barnabas, D. W. Werst and A. D. Trifunac

Chemistry Division

Argonne National Laboratory

Argonne, IL 60439

ABSTRACT

Toluene radical cations produced by γ irradiation at 77 K in ZSM-5 and Silicalite undergo a reversible transformation to the norbornadiene radical cation at temperatures ≤ 150 K. The transformation occurs to a greater extent in the more polar zeolite (ZSM-5). The substrate concentration plays an important role. Toluene radical cations undergo ion-molecule reactions to give benzyl radicals at low substrate loading at temperatures > 200 K. At higher concentration, different adsorption sites become populated which allow the transformation to norbornadiene radical cation to take place.

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The toluene radical cation and the $C_7H_8^{+\bullet}$ family have been examined in the gas-phase and condensed-phase by several groups using various techniques¹⁻⁶. In this communication we show that the toluene radical cation generated by γ irradiation in two different zeolites undergoes a transformation to the norbornadiene radical cation. This reaction has not been observed previously, and its occurrence in zeolites is due in part to a matrix effect. Only toluene radical cations that occupy certain adsorption sites undergo transformation.

We have examined several members of the $C_7H_8^{+\bullet}$ family in zeolite matrices (ZSM-5) at low temperatures and have observed an unprecedented number of transformations,⁷ many of which were either observed or suggested in the gas-phase studies. Kelsall and Andrews² have shown that some rearrangements observed in the gas phase can be realized by photolysis in the low temperature matrix.

Figure 1 shows the EPR spectra observed in a polar zeolite, ZSM-5 (SiO_2/Al_2O_3 ratio of 170), with 0.3% w/w adsorbed toluene following γ irradiation at 77 K. The spectrum observed at 77 K (Figure 1a) is assigned to the toluene radical cation.⁸ At this substrate concentration, no transformation to the norbornadiene radical cation is observed. Increasing the temperature eventually promotes diffusion of substrate molecules, and encounters between radical cations and neutral substrate molecules result in ion-molecule reactions, generating the benzyl radical. The benzyl radical spectrum begins to replace the toluene radical cation spectrum above 200 K and is dominant at 220 K (Figure 1c).

Figure 2 shows the EPR spectra observed in the same zeolite with 1.5% w/w adsorbed toluene. The toluene radical cation is the dominant species observed at 50 K. The spectrum observed at 120 K is shown in Figure 2b and is due to a mixture of the toluene radical cation and the norbornadiene radical cation; the extent of conversion can be estimated to be 60%. This reaction is reversible below 150 K. Above 150 K the spectrum becomes complicated by neutral radical products of ion-molecule reactions as well as radical cations generated by transformation of the norbornadiene radical cation⁷.

The transformations of the toluene radical cation are shown in the following scheme:

Parallel experiments were carried out in Silicalite, which is isomorphous with ZSM-5 but is nonpolar (<0.01% Al_2O_3). The ion-molecule reaction between toluene radical cations and toluene molecules was observed, but the transformation to norbornadiene radical cation occurred to a lesser extent (<10% conversion) than in ZSM-5.

The predominance of the bimolecular reaction at low substrate concentration and the emergence of the unimolecular process only at higher concentrations, can be explained by the existence of at least two different adsorption sites in the zeolite. The active sites from which the transformation is allowed become populated to a significant degree only after the inactive sites are nearly saturated.

Zeolites can influence chemical processes *via* electronic interactions between substrate species and the cavity walls or by excluding molecules or molecular motions that exceed the space restrictions in size or amplitude. A geometry effect cannot be ruled out in this case since the bicyclic norbornadiene cation has a significantly different shape than planar toluene. However, the contrast in the extent of the transformation in ZSM-5 and Silicalite, which differ only in polarity, indicates that there must be a strong electronic influence.

As we have shown previously⁹, electronic matrix effects in zeolites can lead to the stabilization of different radical cation electronic states in different adsorption sites and perhaps lead to site-dependent reactivity. In the present example there is no direct spectroscopic evidence that

more than one electronic state of the toluene radical cation is involved. The occurrence of radical cation transformations requires that significant matrix stabilization of either the radical cation excited states or significant lowering of the reaction barrier must take place. Zeolite polarity, by analogy to polar solvent effects on ionic reactions in solution, can cause different stabilization of reactants and the transition state and lead to a change in the reaction barrier height.

The zeolite polarity is determined by the Si/Al ratio because each Al atom must be balanced by one positive charge. The positive charge is supplied by metal cations, Na^+ in the zeolites we used. Since an increase in polarity facilitates the transformation of the toluene radical cation, we surmise that the active site in ZSM-5 is more polar than the inactive site. Alternatively, ZSM-5 sites of equal polarity and different size may account for the difference reactivity. The lesser number of active sites in Silicalite are presumed to be due to the small amount of impurities that give rise to some polar sites.

Compared to other condensed-phase media that are capable of stabilizing radical cations, zeolites permit much wider variation of experimental conditions such as temperature, polarity and reaction volume. These fascinating microreactors are enabling unprecedented control of radical cation reactions. A comprehensive study of the $\text{C}_7\text{H}_8^{+\bullet}$ system in zeolites will be published elsewhere.

Figure Legends:

1. EPR spectra of the sample with 0.3%w/w toluene in ZSM-5 irradiated at 77K and observed at (a) 77K, and (c) 220K.
(b) and (d) are the simulations of the toluene radical cation with hyperfine couplings of 18.5G (3H) and 12.5G(H) and the benzyl radical with hyperfine couplings of 17G(2H), 6.6G(H), 5.5G(2H) and 2.2G(2H).⁸
2. EPR spectra recorded after γ -radiolysis at 77K:
(a) 1.5%w/w toluene in ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 170); recorded at 50K after sample was annealed 120K;

(b) 1.5%w/w toluene in ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 170); recorded at 120K;

(c) 0.15%w/w norbornadiene in ZSM-5($\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 400); recorded at 150K.

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(b)

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