11594 *J. Am. Chem. Soc.* **1995,** *117,* 11594−11595

Kinetic NMR and Density Functional Study of Benzene H/D Exchange in Zeolites, the Most Simple Aromatic Substitution

Larry W. Beck,[†] Teng Xu,[†] John B. Nicholas,[*,‡] and
James F. Haw[*,†]

Laboratory for Magnetic Resonance and Molecular Science
Department of Chemistry, Texas A&M University
College Station, Texas 77843
Environmental Molecular Sciences Laboratory
Pacific Northwest Laboratory, Richland, Washington 99352

Received July 17, 1995

Both theoretical calculations and kinetic measurements are important for the development or verification of a reaction mechanism. Nuclear magnetic resonance (NMR) studies of reactions on solid acids and bases, including zeolites,[1−3] metal oxides,[4] and metal halides,[5] have characterized persistent intermediates, and the range of these investigations has been extended by monitoring label scrambling.[6] However, there have been no detailed in situ NMR kinetic measurements. We have carried out the first such study, a detailed investigation of the H/D exchange reaction of benzene, which is the most simple example of the class of aromatic substitution reactions that includes important processes such as toluene alkylation. The results of theoretical and experimental investigations of H/D exchange in alkanes have led to mechanisms contrary to traditional views of acid catalysis,[7−12] as is the case here for aromatic substitution.

The theoretical calculations were done using density functional theory (DFT) as implemented in the program Dmol,[13] the BLYP[14,15] exchange-correlation functional, a double numerical polarized basis set,[16] and an XFINE mesh. The model[17] for the zeolite ($AlSi_2O_4H_9$) is taken from zeolite Y. We determined the minimum energy geometries for benzene, the zeolite, the van der Waals (VDW, Figure 1a) complex between benzene and the zeolite, and the transition state (TS, Figure 1b) for H/D exchange. In all cases we optimized the central AlO_2H of the zeolite model, while the rest of the atoms were held fixed in crystal positions. To determine the contribution of zero-point energy to the reaction barriers, we performed frequency calculations for both the VDW and TS geometries.

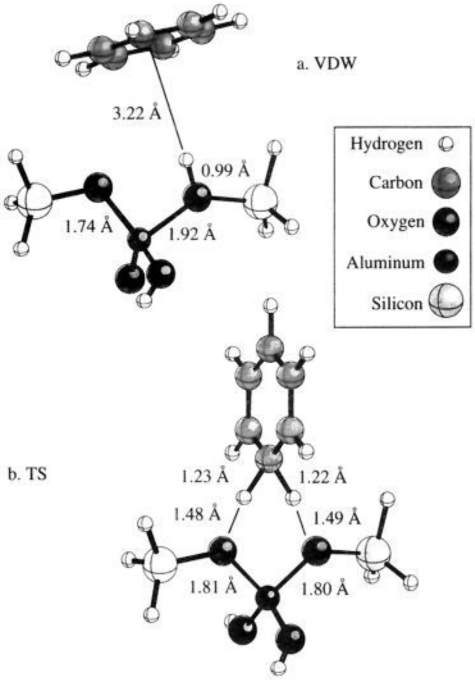

Figure 1. Optimized BLYP/DNP structures and selected bond distances: (a) van der Waals complex (VDW); (b) transition state (TS) for H/D exchange.

In the VDW complex benzene is η^6 coordinated to the acidic zeolite proton with an interaction energy of 1.3 kcal/mol. The calculated TS geometry corresponds to the asymmetric exchange of the hydrons (these calculations do not distinguish between isotopes). Although the TS resembles a benzenonium cation, the charge on C_6H_7 is only $0.56|e|$. In addition, the bond lengths between the exchanging hydrons and the carbon are $\approx$0.1 Å longer than in a free benzenonium cation. More importantly, the TS collapses to the VDW complex with no barrier; thus no stable benzenonium is involved. The energy barrier for H/D exchange, taken as the difference in total energy between the VDW and TS geometries, is 21.2 kcal/mol. Inclusion of the change in the zero-point energy lowers the theoretical barrier to 17.9 kcal/mol. Graphical analysis of the normal mode displacements verifies that an imaginary frequency (-423 cm^{-1}) corresponds to hydron exchange (the TS frequency calculation has more than one imaginary frequency because we constrain the geometry to that of zeolite Y).

Previous transition state calculations using DFT methods[18] suggested that the BLYP functional tends to underestimate reaction barriers, a deficiency which hybrid functionals (i.e., B3LYP[19]) that include the exact exchange appear to correct. To explore this possibility, we used Gaussian94[20] to obtain the single-point B3LYP/6-31G* energies at the BLYP/DNP geometries for the VDW and TS. The B3LYP/6-31G* energy barrier is 23.9 kcal/mol, which decreases to 20.6 kcal/mol when the

---

[*] Authors to whom correspondence should be addressed.
[†] Texas A&M University.
[‡] Pacific Northwest Laboratory.

(1) Haw, J. F.; Richardson, B. R.; Oshiro, I. S.; Lazo, N. D.; Speed, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 2052−8.

(2) Xu, T.; Haw, J. F. *J. Am. Chem. Soc.* **1994**, *116*, 10188−94.

(3) Aronson, M. T.; Gorte, R. J.; Farneth, W. E.; White, D. *J. Am. Chem. Soc.* **1989**, *111*, 840−6.

(4) Kheir, A. A.; Howard, T.; Haw, J. F. *J. Am. Chem. Soc.* **1994**, *116*, 10839−40.

(5) Xu, T.; Torres, P. D.; Beck, L. W.; Haw, J. F. *J. Am. Chem. Soc.* **1995**, *117*, 8027−8.

(6) Munson, E. J.; Xu, T.; Haw, J. F. *J. Chem. Soc., Chem. Commun.* **1993**, 75−6.

(7) Mota, C. J. A.; Martins, R. L. *J. Chem. Soc., Chem. Commun.* **1991**, 171−3.

(8) Mota, C. J. A.; Noguera, L.; Kover, W. B. *J. Am. Chem. Soc.* **1992**, *114*, 1121−2.

(9) Sommer, J.; Hachoumy, M.; Francois, G.; Barthomeuf, D. *J. Am. Chem. Soc.* **1994**, *116*, 5491−2.

(10) Sommer, J.; Hachoumy, M.; Garin, F. *J. Am. Chem. Soc.* **1995**, *117*, 1135−6.

(11) Kramer, G. J.; van Santen, R. A.; Emeis, C. A.; Nowak, A. K. *Nature* **1993**, *363*, 529−31.

(12) Kramer, G. J.; van Santen, R. A. *J. Am. Chem. Soc.* **1995**, *117*, 1766−76.

(13) DMol is sold by Biosym Technologies, San Diego, CA. Delley, B. *J. Chem. Phys.* **1990**, *92*, 508−17.

(14) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098−100.

(15) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−9.

(16) Delley, B.; Ellis, D. E. *J. Chem. Phys.* **1982**, *76*, 1949−60.

(17) (a) Sauer, J. *Chem. Rev.* **1989**, *89*, 199−255. (b) Haase, F.; Sauer, J. *J. Am. Chem. Soc.* **1995**, *117*, 3780−9.

(18) (a) Andzelm, J.; Sosa, C.; Eades, R. A. *J. Phys. Chem.* **1993**, *97*, 4664−9. (b) Barone, V. *J. Chem. Phys.* **1994**, *101*, 10666−76.

(19) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(20) Gaussian 94, Revision B.1: M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh, PA, 1995.

0002-7863/95/1517-11594$09.00/0

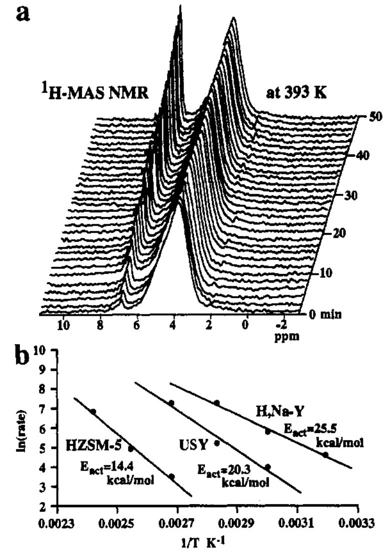

Figure 2. (a) Representative in situ kinetic study showing exchange between benzene-d_6 and zeolite NaHY at 393 K; 360-MHz ^{1}H magic angle spinning spectra acquired every 50 s over total measurement times of up to 1 h clearly showed the growth of the benzene signal at 7.0 ppm at the expense of the signal for the Brønsted site. (b) Arrhenius plots constructed from in situ kinetic studies at various temperatures for zeolites HZSM-5, USY, and NaHY.

zero-point energy corrections are included. While we expect that even higher levels of theory will alter the numerical result, the qualitative aspects of the reaction will not likely change.

Zeolite powders were activated in a variant of the CAVERN device[21] that permits adsorption of reagents onto an "ultra-shallow bed" (for uniform distribution) at reduced temperatures. Benzene-d_6 was adsorbed at temperatures well below the onset of isotopic exchange, and the sample was transferred into the MAS rotor, sealed, and then rapidly placed in a MAS probe. H/D exchange[22] was initiated by jumping the probe temperature to a final value typically between 333 and 393 K on a time scale usually much shorter than that required for the formation of a measurable ^{1}H signal for partially exchanged benzene. Figure 2 shows representative results for the case of a partially sodium exchanged HY zeolite (NaHY). Plots of integrated intensity of the benzene signal vs time are invariably linear over the first 5−10 min, and the initial slopes of such graphs are taken as the rates of H/D exchange. Since benzene is completely adsorbed at the loadings and temperatures used, and since mass transport is not required for a net increase in the benzene proton signal early in the reaction, the measured rates do not require correction for adsorption equilibria or diffusion. The experimental activation energies for benzene H/D exchange on various acidic zeolites (Figure 2) ranged between 14.4 and 25.5 kcal/mol, and the experimental value (20.3 kcal/mol) that most closely agreed with the 20.6 kcal/mol theoretical barrier was obtained on the zeolite (USY) most closely modeled by the cluster in Figure 1.[23]

These calculated structures in Figure 1 require that the equilibrium structure of benzene in the zeolite is a VDW complex rather than a benzenonium cation. Figure 3 reports ^{13}C MAS spectra of benzene in zeolite HY and in magic acid (HSO_3F/SbF_5). The NMR spectrum acquired at 83 K in frozen magic acid shows a static benzenonium cation, and a rapidly equilibrating benzenonium cation in the liquid at 233 K with a single exchange-averaged resonance at 146 ppm.[24] In zeolite HY, however, the isotropic ^{13}C shift (129 ppm) indicates negligible protonation over a wide range of temperatures. The spinning sidebands in the spectra acquired in the zeolite at low temperatures are indicative of restricted large amplitude reorientation of the C_6 axis of benzene.[25]

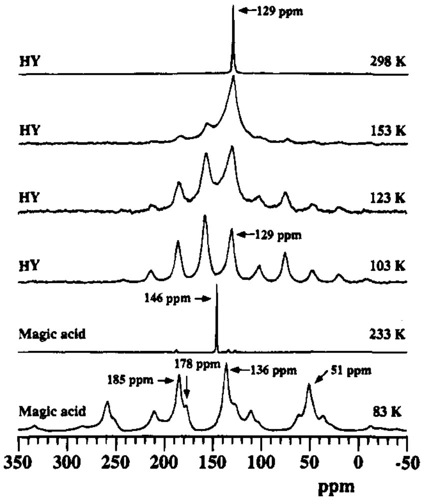

Figure 3. ^{13}C MAS NMR spectra of benzene-$^{13}C_6$ in zeolite HY (90.5 MHz, <0.1 equiv) or magic acid (75.4 MHz). A static benzenonium cation is seen in frozen magic acid at 83 K. Benzene shows no protonation shift in the zeolite, and the line shape reflects large amplitude reorientation. Chemical shifts of the isotropic peaks are indicated.

The transition state structure in Figure 1 has a strong resemblance to those determined for H/D exchange for methane by Kramer and van Santen[11,12] and for hydrogen by Evleth and co-workers.[26] The experimental and theoretical barriers reported for methane are ca. twice what we observe for benzene. The avoidance of a free cation even for the energetically less demanding reaction studied here suggests that free cations in acid catalysis by zeolites at low temperature may be the exception rather than the rule; indeed, the only such species observed spectroscopically have been exceptionally stable cations.[2,27]

Acknowledgment. Work at Texas A&M University is supported by the Basic Energy Sciences program of the U.S. Department of Energy (DE-FG03-93ER14354) and the National Science Foundation (CHE-9221406). J.B.N. is supported by the Advanced Industrial Concepts Division of the DOE Office of Energy and Efficiency under Contract No. 16696 and Laboratory Directed Research and Development funding provided by PNL. Computer resources were provided by the Scientific Computing Staff, Office of Energy Research, at the National Energy Research Supercomputer Center (NERSC), Livermore, CA. Pacific Northwest Laboratory is a multiprogram national laboratory operated by Battelle Memorial Institute for the DOE.

JA9523496

---

[21] Munson, E. J.; Murray, D. K.; Haw, J. F. *J. Catal.* **1993**, *141*, 733−6.

[22] For the first in situ NMR observation of H/D exchange for benzene in a zeolite, see: White, J. L.; Beck, L. W.; Haw, J. F. *J. Am. Chem. Soc.* **1992**, *114*, 6182−9.

[23] The zeolites used in this study were received from UOP Corp. and have previously been described by the authors. USY refers to Y-84, and NaHY refers to Y-64.

[24] For prior NMR investigations of benzenonium, see: (a) Olah, G. A.; Schlosberg, R. H.; Kelly, D. P.; Mateescu, G. D. *J. Am. Chem. Soc.* **1970**, *92*, 2546−8. (b) Olah, G. A.; Schlosberg, R. H.; Porter, R. D.; Mo, Y. K.; Kelly, D. P.; Mateescu, G. D. *J. Am. Chem. Soc.* **1972**, *94*, 2034−43. Calculations of the structure of benzenonium and the predicted NMR chemical shifts are given in the following paper: (c) Sieber, S.; Schleyer, P. v. R.; Gauss, J. *J. Am. Chem. Soc.* **1993**, *115*, 6987−8.

[25] For prior NMR investigations of benzene mobility in zeolites, see: (a) Wilhelm, M.; Firouzi, A.; Favre, D. E.; Bull, L. M.; Schaefer, D. J.; Chmelka, B. F. *J. Am. Chem. Soc.* **1995**, *117*, 2923−4. (b) Kustanovich, I.; Vieth, H. M.; Luz, Z.; Vega, S. *J. Phys. Chem.* **1989**, *93*, 7427−31. (c) Silbernagel, B. G.; Garcia, A. R.; Newsam, J. M.; Hulme, R. *J. Phys. Chem.* **1989**, *93*, 6506−11. (d) Zibrowius, B.; Bulow, M.; Pfeifer, H. *Chem. Phys. Lett.* **1985**, *120*, 420−3.

[26] Evleth, E. M.; Kassab, E.; Sierra, L. R. *J. Phys. Chem.* **1994**, *98*, 1421−6.

[27] Xu, T.; Haw, J. F. *J. Am. Chem. Soc.* **1994**, *116*, 7753−9.