The Nature of Species Formed from Allyl Alcohol on H-ZSM-5 Zeolite

Dan Fărcaşiu

Department of Chemical and Petroleum Engineering, University of Pittsburgh, 1249 Benedum Hall, Pittsburgh, PA 15261, USA

Contrary to a recent claim, no significant amount measurable directly by NMR of allyl cation at equilibrium is formed from allyl alcohol on H-ZSM-5.

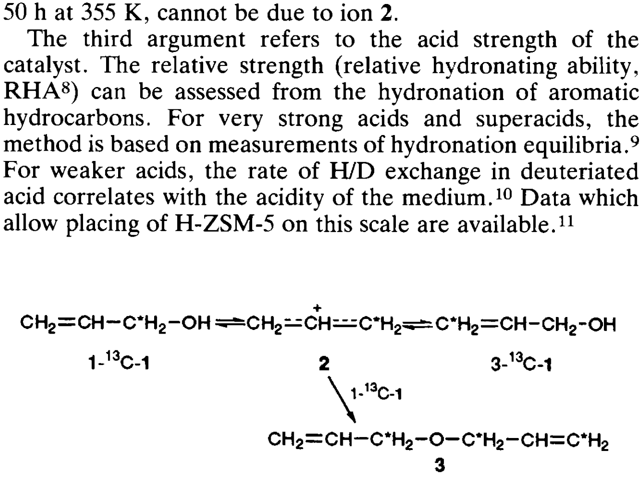
Two communications have reported on ^{13}C NMR spectroscopic studies *in situ* of the reaction of [1-^{13}C]allyl alcohol (1-^{13}C-**1**) on acidic zeolites. The first confirmed[1] the conversion on H-ZSM-5 to a mixture of hydrocarbons reported earlier,[2] but also found that on a solid of lower acidity label migration from C(1) to C(3) occurred first. This observation indicates reversible formation of the allyl cation **2** as an unstable intermediate (Scheme 1), which then reacts with another molecule of **1** to form diallyl ether **3** before transformation to hydrocarbon products. A concerted mechanism[3] for scrambling and formation of the ether by an S_N2 or S_N2' reaction appears less likely but it cannot be definitely ruled out.

In a subsequent study, prolonged heating of the mixture prepared at 85% acid site coverage with **1** led to the growth of a signal at δ_C 218, which was assigned to cation **2**.[4] This communication demonstrates that cation **2** could not have been formed in measurable quantities under these conditions and, therefore, the spectral features observed[4] had a different origin.

The first argument comes from a comparison of the two series of experiments with **1** on H-ZSM-5.[2,4] Isotope scrambling in **1** was observed[2] on a zeolite of low acidity (CsHX) and thus results from internal return of a tight ion pair.[5] At higher acidity (in H-ZSM-5), cation **2** was trapped by starting alcohol **1**, to form **3** (Scheme 1).[2] Mechanistically this reaction is either a rate-determining separation of the tight ion pair followed by reaction of **2** with **1**, or (more likely) trapping of **2** in the tight ion pair by **1**.[5] Upon longer heating, **1** and **3** were converted to hydrocarbons and carbonyl compounds.[2] It is at this stage that the signal at δ 218 assigned[4] to **2** developed. If this assignment were correct it would mean that the products (scrambled **1** and **3**) appear faster than the intermediate **2**. (Signals in that region of the spectra were seen in the other study[2] as well, but were given a different assignment.)

The second argument is one of thermal stability. The parent allyl cation **2** has not been obtained as a persistent[6] carbocation. The next homologue, but-1-en-3-yl cation, stabilized relative to **2** by a methyl group, could be prepared in FSO_3H–SbF_5–SO_2ClF (1 : 1) solution, but decomposed upon heating to 253 K.[7] The signal at δ 218, growing in intensity for 35 h at 325 K and then persisting for another 35 h at 325 K, and 50 h at 355 K, cannot be due to ion **2**.

The third argument refers to the acid strength of the catalyst. The relative strength (relative hydronating ability, RHA[8]) can be assessed from the hydronation of aromatic hydrocarbons. For very strong acids and superacids, the method is based on measurements of hydronation equilibria.[9] For weaker acids, the rate of H/D exchange in deuteriated acid correlates with the acidity of the medium.[10] Data which allow placing of H-ZSM-5 on this scale are available.[11]



Scheme 1

Attempts to prepare **2** as a long-lived species were unsuccessful even in 1 : 1 HF–SbF_5.[12] This acid is too strong to be investigated with aromatic hydrocarbons as bases. The significantly weaker[13] HF–SbF_5 (30 : 1) and HBr–$AlBr_3$ (4 : 1) still hydronate benzene fully.[9] The acid strength drops by another factor of ten in HF–TaF_5 (30 : 1); this mixture protonates benzene partially and toluene fully.[9a,b] Furthermore, the weak superacid[9d] trifluoromethanesulfonic acid, which has a lower RHA than HF–TaF_5 (30 : 1) by 11 orders of magnitude, does not hydronate toluene to any measurable extent at equilibrium.[14] We found, however that H/D exchange of toluene in CF_3SO_3D is very fast. Even at 200 K in SO_2 solution, all toluene was at least monodeuteriated in less than one minute. Less than complete exchange was obtained at this temperature and reaction time only when 1.3% D_2O was added to weaken the acid.†

Toluene also formed a 1 : 1 complex **4** with the acid sites of H-ZSM-5; recovery of toluene from a complex with D-ZSM-5 by heating to 400 K gave material 53% non-, 33% mono-, and 14% di-deuteriated; repetition of the experiment with the recovered acid gave a similar deuterium distribution in toluene (58 : 31 : 11%), demonstrating the presence of a large excess of deuterium on the solid.[11] If complex **4** were the Pfeiffer–Wizinger complex[9c] (arenium ion salt) the product would be less than 15% nondeuteriated, because the primary kinetic isotope effect is 6–9 : 1. Therefore, **4** is a weak π complex,‡ and deuteriation results from repeated exchange of largely non-hydronated toluene. Comparison of the extent of exchange with that obtained after a much shorter reaction time and at much lower temperature in CF_3SO_3D indicates that the strength of H-ZSM-5 is several orders of magnitude below the superacidic range. Such a medium could not stabilise persistent cations **2**.§

We conclude that the published spectrum was not that of **2**; its features can be accounted for by a mixture of **1** with its ethers (allyl and surface silyl), hydrocarbons, and carbonyl compounds.¶

Received, 22nd March 1994; Com. 4/01713G

Footnotes

† Experiments conducted by S. Sharma and J. Hutchison.

‡ The easy removal of toluene from **4** by pumping points to the same conclusion. Thus, benzene, 50% hydronated in HF–TaF_5, is extracted from the latter by pentane, whereas toluene, which is fully hydronated, is not extracted.[9b] Albeit there is no direct correspondence between volatility and extractibility, both processes require the presence of free base at equilibrium.

§ Likewise, tertiary alkyl cations can be generated in HF–TaF_5 (30 : 1)[15] whereas silyl ethers are formed on H-ZSM-5.[16]

¶ This work was supported by a grant (CTS-9121454) from NSF. The paper has benefited from the suggestions of a reviewer.

References

1 E. J. Munson, T. Xu and J. F. Haw, *J. Chem. Soc., Chem. Commun.*, 1993, 75.

2 G. J. Hutchings, D. F. Lee and C. D. Williams, *J. Chem. Soc., Chem. Commun.*, 1990, 1475.

3 R. L. Yates, N. D. Epiotis and F. Bernardi, *J. Am. Chem. Soc.*, 1975, **97**, 6615.
4 A. I. Biaglow, R. J. Gorte and D. White, *J. Chem. Soc., Chem. Commun.*, 1993, 1164.
5 D. Fărcaşiu, G. Marino, J. M. Harris, B. A. Hovanes and C. S. Hsu, *J. Org. Chem.*, 1994, **59**, 154.
6 D. Fărcaşiu, in *Nucleophilicity*, ed. J. M. Harris and S. P. McManus, American Chemical Society, Washington, 1987, ch. 20.
7 G. A. Olah and H. Mayr, *J. Am. Chem. Soc.*, 1976, **98**, 7333.
8 D. Fărcaşiu and A. Ghenciu, *J. Am. Chem. Soc.*, 1993, **115**, 10901.
9 (*a*) D. Fărcaşiu, M. T. Melchior and L. Craine, *Angew. Chem.*, 1977, **89**, 323; (*b*) D. Fărcaşiu, S. L. Fisk, M. T. Melchior and K. D. Rose, *J. Org. Chem.*, 1982, **47**, 453; (*c*) D. Fărcaşiu, *Acc. Chem. Res.*, 1982, **15**, 46; (*d*) D. Fărcaşiu, G. Marino, G. Miller and R. V. Kastrup, *J. Am. Chem. Soc.*, 1989, **111**, 7210.
10 C. Rochester, *Acidity Functions*, Academic Press, New York, 1970, p. 186.
11 W. E. Farneth, D. C. Roe, T. J. G. Kofke, C. J. Tabak and R. J. Gorte, *Langmuir*, 1988, **4**, 152.
12 (*a*) G. A. Olah, P. R. Clifford, Y. Halpern and R. G. Johanson, *J. Am. Chem. Soc.*, 1971, **93**, 4219; (*b*) G. A. Olah and R. J. Spear, *J. Am. Chem. Soc.*, 1975, **97**, 1539.
13 D. M. Brouwer and J. A. van Doorn, *Recl. Trav. Chim. Pays-Bas*, 1973, **92**, 895.
14 D. Fărcaşiu and G. Miller, *J. Phys. Org. Chem.*, 1989, **2**, 425.
15 D. Fărcaşiu, *J. Org. Chem.*, 1979, **44**, 2103.
16 M. T. Aronson, R. J. Gorte, W. E. Farneth and D. White, *J. Am. Chem. Soc.*, 1989, **111**, 840.