# A Report of a Persistent Allyl Cation on H-ZSM-5 Zeolite was due to Propanal

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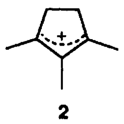
A controversial report of a stable allyl cation intermediate formed during allyl alcohol converson in a zeolite was based on the misinterpretation of the $^{13}$C NMR signal of [1-$^{13}$C]propanal by the claimants.

A recent controversy in this journal has important implications for the mechanisms of zeolite catalysis and the properties of solid acids. In 1990 Hutchings reported straightforward flow reactor studies which showed that the initial catalytic conversion of allyl alcohol on zeolite H-ZSM-5 produced hydrocarbons, but with catalyst use the selectivity switched to oxygenated products including acetone and propanal.[1] Hutchings proposed an allyl cation intermediate in hydrocarbon formation. In early 1993 our laboratory reported *in situ* $^{13}$C NMR studies of allyl [1-$^{13}$C]alcohol and acetone in diverse zeolites; our observation of 1,3-$^{13}$C label scrambling was indirect evidence of a transient allyl species, and we stated that attempts to observe the allyl cation directly were unsuccessful.[2] Downfield signals in our study were attributed to propanal. Later that year, Biaglow, Gorte and White (BGW) reported similar experiments on zeolite H-ZSM-5, but they attributed their downfield signals to the allyl cation **1** and unspecified secondary cations.[3] If confirmed, this would be a remarkable finding. Although transient carbocations are certainly reasonable intermediate species, NMR evidence for high concentrations of persistent carbocation intermediates in zeolites is scarce and limited to cations such as substituted cyclopentenyl cations,[4,5] *e.g.* **2**, that are so stable as to also persist in diluted $H_2SO_4$ solutions. Furthermore, the allyl cation is thermodynamically unstable relative to the isopropyl cation and has never been observed in superacid solutions, even at cryogenic temperatures. The persistence of the allyl cation in appreciable concentration at room temperature would imply remarkable properties for zeolites including almost unparalleled acid strength, but other recent reports have questioned whether zeolites are superacids[6–8] and whether free cations are intermediates in some reactions.[9,10] The allyl cation claim stands counter to an emerging paradigm shift in zeolite catalysis.

In early 1994, Schleyer and coworkers reported the first unequivocal observation of the free allyl cation in any condensed medium; the cation was formed by codepositing allyl chloride and $SbF_5$ at 130 K and then warming to 170 K.[11] The observed IR spectrum of the allyl cation was assigned with the aid of *ab initio* calculations. Other high level *ab initio* calculations of the NMR shifts of the allyl cation 'cast some doubt on the BGW's suggestion that the zeolite species was a free allyl cation', because the calculated shift was δ 227.4 for the 1 and 3 carbons. Schleyer concluded that 'BGW's NMR evidence for [the allyl cation] is equivocal . . . confirmation is desirable.'

A few months later Fărcaşiu independently disputed the claim of BGW based on three lines of reasoning.[12] The first was, 'If this assignment were correct it would mean that the products appear faster than the intermediate.' The second argument was similar to one of Schleyer's—the allyl cation is thermally unstable. The third argument was that zeolite H-ZSM-5 is not a sufficiently strong acid to form a significant concentration of the allyl cation. Fărcaşiu concluded that the published spectra could be accounted for by various products including carbonyl compounds.

**1**



**2**

This controversy prompted us to reopen our investigation of allyl [1-$^{13}$C]alcohol and conduct a detailed study of [1-$^{13}$C]propanal on zeolites. We were able to reproduce the spectra of ref. 3, both non-spinning (Fig. 1) and with magic angle spinning (Fig. 2) in all important respects, with the exception that all of our chemical shifts (including unreacted

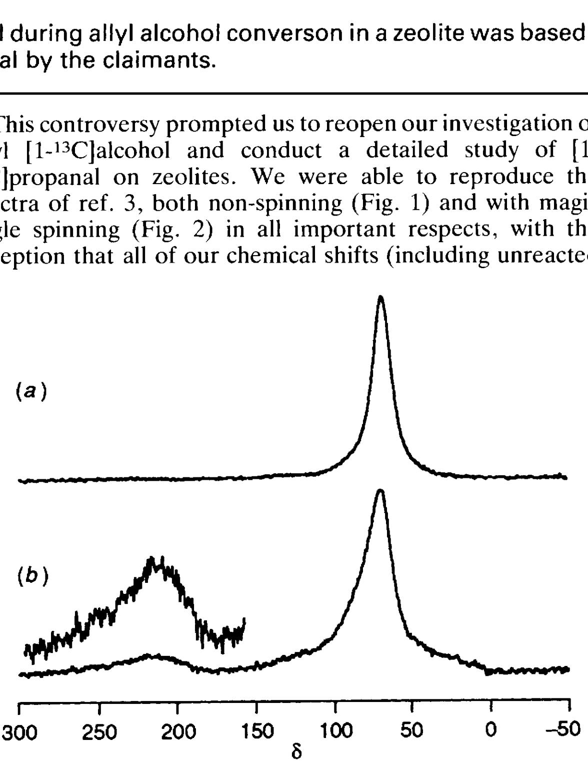


**Fig. 1** Nonspinning 50.1 MHz $^{13}$C cross polarization spectra (20000 scans and 0.1 s pulse delay) of allyl [1-$^{13}$C]alcohol on zeolite H-ZSM-5 obtained at 298 K with a surface coverage of 0.4 molecule per Bronsted acid site; (*a*) prior to heating; (*b*) after heating for 5 h at 323 K. Note the broad carbonyl resonance in the lower spectrum.

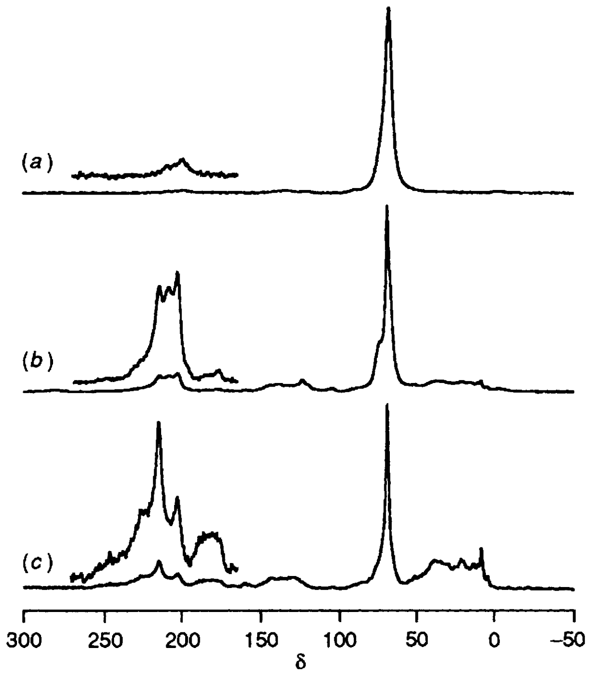


**Fig. 2** 50.1 MHz $^{13}$C CP–MAS spectra of allyl [1-$^{13}$C]alcohol on zeolite H-ZSM-5 (the same sample as in Fig. 1): (*a*) prior to heating, 10000 scans; (*b*) after heating for 5 h at 323 K, 17000 scans; (*c*) after heating for 0.5 h at 393 K, 10000 scans. The downfield regions are highlighted to show the [1-$^{13}$C]propanal signal at δ 216 and signals from the aldol products in Scheme 1.

allyl alcohol) were consistently 2–3 ppm lower than BGW's. Although we found inconsequential variations in the relative intensities and line widths of different peaks depending on catalyst preparation, loading, heating protocol and acquisition parameters,† the overall picture is unchanged from our previous paper;[2] in particular, we always formed the signal at $\delta$ 216 (218 according to BGW), and that signal is clearly visible in our earlier work. Fig. 2 shows illustrative $^{13}$C CP–MAS spectra with the downfield regions highlighted; the reader is referred to the earlier papers for other assignments. After mild sample heating, we reproducibly observed at least three isotropic peaks in the range $\delta$ 200–220; the peak at $\delta$ 216 forms first and is followed by peaks at $\delta$ 208 and 203. BGW reported peaks at $\delta$ 218 and 205, but a close examination of Fig. 2(*a*) in ref. 3 suggests a third resonance at $\delta$ *ca.* 211. Further heating of our samples resulted in the decrease of the $\delta$ 208 peak and growth of the $\delta$ 203 peak accompanied by a broad signal at $\delta$ 178.

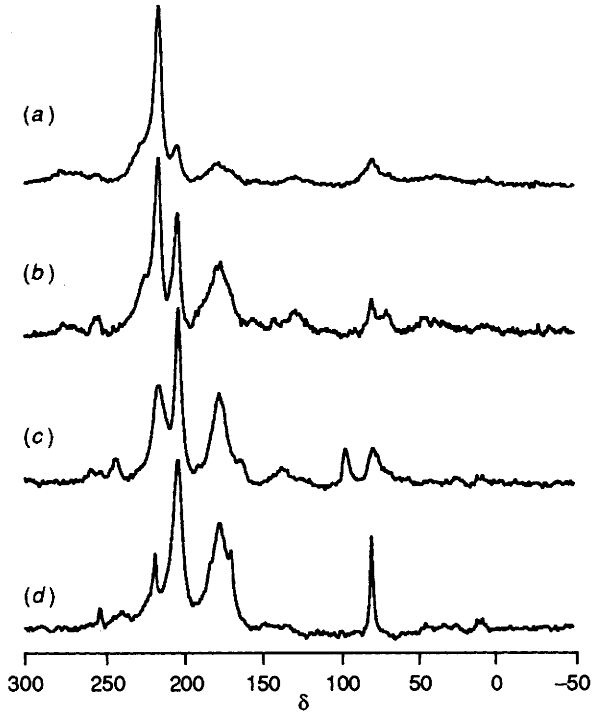
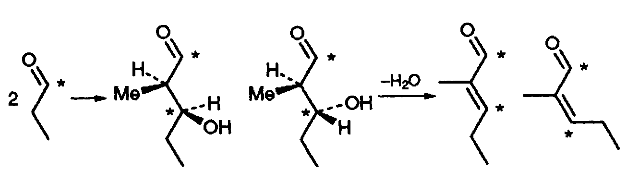
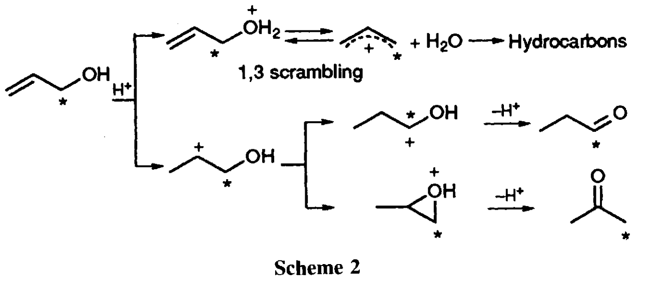


**Fig. 3** 90.5 MHz $^{13}$C CP–MAS spectra of [1-$^{13}$C]propanal on zeolite H-ZSM-5. (*a*) and (*b*) are the spectra of a sample with a surface coverage of *ca.* 0.1 molecule per Bronsted acid site, and the average of 80000 scans with 0.2 s pulse delay. Spectra (*c*) and (*d*) are those of the sample with a surface coverage of *ca.* 0.4 molecule per Bronsted acid site, and the average of 2000 scans; in the latter sample the catalyst was saturated with water before adsorption. (*a*) Prior to heating; (*b*) after heating at 353 K for 0.5 h; (*c*) prior to heating; (*d*) after heating at 353 K for 0.5 h.



Scheme 1



Scheme 2

We easily reproduced this reaction sequence by adsorbing [1-$^{13}$C]propanal onto the zeolite directly, either alone or in the company of water—another product of the reaction of allyl [1-$^{13}$C]alcohol. Fig. 3 shows representative spectra; a full paper on the chemistry of aldehydes on zeolites will be forthcoming.

We reproducibly observed unreacted propanal at $\delta$ 216—the same shift as the contentious peak obtained from allyl alcohol. Propanal reacted in the same pattern of aldol condensations and dehydrations that we reported previously for acetaldehyde,[13] acetone and cyclopentanone,[7] except that propanal is expected to condense to diastereoisomeric alcohols (one enantiomer of each shown in Scheme 1). Unfortunately, the resolution in Figs. 2 and 3 was not sufficient to resolve these products and measure selectivity; we saw a single carbonyl resonance at $\delta$ 208 and a hydroxy carbon at $\delta$ 75–78 [visible as a shoulder in Fig. 2(*b*)]. As seen in all of the other studies of aldol chemistry on zeolites, dehydration of the aldol condensation products produced $\alpha,\beta$-unsaturated aldehydes. The reaction of [1-$^{13}$C]propanal in H-ZSM-5 produced a carbonyl signal at $\delta$ 203 and a broad olefin signal at $\delta$ 178. As demonstrated previously for other $\alpha,\beta$-unsaturated aldehydes and ketones, the $^{13}$C NMR signals for those compounds were shifted in zeolites and acidic solutions from their values in $CDCl_3$ to an extent reflecting the acid strength of the medium.[7,14] All of our assignments were also supported by interrupted decoupling[15] spectra (not shown).

*Thus, the overwhelming evidence of this study as well as other recent reports,[11–12] is that a persistent allyl cation was* not *observed in BGW's NMR study.* The claimants misinterpreted the carbonyl signal of propanal, a known product of allyl alcohol conversion on the zeolite.[1] The peak at $\delta$ 216 (218 according to BGW) was due to propanal as confirmed by direct adsorption as well as by observing the diagnostic aldol reaction sequence for propanal derived from allyl alcohol *in situ*. In light of this misassignment, the claim of unspecified persistent secondary cations[3] should also be considered unproved.

Our view of the mechanism of allyl alcohol conversion on H-ZSM-5 (Scheme 2) is that protonation of the hydroxy and subsequent dehydration form a transient, symmetrical allyl cation, and this leads to label scrambling and hydrocarbons. Alternatively, protonation of the double bond forms a transient secondary cation which has at least two possible fates: 1,2-hydride transfer to form propanal, or ring closure to form a transient protonated epoxide which rearranges to form acetone. If this view is correct, it makes the initial work of Hutchings all the more interesting. That study, which inadvertently originated the allyl cation controversy, reported a change in product selectivity with catalyst use. Could this shift reflect an underlying change in protonation selectivity as a result of the accumulation of other products?

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## Footnote

† The zeolite H-ZSM-5 sample was described in ref. 2, and adsorptions were done using an improved version of the device in ref.

16. All $^{13}C$ spectra were acquired either on a CMX-360 spectrometer operating at 90.5 MHz or on a home built 50.1 MHz spectrometer. The spectra reported were obtained using cross polarization [1.2 ms contact time and 0.5 s pulse delay (unless otherwise noted) to approximate the conditions in ref. 3 but without partial saturation].

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