Microwave Study of the Reactions of n-Butenes over Deuteriated Zeolites

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Summary The hyperfine distribution of the $[^2H_1]$but-1-enes obtained by the reaction of n-butenes over deuteriated zeolites at 100 °C demonstrates that the reactivity of (*Z*)-but-2-ene on mordenite differs widely from that of the other isomers.

The isomerization of n-butenes over zeolite catalysts is well documented and, from kinetic and tracer studies, it seems that the most probable reaction path involves the formation of a common s-butyl cation intermediate which affords all the product isomers by protonation–deprotonation steps.[1–3] The development of microwave spectroscopy, which allows quantitative measurement of the deuterium content at each hydrogen position in the butene molecule, provides a new powerful tool for mechanistic studies.[4,5] This technique, combined with gas chromatography and mass spectrometry, has been used in this work to study the reactions of n-butenes over deuteriated zeolites. A difference in reactivity of the different isomers, not observable using mass spectrometry alone, has been demonstrated.

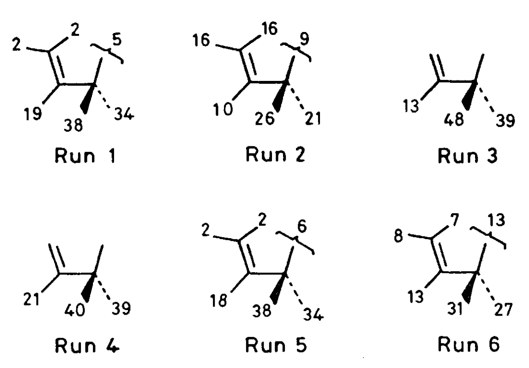
An H-mordenite (Zeolon 100H from Norton) and an H-faujasite (obtained by activation at 450 °C of a commercial Linde NH_4Y zeolite in a stream of air) were used. Catalytic reactions were carried out at 100 °C in an all-glass grease-free flow apparatus. Reactants [Fluka puriss but-1-ene, (*Z*)-but-2-ene, and (*E*)-but-2-ene] were introduced at constant pressure in a flow of purified hydrogen (1 atm) into an isothermal reactor where the catalytic bed (100 mg) operated under differential conditions. Different conversion levels were obtained by varying the olefin flow rates. Before each run, the zeolite was heated for 2 h in hydrogen at 200 °C and then transformed into a deuteriated form by passage of a constant partial pressure of D_2O through the catalyst bed at 200 °C for 2 h, and at 100 °C for an additional hour. Products were collected in a liquid-nitrogen trap and fractionated and purified by gas chromatography.

The deuterium distributions in the but-1-ene molecules, determined by mass spectrometry,[5] and the hyperfine distributions of the $[^2H_1]$but-1-ene species, determined by microwave spectrometry,[6] are given in the Table, together with the total conversions and the ratios between the isomers.

Table. Distribution and localization of deuterium in the but-1-enes formed at 100 °C.

Catalyst		Mordenite				Faujasite	
Run		1	2	3	4	5	6
Reactant		(*E*)-But-2-ene	But-1-ene	(*Z*)-But-2-ene	(*Z*)-But-2-ene	(*Z*)-But-2-ene	But-1-ene
Total conversion/%[a]		23·4	76·4	22·6	53·5	46·9	85·1
But-1-ene/but-2-ene[b]		0·35	—	0·30	0·30	0·30	—
(*E*)-But-2-ene/(*Z*)-but-2-ene		—	1·37	—	—	—	1·38
% Deuterium distribution	$[^2H_0]$	62·2	82·4	80·3	52·4	45·6	62·2
	$[^2H_1]$	28·9	12·0	17·6	32·4	31·5	21·7
	$[^2H_2]$	6·7	3·9	1·7	10·8	12·9	10·3
	$[^2H_3]$	1·6	1·2	0·3	3·4	6·0	4·0
	$[^2H_4]$	0·5	0·3	—	1·0	2·6	1·4
	$[^2H_5]$	—	—	—	—	1·0	0·4

[a] All butene isomers. [b] But-1-ene/(*E*)-but-2-ene in runs 3, 4, and 5; but-1-ene/(*Z*)-but-2-ene in run 1.



Hyperfine distribution of the $[^2H_1]$but-1-enes in runs 1—6 (see Table).

In the reaction of (*Z*)-but-2-ene, the ratio of but-1-ene to (*E*)-but-2-ene was 0·30 : 1 on both mordenite (runs 3 and 4) and faujasite (run 5) and was independent of the total conversion. Similarly, in the reaction of but-1-ene, an identical value of the ratio of (*E*)-but-2-ene to (*Z*)-but-2-ene was obtained on both zeolites (runs 2 and 6).

In all experiments the most abundant but-1-enes formed were the $[^2H_0]$ and $[^2H_1]$ species; this showed that only one H (or D) from the catalyst was incorporated into the olefin for each isomerization process, in agreement with previous studies.[3] In some runs a small scrambling due to readsorption occurred, shown by the increase of the multi-labelled $[^2H_2]$ to $[^2H_5]$ species.

Microwave analysis of the $[^2H_1]$but-1-ene obtained from (*Z*)-but-2-ene on mordenite (runs 3 and 4) revealed that the deuterium was bound exclusively to C-2 and C-3 and that the percentages of $[^2H_1]$but-1-ene labelled at position 2 increased when the total conversion increased. Other species could not be detected. In contrast, although the $[^2H_1]$but-1-ene produced on faujasite was labelled mainly at positions 2 and 3 (run 5), small but definite amounts of deuterium were detected on the terminal carbon atoms (4 ± 2% in position 1 and 6 ± 3% on carbon 4). A similar difference in extent of labelling of the internal and terminal positions of the butene molecule was not observed in the reactions of but-1-ene (runs 2 and 6) since, in the $[^2H_1]$-but-1-enes obtained on both zeolites, deuterium was detected on all four positions. Lastly, the hyperfine distribution of the $[^2H_1]$but-1-ene formed from (*E*)-but-2-ene on mordenite (run 1) is identical to that obtained from (*Z*)-but-2-ene on faujasite (run 5).

From a comparison of the mass spectrometric analysis of the but-1-enes produced in runs 1 and 4 on the one hand, and of those in runs 4 and 5 on the other, it is clear that readsorption steps cannot account for the observed differences of the $[^2H_1]$but-1-ene hyperfine distributions.

The simple specific labelling of the $[^2H_1]$but-1-enes in runs 3 and 4 suggests that on mordenite, but *not* on faujasite, (*Z*)-but-2-ene has a different reactivity from that of the other two isomers.

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