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A ^2H NMR Investigation of the Exchange of Simple Alkenes with D_2 over Alumina

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The exchange of hydrogen for deuterium in alkenes in the presence of Al_2O_3 is a useful method of preparing deuterated alkenes [1]. The reaction has been proposed to involve a dissociative mechanism in which there is preferential cleavage of a vinyl C–H bond [2]. Although there have been several mechanistic investigations of these reactions [2] and both microware spectroscopy and mass spectrometry have been used to evaluate the position of deuterium incorporation [3], the relative rates of exchange of the hydrogens in various simple alkenes have not been measured by the more precise technique of ^2H NMR spectroscopy. We now report the use of this technique to obtain the relative rates for propene, 1-butene, isobutylene, *E*- and *Z*-2-butene and cyclopentene.

Experimental

Alumina was prepared by the hydrolysis of sublimed aluminum isopropoxide and activated following the procedure of Larson *et al.* [1]. The exchanges were carried out by allowing a mixture of the alkene (1 mmol) and D_2 (3 mmol) to stand in contact with the alumina for 3 h at 300 °C. The alkenes and deuterium were purchased from Matheson.

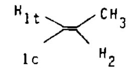
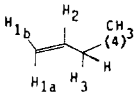
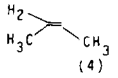
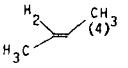
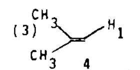
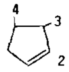
The ^2H NMR spectra of the recovered alkenes were recorded at 61.4 mHz on a Brucker AM400 spectrometer.

Results

Table I shows the alkenes used in this study along with the relative rate of exchange (per H) of the various hydrogens. The total meq D incorporated is also indicated for alkenes.

Earlier investigations of this reactions, which were carried out at temperatures below 100 °C [1, 2] indicated that only the vinyl hydrogens were exchanged, with terminal Hs exchanging more rapidly than the internal protons. The results of the present study are consistent with a mechanism involving preferential exchange of terminal vinyl hydrogens via an insertion of the Al_2O_3 into the vinyl C–H bond followed by rapid 1,3 hydrogen migration as illustrated in eqn. (1) for propene. The fact that 1,3 hydrogen migration occurs and is more rapid than hydrogen exchange is indicated by the fact that butene isomerization

TABLE I. Extent of D Exchange of Alkenes over Al_2O_3–D_2 Matrices

Substrate	Time (h)	Relative amount of D at each position	meq D in total sample × 10^2	
			Alkene	Alkane
	3	H_{1t} = 3.1 H_{1c} = 3.1 H_2 = 1.0 H_3 = 2.8	8.85	trace
	3	H_2 = 9.3 H_{1b} = 1.3 H_{1a} = 1.3 H_3 = 1.0 H_4 = 0.88 also *E*/*Z*-2-butene (1.2:1 ratio)	11.70 0.47	0.50
	3	H_2 = 1.0 H_4 = 1.1 also 1-butene and *E*-2-butene (1:1.3 ratio)	28.30 14.00	trace
	3	H_2 = 1.0 H_4 = 1.0 also 1-butene and *Z*-2-butene (1:5.2 ratio)	17.30 2.72	2.50
	3	H_1 = 1.0 H_3 = 1.05	20.50	
	3	H_2 = 1.6 H_3 = 1.0 H_4 = 1.01	16.60	1.21

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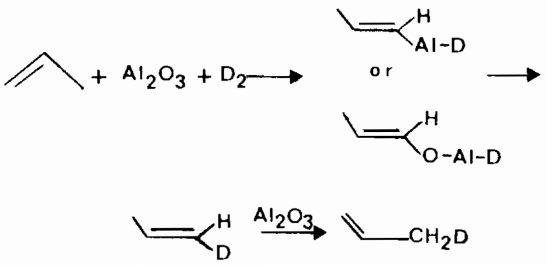
proceeds to a greater extent than D exchange. Thus, 1 mmol of 1 butene is 53% isomerized to a 1.15:1 mixture of *E* and *Z*-2 butene while only a total of 0.19 meq of D is introduced into the system. The isomerization of the butenes over Al has been extensively investigated and is thought to involve the participation of a alkyl intermediate in a 1,3 hydrogen migration [4]. These experiments illustrate the difficulty of evaluating mechanisms in the reactions of alkenes with Al_2O_3 due to the variety of reactions which are catalyzed.



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