Mechanisms of the Isomerization of Butenes on Titanium Dioxide

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Summary The isomerization of butenes on TiO_2 proceeds through three different mechanisms, involving, respectively, protonic sites, Lewis acid sites, and basic sites, depending on the pretreatment temperature of the TiO_2 catalyst.

The behaviour of TiO_2 has recently been shown[1] to be very complex by experiments involving the co-isomerization of normal and perdeuteriated butenes. The use of but-2-enes selectively deuteriated in the allylic or vinylic position has proved to be[2] a very convenient means of studying the isomerization of ethylenic compounds: it allows the detection of *cis–trans* isomerization and double bond migration with or without hydrogen exchange between the olefin and the catalyst, and the characterization of each of these reactions. The first results obtained on TiO_2 at 120 °C are reported here.

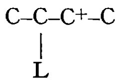
TiO_2 was prepared by hydrolysing $TiCl_4$ with NH_4OH. It contained *ca.* 0·03% Na but no Cl^-, and showed the anatase structure. Before each experiment, the catalyst was dried overnight in a flow of dry N_2 at 350 or 550 °C. The surface areas of these samples were, respectively, 134 and 90 $m^2 g^{-1}$. On TiO_2 pretreated at 350 °C (T-350) double bond migration occurs with exchange of an allylic deuterium (Table): [1,4-$^2H_6$]-*cis*-but-2-ene gives [$^2H_5$]but-1-ene, whereas [2,3-$^2H_2$]-*cis*-but-2-ene yields [$^2H_2$]but-1-ene. Comparison of isomerization rates for the deuteriated *cis*-but-2-enes with that of [$^2H_0$]-*cis*-but-2-ene shows that the former reaction gives rise to an isotope effect (k_H/k_D 2·1), whereas the latter occurs with no isotope effect (k_H/k_D 1·0). The *cis–trans* isomerization involves the partial exchange of a vinylic deuterium; a small isotope effect is detected (k_H/k_D 1·3) which can be ascribed to the breaking of the C–^{2}H bond during the exchange reaction. On TiO_2 predried at 550 °C (T-550) all the reactions occur without any hydrogen exchange between the olefin and the catalyst (see Table). Double bond migration gives rise to an important isotope effect (k_H/k_D 4·0), but *cis–trans* isomerization occurs without any isotope effect.

T-350 catalyses both the double bond migration with exchange of an allylic hydrogen, and the *cis–trans* isomerization with exchange of a vinylic hydrogen; the breaking of the C–H bonds occurs during the rate-determining step. These reactions, which have been observed

Table. Isomerisation of [2,3-$^2H_2$] and [1,4-$^2H_6$]-*cis*-but-2-enes

Reactant	Catalyst	Product	% Product	% Isotope distribution								^{2}H atoms per molecule	k_H/k_D
				$^2H_0$	$^2H_1$	$^2H_2$	$^2H_3$	$^2H_4$	$^2H_5$	$^2H_6$	$^2H_7$		
[2,3-$^2H_2$]-*cis*-But-2-ene				0·3	0·7	98·8	0·2	—	—	—	—	1·99	
	T-350	But-1-ene	1·7	2·0	3·9	93·1	1·0	—	—	—	—	1·93	1·0
		trans-But-2-ene	1·9	2·1	49·2	48·6	0·1	—	—	—	—	1·47	1·3
	T-550	But-1-ene	2·0	1·1	2·6	96·1	0·2	—	—	—	—	1·95	1·0
		trans-But-2-ene	0·4	1·8	3·9	94·0	0·3	—	—	—	—	1·93	1·0
[1,4-$^2H_6$]-*cis*-But-2-ene				—	—	—	0·05	0·95	10·7	88·3	—	5·87	
	T-350	But-1-ene	0·9	—	—	—	1·4	10·2	85·8	2·6	—	4·90	2·1
		trans-But-2-ene	2·4	—	—	—	—	1·4	12·5	85·1	1·0	5·86	1·0
	T-550	But-1-ene	0·7	—	—	—	—	1·1	13·0	85·8	0·1	5·85	4·0
		trans-But-2-ene	0·5	—	—	—	0·1	0·9	11·3	87·4	0·3	5·87	1·0

on alumina,[2] probably take place on Brönsted acid sites of the catalyst. T-350 also catalyses *cis–trans* isomerization without exchange; this reaction occurs without any isotope effect and consequently without any C–H bond-breaking during the rate-determining step. This same reaction is observed on T-550, accompanied by a double bond migration, without exchange, with the breaking of the allylic C–H bond (k_H/k_D 4·0). It is impossible to explain these two reactions by a single mechanism since they occur simultaneously on T-550 but not on T-350. Therefore two different mechanisms must be invoked. Double bond migration could take place on the basic sites[1] of TiO_2, through allylic carbanions as on MgO.[3] *cis–trans* isomerization may occur through σ-bonded carbocations as in the case of Webb's carbonium ion (**A**),[4] where L is a Lewis acid site. Indeed, such an intermediate, which allows only geometrical isomerization, can be formed without any C–H bond-breaking.



$\mathrm{C{-}\underset{\underset{\displaystyle L}{|}}{C}{-}C^{+}{-}C}$

(**A**)

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