Brønsted Acidity of Rutile Developed During Alcohol Dehydration as Shown by Simultaneous Alkene Isomerization: Microwave Spectroscopic Analyses

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Summary Microwave spectroscopic analyses of deuteriopropenes produced from $CD_2{=}CH{-}CH_3$, and of deuterioisobutenes from $CD_2{=}C(CH_3)_2$, indicate conclusively that on rutile in the presence of water and/or alcohol carbonium ion intermediates are involved in alkene isomerization; in contrast, comparison of rates of reaction of $CD_2{=}CH{-}CH_3$ and $CD_2{=}C(CH_3)_2$ implies that π-allylic species with partial carbonium ion character are the intermediates in isomerization in the absence of water or alcohol.

Some recent studies of reactions of primary alcohols over rutile (TiO_2) indicated that dehydration (to alkene and water) occurred at *ca.* 550 K. It became desirable to establish if the product alkenes could isomerize under the reaction conditions or whether the primary product distribution was sensibly preserved.

Recently the reaction of $CD_2{=}CH{-}CH_3$ with D_2O was successfully employed to demonstrate the Brønsted acid nature of alumina at *ca.* 470 K.[5] The present work was undertaken to establish if a similar reaction mechanism was operative for labelled propene over TiO_2 at *ca.* 570 K in the presence of D_2O or pentan-1-ol, *i.e.*, to investigate if the reaction proceeded by a different route in the presence of such species. Additionally the reaction of a selectively labelled isobutene, $CD_2{=}C(CH_3)_2$, with water was examined to provide further information of the Brønsted acid nature of the rutile surface.

The source and pretreatment of the rutile were as previously reported.[3] Samples of 1 g were used with *ca.* 1×10^{20} molecules of alkene and a similar amount of D_2O or pentan-1-ol as appropriate. Reaction was followed by mass spectrometry to the desired extent, at which time a gas phase sample was removed for subsequent microwave analysis.[2] The experimental details and results are summarised in the Table.

Table. Percentage analyses[a] of deuteriopropenes and deuterioisobutenes produced over TiO_2

Experiment no.	1	2	3	4	5
Reactants	$CD_2{=}CH{-}CH_3 + D_2O^c$	$CD_2{=}CH{-}CH_3 + D_2O^d$	$CD_2{=}CH{-}CH_3$ + Pentan-1-ol[e]	$CD_2{=}C(CH_3)_2{}^f$	$CH_2{=}C(CH_3)_2 + D_2O^c$
Reaction temperature/K	523	523	553	283	390
$CD_2{=}CR{-}CH_3{}^b$	87·6(96)	68·8(89)	46·0(57)	12·6(17)	—
$CHD_2{-}CR{=}CH_2$	3·6(4)	8·4(11)	33·6(46)	34·9(47)	—
$CH_2D{-}CR{=}CH_2$	0	0	5·8(34)	6·0(54)	24·9(73)
$CH_3{-}CR{=}CHD$	1·0(100)	2·1(100)	11·1(66)	5·0(45)	9·2(27)
$CD_2{=}CR{-}CH_2D$	1·0(13)	3·3(16)	0·4(17)	—	—
$CD_3{-}CR{=}CH_2$	6·8(87)	17·4(84)	2·0(83)	—	—

[a] Numbers in parentheses are normalised distributions of $[^2H_1]$-species for various i. [b] R is either H (propene) or CH_3 (isobutene). [c] Reactants both added at 283 K and warmed to reaction temperature. [d] D_2O added initially at *ca.* 700 K prior to cooling to 283 K and admitting $CD_2{=}CH{-}CH_3$. [e] Pentan-1-ol added initially at 550 K and partially dehydrated for 20 min prior to cooling to 283 K and admitting $CD_2{=}CH{-}CH_3$. [f] Also contained 26·9% $CHD{=}C(CH_3)CH_2D$ [and $CH_2{=}C(CH_2D)_2$] with 11·7% unknown $[^2H_3]$-species.

It is known that in the absence of alcohol or water, n-butenes[1] and propene[2] isomerize over TiO_2 at rates of *ca.* 1×10^{15} molecule m^{-2} s^{-1} at 430 K, with the reaction of propene (as $CD_2{=}CH{-}CH_3$) being predominantly intramolecular and involving π-allylic species. However, Hughes *et al.*[3] reported that the exchange of propene, with D_2 or D_2O, achieved such a rate only at *ca.* 570 K, and the deuteriopropenes produced had D randomly distributed over the five terminal positions. Such a distribution is characteristic of carbonium ion intermediates if the supply of D is not rate determining for the exchange reaction. With D_2 as the source, the supply of D was indeed shown to be rate determining but this was somewhat uncertain with D_2O. The exchange reaction of isobutene over rutile at 530 K has been reported[4] as some thirty times faster with D_2O than with D_2 which suggests that water can indeed induce a carbonium ion reaction.

Experiments 1 and 2 provide clear evidence that in the presence of water (D_2O) exchange of propene with D and double bond migration (DBM) occurred at essentially the same rate. Furthermore, the highly selective production of $CD_3{-}CH{=}CH_2$ at *ca.* 520 K is strongly indicative[5] of classical carbonium ion intermediates reacting on Brønsted acid centres produced with D^+ from D_2O, irrespective of whether water was initially added at 300 or 700 K.

Exposure of TiO_2 to $CD_2{=}CH{-}CH_3$ and pentan-1-ol at 298 K, with subsequent warming to *ca.* 550 K, showed that alcohol alone was sufficient to poison the (π-allylic) reaction of propene at *ca.* 450 K as dehydration products were only detectable by g.l.c. at *ca.* 550 K. Experiment 3 confirms that in the presence of pentan-1-ol and its dehydration products, propene reacts on Brønsted acid centres which initially contain H^+ leading to the selective production of $CHD{=}CH{-}CH_3$, $CHD_2{-}CH{=}CH_2$, and $CD_3{-}CH{=}CH_2$.

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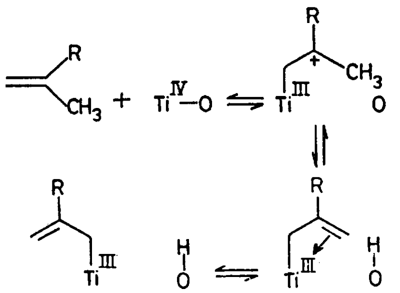
Compound CD_2=$C(CH_3)_2$ reacted on TiO_2 at a rate of *ca.* 1×10^{15} molecule $m^{-2}\,s^{-1}$ at 283 K (experiment 4); 450 K was needed for similar reaction of CD_2=CH–CH_3.[2] Microwave analysis of deuterioisobutenes produced[6] indicates that predominantly intramolecular DBM occurred; CHD=$C(CH_3)CH_2D$ was produced from CH_2=$C(CH_3)CHD_2$ in preference to [$^2H_1$]-species. In previous work on D_2 exchange with both propene and isobutene, therefore, the rate of supply of D from D_2 was rate determining. In addition, substitution of H on C(2) in propene for CH_3, to give isobutene, confers greatly enhanced reactivity which, with the intramolecular nature of the reaction, implies the involvement of allylic species with carbonium ion character, in contradiction to the conclusion of π-allylic carbanions reached[7] on the more subjective basis of product distribution in butene isomerization. Such species might be formed[8] on the Lewis acid centres of rutile as shown in the Scheme.



SCHEME. Schematic representation of the active site for alkene isomerization over rutile.

Intermolecular reaction of either CD_2=$C(CH_3)_2$ or CH_2=$C(CH_3)_2$ with D_2O occurred at very similar rates at 390 K. The ratio, CH_2=$C(CH_3)CH_2D$: CHD=$C(CH_3)_2$ was 2·7 ± 0·3 : 1 in the latter case (experiment 5) whereas DBM in the former was predominantly intermolecular and occurred at sensibly the same rate as exchange. These observations confirm directly that isobutene reacts on TiO_2 in the presence of D_2O through the carbonium ion intermediate, $(CH_3)_2$–C^+–CH_2D; random loss of H^+ gives the above [$^2H_1$] product ratio whereas a π-allylic intermediate would give only CH_2=$C(CH_3)CH_2D$. Thus, reaction through a tertiary carbonium ion (from isobutene) occurs at similar rates to that through a secondary ion (from propenes) in the presence of the same quantity of water, but at 160 K lower in agreement with its greater stability.

It is clear, therefore, that reaction of both propene and isobutene on TiO_2 in presence of water or alcohol occurs by a different mechanism (carbonium ions on Brønsted centres) to that found previously (π-allyls) in their absence. Studies of alkene isomerization in the absence of water or alcohol cannot therefore be used to describe such reactions in their presence, a conclusion also reached with water on alumina[5] which should probably, therefore, be regarded as of general validity for metal oxide catalysts.

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