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Interaction of *n*-Butenes with Tin Oxide

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The isomerization of but-1-ene was observed to occur readily over SnO_2 at temperatures ca. 300 K. A feature was the formation of large amounts of butadiene as well as *cis*- and *trans*-but-2-ene. The major role played in the reaction by the catalyst was emphasized by the extensive loss of deuterium from but-1-ene-d_8 to the catalyst surface. It was postulated that the reaction mechanism was largely dependent upon the existence of a butadiene surface species—formed by the simultaneous loss of two hydrogen atoms from adjacent carbon atoms on the adsorbed but-1-ene molecule.

Different characteristics were exhibited by the *cis*-but-2-ene isomerization. Exclusive *cis–trans* isomerization was observed with no detectable double-bond migration (to give but-1-ene) or butadiene formation. An intramolecular mechanism involving as an intermediate a secondary butyl carbonium ion was invoked to rationalize the data. Coisomerization of *cis*-but-2-ene-d_0 and *cis*-but-2-ene-d_8 indicated that the exchange process was stepwise in nature and did not involve loss of deuterium to the catalyst surface.

INTRODUCTION

Studies of the isomerization of but-1-ene on metal oxide catalysts have been previously reported from these laboratories (*1–3*). It is a useful test reaction as the relative rates of *cis–trans* isomerization and double-bond migration give an insight into the nature of the reaction mechanism, and the initial *cis–trans* product ratio has been interpreted by various authors (*4–9*) in terms of possible ionic or radical intermediates.

Simons *et al.* (*10*) in a study of the reduction of SnO_2 by but-1-ene in the temperature range 573–823 K reported that the conversion to butadiene was accompanied by considerable isomerization (with a *cis–trans* product ratio between 1 and 2). More recently Takte and Rooney (*11*) noted that temperatures of 473 K were required for the isomerization over a pure sample of SnO_2, but that the reaction proceeded smoothly at 293 K over SnO_2 containing small amounts of sulfide. Trifirò, Villa, and Pasquon (*12*), in a study of the oxidative dehydrogenation of but-1-ene to butadiene, have also noted the ability of SnO_2 to catalyze the isomerization process at temperatures around 473 K. They attributed this activity to the presence of Sn ions with a valency lower than 4.

In the present study the isomerization of but-1-ene and *cis*-but-2-ene over SnO_2 was examined. Further evidence of the operative reaction mechanisms was inferred from an examination of the distribution of deuterium in reaction products after (a) the isomerization of but-1-ene-d_8, and (b) the coisomerization of *cis*-but-2-ene-d_0 and *cis*-but-2-ene-d_8.

EXPERIMENTAL METHODS

The apparatus and experimental techniques employed have been described previously (*1*). A static system, with a reaction vessel of 1.03×10^{-4} m^3 volume and a butene pressure of 2.1 kN m^{-2}, was used with samples being removed from the gas phase for analysis by glc at appropriate intervals.

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The source and purification of reagents was as before (*1*). The SnO_2 was supplied by B. P. Chemicals (U. K.) Ltd. It was prepared from reaction of tin with nitric acid, and possibly contained some nitrate ions as impurity. After drying in air at 400 K the catalysts were ground to pass a 30 mesh sieve. Two such samples were examined with specific surface areas of 110 $m^2\ g^{-1}$ (sample A) and 123 $m^2\ g^{-1}$ (sample B), respectively. The SnO_2 (0.5 g) was outgassed at 473 K for 17 hr prior to use and fresh samples were taken for each experiment.

In experiments involving the isomerization of deuterated butenes the mixture after reaction was condensed into a liquid nitrogen trap. The products were then separated by gas chromatography, and each individual product analyzed by a mass spectrometer for deuterium content. In the coisomerization experiments with "light" and "heavy" but-1-ene the mass spectra of the butadiene species were corrected for fragmentation in a similar manner to that described for the butenes (*1*).

RESULTS

The isomerization of but-1-ene occurred at conveniently measurable rates over the SnO_2 samples in the temperature range 310–340 K. Analysis of the gas phase above the catalysts indicated the major reaction products to be *cis*- and *trans*-but-2-ene with initial *cis/trans* product ratios in the range 1.2–1.5. Smaller, but significant, amounts of butadiene were also detected in the gas phase; in subsequent experiments, where the total reaction mixture was condensed into a liquid nitrogen trap, a higher butadiene percentage was observed. Presumably the butadiene was the most strongly adsorbed product on the catalyst surface, and consequently not so prominent in the gas phase.

The initial rate of disappearance of but-1-ene could be estimated from the gradients of the graphs of but-1-ene concentration versus time (the data obeyed zero order kinetics). Values of the initial rate of disappearance of but-1-ene of 3.9×10^{15} (sample A) and 7.5×10^{15} (sample B) molecules $m^{-2}\ s^{-1}$ at 321 K typify the observed data, and indicate the similarity of the results over the two SnO_2 samples.

The isomerization of *cis*-but-2-ene was examined in the temperature range 296–316 K. The rate of disappearance of *cis*-but-2-ene was calculated from the data plotted according to the following first order expression:

$$\ln(x - x_\infty) = -100kt/(100 - x_\infty) + \ln(100 - x_\infty),$$

where x is the percentage of *cis*-but-2-ene at time t, and x_∞ the percentage at equilibrium. For sample A a rate of 1.8×10^{16} molecules $m^{-2}\ s^{-1}$ was observed at 311 K, and for sample B a rate of 1.4×10^{16} molecules $m^{-2}\ s^{-1}$ at 310 K.

The striking feature of these latter experiments was that *trans*-but-2-ene was the only reaction product detected in the gas phase, and also when the reaction mixture was condensed into a liquid nitrogen trap. Even when the reaction temperature was raised to 473 K (where the equilibrium amount of but-1-ene is much higher) no but-1-ene or butadiene was observed.

The coisomerization of light (perhydro) and heavy (perdeutero) *cis*-but-2-ene was examined over sample A in two experiments at ca. 300 K; these corresponded to 6.5 and 19.8% conversion, respectively. The isotopic composition of the subsequent but-2-enes was analyzed mass spectrometrically (Table 1). The data show that although some "scrambling" had occurred the light and heavy fractions (of reactant and product) remained essentially separate. The average ϕ values (i.e., number of deuterium atoms in 100 molecules) of the initial reactants were 327 and 302 for the two experiments. Analysis of the two sets of reaction products gave ϕ values of 326 and 301, respectively. Such agreement is a clear indication that no dilution of the deuterium content of the but-2-enes occurred during reaction, and hence independent exchange processes with the catalyst surface are playing no part in this reaction system.

TABLE 1

COMPOSITION AND DEUTERIUM CONTENT OF THE PRODUCTS OF THE *cis*-BUT-2-ENE COISOMERIZATION EXPERIMENTS

Compound	%	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	ϕ
1st Expt											
cis	93.5	46.7	9.2	1.1	0.2	0.2	0.5	2.7	12.5	26.9	334
trans	6.5	63.3	8.9	1.2	0.2	0.2	0.4	1.5	6.6	17.8	212
2nd Expt											
cis	80.2	41.0	12.7	2.2	0.3	0.2	0.9	4.7	15.8	22.2	340
trans	19.8	68.7	12.2	1.5	0.2	0.1	0.5	1.9	5.7	9.1	143

Another feature of Table 1 worthy of comment is the clear indication that the light fraction isomerized more rapidly than the heavy fraction (with $k_H/k_D \approx 2.5$).

A comparison of the experimentally observed deuterium distribution for the light and heavy fractions of *cis*-but-2-ene (after 6.5% conversion) with the appropriate binomial distributions is illustrated in Table 2. The extent of agreement is a strong indication of the stepwise nature of the exchange process. A similar correlation was exhibited by the data for the *trans*-but-2-ene product.

Further analysis of the exchange data indicates that the exchange reaction occurred more readily than the isomerization, e.g., after 6.5% of the *cis*-but-2-ene had isomerized some 27% had exchanged, similarly after 19.8% isomerization 43% of the *cis*-but-2-ene had undergone exchange. Furthermore the *trans* product was no more exchanged than the *cis* reactant, suggesting that the isomerization reaction was intramolecular in nature.

The coisomerization of light and heavy but-1-ene was examined over sample A at 343 K. The composition and deuterium content of the reaction mixture after 38.3% conversion is indicated in Table 3; butadiene was the major product. A feature of the data is the relatively large amount of d_5 and d_6 butenes. This incorporation of 2–3 hydrogen atoms into the heavy molecules was not accompanied by a corresponding increase in the d_2 and d_3 content of the light molecules. Thus, in this instance, it is apparent that there has been some loss of deuterium from the hydrocarbon—presumably to the catalyst surface.

Subsequent to the but-1-ene coisomerization experiment the isomerization of perdeuterobut-1-ene was examined over sample A. Table 4 indicates the data obtained after 60% conversion: the large butadiene production and formation of relatively large amounts of the d_5 and d_6 butenes were again observed. A comparison of the ϕ value for the initial reactant (=782) with an approximate average ϕ value for the products of 543 demonstrated the extensive dilution of the deuterium content occurring during this isomerization process (in marked contrast to the *cis*-but-2-ene data). It should also be noted that the hydrogen content of the butadiene produced is higher than that which would result from the stripping of two deuterium atoms from the perdeuterobut-1-ene. An attempted correlation of the experimentally observed deute-

TABLE 2

COMPARISON OF THE "LIGHT" AND "HEAVY" FRACTIONS OF *cis*-BUT-2-ENE WITH THE BINOMIAL DISTRIBUTIONS

	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	ϕ
Light fraction	81.5	15.9	2.0	0.4	0.3	—	—	—	—	22
Binomial	79.8	18.3	1.8	0.1	—	—	—	—	—	22
Heavy fraction	—	—	—	—	0.4	1.0	6.3	29.2	63.0	753
Binomial	—	—	—	—	0.1	0.8	6.6	30.6	61.9	753

TABLE 3

Composition and Deuterium Content of the Products of the But-1-ene Coisomerization Experiment

Compound	%	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	ϕ
But-1-ene	61.7	35.8	16.0	3.2	1.0	5.8	15.8	17.6	3.8	0.9	267
cis	10.0	30.3	16.1	3.5	1.0	4.2	14.1	20.9	8.2	1.6	310
trans	6.0	34.1	15.5	3.2	0.8	3.8	12.1	19.2	8.6	2.8	297
Butadiene	22.3	39.1	17.2	9.5	10.0	11.9	9.4	2.9	—	—	178

rium contents of the products with those predicted from the appropriate binomial distributions gave poor agreement. It was concluded that the exchange of but-1-ene did not therefore take place in a simple stepwise manner.

After outgassing at 473 K for 17 hr the SnO_2 catalyst (sample A) gave an ESR signal at liquid nitrogen temperature with a *g*-value of approximately 2.07. This signal was enhanced by the presence of oxygen but unaffected by the addition of but-1-ene.

Discussion

The formation of butadiene as a product in the but-1-ene isomerization reaction indicates the role of SnO_2 as a reactant. This can be contrasted to the behavior of the majority of other oxides where there is no evidence of butadiene formation under similar circumstances. The data of Tables 3 and 4 show clear evidence that during this isomerization process there was extensive exchange with hydrogen from the catalyst surface, which must provide at least two hydrogen atoms per butene molecule to account for the loss of deuterium observed. The butene concentration was approximately 1 molecule/nm^2 and so the value for the exchangeable hydrogen atoms of about 2 per nm^2 could well correspond to the concentration of hydroxyl groups on the oxide surface after outgassing at 473 K.

The temperature range for the but-1-ene isomerization, and the observed product ratios, is similar to that reported by Takte and Rooney (*11*). They postulated that the reaction over their sulfided SnO_2 catalyst proceeded via the formation of 1-methylallyl radicals at paramagnetic centers. Such centers were believed to be low valency Sn ions formed by electron transfer from sulfide ions to the Sn^{4+} species.

The present SnO_2 samples gave an ESR signal indicative of the presence of paramagnetic species albeit with a different *g*-value to that reported by Takte and Rooney (*11*). However, the fact that but-1-ene addition did not cause any reduction in this signal prevents the establishment of a clear correlation between such paramagnetic species and the isomerization activity.

It is suggested that the but-1-ene to butadiene interconversion proceeds *via* the formation of a surface butadiene species with an operative reaction scheme as shown:

$$\begin{tikzcd}
\text{but-1-ene (g)} \arrow[d, shift right] & \text{butadiene (g)} \arrow[d, shift left] \\
\text{but-1-ene (a)} \arrow[u, shift right] \arrow[r, shift left] & \text{butadiene (a)} \arrow[u, dashed, shift left] \arrow[l, shift left]
\end{tikzcd}$$

The notations (g) and (a) refer to the gaseous state and the adsorbed state, respectively, and the broken arrow indicates the relatively strong adsorption of the butadiene species. In such a process the catalyst

TABLE 4

Composition and Deuterium Content of the Products of Perdeuterobut-1-ene

Compound	%	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	ϕ
But-1-ene	40	0.5	0.7	0.5	1.0	8.2	22.1	36.0	15.8	15.1	595
trans	9.2	0.5	0.9	0.6	2.6	7.8	14.9	20.3	16.4	36.3	643
cis	9.9	0.5	0.7	1.3	2.3	7.6	14.3	16.5	13.6	43.1	651
Butadiene	40.9	0.6	4.4	12.7	21.6	27.5	24.3	9.0	—	—	380

would simultaneously remove two hydrogen (deuterium) atoms from adjacent carbon atoms on the but-1-ene molecule. The buildup of the d_5 and d_6 isomers from the isomerization of perdeuterobut-1-ene can be rationalized by such a mechanism, i.e., loss of two deuterium atoms with the subsequent gain of two hydrogens from the catalyst surface would give the butene-d_6 species. The requirement of *simultaneous* removal of two hydrogens would also explain why the exchange process did not occur in a stepwise fashion. The perdeuterobut-2-enes are probably formed directly from the reactant and the other but-2-enes, centered around the d_6-compounds, from but-1-enes which have taken part in the scheme shown above. The but-2-enes retain a higher deuterium content than the but-1-enes (see Table 4) because once formed they do not exchange with the surface *via* the butadiene species.

The formation of butadiene from the but-2-enes would require the removal of two hydrogen atoms from carbon atoms 1 and 4. The differences in behavior of the butenes can be explained if it is assumed that this process is much more difficult on SnO_2 than the simultaneous removal of two adjacent hydrogen atoms as in the but-1-ene case. Thus, the but-2-enes will not take part in the scheme shown for but-1-ene and no butadiene formation or exchange with the catalyst hydrogen will occur. Furthermore, small amounts of but-1-ene formed from *cis*-but-2-ene by the reverse of the reaction which takes place with but-1-ene as reactant are likely to be retained on the surface as adsorbed butadiene. This may account for the absence of any observed double-bond migration and the apparently exclusive *cis–trans* isomerization.

There are other cases in which the formation of the butadiene occurs more readily from but-1-ene than from the but-2-enes, such as catalytic oxidation over bismuth molybdate reported by Adams *et al.* (*13*). The low temperatures used in the present study, relative to those in the oxidation reactions, would tend to accentuate any differences in reactivity.

Exclusive *cis–trans* isomerization, with *cis*-but-2-ene as initial reactant, has previously been reported by Foster and Cvetanovic (*7*) over H_2SO_4. They proposed a reaction mechanism involving as an intermediate the secondary butyl carbonium ion. SnO_2 prepared as in the present study (by the action of concentrated nitric acid on tin) is known to be acidic so that present samples could act as acidic catalysts—with the active sites being different to those involved in the but-1-ene reactions. In an examination of butene isomerization over alumina and silica–alumina catalysts Hightower and Hall (*6*) postulated the secondary butyl carbonium ion as a common intermediate and considered in detail the energetics of the system. Their results suggested that but-1-ene was somewhat less likely to be formed from the carbonium ion than the but-2-ene isomers. However, they also made the point that product selectivities are a very sensitive function of the nature of the catalyst; and dependent upon factors such as method of preparation, reaction temperature, mode of pretreatment, etc.

The coisomerization experiments with light and heavy *cis*-but-2-ene can be assessed in terms of (a) the relative rates of exchange and isomerization, and (b) the nature of the isomerization process (intermolecular or intramolecular) (*1*). The present data are consistent with a situation in which the rate of exchange of *cis*-but-2-ene is slightly faster than its rate of isomerization but the latter process is mainly intramolecular. This implies that when the *trans* isomer is formed from the secondary butyl carbonium ion there is a tendency to lose the same proton originally added (presumably from the catalyst) in the formation of the intermediate.

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