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The Isomerization of *n*-Butenes Over Platinum Black in the Absence of Molecular Hydrogen

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The isomerization reaction (double-bond migration) of 1-butene over platinum black at temperatures between 135 and 180°C in the absence of molecular hydrogen has been studied by means of a flux and a batch reactor. The reaction has also been studied in the presence of oxygen. Experiments have also been conducted by feeding *cis*-2-butene into the batch reactor at 135°C.

It has been proved that by means of a suitable residence time platinum black isomerizes *n*-butenes in the absence of added hydrogen; 1,3-butadiene and traces of *n*-butane have been found. Oxygen strongly inhibits the isomerization reaction. *cis*-2-butene isomerizes to *trans*-2-butene after a noticeable induction time and 1-butene is a significant reaction product.

Two reaction mechanisms are discussed, addition–abstraction and abstraction–addition.

1. INTRODUCTION

During the last 15 yr many studies have been made of the catalytic double-bond isomerization of *n*-butenes in the absence of molecular hydrogen. Extensive investigations have been made on alumina-supported Group VIII metals (*1*, *2*), and other work has involved unsupported Group VIII and IB metals, as wires, powders, or alloys. Silver pellets have been used at 375°C (*3*), palladium, gold and palladium–silver alloys at temperatures between 300 and 400°C (4), and cobalt wires at 197°C (*1*a).

It has been proved that molecular hydrogen increases the isomerization rate (double-bond migration) of *n*-butenes (*4*–*7*) although the rate decreases at high hydrogen pressure (*4*, *6*b); molecular oxygen decreases the rate of isomerization in all cases (*1*c, *4*).

The mechanism of double-bond migration in homogeneous catalysis and on basic and acid heterogeneous catalysts has been established. On supported metal catalysts (Group VIII) observations on hydrogen–deuterium exchange, OH group density on the alumina (*8*) and kinetic calculations, seem to prove that the addition–abstraction rather than the abstraction–addition mechanism is effective (*1*b,c) (see Fig. 1).

On pure metals less interpretative and experimental work has been carried out. This prompted the present study on the isomerization of 1-butene and *cis*-2-butene on platinum black. The experimental runs were not aimed at obtaining quantitative kinetic parameters, on *n*-butene isomerization by platinum black, but at solving the following problems: (i) catalyst deactivation, (ii) eventual dehydrogenation by products, (iii) catalyst deactivation by oxygen.

2. EXPERIMENTAL METHODS

Materials. The 1-butene and *cis*-2-butene were Phillips Petroleum Co. "Pure grade" products. Analysis showed molar percentages in 1-butene of 98.60% 1-butene, 1.04% isobutene, 0.24% *n*-butane, 0.05% isobutane and 0.07% *cis*-2-butene. The *cis*-2-butene consisted of 99.50% *cis*-2-butene.

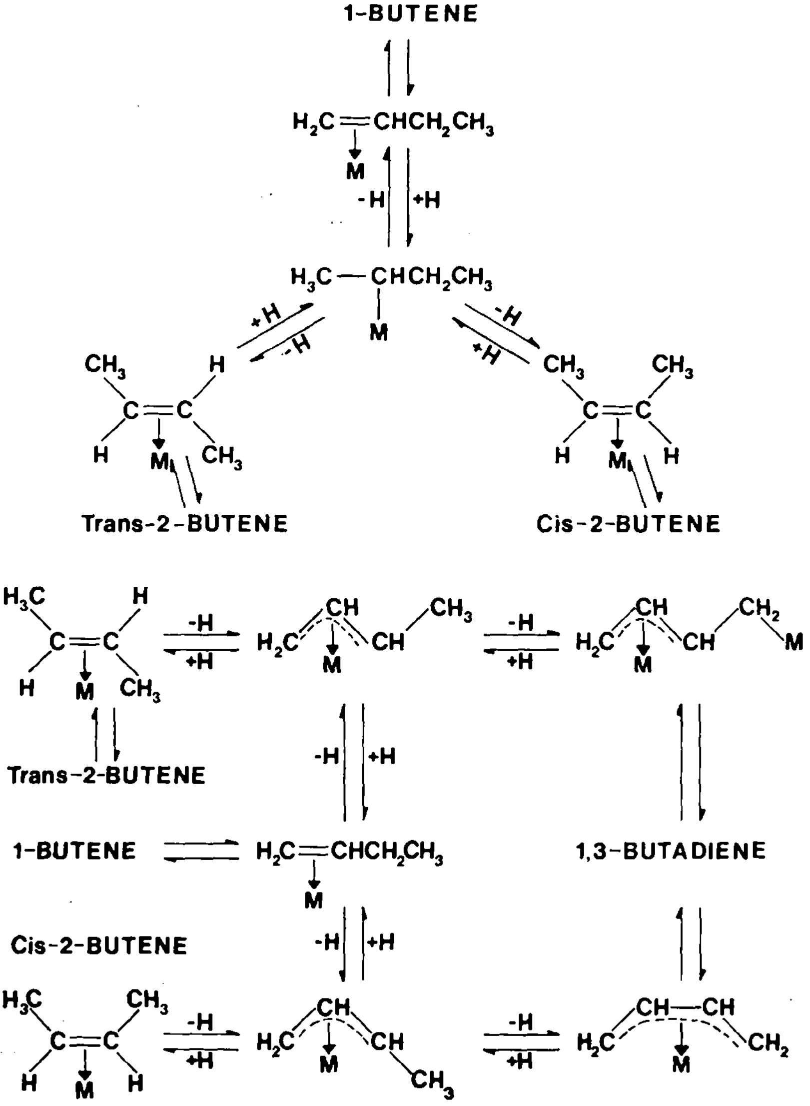

Fig. 1. Mechanisms for the isomerization of *n*-butenes (*14*). (a) Addition-abstraction mechanism (AD-AB) or alkyl reversal; (b) abstraction-addition mechanism (AB-AD) or π-allylic intermediate.

0.30% *trans*-2-butene and 0.20% 1-butene. Helium and hydrogen were gas-chromatographically pure gases. Platinum black was an Engelhard Industries product (Lot No. 2304). Its purity was 99.92 wt%. The surface area determined by Ar adsorption was 26.6 $m^2\ g^{-1}$ for a fresh sample and 4.9 $m^2\ g^{-1}$ after treatment with 1-butene at 181°C (*9*); the pore volume was 0.08 $cm^3\ g^{-1}$.

Analysis. Feeds and products were analysed by a gas chromatograph equipped with a thermal conductivity detector using a 15.4 m copper column 6 × 4 mm filled with Chromosorb P (40–60 mesh) at 15°C; helium was used as carrier gas at 1.3 kg/cm^2. The liquid phase (23 wt%) was glutaronitrile and propylenecarbonate (wt ratio 4:6). Under constant gas flow conditions the relative retention times were the following (analytical calibration factors in parentheses): air and methane, 0.373

(0.967); isobutane and carbon dioxide, 0.607 (0.763); *n*-butane, 0.704 (0.870); 1-butene, 1 (1); isobutene, 1.076 (1.230); *trans*-2-butene, 1.181 (1.068); *cis*-2-butene, 1.368 (1.051); 1,3-butadiene, 1.932 (1.115).

Reaction. The reaction of 1-butene and *cis*-2-butene on platinum black was studied between 135 and 180°C in a tubular glass reactor (100 mm high; 6 mm diameter) according to the following procedure. The catalyst, supported on glass wool, was inserted in the reactor and evacuated at 1×10^{-5} mm Hg at 180°C for 2 hr; then a small flow of hydrogen was admitted for 1 hr at 180°C. The reactor was evacuated for 3 hr at 1×10^{-5} mm Hg at 180°C, and a flow of 1-butene or *cis*-2-butene was then fed for about 5 hr at 140°C. This treatment, according to Taylor, Thomson and Webb (*10*), assured the best elimination of the hydrogen from the catalyst.

Finally the reactor was fed with a flux of 1-butene or *cis*-2-butene and helium (or air) which were measured with soap flow meters and then dried. The inlet and outlet of the reactor were then closed and after a given reaction time a sample of reacting gas was withdrawn for analysis. After each sampling the reactor was flushed with a mixture having the initial partial pressure of the components for 15 min; then it was closed for a new run.

A blank run at 135°C with 1-butene (148 mm Hg) in the batch reactor did not show any thermal conversion of 1-butene in 24 hr.

3. RESULTS

The experiments include: (i) isomerization of 1-butene in a flow reactor (ii) isomerization of 1-butene and *cis*-2-butene in a batch reactor. As regards (i), no conversion of 1-butene was found for the following conditions: temperature, 135°C; contact time $\tau = 25.7$ g $(\text{mole/hr})^{-1}$; partial pressure of 1-butene from 267 to 675 mm Hg. In Table 1 molar fractions (percentage) of reactants and products at different reaction times, temperatures and feeds are reported for the experiments in the batch reactor. The runs from 1 to 9 and the runs 14 and 15 have been made with the same sample of platinum black (sample I, 0.5120 g); the runs from 10 to 13 with another sample of the same platinum black (sample II, 0.3017 g). Samples I and II have been submitted to the same treatment, as previously described, before being used.

TABLE 1

ISOMERIZATION OF 1-BUTENE AND *cis*-2-BUTENE USING A BATCH REACTOR

Run no.	Feed	*T* (°C)	Butene pressure (mm Hg)	Time (min)	Butenes			1,3-Butadiene	CO_2	*n*-Butane
					1	2-*cis*	2-*trans*			
1	1-Butene	135	148	30	89.89	4.72	3.49	na[a]	—	0.24
2		135	148	60	86.26	6.50	5.38	na	—	0.25
3		135	148	90	74.16	12.70	11.04	na	—	0.31
4		135	148	1440	17.81	26.43	51.02	na	—	2.22
5		135	148	30	90.31	4.20	3.05	0.31	—	0.21
6		135	148	60	87.64	6.31	4.16	0.21	—	0.30
7		150	148	30	88.91	5.23	3.89	0.22	—	0.23
8		165	148	30	86.72	5.77	4.77	0.25	—	0.25
9		180	148	30	91.69	3.33	2.46	0.28	—	0.11
10	*cis*-2-Butene	135	170	30	0.20	99.50	0.30	na	—	—
11		135	170	60	0.20	90.50	0.30	na	—	—
12		135	170	120	0.48	98.93	0.59	na	—	—
13		135	170	1440	2.60	92.78	4.40	na	—	—
14	1-Butene + air	135	150, *p*(air) = 610	10	69.73	0.85	0.75	0.24	25.91	1.71
15		135	150, *p*(air) = 610	30	76.71	0.74	0.59	0.21	20.53	0.17

[a] na = not analyzed.

The runs from 1 to 6 have been made cyclically at 135°C and $p_{1\text{-butene}} = 148$ mm Hg in order to verify the reproducibility of the results and the deactivation of the catalyst. The runs from 7 to 9 have been performed at 150, 165, 180°C and $p_{1\text{-butene}} = 148$ mm Hg. For the runs from 10 to 13 a feed of *cis*-2-butene and helium has been used. Finally experiments 14 and 15 were made by feeding the reactor with a mixture of 1-butene and air ($p_{1\text{-butene}} = 150$ mm Hg; $p_{\text{air}} = 610$ mm Hg).

4. DISCUSSION

From an analysis of Table 1 it follows that: (i) at suitable conditions of residence time platinum black can isomerize *n*-butenes, (ii) a dissociative process takes place on platinum black with the formation of 1,3-butadiene (which is not present in the feed).

Platinum black does not isomerize *n*-butenes in the flow reactor. This failure is clearly connected with the small residence time of the flow runs (about 0.5 sec); this value is three orders of magnitude smaller than the least residence time employed in the batch experiments (10 min). There was substantial difficulty in increasing the contact time, τ, in the flow reactor beyond the value of 25.7 g $(\text{mole/hr})^{-1}$.

The lack of activity in the flow experiments could also be due to the presence of helium in the flow stream. Assuming 1-butene to be adsorbed dissociatively, helium could act as a vacuum on the $H_2(g)$ obtained in the reaction:

$$H(a) + H(a) \rightarrow H_2(g),$$

so reducing the concentration of the adsorbed hydrogen atoms, H(a), taking part in the isomerization reaction.

As previously reported, the surface area of the platinum black was reduced from 26.6 m^2g^{-1} to 4.9 m^2g^{-1} [a value close to the surface area of platinum powders ($\leqslant 1$ m^2g^{-1})] by treatment with 1-butene at 181°C. This effect was also shown by another platinum sample (Lot No. 19779) at temperatures higher than 105°C. The reduction of surface area has an obvious influence on the catalytic activity of platinum. The employement of platinum powders and small residence times can perhaps justify the conclusions reported by some authors about the inactivity of unsupported platinum in the isomerization of 1-butene in the absence of molecular hydrogen (*1*b).

The results reported in Table 1 give useful indications for elucidating the probable mechanism of the nonskeletal isomerization of *n*-butenes. The results at 135°C show that the catalyst does not deactivate during runs 1–6 and that the analyses are reproducible.

The runs reported in Table 1 have not been planned in order to calculate kinetic parameters, but to ascertain the conditions in which platinum black could isomerize *n*-butenes. However, some kinetic considerations are justified. External diffusion could be rate-controlling due to the type of reactor employed (not a stirred batch reactor), although it has been verified that internal diffusion is not rate-controlling since the effectiveness factor for the employed platinum black is greater than 0.95. An overall reaction rate for 1-butene is easily calculated from its initial partial pressure and its conversions, taking also into account the volume of the reactor, the weight and surface area of the catalyst. The mean results at 135, 150, 165 and 180°C as moles 1-butene converted/(min · m^2Pt) are, respectively (times 10^8): 8.66, 10.58, 11.37 and 6.57.

The decrease in reactivity at 180°C, at constant 1-butene partial pressure, rules out external diffusion as the rate-controlling step. So this decrease could be due to: (i) some surface phenomena of self-poisoning, such as formation of surface residues (*11*), or (ii) to a decrease of the product bk, b being the adsorption constant for 1-butene on platinum and k the overall rate constant.

As regards (i), it was verified (*11*) that on alumina-supported palladium "carbon–carbon bond rupture appears to be unimportant except at 200°C"; the temperature of 180°C is near enough to 200°C to justify the formation of surface residues also on platinum black. The formation of CO_2

as a major product in 1-butene/O_2 runs at 135°C could support this conclusion. However, at 135°C the runs without oxygen show a good reproducibility showing that at this temperature either no carbonaceous residues are formed on the surface or the whole surface is poisoned within 30 min. The results quoted from Taylor, Thompson and Webb (*11*) suggest that this second hypothesis is not probable at 135°C. For this reason the runs with 1-butene and oxygen seem to be not particularly useful to clarify the reasons for the reactivity decrease at 180°C. In a recent paper (*12*) it was shown that on a foil of platinum the rate of carbon deposition from *cis*-2-butene and hydrogen (100 and 50 Torr, respectively) at 550°C is zero. Such a result is not easily extended to our conditions, both on accounts of the presence of hydrogen and the different surface area of platinum foil, which is two orders of magnitude smaller than that of platinum black. To obtain a better understanding of the kinetic aspects of the isomerization of n-butenes on platinum black and the irreversibility of the poisoning at 180°C, work is in progress using a mixed flow reactor (*13*).

As to the mechanism of the double-bond migration we refer to Fig. 1 (*14*) where the paths for addition–abstraction (AD–AB) mechanism (alkyl-reversal) and abstraction–addition (AB-AD) mechanism (π-allylic intermediate) are reported.

Two remarkable differences exist between the mechanisms: in the former there is a direct *cis–trans* isomerization, that is 1-butene is not a necessary intermediate, while in the latter there is not a direct *cis–trans* isomerization (1-butene is a necessary intermediate) but there is a formation of 1,3-butadiene.

From the presence of 1,3-butadiene in all the experiments where it has been analyzed, from the induction period in the experiments with *cis*-2-butene as a feed (analyses 10 and 11 are the same as the blank) and from the high fraction of 1-butene in experiments 12 and 13 it is easy to conclude that in our case the AB-AD mechanism is operative.

However, it must be noted that the 1,3-butadiene concentration is quite constant over all the runs. It is therefore possible that the AD-AB mechanism is simultaneously operative by means of the hydrogen deriving from the formation of 1,3-butadiene. This explanation is similar to that proposed for the isomerization of 1-butene over pure gold at 300°C (*4*).

From Table 1 we note that the molar fraction of n-butane in each experiment is very close to that of the blank. So it is possible to rule out the process: 2(1-butene) → 1,3-butadiene + n-butane. However, at very high residence time (run No. 4), self-hydrogenation is realized.

The mechanism AD-AB could become relevant at 180°C where besides 1,3-butadiene surface residues could be present. This process at the beginning would be a type of partial self-hydrogenation of the kind studied on nickel by McKee (*15*).

The runs 14 and 15 (Table 1) with 1-butene and oxygen as a feed confirm that the latter reagent is a strong inhibitor of the isomerization reaction. We think, however, that this fact cannot discriminate between the two mechanisms because the availability of surface hydrogen should decrease in any case in the presence of oxygen.

We conclude agreeing with Rooney and Webb (*14*) that "although both mechanisms may occur simultaneously, their relative importance should depend on the metal and the experimental conditions."

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