JOURNAL OF CATALYSIS **151**, 26–32 (1995)

A Skeletal Rearrangement Study of Labelled Butanes on a Solid Superacid Catalyst : Sulfuric Acid Treated Zirconium Oxide

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Received February 7, 1994; revised June 10, 1994

The reactions of *n*-butane and isobutane have been studied in a flow system in the presence of hydrogen at 250°C using sulfuric acid treated zirconia as catalyst. The conversion of the butanes occurs with high selectivity in isomerization. The branched isomer reacts much faster than the linear one. The use of ^{13}C labelled starting material and analysis of the isotope distribution in the products show that the rearrangement is of intramolecular nature in accord with the superacidic properties of the catalyst. © 1995 Academic Press, Inc.

INTRODUCTION

Under the pressure of the worldwide trend towards more severe environmental legislation the refining industry has started to produce cleaner fuels. In order to maintain a high octane number in the absence of lead additives and aromatic octane boosters because of their toxicity, gasoline is reformulated and includes more branched alkanes as well as oxygenates such as methyl *tert*-butyl ether (MTBE) or *t*-butanol (1). In this respect the isomerization of butane to isobutane is of significant importance. Isobutane is the main intermediate in the paraffin alkylation process in which butane and propane are converted into C_7, C_8, branched paraffins with high octane numbers. Further, its dehydrogenation to isobutene is directly tied to the manufacture of MTBE and ethyl *tert*-butyl ether (ETBE).

Industrial processes for butane isomerization (such as those of UOP or BP) use chlorinated alumina with supported platinum in the 150–300°C range. As the temperature-dependent thermodynamic equilibrium is in favor of isobutane below 200°C it is most beneficial to carry out the reaction at the lowest temperature possible. In the past decade an important research effort has been made to find selective and active catalysts for this reaction; however, solid catalysts effective for *n*-alkane isomerization are known to show poor selectivity (2). On the other hand, liquid superacids (3) based on HF, which are efficient and selective at room temperature (4), are not suited for industrial processes due to separation problems tied with environmental protection. Further, solid superacids such as SbF_5-inserted graphite (5) and SbF_5 deposited on SiO_2 (6), which are also selective, deactivate rapidly.

The discovery by Tanabe and Hattori (7) of the superacidic properties of sulfuric acid treated zirconium oxide (ZrO_2/SO_4^{2-}), the acidity of which was estimated to be as high as $H_0 \leq -14.5$ by the adsorbed Hammett base technique, has given a new impulse to solid superacid catalysis. A variety of oxides (Zr, Fe, Sn, Ti) treated with sulfuric acid showed activities for acid-catalyzed reactions in a low temperature range, including *n*-butane isomerization (8).

The importance of solid-acid catalysis in petroleum refining has favored extensive studies of the acidic properties, the structure of the acid site and their catalytic action (9). Until now, however, very little is known about the mechanism of the skeletal rearrangement, and the nature of the cationic intermediates has recently been questioned (10). Labelled hydrocarbons have been used earlier to study zeolite-catalyzed conversions (11, 12). In this paper we contribute to the mechanistic studies by using ^{13}C-labelled butanes and isobutanes as starting material and analyzing the isotopic distribution in the reaction products in order to check the intramolecular nature of the isomerization reaction catalyzed by sulfated zirconium oxide.

EXPERIMENTAL

Catalyst Preparation

The catalysts were prepared following procedures already described in the literature. ZrO_2/SO_4^{2-} was prepared as follows: $Zr(OH)_4$ was obtained by hydrolyzing zirconyl chloride (30 g of $ZrCl_2$, 0.8 H_2O Ventron product of purity 99.99% were dissolved at room temperature in 500 ml of pure water) with an aqueous solution of ammo-

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nium hydroxide at pH = 9 (solution of NH_3 Prolabo at 33%). The precipitate was stirred for 15 min at room temperature then filtered and washed with deionized water until the filtrate was neutral, dried at 110°C for 16 h and ground. The sulfate ion was introduced by pouring 6 ml of H_2SO_4 (0.5 *M*) per gram of $Zr(OH)_4$ under stirring for 1 h, then filtered, not washed, and dried at 110°C for 24 h. Then $Zr(OH)_4/SO_4^{2-}$ was calcined in an air flow at 650°C for 3 h. The powder was crushed and kept under argon before use. ZrO_2/SO_4^{2-} is the resulting solid.

$-Pt/SO_4^{2-}/ZrO_2$ was prepared by impregnation of 2.5 g of ZrO_2/SO_4^{2-} and immersed in 4 ml of H_2PtCl_6 solution (0.3 weight % of Pt). After filtration, drying at 110°C, and calcination at 600°C (3 h) the catalyst was stored as described above.

Materials

Hydrocarbons (Fluka puriss grade) were used without further purification. Hydrogen was purchased from Air Liquide (purity 4*N*).

The syntheses of the ^{13}C-labelled hydrocarbons used as reactants have been described (13). We obtained 1-^{13}C-2-butanol by the reaction of propanal with ^{13}C-methylmagnesium iodide, followed by acidic hydrolysis. Before each experiment 7 μl of 1-^{13}C-2-butanol was dehydrated on Al_2O_3 and hydrogenated on Pt/Al_2O_3, and the hydrocarbon was purified by preparative GC before the catalytic experiment. To obtain 2-^{13}C-2-methyl propane we started from $CH_3-^{13}CO-CH_3$ and CH_3MgI. To obtain 1-^{13}C-2-methyl propane, we started from acetone and $^{13}CH_3MgI$. In both cases the alcohol was dehydrated, hydrogenated, and purified as described above. The isotopic purity was around 80%.

Apparatus and Procedure

The isomerization reactions were carried out in an all-glass, grease-free flow system (14). The catalyst bed (200 mg) was isothermal and isobaric. A small amount of labelled hydrocarbon (approx. 5 μl) was used for each run and injected into the reactor at a constant pressure (10 and 20 Torr for *n*-butane and isobutane, respectively). Under such conditions, with the same hydrogen flow rate for both experiments the space velocity for 2-methyl propane will be twice that of *n*-butane. In other words, for a given conversion, the reaction rate for isobutane is twice the rate of *n*-butane. The pressure-vs-time curve recorded by means of a katharometer inserted in the flow line closely approximated a square-wave pulse. From this curve, the hydrocarbon pressure and the hydrocarbon flow rate could be determined. Samples for GLC analysis were removed directly from the gas phase by a gas syringe as the pulse passed a rubber septum located close to the reactor. Most of the hydrocarbons were collected at the exit of the reactor during the plateau of the $P-f(t)$ curve, which lasted several minutes. A chromatographic separation was then performed at 25°C on 5 m × 0.25 mm silicone SE 30 column, and the two fractions containing the C_4 products were analyzed by direct injection into the mass spectrometer.

Activity Test

The reaction conditions were as follows:

—hydrogen flow rate 15 ml min^{-1}

—hydrocarbon flow rate 0.17 ml min^{-1} (30 ml of hydrocarbon was trapped in a U-tube at −78°C).

Unlabelled hydrocarbons were passed through the catalyst for 2 or 3 h at a constant pressure. Only labelled hydrocarbons were injected as a pulse.

—Catalyst weight : 200 mg.

Before catalytic experiments, the catalyst in the reactor was evacuated under vacuum to 10^{-2} Torr at 400°C for 3 h. Afterwards the temperature was lowered to 250°C and the catalytic bed was kept under hydrogen flow.

—Reaction temperature : 250°C.

Physicochemical Characterization

X-ray diffraction measurements were carried out on a Siemens diffractometer using Co*Kα* radiation.

—$Zr(OH)_4$ and $Zr(OH)_4$, SO_4^{2-} are amorphous;

—ZrO_2/SO_4^{2-} shows a tetragonal structure predominantly with some monoclinic phase. This structure is stable. The same diffraction pattern is present after a catalytic experiment;

—ZrO_2 has a monoclinic structure.

FTIR. Spectra of ZrO_2 and ZrO_2/SO_4^{2-} were recorded at room temperature on a Nicolet 5DXC FT spectrometer.

BET measurements were performed at liquid-nitrogen temperature on 100 mg catalyst sample under nitrogen and helium with the Perkin–Elmer shell sorptometer. The results are reported in Table 1.

Nota bene : Considering the importance of the activation and deactivation processes (15, 16) we have run all our experiments with the labelled butanes on a stabilized catalyst using a fresh sample for each run. All experiments were performed with the same space velocity.

RESULTS AND DISCUSSION

Skeletal isomerization of *n*-butane into isobutane has often been used as a test reaction for the activity of solid-acid catalysts. Among the light alkanes, *n*-butane is a convenient model compound as it yields a very simple

TABLE 1

Effect of Sulfuric Acid Treatment on the Specific Surface Area of Zirconium Oxide

	0.5 M H_2SO_4 contact time (min)	BET surface area (m^2/g)
ZrO_2	0	32
ZrO_2/SO_4^{2-}	15	104
ZrO_2/SO_4^{2-}	60[a]	118
ZrO_2/SO_4^{2-} (Ref. (8f))	60	124
ZrO_2/SO_4^{2-}	After experiment[b]	120

[a] Catalyst used for the catalytic tests.

[b] 3 h flow of butane at 250°C.

product distribution. Two competitive mechanistic pathways are generally proposed which are of either intra- or intermolecular nature.

The intramolecular process (as shown in Scheme 2 with ^{13}C-labelled material) is energetically disfavored as it necessitates the formation of a primary carbenium ion intermediate, the 2-methyl-1-propylium ion.

In the bimolecular process, the skeletal rearrangement occurs before β-scission of an octyl cation obtained by alkylation of butene by the secondary butyl cation. The formation of the alkene by proton loss of the carbocation, unfavorable under superacidic conditions (18), is the reason for the polymerization–coke formation which deactivates the catalyst (19). The β-scission of the octyl cation gives preferentially C_4 moieties but is nevertheless at the origin of C_3 and C_5 alkanes.

In a previous paper (16) we have shown the essential role of hydrogen for maintaining the catalyst activity. If the hydrogen pressure is high enough the presence of platinum is not necessary to maintain the catalyst activity. As the purpose of this work was mainly to investigate the mechanism (mono- or bimolecular process) of butane isomerization on the solid superacid using ^{13}C-labelled starting material we first studied the selectivity of the reaction on unlabelled compounds.

The product distribution based on GC analysis is collected in Table 2 in order to compare the experiments performed with n-butane and 2-methyl propane on sulfated zirconium oxide with and without platinum (ZrO_2/SO_4^{2-} and $Pt/ZrO_2/SO_4^{2-}$). The following points can be observed. The selectivity in isomerization is always very high (>80%) compared to cracking and homologation. As each run is made with a fresh catalyst sample we notice a good reproducibility of each experiment, the catalyst being first stabilized with unlabelled hydrocarbon.

The products of higher molecular weight than the starting material are always 5–10 times less important than the cracking products. This can be ascribed to the fact that cracking of the C_5 is easier than that of the smaller C_3 hydrocarbons formed in the $C_4 + C_4 \rightarrow C_8 \rightarrow C_3 + C_5$ dimerization β-scission reaction, unless a part of the C_1–C_3 material is obtained directly by protolytic cleavage of a C–C bond in butane (17). This point can be stressed, as very little C_2 product is observed on ZrO_2/SO_4^{2-} when isobutane is the starting material. We note also that in the experiments with the platinum-containing catalyst only negligible homologation appears.

The conversion appearing in the last column of Table 2 is only an apparent conversion because the GC results do

TABLE 2

Reactant and Product Distribution (in Moles)

			Cracking[a]		Isomers		Homologation			
Run	Catalyst	Hydrocarbon	$C_1 + C_2$	C_3	iC_4	nC_4	iC_5	nC_5	Selectivity[b] (%)	Conversion[c] (α)
1	ZrO_2/SO_4^{2-}		1.5	1.2	15	82	0.16	0.06	84	18
2	ZrO_2/SO_4^{2-}		0.7	1.1	13	85	0.16	0.05	86	15
13	ZrO_2/SO_4^{2-}		ε	ε	4.5	95.5	—	—	100	4.5
9	With Pt		1.1	0.7	14.4	83	0.8	ε	84	17
3	ZrO_2/SO_4^{2-}		0.5	1.4	83	14.5	0.54	0.13	85	17
4	ZrO_2/SO_4^{2-}		—	1.3	83.5	14.7	0.5	—	89	16.5
12	ZrO_2/SO_4^{2-}		0.2	0.6	92	7.1	ε	—	88	8
6	With Pt		1.5	0.5	91	6.9	0.07	—	77	9

[a] C_1 and C_2 were not separated.

[b] Selectivity in isomerization.

[c] Apparent conversion (see text).

TABLE 3

Product and Label Distribution Obtained from 1-^{13}C Butane, Expressed as Percentages

Run no.	Catalyst	Cracking products	Homologation	Self-isomerization[c] 	Isomers 		Multilabelling	Conversion (%) Total (α_T)	Apparent (α)
1	ZrO_2/SO_4^{2}	14.0	1.0	5.5	23.0 (29)[a]	56.5 (71)	<3	19.0	18.0
2	ZrO_2/SO_4^{2-}	12.0	1.5	~0.0	26.5 (30)	60.0 (70)	<3	15.0	15.0
13	ZrO_2/SO_4^{2}	0.0	0.0	~0.0	20.0 (20)	80.0 (80)	<3	4.5	4.5
9	With Pt	10.5	4.5	~0.0	22.0 (26)	63.0 (74)	~0	17.0	17.0
Stat.[b]					(25)	(75)			

[a] The relative percentages of each 2-methylpropane isotopomer are in brackets.

[b] Statistical isotopomer distributon.

[c] Isomerization, 1-^{13}C butane to 2-^{13}C butane.

not take into account the self-isomerization reaction and the eventual multilabelling indicated by the mass spectrometry, as will be discussed below. However, we may note that the experiments were performed at an apparent conversion lower than 20%.

^{13}C labelling of the starting material and mass spectrometric analysis of the resulting products give a much deeper insight into the acid-catalyzed hydrocarbon transformation.

The isotopic label redistribution which occurs during the isomerization process of 1-^{13}C butane, 1- and 2-^{13}C 2-methyl propane is apparent in Tables 3 and 4.

The last column of both tables shows the difference between the apparent conversion, which is measured by GC when the compounds are unlabelled, and the real conversion or "total conversion," which can be seen only when self-isomerization and double labelling are measured via isotope redistribution. In this way we can note (Table 3) that the rate of self-isomerization of 1-^{13}C-*n*-butane to 2-^{13}C-*n*-butane accounts for 5% (Experiment 1) and is below the limit of sensitivity in Experiments 2, 13, and 9 in the product distribution of ZrO_2/SO_4^{2-}, whereas the double labelling is lower than 3% and even nonexistent on the $Pt/ZrO_2/SO_4^{2-}$ catalyst (Experiment 9). On the contrary, in the case of isobutane (Table 4), the rate of self-isomerization is of the same order of magnitude as the skeletal isomerization, in the presence as well as in the absence of platinum. Taking into account that the space velocity of 2-methylpropane is twice that of *n*-butane in our experiments, we note by comparison of total conversions in Tables 3 and 4 that the respective reaction rates of these two hydrocarbons is about 3 to 6 in the absence of platinum and only above 1.5 in the presence of this metal.

The double labelling is observed only in the absence of Pt (Experiments 3, 4, and 12). We may note that, as the relative contribution of the homologation reaction is lower than 5%, the percentage of the multi-labelled hy-

TABLE 4

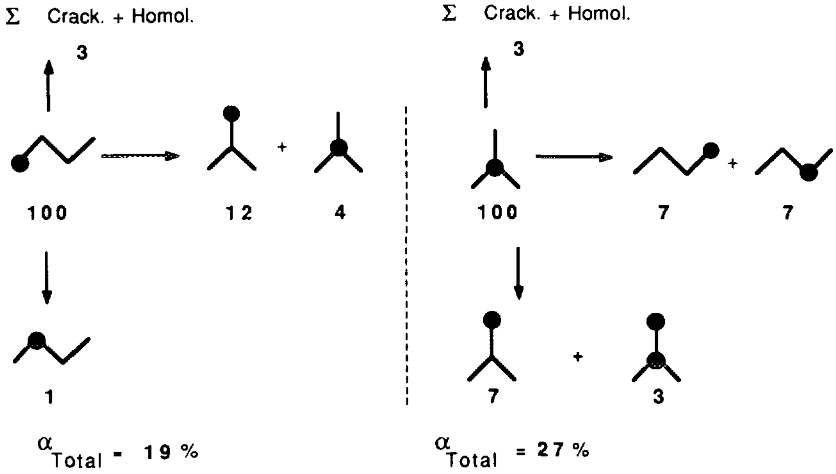
Product and Label Distribution Obtained from 2-^{13}C and 1-^{13}C-2-Methyl-propane, Expressed as Percentages

Experiment no.	Catalyst	Hydrocarbon	Cracking products	Homologation	Self-isomerization[c]	Isomers 		Multilabelling[b]	Conversion (%) Total	Apparent
3	ZrO_2/SO_4^{2-}		7.0	2.5	26.5	26.0 (49)[a]	27.0 (51)	11	27.0	17.0
4	ZrO_2/SO_4^{2}		4.5	1.5	35.5	24.0 (48)	25.5 (52)	8	29.5	16.5
12	ZrO_2/SO_4^{2}		5.5	0.0	42.0	24.0 (47)	27.5 (53)	2.5	14.5	8.0
6	with Pt		16.5	0.5	25.0	29.0 (50)	29.0 (50)	0	12.0	9.0
Stat.[b]						(50)	(50)			

[a] The relative percentages of each isotopomer are in brackets.

[b] The multilabelled hydrocarbon is essentially [1-^{13}C 2-^{13}C] 2-methylpropane.

[c] Isotopomerization only.



SCHEME 1. Isomer and isotopomer distribution.

drocarbons formed will show large experimental errors. This explains why no general trend occurs.

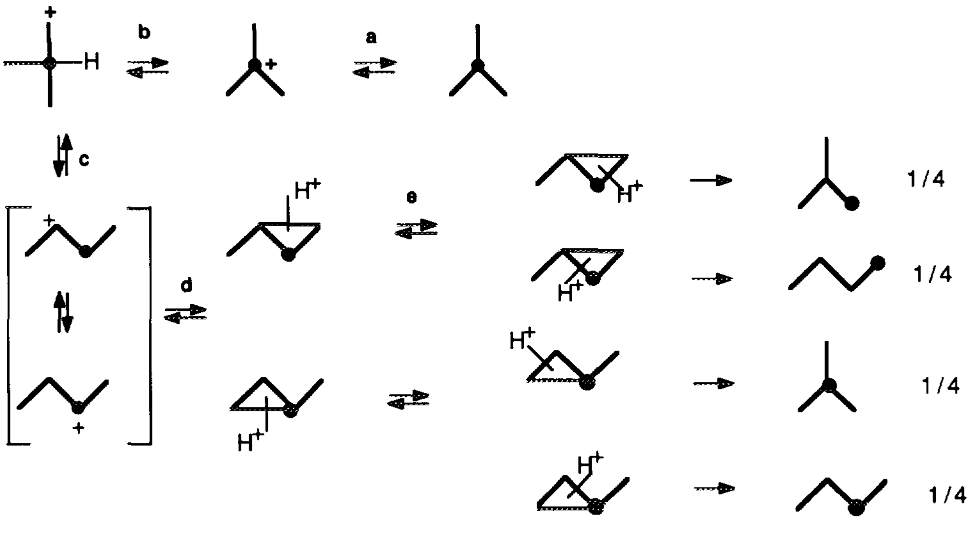
On the other hand, only 2-methyl propane is double labelled independently of the starting material. This makes it easier to understand why, when 1-^{13}C-n butane is the starting material, the relative amount of double labelling is independent of the importance of the homologation reaction as 2-methyl propane is essentially an isomerization product. The process giving the double-labelled hydrocarbon is a repetitive process, the contribution of which is difficult to estimate.

Considering the isotopomer distribution, the *n*-butanes which are formed from labelled 2-methyl propane show a statistical label distribution (Table 4). The labelled isobutanes which are formed when 1-^{13}C *n*-butane is the starting material also show a close to statistical distribution (Table 3).

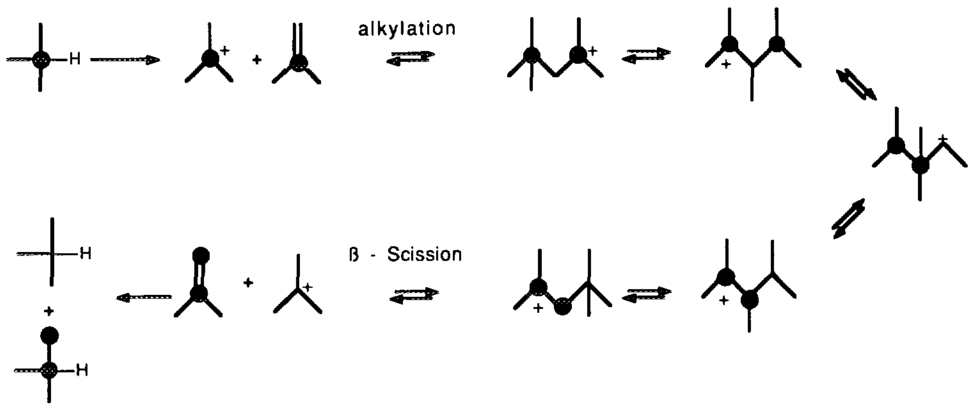
All these results can be expressed in Schemes 1–3. Experiments 1 and 3 are taken as examples. The numbers indicate the distribution of the various products. The sum of these numbers is equal to the total conversion of the reaction. In order to compare the rates of formation of the products we have to keep in mind that the space velocity used for isobutane was double that of its linear isomer.

The label redistribution seems to be very fast as the statistical distribution is reached in the skeletal isomers. In the case of isobutane isomerization, the formation of an adsorbed protonated cyclopropane intermediate is in accord with the label distribution in the *n*-butane as well as in the autoisomerization product.

Despite the important role of solid-acid catalysis in oil refining the mode of formation of the carbocation from the starting hydrocarbon (step a) is still very controver-



SCHEME 2. Skeletal rearrangement.



SCHEME 3. Double-labelling process via alkylation-β-scission.

sial. Whereas in liquid superacids the protolytic cleavage of C–H and C–C bonds at low temperature is well documented (3, 20) such behaviour has only been partly demonstrated on acidic zeolites at temperatures above 400°C (17, 21). The reversible protonation of hydrocarbons at 100°C on acidic zeolites was recently suggested (22) but it has been shown meanwhile that this reaction does not occur, at least at these temperatures (23).

The rearrangement of the *t*-butyl ion into the primary 2-methyl-1-propylium ion is the slowest step of the reaction scheme. Olah *et al.* have recently suggested that in strong superacidic media this rearrangement (steps b and c) was activated by a second protonation (protosolvation) of the *t*-butyl cation (24).

The carbon label scrambling in the *sec*-butyl cation via protonated cyclopropyl intermediates (steps d and e) is a rather facile process which has been studied on the stable ions in liquid superacid media (25, 26).

In the case of *n*-butane isomerization (Table 3), the label redistribution is close to the statistical one and can be best explained by a protonated cyclopropane intermediate which can engender both rapid proton and methyl migration.

The double labelling is noted when isobutane is the starting material or the isomer formed necessitates a bimolecular pathway with classical (1, 2) alkide and hydride group migrations which are well known in acid catalysis. Moreover, the double-labelled isobutane was found to be essentially [1-^{13}C, 2-^{13}C,] 2-methylpropane as it appears in Scheme 3.

CONCLUSION

The main catalytic pathway on the ZrO_2/SO_4^{2-} solid superacid catalyst is a monomolecular process when the total conversion is less than 30%. Nevertheless at this level of conversion there is already a statistical distribution of the isotopomers which are formed, in accord with a mechanism via adsorbed protonated cyclopropanes.

The branched isomer reacts much faster than the linear one with a high rate of isotopomerization. An interesting point is that the double-labelled hydrocarbon is exclusively 2-methylpropane independently of the nature of the starting isomer. This strengthens the mechanism of alkylation-β scission which is not in this case such a major pathway as it is in the zeolite-catalyzed conversion of butane at higher temperatures.

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