Superacidic FSO_3H/HF catalyzed butane isomerization [1]

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Superacid catalyzed isomerization of butane was studied. Highly efficient isomerization of butane to 2-methylpropane (isobutane) was achieved using fluorosulfuric acid containing up to 5% of hydrogen fluoride acting as a protic co-acid. The isomerization when carried out in excess FSO_3H at 21 °C in a flow system gave ~ 70% conversion to 2-methylpropane with generally less than 3% cracking. When 2-methylpropane was isomerized under similar conditions about 12% butane was formed. Attempted isomerization of pentane and hexane with prolonged reaction times in a static system results in predominant protolytic cleavage (cracking).

Keywords: Butane isomerization; superacid catalysis

1. Introduction

The isomerization of butane to 2-methylpropane (isobutane) is of substantial significance [2]. Butane is available from natural gas sources which usually contain only very limited amounts of the branched chain isomer isobutane which is significant in the manufacture of high octane gasoline. Further its dehydrogenation to isobutylene can become significant in the manufacture of polyisobutylene, *tert*-butyl alcohol, methyl *tert*-butyl ether, and other products.

The isomerization of butane to 2-methylpropane is generally carried out by using chlorinated alumina in adjunction of supported platinum [3]. Industrial processes operate in the 150–300 °C temperature range. The two major available processes are those of Universal Oil Products (UOP) and British Petroleum (BP). The UOP process operates with a platinum containing catalyst at 250–300 °C whereas the BP isomerization process uses a platimun catalyst and operates between 15 and 30 atms pressure at a temperature of between about

Table 1
Equilibrium composition of butane and 2-methylpropane

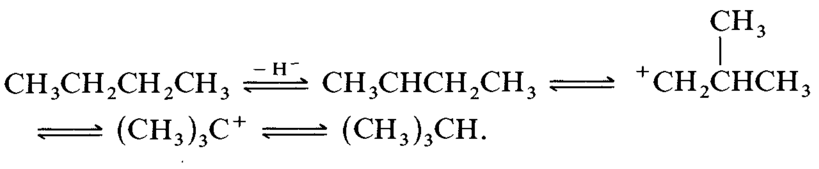
	Temperature (°C)				
	−6	38	66	93	180
2-methylpropane	85	75	65	57	45
butane	15	25	35	43	55

150–200 °C [3]. Under these conditions, butane under hydrogen pressure is brought to near equilibrium conversion to 2-methylpropane. The butane $\rightleftharpoons$ 2-methylpropane equilibrium is temperature dependent [4] (table 1).

The product composition in butane isomerization is determined by the thermodynamic equilibria. At a temperature of 180 °C the equilibrium represents about 45% 2-methylpropane and 55% butane, but at −6 °C the equilibrium is 85% 2-methylpropane and 15% butane. Lowering the temperature thus greatly increases the 2-methylpropane content of the equilibrium mixture. In order to obtain a maximum ratio of 2-methylpropane over butane, it would be advantageous to carry out the isomerization at the lowest feasible temperature. However, the rates of the isomerization at lower temperatures are too slow and consequently so far no practical low temperature isomerization was possible. The acid catalyzed isomerization of alkanes is well studied and was reviewed [4].

The discovery of superacidic systems (i.e., acids up to billion times stronger than 100% H_2SO_4 or anhydrous hydrogen fluoride) [5] opened up extensive research into superacid catalyzed hydrocarbon conversions, including the isomerization of alkanes. Olah disclosed [6] processes for the alkylation of hydrocarbons with alkenes and the isomerization of alkanes, utilizing superacidic catalysts composed of a Lewis acid halide, such as antimony pentafluoride, tantalum pentafluoride, niobium pentafluoride, vanadium pentafluoride, titatium tetrafluoride, molybdenum hexafluoride, bismuth pentafluoride, phosphorus pentafluoride, arsenic pentafluoride, and the like, and strong Bronsted acids such as fluorosulfuric acid or trifluoromethanesulfonic acid [7].

In the acid catalyzed isomerization of alkanes, isomerization of butane represents a case different from that of higher alkanes (pentanes, hexanes, heptanes, etc.). The reason for this is that in the isomerization of butane to isobutane the reaction is either bimolecular (in the presence of butenes) or intramolecular, where it must proceed through the isobutyl cation, a relatively high energy primary carbocation (although of partially delocalized protonated cyclopropane nature) which raises the activation energy of the process.



$$CH_3CH_2CH_2CH_3 \overset{-H^-}{\rightleftharpoons} CH_3CHCH_2CH_3 \rightleftharpoons {}^{+}CH_2\overset{\overset{CH_3}{|}}{C}HCH_3 \rightleftharpoons (CH_3)_3C^+ \rightleftharpoons (CH_3)_3CH.$$

Table 2
Isomerization of butane with fluorosulfuric acid/hydrogen fluoride at 21° C under continuous flow condition

on stream time (hrs)	mol% C_3	i-C_4	n-C_4	SO_2
0.5	5.7	44.9	48.9	0.5
1	1.9	53.5	42.6	1.7
1.5	3.6	60.8	33.6	1.9
2	8.0	64.8	24.6	2.6
4	3.4	61.5	33.2	1.8
6	2.8	68.4	26.4	2.2
11	3.4	70.3	23.8	2.4
12	3.3	69.9	24.5	2.2

There is, however no ready β-cleavage involved in the C_{4+} system, although direct C–C bond protolysis by strong superacids can cause hydrocracking of butane. This is the reason, for example, why Brouwer et al. found [10] that the extremely strong 1 : 1 HF-SbF_5 superacid is not efficient to isomerize butane to isobutane, but causes extensively hydrocracking besides carbon/and hydrogen scrambling. Similarly treatment of butane with 1 : 1 FSO_3H-SbF_5 results also in extensive hydrocracking and only limited isomerization [11].

2. Results and discussion

We report now that in the course of our continuing study of superacid-catalyzed reactions of hydrocarbons we have found an efficient way to carry out the isomerization of butane to 2-methylpropane with fluorosulfuric acid containing hydrogen fluoride as co-acid. The isomerization can be carried out in a flow system with relatively short contact times (around 30 sec) at room temperature (21° C) while obtaining high conversion to 2-methylpropane with limited ($< 5\%$) formation of hydrocracking and secondary reaction products. Results are summarized in table 2. Overall butane recovery from the system was generally $\geqslant 90\%$, the balance besides propane being methane.

In superacid catalyzed isomerization of alkanes product composition is affected by the equilibria of the neutral hydrocarbons and the related carbocations. For example the thermodynamic equilibrium of the isomeric xylenes is about 18% ortho, 61% meta and 21% para isomer. This is the equilibrium reached in isomerization of excess xylenes with aluminum trichloride or related Friedel-Crafts catalysts. When, however, xylenes are treated in excess of superacidic HF/BF_3, 100% meta-xylene is obtained. This process, however, is not a catalytic isomerization, but selective formation of the most stable carbocations. In the superacid solution xylenes are protonated giving their arenium ions. The

Table 3
Isomerization of 2-methylpropane with fluorosulfuric acid/hydrogen fluoride at 21 °C under continuous flow condition

on stream time (hrs)	mol% C_1	C_2H_6	C_3	i-C_4	n-C_4	SO_2
0.5			0.1	98.4	1.5	
5	0.8		1.5	91.9	5.9	
6	< 0.1		3.6	85.3	10.7	0.4
7	< 0.1		3.8	83.7	12.0	0.6
8			2.7	84.9	11.7	0.7
9			2.1	86.1	11.0	0.7

2,4-dimethylbenzenium ion (i.e. protonated meta-xylene) is the most stable of these ions. Consequently all the other isomeric ions rapidly rearrange into this ion. In case by the butyl cations the tertiary-butyl cation is the most stable isomeric carbocation. In excess superacidic media, such as FSO_3H-SbF_5, butane is protolytically converted into the most stable *tert*-butyl cation. If this ion undergoes hydride abstraction from excess butane 2-methylpropane is obtained. However, if there is an equilibrium with excess butane still present, the isomer distribution will reflect the isobutane-butane equilibrium.

When 2-methylpropane (isobutane) was treated under the same isomerizing conditions 10–12% butane was formed (table 3). Cracking again was limited.

In the isomerization of 2-methylpropane, the low concentration (10–12%) of butane, reflects the low thermodynamic equilibrium concentration of butane compared to 2-methylpropane (i-C4).

Fluorosulfuric acid used in our studies generally contained 2 to 5% (weight) anhydrous hydrogen fluoride. HF acts as an activator for the isomerization. Highly purified fluorosulfuric acid with careful exclusion of atmospheric moisture showed poorer isomerizing properties. HF in fluorosulfuric acid is acting as a base and is protonated to $H_2F + FSO_3-$ [12]. The self ionization of fluorosulfuric acid gives $H_2SO_3F^+FSO_3-$. It is known that HF-SbF_5 is a stronger superacid than FSO_3H-SbF_5. In these systems the proton is again solvated as H_2F^+ and $H_2SO_3F^+$, respectively, accounting (in part) for the differing acidity. The effect of HF as co-acid in fluorosulfuric acid can be similarly interpreted. It is also of interest to note, that "magic acid" i.e. FSO_3H-SbF_5, if not carefully purified, also contains some HF, which leads to the formation of $H_2F^+SbF_6-$, enhancing the acidity of the system.

It should be mentioned that initiators such as a butyl fluorosulfates or butyl fluorides were also used in some experiments, but did not alter significantly results obtained, except speeding up initial isomerization. These initiators are conveniently formed *in situ* when small amounts of butenes are added as promoters. Observed limited (3–5%) cracking of butane to propane, ethane and methane can be even further decreased, as observed in some experiments, to 1–3% when carrying out the isomerization under hydrogen pressure (10–30 atm). When using neat fluorosulfuric acid for the isomerization there is always some (~ 1%) SO_2 detected in the products, indicating the oxidative nature of the system contributing to maintain the needed butyl cation concentration in the acid layer.

HF as co-acid in the FSO_3H catalyst system, as discussed, enhances the activity. If the amount of co-acid in relation to fluorosulfuric acid is, however, substantially increased the acidity of the system is significantly decreased. A 2:1 w/w mixture of FSO_3H and HF, for example, is too weak to catalyze efficient isomerization and has been found to give only 5–7% conversion, even with prolonged reaction times. Fluorosulfuric acid with 2 to 5% (w/w) HF in contrast is very effective and fast isomerization is achieved at room temperature. 10 w% HF started to show decreased activity and the need for more prolonged reaction times or elevated temperatures (disadvantageous for the isomerization).

The isomerization reaction was carried out by contacting butane with the catalyst under liquid phase conditions for a period of time sufficient to effect the reaction, while minimizing side reactions. The length of the contact time depends upon the temperature and the acid to hydrocarbon ratio. Typical contact times ranged from 10 seconds to a few minutes. Generally contact times of about 30 sec were used in the reported experiments. These contact times allow the reaction to be carried out in a flow system passing butane through a reactor tube filled with the acid catalyst. The acid to butane ratio any time during the isomerization in the flow system can only be estimated, but represents a ratio of at least 10:1 to 20:1. The preferential temperature employed is in the range of 0 ° C to 30 ° C (a temperature of 21° C was generally used in the reported experiments), with pressure sufficient to maintain the flow rate of the hydrocarbon.

Due to the high rate of butane isomerization in FSO_3H the reaction was carried out in a continuous flow manner with short contact times (~ 10–30 sec). Since it is important to achieve good contact between the catalyst and the hydrocarbon, passing butane through from the bottom of the vertical reactor is convenient. The reactor and other apparatus which is in contact with the acid catalyst should be substantially inert (Teflon, stainless steel, Monel, etc.; even quartz reactor tubes can be used at lower temperature).

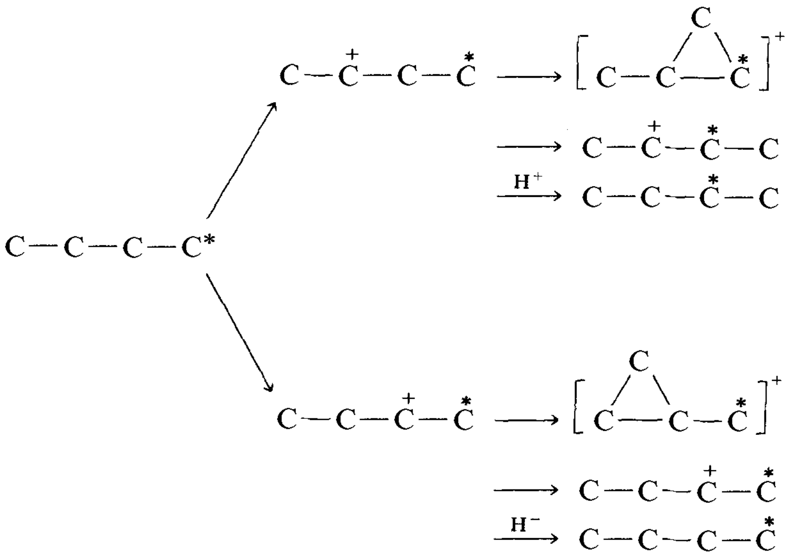
Considering the mechanism of the butane isomerization under conventional acid catalyzed conditions after initial butyl cation formation preferentially involves a bimolecular mechanism. The reason for this is the inevitable equilibrium of the butyl cations with their deprotonation products, i.e. buteness under conventional acidities.

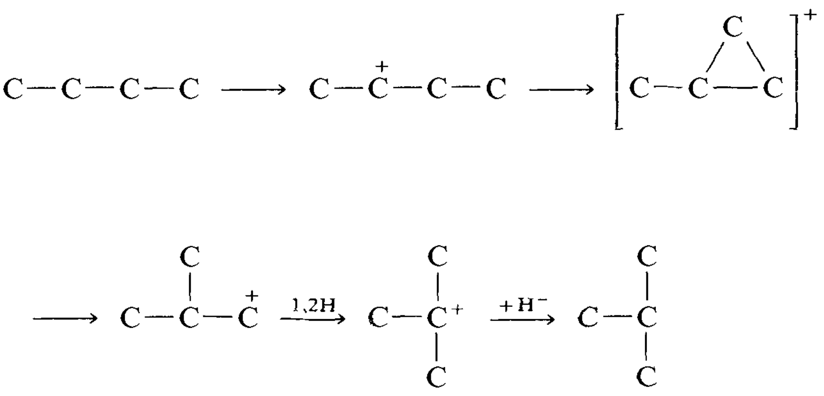
$$(CH_3)_3C^+ \overset{-H^+}{\rightleftharpoons} (CH_3)_2C{=}CH_2$$

$$CH_3\overset{+}{C}H{-}CH_2CH_3 \overset{-H^+}{\rightleftharpoons} CH_3CH{=}CHCH_3 + CH_2{=}CH - CH_2CH_3.$$

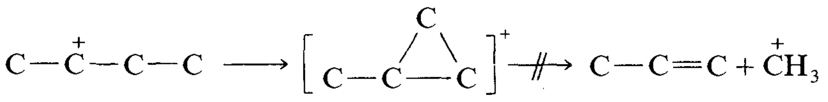
Consequent very facile butylation of the olefins by the butyl cations leads to octyl cations, which then undergo β-cleavage giving 2-methylpropane (via intermolecular hydride transfer).

In contrast in superacidic media the deprotonation equilibria are suppressed (the reason for being able to observe "stable ions"). The butane $\rightleftharpoons$ 2-methylpropane isomerization consequently is becoming intramolecular proceeding through rearrangement of butyl cations to the most stable *tert*-butyl cation involving protonated methylcyclopropanes. Brouwer et al. have shown that in HF/SbF_5 the isomerization of butane-1-^{13}C to butane-2-^{13}C takes place without concurrent isomerization to 2-methylpropane. This clearly indicates that the opening of the protonated cyclopropane to the primary isobutyl cation is a relatively slow process, making the isomerization of the butane to 2-methylpropane distinct from the isotopic $^{13}C1 - ^{13}C2$ scrambling.

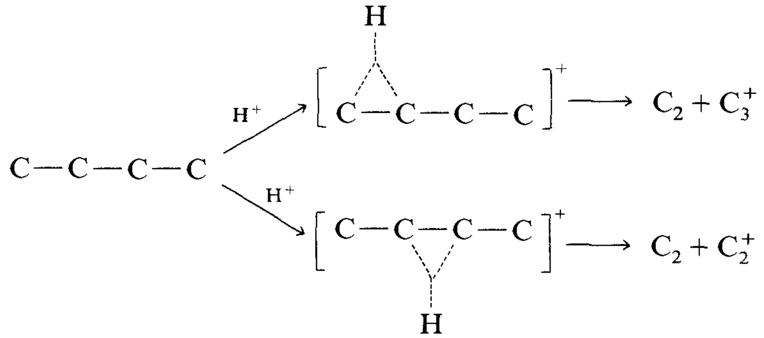




The intramolecular isomerization of butanes differs from that of the higher alkanes in that the secondary 2-butyl cation can not undergo facile β-cleavage.



Consequently $C_4 \rightarrow C_3 + C$ β-cleavage plays no significant role. This explains why hydrogen pressure does not significantly affects the studied butane isomerization. Direct protolytic C–C bond cleavage with the stronger superacids, however, can cause hydrocracking.



This is the reason why in superacids, such as HF/SbF_5 or FSO_3H/SbF_5 (with high SbF_5 proportions) preferential protolytic cleavage takes place even when hydrogen pressure is used (which is capable to moderate β-cleavage by quenching the trivalent butyl cations).

In the butane isomerization the temperature dependent composition of butane and methylpropane is determined by their thermodynamic equilibria. Reaching the equilibria, however, in acid catalyzed alkane isomerizations is generally relatively slow. The fact that in oxidative superacidic solutions, such as in fluorosulfuric acid, rapid high conversion isomerization takes place indicates the ease with which the *t*-butyl cation is formed and its efficient hydride transfer-isomerization equilibria with excess butane.

For comparison we also carried out studies of the isomerization of pentane and hexane with FSO_3H/HF and found it even when using prolonged reaction times (in a static reactor) rather ineffective. It tends to cause excessive cracking (table 4) showing the rather unique effectiveness of the FSO_3H/HF system in isomerizing butane.

3. Conclusions

It was found that the isomerization of butane in fluorosulfuric acid containing 2–5% hydrogen fluoride gives at room temperature and with short contact times (10–30 sec) a 70% conversion to isobutane.

Table 4
Isomerization of pentane and hexane with FSO_3H/HF at 25 °C in a static reactor

n-pentane								
RH:acid 1:1								
time (hrs)	mol% C_1-C_4	n-C_5	i-C_5	i-C_4				
2	<1	74	9	16				
2	<1	69	11	19				
22	~1	45	18	36				
43	~4	29	16	51				
n-hexane								
time (hrs)	mol% i-C_4	n-C_5	i-C_5	n-C_6	2-MeC_5	3-MeC_5	2.2-diMeC_4	$> C_6$
2	1	1	–	84	4	2	–	8
5	2	2	0.5	81	5	3	–	6
24	2	1	0.4	76	10	3	0.7	7

4. Experimental part

Butane of 99%$^+$ purity was passed continuously through a jacketed vertical quartz (Teflon or stainless steel can also be used) 50 × 1.25 cm reactor tube charged with fluorosulfuric acid containing 2 to 5% hydrogen fluoride. The gaseous butane from a pressure cylinder was introduced at the bottom of the column (through a perforated dispersion plate). The flow rate was ~ 50–100 ml/min with a contact time of butane with the acid catalyst from 15 to 30 seconds. LHSV's would correspond to 0.5–1. The temperature was kept at 21 °C. Reactions were carried out in a continuous fashion for up to 48 h without appreciable change of product composition of an average 70–72% 2-methylpropane, 25–27% butane, with only 1–3% propane, and traces of ethane, and methane (analyzed by GLC and MS-GC). 2-Methylpropane (bp. −12 °C) can be readily separated from the reactor effluent gases and excess butane to by recycled, if needed for further isomerization.

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