CHEMISTRY LETTERS, pp. 1485-1488, 1981. © The Chemical Society of Japan 1981

SOME GRAPHITE LAMELLAR STRONG AND SUPER ACIDS AS CATALYSTS IN THE ISOMERIZATION AND CLEAVAGE REACTIONS OF PENTANE AND HEXANE

Norihiko YONEDA,* Tsuyoshi FUKUHARA, Takafumi ABE, and Akira SUZUKI
Department of Applied Chimistry, Faculty of Engineering, Hokkaido University, Sapporo 060
Kazuyoshi KUDO
Research and Development Center of Maruzen Oil Co. Ltd., Satte Saitama 340-01

Graphite lamellar catalysts of acids; SbF_5, SbF_5-HF and $AlBr_3$-Br_2 were found to be effective for the isomerization and cleavage reactions of pentane and hexane at room temperature. Graphite-SbF_5-HF catalyst was excellent and gave skeletal isomerization products exclusively from pentane and hexane. Graphite-$AlBr_3$-Br_2 catalyst showed a highly catalytic activity to yield $C_4 \sim C_7$ alkanes which were formed via the β-cleavage reaction of oilgomeric alkyl cations derived from starting alkanes. Graphite-SbF_5 catalyst exhibited catalytic behavior and gave skeletal isomerization products exclusively for pentane but gave $C_4 \sim C_7$ alkanes as the major products for hexane.

Effective catalytic ionization of saturated hydrocarbons followed by skeletal isomerization, alkylation has been recently achieved by using super acidic solutions such as SbF_5-SO_2ClF, SbF_5-HF, SbF_5-FSO_3H and TaF_5-HF, whereas such reactions were not possible in ordinary acidic media such as H_2SO_4, $AlCl_3$ and BF_3.1) However, these super acidic media are highly hygroscopic and somewhat troublesome to handle and also show some difficulties for the separation of products. One of the possible solutions of such problems would be improved by supporting these acids by way of intercalation into the graphite lattice. In the course of our studies on such super acids catalysts, the reaction of alkanes in the presence of graphite lamellar SbF_5-HF was carried out.2) We now wish to report here the characteristics of catalytic behaviors of various acids intercalated into the graphite lattice in the isomerization and cleavage reactions of pentane and hexane.

The reactions of 10 ml (76.5~86.8 mmol) of alkanes were carried out under thorough stirring in a 100 ml Kel-F flask equipped with a gas holder in the presence of given amounts of various acids or acids intercalated in graphite. Both gaseous and oily products were analyzed by VPC using a 45 m capillary column (U-45) at -10 to +30°C. Graphite lamellar catalysts of SbF_5, SbF_5-FSO_3H, FSO_3H, H_2SO_4, $SbCl_5$, NbF_5 and TaF_5 were prepared by known procedures.3) It was reported that only in the presence of chlorine or bromine, $FeCl_3$, $AlCl_3$ and $AlBr_3$ are intercalated into the graphite lattice.4) Thus, graphite lamellar catalysts of $FeCl_3$, and $AlBr_3$, in the present work were prepared in such a manner. Graphite-SbF_5-HF was prepared by exposing graphite-SbF_5 to gaseous HF at 20°C until the expected weight of the catalyst was observed.

Some of the results obtained by the reaction of pentane and hexane in the presence of graphite lamellar catalysts are shown in the Table.

Graphite lamellar catalysts of FSO_3H, H_2SO_4, $AlCl_3$-Br_2, $FeCl_3$, TaF_5-HF, SbF_5-FSO_3H and NbF_5-HF showed none or small catalytic activity for the reactions. On the other hand, SbF_5, SbF_5-HF and $AlBr_3$-Br_2 with or without graphite systems exhibit considerably high catalytic activity for the reaction.

Tabl 1. Isomerization and Cleavage Reaction of Pentane and Hexane a)

Catalyst b) (mmol)	Alkane c)	Conversion d) (%)	Product Distribution d) (%)				Skeletal Isomerization d) (%)
			C_4 k)	iso-C_5	iso-C_6	iso-C_7	
$AlBr_3$ (14.2)	H	2.1			1.5	0.6	71.4
$AlBr_3$-Br_2 (14.2)-(0.3)	P	62.9	21.5	34.0	7.4	0	54.1
	H	35.7	9.8	8.5	14.1	3.3	39.5
Gr-$AlBr_3$-Br_2 e) (14.2)-(14.2)	P	95.6	52.9	22.7	20.0	0	23.7
	H	92.6	31.0	25.0	23.6	13.0	25.5
Gr-$AlCl_3$-Br_3 f) (17.8)-(0.3)	P	18.3	5.1	10.5	2.7	0	57.4
	H	15.6	4.4	3.2	7.8	0.3	50.0
Gr-H_2SO_4 f) (20.4)	H	0					
Gr-FSO_3H f) (20)	P	0					
	H	0					
Gr-$SbCl_5$ e) (12.7)	P	0					
Gr-$FeCl_3$-Br_2 f,h) (26.2)-(0.3)	P	0					
TaF_5-HF i) (13.8)-(5.0)	P	14.0	0.9	12.6	0.5	0	90.3
	H	38.8	3.1	2.6	32.2	0.9	83.0
Gr-TaF_5-HF g) (13.8)-(50)	P	11.3	0.5	9.6	1.2	0	85.0
	H	7.2	0	0	6.0	1.2	83.3
SbF_5 (17.5)	P	34.1	8.8	16.8	8.5	0	49.3
	H	60.6	29.3 l)	14.5	14.7	2.1	24.3
Gr-SbF_5 e) (17.5)	P	48.0	0.2 l)	47.5	0.3	0	99.0
	H	90.8	30.3	24.1	28.3	8.1	31.2
SbF_5-HF (17.5)-(17.5)	P	64.4	0.5	63.4	0.5	0	98.4
	H	85.8	2.3	1.3	82.0	0.2	95.6
Gr-SbF_5-HF (17.5)-(17.5)	P	78.2	0.2	77.8	0.2	0	99.5
	H	86.6	0	0	86.1	0.5	99.4
Gr-SbF_5-FSO_3H j) (17.5)-(17.5)	H	20.8	2.2	5.6	8.0	5.0	38.5
Gr-NbF_5-HF g) (8.5)-(18.0)	H	2.2	0	0.1	1.3	0.8	59.1

a) Unless otherwise stated, the reaction was carried out at 20°C for 2h.

b) Gr; graphite (1~2 mmϕ), Highly oriented pyrolyte gtaphite obtained from Tōkai Carbon Co..

c) P; pentane 86.6 mmol, H; hexane 76.5 mmol. Both alkanes were commercial chemicals with high purity (~99.5%)

d) mol % e) first stage f) second stage g) in HF solution

h) Reaction Temp. 30°C. Reaction Time 16h.

i) Reaction Temp. 30°C. Reaction Time 3h.

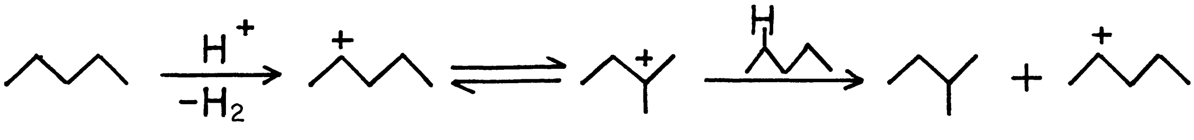
j) Reaction Temp. 50°C.

k) Mainly isobutane.

l) Small amounts of ethane and propane were observed.

Interestingly, the catalytic activity of these acids intercalted in graphite was higher than that of acids without graphite under the same conditions. The reason is not yet clear but may be due to the well dispersible nature of graphite lamellar acids in the reaction.

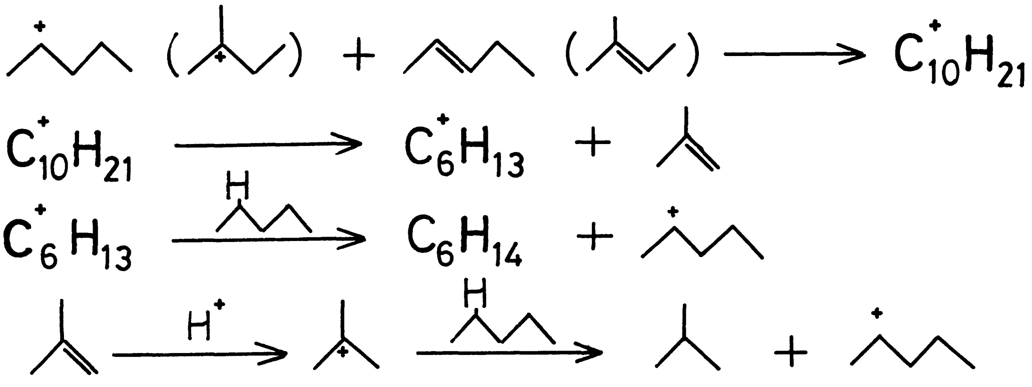
The isomerization of pentane and hexane in the presence of graphite-SbF_5-HF takes place exclusively in a high conversion. The reaction can be explained to be initiated by the direct electrophilic attack of H^+ on the C-H bonds in alkane to give corresponding alkyl cations followed by skeletal isomerization, and then by hydride absorption from another alkane to yield isomeric alkanes and alkyl cations as shown in the following scheme:



Graphite-$AlBr_3$-Br_2 is a reactive catalyst and gave products with different carbon numbers from starting alkanes together with skeletal isomeric alkanes as minor products. $AlBr_3$ itself exhibited little catalytic activity, but was enhanced by the addition of bromine. This may be caused by alkyl bromides photochemically produced from alkanes and bromine. Alkyl bromides can afford corresponding alkyl cations readily in the presence of $AlBr_3$ followed by subsequent reactions involving skeletal isomerization and hydride abstraction from alkane. Thus, dark conditions can prevent the reaction of alkanes in the presence of $AlBr_3$-Br_2 or graphite-$AlBr_3$-Br_2.

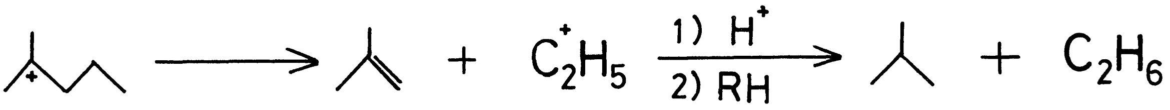
A big difference in the product distributions observed between the reactions using graphite-$AlBr_3$-Br_2 and graphite-SbF_5-HF may be attributed to the characteristic features of alkyl cation appearing in the reactions. Pentyl and hexyl cations produced over the graphite-SbF_5-HF may have sufficiently high concentrations to induce skeletal isomerization. On the contrary, alkyl cations, R^+, formed as intermediates over the graphite-$AlBr_3$-Br_2 may not be highly concentrated and the equilibrium is inclined toward corresponding olefins, which reacts with alkyl cations to give oligomeric alkyl cations. Such oligomeric alkyl cations would readily undergo the β-scission to afford C_4 or species with a higher carbon number as shown in the following reaction:

$$R^+ \rightleftharpoons R^= + H^+$$

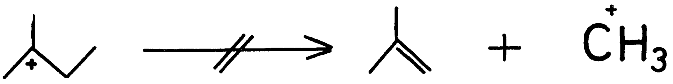


There should not be any cleavage of pentyl and hexyl cations themselves because no fromation of hydrocarbon products with carbon numbers of 1~3 were observed.

In the reaction using graphite-SbF_5,[5] pentane was subjected to skeletal isomerization to give isopentane exclusively but hexane gave cleavage products such as isobutane, pentanes and heptanes mainly together with small amounts of isohexanes, ethane and propane. Such a different type of reaction behavior observed can not be well explained as yet. However, judging from the formation of ethane and propane in the reaction of n-hexane, it might be considered that graphite-SbF_5 seems to provide an environment to carry out β-scission of isohexyl cations to give C_2 and C_4 species, which is difficult to happen under usual acidic conditions. β-Cleavage species of hexyl cations may react with hexyl cations (and/or olefins) to give oligomeric hydrocarbons which then cleave to smaller hydrocarbons.



Pentyl cations derived from pentane, on the other hand may hardly induce the β-cleavage reaction because it requires the formation of energetically unstable methyl cation. Thus, pentane in the presence of graphite-SbF_5 catalysts gave isopentane exclusively.



It should be pointed out that these graphite lamellar acids having high catalytic activity in the isomerization and/or cleavage reaction of alkanes can be more readily handled than acids without graphite in terms of their less sticky nature and high resistance to hydrolysis. Moreover, such solid catalysts can be expected to have valuable usability for industrial applications.

References

1) a G.A.Olah, Science 206, 13 (1979).
b R.Bonifay, B.Torch and M.Hellil, Bull.Soc.Chem.Fr., 808 (1977).
c M.Siskin, J.Am.Chem.Soc., 100, 1838 (1978).
d V.R.Miethchen and C.F.Kroger, Z.Chem., 15, 135 (1975).
e V.R.Miethchen, A.Gartner, U.Roth, K.Wiechert and C.F.Kroger, J.Prakt. Chemie., 319, 383 (1977).
2) a N.Yoneda, A.Suzuki and K.Kudo, the 9th Symposium on Petroleum Chemistry of Japan, Fukuoka, October 1979.
b N.Yoneda, T.Fukuhara, A.Suzuki and K.Kudo, the 1980 Winter meeting of Hokkaido Div. of the Chemical Socity of Jappan, Sapporo, Jannary 1980.
c N.Yoneda, T.Abe, T.Fukuhara, A.Suzuki and K.Kudo, the 1981 Summer Meeting of Hokkaido Div. of the Chemical Society of Japan, Kitami, July 1981.
3) a J.M.Lalancette and J.Lafintaine, J.Chem.Soc., Chem.Comm., 815 (1973).
b J.Bertin, H.B.Kagan, J.L.Lusche and R.Setton, J.Am.Chem.Soc., 96, 8113 (1974).
c J.Melin and A.Herold, C.R.Acad.Sc. Paris, 280. C-641 (1975).
d J,Melin and A.Herold, Carbon, 13, 357 (1975).
4) T.Sasa, Y.Takahashi and T.Mukaibo, Bull.Chem.Soc.Jpn., 45, 2250 (1972).
5) Recently, the isomerization of cis-to trans-decaline has been reported in the presence of graphite-SbF_5. K.Laali, M.Muller and J.Sommer, J.Chem.Soc., Chem.Comm., 1088 (1980).

(Received August 14, 1981)