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SHORT COMMUNICATION

Catalytic Isomerization of n-Hexane by the Ternary Compound Mesitylene: $HCl:2AlCl_3$

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Abstract. Equal volumes of n-hexane and mesitylene:$HCl:2AlCl_3$ when shaken together for 16 hours at 70°C yield some 6% hexane isomers (on n-hexane). No HCl or other gas was formed. The resulting phases appeared to be stable. Mesitylene:$HCl:2AlCl_3$ is an active isomerization catalyst for paraffins.

Introduction

The conversion of normal chain paraffins to their isomers is an important catalytic process. The isomate process was developed by Standard Oil of Indiana to upgrade by isomerization the light straight run fraction of oil (LSR). This process isomerised n-hexane with a complex hydrocarbon-aluminum chloride sludge catalyst. The conditions used were 115-120°C, HCl gas pressure of 1.37 MPa, a hydrogen gas pressure of 3.4 MPa and a space velocity of 1 to 2 volumes of n-hexane per volume of catalyst per hour. The hydrogen was used to suppress cracking side reactions. The HCl was necessary to maintain the catalytic activity. To maintain the catalyst activity it was necessary to add fresh aluminium chloride at about 0.3 wt. % on the n-hexane fed [1,2].

The present commercial process for isomerization of LSR is limited in the quality of the product octane number because it must operate near 200°C in order to have reasonable activity. A catalyst which is active at room temperature can isomerize the LSR naphtha cut to a much higher quality gasoline than the presently used commercial catalyst.

Lieser and Pluger [3] first reported the existence of the ternary compound Mesitylene:$HCl:2AlCl_3$, where mesitylene = 1,3,5-trimethyl benzene. This compound appears to be a close analoguc of the complex sludge catalytst of the isomate process. It was decided to synthesize this compound and to measure some of its physical properties. If it was sufficiently stable it was planned to test it for its catalytic activity on n-hexane.

Methods

The compound was made by shaking solid anhydrous aluminium chloride together with mesitylene while passing a stream of dry HCl gas through the slurry at ambient pressure and temperature. The reaction went smoothly and was complete in 3 hours.

$$Mesitylene_{(l)} + HCl_{(g)} + Al_2Cl_6 \rightarrow Mesitylene{:}HCl{:}2AlCl_3$$

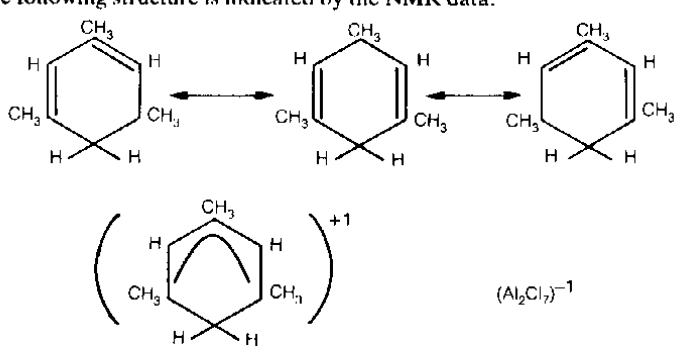
Compound characterization and handling

The liquid compound was stored over excess solid aluminium chloride under a nitrogen blanket. Aliquote samples were withdrawn by pipette under a nitrogen purge. Compound density = 1.36 g/ml. A chloride analysis was done by hydrolyzing a weighed aliquote with excess water and dilution of the resulting water to a standard volume. A standard silver nitrate solution was used to determine the chloride content of the sample. Weight % chloride found = 57.3, while the weight % chloride calculated for mesitylene:$HCl{:}2AlCl_3$ = 58.7.

The compound was further characterized by a neat NMR spectrum. Three peaks were obtained at 6.05, 3.05 and 1.12 (PPM from TMS). The areas of these peaks were respectively in a ratio of 2:2:9.4.

The NMR spectra and the chloride content suggest that the structure is that of a protonated aromatic compound. Small amounts of free mesitylene when added to the sample cause the NMR spectra to collapse to a spectra typical of a distorted mesitylene. Some proton exchange mechanism causes this. From this one concludes that no free mesitylene is present in the synthesized sample.

The following structure is indicated by the NMR data:



where the 3 different kinds of hydrogen should be in th ratio 2:2:9.

The compound is very sensitive to moisture but under nitrogen is stable for long periods of time at ambient temperature. High vacuum may be pulled over the compound for hours without detectable evolution of HCl or other gas.

Isomerization reaction

Equal volumes of an n-hexane containing 5.4% of benzene (an inhibitor) and the catalyst were mixed in a dry glass tube under nitrogen. The sample was then cooled with liquid nitrogen and sealed off by fusion with a torch under high vacuum. The sealed glass reactor was shaken continuously at 70°C for 16 hours. The sample was then cooled and opened. The system was two-phase: a paraffin-rich upper phase and a catalyst-rich lower phase. An aliquote of the upper liquid phase was analyzed by gas chromatograph (GC) to determine paraffin phase composition in terms of hexane isomers.

Results and Discussions

The results of the GC analysis are shown in Table 1.

Table 1. Results of the GC analysis

Isobutane	0.07
2,2-dimethyl butane	0.11
2,3-dimethyl butane and 2-methyl pentane	3.83
3-methyl pentane	1.40
n-hexane	92.72
benzene	1.87

The pure compound mesitylene:HCl:2$AlCl_3$ has a slow but definite catalytic activity for the isomerization of n-hexane at 70°C when equal volumes of catalyst and n-hexane are employed. The catalyst needs no HCl gas pressure and is undecomposed under the conditions of the experiment. It has an intrinsically lower catalytic activity than the previously studied phases containing dimethyl ether:2$AlBr_3$ and methyl bromide:$AlBr_3$ [4].

Approximately after 16 hours we did not reach the equilibrium, indicating a slow reaction. This low rate of the reaction may be attributed to benzene which is deliberately added as an inhibitor to n-hexane initially and to the low temperature.

It is planned to study this catalyst at higher temperatures (100–125°C) where the catalytic activity should be much higher than at 70°C. The catalyst is homogeneous liquid and of simple structure. The hexane solubility in the catalyst phase can be determined. After this is done simple clean kinetic interpretations can be made on this catalyst for the isomerization of paraffins.

References

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التشاكل الحفزي للهكسان باستخدام المركب الثلاثي ميسيتيلين : حمض الهيدروكلوريك : كلوريد الألمنيوم

(Mesitylene: HCl: $2AlCl_3$)

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ملخص البحث. عندما خلطت أحجام متساوية من كل من الهكسان والمركب الثلاثي Mesitylene: HCl: $2AlCl_3$ عند ٧٠°م ولمدة ١٦ ساعة نتج من متشاكلات الهكسان، نتيجة للتفاعل، ما يعادل ٦ بالمائة (من الهكسان). لم يظهر حمض الهيدروكلوريك ولا أي غاز آخر، كما أن الأطوار المتكونة بدت مستقرة تمامًا. يمكن اعتبار المركب الثلاثي هذا حافزًا فعّالاً في عملية تشاكل البارافينات.