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# Alkylation of isobutane by ethylene using a solid Friedel–Crafts catalyst

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Alkylation of isobutane with ethylene was investigated over a $\gamma$-$Al_2O_3$-Cl catalyst at temperatures below 380 K. Ethylene was fully converted over a period of 5–20 h, then conversion steadily decreased. The only products were alkanes, mainly $C_6$ and $C_8$. The composition of the alkylate varied with the isobutane/ethylene ratio and with time-on-stream. Among the $C_6$, 2,3-dimethylbutane became predominant (>95%) after a few hours. The composition of octanes appeared less selective. The kinetic distributions of isomers are interpreted by a new mechanism based on cyclopropane-carbonium ions. Upon catalyst ageing, alkane isomerization decays faster than alkylation, oligomerization being least affected.

**Keywords:** isobutane alkylation; catalysis with superacids; chlorinated alumina; carbonium ion

## 1. Introduction

The alkylation of isobutane by light alkenes, especially by linear butenes, is a unique method of tailoring isoparaffins with high octane index. Large amounts of alkylate are currently produced in units operating at temperatures between −10 and +10°C, with the aid of liquid acids: HF or $H_2SO_4$ [1,2]. Solid catalysts are now being developed, to be used instead of the liquid acids, which are under increasing environmental pressure [3]. Obviously, such solids should possess a strong surface acidity, but a high selectivity is also required. Firstly, the alkylate should contain highly branched alkanes; secondly, oligomerization of the alkene should be avoided since it leads to by-products.

Many solid catalysts are mentioned in the current and patent literature. Zeolites, especially HY or β type, and sulfated zirconia, are intrinsically active for alkylation, but they suffer a very rapid decay with time-on-stream [4–7]. A variety of protonic or Lewis acids, either supported or confined on a porous solid, have been patented [8–10].

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We were interested in supported Lewis acids, and especially in chlorided alumina, which was cited among alkylation catalysts [11,12]. Indeed, chlorided alumina and its variant aluminium chloride fixed on alumina are strongly acidic, with reported Ho values around −14 [13]. Such solids catalyze the isomerization of alkanes at low temperature [14,15]. Moreover, the $AlCl_3 + HCl$ system provokes the alkylation of isobutane by ethylene in the liquid phase [16].

Thus we checked whether chlorided alumina could be a catalyst for the same conversion, with a similar selectivity for dimethylbutanes. Using a continuous flow reactor, the composition of the alkylate could be determined at various times-on-stream.

In the current formalism of acid catalysis [17] alkylation of isobutane with an alkene was considered as alkylation of the alkene by a tertiary-butyl carbenium ion.

However, the concept of carbonium ions with a positive charge on a five-coordinated carbon is now well established in superacidic media [18,19] as well as in heterogeneous catalysis. For instance, isomerization of linear alkanes was explained through a transient cyclopropane carbonium ion [20]. This concept may prove useful in alkylation also.

## 2. Experimental

*Catalyst.* A γ-alumina (Ketjen CK 300, with BET area 183 $m^2\ g^{-1}$) was chlorided by reaction with carbon tetrachloride [14]. The chlorine content was 7% by weight. Infrared spectra of adsorbed pyridine showed the surface to possess Lewis acid sites only, prior to the introduction of the feed. Their number was estimated at 1.13 site $nm^{-2}$, i.e. one sixth of the number of Cl atoms.

*Reactor.* The alkylation was carried out in a flow reactor with a fixed bed of catalyst in an up-flow configuration. Alumina could be chlorided in the reactor, then the flow of isobutane and ethylene was started with a space velocity 0.5–2 ml(liq.) $g^{-1}$(catalyst) $min^{-1}$. The pressure in the reactor was 2.5 MPa and the temperature was typically 323 K, so that all reagents and products were liquid. The molar ratio $\alpha =$ isobutane/ethylene was set between 5 and 18. A space time based on ethylene was defined as $\tau = W(\text{g-cat.})/Q_m(\text{g-}C_2H_4/\text{h})$.

*Analysis.* In the end section of the system operated at atmospheric pressure, samples of the gaseous effluent were taken and analyzed by VPC on a CPSIL-5B capillary column.

## 3. Results and interpretation

### 3.1. CATALYST ACTIVITY

Under the above-stated conditions, chlorided alumina is a very efficient catalyst for alkylation of isobutane by ethylene. In fig. 1A, the rate of product formation

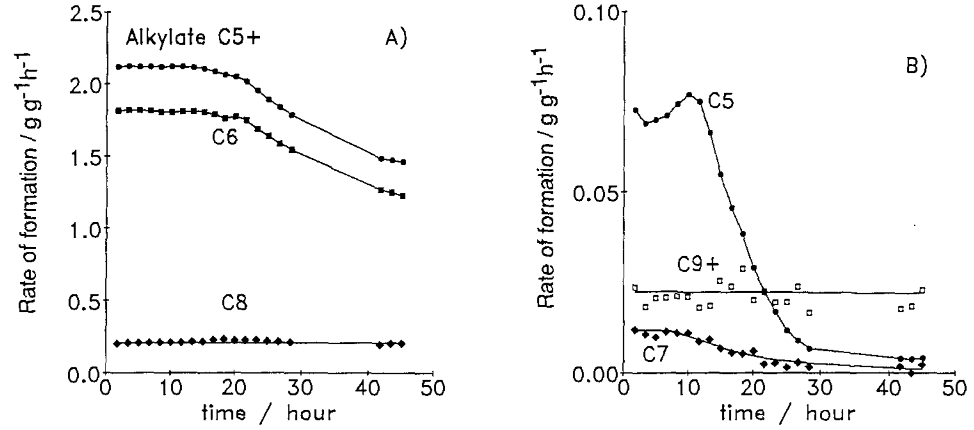


Fig. 1. Rate of alkylate formation versus time-on-stream. $Al_2O_3$-Cl catalyst; $T = 323$ K; $P = 2.5$ MPa; $\alpha = 18$; $\tau = 1.35$ g/g-$C_2H_4$ h. (A) Rate of formation for alkylate $C_{5+}$, hexanes and octanes. (B) Rate of formation for pentanes, heptanes and heavier alkanes.

is plotted as a function of time-on-stream for a run at 323 K, with a dilution $\alpha = 18$. At first, the rate of alkylation is constant, because ethylene is fully converted. Then deactivation starts after some 15 h.

The alkylate contains alkanes exclusively, with no alkenes. Hexanes accounted for most of the products, nearly 85% by weight, octanes for 10%, and heavier alkanes $C_{9+}$ for about 2% (table 1).

Isopentane and heptanes are also observed: the amount of isopentane is initially rather high (up to 4%), but heptanes are much lower. As the deactivation starts, the $C_5$ and $C_7$ rapidly fall to almost zero (fig. 1B). Such products are readily explained by condensation followed by cracking: this cracking is initially very fast, but decays in the early stage of a run. Meanwhile, the $C_6$ decline slowly, the $C_8$ still more slowly, and heavy alkanes remain at a constant level. Trace amounts of ethane are detected, but neither propane nor propene.

Table 1
Distribution of the alkylate by carbon number (wt%) at several working times $\Theta$ (in h). $Al_2O_3$-Cl catalyst; $T = 323$ K; $P = 2.5$ MPa; $\tau = 1.35$ g/g-$C_2H_4$ h. Comparison with thermodynamic control (th. ctrl.)

| | $\alpha = 18$ | | | $\alpha = 9$ | | |
|---|---|---|---|---|---|---|
| | $\Theta = 2$ | $\Theta = 45$ | th. ctrl | $\Theta = 2$ | $\Theta = 35$ | th.ctrl. |
| conv. (%) | 100 | 71 | (100) | 95 | 12 | (100) |
| $C_5$ | 3.4 | 0.3 | – | 1.9 | 0.9 | – |
| $C_6$ | 85 | 84 | 96.2 | 57 | 49 | 92.4 |
| $C_7$ | 0.5 | 0.2 | – | 1.1 | 0 | – |
| $C_8$ | 9.6 | 14 | 3.7 | 21 | 30 | 7.1 |
| $C_{9+}$ | 1.1 | 1.6 | 0.1 | 19 | 19 | 0.5 |

### 3.2. ISOMER SELECTIVITY

The distribution of the hexane isomers confirms that there are two successive regimes of the catalyst (fig. 2A and table 2).

Over the fresh catalyst, when ethylene is fully converted, all $C_6$ isomers are formed. The dimethylbutanes (DMB) are dominant (the 2,3-isomer in majority). Then come the methylpentanes, with very little *n*-hexane.

The second period starts as soon as the ethylene conversion falls below 100%. Then the selectivity for 2,3-DMB increases, and becomes nearly complete when the conversion has declined to 70%. Such a high selectivity has been reported for the same reaction catalyzed by an $AlCl_3$–imidazolium chloride liquid mixture [21].

The composition of the octanes is more complex (fig. 2B and table 2). During the initial period there are about 60% dimethylhexanes (DMH) and 15% trimethylpentanes (TMP). Over the aged catalyst the TMP nearly equal the DMH.

### 3.3. INFLUENCE OF DILUTION

When the dilution of ethylene is lowered from $\alpha = 19$ to 9 with the ethylene flow rate maintained constant, the conversion declines more rapidly. The distribution of products changes somewhat (table 1): the octanes and heavier alkanes increase. Otherwise the internal selectivities are not very different, especially among the $C_6$. In the $C_8$ there are more TMP at all times, but the importance of 2,3-DMH at low conversion is confirmed (table 2).

Fig. 3 shows a plot of the ratio hexane to octane versus catalyst age, for two dilutions of ethylene, 9 and 18. Clearly the relative amount of $C_8$ grows as the catalyst deactivates.

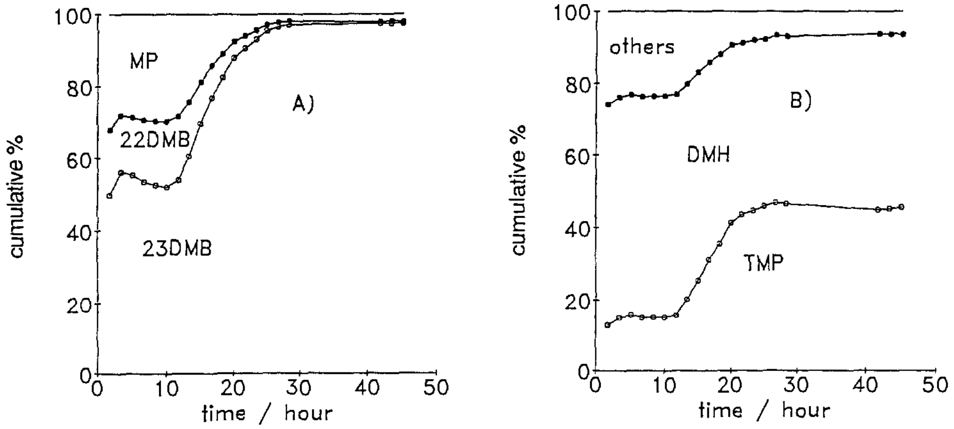


Fig. 2. Distribution of hexane and octane isomers versus time-on-stream. $Al_2O_3$-Cl catalyst; $T = 323$ K; $P = 2.5$ MPa; $\alpha = 18$; $\tau = 1.35$ g/g-$C_2H_4$ h. (A) Distribution of hexane isomers. (B) Distribution of octane isomers.

Table 2
Distribution of the $C_6$ and $C_8$ isomers (%) at several working times $\Theta$ (in h). $Al_2O_3$-Cl catalyst; $T = 323$ K; $P = 2.5$ MPa; $\tau = 1.35$ g/g-$C_2H_4$ h. Comparison with thermodynamic control (th. ctrl.)

| | $\alpha = 18$ | | $\alpha = 9$ | | th.ctrl. |
|---|---|---|---|---|---|
| | $\Theta = 2$ | $\Theta = 45$ | $\Theta = 2$ | $\Theta = 35$ | |
| conv. (%) | 100 | 71 | 95 | 12 | (100) |
| *distribution of $C_6$ isomers* | | | | | |
| 2,2-DMB | 18 | 1 | 3 | 0 | 57 |
| 2,3-DMB | 50 | 97 | 88 | 90 | 8 |
| 2 + 3-MP | 32 | 2 | 9 | 10 | 30 |
| *n*-hexane | 1 | 0 | 0 | 0 | 4 |
| *distribution of $C_8$ isomers* | | | | | |
| TMP *(total)* | *13* | *46* | *38* | *44* | *8* |
| 2,2,3-TMP | 3 | 0 | 0 | 0 | 17 |
| 2,2,4-TMP | 60 | 54 | 54 | 51 | 70 |
| 2,3,3-TMP | 24 | 21 | 26 | 12 | 8 |
| 2,3,4-TMP | 13 | 25 | 20 | 37 | 5 |
| DMH *(total)* | *61* | *48* | *52* | *53* | *65* |
| 2,2-DMH | 11 | 1 | 2 | 0 | 33 |
| 2,3-DMH | 12 | 60 | 34 | 79 | 6 |
| 2,4-DMH | 35 | 29 | 33 | 14 | 23 |
| 2,5-DMH | 31 | 9 | 28 | 7 | 26 |
| 3,3-DMH | 4 | 0 | 0 | 0 | 10 |
| 3,4-DMH | 6 | 0 | 2 | 0 | 2 |
| other $C_8$ | *26* | *6* | *10* | *3* | *27* |

### 3.4. COMPARISON WITH THERMODYNAMICS

The repartition of the products by carbon number, and the distribution of isomers, should be compared with the thermodynamic equilibrium. The thermodynamic calculation [22] considers all possible alkylations together with polymer-

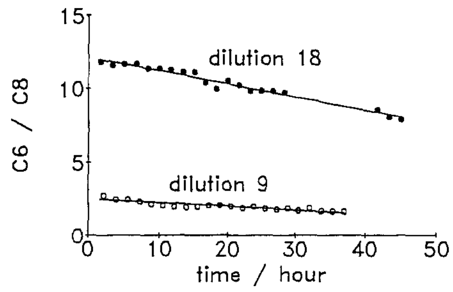


Fig. 3. Plot of the ratio hexanes to octanes for a reaction over $Al_2O_3$-Cl catalyst. $T = 323$ K; $P = 2.5$ MPa; $\alpha = 18$; $\tau = 1.35$ g/g-$C_2H_4$ h.

ization giving all possible isomers. Under alkylation conditions ($T < 520$ K) alkenes are all found unstable.

The thermodynamic repartition between alkane groups $C_n$ calculated at 323 K appears in tables 1 and 2. Hexanes are widely predominant, and the amounts of octanes, decanes etc. decrease rapidly with the carbon number $n$. However, the reaction carried out at $\alpha = 18$ yields up to 14% octanes, which is above the equilibrium value (3.7%). Decanes and heavier alkanes also exceed thermodynamically predicted yields, although the cracking of heavy alkanes appears feasible. The discrepancy is higher at $\alpha = 9$.

The equilibrium between isomers among the $C_6$ and $C_8$ fractions is also shown in table 2. The hexanes produced in the reaction are obviously far from equilibrium, even at low working time. Therefore, 2,3-DMB is the primary product of simple alkylation. Over the fresh catalyst, 2,3-DMB is isomerized into methylpentanes and 2,2-DMB.

Among the octanes, the trimethyl, dimethyl and monobranched isomers are near their equilibrium values during the initial period. Thus, isomerization runs faster with octanes than with hexanes. The primary products may be distinguished at higher working time: these are TMP, with more than 50% of the 2,2,4-isomer and virtually no 2,2,3-isomer, but also DMH, mostly the 2,3-isomer.

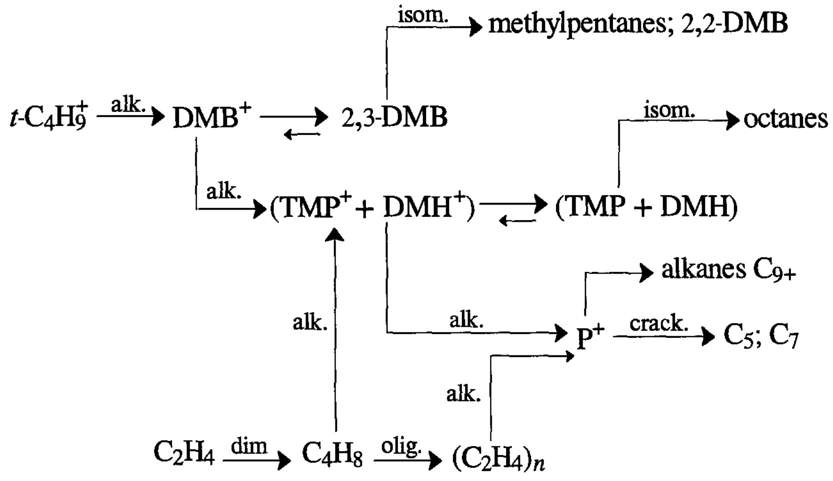
Alkylation of isobutane with 2-butene would give a vast majority of TMP in the $C_8$ fraction, since up to 87% TMP were found when using the $AlCl_3$ catalyst [23]. The alkylation with ethylene over chlorided alumina is less specific.

### 3.5. REACTION NETWORK. INFLUENCE OF TIME-ON-STREAM

The appearance of alkanes with more than six carbons reveals the complexity of the process. Octanes may be readily explained by successive alkylations. If the ethylene were to react exclusively with the alkanes, isobutane, DMB and others, then the concentrations of both $C_6$ and $C_8$ would increase with increasing conversion of ethylene. But the $C_8$ grow faster than the $C_6$, so that the ratio $C_6/C_8$ ought to decrease. This was not observed, as the proportion of $C_8$ in alkylate rose with time-on-stream, while the conversion decreased. Dimerization of ethylene followed by alkylation of the butene is another conceivable source of octanes. Polymerization may occur as well, and likely provokes the deactivation of the catalyst. Some confirmation of the oligomerization path may be found in the amount of $C_{10}$ and heavier products, which may be very large in some instances.

The various reactions may be arranged along the two main reaction paths in scheme 1. Over a fresh $Al_2O_3$-Cl catalyst, the alkylation of $C_4^+$ and $C_6^+$ and cracking of heavy carbenium ions $P^+$ run faster than oligomerization. But isomerization is still faster than alkylation, and lowers the amount of highly branched $C_6$ and $C_8$ isomers.

After some time-on-stream, isomerization becomes slower than alkylation, and isomer selectivity is improved. Also cracking becomes much slower than alkyla-



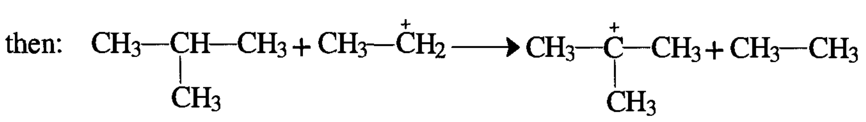
Scheme 1.

tion, but the increase in $C_8$ and $C_{10+}$ shows that oligomerization decays more slowly than any other reaction. Alkylation remains the dominant process, with a high selectivity for dimethylbutanes and branched octanes. Therefore, the catalyst retains sufficient activity for hydrogen transfer. This represents a major difference compared with the alkylation by butenes using zeolite catalysts, where olefins become the main products at high time-on-stream.

## 4. Reaction mechanism

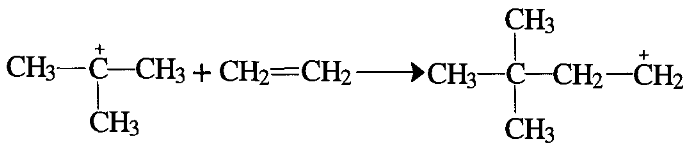
Schmerling [17] assumes that the first tertiary-butyl cation is generated from an ethyl cation:

first: $CH_2{=}CH_2 \xrightleftharpoons{H^+} CH_3{-}\overset{+}{C}H_2$



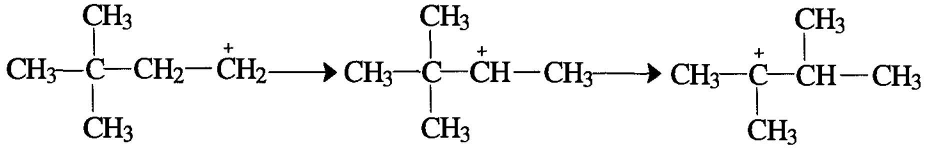
then: $$CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{C}}H{-}CH_3 + CH_3{-}\overset{+}{C}H_2 \longrightarrow CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{\overset{+}{C}}}{-}CH_3 + CH_3{-}CH_3$$

Then alkylation of an ethylene molecule by a tert-butyl cation would produce another primary carbenium ion:



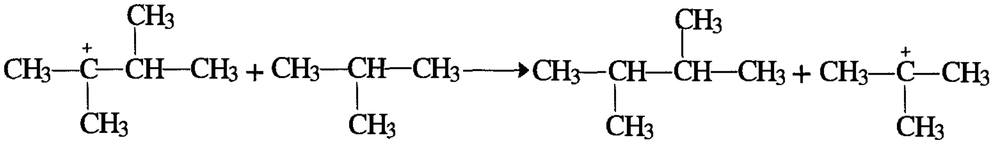
$$CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{\overset{+}{C}}}{-}CH_3 + CH_2{=}CH_2 \longrightarrow CH_3{-}\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}{-}CH_2{-}\overset{+}{C}H_2$$

As the main reaction product is 2,3-dimethylbutane, and not the 2,2-isomer, the primary carbenium ion is supposed to be rapidly transformed into a secondary, then a tertiary ion:



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-CH_2-\overset{+}{C}H_2 \longrightarrow CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-\overset{+}{C}H-CH_3 \longrightarrow CH_3-\overset{+}{\underset{\displaystyle CH_3}{C}}-\overset{\displaystyle CH_3}{CH}-CH_3$$

Finally, the tert-butyl cation is regenerated by a hydride transfer:

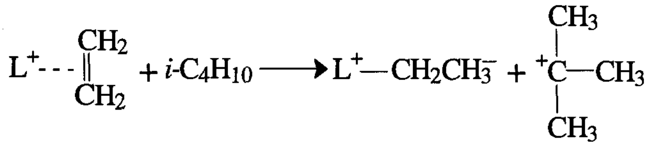


$$CH_3-\overset{+}{\underset{\displaystyle CH_3}{C}}-\overset{\displaystyle CH_3}{CH}-CH_3+CH_3-\underset{\displaystyle CH_3}{CH}-CH_3 \longrightarrow CH_3-\underset{\displaystyle CH_3}{CH}-\overset{\displaystyle CH_3}{CH}-CH_3+CH_3-\overset{+}{\underset{\displaystyle CH_3}{C}}-CH_3$$

Some peculiarities of the $Al_2O_3$-Cl catalyst will now be outlined.

### 4.1. CHAIN INITIATION

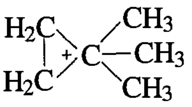
The formation of primary carbenium ions is rather difficult. As there is no evidence for the presence of Brønsted sites on chlorided alumina, a Lewis center $L^+$ may well be involved at this stage:



$$L^+\text{---}\begin{matrix}CH_2\\ \|\\ CH_2\end{matrix}+i\text{-}C_4H_{10} \longrightarrow L^+-CH_2CH_3^- + {}^{+}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-CH_3$$

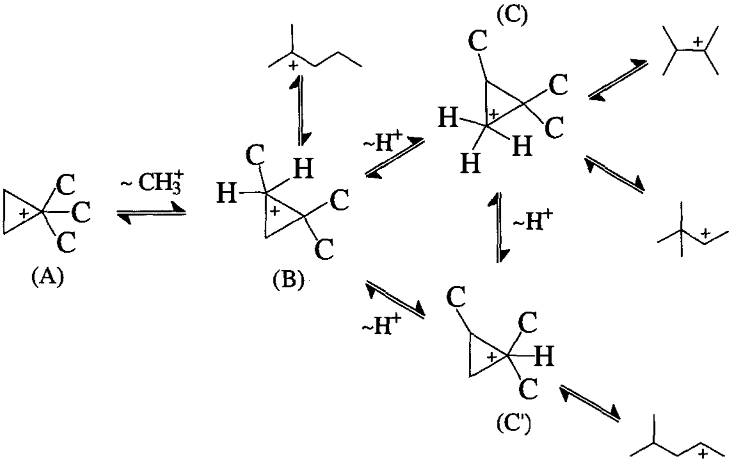
### 4.2. PRIMARY PRODUCTS: HEXANES

According to the concept of cyclic carbonium ions, we propose that the ethylene may add up to the tert-butyl cation to form a transient trimethyl cyclopropane carbonium ion (A):



(A)

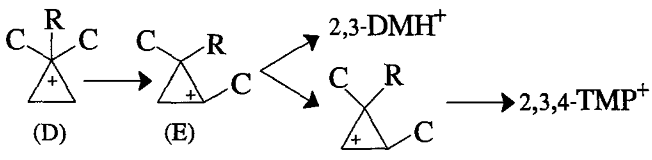
This species cannot be opened directly into a carbenium ion. Instead it may rearrange by jump of a methyl cation into another carbonium ion (B) which is a "protonated cyclopropane". This "pcp" (B) is then rearranged to ions (C) and (C′) by proton jump, then (C) is preferentially opened as the tertiary 2,3-dimethylbutyl carbenium ion:



No 2-methylpentane and very little 2,2-dimethylbutane appeared as primary products, so that proton jump on the carbonium ion (B) followed by opening of (C) to a tertiary carbenium ion occurs faster than the opening of (B) itself. As secondary carbenium ions appear unable to react with isobutane and thus regenerate the tert-butyl cations, these will not be considered further.

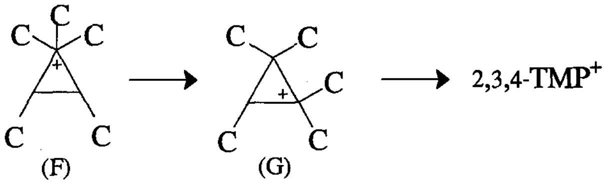
### 4.3. OCTANES

In the secondary alkylation of the 2,3-DMB by ethylene, a mechanism via linear carbenium ions predicts 2,3,3-TMP$^+$ as the only initial $C_8^+$ cation. But introducing cyclic carbonium ions would lead to a different selectivity, since the reaction now reads (with R = isopropyl):



The mechanism correctly predicts the 2,3-DMH as a primary product, along with 2,3,4-TMP. Then the other TMP and DMH may arise from a fast isomerization of the cations. This is not sufficient however to account for more than 50% of 2,2,4-isomer among the TMP.

Indeed, the dimerization route would yield the same octanes as the alkylation with linear butenes. Actually, this reaction produces a vast majority of 2,2,4-TMP, although the linear 2-butyl carbenium ion would be alkylated to the 2,2,3-TMP$^+$ ion which would then isomerize. Then some of the 2,2,4-TMP is thought to occur by another process, either self-alkylation or isomerization of butene to isobutene followed by alkylation [2]. Similarly, a route via cyclopropane-carbonium ions is unable to explain the high initial selectivity for 2,2,4-TMP. The 2-butene would first form a "pcp" ion (F) which would transform into (G) by jump of methyl cation, the end product being the 2,3,4-TMP:



The direct opening of carbonium ion (F) would lead to a secondary 2,2,3-TMP$^+$ carbenium ion. This is considered unlikely, although this ion appears as an intermediate in the classical mechanism.

Therefore, cyclic carbonium ions are important in explaining the repartition among the $C_6$ and $C_8$, but some of the 2,2,4-TMP possibly arises from a self-alkylation.

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