Mechanism for gas formation in polyethylene catalytic decomposition

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Gas formation mechanisms were studied in detail to find means for the selective recovery of specific components through catalytic gasification of polyethylene. Isobutene and butanes were obtained, respectively, by β-scission from chain-end tertiary carbonium ions and by the hydrogenation of butene. The selective recovery of isobutane was possible by controlling reaction conditions such as temperature, reactor shape and, particularly, the exit temperature for gaseous products.

(Keywords: polyethylene; gasification; silica–alumina catalyst; isobutane; gas formation)

INTRODUCTION

Many plastics in daily use are eventually disposed of as waste and, consequently, methods for their recycling are very important. Although land reclamation from the sea and burning at high cost are being avidly pursued, a new technology to conserve energy resources through recycling is urgently required. Liquefaction of fuel is a good example of this. Many studies have been conducted on liquefaction and gasification by thermal decomposition and on the recovery of olefinic constituents which are heavy distillates from polyolefins[1–5]. The energy cost for polyolefin decomposition is high owing to the need for high reaction temperature. Heavy distillates recovered are oxidized or polymerized into unusable components during storage and transportation and, at present, there are no plants available for the recovery of chemically stabilized products. New decomposition technology for these products using low temperature conditions for liquefaction is thus essential.

Isobutane was found to be selectively recovered by the catalytic decomposition of polyethylene (PE) at low reaction temperature using a batch reactor[6]. Although other components are formed by the same catalytic decomposition in a flow reactor[7], gas composition is considerably affected by reactor shape and reaction conditions. The main gaseous products of PE catalytic decomposition are isobutane and propylene[8]. However, the formation mechanism of these products is still unclear.

In this study, gas formation mechanisms were studied in detail to find means for the selective recovery of specific components through the catalytic gasification of PE.

EXPERIMENTAL

Sample and catalyst

The sample was high-density PE ($M_n = 3.1 \times 10^4$, manufactured by Mitsui Petrochemical Industry Co. Ltd, powder with a mesh of >80).

A silica–alumina catalyst with 13 wt% alumina content (Nikki Chemical Co. Ltd) was used after being heated for 3 h in dry air at 540°C. The catalyst was made into powder with a mesh of 100. The physical properties of the catalyst are shown in *Table 1*.

Procedure

A Pyrex glass tube reactor (outer diameter 25 mm, length 240 mm) connected to a trap was used to recover gaseous and liquid products[8]. The experimental procedure was as follows: the sample (2 g) and catalyst (2 g) were mixed by stirring in the reactor tube. The mixture was placed on the bottom of the reactor and the reaction was conducted from 160 to 320°C; nitrogen gas was passed through the reactor at a flow rate of 120 ml min^{-1} for 60 min.

Analysis method

To analyse the reaction products recovered, the molecular weight of the degraded polymer was determined for viscometry ($[\eta] = 5.10 \times 10^{-4} M_n^{0.725}$)[9]. The

Table 1 Physical properties of the catalyst

Catalyst	Silica–alumina
Al_2O_2 (%)	12–14
SiO_2 (%)	86–88
Na_2O (%)	<0.2
Acidity (mmol g^{-1})	0.3
Pore volume (cm^3 g^{-1})	0.6
Specific surface area (m^2 g^{-1})	500
Average pore size (Å)	50

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Table 2 Material balance of the catalytic decomposition products

Temperature (°C)	160	180	220	240	260	280	300	320
Fraction yield (wt%)								
Gas	0	0.1	0.6	1.3	1.9	2.8	4.3	6.2
Liquid	1.6	2.4	6.3	10.2	12.6	19.7	29.2	45.3
Oligomer	23.4	31.2	23.5	44.2	32.1	34.9	34.4	25.4
Degraded polymer	75.0	66.3	69.6	44.3	53.4	42.6	32.1	23.1
Coke	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]

Reaction conditions: time = 1 h; catalyst/sample ratio = 1.0
[a] Trace

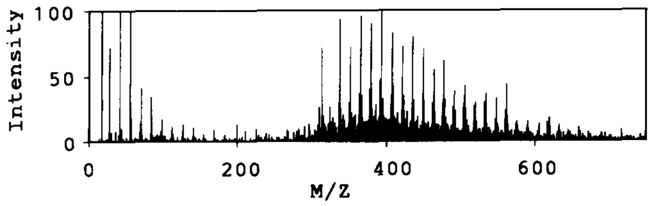


Figure 1 F.d.-m.s. spectrum of the oligomer fraction: temperature = 280°C; time = 1 h; catalyst/sample ratio = 1.0

molecular weights for the oligomer and liquid fractions were determined by field-desorption mass spectrometry (f.d.-m.s.) (Hitachi Data Processing System RUM-7M)[8]. The gas fraction was analysed by gas chromatography (Shimadzu GC-8A)[7]. The chemical structure was determined by ^{1}H n.m.r. (JEOL Ltd, JNM-FX-100) and ^{13}C n.m.r. (JEOL Ltd, JNM-GX270)[8].

RESULTS AND DISCUSSION

Gas yields as a function of reaction temperature

The thermal gasification of PE has generally been conducted by radical chain reactions at high temperatures[10,11] from 400 to 600°C to achieve catalytic decomposition[12–14]. *Table 2* shows the yield of each fraction formed in low temperature gasification (~400°C) by a batch reactor. Gas yields were 0.1 wt% at 180°C and ~6.2 wt% at 320°C. The liquid fraction yield was remarkably high, ~45.3 wt% at 320°C. A previous study[7] showed the liquid fractions to correspond to gasification precursors.

The decomposition products became concentrated mainly into gasification precursors (liquid fractions). The molecular weight of each fraction was $M_w = 200 \sim 400$ (liquid), $M_w = 300 \sim 1000$ (oligomer) or $M_n > 1000$ (degraded polymer). As shown in *Figure 1*, decomposition products whose boiling points correspond to the reaction temperature flowed out into the trap gradually. The lowest boiling point product thus flowed out preferentially. High boiling point products having long residence times remained at the bottom of the reactor tube. The liquid fraction shown in *Table 2* was present in the liquid trap. The remaining products continued to undergo decomposition, isomerization and recombination reactions. The low boiling point products flowed into the trap without being refluxed in the reactor. The liquid fraction flowed out rapidly following a short residence time while the polymer and oligomer fractions decomposed gradually, consequently giving rise to a greater yield of the liquid fraction. As shown by the oligomer yield (23.4 wt%, 160°C), the molecular weights of the oligomer and degraded polymer decreased rapidly. The yield of the gasification precursor (liquid fraction) was controlled by the reaction temperature. Gas components formed by the redecomposition of the liquid fraction were obtained in small yields.

Table 3 shows that the liquid fraction yield changes from ~6.6 wt% (10 min) to 17.7 wt% (120 min) at a constant reaction temperature. Nevertheless, the gas yield was ~3.0 wt%. The extent of secondary decomposition of the liquid fraction was determined by reaction temperature, but not by reaction time.

Thus, it is considered that the increase in liquid fraction yield is determined mainly by the residence time of the oligomer with the catalyst. Contact time is closely related to reactor shape. For instance, in the case of a flow reactor, the residence time is the time the reaction products remain in the catalyst bed and was found[7] to be as much as 20 s. The oligomers and liquid produced flow into the long catalyst bed in a tubular reactor as viscous liquid phase components and are finally gasified by further decomposition of the liquid fraction[7].

In the case of a batch reactor, since the liquid fraction flows into the trap with a short residence time, it does not undergo decomposition for gas formation. This fraction should thus be decomposed over a long residence time. Gas formation takes place through the further decomposition of this fraction by oligomer decomposition.

Gas composition at low temperature decomposition

Table 4 shows the gas composition of the batch reactor. Only isobutane was recovered in the low temperature region (~160°C). The butane yield was ~52.6 mol% and the propylene yield was 13.9 mol% at 320°C. The C_3 and C_4 fractions were the main products and propylene yield increased rapidly with decreasing yield of butane at high temperature.

In contrast, in the case of high temperature gasification

Table 3 Material balance of the catalytic decomposition products

Time (min)	10	20	30	40	50	60	120
Fraction yield (wt%)							
Gas	1.0	1.6	2.1	2.3	2.6	2.8	2.5
Liquid	6.6	9.9	12.7	13.7	13.5	19.7	17.7
Oligomer	20.5	23.6	21.2	22.7	26.4	34.9	20.0
Degraded polymer	71.9	66.0	63.9	61.3	57.6	42.6	59.8
Coke	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]

Reaction conditions: temperature = 280°C; catalyst/sample ratio = 1.0
[a] Trace

Table 4 Composition of the gaseous products

Temperature (°C)	160	180	220	240	260	280	300	320
Yield (mol%)								
Methane	0	0	0	0	0	0	0.3	0.5
Ethane	0	0	0	0	0	0.4	0.9	1.2
Propane	0	0	7.1	7.1	7.3	7.9	7.5	7.3
Propylene	0	0	6.2	6.7	8.1	9.5	12.3	13.9
Isobutane	100.0	99.9	72.0	66.1	60.2	55.3	49.9	45.0
n-Butane	0	0	0	5.3	5.5	5.8	5.3	7.6
Isobutene	0	0	4.4	0	8.6	8.9	11.2	11.9
Trans-2-butene	0	0	2.7	3.2	4.0	4.5	5.6	6.3
Isopentane	0	0	7.4	7.7	6.1	5.9	5.2	4.9
n-Pentane	0	0	0	0.8	1.6	1.8	1.7	1.8

Reaction conditions: time = 1 h; catalyst/sample ratio = 1.0

in the flow reactor[15], the highest yields were noted for propylene, being $\sim$33.3 mol% (C_3), 35.8 mol% (C_2) and 9.1 mol% (C_4). Isobutane was not obtained. For both the batch and flow systems, compositions differed considerably according to reactor shape and temperature.

Vapour pressures of the liquid fraction formed in the flow reactor were high and thus this fraction flowed out following a short residence time. The olefinic gas fraction is thus recovered without catalytic hydrogenation (hydrogen transfer reaction).

As described above, gasification is determined by the decomposition temperature of the liquid fraction and shape of the reactor.

The high yield of propylene indicates β-scission to occur on chain-end secondary carbonium ions at high temperature. The isomerization of primary and secondary chain-end carbonium ions to produce tertiary carbonium ions takes place at low temperature. The isomerization of these ions occurs naturally at lower activation energy ($\sim$63 kJ mol^{-1})[16]. In the high temperature region, gasification thus occurs by high activation energy, such as direct β-scission ($\sim$188 kJ mol^{-1})[16] of chain-end carbonium ions. Gasification takes place to a small extent at low temperature (>200°C) in the batch reactor system; thus, the isomerized oligomer and liquid are produced as shown in the following section.

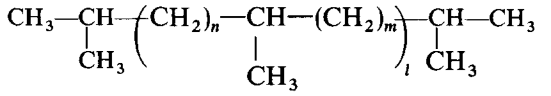
It thus follows that the C_4 fraction is formed mainly by β-scission of chain-end tertiary carbonium ions. It is evident from the compositions in *Table 4* that direct β-scission of chain-end primary and secondary carbonium ions, which requires a higher activation energy than that for C_4 formation at low temperature, does not occur easily. Propylene and ethylene formation was noted at higher temperature in the flow reactor[15]. Olefinic gas components flowed out during short residence times at high temperature while hydrogenated components were produced by long residence times at lower temperature. Increase in isobutene yield thus corresponds to decrease in isobutane yield at high temperature as shown in *Table 4*. Generally, decomposition products should consist of components having chain-end olefins formed by β-scission of the main chains. Isobutane may be produced by hydrogenation with isobutene. The liquid fraction was recovered as olefinic constituents in a short residence time by the flow reactor[7], and paraffinic products in a long residence time by the batch reactor.

As pointed out above, gaseous products were formed by redecomposition of the liquid fraction produced through oligomer decomposition. Thus, clarification of the mechanism for gaseous product formation should be possible through elucidation of the processes of oligomer and liquid fraction decomposition. Chemical structural analysis of the oligomer producing liquid fraction is very important.

Chemical structures of oligomer molecules

The chemical structures of the oligomers were analysed. *Figure 1* shows the f.d.-m.s. of the oligomer fraction. The molecular weight was from 300 to 700 (main peak $M_w = 460$, 280°C). The ^{13}C n.m.r. spectrum[8] of the oligomer fraction differed markedly from that of the starting PE, due to isomerization of polymer chains by the silica–alumina catalyst. For instance, since the isomerization of secondary carbonium ions to tertiary carbonium ions proceeds with lower activation energy ($\sim$63 kJ mol^{-1})[16] than that for chain β-scission, isomerization takes place prior to β-scission and the branching frequency on the main chain increases.

As described previously[8], branched components that have short chains (C_1–C_5) and consisting mainly of methyl groups (27 per 100 methylene carbons) and $M_w = 450$ were detected. From *Figure 1*, the molecular weight of the main fraction was 300–800. Branching of the main fraction was at a frequency of one branch per three ethylene monomer units, except for the chain-end methyl group $\sim CH_2{-}CH_2{-}CH_2{-}CH_2{-}\underset{\displaystyle CH_3}{CH}{-}CH_3$ (ref. 6). The typical oligomer structure was found to be virtually the same as that of polyisoheptyl ($\sim CH_2{-}\underset{\displaystyle CH_3}{CH}{-}CH_2{-}CH_2{-}CH_2{-}CH_2{\sim}$) based on branching frequency. Moreover, oligomer chains showed random branching in an ethylene sequence in regular structures of polyisoheptyl. This is because the ethylene sequence is longer than that of the isoheptyl sequence. A typical structure of the oligomer is:



$$CH_3{-}\underset{\displaystyle CH_3}{CH}{-}\left((CH_2)_n{-}\underset{\displaystyle CH_3}{CH}{-}(CH_2)_m\right)_l{-}\underset{\displaystyle CH_3}{CH}{-}CH_3$$

where $n+m=5$, $n=0$–5, $m=0$–5 and $l=2.3$–6.7.

Mechanism of the catalytic decomposition of PE

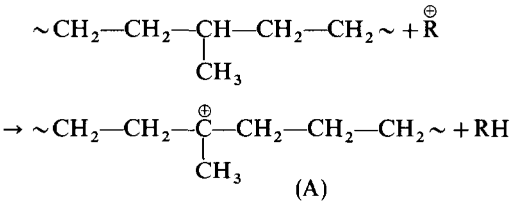
Molecular weight reduction of main chains. As for the functions of the silica–alumina catalyst, cracking, isomerization and carbonization of hydrocarbons are well known. Protonation to olefins by protons released from the silica–alumina catalyst takes place quite easily.

Low molecular weight carbonium ions are produced by the protonation of volatile olefinic products present in a polymer as impurities. Generally, these impurities are produced during oxidation by exposure to daylight and thermal degradation in extruders[17].

The molecular weight of the starting PE decreases without thermal degradation based on radical chain reactions in the presence of the catalyst[6].

The catalytic degradation of PE is initiated by attack of low molecular weight carbonium ions ($\oplus$R) on a very small number of on-chain hydrogen atoms attached to tertiary carbon atoms in polymer chains[18].

The initial stage of molecular weight reduction is shown in equations (1) and (2).

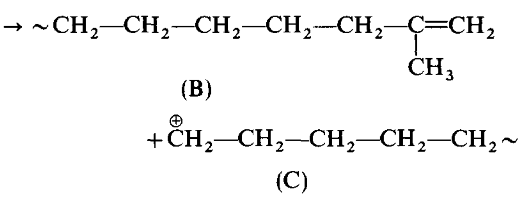


$$\sim CH_2{-}CH_2{-}\underset{\displaystyle CH_3}{CH}{-}CH_2{-}CH_2{\sim} + \overset{\oplus}{R}$$

$$\rightarrow \sim CH_2{-}CH_2{-}\underset{\displaystyle CH_3}{\overset{\oplus}{C}}{-}CH_2{-}CH_2{-}CH_2{\sim} + RH \qquad (1)$$

(A)

from (A)



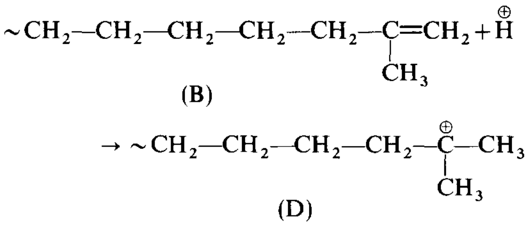
$$\rightarrow \sim CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}\underset{\displaystyle CH_3}{C}{=}CH_2$$

(B)

$$+\overset{\oplus}{C}H_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{\sim} \qquad (2)$$

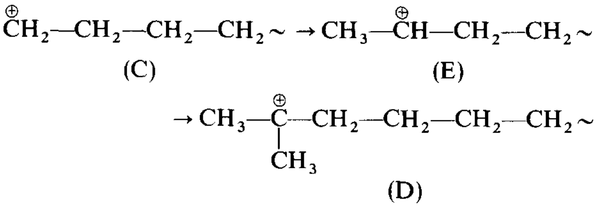
(C)

Chain ends (B) immediately produce stable tertiary carbonium ions by protonation:



$$\underset{\text{(B)}}{\sim CH_2-CH_2-CH_2-CH_2-CH_2-\underset{\substack{|\\ CH_3}}{C}=CH_2}+\overset{\oplus}{H}$$
$$\rightarrow \underset{\text{(D)}}{\sim CH_2-CH_2-CH_2-CH_2-\underset{\substack{|\\ CH_3}}{\overset{\oplus}{C}}-CH_3} \qquad (3)$$

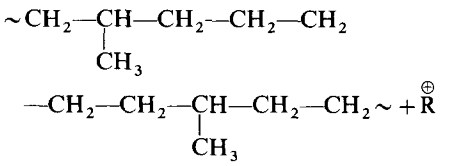
Ions (C) also produce secondary or stable tertiary carbonium ions by isomerization[16]:



$$\underset{\text{(C)}}{\overset{\oplus}{C}H_2-CH_2-CH_2-CH_2\sim} \rightarrow \underset{\text{(E)}}{CH_3-\overset{\oplus}{C}H-CH_2-CH_2\sim}$$
$$\rightarrow \underset{\text{(D)}}{CH_3-\underset{\substack{|\\ CH_3}}{\overset{\oplus}{C}}-CH_2-CH_2-CH_2-CH_2\sim} \qquad (4)$$

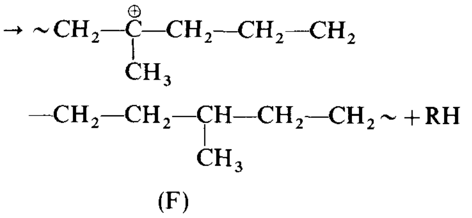
Molecular weight reduction takes place through β-scission of on-chain carbonium ions (A) and, consequently, degraded polymer and oligomer fractions are produced. The oligomer fractions formed by hydrogenation of chain ends (C), (D) and (E) are in agreement with the results by n.m.r. analysis[6].

Gaseous product formation. Gaseous products are produced from the liquid fraction produced by decomposition of oligomers and reactions with typical oligomers are shown in the following scheme.

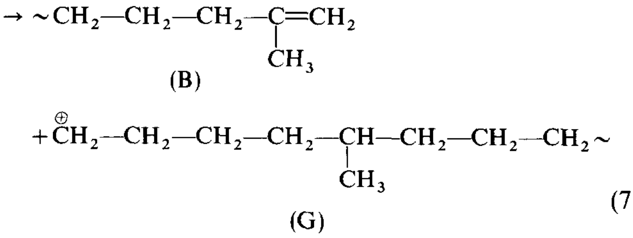


$$\sim CH_2-\underset{\substack{|\\ CH_3}}{C}H-CH_2-CH_2-CH_2$$
$$-CH_2-CH_2-\underset{\substack{|\\ CH_3}}{C}H-CH_2-CH_2\sim+\overset{\oplus}{R} \qquad (5)$$

(where $\overset{\oplus}{R}$ represents the volatile carbonium ion, $CH_3-\underset{\substack{|\\ CH_3}}{\overset{\oplus}{C}}-CH_3$)



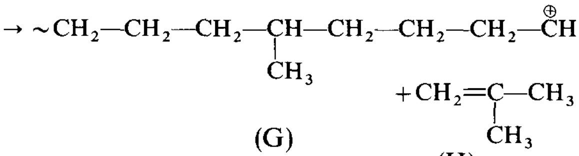
$$\rightarrow \sim CH_2-\underset{\substack{|\\ CH_3}}{\overset{\oplus}{C}}-CH_2-CH_2-CH_2$$
$$\underset{\text{(F)}}{-CH_2-CH_2-\underset{\substack{|\\ CH_3}}{C}H-CH_2-CH_2\sim}+RH \qquad (6)$$



$$\rightarrow \underset{\text{(B)}}{\sim CH_2-CH_2-CH_2-\underset{\substack{|\\ CH_3}}{C}=CH_2}$$
$$+\underset{\text{(G)}}{\overset{\oplus}{C}H_2-CH_2-CH_2-CH_2-\underset{\substack{|\\ CH_3}}{C}H-CH_2-CH_2-CH_2\sim} \qquad (7)$$

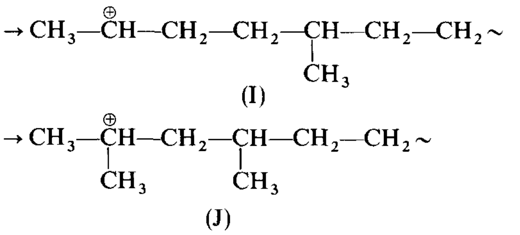
Gas formation takes place by way of the decomposition of these fractions. Liquid fraction (B) immediately produces carbonium ions (D) through equation (3). The unstable reaction intermediate (G) is isomerized to secondary (I) or tertiary carbonium ions (J) as shown by equation (9). Stable ions (D) also produce fraction (H) and chain-end carbonium ions (G).

from (D)



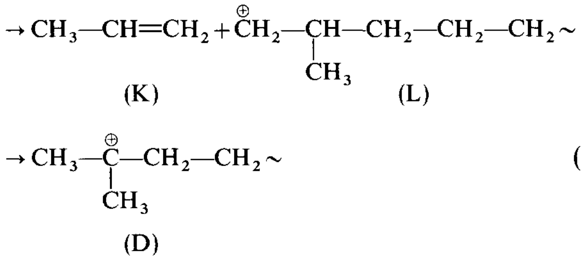
$$\rightarrow \underset{\text{(G)}}{\sim CH_2-CH_2-CH_2-\underset{\substack{|\\ CH_3}}{C}H-CH_2-CH_2-CH_2-\overset{\oplus}{C}H_2}$$
$$+\underset{\text{(H)}}{CH_2=\underset{\substack{|\\ CH_3}}{C}-CH_3} \qquad (8)$$

from (G)



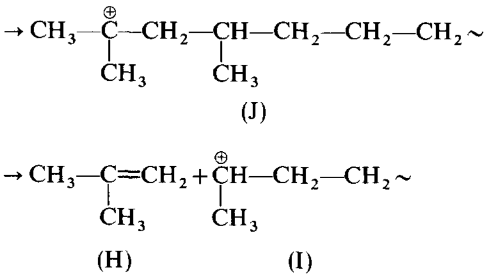
$$\rightarrow \underset{\text{(I)}}{CH_3-\overset{\oplus}{C}H-CH_2-CH_2-\underset{\substack{|\\ CH_3}}{C}H-CH_2-CH_2\sim}$$
$$\rightarrow \underset{\text{(J)}}{CH_3-\underset{\substack{|\\ CH_3}}{\overset{\oplus}{C}H}-CH_2-\underset{\substack{|\\ CH_3}}{C}H-CH_2-CH_2\sim} \qquad (9)$$

from (I)



$$\rightarrow \underset{\text{(K)}}{CH_3-CH=CH_2}+\underset{\text{(L)}}{\overset{\oplus}{C}H_2-\underset{\substack{|\\ CH_3}}{C}H-CH_2-CH_2-CH_2\sim}$$
$$\rightarrow \underset{\text{(D)}}{CH_3-\underset{\substack{|\\ CH_3}}{\overset{\oplus}{C}}-CH_2-CH_2\sim} \qquad (10)$$

from (J)



$$\rightarrow \underset{\text{(J)}}{CH_3-\underset{\substack{|\\ CH_3}}{\overset{\oplus}{C}}-CH_2-\underset{\substack{|\\ CH_3}}{C}H-CH_2-CH_2-CH_2\sim}$$
$$\rightarrow \underset{\text{(H)}}{CH_3-\underset{\substack{|\\ CH_3}}{C}=CH_2}+\underset{\text{(I)}}{\underset{\substack{|\\ CH_3}}{\overset{\oplus}{C}H}-CH_2-CH_2\sim} \qquad (11)$$

Ions (D), (I) and (J) are essential to gaseous product formation and are mainly produced by β-scission of these carbonium ions [(D) and (J)]. In many cases, stable tertiary carbonium ions [(D) and (J)] are produced via isomerization and then isobutene (H) is produced by β-scission, as indicated by equations (8) and (11). Isobutene is converted to isobutane through hydrogen transfer by the catalyst so that its yield is remarkably high. As shown in *Table 4*, the yield of isobutane is high in the low temperature region, but not in the high temperature region. Isobutene flows quickly without hydrogenation with a short residence time and high vapour pressure in the high temperature region.

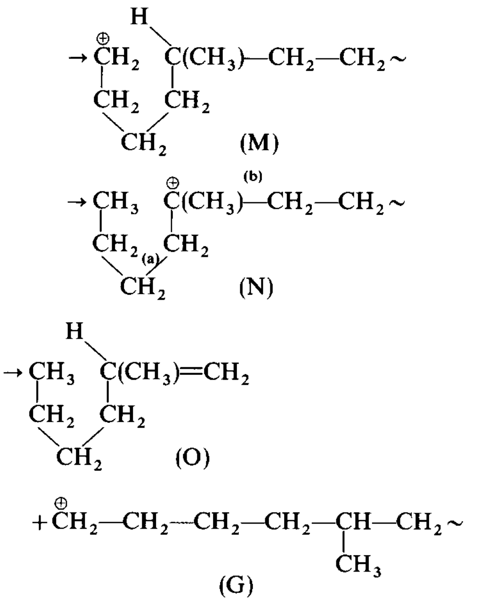
Propylene is produced in high yield by direct β-scission of other important ions (I) at high temperature as shown in *Table 4*. (I) ions are also isomerized directly to (D) ions at low temperature.

(J) ions follow equation (8) again. The propylene yield is low at low temperature since secondary ions (I) are isomerized to stable tertiary carbonium ions (J) by a lower activation energy than that for β-scission.

The propane component is independent of propylene yield and is not produced by hydrogenation of propylene.

The propane component is probably produced from propyl carbonium ions produced by β-scission of volatile tertiary carbonium ions without hydrogenation of propylene. For instance, stabilization of (G) ions takes place with a lower activation energy of isomerization and thus intramolecular rearrangement to inner tertiary carbon atoms occurs. (G) ions cause intermolecular rearrangement by back biting reactions[19]:

from (G)

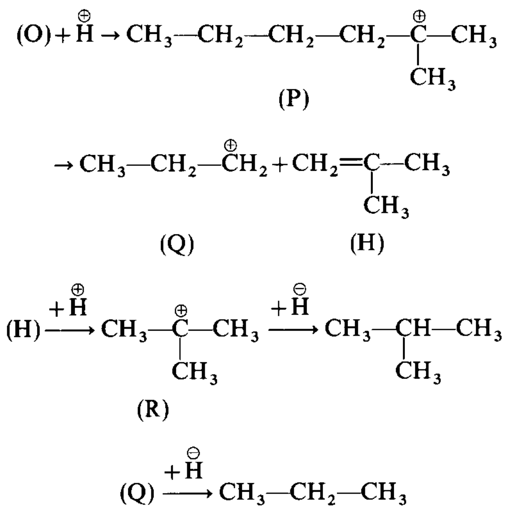


(12)

$$+\overset{\oplus}{C}H_2{-}CH_2{-}CH_2{-}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{C}}H{-}CH_2{\sim} \qquad (13)$$

(G)

from (O)



$$(O)+\overset{\oplus}{H} \rightarrow CH_3{-}CH_2{-}CH_2{-}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{\overset{\oplus}{C}}}{-}CH_3 \qquad (14)$$

(P)

$$\rightarrow CH_3{-}CH_2{-}\overset{\oplus}{C}H_2+CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CH_3 \qquad (15)$$

(Q) (H)

$$(H)\xrightarrow{+\overset{\oplus}{H}} CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{\overset{\oplus}{C}}}{-}CH_3 \xrightarrow{+\overset{\ominus}{H}} CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{C}}H{-}CH_3 \qquad (16)$$

(R)

$$(Q)\xrightarrow{+\overset{\ominus}{H}} CH_3{-}CH_2{-}CH_3 \qquad (17)$$

The stabilization of tertiary carbonium ions (N) proceeds by β-scission at the (b) position to give rise to a more stable fraction (O) than propyl ions [(a) position]. Equations (12)–(17) show isobutane and propane are produced. Propane is not produced by the hydrogenation of propylene, but by propyl carbonium ions (Q) produced by β-scission of the reaction intermediate (P). As shown in *Table 4*, the yields of isobutane and propane are high, demonstrating the importance of equation (15). As shown by equation (16), the fraction (isobutene) produced is converted to volatile carbonium ions by protonation. These ions also contribute to molecular weight reduction via equations (1), (2), (6) and (7).

CONCLUSIONS

In the catalytic decomposition of PE at low temperature, the main product, isobutane, is produced by the hydrogenation of isobutene and then isobutene is produced via β-scission of stable tertiary carbonium ions through the isomerization of the primary and secondary carbonium ions produced to give rise to oligomer decomposition.

In the high temperature region, propylene is produced by direct β-scission of secondary carbonium ions. Primary carbonium ions cause intramolecular rearrangement (back biting) to the inner hydrogenation atoms attached to tertiary carbon atoms. The selective recovery of isobutane was possible by controlling reaction conditions such as temperature, reactor shape and, particularly, the temperature of the exit for gaseous products.

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