Back Biting Reactions during the Catalytic Decomposition of Polyethylene

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Isobutane and isopentane were selectively obtained by polyethylene catalytic decomposition using the NaY-type zeolite catalyst. Back biting reactions are thus essential to gas formation during the catalytic decomposition of polyethylene. Chain-end secondary carbonium ions cause back biting reactions involving intramolecular rearrnagement to form the C_9 fraction. Isobutane and isopentane are then produced by decomposition of the gasification precursor C_9 fraction.

Polymer degradation has mainly been studied for the purposes of attaining greater heat and weather stabilization.[1-4] Many reports describe the mechanisms for this based on radical reactions. However, very little study has been directed to the catalytic degradation of polymers.[5-9] As shown in previous reports,[10,11] unique reactions occur in the catalytic degradation of polyethylene and polystyrene.

For instance, branched ethylene oligomers are produced in the catalytic degradation of polyethylene in the presence of the silica-alumina catalyst.[10] Indan oligomers are produced in the catalytic degradation of polystyrene in the presence of the aluminum chloride catalyst.[11] Gasification was found to occur with the gasification precursor in polyethylene catalytic decomposition. By the zeolite catalyst, the composition of gas resulting from polyethylene catalytic decomposition is unique and differs from that by the silica-alumina catalyst. The gas is composed of isobutane (C_4) and isopentane (C_5), in equimolar amounts at low temperature. The formation mechanisms of these fractions are of interest for the practical utilization of waste polyethylene.

Back biting reactions in gas formation were noted to occur exclusively as elementary reactions. The mechanisms for these reactions are discussed in detail in the following.

Experimental

Sample and Catalyst. The sample was polyethylene (hereafter referred to as PE, $\bar{M}_n$=3.98×10⁴, manufacted by Mitsui Petrochemical Industries Co., Ltd., powder with a mesh of >80).

A NaY-type zeolite catalyst (Na-atoms replacement: Toyo CCI Co., Ltd.) with 24—26 wt% alumina content was used after being heated for 5 h in dry air at 450 °C. It was made into powders of >100 mesh. The physicochemical properties of catalyst are showen in Table 1.

Table 1. Physicochemical Properties of the Catalysts

Catalyst		Zeolite
Al_2O_3	(%)	24—26
SiO_2	(%)	74—76
Na_2O_3	(%)	<0.1
Fe_2O_3	(mmol g^{-1})	0.82
Specific surface area	(m^2 g^{-1})	510—580
Average pore size	(Å)	15—20

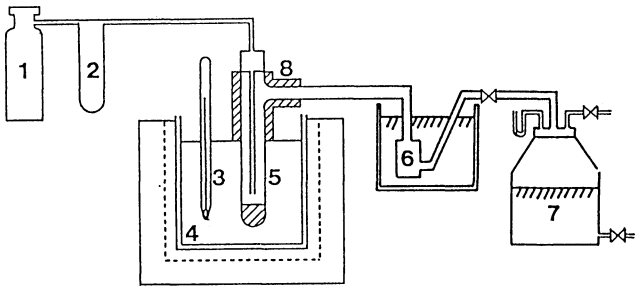

Fig. 1. Batch system reactor for catalytic decomposition. 1) N_2 cylinder, 2) Manometer, 3) Thermometer, 4) Metal bath, 5) Reactor, 6) Trap for liquid, 7) Trap for gaseous products, 8) Asbestos.

Experimental Operation and Procedure. A pyrex glass tube reactor (outer diameter: 25 mm and length: 240 mm) connected to a trap was used to recover gaseous and liquid products as shown in Fig. 1.

The experimental procedure was as follows: 2 g of the sample and 0.06 to 2 g of the catalyst were mixed by stirring. The mixture was placed on the bottom of the reactor and the reaction was conducted from 180 to 300 °C; nitrogen gas was passed through the reactor at a flow rate of 120 ml min^{-1} for 60 min and the ratio of catalyst to sample (C/S) was varied from 0.03 to 1.00.

Analysis Method. To analyze the reaction products recovered, the limiting viscosity method ($[\eta]$=5.10×10^{-4} $[\bar{M}_n]^{0.725}$)[12] was used to determine the molecular weight of the degraded polymer. The molecular weight distributions of the oligomer and liquid were determined by field desorption infrared (FD-), field ionization-mass spectrometers (FI-MS)

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respectively.[13] The gaseous and liquid products were quantitatively analyzed by a gas–liquid chromatograph (GC-8A of Shimadzu).[14] Chemical structure was determined ^{1}H and ^{13}C NMR (JEOL, Ltd., JNM-FX100).[10]

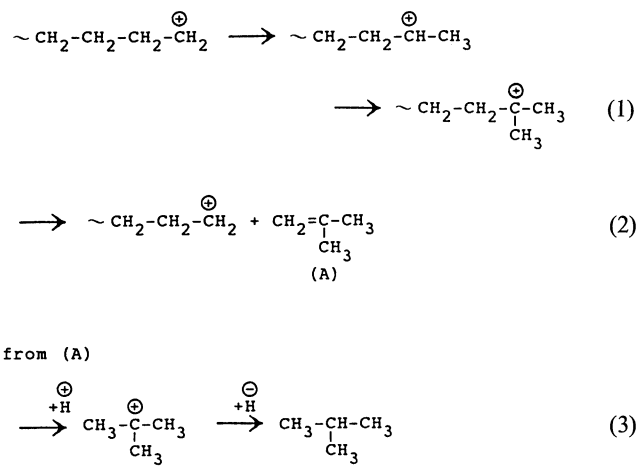
Results and Discussion

Material Balance and Gas Yields by the Zeolite Catalyst. The relationship between reaction temperature and the reaction products of PE decomposition was investigated using the zeolite catalyst. The results are shown in Table 2. The reaction products consisted of 4 fractions, degraded polymer ($\bar{M}_n$=1000<), oligomer ($\bar{M}_w$=300—800), liquid ($\bar{M}_w$=100—250) and gas. The yield of degraded polymer decreased at higher temperature, while that of the liquid fraction containing small amounts of olefins increased rapidly. These results show close agreement with those for PE catalytic decomposition in the presence of the silica–alumina catalyst.[13] As described previously, the gas fraction is produced during liquid fraction (gasification precursor) decomposition and does not derive from chain-end carbonium ions of the oligomer and polymer fractions.[14] If the gas fraction is produced from chain-ends of molecules of the oligomer and polymer fractions, it should be obtainable in a large isobutene yield by isomerization of chain-end carbonium ions without decrease in molecular weight, as shown in Scheme 1.

The formation of 4 fractions indicates that a decrease in molecular weight occurred. From Table 2, the liquid fraction is produced by further decomposition of oligomer and polymer fractions. Gas formation takes place at the chain-ends of the liquid fraction produced by oligomer decomposition, as when using the silica–alumina catalyst.[14]

Table 3 shows the gas composition at each reaction temperature. At a low reaction temperature of 180 °C, the yields of isobutane and isopentane were about 46.5 and 46.9 mol%, respectively.

Gas composition by the silica–alumina catalyst with lower acidity was found to consist of isobutane 54.9 mol%, isopentane 5.9 mol% at 280 °C[13] and thus may possibly depend mainly on the acidity of the catalyst. Isobutane yield was much more than those of the other gaseous products. The formation mechanism of isobutane is possibly direct β-scission of chain-end tertiary carbonium ions produced by redecomposition of the liquid fraction as shown in Scheme 1:



Scheme 1.

In the case of the zeolite catalyst, isopentane yield (36 mol%) was much higher that by the silica–alumina catalyst (6 mol%) at the same temperature 280 °C and isobutane and isopentane would not likely have been formed simultaneously from chain-end primary and secondary carbonium ions. Isopentane was not produced by β-scission from chain-end carbonium ions (primary, secondary and tertiary) in the presence of the zeolite catalyst.

Changes in C_4 and C_5 Fraction Yields as Function of Reaction Conditions. Effects of Reaction Temperature: Figure 2 shows the yields of C_4 and C_5 fractions.

Table 3. Components of Gaseous Products from Catalytic Degradation of PE

Temp/°C	180	200	220	240	260	280	300
Yield/mol%							
Methane	0.0	0.0	0.0	0.0	0.0	0.0	0.3
Ethane[a]	0.0	0.0	0.0	0.1	0.9	0.6	0.9
Propane	2.9	5.1	4.9	4.8	7.4	6.4	6.3
Propylene	0.0	0.5	0.9	4.6	7.4	6.4	6.3
Isobutane	46.5	47.3	41.2	39.9	34.9	44.0	40.7
Butane	3.7	4.6	5.4	4.6	4.8	4.8	4.7
Isobutene	0.0	0.0	0.0	3.3	0.5	2.7	3.8
trans-2-Butene	0.0	0.0	0.3	0.7	0.4	1.3	2.2
Isopentane	46.9	41.2	44.9	42.9	35.9	35.6	34.5
Pentane	0.0	1.3	2.4	2.1	2.0	0.9	1.4

Reaction conditions: zeolite catalyst, time=1 h, C/S =0.25.
a) Ethane, ethylene mixtures.

Table 2. Material Balance of Catalytic Degradation Products from PE

Temp/°C	180	200	220	240	260	280	300
Fraction yield/wt%							
Gas	0.2	1.2	1.7	2.7	3.2	3.1	5.6
Liquid	3.0	7.1	10.3	13.1	16.6	24.5	27.7
Oligomer	25.1	30.0	28.0	27.8	24.8	22.9	24.0
Degraded polymer	71.8	61.8	60.0	56.4	46.0	49.5	42.7
Cake	Trace	Trace	Trace	Trace	Trace	Trace	Trace

Reaction conditions: zeolite catalyst, time=1 h, C/S=0.25.

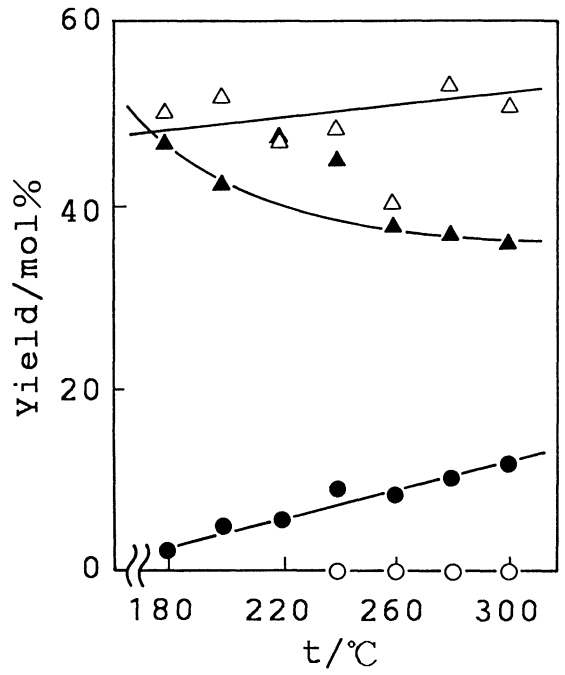


Fig. 2. Composition of gaseous products by polyethylene.
○; C_2, ●: C_3, △: C_4, ▲: C_5.
Reaction conditions; zeolite catalyst, time=1 h, C/S=0.25.

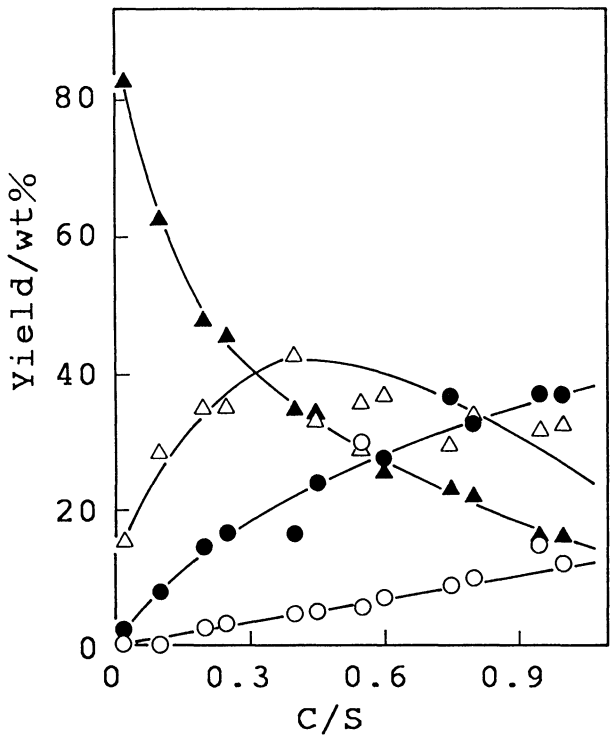


Fig. 3. Material balance of catalytic decomposition products of polyethylene.
○; gas, ●: liquid, △: oligomer, ▲: degraded polymer.
Reaction conditions; zeolite catalyst, temp=260 °C, time=1 h.

C_4 increased slightly with rise in temperature and was about 50.2 mol% at 180 °C and 51.4 mol% at 300 °C. The C_5 fraction decreased while the C_3 fraction increased at high temperature. The compositions of these fractions were independent of reaction temperature.

Table 3 shows the gas fractions to be produced mainly from the liquid fraction. The decrease in C_5 yield corresponds to the increase in C_3 and C_2 yields at high temperature. The C_5 fraction may possibly decompose into C_3 and C_2 fractions at high temperature.

On using the zeolite catalyst, isobutane and isopentane were produced preferentially. Thus, direct β-scission from chain-end carbonium ions is not important.

The stabilization of chain-end carbonium ions has generally been shown to result from rearrangement of ions (15 kcal mol^{-1}) and direct β-scission (45 kcal mol^{-1}).[15] The intramolecular rearrangement of chain-end carbonium ions thus occurs before direct β-scission. Isobutane and isopentane may possibly be formed from the gasification precursor (liquid fraction) produced by decomposition for the stabilization of internal rearranged ions.

Effects of Contact Time: Figure 3 shows the yield of each fraction at various catalyst concentrations at the same reaction temperature. Decomposition was accelerated of high catalyst concentration even though the temperature was the same. The rapid increase in oligomer yield corresponded to the decrease in degraded polymer yield and the liquid fraction also increased with decrease in oligomer yield. Figure 4 shows the yields of the C_4, C_5 and C_3 fractions at various catalyst concentrations. The composition of gas showed virtually no change with catalyst concentration and yield in each case increased with the catalyst/sample (C/S) ratio. The formation of C_4 and C_5 fractions in equimolar amounts was confirmed. Direct β-scission of secondary or primary chain-end carbonium ions with the formation of C_4 and C_5 was not important and thus, intramolecular rearrangement reactions should be required. In Fig. 4, the rates of C_4 and C_5 formation are nearly equal and these fractions may possibly derive from the same reaction intermediate. If isobutane and isopentane are produced from different reaction intermediates, their yields should also differ.

Gas and liquid yields increased with catalyst concentration at the same temperature (Fig. 3), though gas composition showed no change (Fig. 4). Only reaction temperature affected gas yield (Fig. 2). From Fig. 3, the rapid decrease in oligomer yield can be seen to correspond to increase in liquid yield. The liquid fraction (gasification precursor) is thus shown to be produced by decomposition of oligomers. Thus, changes in the molecular weight of oligomer and liquid fractions were carefully examined.

Molecular Weight and Distribution of the Oligomer Fraction. Figure 5 shows the molecular weight distri-

bution of the oligomer fraction: $\bar{M}_w$=200—1000 (top peak $\bar{M}_w$=350, 180 °C (A)), $\bar{M}_w$=200—700 (top peak $\bar{M}_w$=300, 240 °C (B)), and $\bar{M}_w$=200—500 (top peak $\bar{M}_w$=300, 280 °C (C)) were obtained by FD-MS, respectively. The molecular weight and its distribution shifted to the lower molecular weight side with rise in temperature. Figure 6 shows FI-MS spectrum of the liquid fraction recovered at 280 °C. The molecular weight distribution of M_w=100—250 (top peak M_w=130) was measured for the liquid fraction. That is, the liquid fraction for gas formation are formed during decomposition of the oligomer fraction.

Chemical structure of the Oligomer Fraction. The oligomer structure should thus be carefully analyzed to clarify the mechanism for liquid formation. Figure 7 shows the chemical structure of the oligomer fraction by ^{1}H NMR spectrum (280 °C). The liquid fraction structure was essentially the same as that of the oligomer

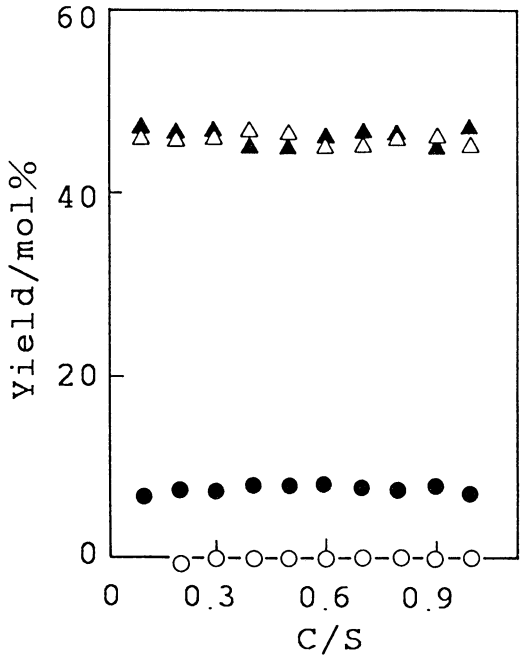


Fig. 4. Composition of gaseous products by polyethylene.
○; C_2, ●: C_3, △: C_4, ▲: C_5.
Reaction conditions; zeolite catalyst, temp=260 °C, time=1 h.

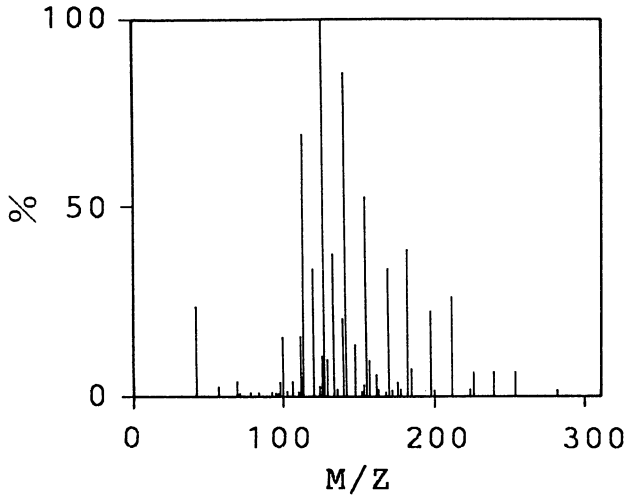


Fig. 6. FI-MS spectrum of the liquid fraction.
Reaction conditions; zeolite catalyst, temp=280 °C, time=1 h, C/S=0.25.

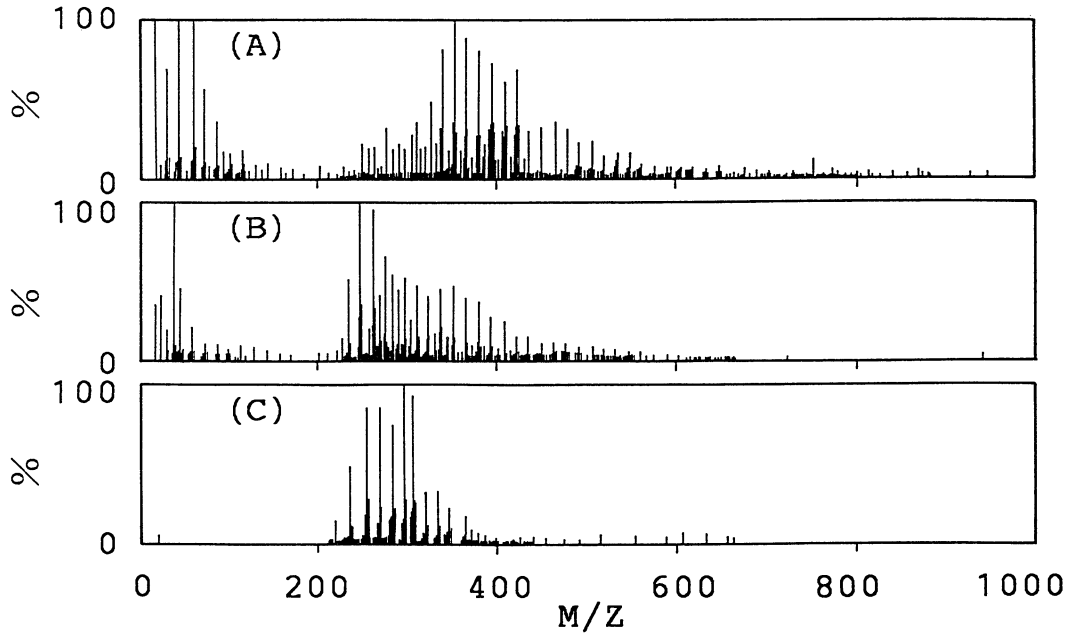


Fig. 5. FD-MS spectra of the oligomer fraction.
Reaction conditions; zeolite catalyst, temp=180 °C (A), 240 °C (B), 280 °C (C), time=1 h, C/S=0.25.

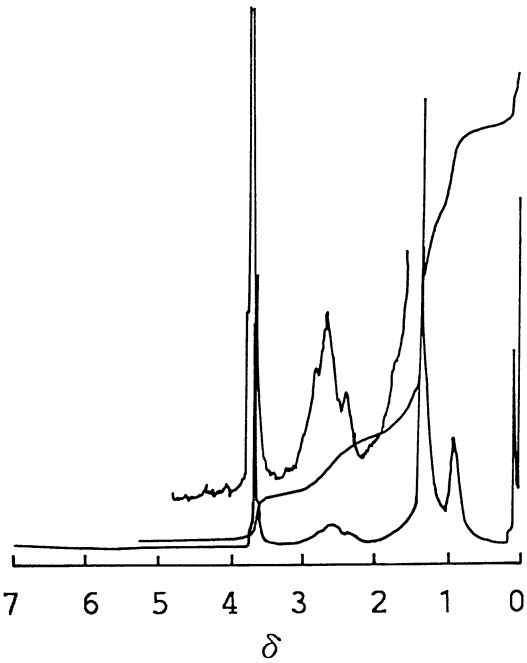


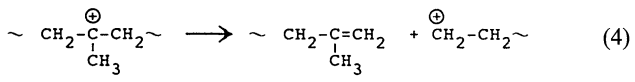
Fig. 7. ^{1}H NMR spectrum of the oligomer fraction. Reaction conditions; zeolite catalyst, temp=280 °C, time=1 h, C/S=0.25.

Table 4. Chemical Shifts of Oligomer and Degraded Polymer Mixture Observed by ^{13}C NMR and Calculated

Branched species	Carbon No.	Calcd[a] (ppm)	Obsd (ppm)
~C-C-C-C-C	1	13.86	14.19
5 4 3 2 1	2	22.65	22.91
	3	32.40	32.27
	4	29.71	29.68
	5	29.96	30.09
4 3 2 1			
~C-C-C-C	1	22.13	22.91
C	2	27.99	27.48
1	3	39.35	39.10
	4	27.20	27.15
1 2 3 2 1			
~C-C-C-C-C~	1	27.27	27.15
C	2	36.91	36.16
4	3	32.52	32.72
	4	20.07	20.31

a) Chemical shifts calculated by Lindeman-Adams method. (L. P. Lindeman and J. Q. Adams, *Anal. Chem.*, **43**, 1245 (1971)).

fraction, though the weakest olefinic signals could be detected. The chemical structure of oligomer and degraded polymer mixture are shown in Table 4. The results of analysis of chain-end structures indicated direct β-scission of on-chain tertiary carbonium ions of oligomers. The liquid fraction also possesses these chain-ends. The β-scission is shown in following Scheme 2.



Scheme 2.

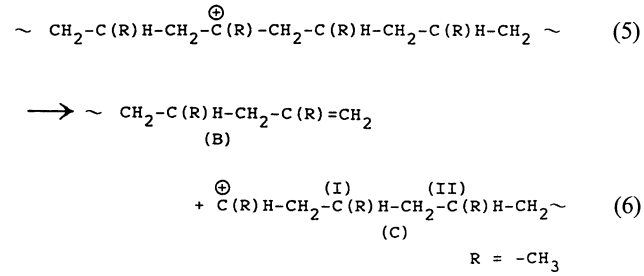
The olefinic liquid fraction flowed into the trap without hydrogenation during a short residence time with high vapor pressure, thus showing it not to possess hydrogenated components.

As shown in Table 5, the oligomer was found to have branched components each possessing short chains of C_1—C_6 6.1 per 20 carbon and $\bar{M}_w$=300 (short chain consist mainly of methyl groups). The extent of branching was essentially the same and showed the back bones of the oligomer structures to be similar to that of copolymer of propylene and 1-butene. The extent of branching has been shown to increase with molecular weight decrease.[13] The extent of branching of further decomposed liquid from oligomers may possible be the same as that of polypropylene back bones (8 per 20 carbon).

It thus follows that secondary carbonium ions are mainly produced at chain-ends of the liquid fraction produced by β-scission of on-chain carbonium ions of the oligomer. The equimoler formation of C_4 and C_5 by direct β-scission of chain-end secondary carbonium ions from the liquid fraction is difficult and thus internal on-chain carbonium ions should be produced through intramolecular rearrangement of chain-end ions by way of least activation energy which ought to be tertiary carbonium ions. The gasification precursor for the C_4 and C_5 fraction formation may possibly be produced by β-scission of on-chain carbonium ions of the liquid fraction.

Mechanism for the Formation of Isobutane and Isopentane. The β-scission for the catalytic decomposition of the oligomer chains possessing short side chains is shown in Scheme 3.

As shown in Tables 2, 4, and 5, yields of the liquid fraction, chain-end structure of oligomer and the extent of branchings indicate that the oligomer fraction undergo random scission to produce the liquid fraction which has chain-end olefin (B) and chain-end secondary carbonium ions (C). The reactions for this are as follows:



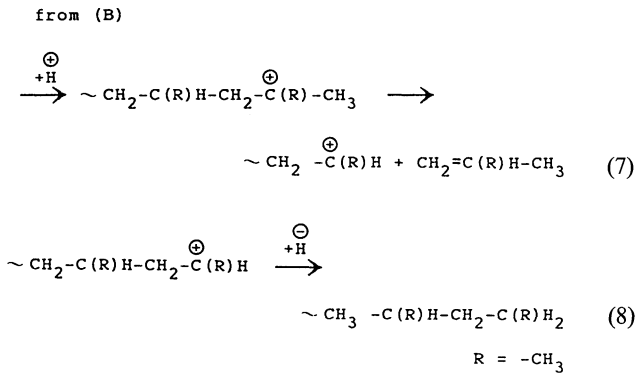
Scheme 3.

Table 5. The Branching Concentration in the Oligomer Fraction

Temp/°C	260	280	300
$CH_3/20CH_2$	2.2	4.3	6.1

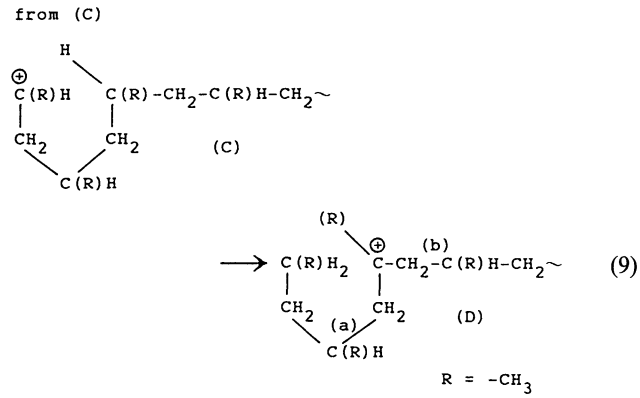
Reaction conditions: zeolite catalyst, time=1 h, C/S =0.25.

Affinity of chain-end olefins for protons released from the catalyst is remarkably high. Consequently, as shown in reaction step (7), olefin (B) immediately undergoes proton addition to form tertiary carbonium ions. These ions are stabilized primarily by β-scission. Hydride ion addition (8) occurs to give the saturated liquid fraction. The reactions for this are as follows:



Only chain-end secondary carbonium ions are produced in the liquid fraction by decomposition of oligomers and are stabilized by an intramolecular rearrangement having the least activation energy. (10—15 kcal mol^{-1}).[15] This occurs most easily through intramolecular rearrangement (15 kcal mol^{-1})[15] rather than by β-scission (45 kcal mol^{-1}).[15] That is, secondary carbonium ions are likely converted preferentially to tertiary carbonium ions.

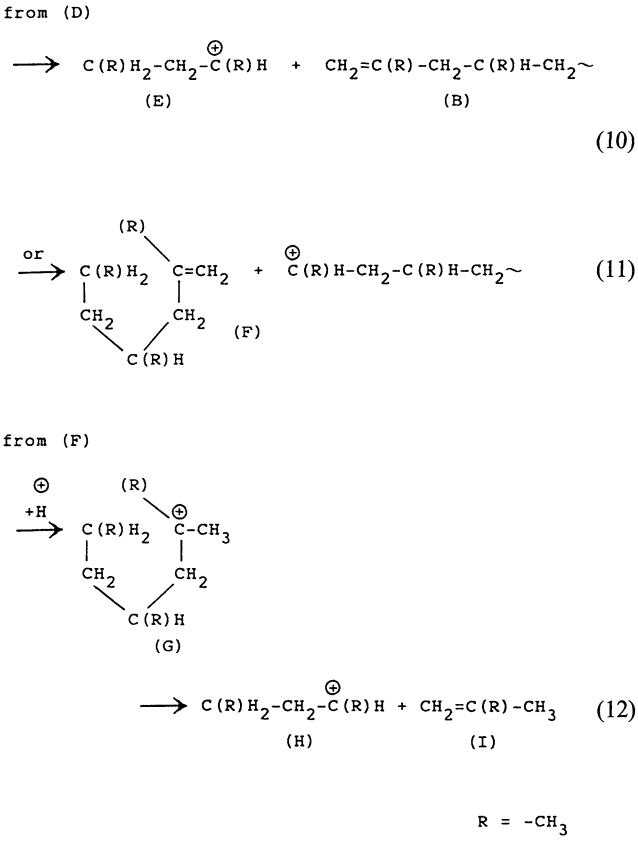
For example, the intramolecular rearrngement of chain-end ions (C) occurs easily on neighboring tertiary carbons by either (I) or (II) (step 6). The formation of ions (I) proceeds via a four membered transition state, while that of ions (II) by a six membered ring. The intramolecular rearrngement of ions (II) occurs exclusively by way of a more stable transition state in step (9).



Chain-end secondary carbonium ions (C) produce internal on-chain tertiary carbonium ions (D) by back biting reactions in step (9). Stabilization of ions (D) occurs by direct β-scission, through either (a) or (b). In the case of the (a) position, 1-methylbutylium ions (E) and chain-end olefins (B) are produced, respectively (step 10). Isopentane is produced by way of hydrogenation and isomerization of (E) ions. The main product produced must thus be only isopentane and the liquid fraction in step (10).

Of course, on the case of this, equimolar yields of C_4 and C_5 could not be recorded. Virtually no gas formation from chain-end olefins occurs continuously. β-scission occurs very little or not at all at the (a) position. Elementary reactions generally lead to the formation of more stable products. The reaction of step (10) is not important.

The stabilization of on-chain carbonium ions (D) occurs through step (11). The C_9 component (F) (branched nonene) is produced by β-scission of (D) ions. From the olefinic branched C_9 fraction (F), reaction intermediate (G) is produced immediately by proton addition in step (12).



The C_4 and C_5 fractions are produced by the redecomposition of intermediate (G). Isobutene is immediately hydrogenated to give isobutane. The 1-methylbutylium ions (H) produced are stabilized by hydride ion addition following isomerization. Isopentane is produced by the hydrogenation of (H) ions.

Table 6. Quantitative Determination of Carbon Number Distribution from the GLC Analysis (Liquid Fraction)

Carbon number	Yield/%
5	0.8
6	2.9
7	6.1
8	7.4
9	17.9
10	17.5
11	20.4
12	11.7
13	13.3

Reaction conditions: zeolite catalyst, temp=260 °C, time=1 h, C/S=O.25.

These steps can be demonstrated by the results of selective formation with equimolar yields of C_4 and C_5 fractions. The continual formation of C_9 is possible only through the reaction intermediate (C) ions in step (9) and not by chain-end olefins (B) in step (10). That is, β-scisssion of (D) ions takes place mainly at the (b) position.

The C_9 fraction (gasification precursor) must first be detected as evidence that these steps actually occur. Table 6 shows the carbon number distribution of the liquid fraction determined by GLC analysis. The liquid fraction consisted of C_9—C_{13} fractions with the C_9 fraction (M_w=128) as the main product. Beltrame, et. al. found the C_9 fraction (saturated and unsaturated isomers) to be the main component in the catalytic decomposition products of PE in the presence of the silica-alumina catalyst.[16]

The C_9 fraction thus corresponds to the reaction intermediate as a gasification precursor. Chain-end secondary carbonium ions of the liquid fraction are formed during the decomposition of the oligomer fraction. These ions are mainly stabilized by back biting involving intramolecular rearrangement. Rearraged on-chain tertiary carbonium ions are also stabilized by β-scission, and consequently, the C_9 fraction is produced. The C_9 fraction cannot be produced by direct β-scission of (a) position, chain-end carbonium ions of the liquid and oligomer fractions but from internal on-chain carbonium ions produced by intramolecular rearrangement via the lowest activation energy than that by β-scission.

The manner in which isobutane and isopentane are formed is shown in Scheme 3. Back biting reactions (step (9)) are quite important to this formation. Isobutane is produced by the hydrogenation of butenes, but no pentenes could be detected in the formation of isopentane and pentane. Pentanes are not produced by hydrogenation of C_5 olefins. That no isopentene could be detected is clear indication of C_9 fraction redecomposition. In this process, only 1-methylbutylium ions are formed. Unstable C_5 ions may possibly be decomposed into the C_3 and C_2 fractions at high temperature. Reaction steps (9) and (11) are repeated. Continuative gasification takes place at step (12) by way of steps (9) and (11).

The oligomer fraction was found to have essentially the same degree of branching as the polypropylene back bone structure. Therefore, the product distribution of polypropylene catalytic decomposition was analyzed. Gas produced by polypropylene decomposition using the silica-alumina catalyst consisted of isobutane 40.4 mol% and isopentane 30.9 mol% at 280 °C.[13] As shown in Table 3, the yield of C_4 and C_5 fractions were 44 and 36 mol% at the same temperature, respectively. The present results confirm the occurrence of these steps PE catalytic decomposition by the NaY-type zeolite catalyst should certainly give rise to isobutane and isopentane as the main products. Back biting reactions are thus shown essential to the formation of the gasification precursor (C_9 fraction) in the catalytic decomposition of PE.

Conclusions

An attempt was made to determine the mechanism for the formation of gas having a peculiar composition in PE decomposition in the presence of the zeolite catalyst. Based on the results obtained, the following conclusions are drawn.

1) The production of isobutane and isopentane in nearly equimolar yields was found at low temperature.

2) The C_9 fraction of the gasification precursor is thus obtained by β-scission of rearrenged on-chain tertiary carbonium ions produced by back biting reactions of chain-end secondary carbonium ions of liquid fraction.

3) Isobutane and isopentane are also produced by redecomposition of the C_9 fraction.

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