Initial Stage of the Oxidation Reaction of Polyethylene by Nitrogen Dioxide

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In a previous paper,[1] the oxidation of polyethylene by nitrogen dioxide was investigated by means of infrared absorption spectroscopy, and the production of nitro, nitrite ester, nitrate ester, carbonyl and hydroxyl groups in polyethylene was recognized. The nitro and nitrite ester groups were produced in the early stage of the degradation by the addition of nitrogen dioxide to the reaction site in polyethylene, and then the nitrate ester, carbonyl and hydroxyl groups were formed as the decomposition products of the nitrite ester group. In that paper, however, no explanation was given of the nature of the reaction sites to which nitrogen dioxide reacted. The present report will attempt to clarify the reaction mechanism in the initial stage of the oxidation reaction of polyethylene by nitrogen dioxide. Particularly, an effort has been made to find out what structure in polyethylene is active in reacting with nitrogen diaxide.

Experimental

The following polyethylenes were used: 1) high pressure polyethylene (HPE), relatively highly-branched polyethylene, called Yukalon, the molecular weight of which as obtained viscosity measurement, was 34000; 2) Phillips-type polyethylene (PhPE), very little-branched polyethylene, called Sholex, the molecular weight of which, as determined by the end group analysis of the infrared spectrum, was 13000; 3) Ziegler-type polyethylene (ZPE), called Hizex, the molecular weight of which as obtained by melt viscosity measurement, was 76000. None of them contained an anti-oxidant. A commercially-available polypropylene called Carlna, was used, from it an anti-oxidant was extractd by propyl alcohol.

The procedure of the reaction of polymers with nitrogen dioxide was the same as that reported in the earlier work.[1] The reaction temperature was 25—120°C, and the partial pressure of nitrogen dioxide in the reaction vessel was 1/3 atm.

Commercial *n*-heptane, decene-1, heptene-2 and 2-ethylhexene-1 were used and purified by fractional distillation. The reaction of the above alkenes with nitrogen dioxide was carried out in the medium of *n*-heptane as follows: the *n*-heptane solution of nitrogen dioxide was added to the *n*-heptane solution of the sample, and the reaction between the sample and nitrogen dioxide was allowed to proceed at 25°C, while the mixture was shaken for an hour. The infrared spectra of the reaction products in the solution of *n*-heptane were measured. Under these conditions, nitrogen dioxide did not react with *n*-heptane. The reaction of *n*-eicosane with nitrogen dioxide was carried out in a sealed tube at 25 and 100°C. The reaction products were dissolved in *n*-octane, washed by an aqueous sodium hydrogen carbonate solution, and water, and dried by sodium sulfate. The products obtained were identified by infrared absorption spectroscopy. Since the infrared spectra of the reaction products of those low molecular hydrocarbons were observed in the solution of *n*-heptane or *n*-octane, the wave number shift of the absorption peak due to the solvent effect was assumed to be similar to that of the reaction products in polyethylene.

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[1] T. Ogihara, This Bulletin, 36, 58 (1963).

The infrared spectra were measured by Perkin Elmer model 13 and Hitachi EPI-S spectrometers, equipped with NaCl and CaF_2 prisms. As the absorption band of the nitro group produced by the reaction was a doublet or had a complex shape, the absorption intensity of the band was of an apparent value. In the present experiment, the absorption intensity of the nitro group produced in polyethylene was the one relative to that of the C-H stretching absorption at 2650 cm^{-1}, i. e., $D(\nu_{NO_2})/D(2650\,cm^{-1})$; therefore, this value represented the absorption intensity of the nitro group formed in a polyethylene film of a constant thickness.

Results and Discussion

Figures 1 and 2 show the absorption band of the N-O anti-symmetric stretching of the nitro group produced by the reaction. The wave number of the band depends on the reaction temperature and on the sample used. It may be seen in Figs. 1 and 2 that the absorption band of the nitro group formed by the reaction has two peaks, i. e., in the region A (1555—1560 cm^{-1}) and in the region B (1568—1570 cm^{-1}). The results are summarized in Table I. All of the polyethylene used, when treated with nitrogen dioxide at various temperatures, showed the absorption peak in the region A. The B absorption band of the nitro group was found in Phillips-type polyethylene (PhPE) oxidized by nitrogen dioxide at both 25 and 120°C. On the contrary, the B band appeared in high-pressure polyethylene (HPE) oxidized above 100°C, while no absorption peak in the region B was observed in HPE treated with nitrogen dioxide at 25°C.

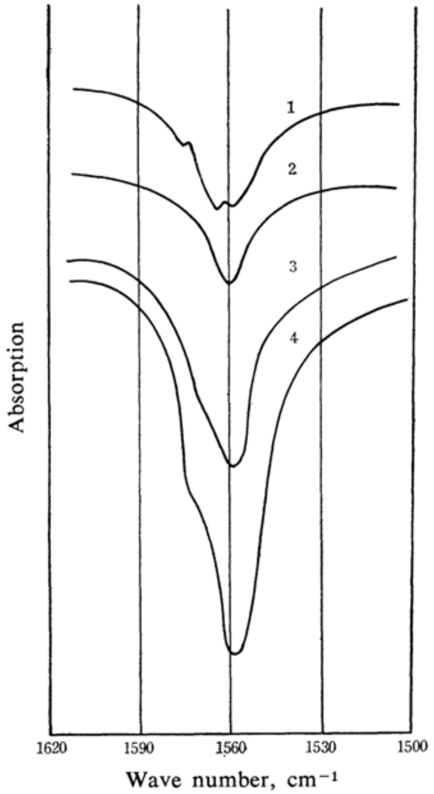


Fig. 1. Absorption band of the anti-symmetric vibration of the nitro group produced in HPE.
The samples are 1 : HPE which was heated to 380°C in the atmosphere of nitrogen gas for 1 hr., and 2, 3, 4 : untreated HPE. The reaction conditions were 1, 2 : 25°C, 0.5 hr., 3 : 80°C, 0.5 hr., 4 : 109°C, 0.5 hr.

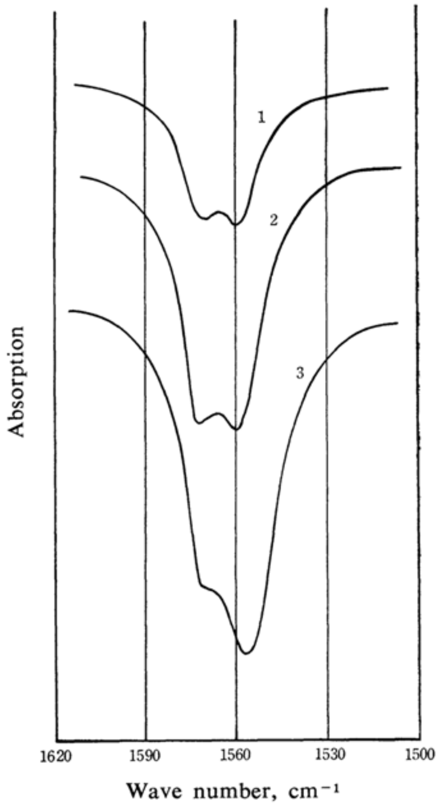


Fig. 2. Absorption band of the anti-symmetric vibration of the nitro group produced in PhPE.
The reaction conditions were 1 : 25°C, 0.5 hr., 2 : 80°C, 0.5 hr., 3 : 120°C, 0.5 hr.

The rate of increase in the absorption intensity of the nitro group formed in PhPE and HPE is given in Fig. 3 as a function of the reciprocal of the reaction temperature. The increment of the rate obtained against the reciprocal of the reaction temperature was not constant in the temperature range of the present experiment; i. e., the negative slope at a high temperature was steeper than that at a low temperature.

TABLE I. WAVE NUMBER OF THE ANTI-SYMMETRIC VIBRATION OF THE NITRO GROUP IN THE REACTION PRODUCTS

Sample*	Reaction temp. and time		Wave number of absorption peak	
			Region A	Region B
	°C	hr.	cm^{-1}	cm^{-1}
HPE	25	0.5	1557	—
	109	0.5	1555	1568
Degraded HPE	25	0.5	1557, 1561	1568
PhPE	25	0.5	1560	1570
	120	0.5	1556	1568
ZPE	28	0.5	1559	1569
	105	0.5	1555	1568
Polypropylene	30	0.5	—	—
	110	0.5	1555	—
n-Eicosane	25	24	—	—
	100	24	1558	1570
Heptene-2	25	1	1559	—
2-Ethylhexene-1	25	1	1561	—
Decene-1	25	1	1562	1568

* HPE: high pressure polyethylene.
Degraded HPE: HPE which was heated to 380°C in the atmosphere of nitrogen gas for 1 hr.
PhPE: Phillips type polyethylene.
ZPE: Ziegler type polyethylene.

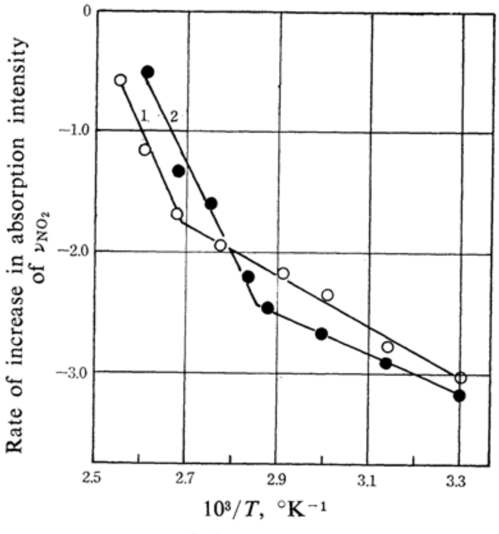


Fig. 3. Rate of increase in the absorption intensity of the nitro group formed in polyethylene. Increasing rate is represented by $\ln d\{D(\nu_{NO_2})/D(2650\,cm^{-1})\}/dt$ hr^{-1}.
1: PhPE, 2: HPE

The absorption intensity of the nitro groups in PhPE and HPE reached a maximum value in a certain reaction time when the reaction with nitrogen dioxide was carried out at 25°C, as may be seen in Fig. 4. However, the absorption intensity of the nitro group increased at an almost constant rate at a high temperature, and the obtained intensity was much larger than that obtained at a low temperature. These results show that the reaction mechanism of polyethylene with nitrogen dioxide at a high temperature differs from that at a low temperature. First, the reaction at low temperature will be discussed.

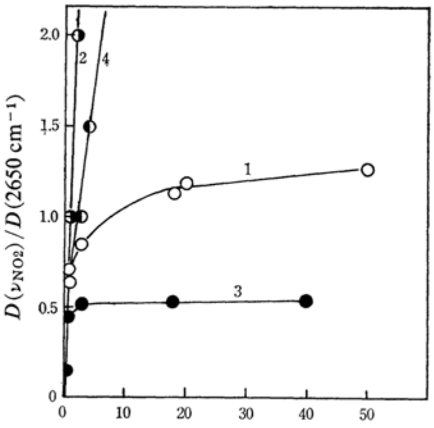


Fig. 4. Rate of formation of the nitro group in polyethylene.
1: PhPE at 25°C, 2: PhPE at 100°C, 3: HPE at 25°C, 4: HPE at 100°C

The Addition Reaction of Nitrogen Dioxide with a Double Bond in Polyethylene. — The absorption intensity of the nitro group which was formed by the reaction with nitrogen dioxide at 25°C did not exceed a certain value, even if a specimen of polyethylene was placed in contact with nitrogen dioxide for a long time, as Fig. 4 shows. This indicates that only a limited number of reaction sites which are active in reacting with nitrogen dioxide at 25°C exist in polyethylene.

The nitro group was not formed in *n*-eicosane (n-$C_{20}H_{42}$), which was left alone in an atmosphere of nitrogen dioxide at 25°C for 24 hr. or longer. Therefore, nitrogen dioxide did not react with the main methylene chain in polyethylene at 25°C. It is well known that polyethylene contains a small amount of structural irregurarity in the main chain, e. g., branchings and double bonds. Nitrogen dioxide, which has an odd electron, easily undergoes the addition reaction with double bonds in olefin. Decene-1, heptene-2 and 2-ethylhexene-1, all of which had double bonds at various positions, reacted with nitrogen dioxide at 25°C, and the products had an absorption band of the nitro group, while the absorption band due to the out-of-plane vibration of a double bond disappeared in the infrared absorption spectra of the products. In that case, after all of the double bonds in the olefin solution had disappeared as a result of the addition reaction of nitrogen dioxide, the absorption intensity of the nitro group in the products retained a constant value even if a longer reaction time and a higher concentration of nitrogen dioxide were adopted. That is, there is a linear relationship between the absorption intensity of the nitro group in the products and the initial amount of olefin in the solution. This is illustrated in Fig. 5. Furthermore, polypropylene, in which double bond was not identified by the infrared spectroscopy, did not react with nitrogen dioxide at 25°C, and no formation of the nitro group could be observed.

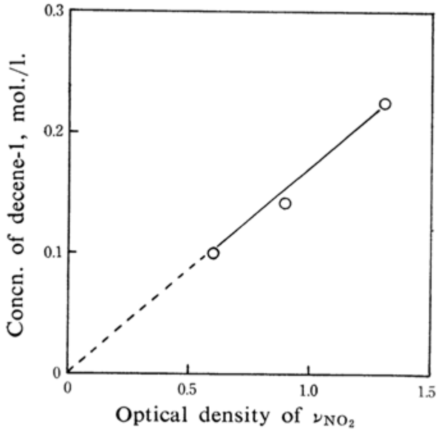
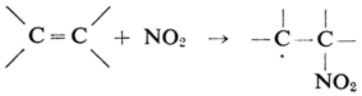


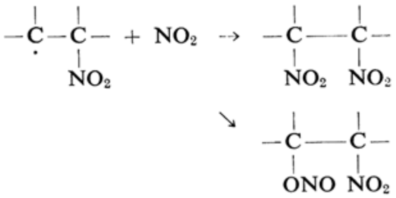
Fig. 5. Relationship between the concentration of decene-1 and the absorption intensity of the nitro group produced. The infrared spectra were measured in *n*-heptane solution and the absorption cell of 0.098 mm. in thickness.

Therefore, it can be concluded that the reaction sites, which react with nitrogen dioxide at 25°C, are double bonds in polyethylene. The nitro group is formed in polyethylene by the addition of nitrogen dioxide to the double bond. Gray and Yoffe have proposed the following mechanism of the addition reaction of nitrogen dioxide with a low molecular olefin[2] first, the nitro group is formed by the reaction:



$$>C=C< + NO_2 \rightarrow -\underset{\cdot}{C}-\underset{NO_2}{C}-$$

and the radical produced is subjected to the further addition of nitrogen dioxide:



$$-\underset{\cdot}{C}-\underset{NO_2}{C}- + NO_2 \rightarrow -\underset{NO_2}{C}-\underset{NO_2}{C}- \quad \searrow \; -\underset{ONO}{C}-\underset{NO_2}{C}-$$

The products are dinitro and nitro-nitrite compounds in almost equal amounts, and the proportion of the nitro to the nitrite ester group of the products is 3 : 1. This explanation is compatible with the present experimental observation that the absorption intensity of the nitrite ester group is much smaller than that of the nitro group in polyethylene treated with nitrogen dioxide at 25°C. However, a quantitative discussion of the number of the nitro group produced from one double bond in polyethylene is difficult as a result of the complex shape of the absorption band of the nitro group. The nitrite ester group is unstable, and it often changes into a nitrate or carbonyl group, as has already been mentioned.[1]

Figure 6 shows the absorption band of the nitro group which has been produced in decene-1, heptene-2 and 2-ethylhexene-1 by the addition of nitrogen dioxide to their double bonds at 25°C. The absorption band of the nitro group formed in decene-1 had two peaks, at 1562 and 1568 cm^{-1}; a similar finding was obtained regarding the absorption band of the nitro group in PhPE, which underwent the addition reaction with nitrogen dioxide at 25°C, as Fig. 2 shows. This can be explained by the fact that most of the double bonds in PhPE are positioned at the terminals of the polymer chains;[3] that is, the double bond in PhPE is of the vinyl type and exactly the same as decene-1. Therefore, the reaction products of PhPE with nitrogen dioxide can be expected to have the same structure as those of decene-1; in other words, it gives the same infrared absorption spectrum. It may be seen in Figs. 1, 2 and 6 that no example of a doublet absorption band of the nitro group, which has been found in the reaction products at 25°C, exists except for the reaction products of PhPE and decene-1. This leads to the conclusion that the absorption band, in which two peaks are observed in the wave number regions A and B is characteristic of the additional reaction product of nitrogen dioxide to the double bond of the terminal vinyl-type in polyethylene. The wave number of the absorption band of the primary nitro compound is slightly larger than that of the secondary or tertiary one.[4] This is probably one of the reasons why the

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[2] P. Gray and A. D. Yoffe, *Chem. Revs.*, **55**, 1069 (1955).

[3] M. Dole, D. C. Milner and T. F. Williams, *J. Am. Chem. Soc.*, **80**, 1580 (1958).

[4] J. F. Brown, ibid., **77**, 6341 (1955).

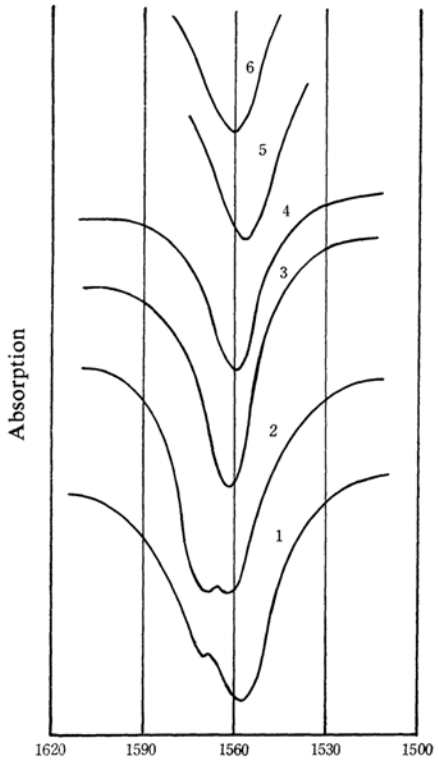

Fig. 6. Absorption band of the anti-symmetric vibration of the nitro group produced in low molecular compounds.
1 : *n*-eicosane, treated with nitrogen dioxide at 100°C for 24 hr., 2 : decene-1, 25°C, 1 hr., 3 : 2-ethylhexene-1, 25°C, 1 hr., 4 : heptene-2, 25°C, 1 hr., 5 : 2-nitropropane, 6 : 1-nitropropane.

nitro group produced in the terminal double bond has two absorption peaks in the regions A and B. Another conceivable reason is the coupling of the NO_2 anti-symmetric stretching vibration of the two nitro groups at the chain terminal. This coupling causes the splitting of the two nitro group vibrations.

The absorption band of the nitro group, which was produced in HPE by the reaction at 25°C, had only one peak in the region A. The same result was obtained in the reaction products of heptene-2 and 2-ethylhexene-1, when nitrogen dioxide was added at 25°C. This result is reasonable, since most of the double bonds in HPE are vinylene and vinylidene in type.[3] The dinitro compound obtained from the double bond of the vinylidene type may have primary and tertiary nitro groups, while only one absorption peak in the region A has been observed here. No satisfactory explanation for this fact has been obtained in the present experiment.

Ziegler-type polyethylene (ZPE) has double bonds of the above-mentioned three types,[3] while the absorption band of the nitro group produced in ZPE has two peaks in the regions A and B as Table I shows. However, the absorption intensity of the B band was smaller than that of the A band, since the nitro group produced from double bonds of vinylene and vinylidene types contributed only to the A band.

Though the nitro group produced in HPE at 25°C had no infrared absorption peak in the region B, a specimen of HPE showed a small absorption peak in the region B when heated to 380°C for 1 hr. in an atmosphere of nitrogen gas and reacted with nitrogen dioxide at 25°C after cooling, as is shown in Fig. 1. This result can be interpreted by means of the fact that double bonds of the vinyl-type are formed at the terminal of the polyethylene chain, probably as a result of the scission of the polymer chain.

Hydrogen Abstraction Reaction by Nitrogen Dioxide.—At a high reaction temperature, the absorption intensity of the nitro group formed in polyethylene was much stronger than that at a low temperature, and it increased linearly with the reaction time, as may be seen in Fig. 4. This finding shows that the reaction site of polyethylene is not double bond, which exists in a limited amount in polyethylene. Both *n*-eicosane and polypropylene, which did not react with nitrogen dioxide at 25°C, produced the nitro group by the reaction at a high temperature. Therefore, it is evident that the reaction site, which has not existed originally in polyethylene, is formed by nitrogen dioxide at a high temperature. The reaction site cannot be expected to be formed by the thermal decomposition of polyethylene at the present reaction temperature. However, it is probable that the hydrogen atom is abstracted by nitrogen dioxide from polyethylene and that the free radical thus produced becomes the reaction site for the addition reaction of nitrogen dioxide.

In the reaction of PhPE with nitrogen dioxide at a high temperature, both A and B absorption bands of the nitro group were observed, while the intensity of the A absorption band was much stronger than that of the B band. The absorption intensity of the A band increased as the reaction temperature was raised, as may be seen Fig. 2. This means that the hydrogen atom in the methylene chain in the polymer is abstracted and that the radical so produced reacts with nitrogen dioxide to form the secondary nitro group, which has an infrared absorption peak only in the region A. Similarly, the increase in the absorption intensity of the A band was observed in the reaction of HPE at 110°C, where the absorption shoulder in the region B was found as shown in Fig. 1. This is considered to be due to the formation of the nitro group bonded to the terminal carbon atom of the polymer chain; it can be explained by the assumption that the scission of the polymer chain occurs in the process of the oxidation by nitrogen dioxide.

In the initial stage of the reaction with nitrogen dioxide at a high temperature, the following reactions are conceivable:

$$RH + NO_2 \xrightarrow{k_1} R + HNO_2 \quad (1)$$

$$R + NO_2 \xrightarrow{k_2} RNO_2 \quad (2)$$

$$R + NO_2 \xrightarrow{k_3} RONO \quad (3)$$

where reaction 1 represents the formation of the free radical as the result of the abstraction of the hydrogen atom from polyethylene by nitrogen dioxide. Nitrogen dioxide adds immediately to the radical produced, and the nitro and nitrite ester groups are formed by reactions 2 and 3. In reactions 1—3, the rate-determining step is reaction 1, since the radical recombination rate of reactions 2 and 3 are considered to be fast. The thermal decomposition of the nitro group does not occur in the temperature range of the present experiment, so that the information about the rate of reaction 1 can be obtained by the measurement of the concentration of the nitro group produced in polyethylene. In the present experiment, the increasing rate of the absorption intensity of the nitro group was observed to be independent of the film thickness in the 0.05—0.2 mm. range, where the absorption intensity of the nitro group was relative to that of the 2650 cm^{-1} band and the effect of film thickness was removed. Therefore, it can be assumed that the diffusion of nitrogen dioxide into a polyethylene film has no considerable effect on the rate of the reaction.

The rate of the formation of the nitro group is represented by the following equation:

$$d[RNO_2]/dt = k_1[RH][NO_2]/\{1+(k_3/k_2)\}$$

where k_1, k_2 and k_3 are the rate constants of reactions 1, 2 and 3 respectively, and a steady condition is assumed. It has been reported in a previous paper[5] that the ratio of the nitro to the nitrite ester group formed in the reaction at 100°C is about 2:1; it is reasonable to consider that this ratio does not vary upon a small change in the reaction temperature. Therefore, k_3/k_2 can be assumed to be independent of the reaction temperature. Figure 3 shows the increasing rate of the absorption intensity of the nitro group in the initial stage of the reaction. Here the absorption intensity of the nitro group is approximately proportional to the concentration of the nitro group in polyethylene, and it is further assumed that polyethylene and nitrogen dioxide exist in excess in the reaction system. As has already been mentioned, it may be seen in Fig. 3 that the slope of the straight line in the high temperature region differs from that in the low temperature region. The former slope corresponds to the activation energy of the hydrogen abstraction reaction by nitrogen dioxide, while the latter corresponds to that of the addition reaction of nitrogen dioxide to the double bonds contained in polyethylene.

The apparent activation energy obtained is shown in Table II. The present value of the activation energy is not very accurate, because a number of samples should be used in following the reaction process at a given temperature and so it has been difficult to obtain the complete reproducibility of the reaction. However, the activation energy of the hydrogen abstraction reaction from HPE or ZPE seems smaller than that of PhPE. This is perhaps due to the existence of branching in the polymer chain of HPE or ZPE. Harnsberger[6] obtained the activation energy of the overall reaction, $CH_4 + NO_2 \rightarrow CH_3NO_2$, as 21 kcal./mol. Semenov's empirical formula[7] to obtain the activation energy of the hydrogen abstraction reaction gives a value of 19 kcal./mol. in the $C_3H_8 + NO_2 \rightarrow iso\text{-}C_3H_7 + HNO_2$ reaction. Compared with these values, the present result is considered to be reasonable. Of course, it is

TABLE II. APPARENT ACTIVATION ENERGY IN kcal./mol.*

Sample**	Hydrogen abstraction reaction	Addition reaction with double bond
HPE	14	2
PhPE	17	4
ZPE	14	2
Polypropylene	15	—

* The error in activation energy is about ±2 kcal./mol.

** See Table I for abbreviations.

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[5] T. Ogihara, S. Tsuchiya and K. Kuratani, *Collected Papers of Aero. Res. Inst., Univ. Tokyo* (*Kôkû Kenkyûsho Shûhô*), 3. 260 (1963).

[6] H. F. Harnsberger, Thesis, Univ. of California, Berkeley (1951), cited in Ref. 2.

[7] N. N. Semenov, "Some Problems in Chemical Kinetics and Reactivity," translated by M. Boudart, Princeton Univ. Press, N. J. (1958), p. 29.

unlikely that the present experimental value is the activation energy of the elementary reaction, because the present reaction system is not homogeneous and many assumptions are made.

Conclusion

The reaction mechanism in the initial stage of the reaction between polyethylene and nitrogen dioxide differs with the reaction temperature. At room temperature, nitrogen dioxide adds to the double bond which exists originally in polyethylene, and dinitro or nitro-nitrite compounds are produced. At a high temperature, above 100°C, in addition to the above reaction, nitrogen dioxide reacts with the methylene chain of polyethylene. That is, the reaction is initiated by the hydrogen abstraction from polyethylene, and the free radicals produced undergo the combination reaction with nitrogen dioxide. The activation energy of hydrogen abstraction reaction by nitrogen dioxide is estimated to be 14—17 kcal./mol. on the basis of the measured data of the absorption intensity of the nitro group.

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