

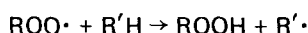
# E.s.r. studies on oxidation processes in irradiated polyethylene: 3. Direct detection of the reaction $\text{ROO}\cdot + \text{R}'\text{H} \rightarrow \text{ROOH} + \text{R}'\cdot$ , in urea—polyethylene complexes

Yasurō Hori, Shigetaka Shimada and Hisatsugu Kashiwabara,

Nagoya Institute of Technology, Showa-ku, Nagoya 466, Japan

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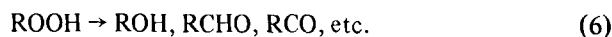
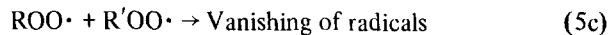
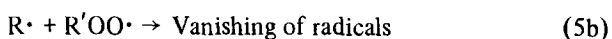
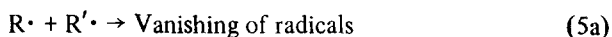
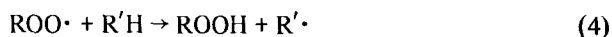
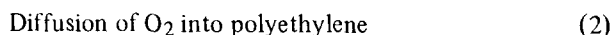
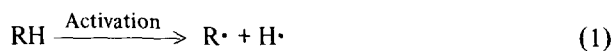
Conversion of peroxy radicals into alkyl radicals



has been directly observed by the e.s.r. method in the case of polyethylene in a urea—polyethylene complex system. Abstraction of hydrogen atoms was found to be an intramolecular reaction in this case, of activation energy 24.6 kcal/mol. Evidence confirming this was provided by i.r. spectrometry.

## INTRODUCTION

The oxidation of polyethylene has been studied by many authors<sup>1-8</sup>. The mechanism of oxidation of polyethylene is presented in each study, and the following reaction equations are generally accepted for all the cases of oxidation in polyethylene:



The equations described above are schematic oxidation processes for polyethylene but observation and detailed study of each reaction is very important in order to elucidate the oxidation mechanism. Many investigations into the oxidation of polyethylene have been undertaken by detecting the final products of the reaction. Reactions (1) and (5a) have been studied by many authors from the viewpoint of the production and decay of carbon radicals, and reactions (2) and (3) have been studied by our group in detail<sup>9-12</sup>.

Reaction (4) is important in a chain mechanism during the oxidation process, but it has not been reported until now. Reactions (5b), (5c) and (6) are also important but they have not been reported. Recently, direct observation of reaction (4) was successfully carried out by us for mate-

rials in urea—polyethylene complexes by means of the e.s.r. technique. These results will be discussed in the present paper.

The method preparation of urea—polyethylene complexes (UPEC) was reported recently<sup>13</sup> and the structure of the model compound was also studied extensively<sup>14</sup>. In UPEC, the polyethylene chain is extended and contained by a wall of urea. The distance between the polyethylene chain and the urea wall is larger than the distance between the nearest neighbour polyethylene chains in the normal polyethylene crystal. Thus, there is little nearest neighbour interaction.

When UPEC was irradiated by  $\gamma$ -rays *in vacuo* at room temperature only the alkyl radicals trapped in polyethylene were observed; radicals trapped in urea molecules were not observed. The former were stable at room temperature and converted completely to the peroxy radicals by reaction with oxygen at room temperature for 1 day. These peroxy radicals were also stable at room temperature. Hence, it should be possible to observe reaction (4) in UPEC. However, this reaction is not observed in normal polyethylene because of absence of those conditions present in UPEC.

In a recent paper<sup>12</sup>, the properties of peroxy radicals trapped in UPEC were reported in detail. The structure of the peroxy radical in the pores of urea is illustrated in *Figure 1*. The C—O—O plane is perpendicular to the direction of the chain axis. This radical rotates rapidly around the chain axis even at room temperature, and the rotation around the C—O bond, although not a main motion of the peroxy radical, becomes faster with rising temperature.

## EXPERIMENTAL

The samples used in this study were powdered urea—polyethylene complexes (UPEC) and (urea-*d*<sub>4</sub>)—polyethylene complexes (*d*-UPEC). UPEC and *d*-UPEC were prepared according to the method of Monobe and Yokoyama<sup>13</sup>; i.e.,

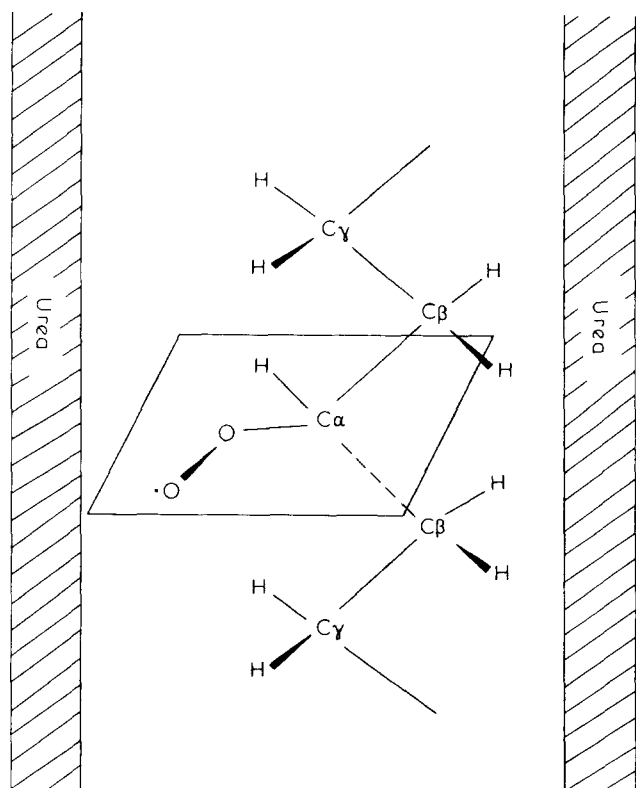


Figure 1 Schematic illustration of structure of urea-polyethylene complex (UPEC)

UPEC by mixing a xylene solution of linear polyethylene (Sholex 6050) with urea-*n*-hexadecane complex at 393K. In the preparation of *d*-UPEC, urea-*d*<sub>4</sub> of 99% purity was used instead of urea-*h*<sub>4</sub>. These complexes were identified by d.s.c. measurement and had purities of about 100%.

All samples were irradiated *in vacuo* at room temperature using a <sup>60</sup>Co source. The total dose was 11.2 Mrad or 3.0 Mrad at a dose rate of 0.17 Mrad/h. All the alkyl radicals produced by  $\gamma$ -irradiation were reacted with oxygen under a pressure of 200 torr and converted to peroxy radicals.

The decay of the peroxy radicals was observed for two cases. One in which radicals were reconverted to the alkyl form by heat treatment when the samples were *in vacuo*; the other in which vanishing of peroxy radicals only occurred on heat treatment when the samples were in an atmosphere of oxygen at 200 torr. For both cases the samples were treated in an oil bath at the desired temperature ( $\pm 0.5^\circ\text{C}$ ) for the appropriate length of time, and the e.s.r. spectra were observed at room temperature.

The e.s.r. measurements were made using an X-band spectrometer with 100 kHz field modulation. The microwave power was kept so small ( $< 0.1\text{ mW}$ ) that the effect of power saturation was not observed even for the carbon radicals. The modulation width was 2.0 gauss. The signals were recorded using a Jeol spectrum computer Model JEC-6.

Changes in the relative concentration of peroxy radicals were obtained by observing the change in the height of the peak indicated by an arrow in Figure 2. The total concentration of all radicals and the concentrations of the peroxy and alkyl radicals were obtained by double integration of the first derivative patterns recorded.

I.r. measurements were also made in order to detect the oxidation products after these reactions. Three different samples were prepared by dissolving UPEC in boiling methanol and filtering. One was untreated UPEC; the second was irradiated up to 11.2 Mrad *in vacuo* at room temperature

before dissolution. The third was similarly irradiated and then exposed to oxygen for 24 h (to convert all alkyl radicals to peroxy radicals) and then heated at 360K for 4 h *in vacuo* (to convert peroxy radicals to alkyl radicals): this cycle was repeated twice (i.e. three cycles). The i.r. measurements were made by the KBr method.

The *G* values of alkyl radicals and hydrogen molecules evolved in UPEC by  $\gamma$ -irradiation were measured, and the amount of gas, which remained after heat treatment of UPEC containing the peroxy radicals *in vacuo*, was also estimated.

## RESULTS AND DISCUSSION

The changes of the e.s.r. spectra due to the heat treatment were observed and an example of these changes is shown in Figure 2 for the case of heat treatment *in vacuo*. Spectrum A in Figure 2 is that obtained from peroxy radicals and spectrum D is that obtained from alkyl radicals. Spectra B and C are superpositions of peroxy and alkyl signals, showing a course of conversion of the peroxy radicals into the alkyl radicals. Of course, when the samples were treated in oxygen at 200 torr, the intensity of the e.s.r. spectra of the peroxy radicals decreased without conversion to alkyl radicals. For the case of treatment *in vacuo*, these changes are caused by reaction (4) or by the back reaction of equation (3):

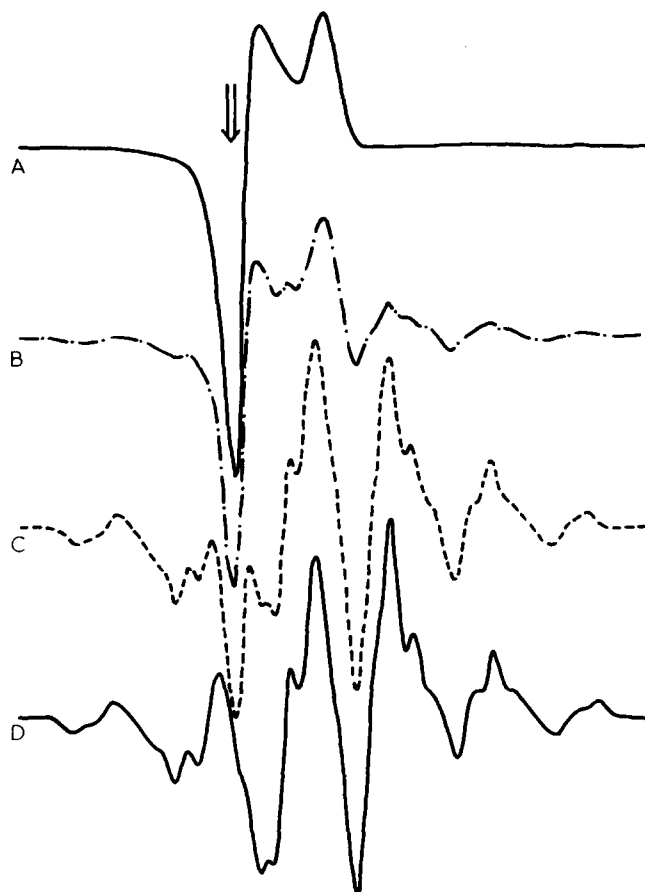
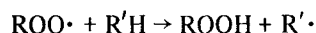


Figure 2 Change of the e.s.r. spectra of radicals trapped in UPEC by the heat treatment *in vacuo* at 361K for A, 0 min; B, 21 min x 1.25; C, 90 min x 2.8; and D, 210 min x 2.8

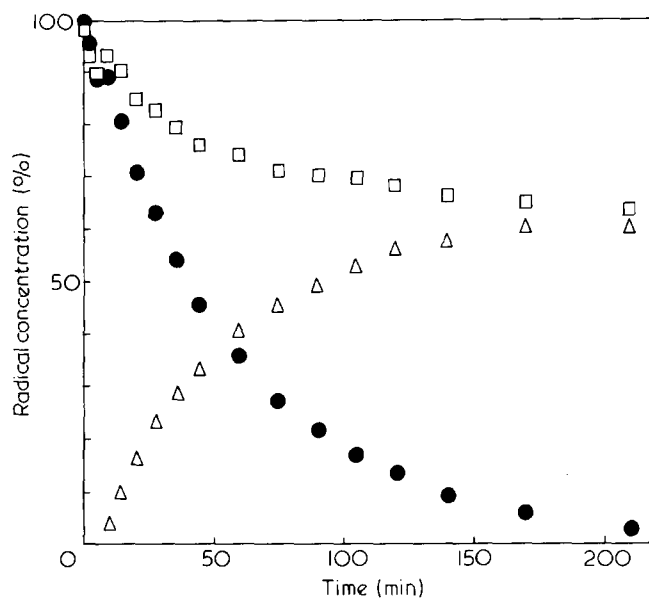


Figure 3 Change of the concentrations of various radicals in UPEC with the time of heat treatments at 361K *in vacuo*; □, total radicals, ●, peroxy radicals, △, alkyl radicals

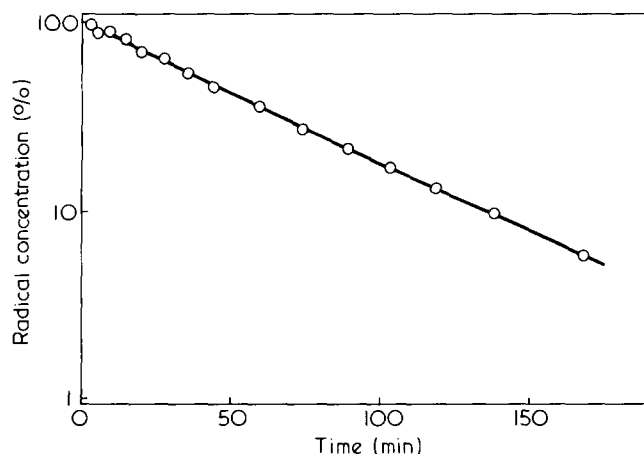
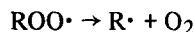


Figure 4 Decay of the peroxy radicals in UPEC due to the heat-treatment at 361K *in vacuo*

or



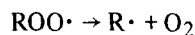
We concluded that reaction (4) occurred for the reasons given below.

The relative concentrations of the peroxy radicals, the alkyl radicals, and the sum of them were determined from the peak height and the value of integration during heat treatment. These measurements were made at various temperatures when the samples were heated *in vacuo* or in oxygen at 200 torr. An example of the changes of relative concentrations is illustrated in Figure 3, which shows that the total concentration of the radicals decays due to the heat treatment, and indicates the partial occurrence of the decay reactions in UPEC, equations (5a), (5b) or (5c).

The logarithms of the relative concentrations shown in Figure 3 were plotted against the reaction time to obtain Figure 4 which shows that the experimental data are in very good agreement with a first order reaction scheme. However, some plots in the earlier stage of the reaction are not explained by the first order reaction scheme, but appear to

be faster. This may indicate that a decay scheme faster than first-order exists in the initial stage of the reaction or that the experimental error is larger in the initial stage. We could not determine which was the case, but if it were the former, these radicals comprise less than 20% of the total. In all cases of heat treatment of UPEC or *d*-UPEC *in vacuo* or in oxygen at various temperatures, the decay of the peroxy radicals was a first order reaction after a few minutes (see Figure 4). The values of the rate constants of these first order reactions were estimated for all cases and are tabulated in Table 1.

The reaction equation (4) and the back reaction of equation (3), which occur if the sample containing peroxy radicals is heated *in vacuo*, will be discussed. For peroxy radicals trapped in polytetrafluoroethylene (PTFE), it has been reported that conversion to alkyl radicals occurs by heat treatment *in vacuo*<sup>15-17</sup> in a similar manner. Tsvetkov *et al.*<sup>15</sup> and Matsugashita and Shinohara<sup>16</sup> claimed that the back reaction of equation (3),



occurred in these cases. But Hagiwara *et al.*<sup>17</sup> analysed the species of gases produced by these reactions by means of mass spectrometry, and they observed only the oxidation products, CO<sub>2</sub> etc., and no oxygen. Therefore, they claimed that reactions (4) and (6) occurred, instead of the back reaction of equation (3).

Similarly in the case of PTFE, our experimental results indicate that the major part of the reaction in UPEC is reaction (4) for the following reasons.

(a) The results of i.r. measurements in our study are illustrated in Figure 5, in which the i.r. spectrum of polyethylene in UPEC before  $\gamma$ -irradiation (A), the spectrum after the  $\gamma$ -irradiation (B) and the spectrum after three cycles of post-oxidation heating at 360K for 4 h *in vacuo* (C), are shown. Spectra B and C are the same except in the range from 1550 to 1800 cm<sup>-1</sup> and the peaks in this range (peaks from oxida-

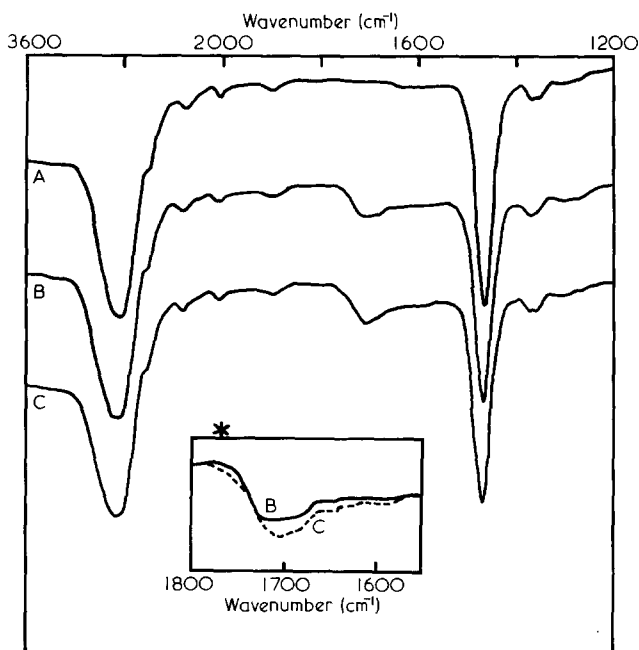


Figure 5 Change of the i.r. spectra of polyethylene due to the heat treatments of UPEC at 360K; (A): materials without any treatment; (B): materials subjected only to the  $\gamma$ -irradiation of 11.2 Mrad; (C): materials subjected to heat treatment for 4 h *in vacuo* three times. Spectra B and C are the same except the region indicated in the inset

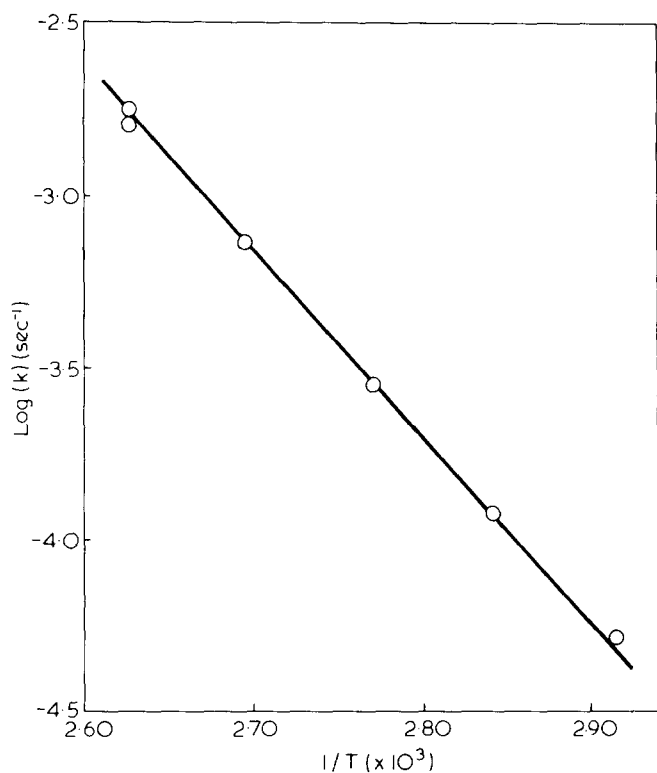
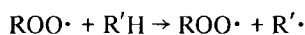


Figure 6 Arrhenius plot of the rate constants of decay of peroxy radicals trapped in UPEC due to the heat treatment *in vacuo*. Activation energy is 24.6 kcal/mol

tion products) increase during heat treatment as shown by the inset enlargement. Such a large quantity of oxidation products could not be produced by the back reaction of equation (3) alone so reactions (4) and (6) must also occur.

(b) The amount of residual gas after the reaction *in vacuo* may be nearly equal to the amount of radicals trapped initially if only the back reaction of equation (3) occurs but the amount of residual gas was measured to be about a quarter of the amount of the radicals. Therefore, reaction (4) must obtain. We thought that the residual gasses after the reaction might be those which were made by degassing from absorbing sites due to heat treatment.

(c) Finally, as shown in Table 1, the reaction rates were nearly equal for the reactions *in vacuo* and in O<sub>2</sub> atmosphere when the reaction temperatures were the same. If the back reaction of equation (3) is a main part of the reaction, the reaction rate in oxygen must be different from that *in vacuo* and might be smaller, because the decay of the peroxy radicals in oxygen is controlled by the equilibrium in the reaction (3) and by the reaction rate of equation (4), but the decay *in vacuo* is controlled only by the rate of back reaction of equation (3). However, if reaction (4) is a main part of the reaction and reaction (3) is very fast in the presence of oxygen molecules, the reaction rate *in vacuo* is equal to that in oxygen. In fact, the reaction is known to be very fast when many oxygen molecules exist around an alkyl radical. Therefore, the equality of the reaction rates between *in vacuo* and in oxygen indicates that the major process of the peroxy radical decay in UPEC by heat treatment is the reaction (4):



Further, we must determine whether R'H in reaction (4) comes from polyethylene or from urea molecules. It was reported by us<sup>12</sup> previously that the peroxy radicals trapped

in UPEC are very stable at room temperature even though they are rotating rapidly around the polyethylene chain at the same temperature. This fact may indicate that the peroxy radicals in UPEC cannot react with the hydrogen atoms of urea. This prediction was confirmed by experimental results for isotope effects. As shown in Table 1, the decay rate of the peroxy radicals by heat treatment *in vacuo* did not change when hydrogen atoms in urea were substituted by deuterium. If the peroxy radicals extract hydrogen atoms from urea molecules in UPEC, the reaction rate may decrease due to the isotope effect when the decay reaction of the peroxy radicals proceeds in *d*-UPEC. Since this reaction shows no isotope effects, the peroxy radicals do not extract hydrogen atoms from urea, but from polyethylene molecules during heat treatment. The decay of the peroxy radicals in UPEC is therefore an intramolecular reaction. From the steric point of view, it can be said that the peroxy radicals probably react with the hydrogen on the  $\gamma$ -carbons shown in Figure 1. Also, experimental facts reflect that the decay reaction begins above the temperature at which the motion of peroxy radical around the C—O bond becomes rapid.

The temperature dependence of the rate constants of reaction (4) in UPEC is illustrated in Figure 6, which shows that the rate constant,  $k$ , can be expressed satisfactorily by the Arrhenius expression:

$$k = k_0 \exp(-\Delta E/RT)$$

The activation energy,  $\Delta E$ , of the decay reaction of peroxy radicals in UPEC was estimated to be 24.6 kcal/mol from Figure 6. This activation energy may be a combination of the activation energy of the rotation of peroxy radical around the C—O bond and the activation energy of the extraction of the hydrogen atom from a  $\gamma$ -methylene group. These values could not be estimated separately.

The reaction rate seemed to be dependent on dose (shown in Table 1) to an extent larger than experimental error. This dependence may be caused by the scission of polyethylene chains due to  $\gamma$ -irradiation. The shorter chain lengths in the sample irradiated to larger dose probably increased the reaction rate by faster molecular motion, and the second order reaction from reactions (5b) and (5c) may also partly be a cause of variation of the reaction rate. These problems will be discussed in a future study.

## CONCLUSION

We have observed directly the reaction:

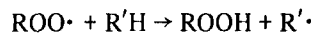


Table 1 Rate constants of the decay of peroxy radicals trapped in UPEC by heat treatment

Temperature (K)	Dose (Mrad)	Rate constant (sec <sup>-1</sup> )	In vacuo or in O <sub>2</sub>	In UPEC or in <i>d</i> -UPEC
343	11.2	5.08 × 10 <sup>-5</sup>	<i>In vacuo</i>	In UPEC
352	11.2	1.19 × 10 <sup>-4</sup>	<i>In vacuo</i>	In UPEC
361	11.2	2.80 × 10 <sup>-4</sup>	<i>In vacuo</i>	In UPEC
371	11.2	7.38 × 10 <sup>-4</sup>	<i>In vacuo</i>	In UPEC
381	11.2	1.6 × 10 <sup>-3</sup>	<i>In vacuo</i>	In UPEC
361	11.2	2.80 × 10 <sup>-4</sup>	<i>In vacuo</i>	In UPEC
361	3.0	2.59 × 10 <sup>-4</sup>	<i>In vacuo</i>	In UPEC
361	11.2	2.82 × 10 <sup>-4</sup>	In O <sub>2</sub>	In UPEC
361	3.0	2.70 × 10 <sup>-4</sup>	In O <sub>2</sub>	In UPEC
361	3.0	2.59 × 10 <sup>-4</sup>	<i>In vacuo</i>	In <i>d</i> -UPEC

in UPEC by means of the e.s.r. technique. In this case, it was an intramolecular reaction with activation energy 24.6 kcal/mol. Since the reaction may be intermolecular for the oxidation processes in normal polyethylene, further study of a similar nature is necessary.

#### ACKNOWLEDGEMENT

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