

## Atactic Polypropylene Hydroperoxide Decomposition in the Neat Liquid Phase

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### Synopsis

Low molecular weight atactic polypropylene hydroperoxide (APPH), *m.* (onset)  $\approx 80^\circ\text{C}$ , was prepared via oxidation of uninhibited low molecular weight atactic polypropylene (APP). The APPH was thermally decomposed over a temperature range of  $115^\circ\text{--}125^\circ\text{C}$  in which the APPH was in a neat molten state. The reaction order ( $n$ ) was found to be close to 2,  $n = 2.2 \pm 0.2$ , and the activation energy of decomposition ( $E$ ) was ca. 27 kcal/mole<sup>1</sup>. In contrast to solid-state decompositions, such values would be anticipated for liquid-phase decompositions due to enhancement of molecule mobility and hydrogen bonding.

### INTRODUCTION

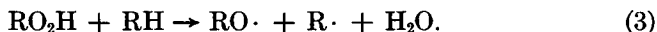
In order to explain various experimental data obtained in the liquid phase during autoxidation of various olefinic hydrocarbons, various workers postulated a bimolecular decomposition of hydroperoxide ( $\text{RO}_2\text{H}$ ) in the initiation step (see Reich and Stivala<sup>1</sup> for leading references), viz.,



However, at low hydroperoxide concentrations, other workers found it necessary to postulate a first-order process to explain their kinetic findings:



and/or



From an energetic viewpoint, reactions (1) and (3) would be favored. Further, these reactions would be enhanced by conditions favoring hydrogen bonding.

In the bulk phase, due to a highly viscous medium which does not favor molecule mobility (and hence hydrogen bonding), step (2) may be anticipated to predominate. Many investigators of bulk polymer decompositions have postulated unimolecular hydroperoxide decompositions to explain their experimental data.<sup>2-9</sup> Thus, for example, during the high-temperature

oxidation of polyethylene, various workers<sup>3-5</sup> have utilized the unimolecular hydroperoxide decomposition mechanism. However, for the decomposition of polypropylene hydroperoxide (PPH), both unimolecular and bimolecular mechanisms have been advanced. Thus, during the oxidation of polypropylene, mechanisms have been put forth which involve unimolecular decomposition of PPH<sup>1,2,5,6</sup> and bimolecular decomposition of PPH.<sup>5,7-9</sup>

Recently, Van Sickle<sup>10</sup> investigated the decomposition of atactic polypropylene hydroperoxide (APPH) in *tert*-butylbenzene during a study of the oxidation of atactic polypropylene (APP) in benzene solution. He reported that the data for APPH decomposition (125°C) approximated a second-order relation for the relatively high APPH concentration of  $\sim 0.1$  g/ml<sup>1</sup>. Such a result may be anticipated based upon the preceding discussion. Thus, for relatively high concentrations of PPH in solution, molecule mobility leading to hydrogen bonding may be enhanced, thereby favoring step (1). In view of this result, it appeared to be of interest to investigate the decomposition of APPH in the neat liquid phase. The purpose of this paper is to report on the kinetic order ( $n$ ) and activation energy ( $E$ ) for the decomposition of low molecular weight APPH at reaction temperatures wherein the APPH is in the molten state.

## EXPERIMENTAL

### Materials

A sample of uninhibited APP (Eastobond M-5W, Eastman Kodak Co.) was dissolved in benzene and centrifuged. The insoluble material was apparently isotactic polypropylene (based on IR measurements). The supernatant liquid was passed through alumina and APP was precipitated with methanol. After drying in a vacuum oven for several days at 35°C, intrinsic viscosity measurements afforded a  $\bar{M}_v \approx 20,000$  and IR measurements indicated virtually complete atacticity.

### Apparatus and Procedure

The sample of APP was dissolved in chlorobenzene ( $\sim 1.5M$ ) in a three-necked flask equipped with reflux condenser, thermometer, and gas sparger. Di-*tert*-butyl peroxide ( $\sim 0.015M$ ) was added, and oxygen was then passed into the solution for ca. 15 hr at 105°C. The resulting solution was treated with carbon black and filtered, and acetone was then added. The APPH which precipitated was dried several days in a vacuum oven at 35°C and was found to possess a  $\bar{M}_v \approx 10,000$  and a hydroperoxide content of ca. 0.2% by weight using iodimetry,<sup>11</sup> and melted (onset) at ca. 80°C. No carbonyl moieties could be detected by IR measurements.

Approximately 1-g samples of APPH were placed at the bottom of glass tubes connected in series. Nitrogen was passed through the tubes and reaction temperatures of 115°, 120°, and 125°C were employed using a silicone oil bath. After allowing ca. 30 min for equilibration, tubes were re-

moved from the bath at various time intervals (up to ca. 270 min), immersed in an ice bath, and titrated iodimetrically for hydroperoxide content.<sup>11</sup> Conversions were carried out up to ca. 40%.

### Results and Discussion

Recently, MacCallum and Schoff<sup>12</sup> reported on a relatively simple equation for estimating  $n$ , viz.,

$$t/p = 1/k + nt/2 \quad (4)$$

where  $t$  is the time at which the reaction reaches a fractional conversion  $p$  and  $k$  is a rate constant. Although eq. (4) involves several approximations, it was shown to be reliable for values of  $p$  as high as 0.4 and for values of  $n = 0$  to 3. In Figure 1 is depicted a typical plot of  $t/p$  versus  $t$  for the decomposition of APPH at 115°C. It should be mentioned that at such

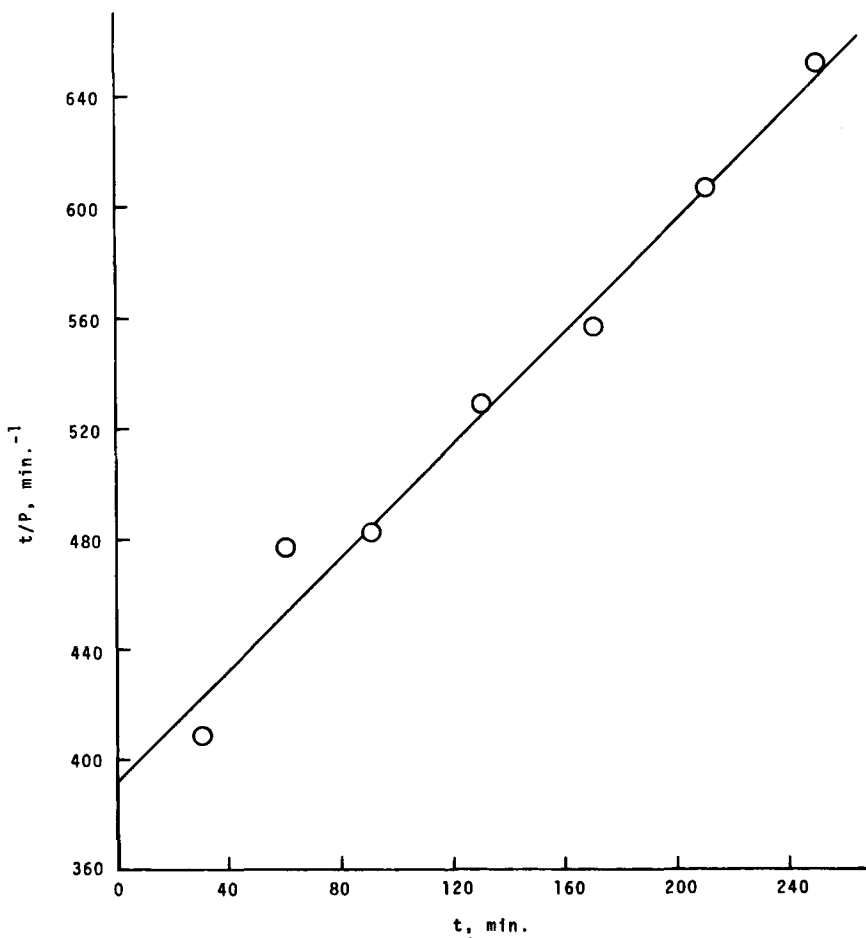


Fig. 1. Plot of  $t/p$  vs.  $t$  during APPH decomposition at 115°C in the molten phase.

temperatures, the APPH was in a free-flowing molten state. Using least-squares treatment, the following values of  $k \times 10^3$  ( $\text{min}^{-1}$ ) were obtained at 115°, 120°, and 125°C, respectively: 2.5, 3.8, and 6.0. From an Arrhenius plot,  $E = 27$  kcal/mole<sup>1</sup>. The average value of  $n$  is  $2.2 \pm 0.2$ . In this connection, it may be remarked that Van Sickle's data were plotted according to eq. (4) for the decomposition of APPH in *tert*-butylbenzene<sup>10</sup> to afford the following values at 125°C:  $n = 2.2$  and  $k = 2.4 \times 10^{-3}$   $\text{min}^{-1}$ . These values are in fair agreement with those reported in this paper. Further, values of  $E$  for the bimolecular decomposition of hydrocarbon hydroperoxides are of the order of 25–30 kcal/mole<sup>1,11</sup>.

From the preceding, it would appear that the decomposition of APPH in the molten phase in an inert atmosphere involves a second-order reaction, cf. eq. (1). A bimolecular reaction would be anticipated based upon enhanced hydrogen bonding due to mobility in the liquid phase. However, some factors which should also be considered in the APPH decomposition are: the effect of carbonyl and other functional moieties<sup>1,2</sup> (see experimental section); and the effect of the position of —OOH moieties relative to each other upon the decomposition mechanism. Thus, according to Zolotova and Denisov,<sup>5</sup> the presence of adjacent —OOH groups may tend to favor a bimolecular mechanism, whereas a unimolecular mechanism may predominate when isolated —OOH groups are present. (However, such a consideration may be important mainly for stereoregular polypropylene.)

This work was supported, in part by a grant from the Office of Naval Research to Stevens Institute of Technology.

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Received December 7, 1972