

## Supporting Information

Real Time Analysis of Volatile Organic Compounds from Polypropylene Thermal Oxidation using Chemical Ionization FTICR Mass Spectrometry.

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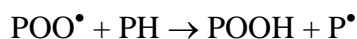
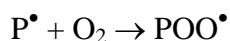
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ABSTRACT. The material therein is a discussion of possible mechanisms responsible for the formation of the major Volatile Organic Compounds emitted during polypropylene thermal oxidation, whose analysis is described in the primary article.

### Tentative mechanisms for VOC formation

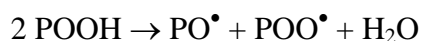
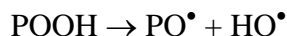
As reported in the primary article, four major VOCs, analyzed in real time by PTR-FTICR, are emitted from polypropylene thermal oxidation: acetone, formaldehyde, acetaldehyde and methylacrolein. Mechanisms accounting for their formation are proposed below.

The generally admitted mechanism of PP thermal oxidation<sup>1, 2</sup> is radical chain reaction. The propagation is composed of two elementary steps, P designating a polymer chain:

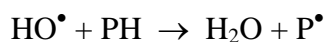


Hydrogen abstraction by  $PO_2^{\bullet}$  occurs preferentially on tertiary CH groups, yielding the most stable tertiary radicals.

The most probable initiation is hydroperoxide decomposition with cleavage of the relatively weak O-O bond, occurring according to either monomolecular or bimolecular mode:

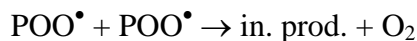
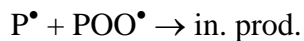
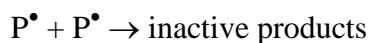


The resulting radical intermediates  $HO^{\bullet}$  and  $PO^{\bullet}$  react very rapidly. The hydroxyl radical  $HO^{\bullet}$  react by H abstraction on the polymer:

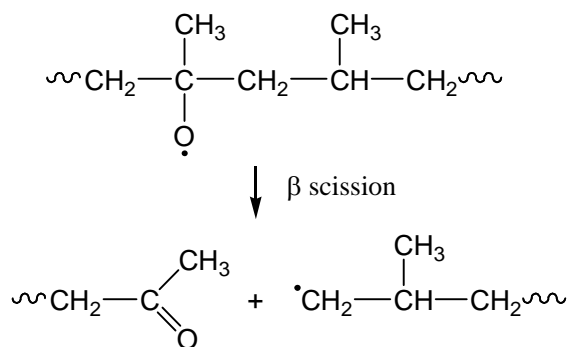


The alkoxy radical  $PO^{\bullet}$  may react either by H abstraction similarly as above giving an alcohol POH or by  $\beta$ -scission leading to a carbonyl group as explained further, which is the major pathway.

Termination of the chain consists in coupling or disproportionation reactions between the different radical intermediates:

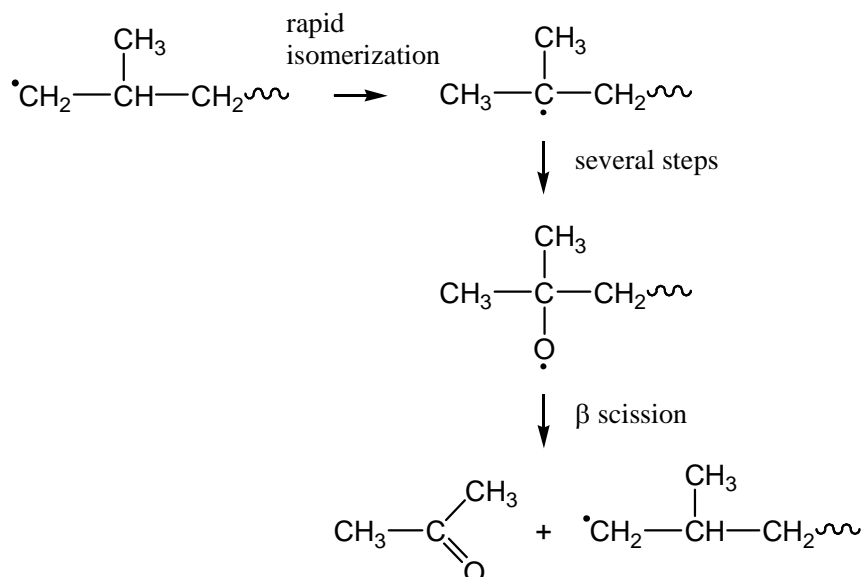


The  $\beta$ -scission of  $PO^{\bullet}$  is schematized on Scheme S-1, starting from the alkoxy radical resulting from a tertiary  $P^{\bullet}$ . This reaction results in scission of the polymeric chain and formation of carbonyl groups, observed by IR spectroscopy (at about  $1710\text{-}1720\text{ cm}^{-1}$ ), and a primary radical (radical A).



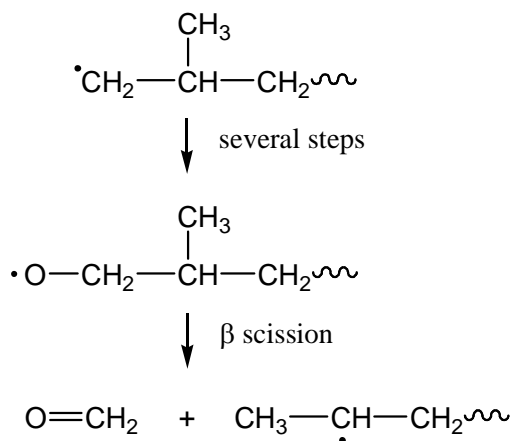
Scheme S-1:  $\beta$ -scission of a tertiary alkoxy radical.

It is generally assumed that this primary radical isomerizes rapidly to give a new tertiary radical,<sup>3</sup> which leads, after several steps ( $O_2$  addition, H abstraction on a tertiary carbon and hydroperoxide decomposition), to acetone formation (see Scheme S-2).



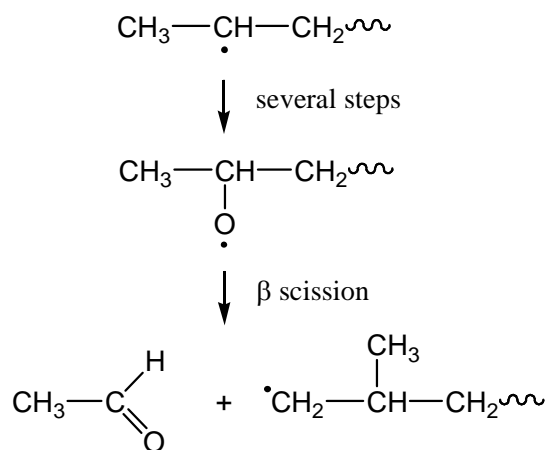
Scheme S-2: Acetone formation by  $\beta$ -scission of a tertiary alkoxy radical.

But, it cannot be excluded that the starting very reactive primary radical adds to oxygen and thus leads, after several steps (H abstraction on a tertiary carbon and hydroperoxide decomposition), to formaldehyde formation (Scheme S-3).



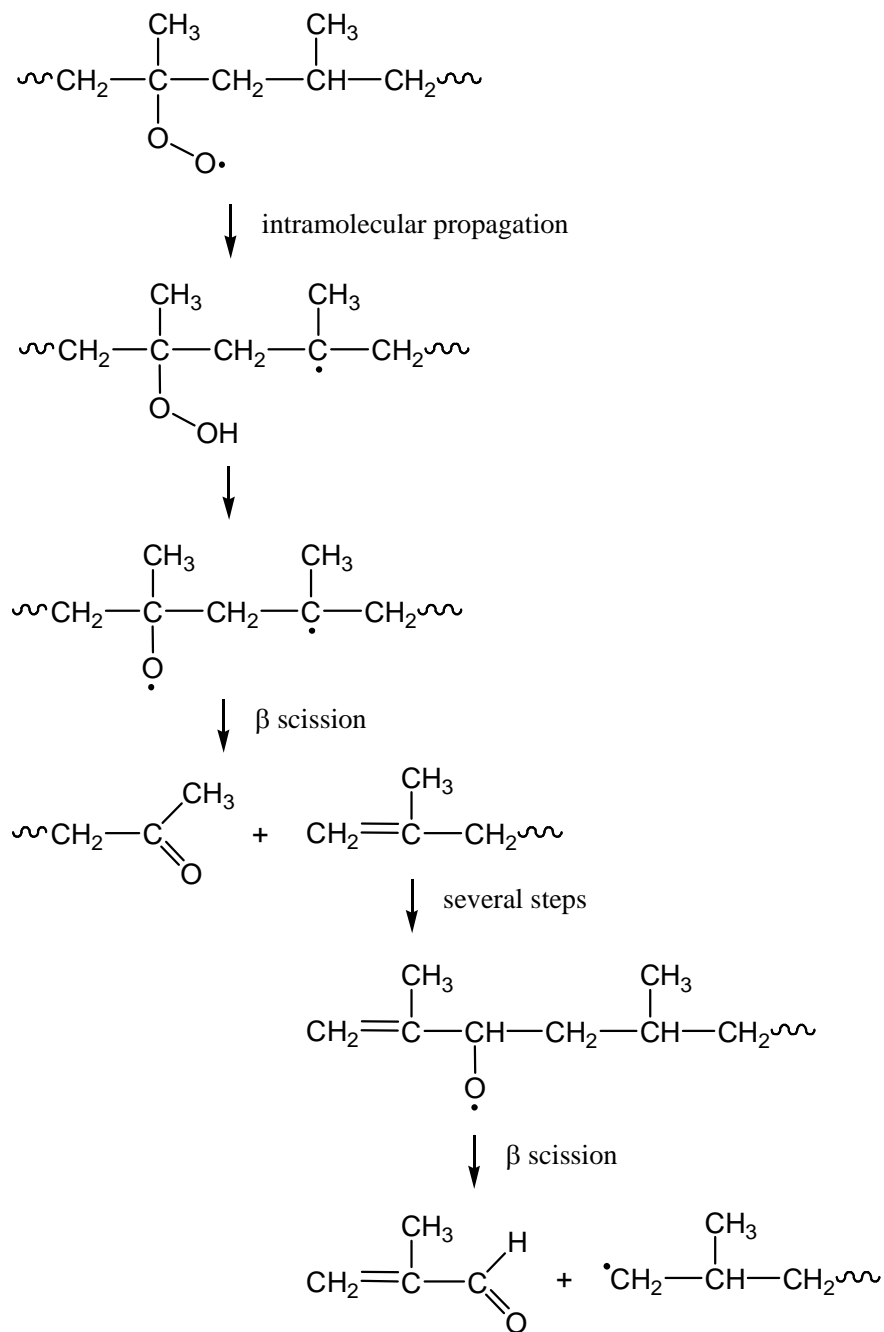
Scheme S-3: Formaldehyde formation by  $\beta$ -scission of a primary alkoxy radical.

The resulting secondary radical can, in turn, add to oxygen and leads, after several steps (H abstraction on a tertiary carbon and hydroperoxide decomposition), to acetaldehyde formation (Scheme S-4).



Scheme S-4: Acetaldehyde formation by  $\beta$ -scission of a secondary alkoxy radical.

Schemes S-2, S-3, S-4 and S-5 allow to explain the formation of three major VOCs detected by the PTR-FTICR-MS apparatus developed by Alyxan: acetone, formaldehyde and acetaldehyde. The remaining VOC is thus methylacrolein. At this stage, it appears impossible to explain the formation of this last compound with a classical radical chain reaction of which propagation is exclusively intermolecular (i.e. involving two distinct polymer chains). Nevertheless, several prestigious authors have proposed a radical chain reaction of which propagation is mainly intramolecular for PP thermal oxidation (i.e. involving a single polymer chains), but without succeeding in proving the validity of this assumption<sup>4, 5</sup>. A combination between both mechanisms has been explored in the present study, which has led us to propose scheme S-5.



Scheme S-5: Methylacrolein formation by  $\beta$ -scission of an allylic alkoxy radical.

This latter scheme leads well to methylacrolein formation. It is a quite realistic scheme because two conditions, necessary to its validity, are well fulfilled:

i) The first  $\beta$ -scission can occur only when oxygen is not in excess in PP. It is well established that oxygen excess is obtained in PP for very high oxygen partial pressure, of the order of 1 MPa.<sup>6, 7</sup> Let's recall that the experiments were conducted in atmospheric air in the present study.

ii) The second  $\beta$ -scission can occur only if allylic alkoxyl radical is formed. Recent studies made on unsaturated elastomers<sup>8, 9</sup> have clearly shown that allylic CH groups are noticeably more sensitive to oxidation than tertiary CH groups.

Thus, thermal oxidation of PP appears as a complex radical chain reaction involving tertiary, secondary and primary alkyl radicals, and in which two propagations compete: intermolecular (i.e. involving two distinct polymer chains) and intramolecular (i.e. involving a single polymer chains) modes. However, the fact that methylacrolein is the minor VOC detected by the PTR-FTICR-MS apparatus, during all the experiment duration, suggests that, even at 256°C, propagation is essentially intermolecular.

The sharp acceleration of VOC emissions observed at stage (iv) of the emission time profile is more difficult to explain. It can be imagined that when a large amount of the initially present tertiary CH groups have been oxidized, the rapid isomerization of primary radical into a new tertiary radical could be less frequent and thus, the formation of primary alkoxy radicals could be privileged. A kinetic analysis of a realistic kinetic scheme of PP thermal oxidation would allow to check this assumption.

## REFERENCES

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## SCHEME CAPTIONS

**Scheme S-1.**  $\beta$ -scission of a tertiary alkoxy radical.

**Scheme S-2.**  $\beta$ -scission of a tertiary alkoxy radical.

**Scheme S-3.** Formaldehyde formation by  $\beta$ -scission of a primary alkoxy radical.

**Scheme S-4.** Acetaldehyde formation by  $\beta$ -scission of a secondary alkoxy radical.

**Scheme S-5.** Methylacrolein formation by  $\beta$ -scission of an allylic alkoxy radical.