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Organophosphorus Antioxidants: Part X—Mechanism of Antioxidant Action of Aryl Phosphites and Phosphonites at Higher Temperatures

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ABSTRACT

By means of kinetic and product studies using ^{31}*P-NMR-spectroscopy and HPLC it is shown that in the autoxidation of hydrocarbons (tetralin and a normal paraffin blend) inhibited by aryl phosphites and phosphonites at 150–180°C, the phosphorus acid esters are hydrolysed to give phenols and hydrogen phosphites and phosphonites respectively. Under certain conditions, these hydrogen esters hydrolyse further to form phosphorous and phosphonic acid respectively. The mixture of antioxidants thus generated is responsible for the high stabilizing efficiency of phosphite and phosphonite esters in autoxidations at these temperatures.*

In addition to hydrolysis, oxidation of the phosphorus compounds by hydroperoxides and peroxyl radicals takes place in the course of the reaction giving the corresponding phosphates and phosphonates. The ratio of oxidation to hydrolysis depends on the oxidizability of the particular hydrocarbon and on the reaction conditions (temperature). In the inhibited oxidation of the highly oxidizable aralkyl hydrocarbons (tetralin), oxidation of the phosphorus compounds is faster than hydrolysis, whereas in the less oxidizable paraffin hydrocarbons at 150°C, hydrolysis exceeds oxidation. In the paraffin oxidation at 180°C, the two processes take place in a 1:1 ratio.

In the inhibited oxidation of a polyether (polyethylene–propylene oxide) at 100–150°C only oxidation and no hydrolysis of the phosphorus inhibitors occurs. Obviously, this is due to the reduced reactivity of water complexed by the polyether in this case.

INTRODUCTION

Organic phosphites and phosphonites are used on a large scale in the stabilization of polymers against oxidative degradation during processing and long-term application. Aryl phosphites function as antioxidants by decomposing hydroperoxides to give phosphates and alcohols

$$\mathrm{ROOH} + \mathrm{P(OAr)_3} \longrightarrow \mathrm{ROH} + \mathrm{O{=}P(OAr)_3} \qquad (1)$$

and by trapping peroxyl radicals to form phosphates and alkyl aryl phosphites releasing sterically hindered phenoxyl radicals

$$\mathrm{ROO\cdot} + \mathrm{P(OAr)_3} \longrightarrow \mathrm{RO\cdot} + \mathrm{O{=}P(OAr)_3} \qquad (2)$$

$$\mathrm{RO\cdot} + \mathrm{P(OAr)_3} \longrightarrow \mathrm{RO{-}P(OAr)_2} + \mathrm{\cdot OAr} \qquad (3)$$

which terminate the oxidation chain reaction.[1,2] At lower temperatures (< 100°C) the chain-breaking antioxidant activity of aryl phosphites and phosphonites is less than that of hindered phenols, because their rate constants with peroxyl radicals and their stoichiometric factors of inhibition are lower than those of phenols.[3] At these temperatures, therefore, aryl phosphites and phosphonites are antioxidatively active only at rather high concentrations predominantly in substrates of low oxidizability.

In the oxidation of polymers at higher temperatures (150–200°C), however, sterically hindered aryl phosphites and phosphonites exhibit a rather high antioxidative activity resembling or even surpassing that of the underlying hindered phenols.[4]

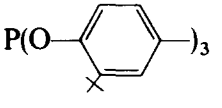
Occasionally it has been suggested, but was not generally accepted, that phenols formed by hydrolysis of the parent phosphites are the species responsible for the antioxidant activity of phosphites in higher-temperature oxidation,[5-8] and in some cases, the formation of phenols and phosphorous acid (H_3PO_3) has been shown to take place in phosphite-inhibited thermo-oxidations.[6-8] Other authors have considered the hydrolysis of phosphates formed from the parent phosphites to be the source of phenols.[9]

Water is always present in autoxidations at somewhat higher temperatures, especially in those inhibited by phosphorus compounds, resulting from dehydration of alcohols formed in reaction (1) and from thermal decomposition of hydroperoxides. It is well known, too, that alkyl and non-hindered aryl phosphites and phosphonites easily hydrolyse at ambient temperatures. Hydrolysis of hindered aryl phosphites is more restrained, and does not occur under the conditions of autoxidation at low temperatures. At higher temperatures, however, it may become relevant.

To settle the question, whether and to what extend hydrolysis takes place in autoxidations of polymers inhibited by aryl esters of phosphorous acids, we

$P(OPh)_3$

I



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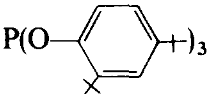
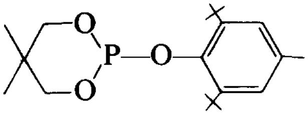
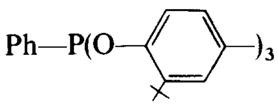


III



IV



V

have studied the fate of various aryl phosphites and phosphonites **I** to **V** in the course of the inhibited oxidation of some hydrocarbons (tetralin and a blend of normal paraffins $C_{14}H_{30}$–$C_{18}H_{38}$, which is a good model for molten polyethylene) and of a polyether (polyethylene–propylene oxide) by means of ^{31}P-NMR spectroscopy and high performance liquid chromatography (HPLC).

EXPERIMENTAL

Phosphites and phosphonites

The phosphorus compounds used were prepared and purified as previously described.[10]

Hydrocarbons and polyether

Tetralin and the $C_{14}H_{30}$–$C_{18}H_{38}$ paraffin blend Parex II (from VEB Petrolchemisches Kombinat Schwedt, GDR) were stirred with conc. sodium hydroxide solution, washed with $NaHSO_3$ solution and shaken repeatedly with conc. sulphuric acid until the acid only became weakly coloured. The hydrocarbon was neutralized with a conc. solution of $NaHCO_3$, washed with water, predried with $CaCl_2$, stored over sodium in a refrigerator and rectified over sodium before use (Tetralin, b.p. 205·5°C; Parex II, b.p. 70–95°C/1 mmHg).

The polyether SYSTOL T 154 from VEB Synthesewerk Schwarzheide, GDR, was a copolymer of ethylene and propylene oxide 1:3 of mean molecular weight 3000.

Kinetic measurements

The reaction solutions were placed in a 100-ml three-necked flask equipped with an efficient reflux condenser, gas inlet tube and thermometer, and immersed in an electrically heated silicone oil or metal bath. A light stream of pure dried oxygen was passed through. All oxidations were performed without using a special initiator. During the course of reactions, samples were taken and analysed.

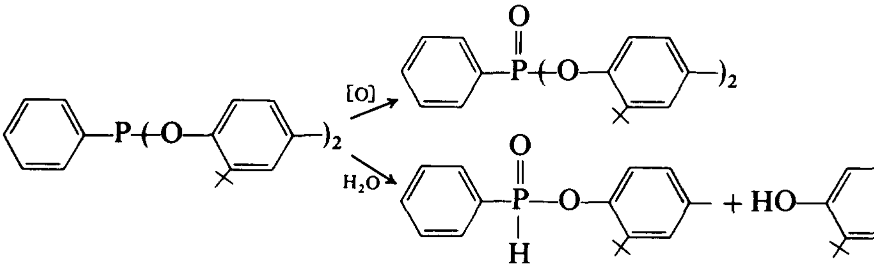
The phosphorus-containing species were characterized by their ^{31}P-NMR spectra measured with a FT-NMR spectrometer Bruker WH 90 at 36·44 MHz (standard, 85% H_3PO_4).

The phenols were detected by HPLC using the high performance liquid chromatographs Hewlett-Packard HP 1084 A with a LiChrosorb RP-18 10 μm (250 mm × 4·6 mm) column and HP 1090 M with a Hypersil ODS 5 μm (100 mm × 2·1 mm) column, water/methanol as eluent (gradient program) and benzonitrile as internal standard. In the case of Parex II oxidations, the samples were extracted 4 times with methanol and the extracts were used for HPLC analysis.

RESULTS

Phosphites and phosphonites in the inhibited oxidation of hydrocarbons

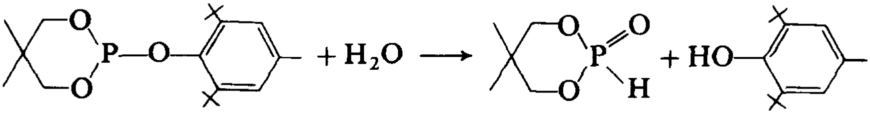
In the course of the oxidation of hydrocarbons (tetralin, Parex II) at 150–189°C inhibited by the aryl phosphites **I**–**III** and phosphonite **V**, the phosphorus species were oxidized to form the corresponding phosphates and phosphonates respectively as well as being hydrolysed to give hydrogen phosphites **VI** and phosphonites respectively, and phenols, for example:



(4)

(5)

In the hydrolysis of the mixed alkylene aryl phosphite IV, the exocyclic aryloxy group is split off:



IV **V**

(6)

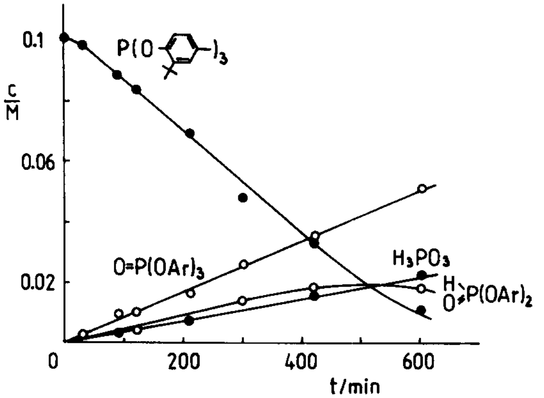
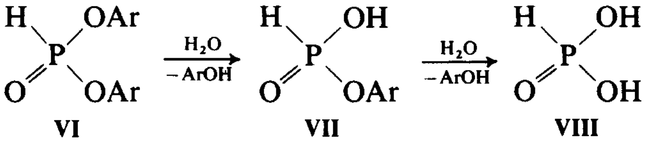


Fig. 1. Formation of phosphorus compounds during the oxidation of tetralin inhibited by tris(2-*tert.*-butyl-4-methyl-phenyl)phosphite (**II**) at 150°C.

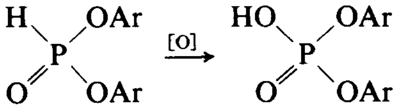
In the later stages of reaction the initially formed monohydrogen phosphites and phosphonites are further hydrolyzed to phosphorous acid (**VIII**) and phosphonic acid ($PhPO_2H_2$) respectively.



(7)

The intermediate dihydrogen phosphites (**VII**) are very unstable and have never been observed (Fig. 1).

In the inhibited oxidation of the normal paraffin hydrocarbon Parex II, the hydrogen phosphites are further oxidized to give hydrogen phosphates (Fig. 2):



(8)

The rates of phosphite (phosphonite) consumption and phosphate (phosphonate) and hydrogen phosphite (hydrogen phosphonite) formation depend on the oxidizability of the hydrocarbon. At the same temperature they are larger in tetralin than in Parex II (Tables 1 and 2). The non-hindered triphenyl phosphite **I** always reacts faster than the sterically hindered esters **II** to **V**, whereas the reactivities of the various hindered phosphorus compounds **II** to **V** are almost identical (Tables 1 and 2). The consumption of the hindered phosphorus compounds and the formation of reaction products occur with constant rates, obeying zero-order kinetics (see Figs 1 and 2). The hydrocarbon oxidation is obviously completely inhibited by

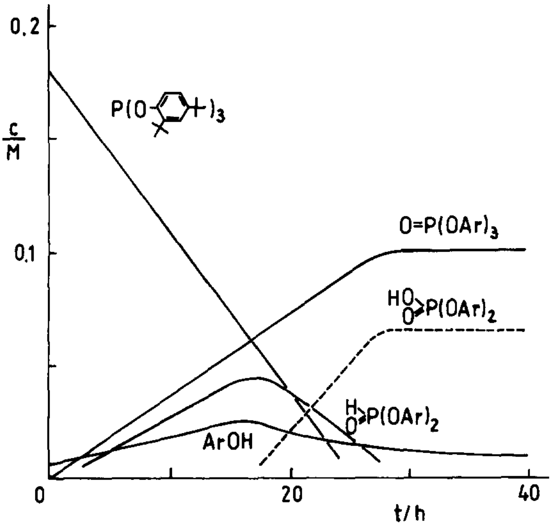


Fig. 2. Formation of 2,4-di-*tert*.-butyl-phenol and phosphorus compounds during the oxidation of the normal paraffin blend Parex II inhibited by tris(2,4-di-*tert*.-butyl-phenyl) phosphite at 180°C.

these antioxidants under the reaction conditions, so that the consumption rates of the P-compounds equal the spontaneous initiation rate of oxidation which is independent of the nature of the inhibitor.

The ratio of formation of phosphate to hydrogen phosphite in the inhibited hydrocarbon oxidation also depends on the oxidizability of the particular hydrocarbon and on the reaction conditions (temperature). In the inhibited oxidation of the highly oxidizable aralkyl hydrocarbons (tetralin), oxidation of the phosphorus compounds is faster than hydrolysis (Table 1), whereas in the less oxidizable paraffin hydrocarbons at 150°C, hydrolysis exceeds oxidation (Table 2). In the paraffin oxidation at 180°C, the two processes take place in a 1:1 ratio (Table 2). The mixed alkylene aryl

TABLE 1

Initial Rates (mol litre^{-1} s^{-1}) of Phosphite (Phosphonite) Consumption (r) and Phosphate (Phosphonate) and Hydrogen Phosphite (Phosphonite) Formation (r_{ox} and r_{hy}) in the Thermo-oxidation of Tetralin Inhibited by Phosphorus Compounds (0·1 mol litre^{-1}) at 150°C

Inhibitor	$10^6 \times r$	$10^6 \times r_{ox}$	$10^6 \times r_{hy}$	r_{ox}/r_{hy}
I	160 ± 20	100 ± 40	70 ± 20	2
II	2·8 ± 2·0	2·4 ± 1·6	0·6 ± 0·6	3
IV	7·2 ± 1·4	4·6 ± 0·4	2	2
V	38 ± 10	34	2	17

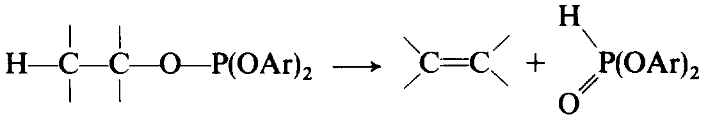
TABLE 2

Rates (mol litre^{-1} s^{-1}) of Phosphite (Phosphonite) Consumption (r) and Phosphates (Phosphonite) and Hydrogen Phosphites (Phosphonite) Formation (r_{ox} and r_{hy}) in the Thermo-oxidation of Paraffin Hydrocarbon Parex II Inhibited by Phosphorus Compounds (0·2 mol litre^{-1})

Inhibitor	*At 150°C*			*At 180°C*		
	$10^6 \times r$	$10^6 \times r_{ox}$	$10^6 \times r_{hy}$	$10^6 \times r$	$10^6 \times r_{ox}$	$10^6 \times r_{hy}$
I	4·2	3·2	3·3	16	12	–
II	0·75	0·13	0·63	4·1	2·1	2·0
III	0·25	0·06	0·20	2·0	1·0	0·8
IV	0·14	0·14	—	1·9	1·8	—
V	0·92	0·56	0·50	2·8	1·9	2

phosphite **IV** is an exception giving only the corresponding phosphate and no hydrolysis products in the oxidation of Parex II.

The phenols generated by hydrolysis of the parent phosphorus compounds act as inhibitors of the hydrocarbon oxidation and are therefore consumed in the further course of the reaction (Fig. 2). In the inhibited oxidation of tetralin at 150°C, they are initially formed in an equimolar ratio with the hydrogen phosphites and phosphonites. In the Parex II oxidations, however, the amount of phenols is less than that of the hydrogen esters (see Fig. 2). Obviously, there is, in addition to hydrolysis of the parent compounds, a minor second route to hydrogen phosphites and phosphonites, in which no phenols are generated. This might be the elimination of olefins from alkyl aryl esters formed in reaction (3):



$$H{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}O{-}P(OAr)_2 \longrightarrow {>}C{=}C{<} + \underset{\displaystyle O}{\overset{\displaystyle H}{P}}(OAr)_2 \qquad (9)$$

It is well known that alkyl phosphites, especially tertiary and secondary ones, readily decompose to give olefins and hydrogen phosphites at higher temperatures.[7,11]

Phosphites in the inhibited oxidation of polyether

In the inhibited oxidation of the polyether SYSTOL T 154 at 100–150°C, the fate of the triaryl phosphites studied is entirely different from that in the hydrocarbon media. They are completely oxidized to the corresponding phosphates, and no hydrogen phosphites are formed. This difference is possibly due to the reduced reactivity of water which is completely

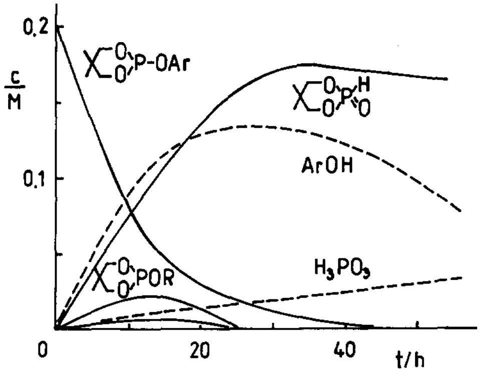
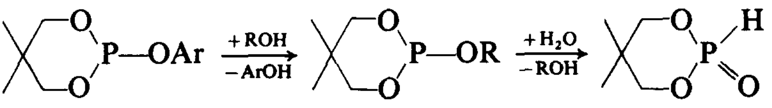


Fig. 3. Formation of 2,6-di-*tert*.-butyl-4-methyl-phenol and phosphorus compounds during the oxidation of polyether SYSTOL T 154 in *o*-dichlorobenzene (1 : 1) inhibited by 2,2-dimethyl-propylene 2,6-di-*tert*.-butyl-4-methyl-phenyl phosphite at 100°C.

complexed by the polyether via hydrogen bonding. It is known that hydrolysis reactions in non-polar solvents, where water is present in polymeric form, are faster than in more polar media in which water exists as a monomer complexed with the solvent by hydrogen bonds.

The rate of consumption of the phosphites in the inhibited oxidation of polyether T 154 is highest for the non-hindered triphenyl phosphite, whereas the hindered triaryl phosphites react at lower rates (see Table 3).

In the polyether oxidation, too, the alkylene aryl phosphite **IV** behaves differently from the triaryl phosphites. Oxidation to the phosphate does not take place, and the alkylene hydrogen phosphite **X** (eqn (10)) is formed as the main product (Fig. 3). This product, **X**, is obviously not generated by hydrolysis of the starting material **IV**, because the rate of consumption of **IV** is 25 times larger than that of the triaryl phosphites (Table 3). Possibly, **X** arises via an alkylene phosphite **IX** by transesterification with the OH-end groups of the polyether (ROH).



IV **IX** **X** (10)

TABLE 3

Initial Rates (mol litre^{-1} s^{-1}) of Phosphite Consumption (r) in the Thermo-oxidation of Polyether SYSTOL T 154 Inhibited by Phosphorus Compounds (0·2 mol litre^{-1})

Inhibitor	$(n\text{—}C_8H_{17}O)_3P$	I	II	III	IV
$10^6 \times r$ at 100°C	7·3		0·04	0·02	1·6
$10^6 \times r$ at 150°C	82	12	1·2	0·45	19

An alkylene alkyl phosphite can be seen in the ^{31}P-NMR spectrum as an intermediate in the course of reaction (Fig. 3). It should be hydrolyzed to **X** and this further to H_3PO_3 very much easier than the starting aryl ester **IV**.

CONCLUSIONS

In the oxidation of hydrocarbons inhibited by aryl phosphites and phosphonites at higher temperatures ($\gtrsim$100°C), hydrolysis of the phosphorus acid esters takes place giving rise to phenols and hydrogen phosphites and phosphonites, which may further hydrolyse to form additional phenols and phosphorous and phosphonic acid. The synergistic mixture of phenolic and phosphorus antioxidants so generated is obviously the reason why sterically hindered aryl phosphites exhibit high antioxidative activity at elevated temperatures. Diaryl hydrogen phosphites are known to be antioxidatively active by themselves and, like H_3PO_3, give synergistic mixtures with hindered phenols in higher-temperature oxidations.[7,8,12]

In the inhibited oxidation of polyether at $\geq$100°C, only the mixed alkylene aryl phosphite **IV** is transformed into the hindered phenol and hydrogen phosphite **X**, whereas the triaryl phosphites studied are completely oxidized to phosphates in the course of reaction.

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