Thermochemical destruction of esters of 2-chloro-2-(1-cyclohexenyl) ethylenylphosphonic acid and their inhibitory properties

N. Shopova [*,a], Chr. Angelov [b]

[a] *Institute of Organic Chemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev str., bl. 9, 1113 Sofia, Bulgaria*
[b] *Higher Pedagogical Institute, Department of Chemistry, 9700 Shumen, Bulgaria*

Abstract

The thermal decomposition of four dialkyl esters of 2-chloro-2-(1-cyclohexenyl) ethylenylphosphonic acid has been investigated from room temperature to 600°C. This thermochemical decomposition proceeds as a three-step process. Independently of the thermal changes, the investigated esters inhibit the auto-oxidation process of cumene at 110°C. We followed the formation of the complexes of dibutyl ester and cumyl hydroperoxide, as a result of proton-donor interactions. These complexes affect cumyl hydroperoxide decomposition. It was established that the investigated esters catalysed the decomposition of cumyl hydroperoxide.

Keywords: Auto-oxidation; Catalyst; Cumene; Esters of 2-chloro-2-(1-cyclohexenyl) ethylenylphosphonic acid; Inhibitor

1. Introduction

Studies on the thermochemical decomposition of phosphonic acid esters and their inhibitory properties have been carried out with respect to their application as stabilizers of polymers and antipyrenes [1–5]. The antioxidative stabilizing properties of diethyl esters of phosphonic acid towards some polymeric materials have been proved by means of DTA under both isothermal and nonisothermal conditions [6].

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Phosphorus-containing compounds favour heterolytic reactions, because of the high polarity of their molecules, as has been established in numerous studies [7]. The radical mechanism dominates during reactions of the trivalent phosphor with electron-symmetrical molecules such as O_2 and ROOR. Depending upon the electron asymmetry of the molecule, similar reactions proceed via either ionic or radical mechanisms [8,9].

Kinetic and physicochemical investigations have shown that organo-phosphorus compounds can suppress chain branching during oxidation reactions. These compounds react with the peroxy radicals and thus terminate the radical chains [10].

The final product of oxidation reactions involving trivalent phosphorus-containing compounds is a compound containing a phosphoryl group [8,11].

The antioxidative activity of phosphoro-organic compounds, comprising phosphoryl groups, depends on the structure of the substitutes and on the participation of P=O in the radical reactions.

In a previous study [12] we established that dialkyl esters of 2-chloro-2-(1-cyclohexenyl) ethylenylphosphonic acid are relatively inactive inhibitors of the initiated cumene oxidation (at 60°C). Kinetic investigations have shown that the diethyl ester has better inhibitory properties on cumene auto-oxidation at 110°C than it does at 60°C.

In investigating the properties of dialkyl esters of 2-chloro-2-(1-cyclohexenyl) ethylenylphosphonic acid we studied the thermal decomposition changes occurring therein, by means of DTA and TGA from room temperature up to 600°C. Their inhibitory properties upon the thermally initiated oxidation of cumene at 110°C have also been considered. The results obtained are shown in this paper.

2. Experimental

The dialkyl esters of 2-chloro-2-(1-cyclohexenyl) ethylenylphosphonic acid were synthesized from the dichloride of 2-chloro-2-(1-cyclohexenyl) ethylenylphosphonic acid and alcohols according to the method described in Ref. [13]. Their physicochemical parameters are listed in Table 1.

The cumene had been purified in advance [14]; n_d^{20} was 1.4920. The cumyl hydroperoxide (CHP) (Merck) had been purified by the method described in Ref. [15], and its concentration was determined iodometrically to be 98.7% [16]. The auto-oxidation processes of cumene in the presence of dialkyl esters were carried out at 110°C and $P_{O_2} = 0.1$ MPa in a volumetric oxidation set-up, measuring the absorption directly.

The stoichiometric coefficients of inhibition, f, were calculated from the expression [17]

$$f = \frac{W_i \tau_{ind}}{[InH]}$$

where W_i is the rate of initiation, τ_{ind} is the induction period and [InH] is the inhibitor concentration. In this case $W_i = 8.34 \times 10^{-6}$ mol l^{-1} s^{-1}, measured experimentally during cumene oxidation in the presence of ionol as radical acceptor.

Table 1
Physicochemical parameters of esters of 2-chloro-2-(1-cyclohexenyl) ethylenylphosphonic acid

No.	Formula	Boiling point [a] in °C	d_4^{20}	n_d^{20}	Elemental analysis in wt.%				
					C	H	Cl	P	O
1	$(CH_3O)_2P(O)–R$ [b]	103–104	1.2104	1.5053	47.70	6.61	14.00	11.96	19.74
2	$(C_2H_5O)_2P(O)–R$	107–108	1.1461	1.4930	51.41	6.98	12.48	10.79	18.34
3	$(i\text{-}C_3H_7O)_2P(O)–R$	105–106	1.0967	1.4850	55.00	8.02	11.85	10.32	14.81
4	$(n\text{-}C_4H_9O)_2P(O)–R$	139–140	1.0932	1.4846	57.48	8.31	10.62	9.15	14.44

[a] Boiling point $P = 6.58 \times 10^{-5}$ MPa. [b] R is $–CH=C(Cl)C_6H_9$.

The decomposition of cumyl hydroperoxide was carried out in an argon medium in a reactor, equipped with a device allowing periodical sampling. The concentration of cumyl hydroperoxide was determined iodometrically [16].

DTA and TGA were carried out in a Derivatograph model "Q 1500" in a medium of air (static atm.) and argon (dynamic atm., flow rate 17 l h^{-1}), over a temperature interval from room temperature up to 600°C, in a zirconium crucible at heating rate 5°C min^{-1} with Al$_2$O$_3$ standard.

IR analysis was performed on Bruker IFS 113V apparatus using the KBr technique.

The mass spectra were recorded on a JEOL mass spectrometer.

3. Results and discussion

The structural variety of the molecular fragments of the studied esters and their mutual influence determine their high reactivity and the occurring thermochemical changes. The strongly polarized phosphoryl group in the esters, and the presence of the cyclohexenyl ring and conjugated double bonds therein, enable their interaction with hydrocarbon oxidation products as shown in Scheme 1.

$$
\begin{array}{c}
O \\
\parallel \\
RO–P–CH=CCl- \\
/ \\
RO
\end{array}
$$
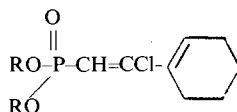
Scheme 1. Reaction (1), R is CH$_3$; (2), R is C$_2$H$_5$; (3), R is C$_2$H$_5$; (4), R is C$_4$H$_9$.

On the basis of data on the thermal decomposition of the studied esters (Figs. 1(a), 1(c) and 1(d)) we found the initial temperature of decomposition to be within the interval 40–60°C. The TG and DTG curves for the dimethyl ester (Fig. 1(a)) registered a three-step weight loss process. During the first step, the phase changes revealed by the endothermic peak at 150°C are accompanied by thermochemical
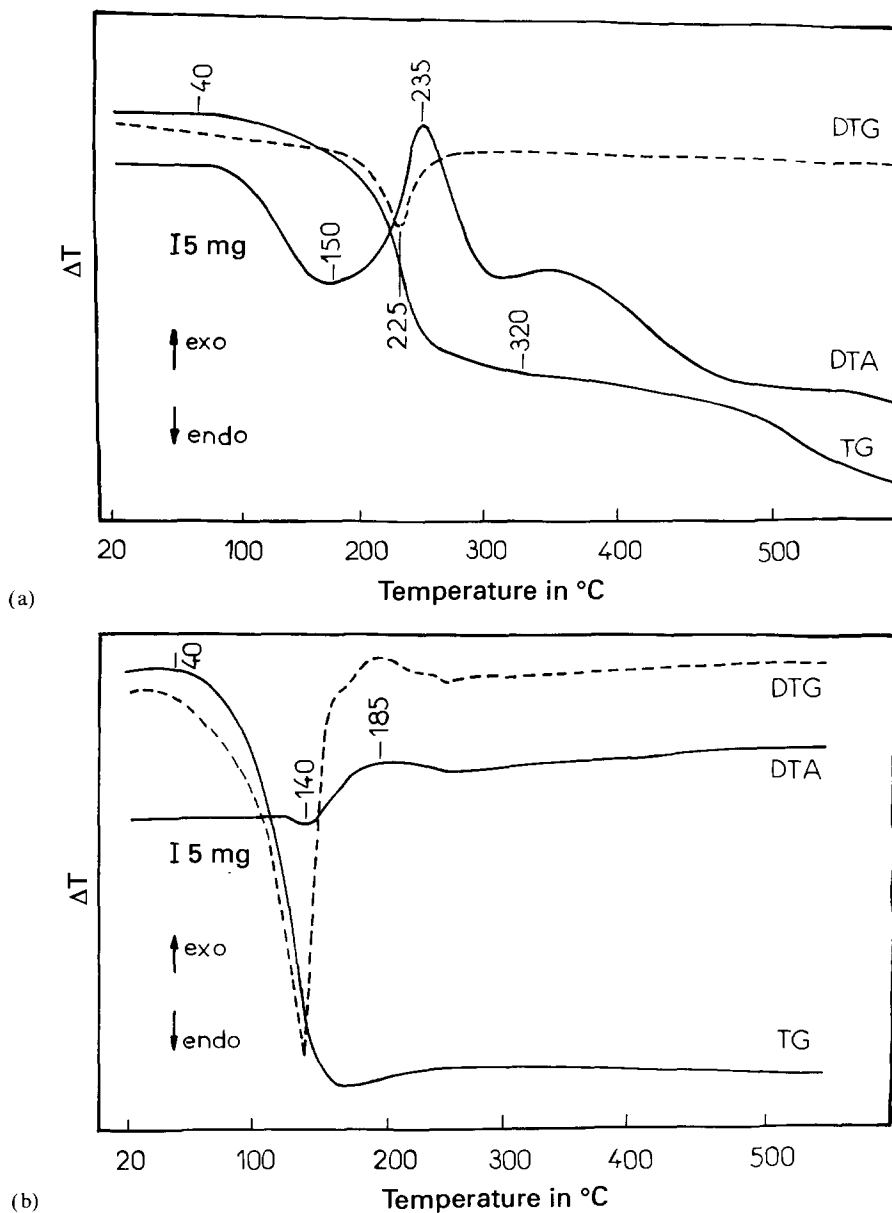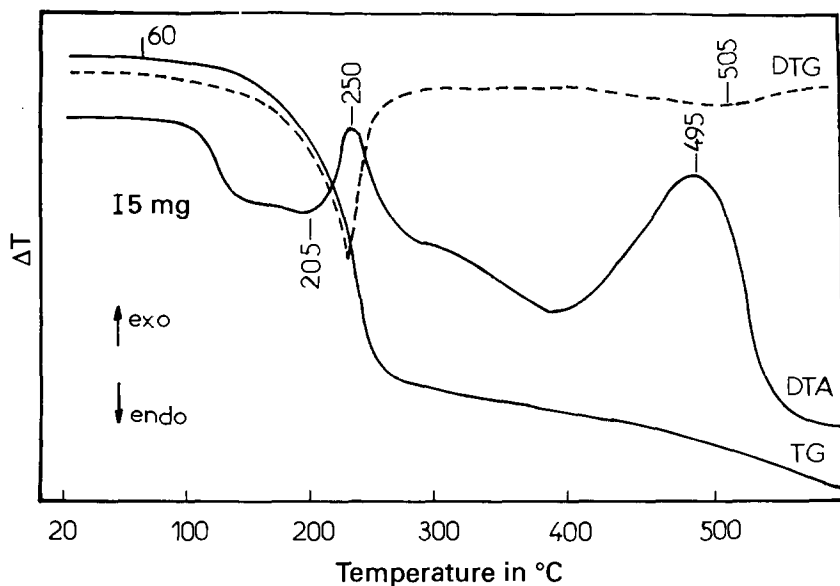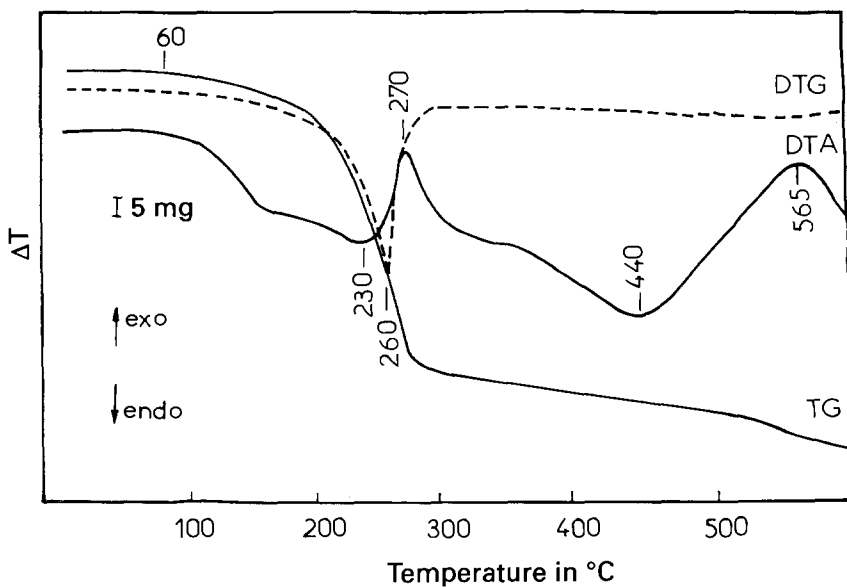
(a)

(b)

Fig. 1 (a,b).

changes. This was confirmed by the weight loss, which was only 37.4% at 225°C, and the temperature of the maximum decomposition rate (DTG_{max}, Fig. 1(a)). The remaining reactant undergoes a thermal oxidative decomposition, which was recorded as an exo-peak at 235°C. The data from the DTA and TG curves in an

(c)

(d)

Fig. 1 (c,d).

Fig. 1. DTA/TGA curves of esters of 2-chloro-2-(1-cyclohexenyl) ethylenylphosphonic acid: (a) $(CH_3O)_2$·$P(O)CH=C(Cl)C_6H_9$; (b) $(CH_3O)_2P(O)H$; $(C_2H_5O)_2P(O)CH=C(Cl)C_6H_9$; (d) $(C_4H_9O)_2P(O)CH=C(Cl)C_6H_9$.

Table 2
Thermal decomposition data of esters of 2-chloro-2-(1-cyclohexenyl) ethylenylphosphonic acid

No.	Formula	Stages, T in °C	W_{max} [b], T in °C	Weight loss in %	Thermochemical effect		Residue in %
					Endo	Exo	
1	$(CH_3O)_2P(O)-R$ [a]	40–300 300–470 470–600	225	37.4	150	235	14
2	$(C_2H_5O)_2P(O)-R$	60–280 280–425 425–560	250	44.7	205, 405	250, 445	15
3	$(n-C_4H_9O)_2P(O)-R$	60–300 300–410 410–550	260	51.6	230, 440	270, 565	14
4	$(CH_3O)_2P(O)-H$	40–165	130	54.2	140	185	–

[a] R is $-CH=C(Cl)C_6H_4$. [b] DTG maximum.

argon atmosphere are evidence of this fact, as the exothermal peak at 230°C was no longer observed, while the weight losses at 220°C (DTG_{max}) are larger than those in an air atmosphere, i.e. 39.1%.

The thermal decomposition of the dimethyl ester proceeds in the vicinity of the temperature of maximum decomposition rate, i.e. 225°C (Fig. 1(a)).

On comparing the data from the DTA and TGA of $(CH_3O)_2P(O)CH=C(Cl)C_6H_9(CH_3O)_2P(O)H$ and $(CH_3O)_2P(O)CH_3$, we observed analogical changes within the temperature range 23–220°C. The thermal decomposition of $(CH_3O)_2P(O)H$ in air proceeds as a one-step process within the temperature interval 40–165°C (Fig. 1(b)). The weight losses up to 165°C are 80% and occur as a result of a rapidly proceeding vaporization process. The exo-peak at 185°C is a consequence of the oxidation of the remaining reactants. Kettrup et al. [1] found, during thermal decomposition investigations, that 90% of the studied ester $(CH_3O)_2P(O)CH_3$ decomposes up to 175°C. The remainder of oxidation products are still in the process of being formed and further decomposition occurs up to 220°C.

It is obvious, from the analysis of these results, that the thermal stability of the dimethyl ester studied here is due to the hydrocarbon chain $-CH=C(Cl)C_6H_9$ attached to the phosphorus atom.

The results from the DTA and TGA analyses of the diethyl and dibutyl esters support an analogical thermal decomposition. The weight losses in air during the first step increase in the order $(CH_3O)_2P(O)R < (C_2H_5O)_2P(O)R < (C_4H_9O)_2P(O)R$ (Table 2).

The positive enthalpy changes during the first step, characterizing the vaporization of the studied esters, shift towards higher temperatures in the above order from $(CH_3O)_2P(O)R$ to $(CH_4H_9O)_2P(O)R$ (Figs. 1(a), 1(c) and 1(d)) as a result of the increasing boiling point (see Table 1).

The remainder of the three studied compounds undergo thermal oxidative destruction, confirmed by the exothermal maxima at 235, 250 and 270°C (Figs. 1(a), 1(c) and 1(d)).
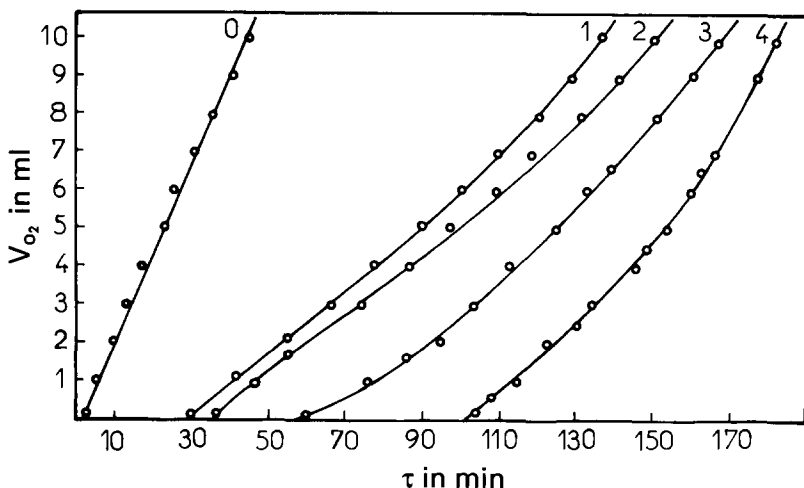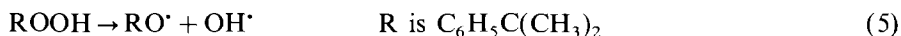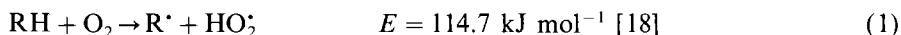
Fig. 2. Kinetic curves of cumene auto-oxidation ($T = 110°C$, $P_{O_2} = 0.1$ MPa), in the presence of (1×10^{-3} mol l^{-1}) esters of 2-chloro-2-(1-cyclohexenyl) ethylenylphosphonic acid: (1) dimethylester; (2) diethyl ester; (3) diisopropyl ester; (4) dibutyl ester.

The processes of thermochemical decomposition above 300°C proceed with a pronounced exo-peak (Figs. 1(a), 1(c) and 1(d)) and weight losses, which are probably the result of the liberation of gaseous products.

The studied esters possess a comparatively low initial temperature of decomposition, $T_i = 40–60°C$. The differences observed in the thermochemical decomposition around the temperature of maximum decomposition rate are probably due to changes in the ester and phosphoryl groups.

The thermochemical stability of the substances depends on the medium in which they are investigated and the reactivity of the substances themselves.

Independently of their thermal changes at 110°C (2–3% weight losses), the studied esters display inhibiting properties with respect to the oxidation of cumene at 110°C (Fig. 2). The products formed during the thermally initiated oxidation of cumene are represented in the following reaction scheme [18]:

$$RH + O_2 \rightarrow R^{\cdot} + HO_2^{\cdot} \qquad E = 114.7 \text{ kJ mol}^{-1} \text{ [18]} \tag{1}$$

$$2RH + O_2 \rightarrow R^{\cdot} + RO^{\cdot} + H_2O \tag{2}$$

$$R^{\cdot} + O_2 \rightarrow RO_2^{\cdot} \tag{3}$$

$$RO_2^{\cdot} + RH \rightarrow ROOH + R^{\cdot} \tag{4}$$

$$ROOH \rightarrow RO^{\cdot} + OH^{\cdot} \qquad R \text{ is } C_6H_5C(CH_3)_2 \tag{5}$$

The inhibitory effect of the studied esters could be due to interaction with cumyl radicals, or to the catalytic effect of cumyl peroxide radicals on the decomposition of the cumyl hydroperoxide. The formation of inactive products is the result of these reactions.

Table 3
Kinetic parameters of the auto-oxidation of cumene in the presence of esters of 2-chloro-2-(1-cyclohex-enyl) ethylenylphosphonic acid ($T = 110°C$, $P = 0.1$ MPa)

No.	Formula	τ_{ind} in min	$W_{max} \times 10^{-5}$ in mol l^{-1} s^{-1}	f
1	$(CH_3O)_2P(O)-R$ [a]	36	1.5	18
2	$(C_2H_5O)_2P(O)-R$	39.5	1.5	20
3	$(i-C_3H_7O)_2P(O)-R$	75	2.2	40
4	$(n-C_4H_9O)_2P(O)-R$	125	2.7	62.5
5	Cumene	–	3.5	

[a] R is $-CH=C(Cl)C_6H_9$.

The higher values of the stoichiometric coefficients of inhibition (f) (Table 3) confirmed the good inhibitory properties of the studied esters and the complex mechanisms in action.

The auto-oxidative character of the kinetic curves (Fig. 2) and the long induction periods (Table 3) are the result of interactions between the studied esters and the peroxide radicals, or hydroperoxide generated in the system.

We can conclude from the values of the kinetic parameters (Table 3) that an increase in the length of the hydrocarbon chain of the esters group causes the duration of the induction period to increase too. The best inhibitory properties are displayed by $(C_4H_9O)_2P(O)CH=C(Cl)C_6H_9$.

In a previous study [12] we established interactions between diethyl ester and the cyanopropyl radicals in an oxidizing system of cumene–azobisisobutyronitrile–$(C_2H_5O)_2P(O)R$ at 60°C, which retards the initiation of an oxidation reaction.

The stationary concentration of the cumyl radicals at 110°C is quite low as reaction (3) (Scheme 1) proceeds quickly, requiring practically no activation energy ($k = 10^7-10^8$ l mol^{-1} s^{-1}). Moreover, the cumyl radicals recombine easily [18]. For this reason we could not be certain that the inhibitory effect of the studied esters is due to the interaction with the cumyl radicals. Cumyl hydroperoxide is the primary thermochemically stable product generated in the studied system.

The thermally initiated decomposition of cumyl hydroperoxide into cumene can be described by the reactions [20]:

$$ROOH \rightarrow RO^{\bullet} + OH^{\bullet} \qquad E = 121.4 \text{ kJ mol}^{-1} \text{ [21]} \tag{6}$$

$$RO^{\bullet} + RH \rightarrow ROH + R^{\bullet} \tag{7}$$

$$RO^{\bullet} + ROOH \rightarrow ROH + ROO^{\bullet} \tag{8}$$

$$OH^{\bullet} + RH \rightarrow H_2O + R^{\bullet} \tag{9}$$

$$R^{\bullet} + ROOH \rightarrow ROH + RO^{\bullet} \quad R \text{ is } C_6H_5C(CH_3)_2 \tag{10}$$
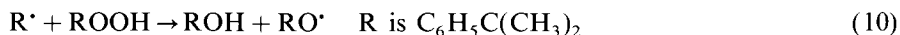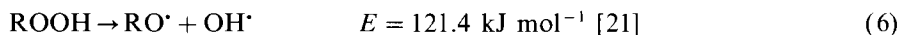
On conducting the decomposition of CHP in a cumene medium at 100°C in the presence of diethyl ester (the ratio $(C_2H_5O)_2P(O)R/CHP$ was mol/mol) we observed a multistep decomposition (Fig. 3(b)). Increasing the CHP concentration in
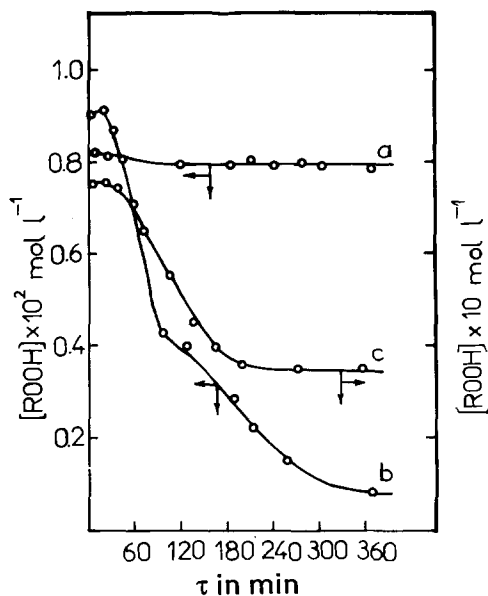
Fig. 3. Decomposition of cumyl hydroperoxide in cumene in the presence of diethyl ester: (a) $C_6H_5C(CH_3)_2OOH$ $(8 \times 10^{-3}$ mol $l^{-1})$ in cumene; (b) $(C_2H_5O)_2P(O)CH=C(Cl)C_6H_9 + C_6H_5C(CH_3)_2OOH$ $(9 \times 10^{-3}/9 \times 10^{-3}$ mol $l^{-1})$ in cumene: (c) $(C_2H_5O)_2P(O)CH=C(Cl)C_6H_9 + C_6H_5C(CH_3)_2OOH$ $(7.8 \times 10^{-3}/7.7 \times 10^{-2}$ mol $l^{-1})$ in cumene.

the system from 1×10^{-2} to 1×10^{-1} mol (CHP) l^{-1} results in 50% decomposition of the CHP (Fig. 3(c)). These data indicate the catalytic effect of the $(C_2H_5O)_2P(O)R$ on cumyl hydroperoxide decomposition. During the first step of decay (Fig. 3(b)) an induction period of 17 min was observed. This effect can be interpreted as follows. The disintegration of the intermolecular associates in the system, formed by hydrogen bonding, requires activation energy during the initial minutes of decomposition. It is known that cumyl hydroperoxide in a cumene medium forms two types of intermolecular associates [22]. The first is an intermolecular associate between the OH group of hydroperoxide and the π-electrons of the cumyl ring (OH$\cdots\pi$). The second is CHP self-association.

The phosphoryl group is strongly polarized because of the p_π–d_π bond, and for this reason is easily associated with CHP. Associates of organo-phosphorus compounds, containing the phosphoryl group, and phenol (1:1 ratio) are cited in the literature [23,24].

We registered the formation of intermolecular associates between the dibutyl ester and CHP using the IR spectrum (Fig. 4). The absorption maximum at 1252 cm^{-1} is assigned to the P=O stretching vibrations (solution in CCl$_4$) (Fig. 4(b)). This maximum is shifted towards lower frequency (1240 cm^{-1}) in the spectrum of the mixture of CHP + dibutyl ester (1:1 ratio in CCl$_4$) (Fig. 4(a)).
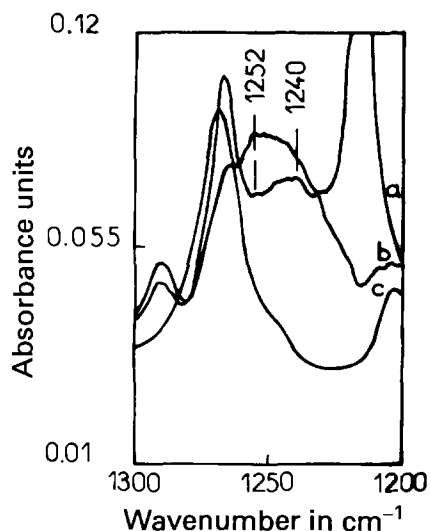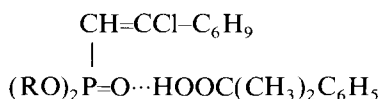
Fig. 4. IR spectra of (a) $(C_4H_9O)_2P(O)CH=C(Cl)C_6H_9$　$(4 \times 10^{-3}$ mol $l^{-1}) + C_6H_5C(CH_3)_2OOH$ $(4 \times 10^{-3}$ mol $l^{-1})$ in CCl_4; (b) $(C_4H_9O)_2P(O)CH=C(Cl)C_6H_9$　$(4 \times 10^{-3}$ mol $l^{-1})$ in CCl_4; (c) $C_6H_5C(CH_3)_2OOH$ $(4 \times 10^{-3}$ mol $l^{-1})$ in CCl_4.

This is characteristic of the effect of an associated phosphoryl group.

$$CH=CCl-C_6H_9$$
$$|$$
$$(RO)_2P=O\cdots HOOC(CH_3)_2C_6H_5$$

The association is proved by the shift of the absorption maximum of the OH group in the CHP from 3452 to 3397 cm^{-1}.

The presence of the intermolecular associates of phosphoric esters and CHP weakens the –O–O– bond in the cumyl hydroperoxide molecule, which facilitates hydroperoxide homolysis.
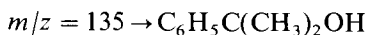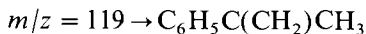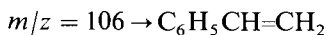
The disintegration of the CHP molecule under the influence of the esters probably proceeds by the formation of an unstable complex with the cumyl peroxy radicals.

In order to trace the sequence of possible changes occurring to the investigated ester during the decomposition of CHP, the reaction was carried out in chlorobenzene medium, the concentration of CHP being equal to that of $(C_2H_5O)_2P(O)R$, i.e. 1×10^{-1} mol l^{-1}.

The homolytic decomposition of CHP in chlorobenzene requires a higher activation energy (129.8 kJ mol^{-1}) [24] than that of cumene (104.7 kJ mol^{-1}) [21]. The high concentration of CHP creates favourable conditions for bimolecular decomposition and increases the concentration of cumyl peroxy radicals:

$$ROOH + ROOH \rightarrow RO^{\cdot} + ROO^{\cdot} + H_2O$$
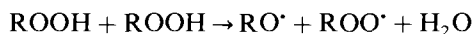
The following molecular products have been detected by means of mass spectral analysis of the reaction mixture after the decomposition (the concentration of CHP was 0.02 mol 1^{-1}):

$$m/z = 279 \rightarrow (C_2H_5O)_2P(O)R$$

$$m/z = 106 \rightarrow C_6H_5CH{=}CH_2$$

$$m/z = 119 \rightarrow C_6H_5C(CH_2)CH_3$$

$$m/z = 121 \rightarrow C_6H_5C(O)CH_3$$

$$m/z = 135 \rightarrow C_6H_5C(CH_3)_2OH$$

$$m/z = 252 \rightarrow (C_2H_5O)_2P(O){=}C{-}C_6H_9$$

The inhibitor is not consumed during the reaction. It probably participates in the formation of an unstable complex with the cumyl peroxy radicals and its inhibitory effect can be expressed by the following alternative scheme:

$$ROO + PO \rightarrow [ROO{\cdots}PO] \rightarrow \text{inactive products}$$
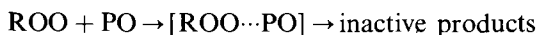
The presence of dimethyl phenyl carbenol gives us reason to conclude that a fraction of the CHP has been homolytically decomposed. CHP (1×10^{-1} mol 1^{-1}) was added to the reaction mixture (Fig. 5). The reaction proceeds in two steps (Fig. 5(c)) — an induction period followed by rapid decomposition of the CHP.
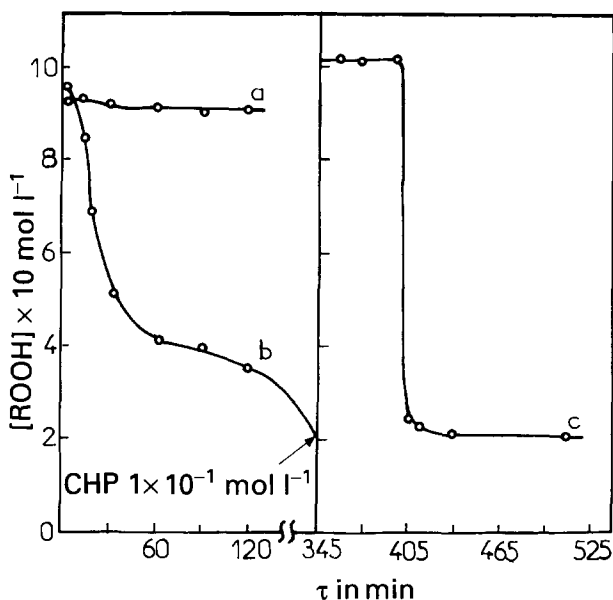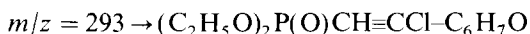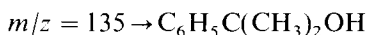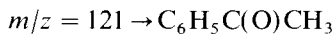

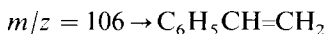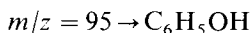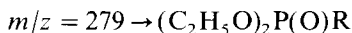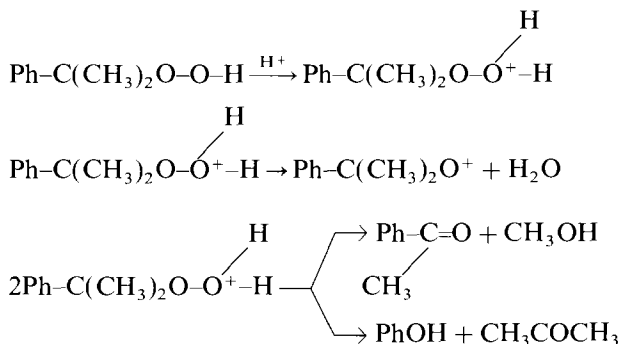Fig. 5. Decomposition of cumyl hydroperoxide in the chlorobenzene: (a) $C_6H_5C(CH_3)_2OOH$ (9.3×10^{-2} mol 1^{-1}) in C_6H_5Cl; (b) $(C_2H_5O)_2P(O)CH{=}C(Cl)C_6H_9 + C_6H_5C(CH_3)_2OOH$ ($9.6 \times 10^{-2}/$ 9.6×10^{-2} mol 1^{-1}) in C_6H_5Cl; (c) $C_6H_5C(CH_3)_2OOH$ (1×10^{-1} mol 1^{-1}) in the reaction mixture.

The mass spectral analysis of the reaction mixture detects the following products:

$m/z = 279 \rightarrow (C_2H_5O)_2P(O)R$

$m/z = 95 \rightarrow C_6H_5OH$

$m/z = 106 \rightarrow C_6H_5CH=CH_2$

$m/z = 119 \rightarrow C_6H_5C(CH_2)CH_3$

$m/z = 121 \rightarrow C_6H_5C(O)CH_3$

$m/z = 135 \rightarrow C_6H_5C(CH_3)_2OH$

$m/z = 252 \rightarrow (C_2H_5O)_2P(O)C\equiv C-C_6H_9$

$m/z = 293 \rightarrow (C_2H_5O)_2P(O)CH\equiv CCl-C_6H_7O$
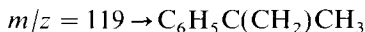
The presence of base peak m/z 279 shows that the diethyl ester has remained unchanged.

The quick decomposition of CHP could be due to the HCl liberated by the ester, and the presence of H_2O in the reaction mixture. The presence of phenol and acetophenon gives grounds to consider that the reaction is probably heterolytic, and proceeds according to

$$Ph-C(CH_3)_2O-O-H \xrightarrow{H^+} Ph-C(CH_3)_2O-\overset{\displaystyle\quad H}{\overset{\displaystyle\diagup}{O}}{}^+-H$$

$$Ph-C(CH_3)_2O-\overset{\displaystyle\quad H}{\overset{\displaystyle\diagup}{O}}{}^+-H \rightarrow Ph-C(CH_3)_2O^+ + H_2O$$

$$2Ph-C(CH_3)_2O-\overset{\displaystyle\quad H}{\overset{\displaystyle\diagup}{O}}{}^+-H \begin{cases} \rightarrow Ph-\overset{\displaystyle\quad}{\underset{\displaystyle CH_3}{C=O}} + CH_3OH \\ \rightarrow PhOH + CH_3COCH_3 \end{cases}$$

The complex of peroxide radicals with the studied esters could be formed under the influence of the π-electrons of the conjugated double bonds in the esters. The stability of such an intermediate also depends on the degree of coplanarity of the phosphorus atom and the cyclohexenyl fragment with the plane of the aromatic ring of the cumene.

The ester groups do not significantly influence the reactivity of the studied esters in a medium of cumene during the oxidation process.

The better inhibiting property of the butyl ester is due to its thermal stability — the phase transitions occur at higher temperatures.

The studied esters continue to manifest their inhibitory properties at 110°C, independently of thermal changes in a medium, generating radicals and electrophilic reactants. The mechanism of their action is quite complicated and we could not confirm it by isolating any stoichiometric reaction products.