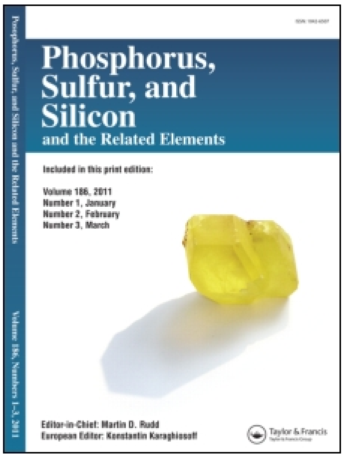

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Study Of The Inhibitory Properties Of Esters Of 2-Chloro-2(1-Cy Clohexenyl)- Ethylenylphosphonic Acid During Cumene Oxidation

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STUDY OF THE INHIBITORY PROPERTIES OF ESTERS OF 2-CHLORO-2(1-CYCLOHEXENYL)-ETHYLENYLPHOSPHONIC ACID DURING CUMENE OXIDATION

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The antioxidant properties of the dialkyl esters and dialkyl thioesters of 2-chloro-2(1-cyclohexenyl)ethylenylphosphonic acid have been investigated in the oxidation of cumene at 333 K and 383 K.

It is found that they inactivate the cumylperoxy radicals. The cyanopropyl radicals of AIBN react with diethyl and diethyl thioesters at 333 K.

The esters studied have better inhibition properties at 383 K than at 333 K.

INTRODUCTION

The antioxidant properties of organophosphorus compounds (OPC) have been intensively studied in the last 15–20 years.[1-9] Reactions of peroxy radicals with OPC are classical subjects of study in the free-radical chemistry of phosphorus.[7,8] Thus, according to the data of Walling,[9] trialkyl phosphites are oxidised by alkylperoxy radicals at 403 K; the oxidation proceeds through a chain mechanism. Pobedimskii *et al.* proved that aryl phosphites react with hydroperoxides and peroxy radicals, formed from an initiator under conditions of liquid-phase oxidation. The antioxidant action of metal-containing derivatives of dithiophosphoric acid at low temperatures (up to about 373 K) is reduced to an interaction with alkylperoxy radicals.[5] Kinetic and physicochemical investigations have shown that OPC can suppress chain branching of oxidation reactions and by reacting with peroxy radicals terminate the kinetic chains.[4,5]

Recently it has been shown that the 2-chloro-1,3-alkadienyl phosphonic acid derivatives are obtained from 1,3-alkadienephosphonic acid dichlorides via their reactions with chlorine.[10,11] The convenience of this method provided a basis for investigation of the chemical behaviour of the 1,3-alkadienephosphonates in reactions with other reagents.[12-14].

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In the present paper we report the results of our studies on the antioxidant properties of the dialkyl esters and dialkyl thioesters of 2-chloro-2(1-cyclohexenyl)ethylenylphosphonic acid in the oxidation of cumene as a model hydrocarbon.

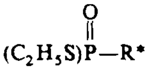
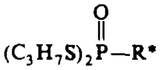
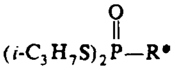
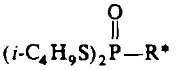
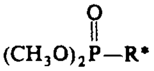
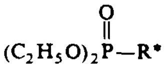
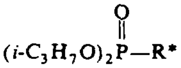
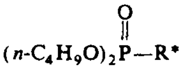
RESULTS AND DISCUSSION

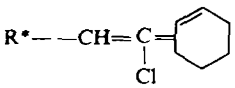
The effect on the initiated cumene oxidation at 333 K, and on its autooxidation at 383 K, of dialkyl thioesters and dialkyl esters was examined. The structure of the esters investigated and kinetic parameters of the initiated oxidation of cumene at 333 K are listed in Table I. The longest induction periods were noted with the systems containing the diethyl thioester–10 min, and with the system containing the diethyl ester–9 min.

During the low temperature initiated cumene oxidation free cumylperoxy radicals have been detected by means of EPR.[15–17] The occurrence of induction periods in

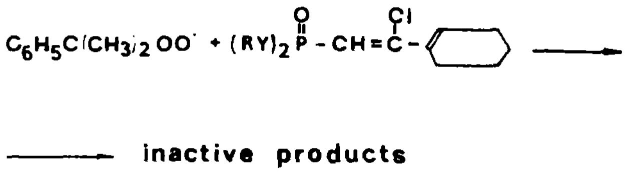
TABLE I

Kinetic parameters of the initiated oxidation of cumene in the presence of dialkyl thioesters and dialkyl esters of 2-chloro-2(1-cyclohexenyl)ethylenylphosphonic acid (T = 333 K)

No	Structure formulas	$\tau_{ind.}$ min.	$W_{max} \times 10^5$ mol/l. sec.	f
1	 $(C_2H_5S)\overset{O}{\overset{\|}{P}}-R^*$	10	1.8	0.4
2	 $(C_3H_7S)_2\overset{O}{\overset{\|}{P}}-R^*$	4.8	1.6	0.4
3	 $(i\text{-}C_3H_7S)_2\overset{O}{\overset{\|}{P}}-R^*$	4.0	1.5	0.1
4	 $(i\text{-}C_4H_9S)_2\overset{O}{\overset{\|}{P}}-R^*$	3.5	1.9	0.1
5	 $(CH_3O)_2\overset{O}{\overset{\|}{P}}-R^*$	3.2	2.1	0.1
6	 $(C_2H_5O)_2\overset{O}{\overset{\|}{P}}-R^*$	9.0	1.8	0.3
7	 $(i\text{-}C_3H_7O)_2\overset{O}{\overset{\|}{P}}-R^*$	8.2	2.4	0.3
8	 $(n\text{-}C_4H_9O)_2\overset{O}{\overset{\|}{P}}-R^*$	2.3	2.6	0.1
9	Cumene and AIBN		2.7	



the oxidation process investigated is a proof of the interaction between the esters investigated and the cumylperoxy radicals. The process can be expressed by reaction (0):

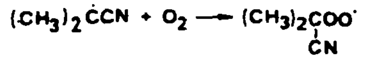


(0)

Y is: O or S

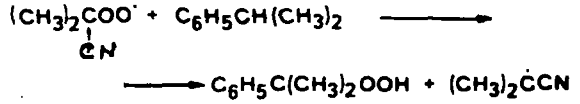
The efficiency of an inhibitor depends on the number of radicals, deactivated by one molecule of inhibitor–i.e. on the stoichiometric coefficient of inhibition (f).[18] The low values of f and induction periods (Table I) show that the esters studied are not very active inhibitors of the initiated cumene oxidation.

At the low partial pressures of O_2 during the initiated cumene oxidation the rate of the reaction (1):



$$(CH_3)_2\dot{C}CN + O_2 \longrightarrow (CH_3)_2\underset{CN}{C}OO^{\cdot} \qquad (1)$$

is slower than the rate of the reaction (2):



$$(CH_3)_2\underset{CN}{C}OO^{\cdot} + C_6H_5CH(CH_3)_2 \longrightarrow C_6H_5C(CH_3)_2OOH + (CH_3)_2\dot{C}CN \qquad (2)$$

and the concentration of cyanopropyl radicals is greater than the concentration of cyanopropyl peroxy radicals in the oxidised system. The data in Figure 1 indicate

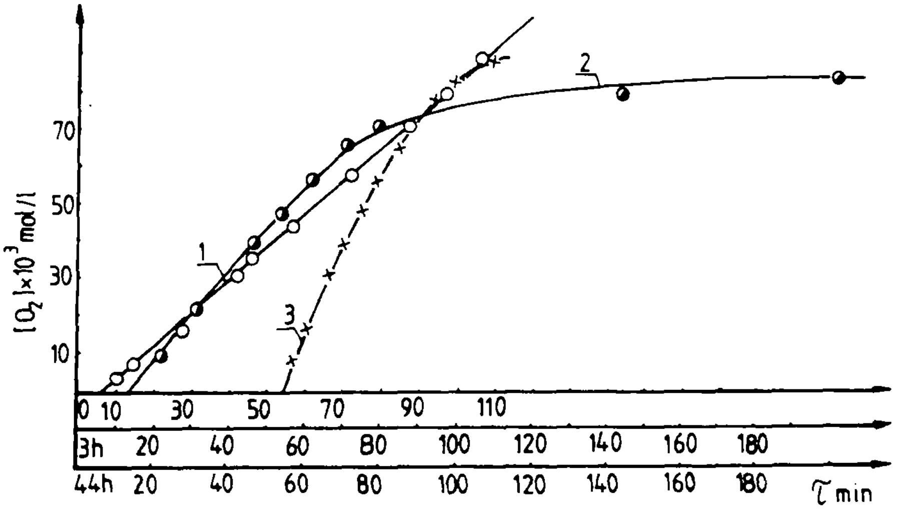
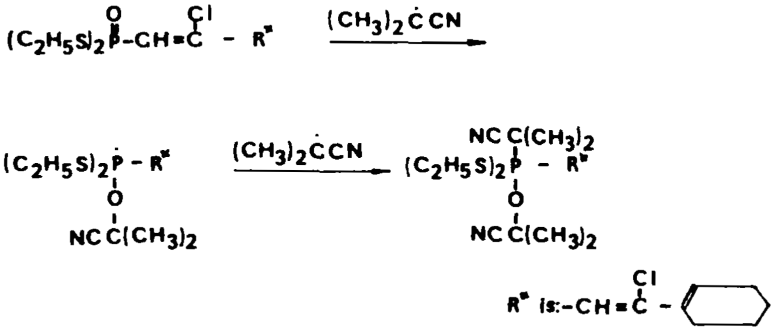


FIGURE 1 Effect of O_2 partial pressure on the initiated oxidation of cumene (W_i = 5.9 × 10^{-7} mol/l. sec., T = 333 K) in the presence of diethyl ester (1 × 10^{-3} mol/l): 1-kinetic curve at O_2 pressure 0.1 MPa; 2-kinetic curve at O_2 pressure 0.025 MPa; 3-kinetic curve at O_2 pressure 0.01 MPa.

that with the decreased partial oxygen pressure during the initiated oxidation in the presence of diethyl thioester, the induction period is significantly longer: 44 hours 54 min. at P_{O_2} = 0.01 MPa. The induction period of the cumene oxidation and AIBN under the same conditions is 10 min. This fact can be explained with the ability of the diethyl thioester to react not only with cumylperoxy radicals but with cyanopropyl AIBN ones. This interaction can be expressed schematically (Scheme 1):



SCHEME 1

We carried out the reaction between the diethyl thioester and AIBN under argon at 333 K. In the IR spectrum of the product obtained we observed a band at 1580–1610 cm^{-1} due to —CH=C<, and another one at 850–810 cm^{-1} due to the C—Cl stretching vibrations. Hence it can be concluded that the cyanopropyl radicals do not attack the double bonds. The absorption band at 1250–1210 cm^{-1}, characteristic for the P=O stretching vibrations was absent. These results lead to conclusion that cyanopropyl radicals attack the P=O group of the diethyl thioester.

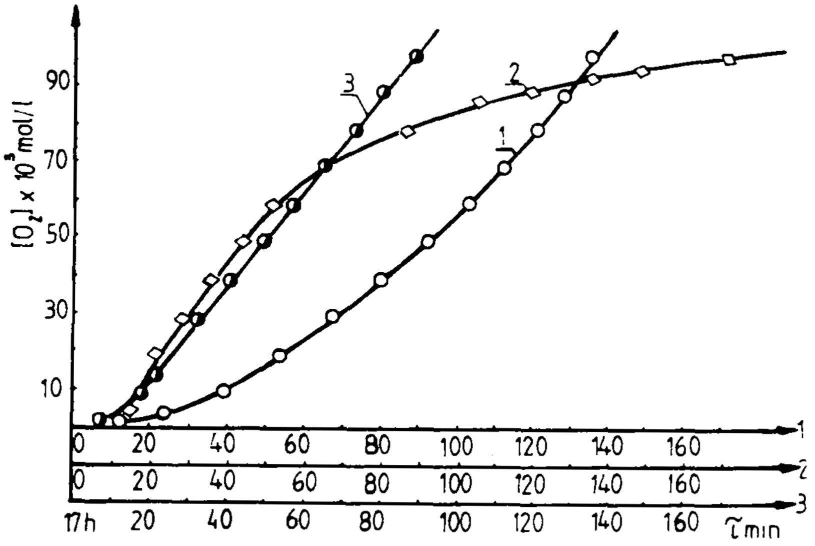


FIGURE 2 Effect of O_2 partial pressure on the initiated oxidation of cumene (W_i = 5.9 × 10^{-7} mol/l. sec., T = 333 K) in the presence of diethyl thioester (1 × 10^{-3} mol/l): 1-kinetic curve at O_2 pressure 0.1 MPa; 2-kinetic curve at O_2 pressure 0.025 MPa; 3-kinetic curve at O_2 pressure 0.01 MPa.

TABLE II

Effect of the partial pressure of oxygen on the initiated oxidation of cumene in the presence of $(C_2H_5S)_2P(O)—R^{\bullet}$(1) and $(C_2H_5O)_2P(O)—R^{\bullet}$(6)
(1 and 6 = 1×10^{-3} mol/l; AIBN = 5×10^{-2} mol/l)

No	Partial pressure of O_2 MPa	$\tau_{ind.}$ min.		f	
		1	6	1	6
1	0.01	2695	1028	95.4	36.4
2	0.025	191	10	6.7	0.3
3	0.1	10	9	0.4	0.3

Analogous results were observed during the initiated cumene oxidation in the presence of diethyl ester at 333 K (P_{O_2} = 0.01 MPa – τ_{ind} is 17 hours and 8 min. Figure 2). The high values of the stoichiometric inhibition coefficients, given in Table II, indicate that diethyl ester and diethyl thioester react repeatedly with cyanopropyl radicals.

A considerable difference in the inhibitory properties of the diethyl ester and the diethyl thioester occurred at an elevated temperature—383 K (Figure 3). Under these conditions the diethyl thioester, which contains sulfur has an induction period two and a half times longer than the diethyl ester. At 383 K the diethyl thioester exhibits $f = 34$ and the diethyl thioester -20, based on $W_i = 8.34 \times 10^{-6}$ mol/l. sec. measured experimentally during cumene oxidation in presence of ionol as radical acceptor.

To summarise it can be concluded that diethyl ester and diethyl thioester react with cumylperoxy radicals and cyanopropyl radicals at 333 K. They have better inhibition properties during the cumene auto-oxidation at 383 K.

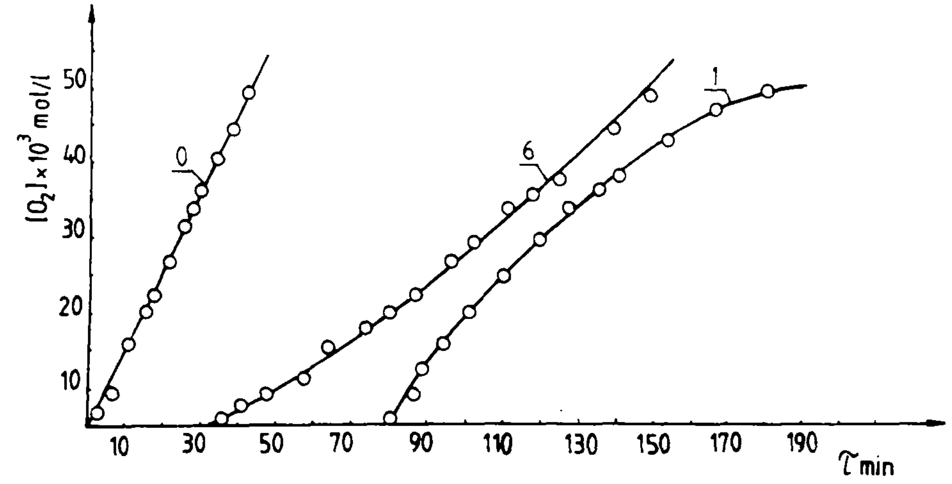


FIGURE 3 Kinetic curves of cumene autooxidation (P_{O_2} = 0.1 MPa, T = 333 K) in the presence of (1×10^{-3} mol/l) diethyl thioester-1 and (1×10^{-3} mol/l) diethyl ester-6, cumene-0.

EXPERIMENTAL

The dialkyl esters and dialkyl thioesters were synthesized from the dichloride of 2-chloro-2(1-cyclohexenyl)ethylenylphosphonic acid and alcohols or thiols in the presence of organic bases according to methods described in the literature.[10,11]

The initiated cumene oxidation was carried out at 333 K, $W_i = 5.9 \times 10^{-7}$ mol/l. sec., $P_{O_2} = 0.1$ MPa; $P_{O_2} = 0.025$ MPa and $P_{Ar} = 0.075$ MPa; $P_{O_2} = 0.01$ MPa and $P_{Ar} = 0.09$ MPa. Cumene was previously purified,[19], $n_D^{20} = 1{,}4920$. The dinitril of azoisobutyric acid (AIBN), after recrystallization from ethanol, acetone and benzene was used an an initiator (M.p. = 378 K).

The autoxidation of cumene was conducted at 383 K, $P_{O_2} = 0.1$ MPa.

The stoichiometric coefficients of inhibition $-\mathbf{f}$ were calculated from the expression:[18]

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

where: W_i is the rate of initiation; τ_{ind} is the induction period; InH is the inhibitor concentration.

The reaction with AIBN and the diethyl thioester was carried out at 333 K, under argon at a diethyl thioester: AIBN mole ratio of 1 : 0.5, without solvent.

The oxidation process was conducted in a manometric apparatus.

The IR spectra were measured on an UR-20 "Carl Zeiss" apparatus as film in KBr cells.

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