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N.A. Shirinova, G.M. Talybov

STUDY OF THE PROPERTIES OF SYNTHESIZED THIIRANE AND THIETANE COMPOUNDS AS ANTIOXIDANT ADDITIVES

Azerbaijan Technical University, Baku, Azerbaijan

The presented article is devoted to the synthesis and study of the antioxidant properties of sulfur-containing heterocyclic compounds. Initially, thiiranes were synthesized by replacing the oxygen atom in the epoxy ring with a sulfur atom. Later, the corresponding thietanes were synthesized under the influence of nucleophilic reagents in an aqueous medium. The structure of the synthesized compounds is confirmed by IR and PMR spectra, and their composition is confirmed by elemental analysis. The antioxidant properties of the compounds were studied in the presence of an initiator in a chlorobenzene medium. For this purpose, the interaction of the compounds with cumene peroxide and cumene hydroperoxide radicals was studied and the kinetic parameters of the reactions were obtained. The antioxidant activity of the samples with and without inhibitors was determined from the kinetic curves based on the obtained parameters. The oxidation products of one of the studied compounds, sulfoxide and sulfone, were obtained and their antioxidant activity was studied. From the obtained results, it was established that this activity is imparted to the newly synthesized thietane compounds by the sulfur atom present in the thietane ring.

Keywords: heterocyclic sulfur compounds, thiirane, thietane, antioxidant, cumene, inhibitor.

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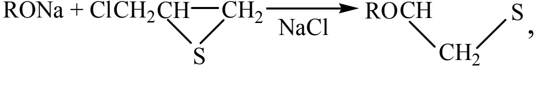
Introduction

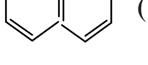
One of the most important challenges in modern chemistry is protecting fuels, lubricants, and other petroleum products from oxidation during long-term storage and use. Antioxidant additives are widely applied to prevent oxidative degradation of fuels and lubricants. Currently, various organic compounds are used as antioxidant additives in industrial practice worldwide [1]. In addition to sulfides, thiophosphates, phenothiazines, benzothiazines, and sulfur-containing heterocyclic compounds such as thiirane and thietanes are successfully employed for this purpose [2].

Experimental, results and discussion

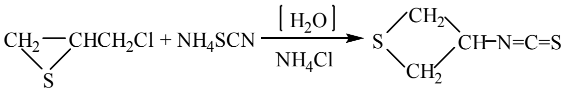
The thiirane and thietane derivatives under study were synthesized via the reaction of 1,2-epithio-3-chloropropane with nucleophiles [3]:



, (I, II)

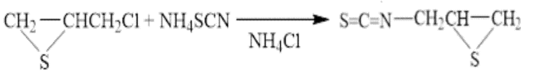
where R=  (I), H- (II).

The corresponding 3-thietanyl isothiocyanates (III) were synthesized by treatment of the synthesized 3-substituted thietanes with ammonium thiosulfate [4]:



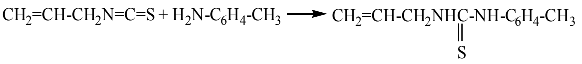
(III)

When the synthesis is carried out in an alcoholic medium, thiirane isothiocyanate (IV) was obtained:



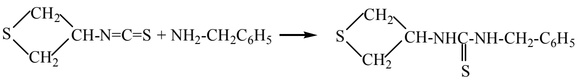
(IV)

3-Thietanyl-substituted thioureas were synthesized by reaction of 3-thietanyl isothiocyanates (V–VI) with primary and secondary amines [5]:



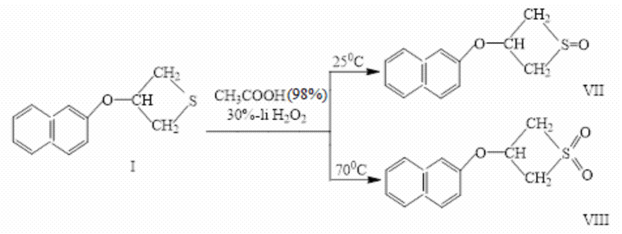
$$CH_2{=}CH{-}CH_2N{=}C{=}S + H_2N{-}C_6H_4{-}CH_3 \longrightarrow CH_2{=}CH{-}CH_2NH\underset{\underset{S}{\|}}{C}{-}NH{-}C_6H_4{-}CH_3$$

(V)



(VI)

To determine the effect of the thietanyl fragment on the antioxidant properties of the synthesized thietane compounds, the corresponding sulfoxides and sulfones of 3-substituted thietanes were obtained by oxidation under various conditions. The sulfoxides and sulfones (VII, VIII) were obtained by oxidation with 30% H_2O_2 in glacial acetic acid or absolute ethanol [6]:



The structure of the compounds was established by IR and PMR spectroscopy, while the composition was confirmed by elemental analysis and purity was assessed by thin-layer chromatography. In the IR spectra of the synthesized 3-substituted thietanes, intense bands corresponding to C–S stretching vibrations of the four-membered thietane ring are observed at 670–680, 720–730, and 1425–1440 cm^{-1}. Bands in the 1590–1610 and 1470–1450 cm^{-1} regions are assigned to C=C stretching vibrations of the aromatic ring, whereas the bands at 1710–1720 and 1730–1740 cm^{-1} correspond to C=O stretching vibrations of the ester group.

In the PMR spectrum of thiethanes, four protons in two equivalent methylene groups located in the four-membered thietane ring are observed in the range of 1.85–4.00 ppm as a quintet with an intensity ratio of 1:4:6:4:1. The signal of the only methine proton in the thietane ring is shifted downfield due to the negative inductive effect of the oxygen atom bonded to it and appears as a quintet in the range of 4.8–5.4 ppm as a result of spin–spin coupling with two neighboring methylene groups. In naphthyl-substituted thietanes, the signal of seven aromatic protons appears as a multiplet in the range of 7.1–8.0 ppm.

Thioureas are white crystalline or oily compounds. To purify crystalline 3-thietanyl-substituted thioureas, they are dissolved in ethyl alcohol and then reprecipitated upon addition of benzene. The IR spectra of 3-thietanyl-substituted thioureas retain absorption bands at 670–680, 720–730, and 1420–1445 cm^{-1}, characteristic of the four-membered thietane ring. The spectra also exhibit an absorption band at 1500–1510 cm^{-1}, corresponding to stretching vibrations of the –NH–C(=S)– fragment. The IR spectra do not show an absorption band corresponding to the isothiocyanate functional group around 2090 cm^{-1}.

In the IR spectrum of 3-thietanyl-substituted thioureas recorded as KBr pellets, a broad absorption band in the region of 3320–3330 cm^{-1} is attributed to N–H stretching vibrations. In the IR spectrum recorded for a 0.005 M solution of these compounds in CCl_4, absorption bands at 3380 and 3480 cm^{-1} correspond to free (non-hydrogen-bonded) N–H stretching vibrations. In addition, a band at 3040 cm^{-1} is observed in the spectrum of the dilute solution, indicating the presence of intramolecular N–H···S hydrogen bonds, which is consistent with literature data [7].

In the NMR spectra of 3-thietanyl-substituted thioureas, the protons of two equivalent methylene groups in the four-membered thietane ring appear as a quintet with an intensity ratio of 1:4:6:4:1 in the range of 2.7–3.75 ppm. The signal of the methine group in the thietane ring appears as a quintet in the region of 4.3–4.7 ppm. The NH proton of the thiourea fragment in all synthesized N-substituted thioureas appears as a singlet in the region of 7.05–7.75 ppm. In addition, depending on the nature of the substituents in the amino moiety, signals corresponding to various substituents are also observed.

Considering the complexity of studying the antioxidant properties of fuel additives and other petroleum products, model reactions were used. The test reaction was carried out in a chlorobenzene solution. 2,2'-Azobisisobutyronitrile (AIBN) was used as an initiator. Oxygen is consumed during the oxidation reaction, and based on this consumption, the oxygen pressure was automatically compensated [8]. The reaction was carried out at 60^{0}C. The concentration of azobisisobutyronitrile was $2\cdot10^{-2}$ mol·L^{-1}. To study the antioxidant properties of thiirane and thietane compounds, their interaction with cumene hydroperoxide radicals was investigated. Chlorobenzene, cumene, and cumene hydroperoxide were purified prior to use [9,10].

The concentrations of the studied compounds were investigated in the range of $3\cdot10^{-4}$—$5\cdot10^{-6}$ mol·L^{-1}. The results showed that the compounds inhibit the initiator-induced oxidation of cumene. The reaction of thiirane and thietane compounds with cumene hydroperoxide was studied in the oxidation of cumene initiated by AIBN. A chlorobenzene solution was placed in a glass reactor maintained in a thermostat, and the reaction was carried out at an initiator concentration of $2\cdot10^{-2}$ mol·L^{-1} in the presence of cumene hydroperoxide. To prevent air ingress, argon was periodically purged through the reaction medium. Samples were periodically withdrawn from the reactor, and the amount of cumene hydroperoxide was determined by the iodometric method. The rate of interaction between hydroperoxides and the studied compounds was evaluated based on the consumption of cumene hydroperoxide:

$$v = \frac{[\mathrm{ROOH}]_0 - [\mathrm{ROOH}]_\infty}{[\text{concentration of the compounds being studied}]}.$$

The stoichiometric coefficient (f) was calculated based on the value of the induction period (τ):

$$f = \frac{\tau \cdot W_i}{[\mathrm{InH}]_0} \qquad (1)$$

The stoichiometric coefficient (f) is defined as the number of oxidation chains terminated by one molecule of the inhibitor or its transformation product. The rate of initiation (W_i) is $2\cdot10^{-7}$ mol·L^{-1}·s^{-1}. $[\mathrm{InH}]_0$ denotes the initial concentration of the inhibitor (mol·L^{-1}).

K_7 is the rate constant for the reaction between the inhibitor and peroxide radicals. It was determined from the slope of the linear plot obtained by transforming the kinetic oxygen absorption curve into coordinates $\Delta[O_2]^{-1}$ versus reciprocal time (t^{-1}) [11]:

$$\mathrm{tg}\alpha = \frac{f \cdot K_7 \cdot [\mathrm{InH}]_0}{K_2 \cdot [\mathrm{RH}] \cdot W_i}. \qquad (2)$$

The rate constant K_7 is determined using Eq. (1):

$$K_7 = \frac{\mathrm{tg}\alpha \cdot K_2 \cdot [\mathrm{RH}] \cdot W_i}{f \cdot [\mathrm{InH}]_0}. \qquad (3)$$

Here K_2=1.51 L/mol·s; RH]=6.9 mol/L [12].

The kinetic curves for the initiator-induced oxidation of cumene in the presence of the synthesized thiiranes and thietanes are shown in Fig. 1.

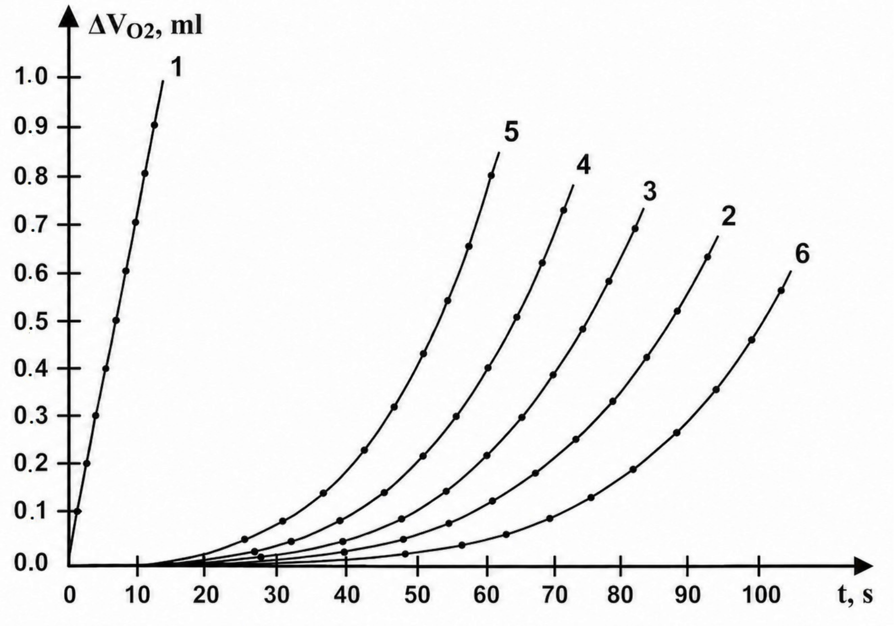


Fig. 1. Kinetic curves of the initiated oxidation of cumene under the action of thiirane and thietane compounds (60^{0}C). AIBN]=$2\cdot10^{-2}$ mol/L; $[\mathrm{InH}_{2,3,4,5,6}]=3\cdot10^{-4}$ mol/L. 1 – without inhibitor; 2 – InH$_1$; 3 – InH$_2$; 4 – InH$_3$; 5 – InH$_4$; 6 – InH$_5$

As can be seen from Fig. 1, the studied compounds slow down the oxidation process by reacting with cumene peroxide. In the absence of the studied compounds, cumene oxidation proceeds at a constant rate and no induction period is detected. However, when the compounds are added to the reaction medium at a concentration of $5 \cdot 10^{-4}$ mol·L^{-1}, the oxygen uptake rate decreases. Figure 2 shows the kinetic curves of cumene autoxidation in the presence of the synthesized compounds. It is evident from the kinetic curves that thiourea derivatives exhibit the longest induction periods. Among them, compound 2 shows the longest induction period (250 min).

The reaction of the synthesized compounds with cumene peroxide was performed in chlorobenzene under a nitrogen atmosphere at 110^{0}C using various molar ratios. The corresponding kinetic parameters characterizing the antioxidant activity of the compounds are summarized in Table 1.

The results showed that the studied compounds promote the decomposition of cumene hydroperoxide. The kinetic curve of decomposition in the presence of the synthesized compounds is S-shaped and is characteristic of autocatalytic processes. The S-shaped behavior has also been reported for other antioxidants currently used in industry [13]. As can be seen in Fig. 3a, a small amount of cumene hydroperoxide is initially consumed over a period of about 10 min, and an induction period is observed for compound 3. Subsequently, the rate of cumene hydroperoxide decomposition decreases as its concentration decreases. This indicates that cumene hydroperoxide decomposition proceeds in the presence of the newly synthesized compounds (Fig. 3b).

The kinetic parameters for the catalytic decomposition of cumene hydroperoxide in the presence of the studied compounds are presented in Table 2.

It was found that the corresponding sulfoxide and sulfone derivatives do not inhibit cumene oxidation (Table 1).

Conclusions

The results show that the key contributor to the antioxidant activity of 3-substituted thietane compounds is divalent sulfur in the thietane ring. The synthesized 3-substituted thietanes, their thiourea derivatives, and functionally substituted thiirane compounds terminate oxidation chains by reacting with peroxide radicals and also catalytically decompose cumene hydroperoxide into molecular products.

Conflict of interest

The authors declare no conflict of interest.

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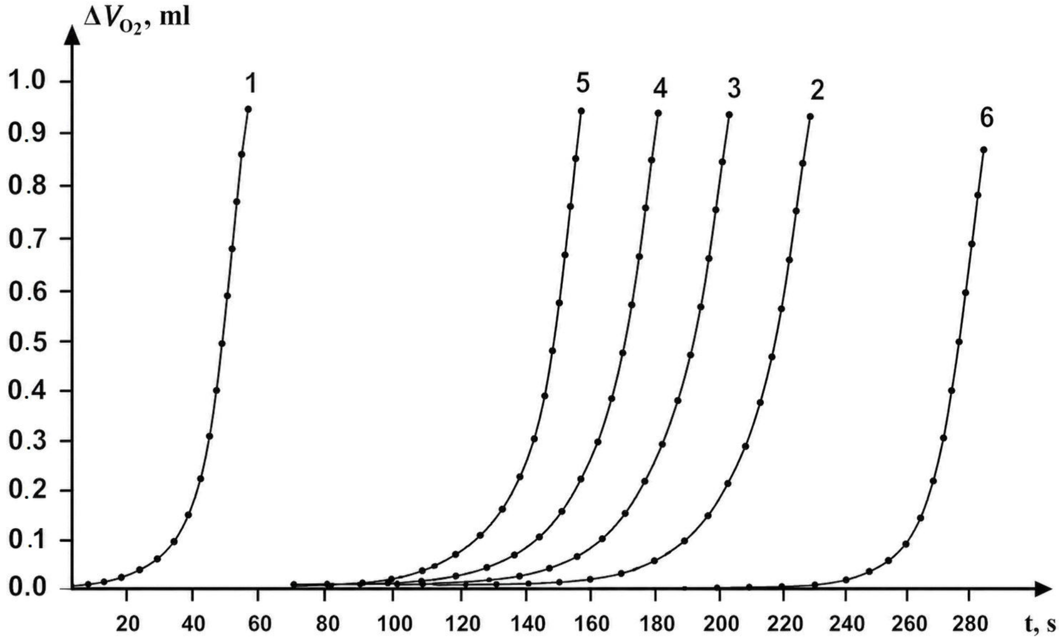

Fig. 2. Kinetic curves of cumene autoxidation under the action of thiirane and thietane compounds (110^{0}C). [$InH_{2,3,4,5,6}$]=$5 \cdot 10^{-5}$ mol/L. 1 – without inhibitor; 2 – InH_1; 3 – InH_2; 4 – InH_3; 5 – InH_4; 6 – InH_5

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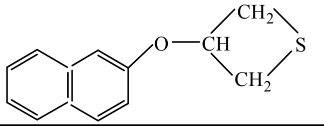
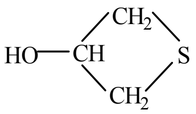
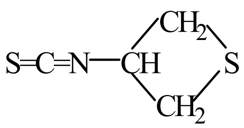
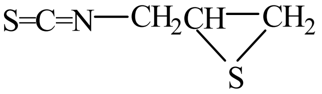
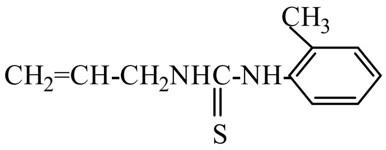
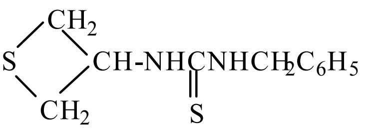
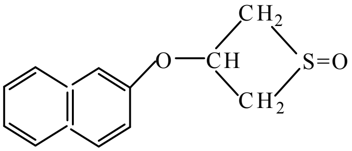
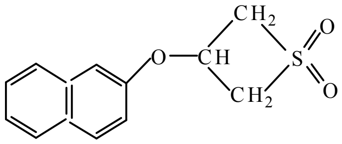
Table 1

Kinetic parameters for the reaction of the synthesized compounds with cumene hydroperoxide radicals

No.	Formula	f	$K_7 \cdot 10^{-4}$, L/mol·s	$[InH] \cdot 10^5$	τ, s
		T=60°C		T=110°C	
1		0.24	2.2	5	105
2		0.24	2.4	5	90
3		0.96	2.23	5	80
4		0.59	2.13	5	65
5		2.20	3.19	5	138
6		34	7.05	$5 \cdot 10^{-6}$	250
7		–	–	5	5
8		–	–	5	5

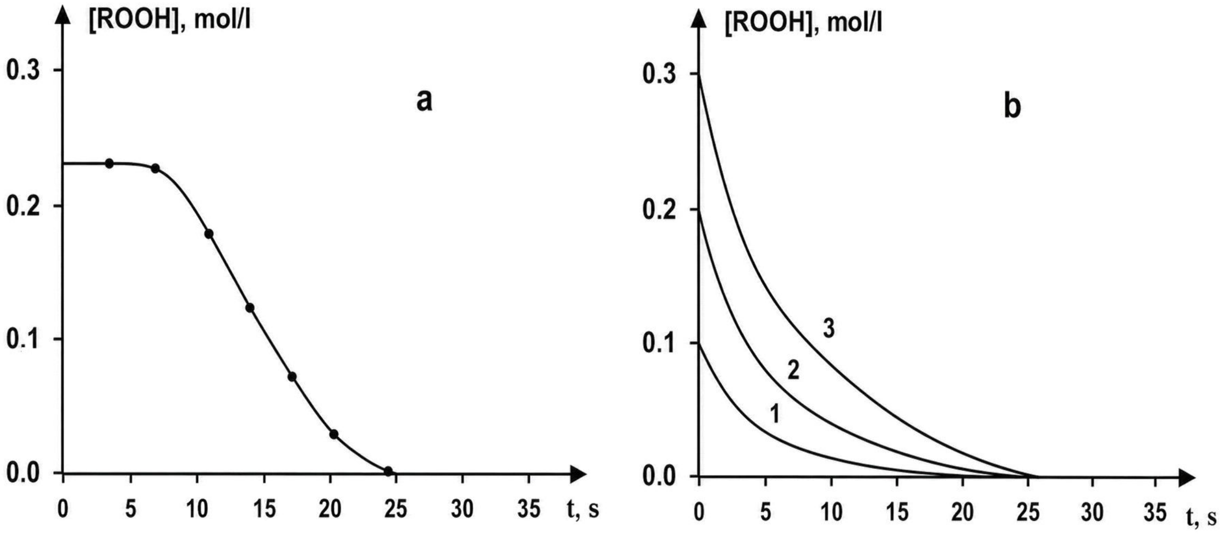
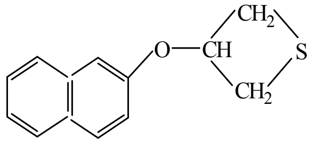
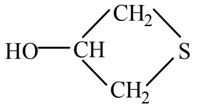
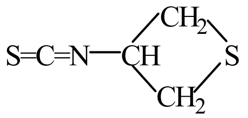
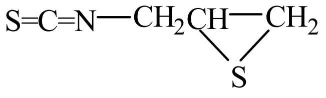
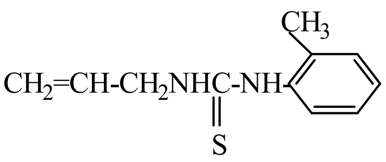
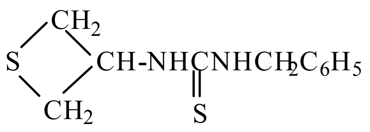


Fig. 3. (a) – kinetic curve of cumene hydroperoxide decomposition under the action of compound (2) (110^{0}C). [InH_2]=5·10^{-5} mol/L. (b) – Kinetic curve of cumene hydroperoxide decomposition of other compounds (110^{0}C). [$InH_{3,4,5}$]=5·10^{-5} mol/L. 1 – InH_3; 2 – InH_4; 3 – InH_5

Table 2

Kinetic parameters for the decomposition of cumene hydroperoxide induced by the synthesized compounds (T=110^{0}C)

No.	Formula	[InH]·10^{-4}	K', L/mol·s	ν
1		5	43	82000
2		5 2 0.5	42	78000
3		5	32	82000
4		2	26	73800
5		1 5	300	860000
6		0.5·10^{-5} 5·10^{-5}	125	586000

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ДОСЛІДЖЕННЯ ВЛАСТИВОСТЕЙ СИНТЕЗОВАНИХ ТІІРАНОВИХ І ТІЕТАНОВИХ СПОЛУК ЯК АНТИОКСИДАНТНИХ ДОБАВОК

Н.А. Ширинова, Г.М. Талибов

Дана стаття присвячена синтезу та дослідженню антиоксидантних властивостей сірковмісних гетероциклічних сполук. Спочатку тіірани були синтезовані шляхом заміщення атома кисню в епоксидному кільці атомом сірки. Згодом у водному середовищі під дією нуклеофільних реагентів були синтезовані відповідні тіетани. Структуру синтезованих сполук підтверджено ІЧ- та ПМР-спектроскопією, а їхній склад – даними елементного аналізу. Антиоксидантні властивості сполук досліджували у присутності ініціатора в середовищі хлорбензену. З цією метою було вивчено взаємодію сполук із радикалами пероксиду кумолу та гідропероксиду кумолу й визначено кінетичні параметри відповідних реакцій. Антиоксидантну активність зразків у присутності інгібіторів і без них оцінювали за кінетичними кривими на основі отриманих параметрів. Додатково було отримано продукти окиснення однієї з досліджуваних сполук, сульфоксид і сильфон, та досліджено їхню антиоксидантну активність. На основі отриманих результатів встановлено, що антиоксидантні властивості новосинтезованих тіетанових сполук зумовлені наявністю атома сірки в тіетановому кільці.

Ключові слова: гетероциклічні сірковмісні сполуки, тііран, тіетан, антиоксидант, кумол, інгібітор.

STUDY OF THE PROPERTIES OF SYNTHESIZED THIIRANE AND THIETANE COMPOUNDS AS ANTIOXIDANT ADDITIVES

N.A. Shirinova, G.M. Talybov *
Azerbaijan Technical University, Baku, Azerbaijan
* **e-mail: gtalibov61@gmail.com**

The presented article is devoted to the synthesis and study of the antioxidant properties of sulfur-containing heterocyclic compounds. Initially, thiiranes were synthesized by replacing the oxygen atom in the epoxy ring with a sulfur atom. Later, the corresponding thietanes were synthesized under the influence of nucleophilic reagents in an aqueous medium. The structure of the synthesized compounds is confirmed by IR and PMR spectra, and their composition is confirmed by elemental analysis. The antioxidant properties of the compounds were studied in the presence of an initiator in a chlorobenzene medium. For this purpose, the interaction of the compounds with cumene peroxide and cumene hydroperoxide radicals was studied and the kinetic parameters of the reactions were obtained. The antioxidant activity of the samples with and without inhibitors was determined from the kinetic curves based on the obtained parameters. The oxidation products of one of the studied compounds, sulfoxide and sulfone, were obtained and their antioxidant activity was studied. From the obtained results, it was established that this activity is imparted to the newly synthesized thietane compounds by the sulfur atom present in the thietane ring.

Keywords: heterocyclic sulfur compounds; thiirane; thietane; antioxidant; cumene; inhibitor.

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