Study of some Heterocyclic Compounds Containing Rhodanide Group as Antioxidant Additives

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Abstract

In the field of synthesis and study of the antioxidant activity of novel derivatives of rhodanides, we carried out a targeted synthesis of this compounds of cyclic thioureas and established a relationship between their structures and antioxidant properties. The antioxidant properties of the synthesized compounds were studied in model reactions. Since the study of the mechanism of the antioxidant action of oxidation inhibitors under real conditions of oxidation of lubricating oils is very difficult, the antioxidant effect of the compounds synthesized by us was studied in the oxidation reaction of a model hydrocarbon-cumene, the oxidation mechanism of which was studied in detail. The study of cumene autoxidation in the presence of these compounds showed that they effectively inhibit the autoxidation process. Thus, the study of the heterocyclic derivatives of rhodanides (E1-E3), which we synthesized by model reactions as hydrocarbon oxidation inhibitors, revealed that these compounds repel peroxide radicals, break oxidation chains, and catalytically decompose hydroperoxides into molecular compounds. The substances studied are antioxidants with a combined effect.

Keywords: *rhodanide, cumene, model reaction, antioxidant, inhibitor.*

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Tərkibində rodanid qrupu saxlayan bəzi heterotsiklik birləşmələrin antioksidant aşqar kimi tədqiqi

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Xülasə

Sintez etdiyimiz rodanidlərin heterotsiklik törəmələrinin (E1-E3) karbohidrogenlərin oksidləşməsinin qarşısını alan inhibitor kimi model reaksiyalarla tədqiqindən müəyyən olunmuşdur ki, bu birləşmələr peroksid radikallarını dəf edərək oksidləşmə zəncirlərini qırır və hidroperoksidləri katalitik olaraq molekulyar birləşmələrə parçalayır. Tədqiq olunan maddələr kombinə təsirə malik antioksidantlardır.

Açar sözlər: *rodanid, kumol, model reaksiya, antioksidant, inhibitor*.

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УДК 547.8

Исследование некоторых гетероциклических соединений, содержащих роданидную группу в качестве антиоксидантных присадок

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Аннотация

Синтезированные гетероциклические производные роданидов (E1-E3) были изучены в модельных реакциях как ингибиторы. При этом было установлено, что полученные соединения отталкивают пероксидные радикалы, разрывают цепи окисления и каталитически расщепляют гидропероксиды до молекулярных соединений. Таким образом, исследуемые соединения являются антиоксидантами комбинированного действия.

Ключевые слова: *роданид, гидропероксид, модельная реакция, антиоксидант, ингибитор.*

Introduction

One of the most important problems of modern hematology is to protect fuels, oils and other petroleum products from oxidation during operation or long-term storage [1-3]. Antioxidant additives are used to protect fuels and lubricants from oxidation. Currently, alkylphenols, amines, aminophenols, various sulfides, metal salts of dithiophosphate, thiourea derivatives and others are widely used as antioxidants [4-6].

Studies have shown that rhodanides are the most effective additives that prevent the oxidation of petroleum products. It is also known from the literature [7] that rhodanides play the role of stabilizers for the stabilization of lubricants, emulsifiers, chlorinated hydrocarbons. They are also widely used in agriculture as insecticides and seed disinfectants. Rhodanides, on the other hand, are the most suitable syntheses for the synthesis of nitrogen and sulfur-containing heterocycles.

It also should be taken into consideration that it is considerably difficult to study the mechanism of action of antioxidants added to fuels and other petroleum products. That is why the antioxidant effect of synthesized compounds has been studied in the oxidation reactions of model hydrocarbons.

To assess the antioxidant activity of synthesized compounds so far, the kinetics of their reactions with cumylperoxide radicals and cumylhydroperoxide have been studied. The model used cumene as a hydrocarbon, and its oxidation mechanism has been studied in detail [8-10].

Numerous studies describing the antioxidant capabilities of nitrogen and sulfur-containing organic compounds have been published in peer-reviewed journals. Sulfides, dithiophosphate, xanthogenate, and different sulfur-containing heterocycles (phenothiazine, benztiazole, etc.) were studied. Prior to our research, however, the antioxidant capabilities of several rhodanide compounds have received little attention.

In light of the above findings, as well as ongoing research in the field of the synthesis of various classes of sulfur compounds, the relationship between their structure and antioxidant properties, rhodanides of various structures can be synthesized and their antioxidant properties studied in model reactions. To put it another way, in order to determine the relationship between the structure of newly synthesized compounds and their antioxidant properties, new rhodanide derivatives were synthesized, their oxidative properties were studied in model reactions, and a theoretical background for the creation of new antioxidants was developed.

Material and method

Compounds produced react with cumylperoxide radicals. To evaluate the reaction with peroxide radicals, initiated oxidation of kumol was done in the presence of these inhibitors. The temperature of the reaction is 60 °C. At a concentration of 2-10-2 mol/l, the initiator was azodiizobutyronitrile (AIBN). At 60°C (K7), his initiation rate is 10-10-5 l/(mol.s.). The inhibitor concentration ranges between l-10-4 and 5-10-4 mol/1. In a monometric apparatus, the process was examined for oxygen absorption. A precisely measured reaction solution is placed in a reactor that is linked to the unit by a grinder. Prior to the experiment, the unit is filled with oxygen and transported to a reactor pre-cooled to -50 °C to prevent solvent evaporation.

The rapid shaking of the reactor guarantees that the oxygen dissolves quickly, allowing the oxidation reaction to proceed in the kinetic area. After the reactor has been heated for 5 minutes, the oxygen pressure in the system is adjusted once more, and measurements begin by turning off the taps. The decrease in oxygen volume is measured using the mercury level in a burette with a constant temperature. A gas is automatically supplied through a pressure regulator and an electrolyzer, which is balanced by a mercury column, to keep the pressure of oxygen on the reaction solution constant.

They add a solvent (chlorbenzene) to the reactor and begin a nitrogen bubble, which lasts throughout the experiment.

Then, with the exception of the hydroperoxide, we add all of the components and start the reactor heater. When the required temperature is reached in the reactor after 10-15 minutes, the final component, hydroperoxide, is introduced and the stopwatch is started. After the requisite temperature has been obtained, the inaccuracy of the reaction temperature should be kept within 0.1°C and controlled by direct measurement in the reactor. The concentration of hydroperoxide in the samples is then determined using a specific iodometric method. Pour a few milliliters of acetic acid and 1-5 milliliters of the sample into conical flasks of 150 milliliters, depending on the number of samples gathered throughout the experiment. Afterwards, the flasks blown with carbon dioxide to remove air. Pour the freshly prepared potassium iodide into a saturated solution of methanol and cover with polished glass stoppers and keep in the dark for 60 minutes.

Reaction of synthesized compounds with cumylhydroperoxide. Kinetic experiments to study the reaction of synthesized compounds with cumylhydroperoxide are carried out in a glass reactor with a constant temperature. A solvent (chlorbenzene) is added to the reactor and nitrogen bubbling is started, which is continued throughout the experiment. Then we include all the components except the hydroperoxide and start the reactor heater. After 10-15 minutes, when the required temperature is reached in the reactor, the last component, hydroperoxide, is introduced and the stopwatch is started. The error of the reaction temperature should be kept within ± 0.1°C and controlled by direct measurement in the reactor after the required temperature has been reached. Samples are then taken at specified time intervals and the concentration of hydroperoxide in them is found by a certain iodometric method. To do this, pour a few ml of acetic acid and 1-5 ml of the sample into the conical flasks of 150 ml, depending on the number of samples taken during the experiment. The flask is then blown with carbon dioxide to remove air. Pour the freshly prepared potassium iodide into a saturated solution of methanol and cover with polished glass stoppers and keep in the dark for 60 minutes.

In this case, the following reaction occurs:

$$ROOH + 2KJ + H_2O \rightarrow J_2 + ROH + 2KOH$$

Preliminary tests with a known starting concentration of hydroperoxide are used to ensure that the reaction is completed completely. When 10 mL of acid is added, the process totally releases molecular iodine after 30 minutes. During this time, very little iodine accumulates in the test sample. Each time a new experiment is introduced, a test sample is taken in addition to the basic samples. When calculating the solids, it was discovered that 2 moles of thiosulfate are utilized in the titration for every mole of hydroperoxide: $J_2+2Na_2S_2O_3 \rightarrow Na_2S_4O_6+2NaJ$

During titration, sodium thiosulfate is taken at a concentration of 0.05 N. The concentration of hydroperoxide is calculated by the following formula:

$$[ROOH] = \frac{(V_T - V_s)[Na_2S_2O_3]0{,}05N}{2V_{exp}}$$

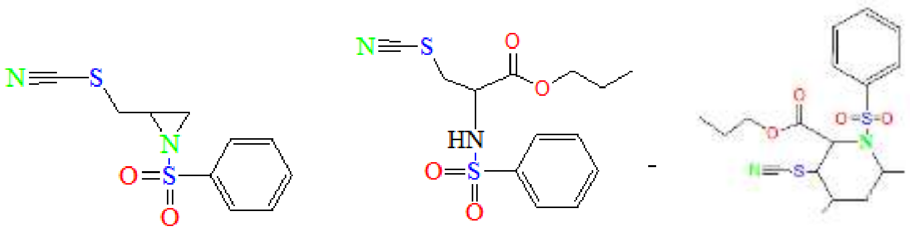
V_T - volume of solution used for titration of the sample, ml

V_s - volume of solution used for titration of test sample, ml

V_{exp} - volume of sample taken, ml.

Result and discussion

The autooxidation of kumol with their participation was investigated in this stage of the study to determine the ability of newly synthesized rhodanide derivatives (E1-E3) [15] to act as oxidation inhibitors (scheme).



E1 **E2** **E3**

Scheme – Some heterocyclic compounds containing rhodanide group

When we study the autoxidation of cumene in the presence of these compounds (E1-E3) at 110°C (Figure 1), we see that they stop the oxidation process. This manifests itself during their induction period (τ) (Fig.1).

Induction of the studied antioxidants (E1-E3) with azodiisobutyronitrile (AIBN) to assess the ability to break the oxidation chain during the oxidation of cumene rilled. The reaction was carried out in a monometric device, the kinetics of the oxidation process was determined by the amount of oxygen absorbed over a period of time.

(E1-E3) to inhibit the oxidation of cumene. As can be seen from the table below, the induction period (τ) of these compounds is much higher than that of ionol. According to the induction period (E3), the combination has a higher value.

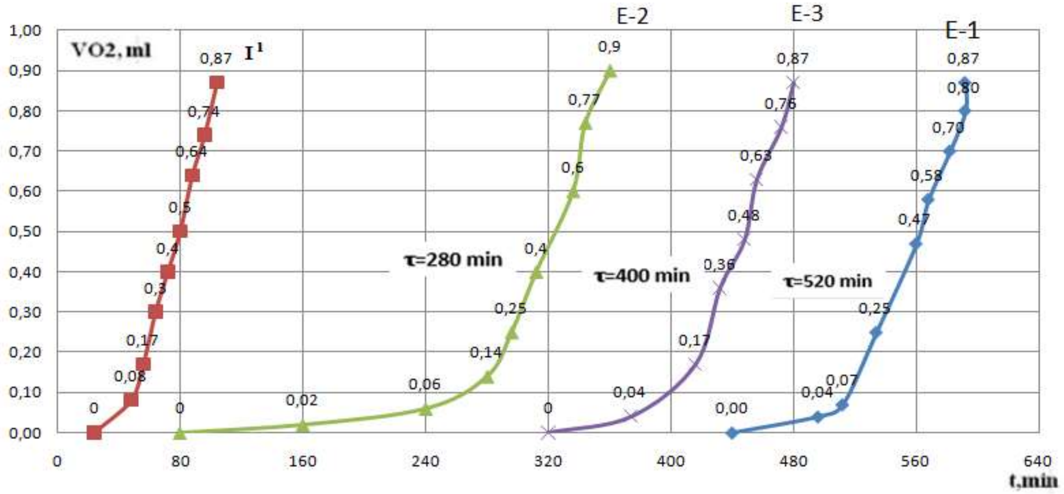


Figure 1 – Kinetic curves of cumene auto-oxidation in the presence of the synthesized compounds: T = 110°C, V_{O2} is a volume of oxygen (ml), τ is a time (min); [InH]= 0 (1^1) [InH]= E-1-E-3 = $5 \cdot 10^{-4}$ mol/l.

In order to evaluate the ability of the studied compounds E1-E3 to break the oxidation chains via the reaction with cumene peroxide radicals, the oxidation of cumene was initiated by azodiisobutyronitrile (AIBN) at 60°C in the presence of these inhibitors. In all experiments, concentration of the initiator was $2 \cdot 10^{-2}$ mol/l, and content of the inhibitor was $5 \cdot 10^{-4}$ mol/l. It was found that all studied compounds, to one degree or another, inhibited the initiated oxidation of cumene (Fig.2):

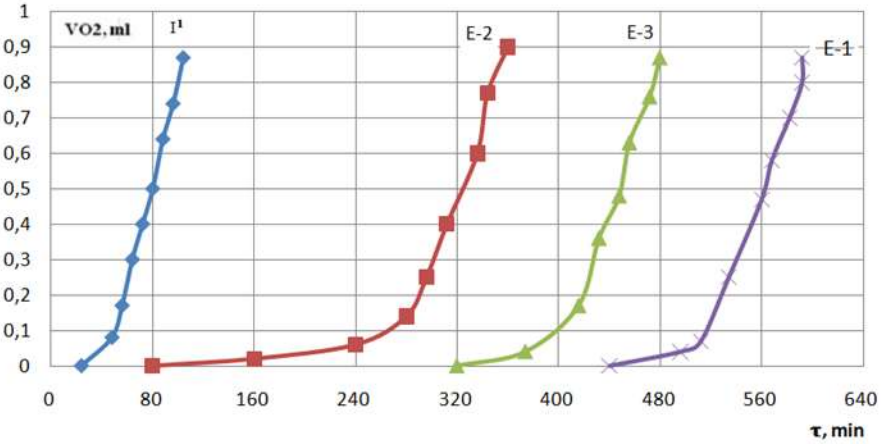


Figure 2 – Kinetic curves of initiated cumene oxidation in the presence of synthesized compounds E-1-E-3: T = 60ºC; V_{O2} is the volume of oxygen (ml), τ is the time (min.), [InH]=0 (1') [InH]=$5 \cdot 10^{-4}$ mol/l = (E-1-E-3).

Using the value of the induction time (τ) of the initiated cumene oxidation, the stoichiometry coefficient *f* was calculated. The latter is equal to the number of oxidation chains breaking under the action of one inhibitor molecule and products of its conversion:

$$f = \frac{\tau \cdot W_i}{[InH]_0}$$

where $\tau_{ind.}$ is induction time, W_i is initiation rate, $[InH]_0$ is initial concentration of the inhibitor. To determine the value of the rate constant of the interaction of inhibitor with cumene peroxide radicals (κ_7), the kinetic curves of the initiated oxidation of cumene were transformed from $\Delta[O_2]$-τ coordinates to $\Delta[O_2]^{-1}$-τ^{-1} coordinates. Using the slope of the straight line

$$\mathrm{tg}\,\alpha = \frac{fk_7[InH]_0}{(k_2[RH]W_i)}$$

it was found that

$$k_7 = \frac{tg\alpha k_2[RH]W_i}{f.[InH]_0}$$

where: k_2=1,51 mol^{-1}·s^{-1}, [RH]=7,17 mol^{-1}·s^{-1} [11].

The kinetic curves of kumol induced oxidation reveal that the oxidation rate of kumol after leaving the induction cycle in the presence of chemicals is less than the oxidation rate of pure kumol (E1-E3). This demonstrates that the intermediate products of the cumyl peroxide radical reaction have an inhibitory impact, or a secondary inhibitory feature.

The table compares the kinetic properties of the examined antioxidants (E1-E3) with cumyl peroxide radicals with ionol.

The values of the kinetic parameters of the reaction of the synthesized compounds with cumene peroxide radicals are given in Table.

To ebaluate the ability of the synthesized compounds (E1-E3) to decompose CHP, the reaction of cumene hydroperoxide with inhibitors has been implemented at 110°C in chlorobenzene under nitrogen atmosphere (at this temperature, CHP is thermally stable). The studies have shown that the inhibitors, which contain a sulfur atom in the molecule, effectively decompose CHP (Fig. 3). Moreover, one molecule of the studied inhibitors is capable of decomposing several thousand CHP molecules, that is, the reaction has a catalytic character.

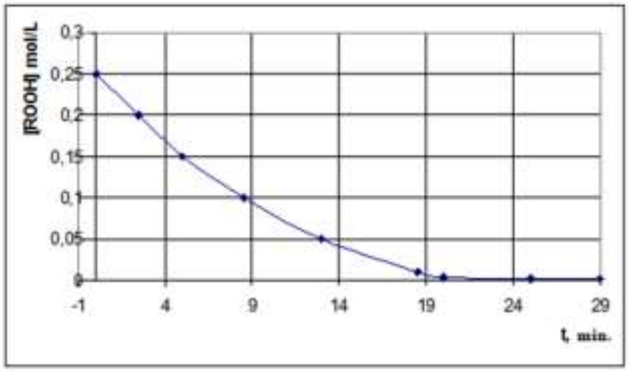


Figure 3 – (E3) The kinetic curve of KHP fragmentation with the participation of the combination:
T = 110° C; [InH] = $5 \cdot 10^{-4}$ mol·l^{-1};
[ROOH] = 0.38 mol·l^{-1}; τ - induction time (minutes).

The number of CHP molecules (ν), decomposed under the action of one molecule of the studied compounds, was calculated by the formula:

$$\nu = \frac{[CHP]_0 - [CHP]_\infty}{[InH]_0}$$

where $[CHP]_0$ and $[CHP]_\infty$ are initial and final concentration of CHP, respectively; $[InH]_0$ is initial concentration of the antioxidant.

It is found that for all compounds, the reaction with CHP is of the first order both in terms of antioxidant and CHP, and the initial reaction rate of the catalytic decomposition of CHP follows the equation:

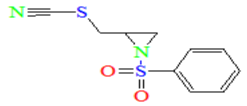
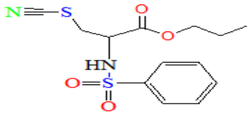
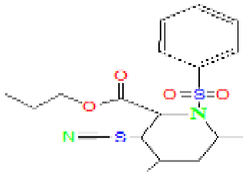
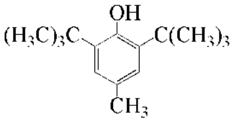
$$w_0 = \mathrm{K}[InH]_0 \cdot [CHP]$$

The values of the rate constant of CHP decomposition under the action of the studied compounds (K) and catalytic factor (ν) are given in Table.

The Table also contains values of the induction time (τ) of cumene autooxidation in the presence of the synthesized compounds, as well as the kinetic parameters of their reaction with cumene peroxide radicals and cumeme hydroperoxide.

According to the literature, the stoichiometric coefficient of alkylphenols, including ionol, is roughly 2 (f2).

Table – The values of the induction time of cumene autooxidation in the presence of the synthesized compounds E-1-E-3, as well as the kinetic parameters of their reaction with cumene peroxide radicals and cumene hydroperoxide

№	The formula of the combination	T=60°C		T=110°C		τ, min
		f	$K_7 \cdot 10^{-4}$ l/(mol·s)	ν	K, l/mol.s	
E1		5.28	3.97	222000	11	520
E2		4.08	3.55	20000	10.5	400
E3		2.88	1.81	17000	8.6	280
Ionol*		2.00	2.10	-	-	150

*Ionol was used as a standard inhibitor.

According to the table, the stoichiometry coefficient of rhodanides (E1-E3) ranges between 2.88-5.28. The price of the K_7 is in a similar scenario. The value of K_7 in rhodanides ranges from 1.81 to 3.97 10^{-4} l/(mol s), and its efficiency is significantly higher than that of ionol.

The investigated rhodanide compounds (E1-E3) catalytically degrade the cumylhydroperoxide produced during the oxidation reaction into molecular products. This is not applicable for ionol.

Table shows the kinetic parameters of the reaction of antioxidants with cumylhydroperoxide. The number of KHP molecules decomposed by one molecule of antioxidant and its conversion products, ie the rate constant of the decomposition reaction with catalytic factor (ν), was calculated. It is known that one molecule of cyanide breaks down two molecules of cumylhydroperoxide. However, when the sulfur atom is located in the rhodanide (SCN) fragment, the decomposition of KHP increases by a thousand times. As can be seen from the table, the value of the catalytic factor varies in the range of 17 000-22 000. They have the highest combination of catalytic factors (E1) and their values reach 22 000, respectively. The value of the velocity constant of the catalytic factor is 8.6-11 l/mol.s. From the above, it is clear that the compounds we studied belong to the class of antioxidants that have a combined effect. Because they interact with cumyl peroxide radicals, they break the oxidation chain and also act on cumyl hydroperoxide, which catalytically breaks it down into molecular products. After interacting with peroxide radicals, the antioxidants investigated entirely lose their catalytic properties in the hydroperoxide breakdown reaction.

Thus, the antioxidants generated react with peroxide radicals, which are the primary oxidation products in the oxidation process and have a high reactivity, and the majority of the time is spent on this reaction. Once generated, the remaining hydroperoxide is catalytically degraded and converted into more active compounds such as antioxidants. In brief, these antioxidants are not reaching their full potential.

In consideration of this, the antioxidants tested for the pre-formation of active compounds were treated with hydroperoxide before being incorporated in the oxidation process. When the antioxidant-hydroperoxide mixture was incorporated in the oxidation process in multiple quantities and for varying durations of time, the antioxidant effect of the mixture rose several times over the initial antioxidant.

Conclusion

To summarize, the chemicals tested break down the oxidation chain by repelling cumyl peroxide radicals, oxidizing with cumyl hydroperoxide to catalytically breakdown cumyl hydroperoxide, and rejecting peroxide radicals more effectively. In short, the compounds investigated are antioxidants with a synergistic impact.

Conflict of Interests

The author declare there is no conflict of interests related to the publication of this article.

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