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SYNTHESIS OF β -KETOSULFIDES BASED ON BENZALACETONE AND RESEARCH INTO THEIR INHIBITORY PROPERTIES

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Abstract: The interaction of benzalacetone with mercaptoacetic acid and its alkyl esters was used to synthesize and characterize new representatives of β -ketosulfides, the structure of which was proved by ^1H and ^{13}C NMR- spectroscopy. The gravimetric method was used to study the influence of the synthesized compounds on the corrosion rate of St-3 in various aggressive medium. It was established that the studied compounds inhibit the corrosion process both in single-phase acidic (0.1N HCl u 0.1N H_2SO_4), and in two-phase (electrolyte-hydrocarbon) media. In the latter case, they are more effective - the corrosion rate of St-3 decreases from 2.1 to 0.06-0.35 g/m^2 hour, while the degree of protection against corrosion is 83.3-97.1 %. The studied compounds exhibit a greater protective effect in hydrochloric acid solution (97.1-92.45%), than in sulfuric acid (76.9-87.1%). Among the tested compounds, β -ketosulfide obtained on the basis of mercaptoacetic acid showed the highest inhibitory efficiency in both mediums.

Keywords: benzalacetone, mercaptoacetic acid, alkyl esters of mercaptoacetic acid, β - ketosulfide, inhibitors of corrosion, single-phase medium, two-phase medium, gravimetric method.

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Introduction

Ketosulfides are of interest as corrosion inhibitors [1, 2], growth stimulators of agricultural crops [3], and synthesis of biologically active compounds [4, 5].

One of the convenient ways to obtain ketosulfides is the addition of thiols to unsaturated ketones by the Michael reaction. A number of β -ketosulfides were synthesized and characterized by conjugate addition of thiols to

α -, β -unsaturated carbonyl compounds in the presence of various catalysts [6–14]. Obtaining new representatives of ketosulfides and studying their useful properties is relevant. For this purpose, we carried out reactions of benzalacetone with mercaptoacetic acid and its alkyl esters. The synthesized β -ketosulfides were studied as steel corrosion inhibitors in various aggressive media.

Experimental part

NMR spectra were taken on a Bruker instrument with an operating frequency of 300 MHz (^1H) and 75 MHz (^{13}C) in C_6D_6 solvent. TMS was used as an internal standard.

Alkyl esters of mercaptoacetic acid were synthesized by the reaction of mercaptoacetic acid with the corresponding alcohols in an acidic medium [15]. The physicochemical constants of the synthesized esters comply with

the literature data.

The reagents used - benzalacetone, mercaptoacetic acid, and triethylamine - were purified by distillation.

4-Methoxycarbonylmethylthio-4-phenylbutan-2-one (I). To a mixture of 10.6 g (0.1 mol) of methyl ester of mercaptoic acid and 3 ml of triethylamine in 50 ml of benzene when mixing, are added 14.6 g (0.1 mol) of

benzalacetone in 50 ml of benzene. While an increase in the temperature of the reaction mixture by 6-8°C is observed.

Stirring is continued for 2 hours at room temperature. Then the temperature is raised to 60-65°C and the reaction is continued for another 3 hours.

The benzene solution was washed with water until neutral, dried over sodium sulfate, and then filtered. After distilling off the solvent, the target product was isolated by vacuum distillation. Yield of 18.82 g (74.5 %), T_b 115-116°C/1.5 mm, n_D^{20} 1.5403. NMR spectra 1H , δ , м.д.: 7.13-7.26 m (5H, C_6H_5), 4.41-4.46 t (1H, PhCHS); 3.55 s (3H, OCH_3); 3.02 s (2H, SCH_2); 2.61-2.80 m (2H, CCH_2C); 2.02 s (3H, $O=C-CH_3$). NMR spectra ^{13}C , δ , м.д.: 205.2 (C=O); 173.4 (O=C-O); 14.1 (C^1 , Ph); 128.6 (C^2 , C^3 , C^5 и C^6 , Ph); 127.3 (C^4 , Ph); 51.2 (CH_2); 50.6 (OCH_3); 38.9 (SCH_2); 37.7 (CH); 29.2 (CH_3). Found, %: C 33.81; H 5.72; S 29.99. $C_3H_6O_2S$. Calculated, %: C 33.96; H 5.66; S 30.19.

Other β -ketosulfides (II-IV) were synthesized by a similar procedure.

Other β -ketosulfides (II-IV) were synthesized by a similar procedure (II). Yield: 73.2 %, T_b 123-125°C/1.5 mm, n_D^{20} 1.5321. NMR spectra 1H , δ , ppm.: 7.10-7.23 m (5H, C_6H_5), 4.31-4.36 m (2H, OCH_2); 4.10-4.15 t (1H, PhCHS); 3.12 s (2H, SCH_2); 2.65-2.84 m (2H, CCH_2C); 2.01 s (3H, $O=C-CH_3$); 1.27-1.32 t (3H, $O-C-CH_3$). NMR spectra ^{13}C , δ , ppm.: 205.2 (C=O); 168.2 (O=C-O); 139.5 (C^1 , Ph); 128.3 (C^2 , C^3 , C^5 and C^6 , Ph); 127.4 (C^4 , Ph); 60.2 (OCH_2); 52.1 (CH_2); 39.8 (SCH_2); 37.2 (CHS); 28.9 ($O=C-CH_3$); 14.3 ($O-CH_2-CH_3$). Found, %: C 39.83; H 6.52; S 26.59. $C_4H_8O_2S$. Calculated, %: C 40.00; H 6.67; S 26.67.

4-i-Propoxycarbonylmethylthio-4-phenylbutan-2-one (III). Yield: 70.1%, T_b 131-133°C/1.5 mm, n_D^{20} 1.5300. NMR spectra 1H , δ , ppm.: 7.11-7.24 m (5H, C_6H_5), 4.86-5.00 m (1H, OCH); 4.31-4.38 t (1H, Ph CH S); 3.31 s (2H, SCH_2); 2.52-2.77 m (2H, $C-CH_2-C$); 1.95 c

(3H, $O=C-CH_3$); 1.29 d (6H, CH_3-C-CH_3). NMR spectra ^{13}C , δ , ppm.: 205.7 (C=O); 168.9 (O=C-O); 139.3 (C^1 , Ph); 128.5 (C^2 , C^3 , C^5 и C^6 , Ph); 127.2 (C^4 , Ph); 69.1 (OCH); 38.5 (SCH_2); 37.5 (CHS); 29.2 ($O=C-CH_3$); 21.3 (CH_3-C-CH_3). Found, %: C 44.68; H 7.26; S 23.69. $C_5H_{10}O_2S$. Calculated, %: C 44.78; H 7.46; S 23.88.

4-Carboxymethylthio-4-phenylbutan-2-one (IV). Yield: 67.5%, T_b 128-130°C/1.0 mm, n_D^{20} 1.5690. NMR spectra 1H (fig.1), δ , ppm.: 10.29 s (1H, COOH); 7.02-7.13 m (5H, C_6H_5); 4.59-4.64 m (1H, PhCHS); 2.79 c (2H, SCH_2); 2.58-2.64 m (2H, $C-CH_2-C$); 1.58 s (3H, CH_3). NMR spectra ^{13}C (fig.2), δ , ppm.: 204.5 (C=O); 175.4 (COOH); 140.8 (C^1 , Ph); 128.5 (C^2 , C^3 , C^5 and C^6 , Ph); 127.2 (C^4 , Ph); 48.8 (CH_2); 44.23 (SCH_2); 32.3 (CH); 29.5 (CH_3). Found, %: C 26.15; H 4.19; S 34.53. $C_2H_4O_2S$. Calculated, %: C 26.09; H 4.35; S 34.78.

The inhibitory properties of the synthesized compounds were studied gravimetrically according to the State Standard (ГОСТ) 9.502-82 in single-phase acidic media and in two-phase electrolyte-hydrocarbon media (3% NaCl+0.02% CH_3COOH + kerosene 5:1), saturated with carbon dioxide.

Before testing, the plates were ground on a grinding machine, polished, washed with distilled water, alcohol, hexane, and then with acetone.

The plates (40 x 20 x 5) were placed in a beaker with 200 ml of an acid solution so that they did not come into contact with each other. After 3 hours, the plates were removed from the solution and washed with running water, dried and a thin coating was removed from the surface of the plates with an elastic band, washed with hexane, and dried with acetone. Then the plates were weighed on an analytical balance with an accuracy of 0.0001 g.

The corrosion rate (ρ) was determined in $g/m^2 \cdot h$ using the following formula:

$$\rho = \frac{m_1 - m_2}{S \cdot \tau}$$

m_1 – mass of plates before testing, g

m_2 – mass of plates after testing, g

S – plate area, m^2

τ – test time, hour.

The degree of protection (Z , %) was determined by the following formula:

$$Z = \frac{\rho_{\text{fon}} - \rho}{\rho_{\text{fon}}} \cdot 100, \%$$

ρ_{fon} - plate corrosion rate without inhibitor, $\text{g}/\text{m}^2 \text{h}$.

ρ - plate corrosion rate with inhibitor, $\text{g}/\text{m}^2 \text{h}$.

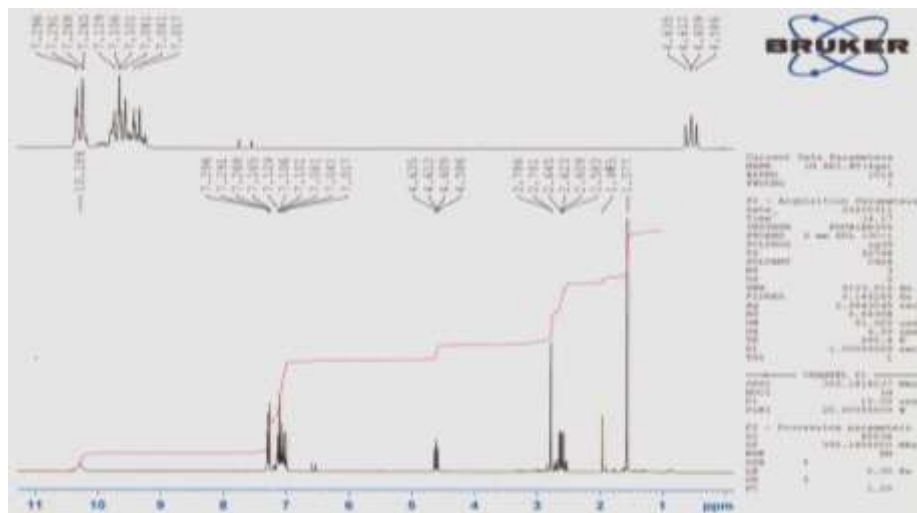


Fig. 1. ^1H NMR spectra of 4-carboxymethylthio-4-phenylbutan-2-one

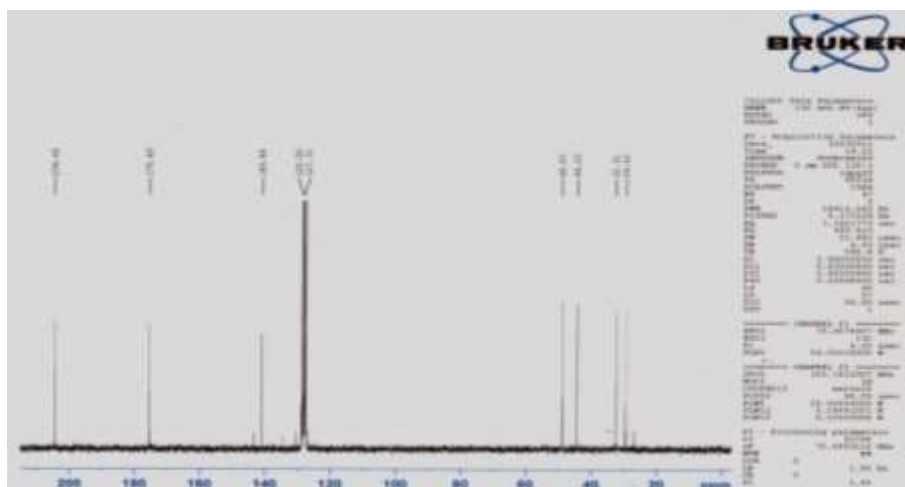
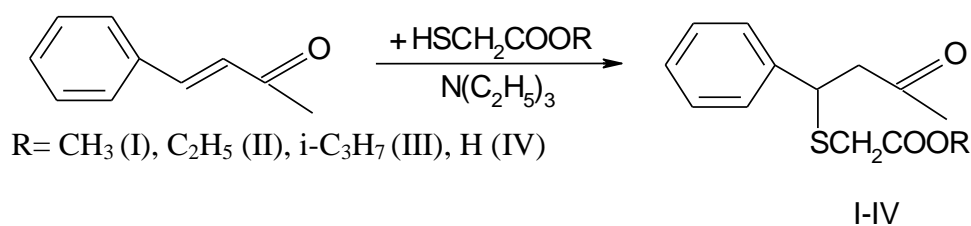


Fig. 2. ^{13}C NMR spectra of 4-carboxymethylthio-4-phenylbutan-2-one

Results and their discussion

The reaction of benzalacetone with benzene solution in equimolar ratios of reagents mercaptoacetic acid and its esters proceeded in a benzene solution in the presence of triethylamine.

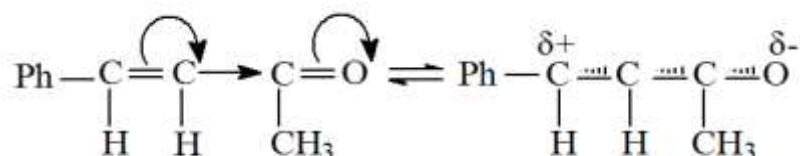
Reaction scheme:



Synthesized β -ketosulfides (I-IV) are light yellow liquids, soluble in organic solvents, stable during storage. Their structure and composition were confirmed by ^1H , ^{13}C NMR spectroscopy and elemental analysis.

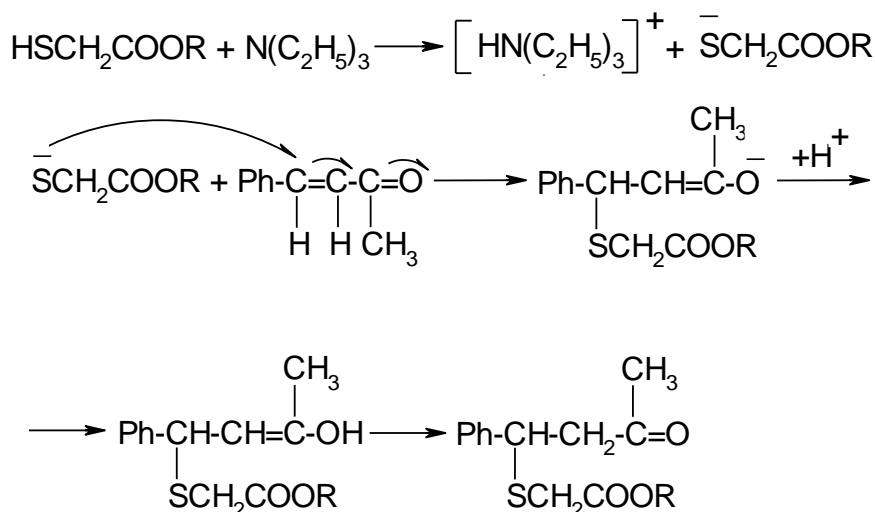
The reaction mechanism is presented as follows. Benzalacetone belongs to α , β -unsaturated ketones, in the molecule of which, by conjugation of π -bonds of the double carbon-

carbon and carbonyl groups, four p-electrons are delocalized on three carbon atoms and an oxygen atom. The influence of -I and -M - effects of carbonyl oxygen leads to the polarization of the conjugated system, as a result of which the β -carbon atom acquires a partially positive charge, and carbonyl oxygen acquires a partially negative charge:



Such a distribution of electron density in the conjugated system leads to the addition of nucleophilic thiolate ion to carbon at the β -position of the ketone, forming an enolate ion,

which, after subsequent protonation, turns into enol. Further, the unstable enol formed as a result of conjugated addition is isomerized into a more stable keto form:



Thus, the final product corresponds to a formal addition at carbon-carbon double bonds without affecting the carbonyl group.

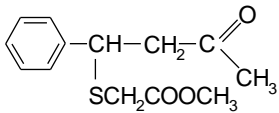
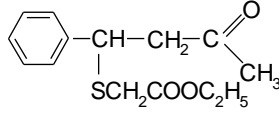
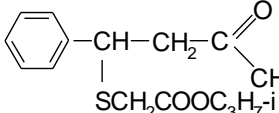
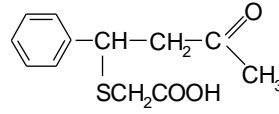
The molecules of β -ketosulfides we synthesized contain various functional groups, including ester and carbonyl groups, as well as a sulfur heteroatom having an unshared electron pair, which can be used to interact with the

metal surface. In this regard, it was of interest to study their inhibitory properties.

The inhibitory properties of β -ketosulfides were studied in a single-phase acid medium (0.1N HCl and 0.1 N H_2SO_4) and in a two-phase system: electrolyte-hydrocarbon saturated with carbon dioxide. The gravimetric test results are presented in Table 1.

Table 1. Inhibitory properties of β -ketosulfides

№№	Formula and name of the compound	Conc., mg/l	0.1N HCl $t = 20^\circ\text{C}$		0.1N H_2SO_4 $t = 20^\circ\text{C}$		3% NaCl+0.02% CH_3COOH +kerosene 5:1, CO_2 , $t = 20^\circ\text{C}$	
			ρ , g/m^2 h	Z, %	ρ , g/m^2 h	Z, %	ρ , g/m^2 h	Z, %

I	 4-Methoxycarbonylmethylthio-4-phenylbutan-2-one	50	0.71	79.1	0.97	76.9	0.35	83.3
		100	0.55	83.8	0.87	79.3	0.27	87.1
II	 4-Ethoxycarbonylmethylthio-4-phenylbutan-2-one	50	0.66	80.6	0.92	78.1	0.31	85.2
		100	0.52	84.7	0.84	80.2	0.23	89.0
III	 i-Propoxycarbonylmethylthio-4-phenylbutan-2-one	50	0.60	82.4	0.87	79.3	0.29	86.2
		100	0.50	85.3	0.79	81.2	0.20	90.5
IV	 4-Carboxymethylthio-4-phenylbutan-2-one	50	0.37	89.1	0.66	84.3	0.17	91.9
		100	0.26	92.4	0.54	87.1	0.06	97.1
V	Without the inhibitor	–	3.40	–	4.20	–	2.10	–

As can be seen from the data in Table 1, the studied compounds effectively inhibit the corrosion of steel in a two-phase system: electrolyte-hydrocarbon saturated with carbon dioxide. At that, the corrosion rate decreases from 2.1 to 0.06-0.35 g/m² h, while the degree of protection is 83.3-97.1%. These compounds have inhibitory properties in acidic medium in 0.1N HCl and 0.1 N H₂SO₄, solutions, but exhibit less inhibitory activity than in a two-

phase system.

The studied compounds exhibit a greater protective effect in a solution of hydrochloric acid (79.1-92.4%) than in sulfuric acid (76.9-87.1%).

It should be noted that among the studied compounds, β -ketosulfide, obtained on the basis of mercaptoacetic acid itself, turned out to be the most effective.

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BENZALASETON ƏSASINDA β -KETOSULFİDLƏRİN SİNTEZİ VƏ İNHİBİTOR XASSƏLƏRİNİN TƏDQIQI

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Xülasə: Benzalasetonun merkaptosirkə turşusu və onun alkil efirləri ilə qarşılıqlı təsirindən β -ketosulfidlərin yeni nümayəndələri sintez edilmiş və xarakterizə olunmuşdur. Onların quruluşu ¹H və ¹³C-spektroskopiyaya ilə təsdiq edilmişdir. Sintez olunmuş birləşmələrin qravimetrik üsulla müxtəlif aqressiv mühitlərdə Ct-3-ün korroziya sürətinə təsiri öyrənilmişdir. Məlum olmuşdur ki, onlar həm birfazlı elektrolit (0.1N HCl və 0.1N H₂SO₄ məhlulları), həm də ikifazlı elektrolit–

karbohidrogen mühitində poladın korroziyasını ləngidirlər. Sonuncu halda onlar daha effektivdirlər – korroziyanın sürəti 2.1-dən 0.06-0.35 q/m²·saat-dək azalır, mühafizə effekti 83.3-97.1% təşkil edir. Tədqiq olunan birləşmələr sulfat turşusu məhlulu (76.9-87.1%) ilə müqayisədə xlorid turşusu məhlulunda (79.1-92.4%) daha yüksək mühafizə effekti nümayiş etdirirlər. Həm elektrolit, həm də elektrolit–karbohidrogen mühitində ən yüksək effektivlik merkaptosikə turşusu əsasında alınmış β -ketosulfidə məxsusdur.

Açar sözlər: benzalaseton, merkaptosirkə turşusu, merkaptosirkə turşusunun alkil efirləri, β -ketosulfidlər, korroziya inhibitorları, mühafizə effekti, birləşmə mühit, ikifazlı mühit, qravimetrik üsu

СИНТЕЗ β -КЕТОСУЛЬФИДОВ НА ОСНОВЕ БЕНЗАЛЬАЦЕТОНА И ИССЛЕДОВАНИЕ ИХ ИНГИБИРУЮЩИХ СВОЙСТВ

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Аннотация: Взаимодействием бензальацетона с меркаптоуксусной кислотой и ее алкильными эфирами синтезированы и охарактеризованы новые представители β -кетосульфидов, строение которых доказано ¹H и ¹³C ЯМР-спектроскопией. Методом гравиметрии изучено влияние синтезированных соединений на скорость коррозии Ст-3 в различных агрессивных средах. Установлено, что исследуемые соединения ингибируют процесс коррозии как в однофазной кислотной (0.1N HCl и 0.1N H₂SO₄), так и в двухфазной (электролит-углеводород) средах. В последнем случае они более эффективны – скорость коррозии Ст-3 уменьшается от 2.1 до 0.06-0.35 г/м² час, при этом степень защиты от коррозии составляет 83.3-97.1 %. Исследуемые соединения проявляют большее защитное действие в растворе соляной кислоты (97.1-92.45%), чем в серной кислоте (76.9-87.1%). Среди испытанных соединений наибольшую ингибирующую эффективность в обеих средах проявил β -кетосульфид, полученный на основе меркаптоуксусной кислоты.

Ключевые слова: бензальацетон, меркаптоуксусная кислота, алкильные эфиры меркаптоуксусной кислоты, β -кетосульфиды, ингибиторы коррозии, однофазная среда, двухфазная среда, гравиметрический метод.