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OBTAINING CORROSION INHIBITORS IN THE PRESENCE OF OXYETHYLIDENE DIPHOSPHONIC ACIDS

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Abstract

In this article the regularities of the urea condensation reaction with glyoxal are considered and studied. It is shown that during the condensation of carbamide with 1,2-dicarbonyl compound in the presence of OEDP as a catalyst the product based on tetrahydroimidazo-[4,5-d]-imidazolidione-2,5 is synthesized with a yield of 80-85%. The obtained products in pure form and in composition with diethylamine, formaldehyde, carbamide and gossypol resin were tested as corrosion inhibitors. It was established that the compositions are effective corrosion inhibitors and protect steel from corrosion by more than 90%.

Keywords: urea, dial, OEDP, tetrahydroimidazo-[4,5-d]-imidazolidione corrosion inhibitor, protection level

Tetrahydroimidazo-[4,5-d]-imidazolidione-2,5 - multifunctional compound, V which urea fragment, actually, defines properties molecules, conditioned presence two reactionary centers V structure: four donor NH groups And two acceptor C=O groups.

As a rule, synthesis tetrahydroimidazo-[4,5-d]-imidazolidione-2,5 is carried out by condensation of 1, 2 - dicarbonyl connections With urea V presence aggressive mineral And organic acid (H_2SO_4 , H Cl and CF_3COOH , $HCOOH$) and alkaline catalysts. Besides that, the main Part processes receipt glycolurils is being carried out V or-

ganic solvents (Kravshenko, A.N., 2018; Li, J.-T., 2010).

Relatively recently V in a row works (30-32, 108, 109) established, What 1-hydroxyethylidenediphosphonic acid (OEDF) showed myself V quality convenient catalyst V 3-x component reactions heterocyclization V water. IN reactions were used carbonyl connections With active methylene group, ureas And aldehydes.

So OEDF - five-base acid With constants dissociations rK_α : 1.7, 2.47, 7.28, 10.29 And 11.13 for five steps respectively, decomposes at temperature about 250 °C, A V water

solutions decomposes at 140 °C (Pansuriua, A.M. 2009). In natural reservoirs OEDF subject to rapid decay under action ultraviolet, A products disintegration are used V quality fertilizers (Vilapara, K.V., 2019). OEDF With grounds forms salts (Savant, M.M. 2009; Bakibaev, A., 2020; Panshina, S., 2020). Unique complexing properties OEDF, contributed synthesis sets new organophosphorus connections and creation on their basis practically valuable substances V quality regulators contents calcium V in the body a person, bactericidal funds, inhibitors corrosion, auxiliary substances V oil production And thermal power engineering And etc.

In molecule OEDF two phosphonyl atom O(H) at both atoms phosphorus, A Also deputies O H And With H₃ at atom WITH located By both sides from specified higher planes. This circumstance minimizes repulsion between atoms H(O), H(C) And phosphonic atoms oxygen. Two groups PO₃ in the structure OEDF have eclipsed conformation relative to axes P - P. By in the opinion of the authors

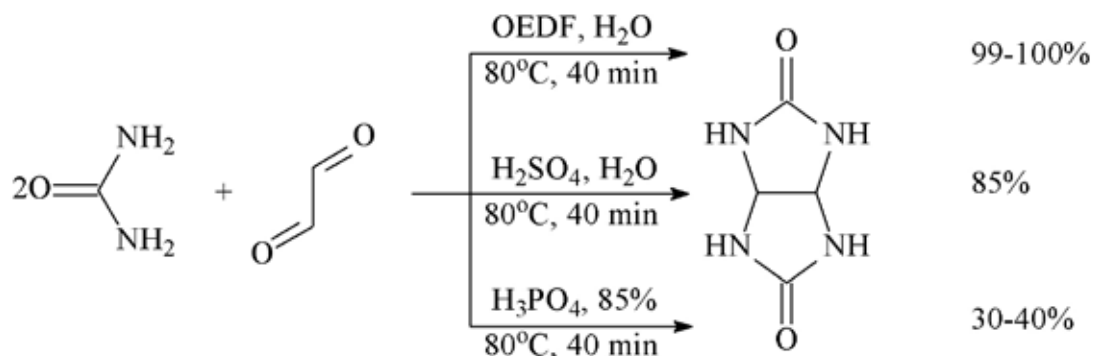
(Belykh, S.I., 2018), obscured con formation molecules, conditioned by presence deputies HE And Me at atom carbon and responsible for weaker acidity V OEDF.

Taking into account the above, we carried out a condensation reaction of urea with 1,2-dicarbonyl compounds in the presence of OEDP as a catalyst in the synthesis of tetrahydroimidazo-[4,5-d]-imidazolidione-2,5.

It is known, What V industrial conditions tetrahydroimidazole-[4,5-d]-imidazolidione-2,5 receive reaction condensation of glyoxal with urea in the presence of sulfuric acids with output 85% (Patent. 2439072).

Us for the first time carried out synthesis tetrahydroimidazo-[4,5-d]-imidazolidione-2,5 reaction condensation ureas With glyoxal in water in the presence of OEDP as “green” catalyst (Mysheletti, G., 2013).

In the course conducted research, by us established, What synthesis tetrahydroimidazo- [4,5-d]-imidazolidione-2,5 With using OEDF leaks for 50-60 minutes With practically quantitative yield of the target product:



The relationships were established components and time reactions. On first stage research We used ratio 1:0.5 (urea: OEDF), Where reaction it was over already on 10 minute With exit glycoluril 44%. Dropped out product tetrahydroimidazole-[4,5-d]-im-

idazolidione-2,5 at 10 minutes reactions was separated by filtering, A filtrate continued heat V flow 2 hours. By expiration time reactions general exit tetrahydroimidazo-[4,5-d]-imidazolidione-2,5 amounted to 87% (Table 1).

Table 1. Exit tetrahydroimidazole-[4,5-d]-imidazolidione-2,5 at various ratio ureas and OEDF

Time	Amount of OEDP, mol (ratios urea (urea , OEDF))			
	0.0005 (1:0.25)	0.001 (1:0.5)	0.002 (1:1)	0.004 (1:2)
10 minutes	35%	44%	61%	66%
120 minutes	79%	87%	99%	97%

Next at working off moths ratios quantities OEDF (table 2.1) was established, What the greatest exit tetrahydroimidazole-[4,5- d]-im-

idazolidione-2,5 (99%) V reactions bicyclization achieved at use relation 1: 1 urea to OEDF respectively.

At use 1 equivalent OEDF V synthesis tetrahydroimidazole-[4,5-d]-imidazolidione-2,5 was established, what already on 40 minute was highlighted product tetrahydroimidazole- [4,5- d]-imidazolidione-2,5 With exit 99%, A at hourly duration tetrahydroimidazole-[4,5-d]-imidazole-2,5 dione process was received With quantitative yield (100%).

Was established, what at long-term heating reactionary masses synthesis tetrahydroimidazole-[4,5-d]-imidazolidione-2,5 V presence OEDF (more 2 hours) finished product yield decreases. In this case, the analysis of the solution revealed that, together with OEDP,

the filtrate contains products of a competitive reaction or rearrangement of tetrahydroimidazole- [4,5- d]-imidazole-2,5-dione.

Considering that the synthesis product and the initial reagents are corrosion inhibitors, the determination of the inhibitory properties was studied in a mixture without additional purification (Table 2). The effect of the concentration of tetrahydroimidazole-[4,5-d]-imidazolidione-2,5 (THID) in pure form and as a composition on the corrosion rate of grade Ct. 20 steel in 15% hydrochloric acid ($t = 60\text{ }^{\circ}\text{C}$; $\tau = 42\text{ hours}$).

Table 2. *The influence of TGID concentration on the corrosion rate of steel grade Ct. 20*

Concentration inhibitor, %	Corrosion rate g/ m ² ·hour	Degree protection, %
Without additives	13	–
0.2	6.5	95.0
0.4	4.7	96.4
0.6	4.1	96.8
0.8	2.0	99.0
1.0	1.4	99.6
1,2	2.4	97.6

The obtained inhibitor has limited solubility in gas condensate. When dissolved in a two-phase medium - gas condensate: water - an independent phase is released, which limits its use as an inhibitor of hydrogen sulfide corrosion.

TGID product was modified with the addition of diethylamine and was called TGID-SHO. Its effect on steel corrosion in hydrogen sulfide (Table 3) and carbon dioxide (Table 4) environments was studied.

Table 3. *The effect of TGID-SHO on the rate of steel corrosion in a hydrogen sulfide environment (strength grade D, T = 25-35 °C, hydrogen sulfide concentration – 2.5–3.0 g/l, gas condensate: water – 1:2, active substance – inhibitor 50%)*

Inhibitor	Concentration, mg /l	Time experience, hour	Corrosion rate, g/ m ² hour	Degree protection, %
Without inhibitor	–	12	1.15	–
TGID-SHO	100	12	0.048	95.1
TGID-SHO	300	12	0.013	98.9
TGID-SHO	500	12	0.015	98.7
Without inhibitor	–	24	0.92	–
TGID-SHO	200	24	0.042	96.6
TGID-SHO	500	24	0.018	98.1
Dodikor (standard)	100	24	0.055	95.0
Without inhibitor	–	48	0.25	–
TGID-SHO	100	48	0.010	93.8
TGID-SHO	300	48	0.008	96.8
Dodikor (standard)	100	48	0.009	96.4

Table 4. *The effect of TGID-SHO on the rate of steel corrosion in a carbon dioxide environment (strength grade D, T – 25-40 °C, Pso₂ -1.0 MPa, stirring)*

Inhibitor	Concentration, mg/l	Time experience, hour	Corrosion rate, g/m ² ·hour	Degree protection, %
Without inhibitor	–	20	3.7	–
TGID-SHO	100	20	0.132	96.29
Without inhibitor	–	40	3.8	–
TGID-SHO	100	40	0.17	96.46
Without inhibitor	–	60	3.5	–
TGID-SHO	100	60	0.138	96.01
Without inhibitor	–	80	3.4	–
TGID-SHO	100	80	0.138	95,94
I-1-A	200	80	0.3	91.17

As can be seen from the data of Table 3, TGID-SHO is an effective corrosion inhibitor for 24 hours, at a concentration of 500 mg/l, with the corrosion rate being 0.018 and the degree of protection being 98.7%, for 48 hours of dosing at 300 mg/l, the corrosion rate is 0.008 and the degree of protection is 96.8%.

Thus, the synthesized product is not inferior in terms of the degree of protection to the corrosion inhibitors imported from Russia “I-1-A” and from Germany “Dodacor”.

The influence of TGID-SHO concentration on the corrosion rate depending on temperature was studied.

Tables 5. *The effect of TGID-SHO on the corrosion rate in different waters depending on temperature, the experiment time is 24 hours*

Solution, % mass.	Corrosion rate	Degree protection, %	Corrosion rate	Degree protection, %	Corrosion rate	Degree protection, %
	g/ m ² h	T=20 °C	g/ m ² h	T=40 °C	g/ m ² h	T=60 °C
NaCl ÷ 25.0	0.042	–	0.99	–	25.80	–
NaCl+ TGID–SHO ÷ ÷ 25.0+0.5	0.0091	78.30	0.079	92.02	0.40	98.45
H ₂ SO ₄ ÷ 20.0	15.7	–	7.7	–	31.20	–
H ₂ SO ₄ + TGID–SHO ÷ ÷ 20.0+0.5	2.2	85.99	3.0	61.03	16.00	48.72
NaCl + H ₂ S ÷ 25.0 + saturated solution	0.23	–	0.94	–	3.10	–
NaCl + H ₂ S + TGID–SHO ÷ 25.0+ saturated p–p+1.0	0.02	91.30	0.072	92.34	0.099	96.81

As can be seen from the data in Table 5, TGID-SHO effectively protects steel from corrosion in aqueous solutions of NaCl and NaCl + H₂S, showing stability with an increase in temperature to 60 °C. At the same time, in a 20% aqueous solution of H₂SO₄, the efficiency decreases with an increase in temperature.

THID was also modified by adding formaldehyde, urea, gossypol resin, copper salts in the ratio: THID: formaldehyde: urea: gossypol resin = 0.6: 0.1: 0.29: 0.01 (the conventional name of this composition is THID – extra).

TGID and TGID - extra was studied ; the results for determining the volatility of the samples are presented in Table 6.

Table 6. Results for determination of sample volatility

Name samples	Load , g	Weight loss, g, after 5 hours.	Weight loss, g, after 25 hours
TGID	1.96	0.81 (41%)	0.97 (49.5%)
TGID -extra	2.6	0.29 (11%)	0.38 (14.6%)

Table 6 shows that the analyzed reagents (except for TGID - extra concentrate) have high volatility. Removal of the solvent from the reagent “TGID - extra” allowed us to obtain a homogeneous stable reagent, the volatility of which did not exceed 0.2%.

The studies of the inhibitory effect of “TGID - extra” were carried out by express determination on metal samples of steel grade St. 20.

The inhibitor concentration was 400 mg/l. The study time was 24 hours, at room temperature in two-phase systems gas condensate - saline solution, oil - saline solution and in saline solution. The analyzed systems were saturated with hydrogen sulfide for 15 minutes.

The results of the inhibitory effect of the “TGID - extra” test on metal plates St.20 are presented in Tables 7 and 8.

Table 7. Results of the inhibitory effect of the TGID sample, inhibitor concentration 1% by weight

No.	Terms and Conditions experience	Average loss mass, gr.	Average corrosion rate g/m ² ·hour	Degree protection, %
	Without inhibitor	0.0255	0.03310	
1	Saline solution containing H2S + 70 ml gas condensate	0.004	0.00519	84.3
	Without inhibitor	0.012	0.01557	–
2	Saline solution containing H2S + 70 ml oil	0.0013	0.00143	89.2
	Without inhibitor	0.0107	0.13889	–
3	Saline solution containing H2S	0.0012	0.01493	89.3

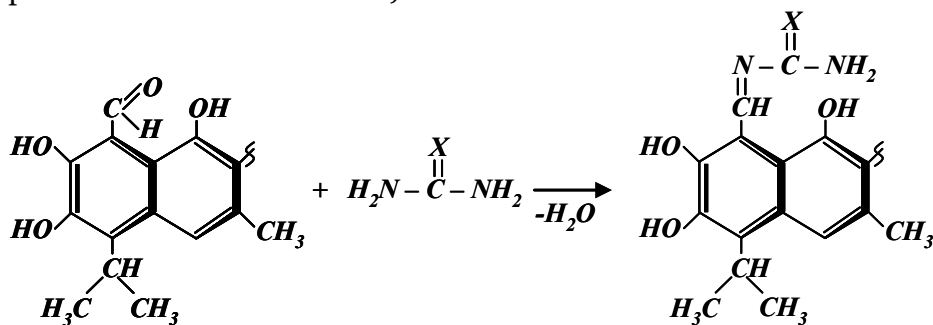
Table 8. Results of the inhibitory effect of the “TGID - extra” sample, inhibitor concentration 1% by weight

No.	Terms and Conditions experience	Average loss mass , gr .	Average corrosion rate g/m ² ·hour	Degree protection, %
	Without inhibitor	0.0031	0.3952	
1	Salt solution containing gas condensate: water 1:2 and H2S	0.0053	0.00365	90.7
	Without inhibitor	0.0051	0.196	
2	Salt solution containing gas condensate: water 1:2 and H2S + 70 ml of oil	0.0022	0.02791	85.8
	Control	0.001	0.01298	
3	Salt solution containing gas condensate: water 1:2 and H2S	0.0002	0.00128	90.1

In order to develop a universal hydrocarbon-soluble inhibitor, PKI-3 was improved by adding urotropine, gossypol resin, acrylic nitrile, formaldehyde, urea and copper salt in the ratios urotropine: gossypol resin: acrylic nitrile: formaldehyde: urea: copper salts = 0.5: 0.1: 0.09: 0.1: 0.2: 0.01 (the conventional name of this composition is “TGID - extra SHO”).

The inhibitor components were selected based on the following considerations: formaldehyde reacts with urea to form mono-, di-, tri- and tetramethylol derivatives.

Urea reacts with gossypol, which is present in gossypol resin, according to the following scheme:



The inhibitor “TGID - extra SHO” has a weak characteristic odor. It dissolves well in gas condensate and hydrocarbons. The main

indicators of the inhibitor “TGID - extra SHO” are given in Table 9.

Table 9. Physicochemical parameters of the inhibitor “TGID - extra SHO”

No.	Name indicators	Meaning
1	Amine number, mg HC l per 1 g of inhibitor, not less than	45.0
2	Protective capacity in water-hydrocarbon environment containing hydrogen sulfide, % not less than	90.0
3	Solubility: in gas condensate in the water	soluble disperses
4	Freezing point, °C not higher	minus - 35
5	Kinematic viscosity at 20 °C mm ² /s no more than	25
6	Dry residue , % not less	67
7	Density of inhibitor at 20 °C, g/cm ³ no more than	1.05

“TGID-extra SHO” was tested as a corrosion inhibitor in hydrogen sulfide, carbon

dioxide and hydrochloric acid environments (Tables 10–12).

Table 10. The effect of the inhibitor “TGID - extra SHO” on the corrosion of steel grade D in a carbon dioxide environment ($PCO_2 = 1.0$ MPa), room temperature

Concentration inhibitor, mg /l	Time experience, hour	Corrosion rate, g/m ² h	Degree protection, %
Without inhibitor	20	3.7	–
200	20	0.137	96.29
Without inhibitor	40	3.8	–
200	40	0.172	96.46
Without inhibitor	60	3.5	–

Concentration inhibitor, mg /l	Time experience, hour	Corrosion rate, g/m ² h	Degree protection, %
200	60	0.138	96.0
Without inhibitor	80	3.4	–
200	80	0.135	95.94
I-1-A standard, 200	80	0.3	91.17
400	80	0.2	94.12

Table 11. Protective action of the inhibitor “TGID - extra SHO” in a hydrogen sulfide environment. Temperature - room

Concentration of H ₂ S in gas condensate g/l	Concentration inhibitor , mg /l	Corrosion rate g/m ² hour	Degree protection , %
	Time 1 day		
	Without inhibitor	3.9	-
2.5 – 2.7	100	0.2	94.87
	250	0.31	92.05
	400	0.036	95.2
	Time 3 days		
	Without inhibitor	0.489	-
2, 9 – 3, 1	100	0,013	97.3
	250	0,011	97.9
	400	0,014	97.0

Table 12. Effect of temperature on the corrosion rate of C.3 in 15% hydrochloric acid. Concentration inhibitor 0.8% by weight

Solution salt acids	Corrosion rate g/m ² hour	Degree protection %
	Temperature room temperature , τ = 24 hours	
Without inhibitor	5.2	–
With inhibitor	1.3	75.0
	Temperature 40 °C, τ = 4 hours	
Without inhibitor	48	–
With inhibitor	0.6	99.0
	Temperature 60 °C, τ = 4 hours	
Without inhibitor	13	–
With inhibitor	2.0	98.0
	Temperature 80 °C, τ = 4 hours	
Without inhibitor	610	–
With inhibitor	2.0	99.6
	Temperature 100 °C, τ = 1 hour	
Without inhibitor	1020	–
With inhibitor	4.3	99.5

As can be seen from the obtained data, the inhibitor “TGID - extra SHO” in all cases shows high protection against corrosion.

Thus, the regularities of the urea condensation reaction with glyoxal have been established. It has been shown that during the con-

denation of carbamide with 1,2-dicarbonyl compounds in the presence of OEDP as a catalyst, a product based on tetrahydroimidazo-[4,5-d]-imidazolidione-2,5 was synthesized with a yield of 80–85%. The products obtained in pure form and in combination with some secondary reagents of the chemical industry were tested as corrosion inhibitors.

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