Inhibitory protection of steels in acid solutions under high-temperature corrosion conditions. A review. Part 3

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Abstract

Literature data concerning the protection of steels in acid solutions at elevated temperatures ($t \leq 200°C$) by organic nitrogen-containing heterocyclic compounds (NHCs) and formulations based on them are generalized. It is noted that individual NHCs are rarely efficient in steel protection in acid solutions at $t > 100°C$. However, composite inhibitors based on some of these compounds allows their protective effect to be expanded to $t = 200°C$ in certain cases. Data on the protection of various steels by composite inhibitors of this kind is discussed. The most outstanding results in the protection of low-carbon and chromium–nickel steels in high-temperature acid solutions are provided by formulations based on triazole derivatives, which effectively inhibit corrosion in mineral (HCl, H_2SO_4, H_3PO_4) and organic (acetic, formic, citric) acids. Problems related to the mechanism of the inhibitory effect of triazoles are discussed. It is shown that the possibility of providing steel protection at these high temperatures is due to the unique mechanism of the inhibitory action of triazoles that are chemisorbed on the metal surface and form a monomolecular layer strongly bound to the surface. Additional physical or chemical polymolecular adsorption of inhibitor molecules occurs on top of that layer, which significantly improves its protective properties. Generalization of data on the inhibitory protection of steels in high-temperature acid solutions with unsaturated organic compounds and NHCs, as well as an analysis of the mechanism of their action made it possible to formulate modern approaches to the creation of high-temperature inhibitors for acid solutions. The bibliography includes 137 sources.

Keywords: *high-temperature acid corrosion, steel, corrosion inhibitors, acidizing, hydrochloric acid, sulfuric acid, phosphoric acid, acetic acid, formic acid, citric acid, nitrogen-containing heterocyclic compounds, triazole, diazole, tetrazole.*

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I. Introduction

In the final part of our review we consider the most significant results achieved over the past decades in the field of inhibitory protection of steels in high-temperature acid solutions ($t \geq 80°C$) and related to studies of various azoles as corrosion inhibitors of steels in acid media. The preceding part of the review [1] generalizes the literature data on the protection of steels in acid solutions by unsaturated organic compounds (UCs) and formulations based on them at temperatures $t \leq 250$°C. It was noted that UCs themselves, *i.e.*, acetylenic compounds (ACs), unsaturated aldehydes, ketones and azomethines, are rarely efficient for steel protection in HCl solutions at $t > 100$°C. The creation of a mixed corrosion inhibitors (CIs) based on some of them sometimes makes it possible to expand the range of their protective action to $t = 250$°C.

Data on the protection of various steels by such CIs was discussed. It was noted that such CIs are most suitable for corrosive high-temperature HCl solutions. Issues related to the mechanism of the inhibitory effect of UCs were discussed. It was shown that the possibility of steel protection at these high *t* is a consequence of the inhibition mechanism of UCs that results from their ability to be chemisorbed on a metal surface and undergo deep chemical transformations to form a protective polymer film. This often leads to the formation of a protective polymer film. The factors that limit the use of formulations containing UCs were analyzed, including their instability in hot corrosive media over time and polymerization in the acid bulk that removes the inhibitor from the corrosive environment. Moreover, the UCs themselves and the additives used in combination with them are very toxic compounds.

In this review, nitrogen-containing heterocyclic organic compounds (NHCs) mainly represented by azoles will be considered as high-temperature CIs (HCIs). These compounds are, to a considerable extent, devoid of the drawbacks inherent in UCs in the protection of steels in mineral acid solutions. Not only the effect of NHCs on the corrosion process but also the possibility of improving their protective effect by creating mixed CIs on their basis will be considered. The analysis of modern concepts concerning the mechanism of metal protection by NHCs is important for the development of a scientific approach to the use of these compounds and creation of formulations based thereon.

Reference information on the possibility of using individual NHCs to protect steels from degradation in acid solutions in the oil and gas industry is given in recent reviews [2–4], but this information is limited to $t = 110$°C. So it does not fully meet the needs of modern production and does not reliably reflect the capabilities of this group of CIs which, in some cases, can efficiently slow down the corrosion of metals at $t \leq 200$°C.

The general issues of steel protection in acid solutions by NHCs were considered in review articles [5, 6]. Some specific features of the mechanism of their inhibitory action are also discussed there. In this review, priority is given to the generalization and analysis of issues related to the use of these CIs against the high-temperature corrosion of steels.

The group of HCIs that protect chromium–nickel steels in phosphoric acid solutions is narrow and they have a specific mechanism of action. It is represented by inorganic compounds that will also be briefly covered in our review.

In the first part of this review [7], we discussed the methodological and technical specifics of studying the corrosion of steels and their electrochemical behavior in acid solutions at elevated temperatures, both in the absence and in the presence of CIs. The chemical composition of steels discussed in this review is given in Table 1.

Table 1. Chemical composition of steels.

Steel brand	Content of elements, mass%
Steel 3	0.14–0.22 C; 0.15–0.33 Si; 0.40–0.65 Mn; up to 0.3 Cr; up to 0.30 Ni; up to 0.008 N; up to 0.30 Cu; up to 0.05 S; up to 0.04 P; up to 0.08 As; remainder Fe
Steel 5	0.28–0.37 C; up to 0.3 Si; 0.5–0.8 Mn; up to 0.05 S; up to 0.04 P; remainder Fe
Steel 10	0.07–0.14 C; 0.17–0.37 Si; 0.35–0.65 Mn; up to 0.15 Cr; up to 0.25 Ni; up to 0.25 Cu; up to 0.04 S; up to 0.035 P; up to 0.08 As; remainder Fe
Steel 20	0.17–0.24 C; 0.17–0.37 Si; 0.35–0.65 Mn; up to 0.25 Cr; up to 0.30 Ni; up to 0.30 Cu; up to 0.04 S; up to 0.035 P; up to 0.08 As; remainder Fe
Steel 45	0.42–0.50 C; 0.17–0.37 Si; 0.5–0.8 Mn; up to 0.25 Cr; up to 0.25 Ni; up to 0.25 Cu; up to 0.04 S; up to 0.035 P; up to 0,08 As; remainder Fe
Steel D	0.41–0.48 C; 0.17–0.37 Si; 0.65–0.90 Mn; up to 0.045 S; 0.045 P; 0.25 Cu; remainder Fe
Mild steel [18–21, 39, 40]	0.14 C; 0.35 Mn; 0.17 Si; 0.025 S; 0.03 P; remainder Fe
Mild steel [86]	0.13 C; 0.39 Mn; 0.18 Si; 0.04 S; 0.40 P; 0,025 Cu; remainder Fe
Carbon steel [76]	0.18 C; 0.25 Si; 0.42 Mn; 0.18 Cr; 0.22 Ni; 0.21 Cu; 0.02 S; 0.02 P; remainder Fe
Cold rolled steel [77]	0.07 C; 0.3 Mn; 0.022 P; 0.010 S; 0.01 Si; 0.030 Al; remainder Fe
N80	0.34–0.38 C; 0.20–0.35 Si; 1.45–1.7 Mn; up to 0.02 P; up to 0.015 S; up to 0.15 Cr; 0.11–0.16 V; remainder Fe
P110	0.26–0.395 C; 0.17–0.37 Si; 0.40–0.70 Mn; up to 0.020 P; up to 0.010 S; 0.80–1.10 Cr; up to 0.20 Ni; up to 0.20 Cu; 0.15–0.25 Mo; up to 0.08 V; remainder Fe
X80	0.064 C; 0.025 Si; 1.56 Mn; 0.013 P; 0.004 S; 0.01 Cu; 0.021 Cr; 0.056 Nb; 0.005 V; 0.025 Ti; 0.0006 B; remainder Fe
Kh18N9T	0.11 C; 9.66 Ni; 18.66 Cr; 0.57 Ti; remainder Fe
1Kh18N9T	17.57 Cr; 9.16 Ni; 71.92 Fe; 0.83 Ti; 0.52 Si
08Kh18N10T	0.08 C; 0.8 Si; up to 2 Mn; 9–11 Ni; up to 0.02 S; up to 0.035 P; 17–19 Cr; up to 0.3 Cu; up to 0.7 Ti; remainder Fe
12Kh18N10T	up to 0.12 C; up to 0.8 Si; up to 2 Mn; 9–11 Ni; up to 0.02 S; up to 0.035 P; 17–19 Cr; up to 0.3 Cu; up to 0.5 Ti; remainder Fe
Kh17N13M2T	up to 0.1 C; up to 0.8 Si; up to 2 Mn; up to 0.035 P; up to 0.02 S; 16–18 Cr; 12–14 Ni; up to 0.3 Cu; 2–3 Mo; up to 0.7 Ti; remainder Fe
Kh17N13M3T	up to 0.1 C; up to 0.8 Si; up to 2.0 Mn; up to 0.035 P; up to 0.02 S; 16–18 Cr; 12–14 Ni; up to 0.3 Cu; 3–4 Mo; up to 0.7 Ti; remainder Fe

II. Protection of steels in acid solutions by nitrogen-containing heterocyclic organic compounds

The first studies of NHCs as HCIs of steels in HCl solutions were carried out in the 1960s and dealt with pyridine derivatives [8]. It was shown that in the protection of steel 5 in 16% HCl (300 atm) by addition of 0.5% catapin A (*p*-alkylbenzylpyridinium chloride $[H_3C(CH_2)_nCH_2C_6H_4CH_2NC_5H_5]Cl$, where $n = 8–10$), with an increase in the acid temperature the corrosion inhibition coefficient passes through a maximum at 65°C (Figure 1). Under the same conditions, a mixture of polyalkylpyridines (I-1-A inhibitor, 1%) is characterized by a higher temperature of the maximum inhibitor efficiency toward steel 5. In individual form, both CIs turned out to be poorly efficient in steel protection at $t > 100$°C. However, their mixtures with urotropine satisfactorily inhibit metal corrosion at $t \leq 110$°C, though urotropine itself is inefficient under these conditions. The strongest protective effect is provided by the three-component formulation 0.4% I-1-A + 0.8% urotropine + 1% Na_2SO_4 that protects steel 5 up to $t = 130$°C, but no detailed information about its properties is reported in the article. A drawback of catapin A as a corrosion inhibitor noted in the article is that it undergoes decomposition due to hydrolysis in the acid solution.

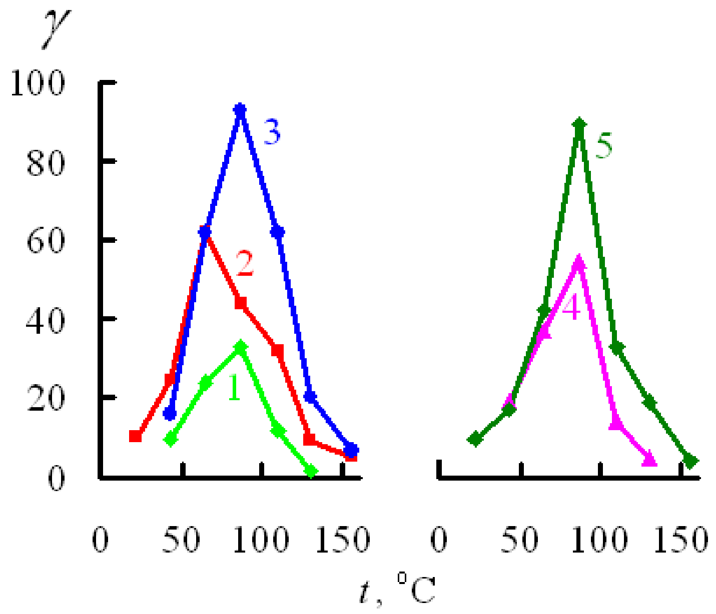
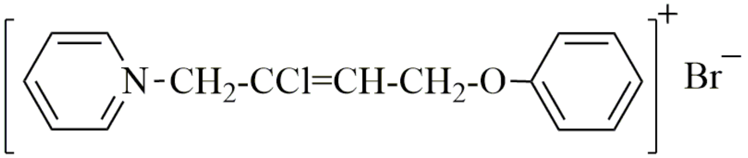
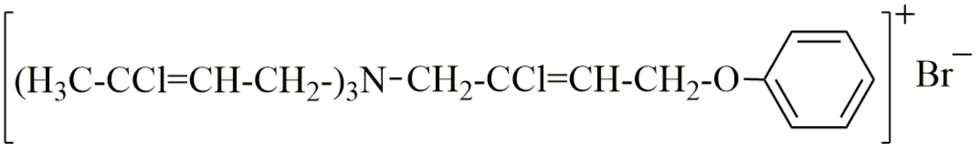


Figure 1. Steel corrosion inhibition factors for steel 5 in 16% HCl (300 atm) with addition of 1% urotropine (1), 0.5% catapin A (2), 0.5% catapin A + 0.5% urotropine (3), 1% I-1-A (4), 0.4% I-1-A + 0.8% urotropine (5).

Various pyridine derivatives protect steel 10 in 15% HCl (25–100°C) where the corrosion rate in the background solution is $k_0 = 5.7–2860$ g/(m^2·h) [9]. In the presence of 0.5% catapin K (*p*-alkylbenzylpyridinium chloride $[H_3C(CH_2)_nCH_2C_6H_4CH_2NC_5H_5]Cl$, where $n = 4–6$), the corrosion rate of steel is $k \leq 5.1$ g/(m^2·h). This parameter is worse in the case of the I-1-A inhibitor, $k \leq 6.3$ g/(m^2·h). It is interesting that 0.5% catapin K effectively slows down the corrosion of steel 10 ($k_0 = 59–230$ g/(m^2·h)) in 5–25% H_2SO_4 (80°C) to give $k \leq 3.0$ g/(m^2·h). In contrast, I-1-A weakly inhibits corrosion in this environment. In 5% HCl (100°C), addition of 0.5% catapin K slows down the corrosion of chromium–nickel steels Kh17N13M3T ($k_0 = 100$ g/(m^2·h)) and Kh17N13M2T ($k_0 = 114$ g/(m^2·h)) to $k = 12$ and 3.0 g/(m^2·h), respectively [10]. The corrosion of chromium–nickel steels is poorly inhibited by combinations of catapin K with urotropine. For example, for steel Kh17N13M2T in the presence of a formulation of 0.5% catapin K + 0.5% urotropine, $k = 4.8$ g/(m^2·h). Works [9, 10] do not report data on the protection of steels at $t > 100$°C, but catapin K and I-1-A decompose in acid solution in 5 days [9]. In hot acid solutions, these CIs will be less stable, so they cannot be efficiently used in high-temperature media. Other things being equal, pyridine derivatives inhibit corrosion more weakly than UCs with similar structures. In fact, in the case of steel 45 corrosion in 14% HCl at 100°C ($k_0 = 2020$ g/(m^2·h)), the following compound (1%)

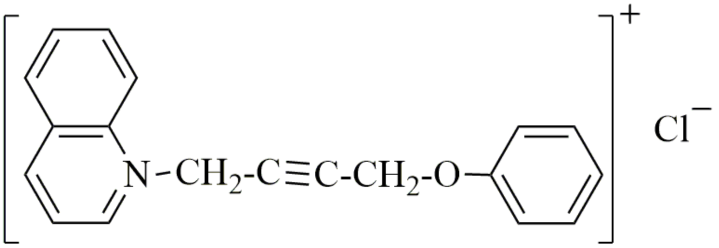


provides an inhibition coefficient of $\gamma = 77$, whereas an equal amount of



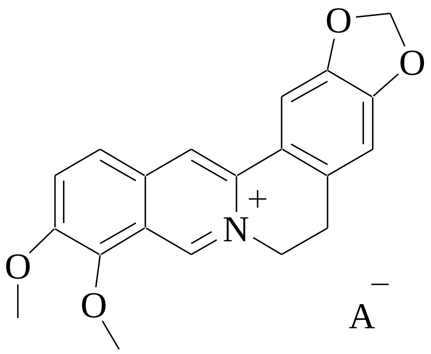
gives $\gamma = 326$ [11].

Along with pyridine derivatives, quinoline derivatives with bulky unsaturated substituents can be used to slow down the corrosion of low carbon steels in hot HCl [12–14]. For example, in the case of steel 3 corrosion in 14% HCl at 95°C ($k_0 = 2240$ g/(m^2·h)), the most efficient protection provided by



in the presence of which (1%) $k = 2.5$ g/(m^2·h).

The patent [15] provides data on the protection of steel P110 in 15% HCl (107°C) by formulations based on the berberine alkaloid:

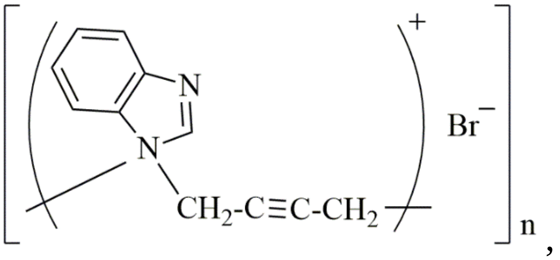


In fact, in the presence of a formulation of 0.7% crude berberine extract, 0.5% urotropine, and 0.36% H1I-1 24B™ CI enhancer (manufactured by Halliburton Energy Services, Inc., Houston, Texas), the k value is 37 g/(m^2·h), whereas in the presence of 0.5% urotropine and 0.36% of the CI enhancer, $k = 187$ g/(m^2·h).

NHC derivatives containing quaternized nitrogen are mainly used to protect steels in acids. Quaternary ammonium salts (QAS) are close to this group of compounds. However, their use in high-temperature environments, even in inhibitor formulations, does not give good results. In fact, in the presence of 3% HOSP-10 (an industrial CI), which is a mixture of QAS, a foaming agent and a synergist, steel D in 12% HCl (30 atm) at $t = 100$, 140, and 160°C gives $k = 128$, 705 and 1190 g/(m^2·h), which corresponds to the degree of protection $Z = 95.4$, 81.4 and 74.8%, respectively [16]. Thus, the presence of an NHC fragment in the structure of the organic cation should make it possible to protect steels by such a cation under high-temperature corrosion conditions.

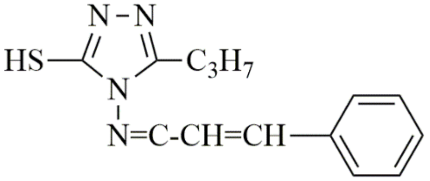
More detailed information on the use of six-membered NHCs for the protection of steels in high-temperature acids in individual form or in formulations based on them is not reported. This indirectly indicates that they are not promising as HCIs, though pyridine and quinoline derivatives are often added to HCI formulations based on UCs, as we discussed earlier [1]. Moreover, pyridine and quinoline derivatives are toxic, which strongly restricts their practical application.

Five-membered NHCs can serve as an alternative to six-membered NHCs for the protection of steels in hot acid solutions. In the earliest study, benzimidazole derivatives were studied as HCIs [17]. In 14% HCl (100°C) for steel 3 ($k_0 = 2080$ g/(m^2·h)) in the presence of the most efficient derivative (1%),



$k = 11$ g/(m^2·h). Later, M.A. Quraishi studied derivatives of 1,2,4-triazole [18, 19], 1-oxa-3,4-diazole [20], and thiazole [21] as CIs in hot HCl solutions.

In 15% HCl (105°C) for mild steel ($k_0 = 11150$ g/(m^2·h) in the presence of 5000 ppm N-cinnamylidene-3-propyl-5-mercapto-1,2,4-triazole-4-amine



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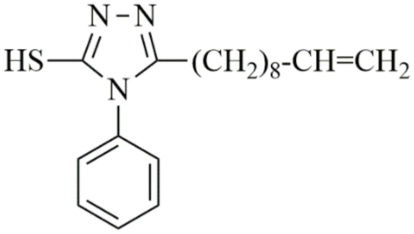
$k = 49$ g/(m^2·h), which is higher than with an equivalent (by weight) addition of the well-known acetylenic HCI, *viz*., propargyl alcohol (PA) ($k = 33$ g/(m^2·h)) [18]. The following compound provides poorer steel protection:



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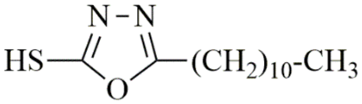
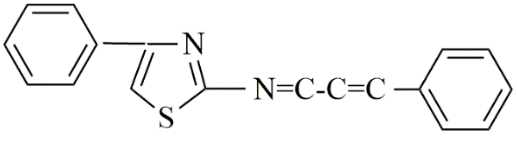
In boiling 15% HCl (105°C), addition of 5000 ppm of this compound decreases the k of mild steel ($k_0 = 12800$ g/(m^2·h)) to 488 g/(m^2·h) [19].

The most efficient 1-oxa-3,4-diazole derivative, namely, 2-undecyl-5-mercapto-1-oxa-3,4-diazole (5000 ppm), in 15% HCl provides $Z = 72\%$ for cold rolled mild steel and $Z = 92.6–94.5\%$ for steel N80, depending on the duration of corrosion tests [20].



Structurally similar compounds, 2-heptadecenyl-5-mercapto-1-oxa-3,4-diazole and 2-decenyl-5-mercapto-1-oxa-3,4-diazole containing unsaturated hydrocarbon radicals, are inferior to it in the protective action. Substituted thiazole (2000 ppm)



in 15% HCl (105°C) on mild steel ($k_0 = 11150$ g/(m^2·h)) reduces k to 202 g/(m^2·h), which is significantly lower than that provided by 2000 ppm PA ($k = 8490$ g/(m^2·h)) [21]. The CAHMT inhibitor (the composition is not disclosed) [22] also deserves attention. It contains an azomethine bond conjugated with a C=C group, a heterocycle containing three nitrogen atoms, and a sulfide group. The CI developers position it as "environmentally friendly". At C_{in} up to 5000 ppm, it reduces the k of N80 steel in 15% HCl (105°C) to 102 g/(m^2·h)

($Z = 98.4–99.2\%$), but parallel studies show that the same amount of PA slows down the corrosion better and allows one to reach a minimum rate of about 40 $g/(m^2 \cdot h)$.

Information on the protection of steels by derivatives of five-membered NHCs considered above is limited to $t = 105°C$, which does not allow us to fully understand the feasibility of their application at higher temperatures. All of these compounds, except for 2-undecyl-5-mercapto-1-oxa-3,4-diazole, are modified by substituents comprising unsaturated carbon–carbon bonds. This feature of their structure indicates that the high efficiency of CIs in inhibiting the corrosion of steels in hot HCl solutions will be largely due to the formation of a polymer film on the steel surface upon deep chemical conversion of these compounds on the steel surface [23, 24]. It should be understood that the presence of unsaturated bonds in their structure will give them the main disadvantage inherent in UCs, *i.e.*, low stability in hot acid solutions that eliminates the CI from the corrosive environment. Moreover, it is known that UCs are efficient only in HCl solutions but not in other mineral acids (H_2SO_4, H_3PO_4, and $HClO_4$). All these factors can significantly limit the practical application of these compounds as HCIs.

From our point of view, NHC derivatives containing substituents without unsaturated carbon–carbon bonds, which should increase their chemical and thermal stability, are more promising as HCIs. Triazoles should be used as a basis for creating such HCIs. It is well known [25] that triazole rings can be chemically and thermally stable. An important property of triazoles is their ability to form strong complex compounds with metal cations, including iron [26–31]. This property indirectly indicates the ability of compounds containing a triazole moiety to chemically bind to steel surface through it, which should favor the most durable retention of such a CI on the metal. It is interesting that interaction of substituted triazoles with metal cations often results in polynuclear polymeric complex compounds with various structures in which they act as bidentate bridging ligands that bind metal cations, including Fe(II) [26–28]. If such structures are formed from triazole and Fe(II) cations on steel and they are strongly bound to its surface, efficient protection of the metal in corrosive media can be anticipated.

Indeed, 1,2,4-triazole derivatives efficiently protect steel in hot acid solutions. For example, 5 mM of 4-substituted 1,2,4-triazole (IFKhAN-96) in 2 M HCl (95°C) slows down the corrosion of steel 3 ($k_0 = 1031$ $g/(m^2 \cdot h)$) by a factor of 69 [32]. Under the same conditions, an industrially produced QAC, catamine AB (alkylbenzyldimethylammonium chloride $[C_nH_{2n+1}N^+(CH_3)_2CH_2C_6H_5]Cl^-$, where $n = 10–18$), slows down the corrosion only 24-fold. The temperature maximum of IFKhAN-96 efficiency is about 80°C, which formally allows us to consider it as an HCI. As a disadvantage of this CI, it may be noted that it strongly accelerates steel corrosion at $t > 80°C$ compared to lower temperatures. The corrosion of steel 3 is significantly hindered by IFKhAN-94, which is a 3-substituted 1,2,4-triazole [33]. At its $C = 5$ mM in 2 M HCl (95°C), k decreases 93-fold, but the temperature maximum of its efficiency also lies at temperatures close to 80°C. Along with the corrosion inhibition in HCl solutions, IFKhAN-94 efficiently inhibits the corrosion of steel 3 ($k_0 = 1033$ $g/(m^2 \cdot h)$) in 2 M H_2SO_4 (95°C), providing an inhibition coefficient of $\gamma = 610$. In the same environment, 5 mM catamine AB protects steel 3 much worse ($\gamma = 63$). Unfortunately, these CIs do not offer equally high protective effects in H_3PO_4. In 2 M H_3PO_4 (95°C) for steel 3 ($k_0 = 519$ g/(m^2·h)) in the presence of these CIs, $\gamma = 2.6$ and 3.1, respectively. IFKhAN-93, a 3-substituted 1,2,4-triazole, is efficient in the protection of steel 3 in hot solutions of HCl and H_2SO_4, but it was studied only up to $t = 80$°C [34].

Along with 1,2,4-triazole derivatives, the protection of steels in hot acid solutions is provided by some tetrazole derivatives [35]. For example, IFKhAN-95, a 5-substituted tetrazole, inhibits the corrosion of steel 3 111- and 103-fold in 2 M HCl and H_2SO_4 (95°C), respectively. It is interesting that lower molecular weight tetrazoles such as 5-phenyltetrazole and 5-(2-dimethylaminoethyl)tetrazole provide $\gamma \leq 4.6$ even at $t \leq 80$°C. In both acids in the selected *t* range of 25–95°C, the maximum of CI efficiency was not reached, indicating that it lies no lower than at 95°C. This is typical of HCIs.

Table 2. Corrosion rates (*k*, g/(m^2·h)) and corrosion inhibition coefficients (γ) of steel 20 in 2 M HCl with addition of an IFKhAN-92 + urotropine mixture at various temperatures.

Inhibitor	**Test duration**					
	0.5 h		**1.0 h**		**2.0 h**	
	***k*, g/(m²·h)**	**γ**	***k*, g/(m²·h)**	**γ**	***k*, g/(m²·h)**	**γ**
0°C						
10 mM IFKhAN-92 + 10 mM urotropine	0.14	28.6	0.11	22.7	0.08	23.8
20°C						
10 mM IFKhAN-92 + 10 mM urotropine	0.24	40.8	0.14	63.6	0.10	56.0
40°C						
10 mM IFKhAN-92 + 10 mM urotropine	0.34	110	0.27	119	0.25	113
60°C						
10 mM IFKhAN-92 + 10 mM urotropine	0.98	93.1	0.91	92.9	0.86	96.5
80°C						
10 mM IFKhAN-92 + 10 mM urotropine	2.86	140	2.40	165	1.66	224
100°C						
10 mM IFKhAN-92 + 10 mM urotropine	10.5	148	8.1	188	7.1	197
10 mM IFKhAN-92 + 20 mM urotropine	10.3	150	8.2	185	8.0	175
120°C						
5 mM IFKhAN-92 + 10 mM urotropine	19.5	255	16.0	259	17.8	–
10 mM IFKhAN-92 + 10 mM urotropine	19.5	255	15.9	261	17.1	–
20 mM IFKhAN-92 + 20 mM urotropine	16.0	312	12.6	329	17.0	–

Inhibitor	**Test duration**					
	0.5 h		**1.0 h**		**2.0 h**	
	***k*, g/(m^2·h)**	**γ**	***k*, g/(m^2·h)**	**γ**	***k*, g/(m^2·h)**	**γ**
140°C						
10 mM IFKhAN-92 + 10 mM urotropine	298	27.0	211	–	144	–
20 mM IFKhAN-92 + 20 mM urotropine	130	62.0	101	–	109	–
20 mM IFKhAN-92 + 100 mM urotropine	49.6	163	65.0	–	68.9	–
160°C						
20 mM IFKhAN-92 + 100 mM urotropine	248	50	284	–	393	–

The most promising results in the protection of steels in hot acid solutions are shown by IFKhAN-92, a 3-substituted 1,2,4-triazole. IFKhAN-92 itself efficiently inhibits the corrosion of steel 20 in 2 M HCl at $t \leq 100$°C (Figure 2), thus significantly surpassing catamine AB [36]. From a practical point of view, formulations of IFKHAN-92 with urotropine that slow down the corrosion of steel at $t \leq 160$°C (Table 2) are important. Formulations of IFKhAN-92 with urotropine inhibit the corrosion of steel 20 in HCl solutions in a wide range of HCl concentrations, $C_{\mathrm{HCl}} = 2–6$ M (Table 3). At the same time, urotropine itself has little effect on the corrosion in hot HCl solutions. In the absence of a CI, the corrosion rate of the samples decreases with exposure due to consumption of the acid in the reaction with iron. In contrast, it often increases in inhibited solutions. However, even at 160°C the *k* values obtained in 0.5- and 2-hour tests differ only 1.6-fold.

Table 3. Corrosion rates (*k*, g/(m^2·h)) and corrosion inhibition coefficients (γ) of steel 20 in 4 and 6 M HCl with addition of an IFKhAN-92 + urotropine mixture at various temperatures.

Inhibitor	**Acid**	**Test duration**					
		0.5 h		**1.0 h**		**2.0 h**	
		***k*, g/(m^2·h)**	**γ**	***k*, g/(m^2·h)**	**γ**	***k*, g/(m^2·h)**	**γ**
100°C							
–	4 M	3380	–	3100	–	2720	–
	6 M	4970	–	4610	–	4020	–
10 mM IFKhAN-92 + 10 mM urotropine	4 M	12.1	279	8.7	356	17.0	160
	6 M	21.3	233	20.0	231	30.1	134
20 mM IFKhAN-92 + 20 mM urotropine	4 M	–	–	–	–	16.8	162
	6 M	–	–	–	–	30.0	134

Inhibitor	**Acid**	**Test duration**					
		0.5 h		**1.0 h**		**2.0 h**	
		***k*, g/(m^2·h)**	γ	***k*, g/(m^2·h)**	γ	***k*, g/(m^2·h)**	γ
10 mM IFKhAN-92 + 100 mM urotropine	4 M	12.7	266	8.3	373	13.3	205
	6 M	20.6	241	14.0	329	14.5	277
120°C							
–	4 M	6630	–	–	–	–	–
	6 M	9340	–	–	–	–	–
10 mM IFKhAN-92 + 100 mM urotropine	4 M	22.9	290	25.6	–	29.9	–
	6 M	43.7	214	51.5	–	60.4	–
140°C							
–	4 M	12000	–	–	–	–	–
20 mM IFKhAN-92 + 100 mM urotropine	4 M	129	93.0	146	–	166	–

A unique feature of formulations based on IFKhAN-92 is the ability to slow down the corrosion of steel in H_2SO_4 solutions at $t \leq 200°C$ [37]. IFKhAN-92 at $C = 20$ mM significantly inhibits the corrosion of steel 20 up to $t = 140°C$, whereas catamine AB does so only up to 100°C. Binary formulations of IFKhAN-92 with KI or KBr protect steel up to $t \leq 200°C$ (Table 4). An increase in the duration of corrosion tests does not lead to a significant acceleration of steel 20 corrosion, both in the presence of IFKhAN-92 itself and with binary mixtures. Though the protective effects of the IFKhAN-92 mixture with KBr are lower than with KI, this mixture is more promising for practice since it does not contain expensive KI. The high efficiency of the mixture of IFKhAN-92 with KI in the protection of steel 3 in 2 M H_2SO_4 ($t \leq 140°C$) was shown in [38].

It is important that no information on such efficient inhibitory protection of steels in high-temperature H_2SO_4 solutions is available in literature. In fact, according to M.A. Kuraishi [39], the macrocyclic compound 2,3,9,10-tetramethyl-6,13-dithia-1,4,5,7,8,11,12,14-octaaza-cyclotetradeca-1,3,6,8,10,13-hexaene (MTAH) deserves attention for steel protection in hot H_2SO_4 solutions. This CI (1000 ppm) provides $Z = 88.9\%$ in 20% H_2SO_4 (95±2°C) according to 10 min tests. Z reaches 99.3% only for the formulation of 500 ppm MTAH + 0.25% KI [40]. However, it is not clear from the article how an increase in the exposure time will affect the protective effect of this CI, which is very important for its practical use.

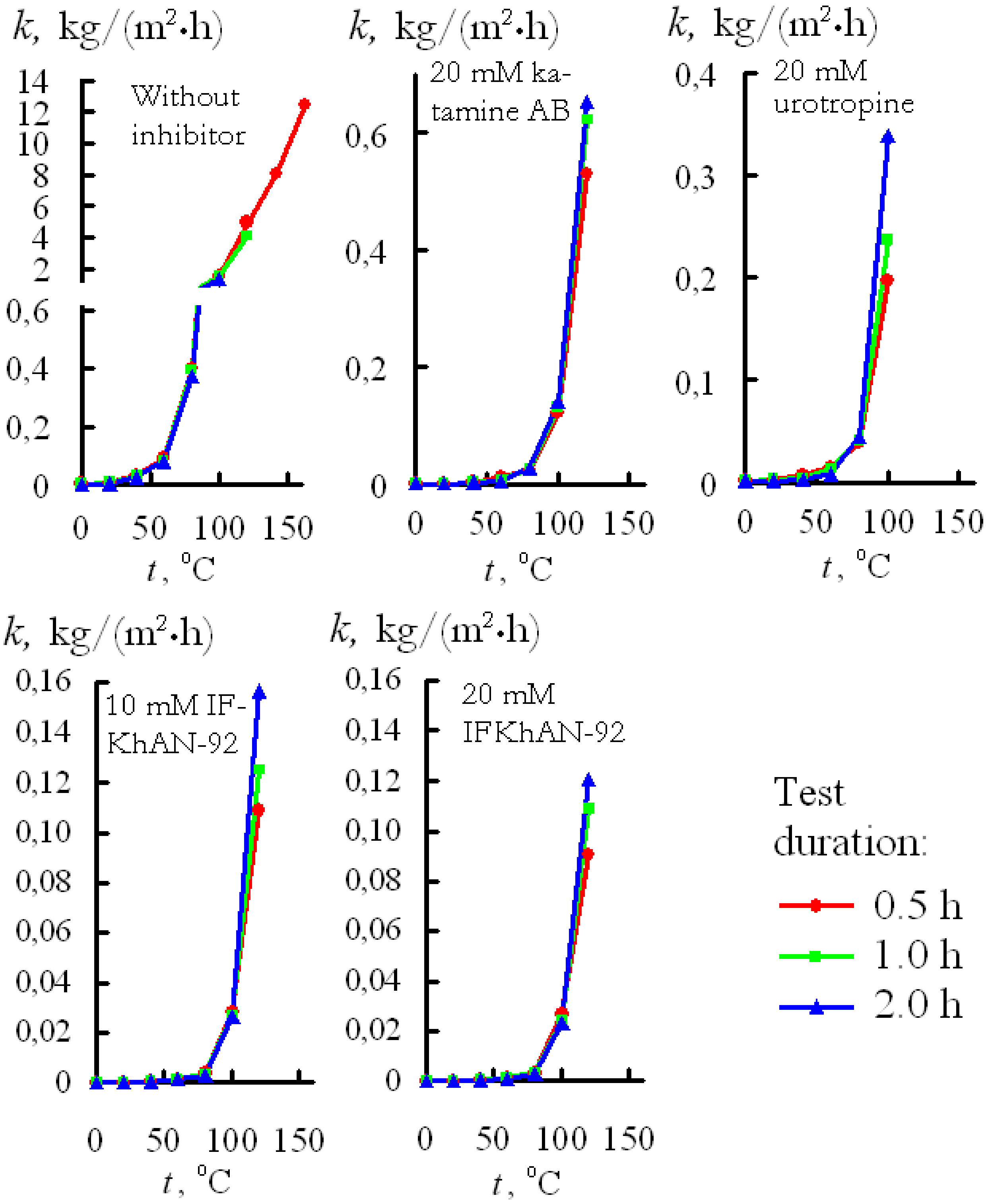


Figure 2. Corrosion rates of steel 20 in 2 M HCl.

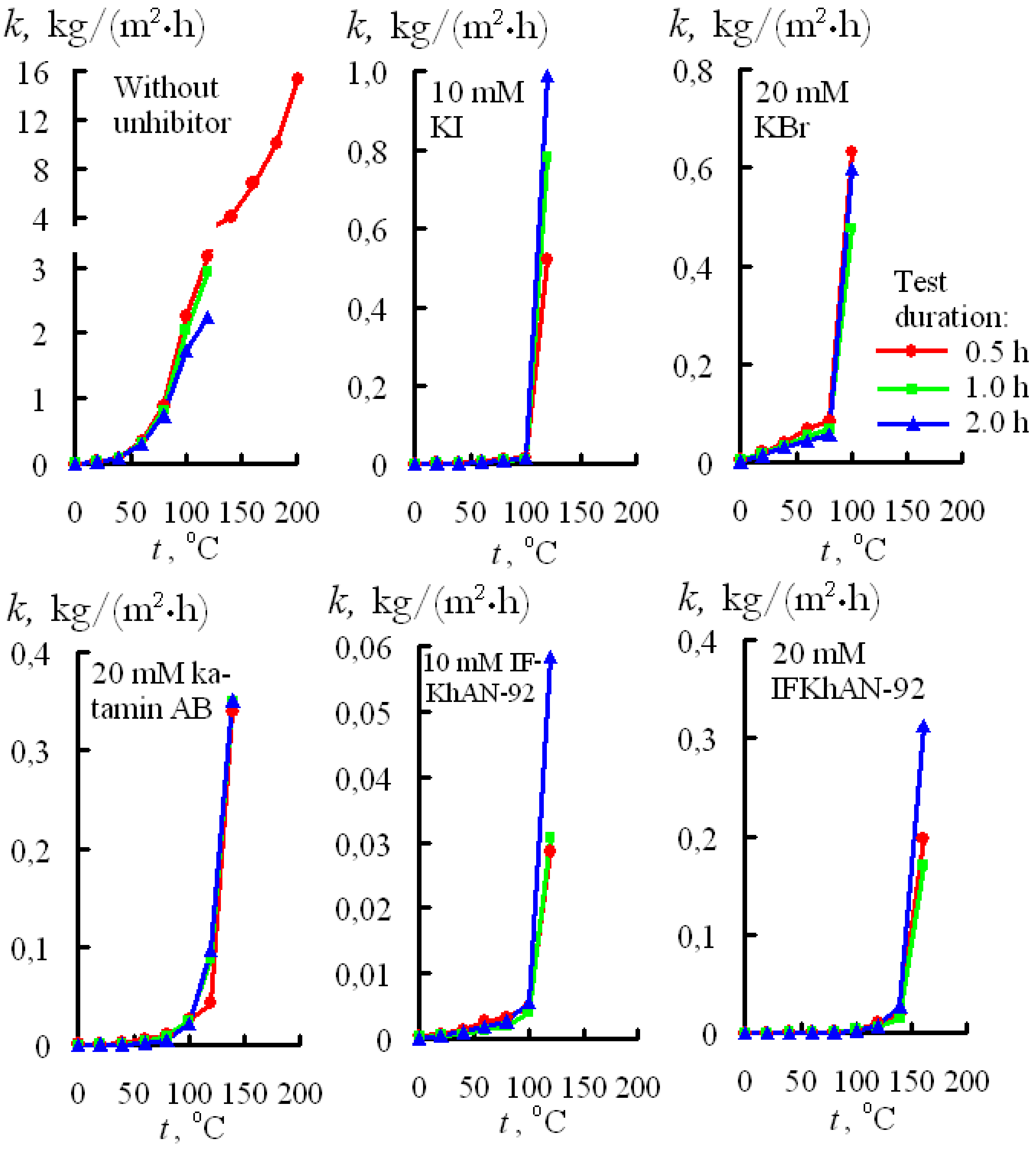


Figure 3. Corrosion rates of steel 20 in 2 M H_2SO_4.

Table 4. Corrosion rates (*k*, g/(m^2·h)) and corrosion inhibition coefficients (γ) of steel 20 in 2 M H_2SO_4 with addition of IFKhAN-92 based mixtures at various temperatures.

Inhibitor	**Test duration**					
	0.5 h		**1.0 h**		**2.0 h**	
	***k*, g/(m^2·h)**	**γ**	***k*, g/(m^2·h)**	**γ**	***k*, g/(m^2·h)**	**γ**
0°C						
5 mM IFKhAN-92 + 5 mM KI	0.21	45.2	0.12	95.8	0.09	95.5
10 mM IFKhAN -92 + 10 mM KBr	0.36	26.4	0.31	37.1	0.20	43.0
20°C						
5 mM IFKhAN-92 + 5 mM KI	0.31	145	0.17	211	0.16	207
10 mM IFKhAN -92 + 10 mM KBr	0.52	86.5	0.41	87.8	0.31	107
40°C						
5 mM IFKhAN-92 + 5 mM KI	0.49	214	0.20	475	0.19	487
10 mM IFKhAN -92 + 10 mM KBr	0.88	119	0.70	136	0.58	159
60°C						
5 mM IFKhAN-92 + 5 mM KI	0.66	530	0.39	874	0.30	1050
10 mM IFKhAN -92 + 10 mM KBr	1.2	292	0.98	348	0.73	432
80°C						
5 mM IFKhAN-92 + 5 mM KI	0.81	1090	0.58	1440	0.53	1400
10 mM IFKhAN -92 + 10 mM KBr	1.8	491	1.4	596	1.5	495
100°C						
5 mM IFKhAN-92 + 5 mM KI	2.0	1130	1.4	1460	1.1	1580
10 mM IFKhAN -92 + 10 mM KBr	2.1	1080	1.7	1200	3.3	527
120°C						
5 mM IFKhAN-92 + 5 mM KI	2.6	1220	2.4	1220	1.8	1240
10 mM IFKhAN -92 + 10 mM KBr	3.7	854	2.1	1400	3.6	622
140°C						
5 mM IFKhAN-92 + 5 mM KI	4.5	898	3.2	–	2.7	–
10 mM IFKhAN -92 + 10 mM KBr	18.9	214	11.2	–	18.0	–

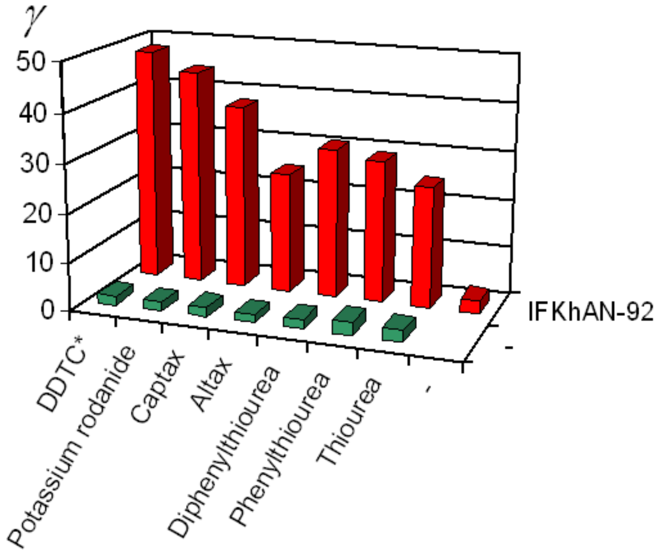
Inhibitor	**Test duration**					
	0.5 h		**1.0 h**		**2.0 h**	
	***k*, g/(m²·h)**	**γ**	***k*, g/(m²·h)**	**γ**	***k*, g/(m²·h)**	**γ**
160°C						
5 mM IFKhAN-92 + 5 mM KI	34.7	195	21.5	–	39.7	–
10 mM IFKhAN-92 + 5 mM KI	19.2	353	20.0	–	37.8	–
10 mM IFKhAN -92 + 10 mM KBr	52.9	128	54.8	–	162	–
20 mM IFKhAN -92 + 20 mM KBr	50.1	135	49.1	–	71.0	–
180°C						
10 mM IFKhAN-92 + 5 mM KI	75.5	134	78.4	–	125	–
20 mM IFKhAN -92 + 20 mM KBr	100	101	133	–	164	–
200°C						
10 mM IFKhAN-92 + 5 mM KI	78.4	195	119	–	160	–
20 mM IFKhAN -92 + 20 mM KBr	237	64.6	217	–	198	–

Stainless steels are most difficult to protect in acid solutions. The surfaces of these materials are heterogeneous in chemical composition, thus certain difficulties to the inhibition of the corrosion process are created. The corrosion of stainless steels in HCl solutions is hindered by IFKhAN-92 itself and the IFKhAN-92 + urotropine (molar ratio of components 1:1), IFKHAN-92 + KBr (1:9) and IFKHAN-92 + KNCS (4:1) mixtures. These formulations inhibit the corrosion of 12Kh18N10T chromium–nickel steel in 2 M HCl and 2 M H_2SO_4 ($t \leq 100$°C) [41, 42]. In solutions of these acids ($t \leq 100$°C) saturated with H_2S, binary formulations of IFKhAN-92 significantly reduce corrosion and, especially important, hydrogenation of 1Kh18N9T chromium–nickel steel [43, 44].

The three-component formulation of IFKhAN-92 + KI + urotropine (1:1:4) [45–47] is most efficient in the protection of chromium–nickel steels. This mixture efficiently inhibits the corrosion of 08Kh18N10T chromium–nickel steel in 2 M HCl at *t* up to 160°C, as well as in 2 M H_2SO_4 at *t* up to 180°C inclusive, and maintains the protective effect for at least 8 hours [45–47]. Along with chromium–nickel steels, the three-component HCI also protects low-carbon steels in the same *t* ranges in HCl and H_2SO_4 solutions, which proves its versatility.

The protection of steels in H_3PO_4 solutions by inhibitors is a complex task [48]. The generalized information on the inhibitory protection of steels in this environment presented in the review [49] refers exclusively to $t \leq 75$°C. The CIs used for the protection of steels in this acid are usually studied at temperatures close to room temperature, while the rare reported data corresponding to higher temperatures indicate a significant decrease in their protective effect under these conditions [50–59]. In view of this, data on the protection of low-carbon steel in H_3PO_4 solutions by the IFKhAN-92 inhibitor are of interest. It was shown [60] that 5 mM IFKhAN-92 weakly protects steel 3 in 2 M H_3PO_4 at 0–95°C ($k_0 = 2.4$–518 g/(m^2·h)), slowing down corrosion by a factor of 2.4–6.2. Modifying this CI by adding 0.5 mM KNCS allows the maximum k value in the range of $t = 0$–95°C to be reduced to 1.2 g/(m^2·h), while addition of 0.5 mM 2-mercaptobenzothiazole, to 1.1 g/(m^2·h). By themselves, these additives fail to inhibit the corrosion of steel satisfactorily in this environment. The temperature maximum of efficiency was not achieved for either of the composite CIs, as it is characteristic of HCIs.

Organic acids are yet another important group of corrosive process fluids. A deception exists that they are not capable of exerting significant corrosive effects on steels with which they come into contact and that inhibitory protection of metals is not required in these environments. It was clearly shown in the first part of our review [7] that an increase in t of these media significantly increases their corrosivity towards steels, making them unstable under these conditions. It should be noted that considerably fewer CIs are recommended for the protection of steels in organic acids than for mineral acid environments. There is but a narrow range of individual CIs that protect steels in hot organic acids. According to the data of 2-hour testing in 20% HCOOH (103±2°C), the following sulfur-containing compounds significantly inhibit the corrosion of mild steel ($k_0 = 405$ g/(m^2·h)) at 1000 ppm concentration: ditolylthiourea ($Z = 99.5\%$), 2-decenyl-5-mercapto-1-oxa-3,4-diazole ($Z = 99.6\%$), 3-heptadecenyl-4-phenyl-5-mercapto-1,2,4-triazole ($Z = 99.7\%$), 3-undecyl-4-phenyl-5-mercapto-1,2,4-triazole ($Z = 99.7\%$), and 3-decenyl-4-phenyl-5-mercapto-1,2,4-triazole ($Z = 99.8\%$) [39]. The range of CIs recommended for use in colder organic acids is mainly represented by NHCs. Literature sources report that mild steels can be protected in acetic acid solutions by aromatic nitrones [61], 3-alkyl-4-amino-5-mercapto-1,2,4-triazole (alkyl = methyl, ethyl, propyl and butyl) [62], 4-(N,N-dimethylamino)-benzylidineimino-3-propyl-5-mercapto-1,2,4-triazole, 4-benzylidineimino-3-propyl-5-mercapto-1,2,4-triazole, 4-salicylideneimino-3-propyl-5-mercapto-1,2,4-triazole, 4-cinnamalideneimino-3-propyl-5-mercapto-1,2,4-triazole [63], 3-heptadecenyl-4-phenyl-5-mercapto-1,2,4-triazole, 3-undecyl-4-phenyl-5-mercapto-1,2,4-triazole, 3-decenyl-4-phenyl-5-mercapto-1,2,4-triazole [64], ditetrazole derivatives [65], tetrahydro-1,2,4,5-tetrazine-3-thione derivatives [66], 5-alkyl-2-amino-1,3,4-thiadiazole (alkyl = methyl, ethyl and propyl) [67], and 1,2-alkane-bis-(ethyl ammonium bromide) [68]. Some of them also exhibit a protective effect in formic acid solutions [62, 63, 66, 67, 69]. In formic acid, the corrosion of steel is inhibited by phenylthiourea, tolylthiourea, diphenylthiourea [70], 5-heptadec-8-enyl-4-phenyl-4*H*-[1,2,4]triazole-3-thiol, 4-phenyl-5-undecyl-4*H*-[1,2,4]triazole-3-thiol, 5-dec-9-enyl-4-phenyl-4*H*-[1,2,4]triazole-3-thiol [71], 2-heptadecenyl-5-mercapto-1-oxa-3,4-diazole, 2-undecyl-5-mercapto-1-oxa-3,4-diazole, 2-decenyl-5-mercapto-1-oxa-3,4-diazole [72], alkanediyl-α,ω-bis(dimethylcetylammonium bromide) [73], undecenoic acid hydrazide, 1-undecyl-4-phenylthiosemicarbazide, and 1-decenyl-4-phenylthiosemicarbazide [74]. Experimental data on the protection of steels by these compounds in organic acid solutions were mainly obtained in cold environments or in solutions with a maximum temperature of 60°C, which does not allow one to judge on the prospects for the use of even the most efficient of them under high-temperature corrosion conditions. The industrial use of many of these CIs will be limited the instability of their protective effect over time and its loss with an increase in *t*. All this indicates that it is impossible to use these compounds in individual form for steel protection in H_3CCOOH and HCOOH solutions under high-temperature corrosion conditions. It might be more promising to create mixed inhibitors based on some of these compounds, primarily triazole derivatives, which might expand the temperature range of their application. We successfully demonstrated the feasibility of creating an HCI for H_3CCOOH and HCOOH solutions by combining substituted triazoles with compounds of various classes [75] for the protection of steel 20 in these media at temperatures up to 100°C. IFKhAN-92 alone poorly inhibits steel corrosion in H_3CCOOH solutions, but its combinations with small amounts (10:1) of hydrophobic sulfur-containing compounds, which themselves are also weak CIs in this medium, protect steels very efficiently (Figure 4). The best mixture, 5.0 mM IFKHAN-92 + 0.5 mM sodium diethyldithiocarbamate (DDTC), protects steel 20 in 2.0–6.0 M H_3CCOOH and HCOOH solutions at 20–100°C (Table 5, Figure 5). In the presence of this CI, the maximum values of *k* for steel 20 in H_3CCOOH and HCOOH solutions at $t \leq 100$°C are 1.0 and 2.5 g/(m^2·h), respectively. In the presence of the mixed CI, the *k* of steel 20 remains low over time even at $t = 100$°C. In both acids, a maximum of the corrosion inhibition coefficient of the CI in the *t* range studied is not achieved. This indirectly indicates that efficient metal protection can be achieved even at higher *t*.

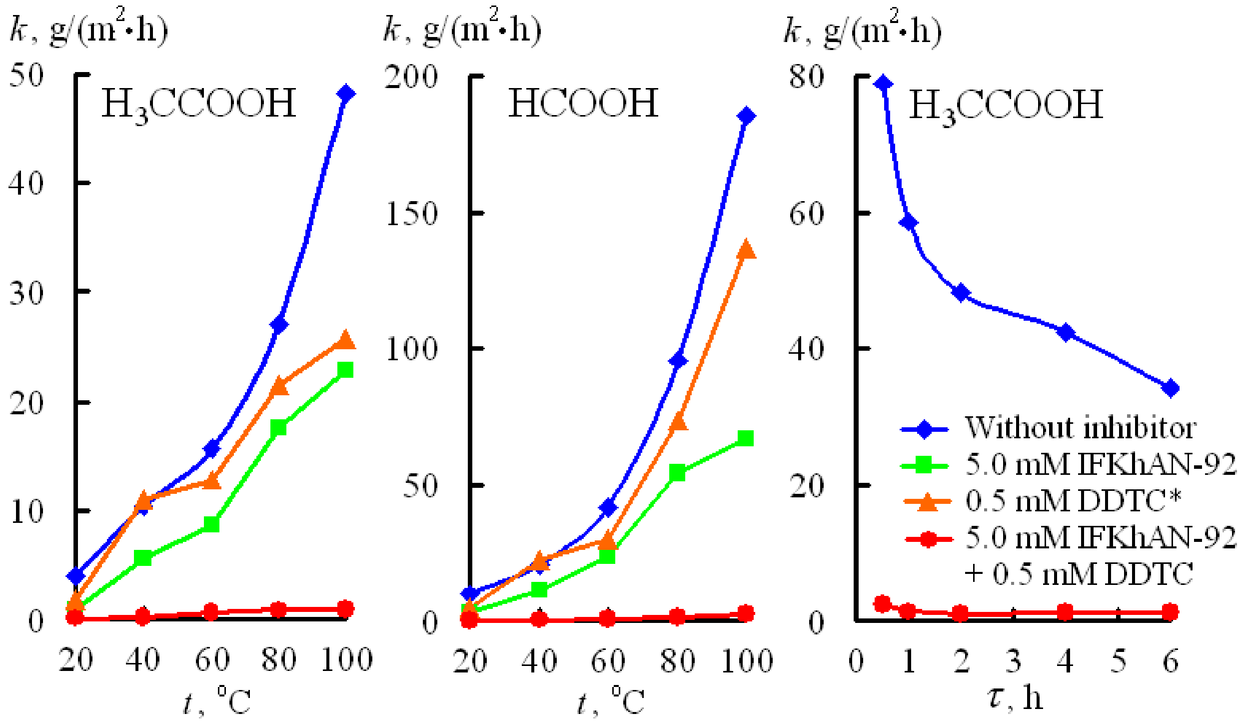


* DDTC - sodium diethyldithiocarbamate

Figure 4. Steel corrosion inhibition factors for steel 20 in 4.0 M H_3CCOOH ($t = 100$°C) by sulphur-containing compounds (0.5 mM) and their mixtures with 5.0 mM IFKhAN-92. Test duration – 2 h.

Table 5. Corrosion rates (k, g/(m^2·h)) and corrosion inhibition coefficients (γ) of steel 20 in H_3CCOOH and HCOOH solutions with addition of IFKhAN-92 + DDTC at t = 100°C. Test duration – 2 h.

Inhibitor	**Acid concentration**					
	2.0 M		**4.0 M**		**6.0 M**	
	***k*, g/(m²·h)**	**γ**	***k*, g/(m²·h)**	**γ**	***k*, g/(m²·h)**	**γ**
			H_3CCOOH			
–	31.7	–	48.1	–	42.9	–
5.0 mM IFKhAN-92	30.8	1.0	22.8	2.1	12.2	3.5
0.5 mM DDTC	12.1	2.6	25.8	1.9	24.6	1.7
5.0 mM IFKhAN-92 + 0.5 mM DDTC	0.81	39.1	1.0	48.1	0.89	48.2
			HCOOH			
–	109	–	185	–	226	–
5.0 mM IFKhAN-92	83.2	1.3	66.4	2.8	18.7	12.1
0.5 mM DDTC	88.4	1.2	137	1.4	187	1.2
5.0 mM IFKhAN-92 + 0.5 mM DDTC	1.1	99.1	2.5	74.0	1.3	174



* DDTC - sodium diethyldithiocarbamate

Figure 5. Corrosion rates of steel 20 in 4.0 M H_3CCOOH and 4.0 M HCOOH. t = 100°C.

The inhibition of steel corrosion in citric acid solutions has been studied insufficiently. To protect carbon steel in 4% citric acid, it was suggested to use 2-undecyl-*N*-carboxymethyl-*N*-hydroxyethyl imidazolium chloride (0.4%) which, according to voltammetry data, decreases the Z value from 89.2 to 84% upon a t increase from 20 to 95°C [76]. Weak protection of cold rolled steel in 0.2 M citric acid is provided by an extract of bamboo leaves, which is a "green CI" [77]. The effect of this CI strongly decreases with a t increase to 50°C. All the more interesting are the results on the protection of low-carbon steel in citric acid with a formulation of 4.5 mM IFKhAN-92 + 0.5 mM KNCS [78]. At 95°C, this CI formulation in 0.25–2.0 M citric acid slows down the corrosion of steel 3 ($k_0 = 57.4$–106 g/(m^2·h) by a factor of 133–185. In inhibited media, the k values of steel 3 are $k \leq 0.57$ g/(m^2·h). The maximum efficiency of the IFKhAN-92 + KNCS mixture is not reached in the t range studied.

Analysis of the results on the protection of steels in solutions of mineral acids by NHC derivatives shows that they have no prospects for this purpose in individual form. Even the most efficient of these CIs, *i.e.*, triazole derivatives, lose their protective capability rather quickly at $t > 100$°C. The best results in the protection of steels in acid environments can be obtained using mixed CIs based on NHC derivatives. The NHC derivatives used as the basis should contain a triazole ring. The triazole ring should be modified with various substituents that contain neither C=C nor C≡C bonds. Otherwise, the thermal stability of the CI in hot acid solutions will decrease and they will suffer many drawbacks typical of unsaturated organic CIs as we discussed in the second part of this review [1].

The protective effect of NHC derivatives on the corrosion of steels in mineral acid solutions can be enhanced and the temperature range of their efficiency can be expanded by combining these compounds with components of various nature. Urotropine is a versatile additive that improves the protective effect of NHC in HCl solutions. It is well compatible with pyridine derivatives (catapin A and I-1-A), but more interesting results can be obtained by using its combinations with substituted triazoles. In fact, a mixture of IFKhAN-92 and urotropine protects low-carbon steel in this environment up to $t = 160$°C. It is interesting that efficient protection of the metal with a mixture of IFKhAN-92 and urotropine, especially at high t, requires urotropine to be the main component, though it is significantly inferior to IFKhAN-92 in the inhibitive effect. Binary mixtures of IFKhAN-92 with alkali metal iodides or bromides make it possible to protect low-carbon steels in sulfuric acid environments up to $t = 200$°C. Alkali metal halides are widely used to enhance the action of organic CIs of various nature in acids [79], but only their combinations with triazoles make it possible to achieve such a good result. In solutions of H_3PO_4 and organic acids, where individual IFKhAN-92 is not a very efficient CI of steel, its effect can be improved considerably by combining it with relatively hydrophobic sulfur-containing compounds of molecular or anionic nature. The best results are provided by compounds of anionic nature, *viz*., KNCS and sodium diethyldithiocarbamate (DDTC).

Three-component formulations of triazole derivatives open wider prospects for the protection of steels in high-temperature acid solutions. The IFKhAN-92 + KI + urotropine mixture is a versatile CI that inhibits the corrosion of not only low-carbon steels but also chromium–nickel stainless steels that are very difficult for inhibitor protection. Three-component CIs containing a triazole derivative and urotropine are new and promising CIs of steels in highly corrosive acid media. As a rule, it is impossible to provide efficient protection of steels in mineral acid solutions containing an additional oxidizing agent, namely, Fe(III) salts [48, 80]. The combination of IFKhAN-92, urotropine and KNCS makes it possible to protect low-carbon steels in such environments at $t \leq 80$°C, which is a unique result [81, 82].

The successful application of composite CIs based on NHCs for the protection of steels in high-temperature acid solutions makes the mechanism of their action an urgent question. Understanding its features for these CIs is not only important for their practical use but also opens a way for creating more efficient new HCIs.

III. Mechanism of the protective action of nitrogen-containing heterocyclic organic compounds

When the mechanism of the protective action of UCs was discussed [1], we noted that the protection of steels in high-temperature acid solutions can be provided only by those compounds which are chemically adsorbed on the metal surface and then form a polymolecular layer in which CI molecules are bound to each other by chemical bonds, on top of the chemisorbed inhibitor monolayer. In the case of UCs, the possibility of their adsorption on a steel surface and formation of a polymolecular protective film is provided by the presence of unsaturated C≡C and C=C bonds in their structure. In NHC derivatives, a nitrogen-containing heterocycle will serve as such an active site. As discussed above and based on experimental data on the protection of steels in high-temperature acid solutions, it is most promising to use a triazole as such an active center. The thermal stability of NHC derivatives in high-temperature acid solutions is extremely important. Otherwise, the CI will undergo destruction in a corrosive environment and will be removed from it. This condition is clearly confirmed by a study on the thermal stability of IFKhAN-92 that protects steels at $t \leq 200$°C. Optical spectrophotometry data for IFKhAN-92 solutions in 2 M H_2SO_4 ($t \leq 200$°C) after exposure for 2 h show that the changes in the IR spectrum begin at $t = 180$°C, indicating its stability at lower temperatures [83]. The intensity of the characteristic signal of IFKhAN-92 decreases by only 7% at 180°C and by 15% at 200°C in 2 h. Note that the resinification of ACs, the well-known HCIs, begins at lower temperatures [84, 85]. In 4 M HCl (150°C) in 3 h, propargyl alcohol turns into a resinous product in 52% yield, while propargyl chloride does so in 70% yield.

The chemisorption interaction of a CI with a steel surface is a prerequisite that allows the CI to protect the metal under high-temperature corrosion conditions. This statement is clearly demonstrated by recent studies. It is believed that if the standard free adsorption energy of a CI ($-\Delta G_{ads}$) is less than 20 kJ/mol, then physical adsorption takes place. Only if ($-\Delta G_{ads}$)≥40 kJ/mol, one can state with high probability that the CI is chemisorbed. The ($-\Delta G_{ads}$) value of 2-[(*E*)-[5-methoxy-1-[4-(trifluoromethyl)phenyl]pentylidene]amino]-

oxyethanamine on mild steel in 1 M HCl is 15.2–21.4 kJ/mol, which indicates the physical nature of the interaction of the CI molecules with the metal surface. In the presence of 0.1 mM of this CI, an increase in t from 30 to 60°C increases Z from 94.4 to 95.1%, but a further increase in t decreases Z. At 90°C, $Z = 88.5\%$ [86]. Most likely, the physically adsorbed CI molecules are desorbed at $t > 60$°C, which impairs the metal protection. The maximum efficiency of this CI lies at $t = 60$°C, so we cannot consider it as an HCI. A similar result is observed for 2-methyl-9-phenyl-1,2,3,4-tetrahydroacridine and ethyl 9-phenyl-1,2,3,4-tetrahydroacridine-2-carboxylate whose $(-\Delta G_{\text{ads}})$ is slightly higher and amounts to 25.4–30.6 kJ/mol. On X80 steel in 15% HCl, both CIs (400 ppm) provide $Z = 96.1$ and 94.4% at 30°C, as well as 82.3 and 79.0% at 90°C, respectively [87]. The results of these studies that are rare due to the wide temperature range they cover show that the absence of a chemical bond between the CI molecules and the metal surface does not allow the CI to provide efficient protection of steels in hot acid solutions.

To understand the nature of the NHC interaction with steel surfaces in acid solutions, the data on their $(-\Delta G_{\text{ads}})$ require systematization. Though the literature available to us contains almost no estimates of NHC adsorption on steel from acid solutions by direct methods, there is plenty of data on the determination of $(-\Delta G_{\text{ads}})$ obtained by a less correct method, *viz*., from the results of measuring the mass loss of steel samples in inhibited acid solutions.

Generalization and analysis of the data on the adsorption of six-membered NHCs on steels in acid media showed that in most cases the observed values of $(-\Delta G_{\text{ads}})$ are insufficient to make an unambiguous conclusion about their chemisorption on a steel surface [6]. This is consistent with the conclusion made above that these compounds are unsuitable as a basis for creating HCIs.

Azole derivatives show more encouraging results. According to the data summarized in review [88], the values of $(-\Delta G_{\text{ads}})$ for various imidazo[1,2-*a*]pyridines on steels in acid solutions are close to or higher than 40 kJ/mol, which allows us to hope that they are chemisorbed on the metals. Our analysis of literature data (Table 6) shows that for some derivatives of imidazoles, triazoles, and tetrazoles, the calculated values of $(-\Delta G_{\text{ads}})$ reach or exceed the threshold value of 40 kJ/mol, which allows one to assume that the azoles are chemisorbed on steel. The data on the adsorption of azoles on steel measured by direct methods, *i.e.*, by a decrease in the capacitance of the double electric layer (DEL) of a steel electrode obtained using the electrochemical impedance spectroscopy (EIS) and by ellipsometry, become even more valuable in this context.

An EIS study of the adsorption of the IFKhAN-92 HCI indicates the chemisorption nature of the interaction between the molecules of this CI and the steel surface. At $t = 22$°C, the adsorption of IFKhAN-92 on cathodically polarized low-carbon steel is described by the Temkin isotherm, while $(-\Delta G_{\text{ads}})$ is 42 kJ/mol in 2.0 M HCl [102], 49 kJ/mol in 2.0 M H_2SO_4 [103], and 51 kJ/mol in 2.0 M H_3PO_4 [104]. It is important to note that the kinetics of IFKhAN-92 adsorption on low-carbon steel from solutions of mineral acids is described by the Roginsky–Zeldovich equation that characterizes chemisorption processes. As discussed earlier, IFKhAN-92 is inefficient in the protection of steels in 2.0 M H_3PO_4, but its combination with 0.5 mM KNCS can improve protection considerably. It was shown that addition of KNCS to 2.0 M H_3PO_4 does not affect the value of ($-\Delta G_{ads}$) of IFKhAN-92 on steel but accelerates its adsorption, as the kinetic adsorption isotherms clearly demonstrate (Figure 6) [104]. Apparently, this effect favors the accelerated formation of a protective CI layer on the metal surface that rapidly degrades in acid solutions, this providing the required protection. It should be noted that this is just one of the possible ways in which the KNCS additive can affect a corroding system.

Table 6. Free adsorption energies of substituted azoles on steels from acid media.

No.	Inhibitor	System	Standard adsorption free energy ($-\Delta G_{ads}$), kJ/mol	Adsorption isotherm	Ref.
		Imidazoles			
1	2-(2-Methyl-5-nitro-1H-imidazol-1-yl)ethanol]	0.5 M HCl (30–60°C). Mild steel	58.2–66.0	Temkin isotherm	[89]
2	5-((4,5-Dihydro-imidazol-2-yl) methyl)quinolin-8-ol	1 M HCl (25°C). Mild steel	40.3	Langmuir isotherm	[90]
3	2-(3-(Carboxymethyl)-1*H*-imidazol-3-ium-1-yl)acetate, 2-(3-(1-carboxyethyl)-1*H*-imidazol-3-ium-1-yl)propanoate, 2-(3-(1-carboxy-2-phenylethyl)-1*H*-imidazol-3-ium-1-yl)-3-phenylpropanoate	1 M HCl (35°C). Mild steel	37.0. 37.5. 37.6	Langmuir isotherm	[91]
4	2-(4-Chlorophenyl)-1,4,5-triphenyl-1*H*-imidazole, 1,4,5-triphenyl-2-(*p*-tolyl)-1H-imidazole	0.5 M H_2SO_4 (25°C). Mild steel	42.1. 41.7	Langmuir isotherm	[92]
5	1,3-Dioctadecylimidazolium bromide	1 M H_2SO_4 (room *t*). Mild steel SAE 1018	37.9	Langmuir isotherm	[93]

No.	Inhibitor	System	Standard adsorption free energy (–ΔG_{ads}), kJ/mol	Adsorption isotherm	Ref.
		Triazoles			
6	3,5-*Bis*(methylene octadecyl dimethylammonium chloride)-1,2,4-triazole	1 M HCl (25°C). Carbon steel	42.1	Langmuir isotherm	[94]
7	3,5-*Bis*(4-pyridyl)-4*H*-1,2,4-triazole, 3,5-*bis*(4-methylthiophenyl)-4*H*-1,2,4-triazole	1 M HCl (30°C). Mild steel	39.4 44.4	Langmuir isotherm	[95]
8	3,5-*Bis*(2-thienylmethyl)-4-amino-1,2,4-triazole	1 M HCl (30°C). Carbon steel	45.7	Langmuir isotherm	[96]
9	3,5-*Bis*(4-methoxyphenyl)-4-amino-1,2,4-triazole, 3,5-*bis*(4-chlorophenyl)-4-amino-1,2,4-triazole	2 M H_3PO_4 (30°C). mild steel	41.1 39.8	Langmuir isotherm	[97]
10	3,5-*Bis*(4-tolyl)-4-amino-1,2,4-triazole, 3,5-*Bis*(3,4-dimethoxyphenyl)-4-amino-1,2,4-triazole	2 M H_3PO_4 (30°C). Mild steel	39.8 40.0	Langmuir isotherm	[98]
		Tetrazoles			
11	(*E*)-3-(4-Hydroxyphenyl)-2-(1*H*-tetrazole-5-yl)acrylonitrile	1 M HCl (35–65°C). Mild steel	37.6–39.7	Langmuir isotherm	[99]
12	2,2′-*Bis*(4-nitrophenyl)-5,5′-diphenyl-3,3′-(3,3′-dimethoxy-4,4′-diphenylene)ditetrazolium chloride	0.5 M H_2SO_4 (25°C). Cold rolled steel	41	Langmuir isotherm	[100]
13	3,3′-(3,3′-Dimethoxy[1,1′-biphenyl]-4,4′-diyl)-bis(2,5-diphenyl-2H-tetrazolium) dichloride	1.0 M H_2SO_4 (20°C). Cold rolled steel	39.1	Langmuir isotherm	[101]

The chemisorptive interaction of triazoles with a steel surface in acid media is characteristic not only of low-carbon steels but also of chromium–nickel ones that are very difficult to protect by inhibitors. In fact, the values of (–ΔG_{ads}) for IFKhAN-92 on 12Kh18N10T steel calculated using the Temkin equation amount to 55±1 and 61±1 kJ/mol for 2.0 M HCl and 2.0 M H_2SO_4, respectively [105]. This result is in good agreement with the data of an ellipsometric study on its adsorption, according to which the $(-\Delta G_{ads})$ values on 12Kh18N10T steel in 0.005–0.05 M HCl and 0.05 M H_2SO_4 calculated from the Temkin isotherm are 55±3 kJ/mol [106].

Important additional information on the nature of binding of CI molecules with a steel surface can be obtained using quantum chemical methods. In recent years, more and more studies were appearing in which quantum-chemical calculations were used to explain the inhibitory effect of azoles [107–113]. A detailed analysis of the prospects of using quantum chemical methods for explaining the inhibitory action of organic compounds, including azoles, was carried out in the review [114], so this issue can be left outside the scope of our review.

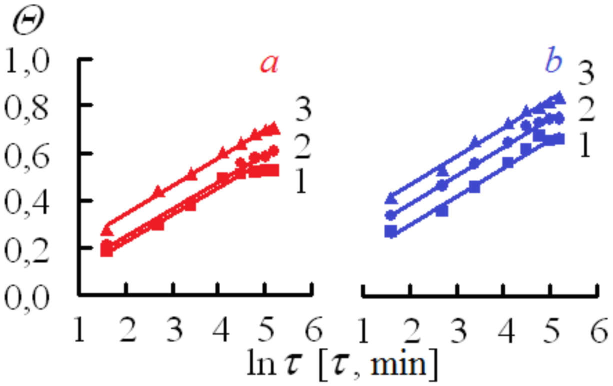


Figure 6. Dependence of the coverage of steel 3 surface with inhibitor (E = –0.30 V) on the logarithm of its adsorption time in 2 M H_3PO_4 (22°C) containing IFKhAN-92 (*a*) and its combination with 0.5 mM KNCS (*b*), with concentrations in μm: 1 – 2.5, 2 – 5.0, 3 – 10. Points – observed plots. Straight lines – theoretical plot for the Roginsky–Zeldovich equation.

To a considerable extent, the unique property of triazoles that gives them the ability to protect steels in high-temperature acid solutions is that they can form polymolecular protective layers from their molecules on the metal surface. X-Ray photoelectron spectroscopy (XPS) combined with argon ion etching of the object surface provides the most productive method for studying such surface layers. This XPS technique allows one to determine the qualitative and quantitative composition of not only the layers directly adjacent to its surface, but also the underlying sample layers that are inaccessible by ordinary methods. Our studies show that, according to XPS data, a 24 h exposure of steel 3 samples in 2.0 M HCl+5.0 mM IFKhAN-92 (20°C) results in the formation of a protective layer of the organic inhibitor 4 nm thick on the metal (no more than 4 monomolecular layers). Upon sixfold ultrasonic cleaning of the steel surface in distilled water (3 min each time), only a tentative inhibitor monolayer with a thickness of no more than 2 nm remains on the metal. The CI monolayer remaining on the steel surface at $t = 20–60$°C provides $Z = 88.9–96.4\%$. This value is slightly worse than that of the polymolecular CI layer ($Z = 94.9–98.8\%$) but high enough to confirm the chemisorptive nature of the CI interaction with the steel surface (Figure 7*a*). Thus, a polymolecular protective CI layer is formed on steel in this medium. It consists of its monolayer chemisorbed on the metal, on top of which there are layers of CI molecules bound to each other and to the chemisorbed layer by weaker physical interaction. Ultrasonic cleaning removes the physically sorbed molecules from the steel surface, leaving only a chemisorbed monolayer. In this case, the metal surface underlying the organic CI layer is oxidized to iron(III) oxide. A CI layer similar in structure and protective properties is formed in 2.0 M H_2SO_4+5.0 mM IFKhAN-92+5.0 mM KNCS (Figure 7b) but, despite the presence of KNCS in the inhibitor formulation, no thiocyanate anions are found in the protective layer [115]. Triazoles do not always form polymolecular layers on a metal being protected. In fact, IFKhAN-96 is adsorbed on steel surface from 2.0 M HCl (25°C) to form only a tentative CI monolayer chemically bound to the metal surface. Under a monolayer of the organic CI, there are phases of iron(II) chloride and oxide 4–7 nm thick that are directly adjacent to the metal [32].

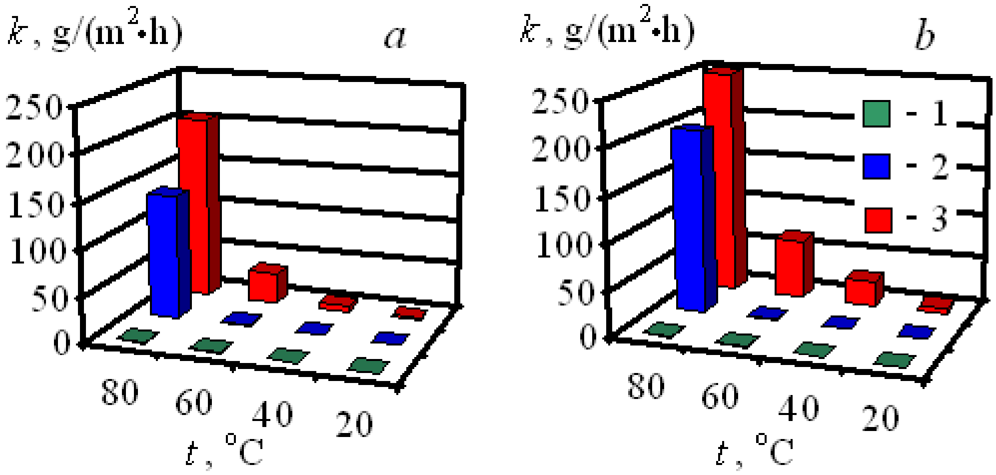


Figure 7. Protective after-effect of inhibitor layers formed at *t* = 20°C on the surface of steel 3 in 2 M HCl + 5 mM IFKhAN-92 (*a*) and 2 M H_2SO_4 + 5 mM IFKhAN-92 + 5 mM KNCS (*b*) in 2 M HCl (*a*) and 2 M H_2SO_4 (*b*) solution (2 h). 1 – samples after preliminary inhibitor adsorption (24 h), 2 – samples after preliminary inhibitor adsorption (24 h) followed by ultrasonic washing, 3 – samples without preliminary inhibitor adsorption.

The protective layers formed by IFKhAN-92 in phosphoric acid solutions have more complex structures [116]. During preliminary adsorption of a IFKhAN-92+KNCS mixture on steel surface from H_3PO_4 solutions, a chemisorbed protective layer more than 4 nm thick is formed, which presumably consists of a complex polymeric compound of IFKhAN-92 molecules, Fe(II) cations, and rhodanide anions (Figure 8). This layer is not removed from the steel surface during ultrasonic treatment and has a protective aftereffect in hot H_3PO_4 solutions, as we discussed in our review [48]. One can see that addition of KNCS not only accelerates the adsorption of the triazole on steel but can also participate in the formation of a protective layer of the organic inhibitor.

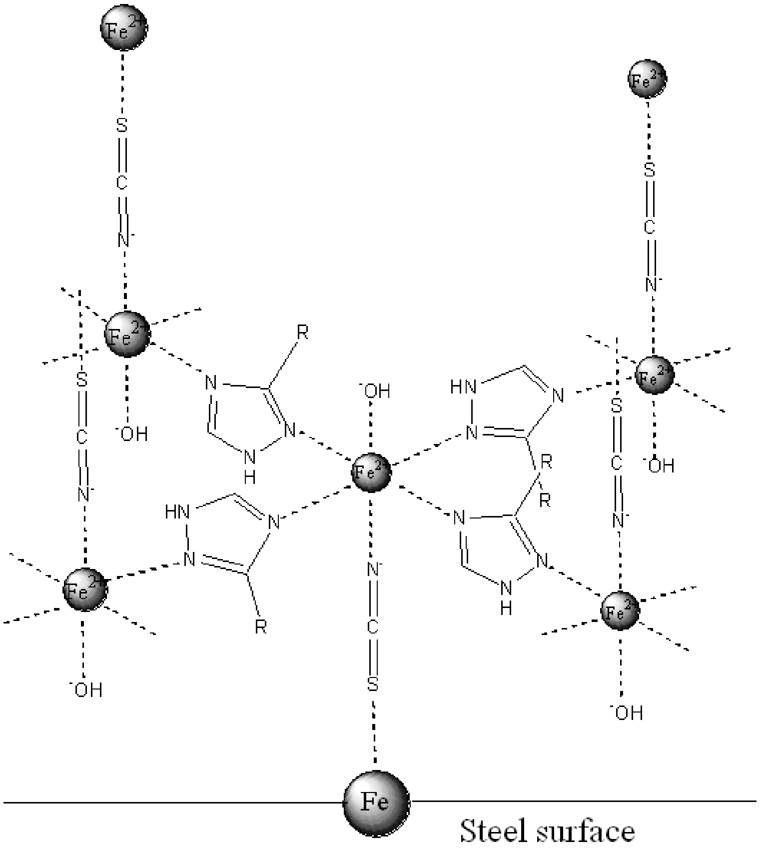


Figure 8. The assumed structure of the protective layer formed on steel 3 surface in 2 M H_3PO_4 + 5 mM IFKhAN-92 + 5 mM KNCS (25°C).

Protective polymolecular layers of IFKhAN-92 are formed not only on low-carbon steel but also on chromium–nickel steels. During preliminary adsorption of IFKhAN-92 on the surface of 12Kh18N10T steel, a polymolecular protective organic CI layer is formed from an HCl solution. It is chemically bound to the phase of Fe, Cr and Ni oxides and hydroxides adjacent to the metal phase [117, 118]. The lower part of the polymolecular protective layer of the organic CI consists of a polymer complex formed by IFKhAN-92 molecules, metal cations (Fe, Cr and Ni) and chloride anions, while the outer part consists of physically sorbed IFKhAN-92 molecules. Weakly bound CI layers are removed from the metal surface during its ultrasonic cleaning in an HCl solution. The CI layer remaining on the metal surface (about 3 monolayers) exhibits a protective aftereffect in 2 M HCl with *t* up to 80°C (Figure 9), which is evidence of the chemical nature of interaction of the organic CI within the layer of its complex polymer with the surface of the oxide–hydroxide phase. We noted the formation of structurally similar protective layers on chromium–nickel steels in case of its protection in H_2SO_4 solutions with composite CIs based on IFKhAN-92 [119].

Thus, an important property of triazole derivatives as CIs of steels in acid solutions is their ability to form polymolecular protective layers on a metal surface. A specific feature of these layers is that the underlying CI layer is chemically bound to the steel surface. Above this layer, there are layers of the organic CI whose molecules are bound either physically or chemically with each other. It is clear that the maximum protective effects will be provided by chemically bound CI layers. Experimental data indicate that organic CI layers consist of a polymer complex of triazole molecules and Fe cations (Cr and Ni in the case of chromium–nickel steels). In addition, the components of the triazole-based CI mixture (for example, thiocyanate anion) can be incorporated into the structure of the polymer complex, which ultimately strengthens the complex structure. It is the formation of such polymolecular layers that allows triazoles to provide efficient protection of steels in high-temperature acid solutions.

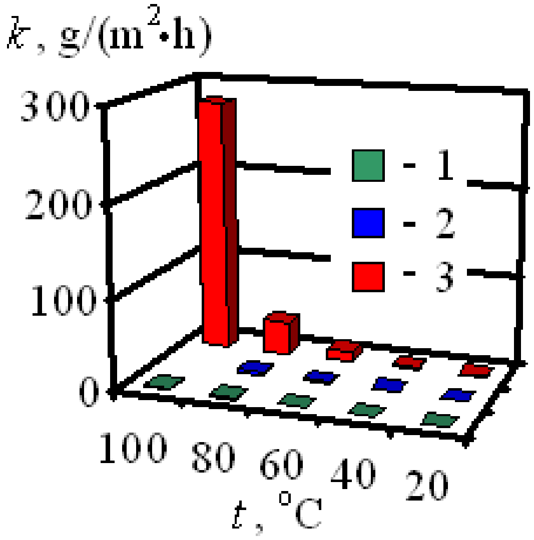


Figure 9. Protective after-effect of inhibitor layers formed on the surface of chromium-nickel steel 12Kh18N10T in 2 M HCl + 5 mM IFKhAN-92 (20°C) in 2 M HCl solution (2 h). 1 – samples after preliminary inhibitor adsorption (24 h), 2 – samples after preliminary inhibitor adsorption (24 h) followed by ultrasonic washing, 3 – samples without preliminary inhibitor adsorption.

Let us consider the possible reasons for the improvement of the protective effect of HCIs upon addition of urotropine. This issue was not studied separately, but XPS data indicate that the combination of IFKhAN-92 with urotropine seals the protective layer formed on the surface of 12Kh18N10T steel in HCl solution, presumably due to chemical crosslinking of the organic parts of CI molecules initiated by formaldehyde, a product of urotropine hydrolysis [117]. In general, this issue requires a more detailed experimental study, considering the practical importance of HCIs that contain urotropine.

Literature sources provide extensive data on the electrochemical behavior of triazoles in acid solutions at temperatures that rarely reach 75°C [120–129]. Voltammetric measurements indicate that these compounds efficiently inhibit the cathodic and anodic reactions that occur on steels. According to EIS results, addition of such CIs into a corrosive environment decreases the capacitance of the double electric layer on steel and increases the polarization resistance. Voltammetry and EIS data are always in good agreement with the *k* of steel samples obtained by measuring their mass loss. In view of this, data related to higher temperatures become even more interesting. Using IFKhAN-92 as an example, it has been shown that individual triazoles or formulations based on them can significantly slow down the electrode reactions on low-carbon [130] and chromium–nickel [41, 42] steels in HCl and H_2SO_4 solutions at temperatures close to 100°C.

Formulations of IFKhAN-92 with sulfur-containing compounds have a similar effect on the electrode reactions on low-carbon steel in solutions of H_3PO_4 [131], acetic, formic [75] and citric [78] acids. In particular, the addition of 5.0 mM IFKhAN-92+0.5 mM DDTC significantly inhibits the electrode reactions of steel 3 in 4.0 M H_3CCOOH and 4.0 M HCOOH ($t = 100$°C), though the individual components of the mixed CI do not affect these reactions considerably (Figure 10). These results are in good agreement with the data of corrosion tests (Table 5) based on the weight loss of metal samples, according to which the IFKHAN-92+DDTC formulation significantly slows down the corrosion of steel 3 in both acids under these conditions [75].

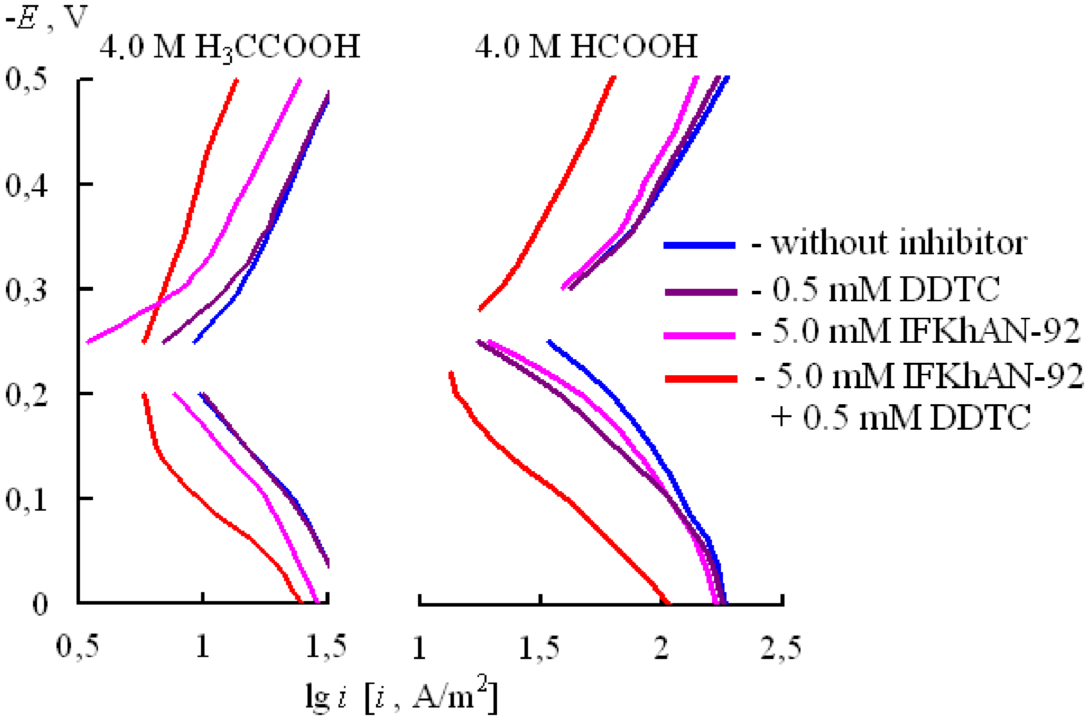


Figure 10. Polarization curves of steel 3 in acetic and formic acids (t = 100°C) with addition of 5.0 mM IFKhAN-92 + 0.5 mM DDTC.

The high protective effects of IFKhAN-92 and its formulations in inhibiting the electrode reaction of steel at temperatures close to 100°C allow us to hope that they will retain their protective effect even at higher temperatures. Thus, the layers formed by triazoles on a steel surface can slow down both electrode reactions on the metal in a wide temperature range, which ultimately determines the possibility of its protection even under high-temperature corrosion conditions.

IV. Protection of chromium–nickel steels in phosphoric acid solutions by inorganic inhibitors

In exceptional cases, steels can be protected in high-temperature acid solutions by inorganic CIs alone. It is known that chromium–nickel steel Kh18N10T is in an unstable passive state in 1–10 M H_3PO_4 at $t = 100–150°C$, so that a few similar samples exposed to a totally identical corrosive environment are destroyed at rates that differ by more than an order of magnitude. In these cases, the maximum corrosion rate (k) of the samples reaches tens of $g/(m^2 \cdot h)$. For example, in 3 M H_3PO_4 (130°C) the k values of steel vary within 0.085 to 7.5 $g/(m^2 \cdot h)$ [132, 133]. In the industrial operation of a metal, such a behavior can cause unpredictable and spontaneous destruction of structures, which is unacceptable, especially where such hazardous process fluids as hot acids are used.

It is recommended to add Cu(II) cations obtained by dissolving CuO in H_3PO_4, or NO_3^- anions in the form of $NaNO_3$ for the protection of Kh18N10T steel in hot H_3PO_4 solutions (up to 130°C). The mechanism of action of these additives that favor the preservation of the stable passive state of chromium–nickel steel in H_3PO_4 solutions was considered. It was shown that Cu(II) ions inhibit the anodic reaction of steel dissolution in the active state. The inhibiting effect of Cu(II) cations becomes even stronger in the presence of nitrate ions, up to complete suppression of the anodic reaction. The synergistic effect is explained by a change in the structure of metallic copper precipitated from a solution in the presence of nitrate ions. It has also been found that copper ions catalyze the nitrate reduction reaction. The activating effect is attributed to Cu(I) ions that are formed as an intermediate product in the chemical reduction of Cu(II) cations. Cu(I) ions chemically react with nitrate to give reactive components which, unlike nitrates, can be easily discharged on the cathode, thus increasing the efficiency of the overall cathodic process and promoting the electrode passivation [134–137].

The protection of steel structures with inorganic compounds in high-temperature acid solutions is possible only if the metal being protected is already in the passive region. In the media we are discussing, this state can be observed in the case of high-alloy steels. The passive state of steels in acid environments can be preserved by oxidizing agents. This study clearly shows that the use of oxidizing-type CIs (nitrate ion, Cu(II)) makes it possible to protect steels in hot acid solutions.

V. Conclusions

Based on the concept of the mechanism of acid corrosion inhibition by UCs and NHCs, let us formulate the basic principles of inhibitory protection of metals in mineral acids at $t > 100°C$. Under high temperature acid corrosion conditions, it is only possible if the CI forms a protective film on the metal surface that is firmly bound to it. A protective film on a metal can be formed by addition to the corrosive environment of monomeric UCs that can polymerize upon adsorption on the metal surface. Such polymerization can decrease the solubility of the adsorbed layer, increase the protective effect, and make the adsorption irreversible. However, UCs are prone to side polymerization reactions in the bulk of the corrosive medium, which is extremely undesirable in practical use [1].

A fundamentally new and more promising method to create protective coatings on steels is to use thermostable azoles. These compounds are chemisorbed on the metal surface and form a monomolecular layer firmly bound to its surface. On top of this layer, additional polymolecular physical or chemical adsorption of the CI occurs, which significantly improves its protective properties. An important way to increase the efficiency of azoles and expand their temperature range of application is to create synergistic formulations based on them.

Thus, a high-temperature CI of steels in acid solutions should:

- be capable of strong adsorption on the corroding metal surface;
- form a polymolecular protective layer on the metal in order to provide the strongest protection;
- be thermally stable in acid solutions (without resinification);
- enhance the protective effect under high-temperature conditions when combined with other thermally stable additives.

Triazole derivatives that fully comply with the requirements listed above should be used as a basis for creating mixed HCIs based on NHCs. Diazoles and tetrazoles can become an alternative to triazoles, but the possibility of their use as HCIs needs to be checked by experiments. It should be borne in mind that the industrial use of UCs, pyridine and quinoline derivatives and additives compatible with them as CIs [1] will be limited by the environmental requirements for such compounds. In view of this, triazole derivatives are more interesting. To create HCIs, they should be combined with safe and cheap urotropine, as well as relatively safe alkali metal iodides and bromides as additives. The use of mixed CIs based on UCs is well justified only for hydrochloric acid solutions. Composite CIs based on triazoles are more versatile. They can be used to protect steels both in mineral (HCl, H_2SO_4, H_3PO_4) and organic (acetic, formic, citric) acids.

To summarize, the authors of the review express their hope that the results they collected concerning the inhibitory protection of steels in high-temperature acid solutions will be interesting and useful to the readers. The regularities of the inhibitory protection of steels in high-temperature acid solutions that we discussed open the possible approaches to the creation of new HCIs urgently required by the oil and gas industry and by metallurgical industry.

Acknowledgements

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