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APPLIED ELECTROCHEMISTRY AND CORROSION PROTECTION OF METALS

Corrosion-Protective Properties of *N*-Phenacylmethylpyridinium Bromides

R. I. Yurchenko, I. S. Pogrebova, T. N. Pilipenko, and E. M. Kras'ko

Kiev Polytechnic Institute, National Technical University of Ukraine, Kiev, Ukraine

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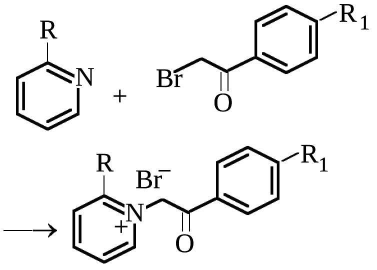
Abstract—The inhibiting action of *N*-phenacylmethylpyridinium bromides on corrosion of carbon steel in a 3 M sulfuric acid solution was studied. A relationship between the structure of the compounds under study and their corrosion-protective properties was revealed. Compounds ensuring high degree of corrosion protection of steel in acid media were found.

Despite that the relationship between the structure of organic compounds and their corrosion-protective properties have been studied for a relatively long time [1–3], this problem still remains topical. Particularly promising is a search for effective corrosion inhibitors among substances exhibiting the so-called intramolecular synergism [4–6]. This effect consists in that the presence of functional groups of varied nature in the inhibitor molecule enables multidimensional action on the corrosion process and ensures effective protection by the inhibitor.

As objects of study were chosen phenacylmethylpyridinium bromides **I**–**XI**, which are of interest in that they are simultaneously quaternary pyridinium salts and aromatic carbonyl compounds, i.e., belong to such types of organic compounds whose inhibiting action is well known [1, 2, 7].

Compounds **I**–**XI** were synthesized by alkylation of 2-substituted pyridines with the corresponding ω-bromoacetophenones:



I–XI

where R = H, CH_3, NH_2, $COCH_3$; R_1 = H, CH_3, OCH_3, Br, Cl, NO_2.

The presence in these compounds of a methylene bridge separating the pyridinium and benzoyl moieties makes it possible to act upon each of them separately by varying the substituents R and R_1 and to reveal factors positively affecting the inhibiting action of the molecule as a whole.

EXPERIMENTAL

Compounds **I**–**IV** were synthesized by published procedures; compounds **V**–**XI** were uknown previously, and their structure was confirmed by IR and ^{1}H NMR spectroscopy.

2-Amino-1-phenacylmethylpyridinium bromide V, 2-amino-1-(4-methylphenacyl)methylpyridinium bromide VII, 2-amino-1-(4-methoxyphenacyl)methylpyridinium bromide VIII, 2-amino-1-(4-bromophenacyl)methylpyridinium bromide IX, 2-amino-1-(4-chlorophenacyl)methylpyridinium bromide X, and 2-amino-1-(4-nitrophenacyl)methylpyridinium bromide XI. Solutions of equimolar amounts (0.02 M) of 2-aminopyridine and appropriate ω-bromoacetophenone in ethyl acetate were mixed. The reaction mixture was refluxed for 3 h for **V** and **VII** and for 5 h for **IX**–**XI**. The next day, the reaction mixture was treated with ether, and the precipitate formed was separated and recrystallized from ethanol–ether. For pyridium bromides **V** and **VII**–**XI**, the yields (%) and melting points (°C) are as follows: **V**, 82, 218–220; **VII**, 75, 191–193; **VIII**, 80, 232–234; **IX**, 77, 215–217; **X**, 82, 220–222; and **XI**, 60, 252–254.

2-Acetyl-1-phenacylmethylpyridinium bromide VI. A mixture of equimolar amounts (0.02 M) of 2-acetylpyridine and ω-bromoacetophenone was heated to 125–130°C for 20 min and treated with a minor

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Table 1. Hindrance factors γ and degree *Z* of corrosion protection of 08KP steel in 3 M H_2SO_4 solution in the presence of phenacylmethylpyridinium bromides **I**–**XI**

Compound	R	R_1	20°C		40°C		60°C		80°C	
			γ	*Z*, %	γ	*Z*, %	γ	*Z*, %	γ	*Z*, %
I	H	H	11.3	91.1	12.7	92.1	221.2	99.5	88.3	98.7
II	H	NO_2	1.7	41.2	2.2	54.5	–	–	15.7	93.6
III	CH_3	H	15.5	93.5	18.7	94.7	209.1	99.5	150.4	99.3
IV	CH_3	NO_2	2.3	56.5	2.9	65.5	–	–	21.7	95.4
V	NH_2	H	23.7	95.8	29.0	96.5	200.3	99.5	144.6	99.3
VI	$COCH_3$	H	7.6	86.8	10.4	90.4	262.8	99.6	198.3	99.5
VII	NH_2	CH_3	26.5	96.2	34.1	97.1	413.6	99.8	207.1	99.5
VIII	NH_2	OCH_3	32.0	96.4	35.4	97.1	643.2	99.8	626.7	99.8
IX	NH_2	Br	3.4	70.6	3.6	72.2	25.4	96.1	63.0	98.4
X	NH_2	Cl	1.8	44.4	2.2	54.5	23.8	95.8	60.0	98.3
XI	NH_2	NO_2	9.7	89.7	12.3	91.9	44.9	97.8	31.3	96.8

amount of ethanol; the precipitate formed was separated. Yield 35%, mp 198–200°C (from ethanol–ether).

To evaluate the corrosion-protective properties of the compounds under study, the hindrance factors γ and the degree *Z* of corrosion protection of steel were determined in the presence of 1×10^{-2} M of inhibitors in 3 M H_2SO_4 solutions at 20, 40, 60, and 80°C. The corrosion was monitored gravimetrically using 08KP steel samples with the working area of 14×10^{-4} m^2. The test duration was 24 h at 20°C, 2 h at 40 and 60°C, and 1 h at 80°C. Polarization curves were measured in the potentiodynamic mode at the potential sweep rate of 2 mV s^{-1} on a steel electrode in the initial and inhibited sulfuric acid solutions.

The test performed demonstrated that most of the compounds under study show noticeable inhibiting properties which are largely determined by the nature of substituents in their molecules (Table 1).

As is known [7], adsorption of quaternary pyridinium salts may occur both through electrostatic attraction of the pyridinium cation to the negatively charged metal surface and via specific π interaction of the pyridine with the metal. Attempts were made, by introducing substituents of varied electronic nature into the position 2 of the pyridine ring of **I** and thereby changing the charge on the nitrogen atom and the π-electron density of the pyridine ring, to reveal the role played by the pyridinium moiety of the molecule and evaluate the effect of the substituents introduced on the inhibiting effect of the forming compounds. It was found that, in going from **I** and **II** to the corresponding compounds with a CH_3 group heading the series of electron-donor substituents, the hindrance factor of steel corrosion grows somewhat. It increases at 20°C from 11.3 to 15.5 for compounds **I** and **III** and from 1.7 to 2.3 for **II** and **IV**. In the case of such a relatively strong electron-donor substituent as NH_2 group, the protective effect is enhanced substantially, with the corrosion hindrance factor for **V** and **XI** being 23.7 and 9.7, respectively.

This can be accounted for by the electronic influence of the amino group on the π system of the pyridine ring, which favors its π-electronic interaction with the steel surface. Also possible is the direct involvement of the amino group in free or protonated state in adsorption processes. On introducing a CH_3CO group into position 2 of the pyridine ring (compound **VI**), the corrosion hindrance factor decreases to 7.6.

It was established that the observed changes in the inhibiting action of **I, III, V**, and **VI** are strictly determined by the electronic nature of substituents R. There exists a linear relationship (*r* = 0.994) between the corrosion hindrance factors for these compounds and the constants σ_c^0 characterizing the combination of the mesomeric and π-induction effects of the substituents R [8]. The fact that this dependence is observed suggests that adsorption of the compounds studied onto steel at room temperature is due to π-electronic interaction of the pyridinium ring with the metal surface, favored by the presence of electron-donor substituents in the pyridinium ring. This also indicates that the amino group in **V** is not involved directly in the adsorption, and the decisive role is played by its influence on the π system of the pyridine ring.

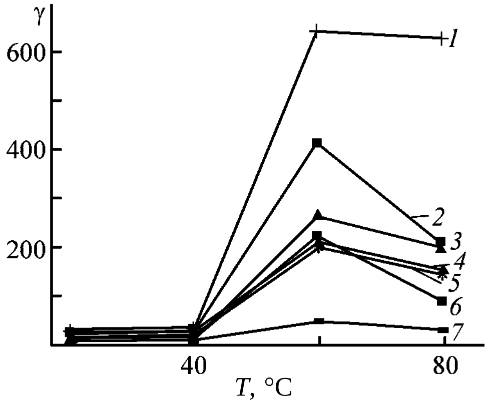

Fig. 1. Hindrance factor γ vs. temperature T in corrosion of 08KP steel in a 3 M solution of H_2SO_4 in the presence of 1×10^{-2} M phenacylmethylpyridinium bromides. Compound: (*1*) **VIII**, (*2*) **VII**, (*3*) **VI**, (*4*) **III**, (*5*) **V**, (*6*) **I**, and (*7*) **XI**.

It should be noted that the linear dependence γ–σ_c^0, observed for compounds **I**, **III**, **V**, and **VI**, is also preserved at 40°C, but the correlation coefficient falls in this case to 0.985. At 60°C, the inhibiting action of the compounds studied increases dramatically (Table 1), but the γ–σ_c^0 relationship is strongly disturbed, being completely eliminated at 80°C. Possibly, raising the temperature leads to manifestation in the corrosion process of a number of other factors. This may be, e.g., reorientation of molecules bound to the metal surface via the π system of the pyridinium moiety, enhancement of the role played by electrostatic interaction of pyridinium cations with the metal surface, and increasing share of the specific adsorption of compounds via the carbonyl group.

As is known [1, 2], the corrosion hindrance under the action of carbonyl compounds is mainly due to involvement of the oxygen from the carbonyl group in adsorption processes because of the presence of a substantial electron density on this atom. Electron-donor substituents make higher the nucleophilicity of the oxygen atom of the carbonyl group, thereby enhancing the donor–acceptor interaction of carbonyl compounds with the metal surface, whereas electron-acceptor substituents passivating the carbonyl group make this interaction weaker. Introduction into the *para* position of the benzene ring of **V** of CH_3 or CH_3O groups, which exhibit electron-donor effect, enhances the protective action of the inhibitor, with the result that the corrosion hindrance factor increases to 26.5 and 32.0 for **VII** and **VIII**, respectively, at 20°C. If these substituents are replaced with a bromine or chlorine atom, the corrosion-protective effect decreases dramatically, with the corrosion hindrance factor for **IX** and **X** being as low as 3.4 and 1.8, respectively.

A comparison of the protective effects of compounds **I**, **III**, and **V** and the corresponding nitro derivatives **II**, **IV**, and **XI** demonstrated that introduction of an NO_2 group into the *para* position of the benzene ring makes their inhibiting action weaker. Since the nitro group is a much stronger electron acceptor than a bromine or chlorine atom, it would be expected that the protective properties should be completely eliminated on replacing these atoms with a nitro group. However, it was found that such a replacement not only fails to make the hindrance factor lower, but even raises it substantially. For example, the corrosion hindrance factor for **XI** is 9.7.

Variation of the substituents R_1 revealed for compounds **V**, **VII**, **IX**, and **X** at 20 and 40°C a correlation between their σ_1 constants and γ values, with the correlation coefficients equal to, respectively, 0.998 and 0.990. The exception are compounds **VIII** and **XI**. Possibly, the substituents R_1 in these compounds are involved, in addition to exerting influence on the carbonyl group and the π system of the benzene ring, in some other processes. For **VIII**, this may be, e.g., independent involvement of the MeO group in the free or protonated form in adsorption, whereas in **XI**, as also in **II** and **IV**, the observed corrosion hindrance, probably, results from the combined influence exerted on corrosion both by these compounds themselves and by the corresponding amino compounds, which could be formed under the experimental conditions.

The results of the corrosion tests demonstrated that, with the temperature increasing to 60°C, the inhibiting action of most of the compounds studied increases substantially (Table 1) and remains rather high at 80°C. The observed temperature dependence of the inhibiting effect of the compounds studied (Fig. 1) is probably associated with a change in the mechanism of their adsorption onto the metal and a transition from physical (or first-order specific) adsorption to chemisorption as a result of the enhanced donor–acceptor interaction between the carbonyl oxygen and *d* levels of iron. A certain decrease in the inhibiting action of some compounds at 80°C is possibly due to desorption of inhibitors from the metal surface, resulting from the high rate of metal dissolution at this temperature.

Voltammetric measurements on steel in the presence of compounds **V**, **VIII**, and **XI** demonstrated that these compounds are inhibitors of mixed type, which inhibit both the cathodic and anodic reactions of the corrosion (Fig. 2). Under stationary conditions, they affect the process to a greater extent by shifting the free corrosion potential E_f of steel in the positive direction. The hindrance factors calculated from the intersection of the Tafel portions of polarization curves for **V**, **VIII**, and **XI** are, respectively, 22.5, 29.2, and 4.0, and those for **V** and **VIII** are close to those obtained from gravimetric measurements (Table 1).

The nature of substituents in these compounds strongly affects the run of the cathodic polarization curves, and to a lesser extent, that of the anodic curves. The influence of compound **XI** containing a nitro group on the cathodic reaction is low, which may be due to its partial reduction on the steel surface. The extent to which compound **XI** affects the cathodic reaction of steel corrosion decreases markedly when the electrode potential is shifted in the negative direction, which may also be due to the reduction of **XI**. Inhibitors **V** and **VIII** enhance substantially the electrode polarization of the cathodic reaction of the corrosion process, thereby markedly changing the run of the cathodic curves at high polarizations. When the electrode potential is shifted in the negative direction, inhibition of the cathodic reaction of the corrosion process is enhanced in their presence. This can be accounted for by an increase in adsorption of **V** and **VIII** onto steel and their reorientation on the metal surface, which ensures formation of a more closely packed protective layer of an inhibitor [7].

The strongest influence on the rate of acid corrosion of metals is commonly exerted by the energetic ($\gamma_{\Delta\Psi_1}$) and blocking (γ_θ) inhibition effects, whose contribution to the overall corrosion hindrance factor can be calculated using a system of equations reported in [7]. The corrosion hindrance associated with the appearance of an additional step of potential, $\Delta\Psi_1$, can be calculated using simple kinetic relations taking into account the Tafel slopes of the polarization curves, b_c and b_a, and the shift of the free corrosion potential, ΔE_f, caused by the inhibitor (Table 2).

A comparison of the experimental (γ_e) and calculated (γ_c) hindrance factors demonstrated that the compounds studied hinder acid corrosion of steel mainly by the energetic mechanism, and the effect of blocking of the metal surface is only of secondary importance in their presence. As also for other cation-like compounds, this is probably due to the presence in the phenacylmethylpyridinium bromides of pyridinium cations ensuring the appearance at the metal–solution interface of a positive adsorption step of potential. The excess of γ_c over γ_e, observed for some compounds, is possibly due to the influence exerted on ΔE_f by a number of additional factors: conjugated reduction of oxygen, occurring in an acid medium in the presence of effective inhibitors; selective adsorption of surfactants on active centers of the metal; etc.

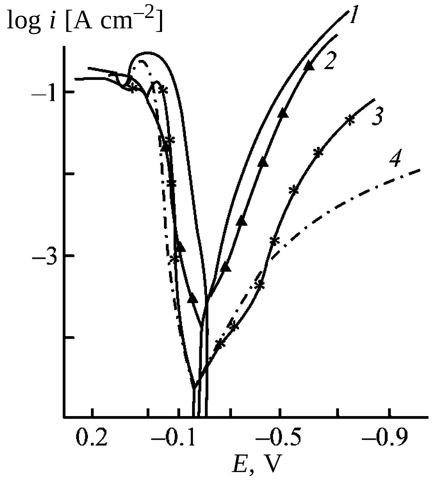

Fig. 2. Polarization curves measured on 08KP steel in a 3 M solution of H_2SO_4 at 20°C in the presence of 1×10^{-2} M phenacylmethylpyridinium bromides. (*i*) Current density and (*E*) potential (vs. standard hydrogen electrode). (*1*) Supporting electrolyte solution; compound: (*2*) **XI**, (*3*) **VIII**, and (*4*) **V**.

CONCLUSIONS

(1) Phenacylmethylpyridinium bromides are effective inhibitors of acid corrosion of steel, whose protective action depends on the nature of substituents present in these compounds.

(2) The inhibiting properties of the compounds under study are enhanced by electron-donor sub-

Table 2. Experimental (γ_e) and calculated (γ_c) corrosion hindrance factors for 08KP steel in a 3 M solution of H_2SO_4 in the presence of **V**, **VIII**, **IX**, and **XI**

Compound	*c*, M	E_f, mV	γ_e	γ_c^*
V	1×10^{-2}	60	23.7	26.8
	4×10^{-3}	56	23.2	21.4
	1.6×10^{-4}	45	17.0	11.8
	6.4×10^{-4}	17	2.6	2.5
VIII	1×10^{-2}	71	32.0	48.9
IX	1×10^{-2}	21	3.4	3.2
XI	1×10^{-2}	50	9.7	10.2
	4×10^{-3}	31	7.8	5.4

* It was taken in calculations that $\gamma_c = 10^{K\Delta\Psi}1$, $K = b_c/b_0(b_a + b_c)$, $\Delta\Psi_1 = \Delta E_c/[1 - b_c b_a/b_0(b_a + b_c)]$, where b_c and b_a are the Tafel slopes of the cathodic and anodic polarization curves in a 3 M solution of H_2SO_4, $b_0 = 2.3RT/F$ [7].

stituents introduced both in the pyridinium and in benzoyl moieties of their molecules and weakened by electron-acceptor substituents. The key role in the corrosion-protective action of the compounds under study at room temperature is the pyridinium moiety, with the corrosion hindrance by the energetic inhibition mechanism, and the benzoyl moiety of the molecule ensures their chemisorption and high performance at elevated temperatures. Such a polyfunctionality of phenacylmethylpyridinium bromides allows them to preserve their strong inhibiting action in a 3 M solution of sulfuric acid in a wide range of solution temperatures (20–80°C).

(3) The most effective of the compounds studied are 2-amino-1-phenacylmethylpyridinium bromide **V**, 2-amino-1-(4-methylphenacyl)methylpyridinium bromide **VII**, and 2-amino-1-(4-methoxyphenacyl) methylpyridinium bromide **VIII**.

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