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BRIEF COMMUNICATIONS

1-Phenacylmethyl-2-(acylaminothiocarbonylamino)pyridinium Bromides as Protectors of Steel Acid Corrosion

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Abstract—Inhibiting effect of 1-phenacylmethylpyridinium bromides containing acylthiourea substituents in the pyridine ring on corrosion of mild steel in sulfuric acid (3 M) was studied.

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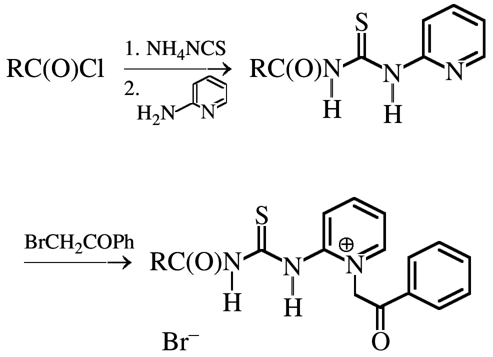
The inhibiting properties of 1-phenacylmethylpyridinium bromides containing, in the 2-position of the pyridine ring, the $-NH_2$ [1], –NH(C)OR [2], –NHC(O)NHR, and –NHC(S)NHR [3] groups have been studied previously. The thiourea derivatives were found to be the most active. In this study, we examined ureides **I**–**VIII** as a logical continuation of the above studies: 1-(2-oxo-2-phenylethyl)-2-(3-phenylureido)pyridinium bromide **I**, 1-(2-oxo-2-phenylethyl)-2-[3-(4-methylphenyl)ureido]pyridinium bromide **II**, 1-(2-oxo-2-phenylethyl)-2-[3-(4-methoxyphenyl)ureido]pyridinium bromide **III**, 1-(2-oxo-2-phenylethyl)-2-[3-(4-bromomethylphenyl)ureido]pyridinium bromide **IV**, 1-(2-oxo-2-phenylethyl)-2-[3-(4-chloromethylphenyl)ureido]pyridinium bromide **V**, 1-(2-oxo-2-phenylethyl)-2-[3-(2-furyl)ureido]pyridinium bromide **VI**, 1-(2-oxo-2-phenylethyl)-2-[3-(adamant-1-yl)ureido]pyridinium bromide **VII**, and 1-(2-oxo-2-phenylethyl)-2-[3-(undec-1-yl)ureido]pyridinium bromide **VIII**.

These compounds are acyl derivatives of thiourea and contain RC(O)NHC(S)NH groups in the 2-position of the pyridine ring. It is known that β-dicarbonyl compounds are often used in organic chemistry as complexing agents. Therefore, we can expect that the structure of substituents taken will be favorable for the protective properties of the compounds studied.

Compounds **I**–**VIII** were synthesized by the reaction of acyl chlorides, ammonium thiocyanate, and 2-aminopyridine, followed by treatment of the compounds obtained with ω-bromoacetophenone:



where R is Ph (**I**), $4\text{-}CH_3C_6H_4$ (**II**), $4\text{-}CH_3OC_6H_4$ (**III**), $4\text{-}BrC_6H_4$ (**IV**), $4\text{-}ClC_6H_4$ (**V**), 2-furyl (**VI**), 1-adamantyl (**VII**), and 1-undecyl (**VIII**).

The composition of the compounds obtained was confirmed by IR and ^1H NMR spectra.

EXPERIMENTAL

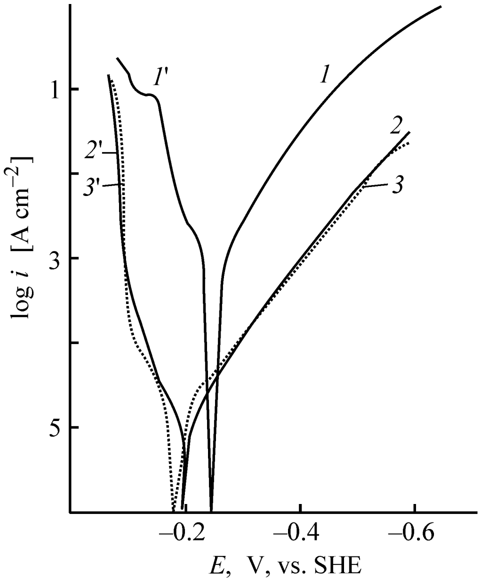
A mixture of an appropriate acid chloride prepared by reaction of the acid with thionyl chloride (2×10^{-2} mol), ammonium thiocyanate (2.5×10^{-2} mol), and anhydrous acetone (15 ml) was stirred for 30 min, after which 2-aminopyridine (2×10^{-2} mol) was added, and stirring was continued for an additional 1 h. The reaction mixture was treated with a small portion of water, and, the next day, the precipitate was separated. Equimolar amounts (1.5×10^{-3} mol) of the compound prepared and ω-bromoacetophenone were refluxed in 15 ml of ethyl acetate for 3 h, and the precipitate was separated. The yields (%) and

Corrosion inhibition coefficient γ and degree of protection, *Z*, for 08KP steel in 3 M H_2SO_4 in the presence of 1-phenacylmethylpyridinium bromides **I–VIII**

Compound	R	40°C		60°C		80°C	
		γ	*Z*, %	γ	*Z*, %	γ	*Z*, %
I	C_6H_5	23.90	95.82	129.40	99.22	41.70	97.60
II	4-$CH_3C_6H_4$	29.87	96.66	373.10	99.73	190.10	99.47
III	4-$CH_3OC_6H_4$	36.70	97.27	396.42	99.75	125.10	99.22
IV	4-BrC_6H_4	22.76	95.60	103.40	99.03	56.55	98.23
V	4-ClC_6H_4	22.76	95.60	121.20	99.17	103.60	99.03
VI	2-Furyl	41.56	97.59	218.70	99.54	119.00	99.16
VII	1-Adamantyl	39.80	97.48	380.56	99.73	192.75	99.48
VIII	1-Undecyl	38.24	97.38	328.10	99.69	102.90	99.02

melting points (°C) of **I**–**VIII** are as follows: **I**, 40, 229–232; **II**, 50, 198–200; **III**, 75, 195–205; **IV**, 70, 210–212; **V**, 71, 196–203; **VI**, 69, 218–220; **VII**, 35, 227–229; and **VIII**, 70, 212–215.

The corrosion-protective properties **I**–**VIII** were evaluated gravimetrically at 20, 40, 60, and 80°C by the inhibition coefficient γ and degree of protection, *Z*, of a 08KP steel in 3 M sulfuric acid [1]. Unfortunately, the poor solubility of the compounds obtained in 3 M H_2SO_4 prevented attaining the same concentration as for the previously studied 1-phenacylmethylpyridinium bromides.



(*1–3*) Cathodic and (*1'–3'*) anodic polarization curves recorded at 20°C on 08 KP steel in 3 M H_2SO_4 and in solutions saturated with **VI** and **VII**. (*i*) Current density and (*E*) potential. Solution: (*1*, *1'*) supporting electrolyte, (*2*, *2'*) with **VI**, and (*3*, *3'*) with **VII**.

Nevertheless, the tests performed showed that compounds **I**–**VIII** are fairly efficient inhibitors of steel acid corrosion (see table). The corrosion inhibition coefficients found for saturated solutions in 3 M H_2SO_4 vary within the ranges 15.79–26.47 at 20°C, 22.76–41.56 at 40°C, 103.40–396.42 at 60°C, and 41.70–192.80 at 80°C. Voltammetric measurements on steel with **VI** and **VII** at 20°C showed that these compounds behave as mixed-type inhibitors affecting the rate of both anodic and cathodic processes (see figure). Calculations based on the "formal theory" of inhibition [4] indicate that corrosion is inhibited by these compounds at 40°C by the energy-blocking mechanism.

Introduction of MeO group into the *p*-position of the benzene ring in **I** or replacement of the phenyl substituent with a furyl group enhances the protective properties, which is in accordance with the chemical nature of the substituents introduced, but the extent of enhancement is substantially lower than that in the series of the previously studied compounds [2, 3]. At 60°C, the corrosion inhibition coefficient for ureide **III** is only three times higher, and for **VI**, two times higher than that for **I**.

CONCLUSIONS

(1) It was found that the steel corrosion inhibition coefficients for saturated solutions of 1-phenacylmethyl-2-(acylaminothiocarbonlylamino)pyridinium bromides in 3 M sulfuric acid vary within the ranges 15.79–26.47 at 20°C, 22.76–41.56 at 40°C, 103.40–

396.42 at 60°C, and 41.70–192.80 at 80°C; the degree of metal surface protection is 95.6–99.7%.

(2) Voltammetric measurements showed that the compounds studied behave as mixed-type inhibitors affecting the rates of both anodic and cathodic processes. Corrosion is inhibited by these compounds by the energy-blocking mechanism.

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