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BRIEF COMMUNICATIONS

Pyridinium Halides and Their Mixtures as Inhibitors of Steel Corrosion in Sulfuric Acid Solutions

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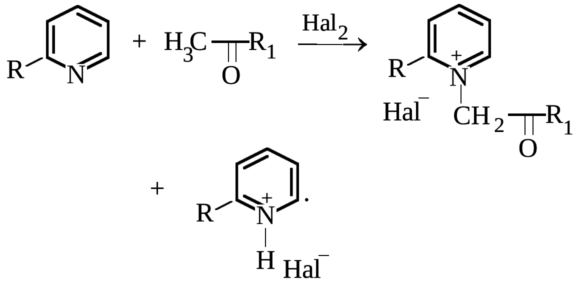
Abstract—Mixtures of 1-acylmethylpyridinium halides with equimolar amounts of pyridinium halides were prepared by the Ortoleva–King reaction. The inhibiting effect of various pyridinium halides and their mixtures on corrosion of steel in sulfuric acid solutions was studied.

Previously we found [1, 2] that some of 1-phenacylmethylpyridinium bromides are relatively effective inhibitors of the acid corrosion of steel, especially at elevated temperatures. These compounds were prepared by alkylation of appropriate pyridine derivatives with ω-bromoacetophenones.

Corrosion inhibitors of this type can be prepared by the Ortoleva–King reaction [3], i.e., the reaction of pyridine derivatives, iodine, and compounds containing labile hydrogen atoms. Since pyridine and its derivatives act as both reagents and acceptors of the forming hydrogen halide, this reaction gives, along with the desired pyridinium salts, also the corresponding pyridinium halides. For example, the reaction of pyridine, acetophenone, and bromine yields an equimolar mixture of 1-phenacylmethylpyridinium bromide and pyridinium bromide:



When the solubility of the resulting salts is strongly different, they can be separated to prepare individual 1-acylmethylpyridinium halides. For example, treatment with alcohol of the salt mixture formed in the reaction of pyridine or 2-methylpyridine with acetophenone in the presence of bromine or iodine allows preparation of the corresponding 1-phenacylmethylpyridinium bromides and iodides with high yields. In many cases, the Ortoleva–King reaction strongly simplifies synthesis of 1-acylmethylpyridinium halides: it can be performed in one step without using halomethyl ketones (lacrimators) and allows preparation of pyridinium salts that cannot be obtained by common methods. Moreover, this reaction yields acylmethylpyridinium halides in mixtures with pyridinium halides, which can enhance their corrosion-protective effect [4].

EXPERIMENTAL

The synthesis was performed according to the procedure described in [3]. The corrosion-protective effect of the compounds prepared was evaluated using the coefficients of corrosion deceleration γ and degree of corrosion protection Z, calculated from the weight loss of 08KP steel samples in 3 M sulfuric acid at 20 and 60°C and inhibitor concentration of 1×10^{-2} M (see table).

The coefficient of corrosion inhibition of 1-phenacylmethylpyridinium bromide (I-1) at 20°C is 11.3 [1]. This compound is formed by the Ortoleva–King reaction from pyridine, acetophenone, and bromine in a mixture with pyridinium bromide and the coefficient of corrosion inhibition of this mixture (inhibitor I-1a) is as high as 18.0. In the case of iodine, the reaction yields 1-phenacylmethylpyridinium iodide (I-2) and pyridinium iodide; the first compound, when isolated pure, exhibits the coefficient of inhibition of 17.7 at 20°C. The coefficient of corrosion inhibition of the resulting mixture (I-2a) is 24.3. In the case of 1-phenacylmethyl-2-methylpyridinium bromide (I-3), the coefficients of corrosion inhibition are 15.5 and 209.1 [1], and for its mixture with

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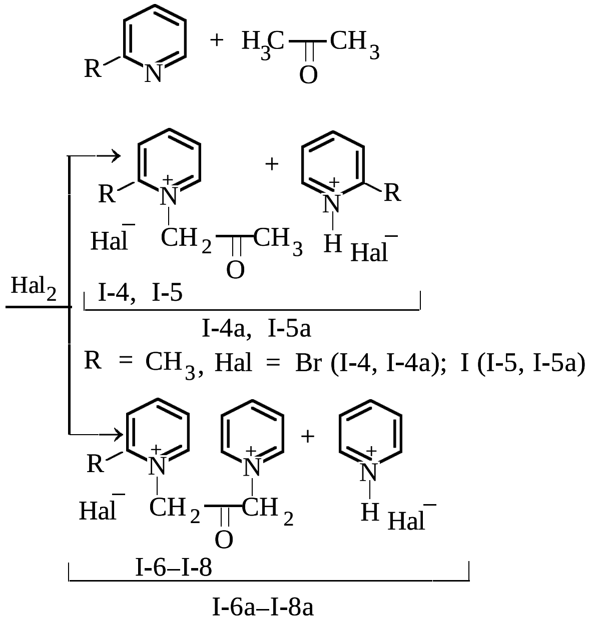
Coefficients of corrosion inhibition γ and degree of corrosion protection Z of 08KP steel in 3 M H_2SO_4 in the presence of acylmethylpyridinium halides (I-1–I-8) and their mixtures with the corresponding pyridinium halides (I-1a–I-8a)

Inhibitor	20°C		60°C		Inhibitor	20°C		60°C	
	γ	Z, %	γ	Z, %		γ	Z, %	γ	Z, %
I-1	11.7	91.45	–	–	I-1a	18.0	94.44	–	–
I-2	17.7	94.35	–	–	I-2a	24.3	95.88	–	–
I-3	15.5	93.55	209.1	99.52	I-3a	21.4	95.33	237.8	99.58
I-4	19.6	94.90	223.9	99.55	I-4a	22.5	95.56	250.3	99.60
I-5	–	–	–	–	I-5a	23.1	95.67	594.6	99.83
I-6	–	–	–	–	I-6a	22.0	95.45	237.9	99.58
I-7	21.4	95.33	333.8	99.70	I-7a	23.1	95.67	464.0	99.78
I-8	–	–	–	–	I-8a	25.0	96.00	864.9	99.88

2-methylpyridinium bromide, 21.4 and 237.9 at 20 and 60°C, respectively.

The reaction with acetone can be performed through one or two methyl groups. The reaction of 2-methylpyridine, acetone, and bromine or iodine in a 2 : 1 : 1 ratio yields the corresponding 1-acetylmethylpyridinium bromide (I-4) or iodide (I-5) in a mixture with 2-methylpyridinium bromide or iodide (I-4a and I-5a). We failed to isolate pure compounds I-4 and I-5 because of their close solubilities with the corresponding pyridinium salts. Pure I-4 was prepared by a common procedure, i.e., by alkylation of 2-methylpyridine with α-bromoacetone. The reaction of pyridine or 2-methylpyridine, acetone, and bromine or iodine (4 : 1 : 2 molar ratio) yields bis-salts (I-6–I-8) in the form of mixtures with the corresponding pyridinium salts (inhibitors 1-6a–I-8a, respectively). Pure I-7 was prepared by treatment of the reaction mixture with alcohol. As seen from the table, the corrosion-protective power of I-7a is higher than that of individual compound I-7 by a factor of 1.5.

Our experimental results show that the corrosion-protective effect of 1-phenacylmethylpyridinium halides increases in the presence of equimolar amounts of the corresponding pyridinium halides and on passing from bromine to iodine. This trend is the most pronounced at elevated temperatures. The products of reaction of pyridine or 2-methylpyridine with acetone and iodine (I-5a, I-7a, and I-8a) are the most effective inhibitors exhibiting at 60°C the coefficients of corrosion inhibition of 594.6, 464.0, and 864.9 and the degrees of corrosion protection of 99.83, 99.48, and 99.88%, respectively:



R = H, Hal = Br (I-6, I-6a), I (I-7, I-7a)
R = CH_3, Hal = I (I-8, I-8a)

CONCLUSIONS

(1) The Ortoleva–King reaction essentially simplifies synthesis of 1-acylmethylpyridinium halides exhibiting corrosion-protective properties and allows preparation of pyridinium salts that are difficultly accessible by common procedures.

(2) The inhibiting effect of the mixtures of pyridinium salts formed by the Ortoleva–King reaction is stronger than that of the individual acylmethylpyridinium halides. The best inhibitors at a concentration of 1×10^{-2} provide the coefficients of corrosion

inhibition and the degrees of corrosion protection of 08 KP steel at 60°C in 3 M sulfuric acid of 464.0–864.9 and 99.58–99.88%, respectively.

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