

# Kolbe Synthesis on a Platinum Anode Modified with Thiocyanate Ions

Sh. Sh. Khidirov<sup>z</sup> and Kh. S. Khibiev

Dagestan State University, Makhachkala, Russia

Received March 9, 2004; in final form, May 5, 2005

**Abstract**—The Kolbe synthesis on a smooth platinum anode modified with thiocyanate ions is studied in acetate buffer solutions. The modification is shown to result in the oxidation of carboxylate ions to percarboxylate ions. The peracetate formation is proved in a preparative synthesis where it is isolated and identified using IR spectroscopy.

**Key words:** Kolbe synthesis, peracetate, modification, platinum, thiocyanate, IR spectrum

## INTRODUCTION

The Kolbe synthesis is a most thoroughly studied reaction in organic electrochemistry, including electrooxidation of carboxylic acids, their salts, and their numerous derivatives. A vast amount of data on the effects of solution composition, solvent nature, anode material, current density, foreign anions, solution pH, and temperature on the Kolbe synthesis were obtained. However, data on the effects the surfactant ions, which modify the platinum electrode surface, exert on the anodic oxidation of carboxylic acids are scarce. For example, during the oxidation of phenylacetic acid and its derivatives at platinum, the yield of the dimer drops to zero in the presence of  $\text{ClO}_4^-$  and the direction of the Kolbe reaction totally changes [1, 2]. Of particular interest is the effect of thiocyanate ions on this reaction, because these ions modify deeply the platinum electrode surface.

In this work, we are studying the effect exerted by ammonium thiocyanate (AT) on the Kolbe synthesis in aqueous solutions of sodium acetate and acetic acid.

## EXPERIMENTAL

Steady-state potentiostatic polarization curves (PC) were taken and a preparative synthesis was performed in an electrochemical cell whose anodic and cathodic compartments were separated with a cationite membrane. The steady-state PC were recorded using a P-5827M potentiostat. Sodium acetate, acetic acid, and AT were of reagent grade. Sodium acetate was additionally purified by recrystallization. Twice-distilled water was used for the solutions' preparation. Saturated silver–silver chloride electrode was the reference elec-

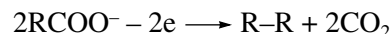
trode; a smooth platinum electrode with a geometrical area of  $2 \text{ cm}^2$  was the auxiliary electrode. All potentials are given in the standard hydrogen electrode scale. The polarization measurements were carried out at room temperature. Prior to recording steady-state PC, the working electrode (smooth platinum, geometrical area  $0.2 \text{ cm}^2$ ) was subjected to anodic and then cathodic polarization at  $0.1\text{--}0.2 \text{ A/cm}^2$  for 10–15 min.

Products of the preparative synthesis were identified using qualitative and quantitative analytical methods. The identification was performed using qualitative reactions for the peroxide group and IR spectra (obtained using Model IKS-9 and Fourier-transform-based Model Infracum FT-801 spectrometers). Measurements with the Infracum spectrometer were carried out under the following conditions: the wave range  $500\text{--}4000 \text{ cm}^{-1}$ , triangle apodization, frequency 8 scans per second, measurement time 60 s, and a ZnSe beam divider. Samples for spectrometric studies were prepared by grinding electrolysis products (peracetates) with sodium bromide and pressing them into microtablets in a mold. The spectrometric data were processed using Get Spektrum and Spektrum Manager software.

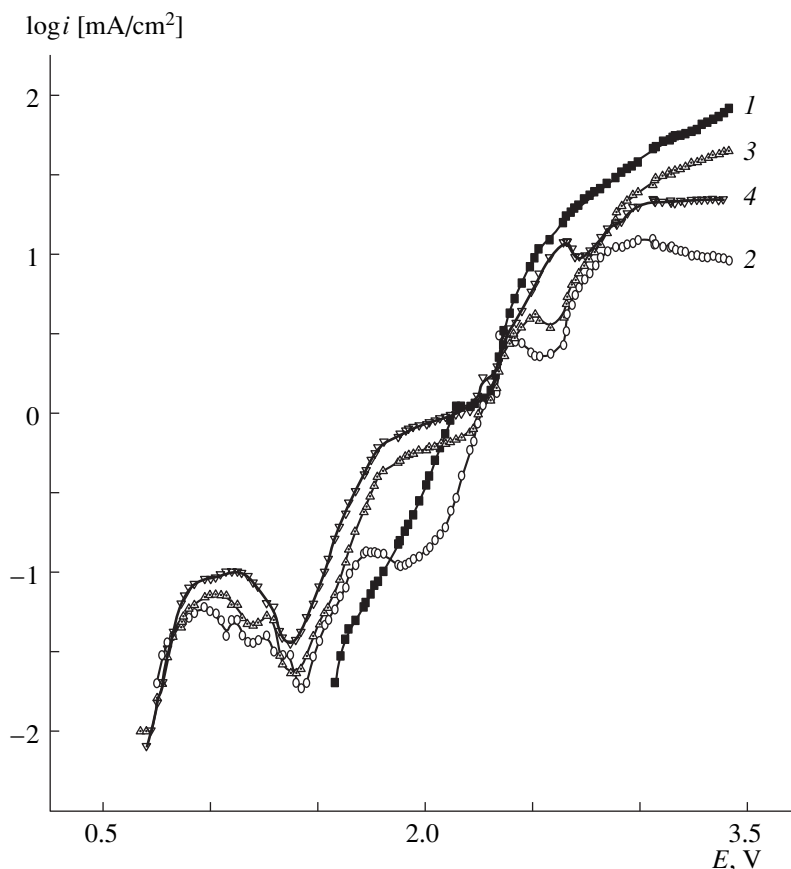
The peracetates in solutions were determined quantitatively using iodometric titration.

## RESULTS AND DISCUSSION

The steady-state PC, recorded in a 1 M acetate buffer with and without AT, are presented in the figure. The background PC can be divided into two segments, with a current delay at 2.1–2.3 V. It is known that the Kolbe reaction at platinum electrodes

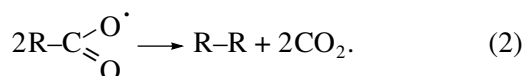
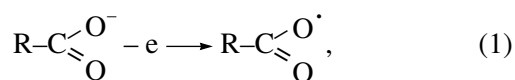


<sup>z</sup> Corresponding author, e-mail: khidirovdgu@rambler.ru

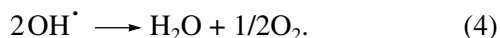
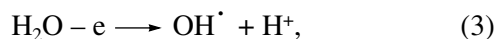


Steady-state potentiostatic PC for smooth Pt in 1.0 M acetate buffer containing (1) 0, (2) 6.15, (3) 13.0, and (4) 26.0 mM  $\text{NH}_4\text{SCN}$ .

starts precisely at these potentials and proceeds by a radical mechanism



In a background solution, the PC segment before 2.1 V corresponds to the beginning of oxygen evolution

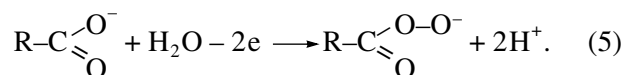


The characteristic feature of reaction (1), (2) is that it requires higher anodic potentials and is preceded by reaction (3), (4). A clear-cut separation of these two conjugated reactions was for the first time revealed by one of us in an alkaline medium using voltammetry [3].

Potentiostatic steady-state PC were taken in an electrochemical cell with and without a cationite membrane. In both cases the curves are similar; however, in the cell with a membrane, the effect of AT on reactions (1)–(4) is more clearly pronounced.

Adding 6.15 mM AT to the 1.0 M acetate buffer (pH 4.6) markedly alters the steady-state PC: it acquires currents prior to the oxygen adsorption and evolution potentials. These currents correspond to the thiocyanate oxidation. The potential range of the oxygen formation and evolution shifts in the direction of anodic potentials up to the potential of the carboxylate ion discharge (curve 2) and the current delay corresponding to the acetate ion discharge occurs at 2.35–2.65 V.

Doubling the AT concentration (to 13.0 mM) also makes the potential domains for the discharge of water molecules and carboxylate ions overlap (curve 3). Raising it to 26.0 mM displaces the current delay caused by the acetate ion discharge to 2.7–2.8 V (curve 4). These data suggest that the high oxygen evolution overvoltage in the presence of AT leads to the oxidation of carboxylate ions to percarboxylate ions and involves water molecules



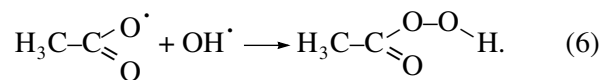
During a further polarization ( $E > 2.8$  V), no current increase is observed with an increase in the concentration of the  $\text{SCN}^-$  ions modifying the platinum electrode.

## Experimental data on sodium peracetate electrosynthesis

<i>c</i> , M		<i>Q</i> , A h	<i>i</i> , A/cm <sup>2</sup>	CE, %
CH <sub>3</sub> COONa	NH <sub>4</sub> SCN			
0.5	—	2	0.1	0
0.5	6.15 × 10 <sup>-3</sup>	2	0.1	52.5
1.0	6.15 × 10 <sup>-3</sup>	3	0.1	60.6
2.0	6.15 × 10 <sup>-3</sup>	5.5	0.1	78.5
0.5	—	2	0.05	0
0.5	1.30 × 10 <sup>-2</sup>	2	0.05	63.6
1.0	1.30 × 10 <sup>-2</sup>	3	0.05	80.0
2.0	1.30 × 10 <sup>-2</sup>	5.5	0.05	87.0
2.5	1.30 × 10 <sup>-2</sup>	7	0.05	78
3.0	1.30 × 10 <sup>-2</sup>	8.3	0.05	40

The most remarkable effect of AT on the Kolbe reaction (background curve) is observed at the AT concentration of 6.15 mM (curve 2). This concentration is optimum, with respect to the current, for changing the Kolbe synthesis direction and the formation of percarboxylate ions. Concentrations below 6.15 mM probably only modify the platinum electrode, while anodic reactions at higher concentrations involve them.

The formation of peralkyl compounds, in particular, peracetate bisulfate CH<sub>3</sub>C(O)OOSO<sub>3</sub>H results from the recombination of radicals acetoxy CH<sub>3</sub>COO\*<sup>-</sup> and HSO<sub>4</sub>\* [4, 5]. It forms when potentials of discharge of the acetate and sulfate ions overlap. Peracetate probably forms in the recombination of radicals CH<sub>3</sub>COO\*<sup>-</sup> and OH\* that are generated in reactions (1) and (3):



We studied the peracetate formation in the AT presence at high anodic potentials using a preparative electrosynthesis, isolating and identifying the final product. By electrolyzing aqueous solutions of acetic acid and acetates in the presence of AT while monitoring the current density *i*, we synthesized solutions of peracetic acid and alkali-metal peracetates. The synthesis was carried out on a platinum anode, for active modification by AT occurs precisely at a platinum electrode [6]. The results concerning the effect of the electrolyte (sodium acetate), AT concentration, and current density on the synthesis appear in the table.

We see that increasing the initial sodium acetate concentration to 2.0 M significantly raises the current efficiency (CE) for peracetate, while at higher concen-

trations, the CE drops. The AT concentration optimum for a preparative synthesis with a satisfactory CE is 6.15–13.0 mM. Higher concentrations reduce the CE. For example, at the AT concentration of 26.0 mM, the CE drops to 42%.

All synthesis experiments were carried out on a smooth platinum anode in a diaphragm electrolyzer with a cationite membrane. The peracetic acid was isolated as follows. On completing the electrolysis, the anolyte was subjected to a vacuum rectification and the yield of the final product was determined in the concentrated sodium peracetate solution. Then the latter was dried in a vacuum chamber until a crystal mass. By acidifying aqueous sodium peracetate solutions, pure solutions of peracetic acid were isolated with a quantitative yield [7].

For a comparison, peracetic acid was also synthesized by a traditional chemical method [8] in which acetic anhydride was oxidized by 90-percent hydrogen peroxide. A mixture of these two substances was rectified in a vacuum, resulting in the removal of unreacted hydrogen peroxide from solution. Then a corresponding alkali-metal peracetate was obtained. When isolating it from concentrated solutions of peracetic acid, a significant portion of active oxygen is lost.

The qualitative reactions for the peroxide group in the case of peracetates prepared by the chemical [8] and electrochemical methods gave identical results. Comparing IR spectra for acetate and peracetate prepared by the electrochemical method shows that the absorption band of the carbonyl group C=O occurs at 1700–1500 cm<sup>-1</sup> for both compounds. The absorption band for the C(O)–O–O-group (1038 cm<sup>-1</sup>) is well pronounced for peracetate but not for acetate. Comparing spectra for peracetates obtained chemically and electrochemically shows that the characteristic absorption bands are observed at similar frequencies.

## CONCLUSIONS

The effect of AT on the Kolbe synthesis at platinum electrodes in aqueous sodium acetate and acetic acid solutions was studied. It was shown that the high oxygen evolution overvoltage, caused by AT, makes potential domains for the discharge of water molecules and acetate ions overlap, leading to the oxidation of acetate ions, which involves water molecules and yields peracetates. The AT concentration optimum for modifying a platinum anode and changing the Kolbe synthesis direction is 6.15 mM. At this concentration, the optimum current density is 0.05 A/cm<sup>2</sup> and the optimum sodium acetate concentration is 2 M. These parameters ensure the formation of peracetates at a maximum CE (87%).

## REFERENCES

1. Coleman, I.P., Lines, R., Utley, I.H.P., and Weedon, B.C.I., *J. Chem. Soc., Perkin Trans. II*, 1974, p. 1064.
2. Smirnova, N.V., Netanova, E.G., Astaf'ev, E.A., Petrii, O.A., Tsirlina, G.A., and Beletskaya, I.P., *Elektrokhimiya*, 2001, vol. 37, p. 1043.
3. Khidirov, Sh.Sh., *Elektrokhimiya*, 1992, vol. 28, p. 158.
4. Veselovskii, V.I., Rakov, A.A., Kasatkin, E.V., and Yakovleva, A.A., *Adsorbtsiya i dvoynoi sloi v elektrokhimii* (Adsorption and the Double Layer in Electrochemistry), Moscow: Nauka, 1972, p. 132.
5. Yakovleva, A.A., Bairamov, R.K., and Veselovskii, V.I., *Elektrokhimiya*, 1979, vol. 15, p. 1114.
6. Kondrikov, N.B., Shcheka, O.L., and Klimenko, O.O., *Elektrokhimiya*, 1993, vol. 29, p. 1292.
7. Khidirov, Sh.Sh. and Khibiev, Kh.S., RF Patent 2216537.
8. Hawkins, E.G.E., *Organic Peroxides: Their Formation and Reactions*, London: Spon, 1961.