

Products of Anodic Oxidation of Carbamide: Effect of Anionic Composition of Solution

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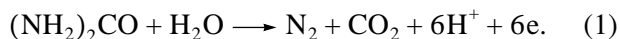
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Abstract—The current efficiency for carbamide oxidation on smooth platinum electrode to molecular nitrogen and nitrate in sulfate, fluoride, chloride, and bromide solutions are determined. The supporting-electrolyte anion has a complex effect on the ratio between rates of these processes. Independence of the current efficiency from the solution pH in electrolysis of sulfate solutions of carbamide is confirmed.

INTRODUCTION

The anodic oxidation of carbamide (urea) had attracted attention of many a researcher; however, the mechanism of this process is not clearly understood yet. It has not even been determined to what products carbamide is oxidized under various conditions. Carbamide oxidation rates on platinum electrodes are sufficiently high only at rather high anodic potentials: from 2.2 to 2.9 V (RHE). In [1], it was concluded that, at these potentials, on smooth platinum in acidic solutions, carbamide is oxidized solely to elementary nitrogen and carbon dioxide, i.e. the anodic process is described by equation



However, no evidence to this conclusion was presented.

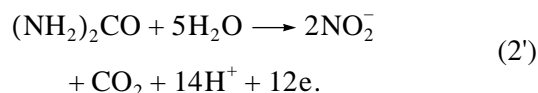
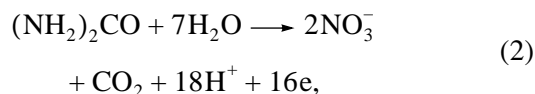
In [2], it was found that, in the electrolysis of carbamide solution in a bicarbonate Krebs–Ringer buffer on platinum black anode in a cell with separated electrode compartments, a charge consumed for the carbamide oxidation corresponded to (1), i.e. $6F$ per mole; however, the anolyte was acidified to a pH value below two.

In [3], carbamide oxidation was studied on platinum black electrodes in a slightly modified Krebs–Ringer solution in a cell with separated electrode compartments. No total analysis of oxidation products was performed; however, it was found that these products contained no noticeable amounts of nitrates and nitrites.

In a recent study [4], mass spectroscopy revealed the presence of nitrogen, carbon dioxide and a small amount of nitrogen oxides (N_2O , NO_2) in gaseous products of the carbamide anodic oxidation on porous platinum electrode in a Krebs–Ringer buffer.

Earlier [5], we found that during the electrolysis of neutral sulfate or buffer phosphate solutions of carbamide on a smooth platinum electrode, the current efficiency (CE) of reaction (1) was negligibly low, and

almost the entire charge was consumed for the formation of nitrates or nitrites in the reactions



It was also supposed that, partially, some radical cation species, which initiated polymerization or oligomerization, formed in the anodic process. By contrast, in the electrolysis of a chloride solution of carbamide, the process proceeded almost solely by reaction (1).

Here, the effect of supporting anion on carbamide anodic oxidation is studied more thoroughly. These results were partly reported earlier [6, 7].

EXPERIMENTAL

Most measurements were conducted in cells with common anodic and cathodic compartments. A platinum plate with an apparent surface area of about 1 cm^2 served as the working electrode. In most experiments the electrolyte was a 0.05 to 2 M carbamide solution in 0.15 or 1 M sodium sulfate, fluoride, chloride, or bromide solutions. A 0.15 M NaCl solution corresponds to the practically important case of carbamide oxidation in “artificial kidney” apparatus with electrochemical regeneration of dialyzing solution. All experiments were carried out at room temperature. As a rule, the rates of anodic gas evolution and carbon dioxide evolution were measured. To do this, the anodic gas was absorbed for a certain time by $\text{Ba}(\text{OH})_2$ solution, and the weight of BaCO_3 precipitate was determined.

To determine the anodic gas evolution rate in a cell with common electrode compartments, the rate of evolution of all gases evolved on both electrodes was measured and the rate of hydrogen evolution on the cathode

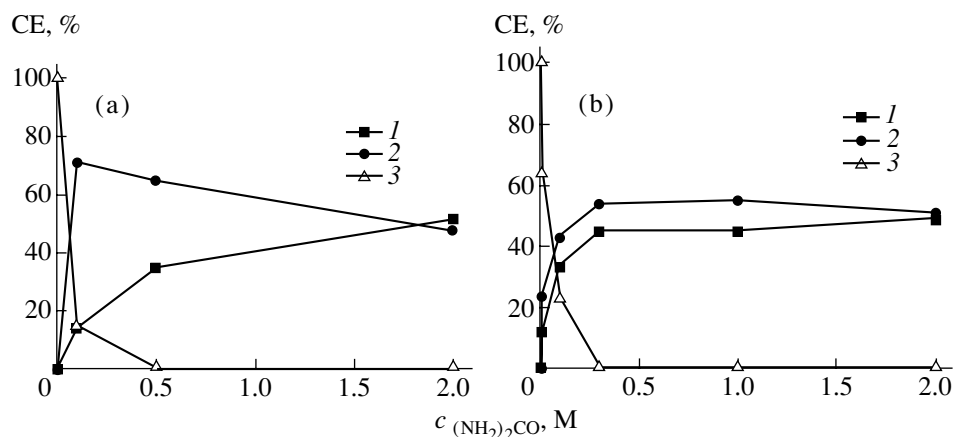
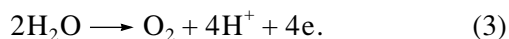


Fig. 1. CE for processes (1)–(3) in (a) 0.15 and (b) 1 M NaF vs. carbamide concentration.

was subtracted from it. The latter was calculated by Faraday's law. It is known that, even in electrolysis of dilute chloride solutions, CE for hydrogen is almost 100% at first minutes of electrolysis. In electrolysis of sulfate and fluoride solutions, the hydrogen evolution is the only cathodic process. In most cases, the electrolysis was conducted at a constant current density of 0.1 A/cm².

As an approximation, we can state that the anodic process consists of concurrent reactions (1) and (2) and the oxygen evolution



At sufficiently positive potentials (i.e. sufficiently high current densities), reaction (2') is barely probable, and the volumetric and gravimetric measurements are not accurate enough for processes (2) and (2') to be distinguished.¹

In principle, the anodic process can involve anions. However, fluoride cannot be oxidized in aqueous solutions, and sulfate oxidation proceeds at much more positive potentials than those used here (when even a fraction of current consumed for oxygen evolution is rather small). Bromide can be oxidized to elemental bromine and its oxygen compounds, and the chloride oxidation yields hypochlorous acid or hypochlorite. These processes are considered in the next section. It is important that these processes have no effect on the derivation of equations for CE.

Assume that, when a certain charge Q was passed under steady-state conditions, the anodic gas of volume V evolved, and, when the gas was absorbed by Ba(OH)₂ solution, BaCO₃ deposit of weight M formed. Then, the

following equations are valid:

$$2A\eta_1/6F + A\eta_2/16F + A\eta_3/4F = V/Q, \quad (4)$$

$$B\eta_1/6F + B\eta_2/16F = M/Q, \quad (5)$$

$$\eta_1 + \eta_2 + \eta_3 = 1. \quad (6)$$

Here, η_1 , η_2 , and η_3 are CEs for (1), (2), and (3); A is the gas molar volume (22.4 l/mol for nitrogen and 22.26 l/mol for carbon dioxide); B is the molar weight of BaCO₃, and F is Faraday's number. Equations (4)–(6) enable one to calculate CE for (1)–(3) from measured values of Q , V , and M .

The polarization measurements were conducted without iR correction in an H-shaped cell with electrode compartments separated by a porous glass membrane. A saturated calomel electrode was the reference electrode. The polarization was not corrected for ohmic component because the larger part of this component was due to the potential drop in the polymeric film that could form on the anode [5].

RESULTS AND DISCUSSION

Fluoride solutions. Figure 1 gives plots of CE for (1)–(3) vs. the carbamide concentration obtained during the electrolysis of carbamide solutions in 0.15 M NaF and 1 M NaF. At low concentrations of both supporting electrolyte and carbamide, for example, 0.1 M (NH₂)₂CO + 0.15 M NaF, a considerable fraction of the current is consumed by process (2); however, CE for (1) is not vanishingly small, as was found when electrolyzing more dilute solutions [5]. With an increase in the carbamide concentration in a dilute fluoride solution, CE for (1), i.e. for the carbamide oxidation to nitrogen, increases at the expense of a decrease in CE for (2). In this case, the oxygen evolution virtually ceases even at a rather low carbamide content. In a more concentrated fluoride solution, values of CE for (1) and (2) are comparable at any carbamide concentration; with an increase in the carbamide concentration, both CEs

¹ Special analysis of solutions after the electrolysis showed that, indeed, nitrite was not detected analytically or was detected in trace amounts. The nitrite content was determined in accordance with [8].

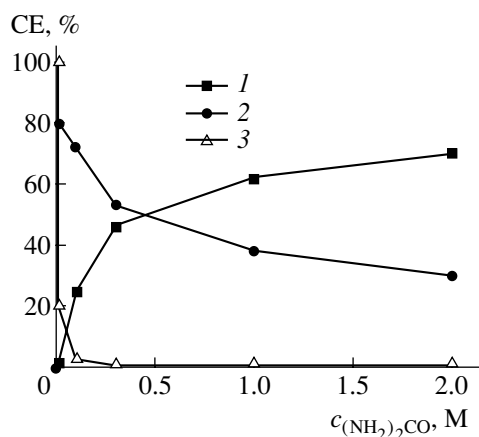


Fig. 2. CE for processes (1)–(3) in 1 M Na₂SO₄ vs. carbamide concentration.

increase at expense of a decrease in the fraction of current consumed for the oxygen evolution. Process (2) becomes severely hampered by an increase in the NaF concentration in sufficiently dilute carbamide solutions (less than 0.2 M), which calls for further thorough investigation.

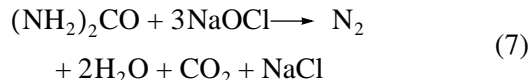
Sulfate solutions. Figure 2 gives plots of CE for (1) and (2) vs. the carbamide concentration in 0.5 M Na₂SO₄. The concentration dependences of CE of both processes are antibatic. In this regard, 1 M sulfate solution is similar to 0.15 M fluoride solution (cf. Figs. 1a and 2). Even at a rather low carbamide content, the water electrolysis that releases oxygen almost ceases. The concentration dependence of CE for process (2), i.e. for the nitrate formation, is of special interest. By definition, in a carbamide-free solution, CE for processes (1) and (2) is zero, and the entire current is consumed for water electrolysis. However, even at a carbamide content of 0.01 M, almost 80% of current is consumed for the carbamide oxidation to nitrate and only

20%, for oxygen evolution; CE for carbamide oxidation to nitrogen is negligibly small.

Bromide solutions. As the anodic oxidation of bromide can yield hypobromite and the standard potential of the BrO[−]/Br[−] system, namely 1.07 V (NHE), is sufficiently positive, we supposed that, in the electrolysis of bromide solutions of carbamide, the process yielding nitrogen will prevail (by analogy with electrolysis of chloride solutions). However, it was found that, in the electrolysis of bromide solution, the major charge is consumed for the anodic formation of elementary bromine, while carbamide is barely oxidized.

Chloride solutions. Figure 3 gives plots of CE for processes (1)–(3) vs. carbamide concentration in 0.15 M and 1 M NaCl. In a dilute chloride solution at not very high carbamide concentrations, nitrate virtually does not form; however, with the carbamide concentration increased to 0.5 M, CE for process (2) becomes noticeable. In more concentrated chloride solutions, the nitrate formation is also appreciable at carbamide concentrations of 0.3 M and higher.

In [5], based on several experiments performed in 0.15 M NaCl, it was concluded that no oxidation of carbamide to nitrate is possible in chloride solutions, due to the action of an efficient oxygen carrier, the hypochlorite ion that forms during the primary anodic oxidation of chloride. It was supposed that the chemical oxidation of carbamide via the reaction



proceeded easier than the oxidation via reaction (1). The results of the present, more thorough study refute this conclusion. At the same time, undoubtedly, carbamide can indirectly be oxidized to nitrogen via reaction (7). We stress that both direct anodic and indirect (with the aid of hypochlorite) carbamide oxidation processes are absolutely identical stoichiometrically. That is why

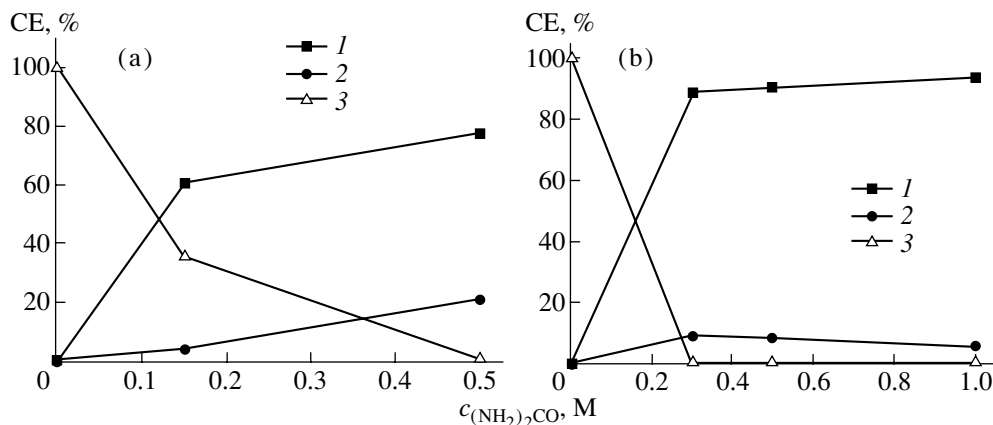


Fig. 3. CE for processes (1)–(3) in (a) 0.15 and (b) 1 M NaCl vs. carbamide concentration.

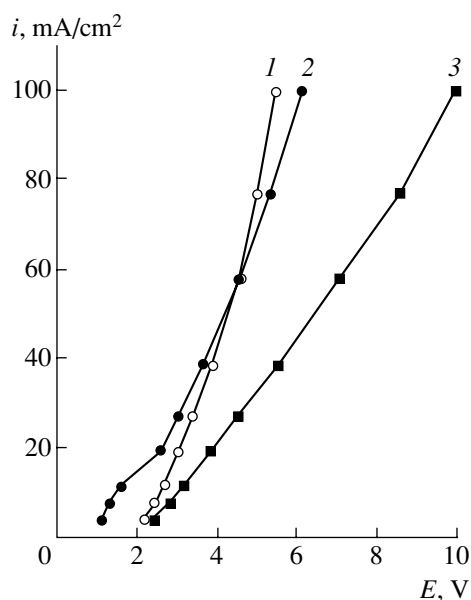


Fig. 4. Anodic polarization curves for 0.1 M carbamide solutions in 0.15 M (1) NaCl, (2) NaBr, and (3) NaF.

taking into account process (7) has no effect whatsoever on the derivation of equations for CE.

The possibility of an indirect oxidation of carbamide with the aid of hypochlorite is supported by polarization measurements. Figure 4 gives anodic polarization curves obtained in halide solutions of carbamide. As seen, the polarization in a fluoride solution is significantly higher than in a chloride solution; this can be associated with the formation of polymeric films on the electrode [5]. In a chloride solution, hypochlorite forms and no polymerization occurs.

The polarization curves were measured in nonbuffered solutions in a cell with separated anodic and cathodic compartments; therefore, the potentials presented in Fig. 4 are slightly overrated (are more positive) due to acidification of a near-anode layer. However, a comparison of Figs. 1a and 3a suggests that CE for the oxygen evolution (this process leads to the acidification) in the fluoride solution is much lower than in the chloride solution. Consequently, the actual difference between the electrode polarization in chloride and fluoride solutions is still larger than it follows from Fig. 4. This is yet one more confirmation of the above conclusion.

The effect of pH value of a sulfate solution of carbamide on CE for processes (1) and (2) was also estimated. The measurements were taken in solutions containing 0.5 M Na_2SO_4 , 0.1 M carbamide, and either H_2SO_4 or NaOH (Fig. 5). As seen, rates of processes (1) and (2) are independent of solution pH. This conclusion is not surprising, because almost identical acidification

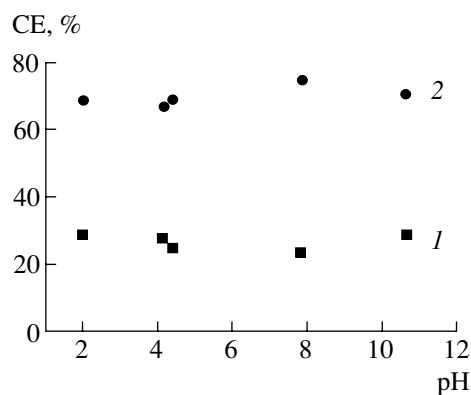


Fig. 5. CE for processes (1) and (2) vs. pH value of 0.1 M carbamide solution in 0.5 M Na_2SO_4 .

of solution occurs in both processes: 1 and 1.125 g-ion H^+ per F in (1) and (2), respectively.

CONCLUSION

The anodic oxidation of carbamide in neutral sulfate and halide (fluoride, chloride, bromide) solutions yields molecular nitrogen and nitrate, and the current efficiencies for both processes are complex functions of the nature and concentration of the supporting salt. Variation in the pH value of sulfate solutions in the range from 2 to 11 scarcely affects the ratio between rates of anodic processes.

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