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Concentration Oscillations in the Oxidative Carbonylation of Non-1-yne in the PdI_2–KI–CO–O_2–CH_3OH and PdI_2–KI–CO–O_2–Phenylacetylene–CH_3OH Systems

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Abstract—The oscillatory mode of the oxidative carbonylation of non-1-yne in the PdI_2–KI–CO–O_2–CH_3OH system has been observed for the first time. Triethylamine affects the formation and development of concentration oscillations in this system. It has been discovered that the character of oscillations of the non-1-yne concentration is changed by the simultaneous introduction of another alkyne (phenylacetylene) into the system.

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Among the numerous organic and inorganic reactions, there are many processes characterized by periodic oscillations of the concentrations of intermediates [1–3]. Investigating the carbonylation of unsaturated compounds in alcoholic solutions of palladium complexes, we showed that these reactions could occur in the oscillatory mode in fairly narrow ranges of conditions. We discovered several oscillation reactions classified as oxidative carbonylation processes [4–12]. Our British colleagues from Newcastle and Leeds Universities repeated our experiments on the oxidative carbonylation of phenylacetylene and gained a considerably deeper insight into the understanding of the processes that occur in this system. In particular, they measured the heat per oscillation, revealed the dependence of the character of oscillations on the particle size of palladium iodide used, and demonstrated the possibility of enhancing the selectivity of the process by conducting it in the oscillatory mode [13–16].

In the present work, we consider the results obtained for the oxidative carbonylation of a new substrate (non-1-yne). The carbonylation of non-1-yne in the PdI_2–KI–CO–O_2–CH_3OH system can proceed in the developed oscillation mode. In addition, the introduction of phenylacetylene (PA) into this system causes nontrivial effects, specifically, changes in the shape and duration of the oscillations of the electrical potential difference (E_{Pt}) and solution acidity (pH).

EXPERIMENTAL

Oscillatory processes in the oxidative carbonylation of non-1-yne were studied in a system closed with respect to the liquid phase. A 250-mL glass reactor, whose temperature was maintained at 40°C, was used. The reactor was connected to a calibrated burette and an Ekspert-004 ionometer, which provided the possibility of measuring the characteristics of concentration oscillations during the process. The experimental procedure for studying oscillatory modes in metal complex catalyzed reactions was reported in detail in earlier works [5, 6] and can briefly be described as follows. Weighed samples of KI and PdI_2 in methanol were successively introduced into a temperature-controlled reactor under vigorous mechanical stirring. The system was sealed, purged with a mixture of CO and O_2 gases, and filled with the same mixture in a volume ratio of 1 : 1. Finally, the substrate to be carbonylated (non-1-yne) was injected with a microsyringe into the reactor. The alkyne addition moment was taken to be the beginning of the run. The total volume of the liquid phase was 10 mL. The difference between the electrical potentials of the platinum and silver chloride electrodes (E_{Pt}), the pH of the reaction medium (measured with a glass electrode), and the gas mixture uptake rate (measured with a calibrated burette) were recorded during the run. The compositions of the gas and liquid phases were monitored by chromatography. The reaction products were identified by NMR spectroscopy (Bruker-300) and gas chromatography coupled with mass spectrometry (Agilent 6890N instrument). Experiments were carried out under standard conditions: constant initial concentrations of the reactants ($[KI]_0 = 0.4$, $[PdI_2]_0 = 0.01$, $[\text{non-1-yne}]_0 = 0.1$ mol/L); gas mixture composition, $CO : O_2 = 1 : 1$ (vol/vol); total pressure of 1 atm; 40°C. Each reactant was stirred for 15 min until its complete dissolution. Non-1-yne was introduced 15 min after purging and filling the system with the gas mixture.

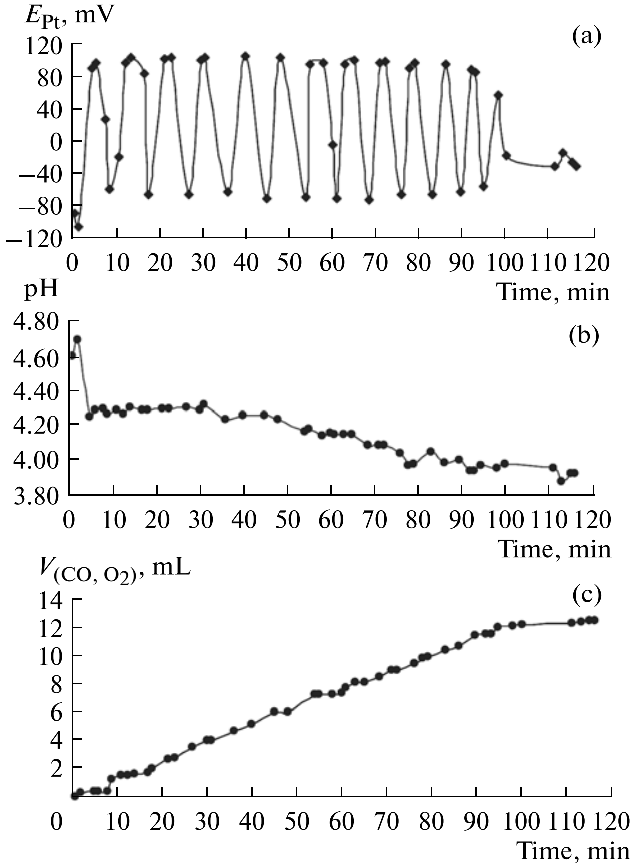

Fig. 1. Oxidative carbonylation of PA in the PdI_2–KI–CO–O_2–CH_3OH system: changes in (a) E_{Pt}, (b) pH of the medium, and (c) the volume of the absorbed gas mixture during the reaction. Concentrations: $[KI]_0 = 0.4$, $[PdI_2]_0 = 0.01$, and $[PA]_0 = 0.1$ mol/L; CO : O_2 = 1 : 1.

RESULTS AND DISCUSSION

We showed that the oxidative carbonylation of non-1-yne in the PdI_2–KI–CO–O_2–CH_3OH system can occur in the oscillatory mode. The oscillations of E_{Pt}, the pH of the medium, and the uptake rate of the gas mixture have several specific features differentiating them from the oscillations in the system containing phenylacetylene under the same conditions. These distinctions can be seen by comparing Figs. 1 and 2.

The oscillations of E_{Pt} in the reaction with non-1-yne have a somewhat smaller amplitude and cease sooner than those in the reaction with PA. This is likely due to the difference between the effects of the heptyl and phenyl radicals at the terminal triple bond. The introduction of a small amount of a base into the system plays a noticeable role in the development of oscillations in the oxidative carbonylation of PA. For example, the addition of 5–10 μL of triethylamine (TEA) significantly increased the amplitude and duration of the oscillations. Experiments with non-1-yne confirmed this characteristic feature of oscillation development upon the addition of a base (Fig. 3).

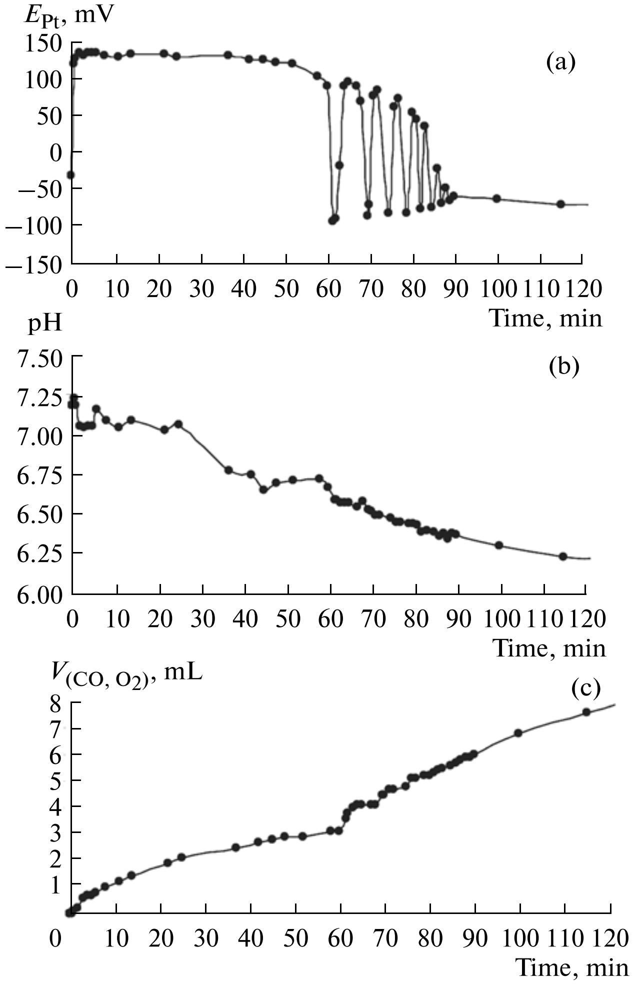

Fig. 2. Oxidative carbonylation of non-1-yne in the PdI_2–KI–CO–O_2–CH_3OH system: changes in (a) E_{Pt}, (b) pH of the medium, and (c) the volume of the absorbed gas mixture during the reaction. Concentrations: $[KI]_0 = 0.4$, $[PdI_2]_0 = 0.01$, and $[\text{non-1-yne}]_0 = 0.1$ mol/L; CO : O_2 = 1 : 1.

Although we failed to exhaustively explain the effect of TEA on the development of oscillations in the system, we can assume, however, that TEA increases the pH of the medium to a value at which the system passes into an unstable state and comes to the thermodynamic equilibrium in the oscillatory mode. Anyway, the role of TEA was demonstrated by several examples involving various alkynes and alkynols as substrates to be carbonylated [7–9].

In addition to observing the above effects, we discovered the mutual effect of two simultaneously present alkynes on the development of oscillations in the PdI_2–KI–CO–O_2–PA–CH_3OH system in oxidative carbonylation in a solution of palladium complexes—a very unusual phenomenon. The essence of this phenomenon is that the character of oscillations (in particular, their shape and duration) in the case of the simultaneous introduction of PA and non-1-yne

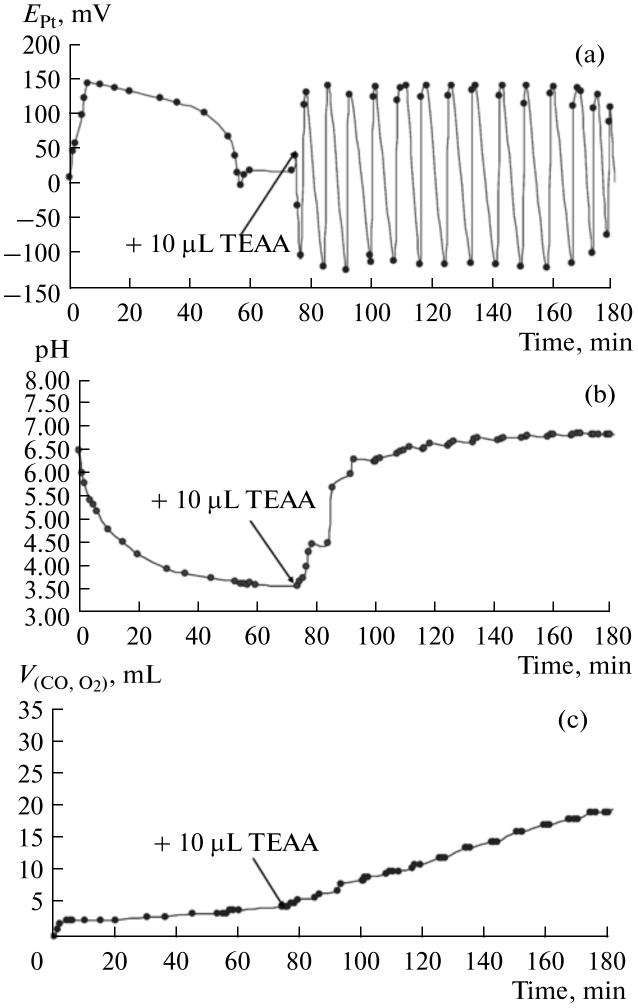

Fig. 3. Effect of TEA on the oxidative carbonylation of non-1-yne in the PdI_2–KI–CO–O_2–CH_3OH system: changes in (a) E_{Pt}, (b) pH of the medium, and (c) the volume of the absorbed gas mixture during the reaction. Concentrations: $[KI]_0 = 0.4$, $[PdI_2]_0 = 0.01$, $[\text{non-1-yne}]_0 = 0.1$, and $[TEA]_0 = 0.008$ mol/L; CO : O_2 = 1 : 1.

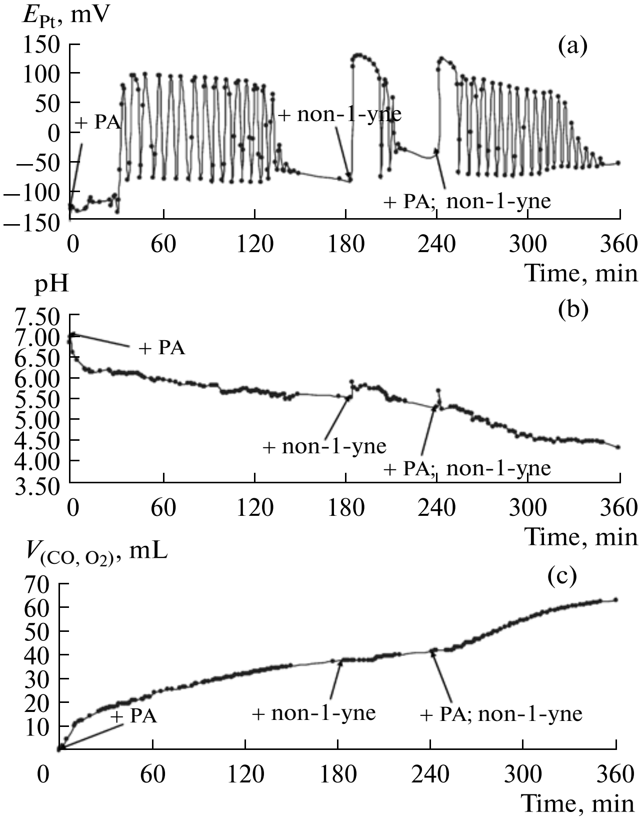

Fig. 4. Mutual effect of non-1-yne and the additional substrate PA on the oxidative carbonylation of non-1-yne in the PdI_2–KI–CO–O_2–CH_3OH system: changes in (a) E_{Pt}, (b) pH of the medium, and (c) the volume of the absorbed gas mixture during the reaction. Concentrations: $[KI]_0 = 0.4$, $[PdI_2]_0 = 0.01$, and $[\text{non-1-yne}]_0 = 0.1$ mol/L; CO : O_2 = 1 : 1.

into the system differs from the character of oscillations in the case of the successive introduction of these substrates. Figure 4 illustrates the changes that occur in the system. The experiments carried out according to the above procedure were characterized by a fairly good reproducibility, which is a necessary condition for drawing correct conclusions from experimental data.

Initially, 1 mmol of PA was introduced into the reactor. An induction period of 30–40 min was observed, during which the system was in the reduced state characterized by low E_{Pt} (−150 to −110 mV), by rapid establishment of an almost invariable acidity value of pH 6.2–6.0, and by intensive absorption of the CO + O_2 mixture (15–20 mL). This was followed by a number of oscillations typical of the oxidation carbonylation of PA: E_{Pt} changed from +100 to −90 mV, pH decreased slowly from 6.0 to 5.5, and vigorous gas uptake was observed. Half an hour after the cessation of the first series of oscillations, 1 mmol of non-1-yne was introduced into the system. The system passed rapidly to the oxidized state (E_{Pt} from +120 to +130 mV) and stayed in it for 15–20 min, after which 5 to 7 rapidly decaying oscillations were observed. The gas uptake was considerably smaller (3–5 mL) than in the reaction with PA. Half an hour after the end of this series of oscillations, PA (0.5 mmol) and non-1-yne (0.5 mmol) were simultaneously introduced into the reactor. The observed series of oscillations was intermediate between the two former series. On the one hand, there were a delay before the oscillations due to the system staying in the oxidized state, which is characteristic of oscillations in the reaction with non-1-yne, and a gradual decay of the E_{Pt} oscillations, also characteristic of the reaction with non-1-yne. On the other hand, the character of oscillations in the intermediate part of this series resembled the PA oscillations: there was only a slight change in E_{Pt}, H continued to decrease, and the gas mixture was taken up at a higher rate than in the case of the separate introduction of PA and non-1-yne.

Thus, our experiments showed that the character of oscillations in non-1-yne carbonylation change significantly when PA is introduced simultaneously with non-1-yne. At present, we attempt to exactly identify the reaction products at the end of the process and directly after each particular series of oscillations. Firstly, it is necessary to elucidate whether new, hitherto unidentified products form upon the simultaneous introduction of the substrates. Secondly, it is necessary to see whether the proportions of the products vary from one stage of the process to another. These data would help us conclude about the processes that occur in the system and make an assumption as to the mechanism of the reaction.

CONCLUSIONS

The oxidative carbonylation of non-1-yne in the PdI_2–KI–CO–O_2–CH_3OH system was observed for the first time to occur in the oscillatory mode. It was shown that TEA affects the formation and development of concentration oscillations in this system. It was discovered that the simultaneous introduction of non-1-yne and PA into the system changes the character of the oscillations. It is expected that this effect will take place in oscillatory reactions involving other substrates. This assumption will be checked in our forthcoming studies.

ACKNOWLEDGMENTS

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