

Research Article

Oxidative Carbonylation of 2-Propyn-1-ol and 2-Methyl-3-butyn-2-ol in an Oscillatory Mode

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The oscillatory modes of oxidative carbonylation reaction of two new substrates—2-methyl-3-butyn-2-ol and 2-propyn-1-ol in homogeneous system PdI₂-KI-CO-O₂-CH₃OH are found. Borders of oscillatory areas are drawn, the basic products of reaction are identified, and probable processes routes are offered.

1. Introduction

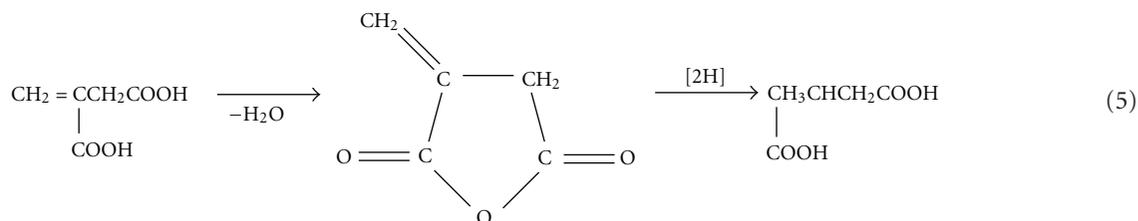
The phenomenon of intermediates concentration oscillations is found already in several tens of homogeneous [1] and heterogeneous [2] chemical systems. The most interesting thing, in our opinion, is the oscillations occurring in homogeneous catalysis conditions. They are evolving out of intermediates complex interactions, which are formed during process. So this type of oscillations has a chemical nature only. Influence of diffusion, processes of mass and heat exchange, certainly, can be observed in these systems, but these processes, to all appearance, are not responsible for an occurrence of concentration oscillations in the homogeneous systems.

We were lucky to find out oscillatory modes of oxidative carbonylation reactions of two new alkynes: 2-methyl-3-butyn-2-ol (**MB**) and 2-propyn-1-ol (**P**). As far as we know it is the first mention of oscillatory process with participation of oxygen containing alkynes in metal complexes catalysis conditions. In early works we investigated the oscillations in palladium halogenide solutions in reactions of alkynes oxidative carbonylation [3–11]. These are examples of reactions

in which complex products—carboxylic acids and their derivatives—are synthesized from simple substances—H₂O, CH₃OH, CO, and so on. The carbonylation reactions are interesting with relation to important products of organic synthesis obtaining 2-methyl-3-butyn-2-ol is that used as semiproduct in synthesis of fragrance compounds, medical products, and vitamins, applied as anticorrosive means to protection of the petroleum equipment, the modifier of motor fuels, emulgators. **MB** is an interesting research object. On the one hand, it has triple bond in the molecule, and so it can participate in reactions of hydrogenation, halogenations and other addition processes on the triple bond. It is active also in reactions of oligomerization and polymerization, and owing to presence of hydroxyl groups **MB** is the participant of reactions that are characteristic for alcohols generally, and for tertiary alcohols particularly. Finally, **MB** participates in reactions of carbonylation as any unsaturated reactant. **MB** reacts in butanol with nickel carbonyl in the presence of HCl even at room temperature and gives as main product butylic ether of 4-hydroxy-4-methyl-2-pentenoic acid with a good yield [12]. After the further hydrogenation and hydrolysis, isohexane acid and corresponding lactone (1).

Hydrolysis of esters allows obtaining itaconic and aconitic acids. The first one passes easily into itaconic anhydride

that turns sequentially by hydrogenation into methylsuccinic acid (5).



2. Experiments

Experiments on oxidative carbonylation **MB** were carried out in closed system at 40°C in glass thermostatic reactor (volume = 200 mL), having a reflux condenser, a liquid sampling unit, and units for glass and platinum electrodes, electrolytic key, and graduated gas burette.

Gas and liquid phases were stirred with a magnetic stirrer. The measurements of the electric potential differences (E_{Pt}) and the acidity of the reaction solution (pH) were managed with platinum and glass electrodes accordingly during experiments. Silver-chloride electrode was used as a reference electrode; it was immersed in the saturated solution of KCl, and connected to the reactor via an electrolytic bridge filled with the colloidal (agar) solution of KI in methanol. For measurement of pH and E_{Pt} pH-meter-ionometer EXPERT-001 was used. The compositions of the initial and reaction gas were determined during the experiment by gas chromatography (3 m * 3 mm packed columns with activated carbon AP-3; determination of air, CO, and CO₂; separation temperature 160°C, and 13X molecular sieves: determination of O₂, N₂, and CO; separation temperature 40°C). In both cases fraction with particles size of 0.25–0.5 mm was used; the heat conductivity detector was also used, the carrier gas-argon. The reaction products were identified with the help of a chromatomass-spectrometry technique. Agilent Technologies gas chromatograph (USA) was used, equipped with mass-detector Agilent 5973 N (length of capillary column was 50 m and internal diameter 0.32 mm, column was covered with polymethylsiloxan; thickness of a layer was 0.52 microns). The temperature of the evaporator was 150°C, temperature of a column was programmed: 5 minutes temperature was supported at 50°C, then during 12 minutes the temperature was lifted with speed of 15°C/minutes up to 230°C, and then the given temperature was maintained 5 minutes more.

2.1. General Experiments Technique. Weighed portions of KI, PdI₂ and methanol were loaded consistently into the dry reactor thermostated at 40°C with electrodes inserted beforehand. The mixture was stirred during 20 minutes for dissolution of palladium salt. A reactor attached to a calibrated burette was pressurized and blown out with gas mixture CO and O₂ (blown gas volume was not less than 500 mL). The burette was used for measurement of the consumed gases volume. An initial gas mixture of carbon

monoxide and oxygen was prepared in gasometer. Thermostated cell with saturated KCl solution connected to the reactor via an electrolytic bridge. Reaction solution was mixed, and pH and E_{Pt} values were measured. Then, without stop the stirring, a prepared beforehand methanol solution of alkyne was added with the help of a microsyringe through a liquid sampling unit, leading to total amount of solution up to 10 mL. The moment of alkyne input was accepted as a start point of the experiment.

3. Results and Discussion

During experiments in the system PdI₂-KI-CO-O₂-CH₃OH oscillations of platinum electrode potential (E_{Pt}) and pH values and also the characteristic step form of consumed gases (CO and O₂) curve (Figures 1 and 2) were obtained.

Oscillations, as one would expect for the closed system, had damped character and continued from 2 to 4 hours according to the experiment conditions. In **MB** carbonylation experiments the relaxation oscillations were observed frequently (see Figure 1) when the system was in the upper (oxidized) state for a long time, doing short-time transitions into the lower (reduced) state. In many experiments with **P** as a substrate it was necessary for oscillations initiation to enter into a system small amounts (5–15 mL) of triethylamine, which led the system into a pH values range where the oscillations can begin. However, it is necessary to notice that the role of bases in oscillations development is not quite clear, and this question requires further researches. Oscillations in the system with **MB** began without adding of the base.

Gases consumption occurs in the portions at those moments only when the system passes in the reduced state; the bottom points on the pH and E_{Pt} change curves were corresponded to these states. In the rest of the time, which surpasses considerably the moments of products synthesis (reduced states), the system does not consume the gas mixture—to these states almost horizontal regions of gases consumption curves corresponded.

The several series of one-factorial kinetic experiments were carried out for the study of influence of reagents initial concentrations that were added into system. As a result of these experiments the area where the advanced oscillations develop was determined. The experiments with **MB** were carried out in interval [PdI₂]₀ concentration from 0.0025 up to 0.02 M. The concentration of other reagents was maintained as follows: [KI]₀ = 0.4 M; [**MB**]₀ = 0.1 M;

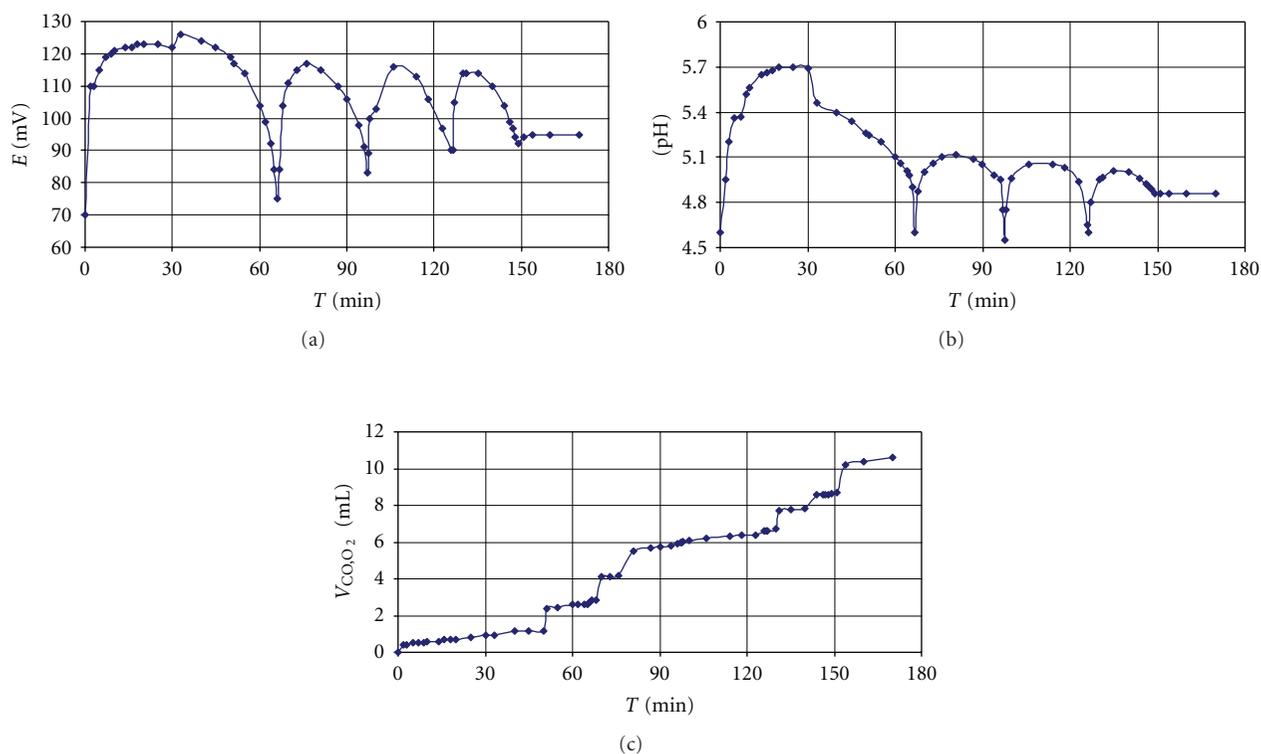


FIGURE 1: Oxidative carbonylation of 2-methyl-3-butyne-2-ol (**MB**) in the system PdI₂-KI-CO-O₂-CH₃OH. [PdI₂]₀ = 0,005 M; [KI]₀ = 0,4 M; [MB]₀ = 0,1 M; [CO]₀ = 60%; [O₂]₀ = 40%.

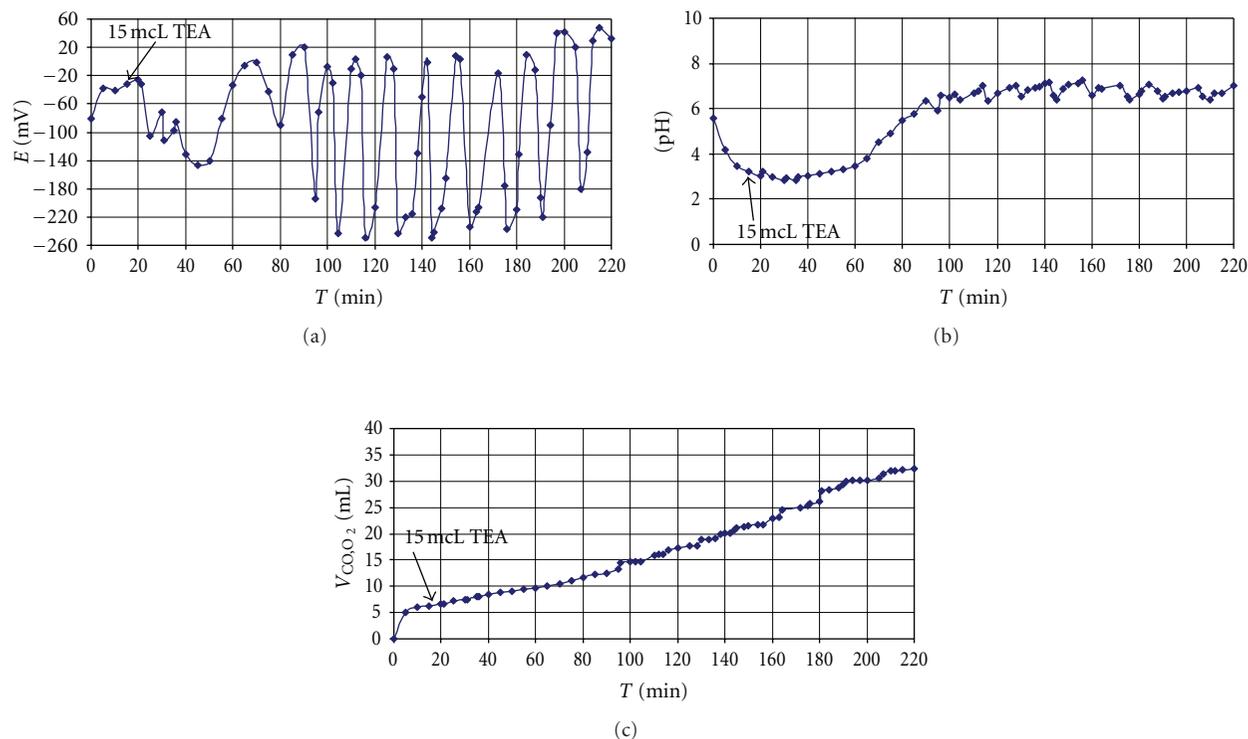


FIGURE 2: Oxidative carbonylation of 2-propyne-1-ol (**P**) in the system PdI₂-KI-CO-O₂-CH₃OH. [PdI₂]₀ = 0,015 M; [KI]₀ = 0,4 M; [P]₀ = 0,1 M; [CO]₀ = 60%; [O₂]₀ = 40%.

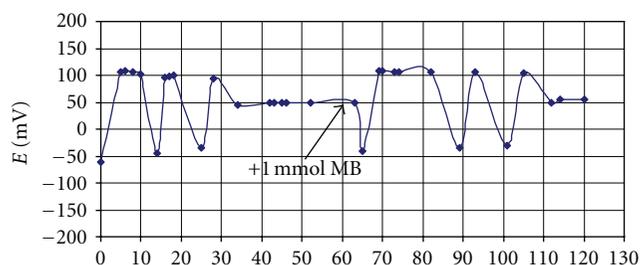


FIGURE 3: Oxidative carbonylation of **MB** with input of an additional substrate portion. $[KI]_0 = 0.4$ M; $[PdI_2]_0 = 0.01$ M; $[MB]_0 = 0.1$ M; $[CO]_0 = 72\%$; $[O_2]_0 = 21\%$; $[N_2]_0 = 7\%$.

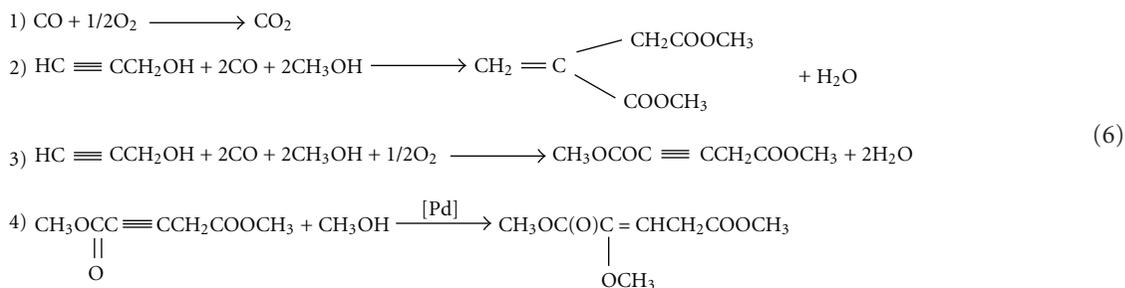
$[CO]_0:[O_2]_0 = 3:2$. The period of oscillations increases with the reduction of $[PdI_2]_0$ concentration up to 0.0025 M while their amplitude does not vary practically. E_{Pt} values are ranged in interval $(-60)/(+130)$ mV. The reduction of oscillations number and also their amplitudes is observed at increasing of $[PdI_2]_0$ concentration up to 0.02 M; at $[PdI_2]_0$ concentration of 0.02 M oscillations are practically away, which can attest a hypothesis about approach to the upper border of concentrations area where the oscillatory mode is realized. Study of gas mixture composition influence on oscillations appearance was carried out at compositions of gas mixture from 44% CO (56% O_2) up to 94% CO (6% O_2). Moderate increase of amplitude and period of oscillations is marked at the increase of initial CO concentration. The oscillations are not found out at concentration of CO in

a gas mixture less than 44% and more than 94%. Also in the case of oxidative carbonylation of phenylacetylene and methylacetylene [6, 7], it was shown that alkyne portion addition (1 mmol e.g., **MB**) after the termination of an initial series of oscillations results in their renewal (Figure 3).

It can be testified that the reasons of oscillations attenuation are connected with substrate consumption and they could be not damping in case of its continuous feeding.

The oscillations area determined in experiments with **P** range in concentration interval for $[KI]_0$ —from 0.20 up to 0.45 M, for $[PdI_2]_0$ —from 0.005 up to 0.035 M, for $[CO]_0$, from 60 up to 93%(vol). An obviously expressed dependence of oscillations appearance on the presence in system triethylamine at $[P]_0$ not less than 0.6 M was observed. The oscillations with the alternation of different periods was noticed during some experiments that can serve as indirect confirmation of two different processes proceeding in the system in parallel. It is quite possible that such processes are the reaction of oxidative and additive carbonylation.

3-Hydroxy-3-methyl-butan-1-on and methyl ester of 3-methyl-2-butenic acid were found out among the products of **MB** oxidative carbonylation. The basic products of **P** carbonylation in the given conditions are dimethyl esters of itaconic, 2-pentyn-1,5-dioic, and 2-methoxy-2-pentendioic acids. Considering the literary data mentioned above and also the experiments results of alkynes carbonylation studying in homogeneous catalytic systems [4, 6, 7, 9–11], it is possible to offer some connected routes where the products found out by us could be formed.



The offered scheme implies presence in the system of several connected processes: reactions of oxidation CO up to CO_2 , reactions of **P** additive carbonylation up to dimethyl ester of itaconic acid, and reactions of **P** oxidative carbonylation up to two other acids esters. Such reaction run was unexpected, as the other reactions investigated by us earlier in similar systems (KI- PdI_2 -CO- O_2 -phenylacetylene or methylacetylene; LiBr- $PdBr_2$ -CO- O_2 -phenylacetylene or methylacetylene; LiBr- $PdBr_2$ - H_2O -(CH_3) $_2$ CO-CO) [3, 4, 6, 7] have been concerned with for processes of alkynes oxidative (only) carbonylation.

4. Conclusion

In the given work the oscillatory mode in oxidative carbonylation reaction of two new substrates—2-methyl-3-butyn-2-ol and 2-propyn-1-ol—for the first time was found out.

The data, which have been found out in experiments with 2-propyn-1-ol, allow to consider that alongside the alkyne oxidative carbonylation in the system its additive carbonylation proceeds. The ranges of reagents initial concentrations and gas mixtures compositions were determined at which E_{Pt} and pH values steady oscillations were observed. It was shown that a new portion of alkyne adding results in recurrence of an oscillatory mode. Thus, it is possible to assert that the first examples of nonlinear behavior of a new class of oscillators—reactions of alkynes oxidative carbonylation—were found out.

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