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Oxidative carbonylation of alkynes in self-oscillating mode. Effect of the nature of substrates on the dynamic behavior of reaction system

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The oxidative carbonylation of alkynes in the oscillation mode was studied. The influence of the nature of substrates, alkynes and alcohols, on the pattern of oscillations was considered. The role of oxidants, I_2 and H_2O_2, in this process was demonstrated. The reaction network of the process was formulated, and four hypothetical mechanisms were selected.

Key words: oxidative carbonylation of alkynes, homogeneous catalysis by metal complexes, self-oscillations, mathematical simulation.

Reactions that occur in the self-oscillating mode have been a matter of research in chemistry and biology for many years.[1,2] It is quite possible that oscillation processes are rather common in nature. Many reactions that follow steady-state or quasi-steady-state kinetics under certain conditions may exhibit, under some other conditions, a nonlinear dynamic behavior, whose prediction is a fairly complicated task.

Unlike all the other known oscillating chemical systems, in the oxidative carbonylation of alkynes discovered recently to proceed in the self-oscillating mode,[3,4] relatively simple substrates are converted into complex molecules:

$$\mathrm{RC{\equiv}CH + 2\,CO + 2\,R'OH + 1/2\,O_2} \xrightarrow{\mathrm{PdI_2,\ KI}} (cis\text{-},\ trans\text{-})\ \mathrm{R'OOCC(R){=}CHCOOR' + H_2O}. \qquad (1)$$

All the other oscillating processes including those driven by heterogeneous catalysts[5] involve oxidation, hydrogenation, or destruction of complex molecules.[6]

Previously,[4] it was shown that reaction (1) is general as regards alkynes. This work is a detailed study of the influence of the nature of the alkyne and alcohol on the region of existence and characteristics of the oxidative carbonylation in the self-oscillating mode.

Experimental

The experiments were carried out in a closed system, in a 250-mL glass reactor maintained at 40 °C using a standard procedure. Weighed portions of KI and PdI_2 were placed into the reactor and dissolved in 10 mL of alcohol with stirring with an efficient power-driven Teflon stirrer with shaft precessing. After complete dissolution of the salts, the stirrer was switched off, and a gas mixture (either CO and O_2 in the case of liquid alkynes, or CO, O_2, and methylacetylene) was passed through the system (total amount was 500 mL). The repeated switching-on of the stirrer was taken as the start of the experiment. The parameters measured during the experiment included the electric potential differences between platinum and silver chloride electrodes (E_{Pt}) and between glass and silver chloride electrodes (pH) (pH and E_{Pt} were measured using pH-121 and pH-673 millivoltmeters, respectively), and the rate of absorption of the gas mixture (using a 100-mL calibrated burette). The volume of the gas phase in the reactor was 240 mL. The compositions of the initial and reaction gas were determined during the experiment by GC (3 m × 3 mm packed columns and AP-3 activated carbon to determine air, CO, and CO_2, separation temperature 160 °C; 13 X molecular sieve to determine O_2, N_2, and CO, separation temperature 80 °C; polysorb-P to determine methylacetylene, separation temperature 100 °C). In all cases, the fraction with a particle size of 0.25—0.5 mm and a heat conductivity detector were used. Argon (or helium in the case of polysorb) was used as carrier gas.

The reaction products were identified by GLC (a 3 m × 3 mm packed column, 10% Apiezon L on Inerton, the 0.25—0.3 mm fraction, heat conductivity detector, helium as carrier gas, separation temperature 230 °C), NMR, and GC/MS.* The major products formed in the alkyne carbonylation under these conditions were esters of unsaturated carboxylic acids.

Results and Discussion

According to previous data,[7,8] conducting the reaction in a dark reactor and a change in the stirring velocity

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may have an effect on the oscillation parameters. The results of our experiments show unambiguously that initiation of oscillating modes in reaction (1) does not depend on these factors. The change in the stirring velocity from 250 to 900 rpm (number of revolutions was measured using an ST-MEI strobotachometer) did not affect the oscillation mode, amplitude, or period. In our opinion, gas diffusion through the interface is not responsible for the appearance of oscillations in this system. The oscillations arise in this case due to specific features of the process mechanism.[4]

With phenylacetylene (PA), methylacetylene (MA), propargyl alcohol (PAlc), and 1,1-dimethylprop-2-ynol (DP) are used in oxidative carbonylation under similar conditions, the reaction proceeds in the self-oscillating mode over a certain period (120—240 min) (Fig. 1—4). This points to some common features of the reaction mechanism responsible for the observed complex behavior of the reaction systems. Nevertheless, oxidative carbonylation reactions with particular alkynes have also some peculiar features.

During carbonylation of phenylacetylene, the self-oscillating mode is established some period after the addition of PA. In the case of MA, the periodic variation of pH, E_{Pt}, and the gas absorption rate can be detected immediately after switching-on the stirrer. With DP as the reactant, no delay before the transition to a self-oscillating mode is observed but the oscillation period is much longer (up to 50 min) (see Fig. 3), while in the case of PAlc, the pH decreases to 1 in the beginning of the experiment and switching to a self-oscillating mode requires addition of some sodium acetate to the reaction system (see Fig. 4).

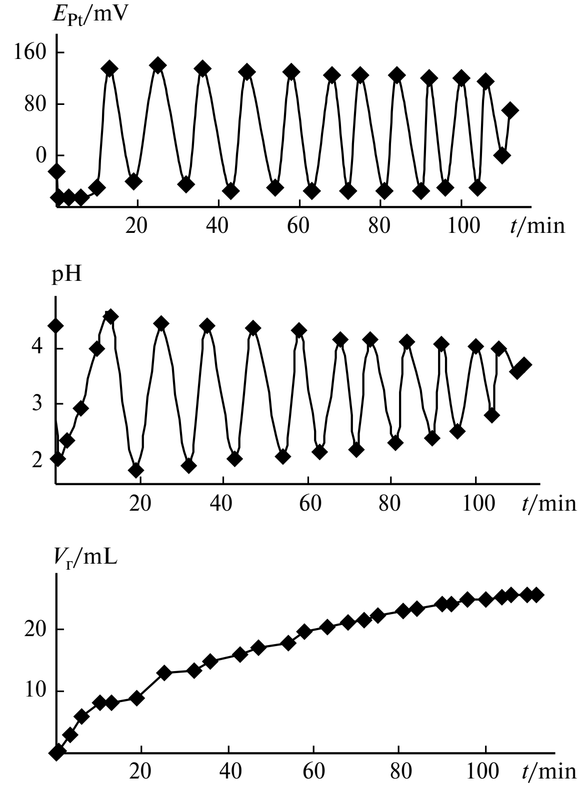

Fig. 1. Oxidative carbonylation of phenylacetylene in methanol. Stirring velocity W = 700 rpm; $[KI]_0$ = 0.4 mol L^{-1}; $[PdI_2]_0$ = 0.01 mol L^{-1}; $[PA]_0$ = 0.1 mol L^{-1}; $[CO]_0 : [O_2]_0$ = 3 : 2.

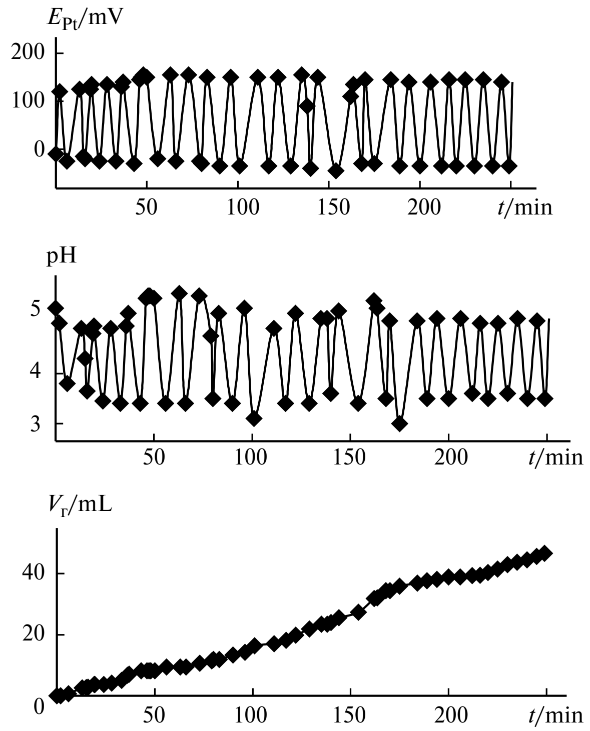

Fig. 2. Oxidative carbonylation of methylacetylene in methanol. $[KI]_0$ = 0.4 mol L^{-1}; $[PdI_2]_0$ = 0.005 mol L^{-1}; $[MA]_0 : [CO]_0 : [O_2]_0$ = 5 : 3 : 2.

In all cases, the oscillations were damped in time, which is usual for processes in closed systems and may be related to the consumption of alkyne. In the reaction with PA, the oscillations appear again after addition of fresh portions of the reactant (0.5—1.0 mmol of PA) (Fig. 5). In the oxidative carbonylation of MA in a closed system, the rate of gas absorption and, hence, the change in the gas composition throughout the experiment were slight (5—8% over 5—6 h).

The regions of stable oscillations and the "boundary" regions found by varying the gas phase composition are shown in the charts (Fig. 6). During PA carbonylation, stable self-oscillation modes appear at higher partial pressures of CO than in MA carbonylation.

Generally, the following regular features are observed. The oscillation period increases with an increase in $[KI]_0$, a decrease in $[PdI_2]_0$, and an increase in the fraction of O_2 in the gas mixture. The amplitude and number of oscillations decrease as the system approaches the limits of the

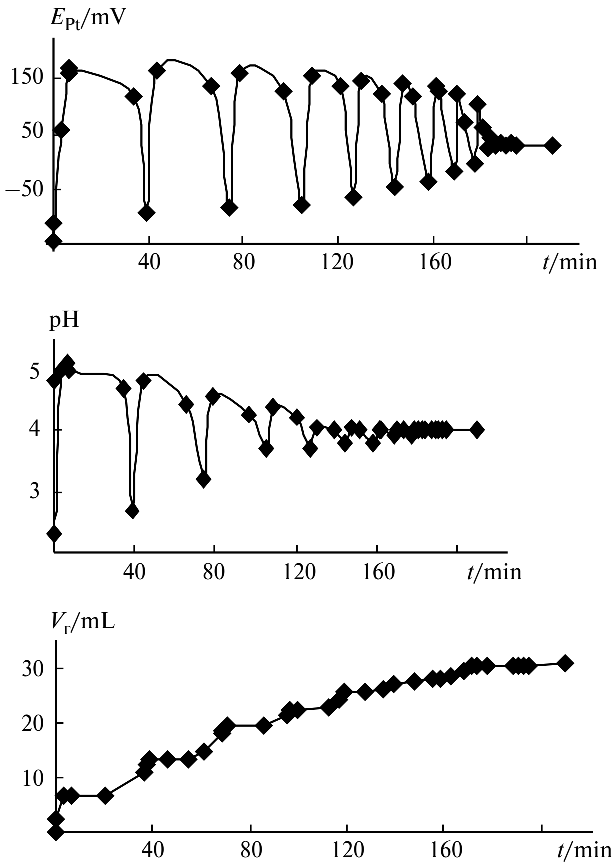

Fig. 3. Oxidative carbonylation of 1,1-dimethylprop-2-ynol in methanol. W = 700 rpm^{-1}; $[KI]_0$ = 0.4 mol L^{-1}; $[PdI_2]_0$ = 0.01 mol L^{-1}; $[DP]_0$ = 0.1 mol L^{-1}; $[CO]_0 : [O_2]_0$ = 3 : 2.

region of existence of self-oscillations regarding any of the above-mentioned parameters. It follows from the results obtained that oscillations can stop not only due to exhaustion of the alkyne but also when the system leaves the self-oscillation region regarding any of the parameters ($[PdI_2]$, [alkyne], and gas composition).

The nature of the cation (Rb^+, Cs^+, NH_4^+, K^+) introduced together with the iodide ion affects insignificantly the pattern of oxidative carbonylation of PA or MA in the self-oscillating mode. Substantial difference from the usual course of experiment in the PdI_2—MI—MeOH system (M is a cation) with PA as the substrate was found for CsI, in particular, the oscillation amplitude E_{Pt} (−50 to +210 mV) and pH (0.8—5.0) increased and the oscillations lasted for 7 h instead of the usual 2 h. This might be due to poor solubility of CsI in methanol. In the PdI_2—NH_4I—MeOH system with MA as the substrate, no oscillations were detected, although E_{Pt} and pH fell in the usual regions.

The course of the process proved to be fairly sensitive to the nature of the alcohol. The reactions with PA and MA proceed in the self-oscillating mode only in methanol and *n*-butanol solutions. In ethanol and isopropanol, gas absorption was slight, E_{Pt} and pH varied little with time, and no self-oscillating modes were detected under any experimental conditions. According to our data, carbonylation of alkynes did not occur under these conditions either. This is all the more strange in view of the fact that carbonylation of acetylene in similar PdI_2—LiI—HI (HCl) systems takes place in solutions of lower alcohols under the same conditions with comparable parameters.[9] This point requires further research.

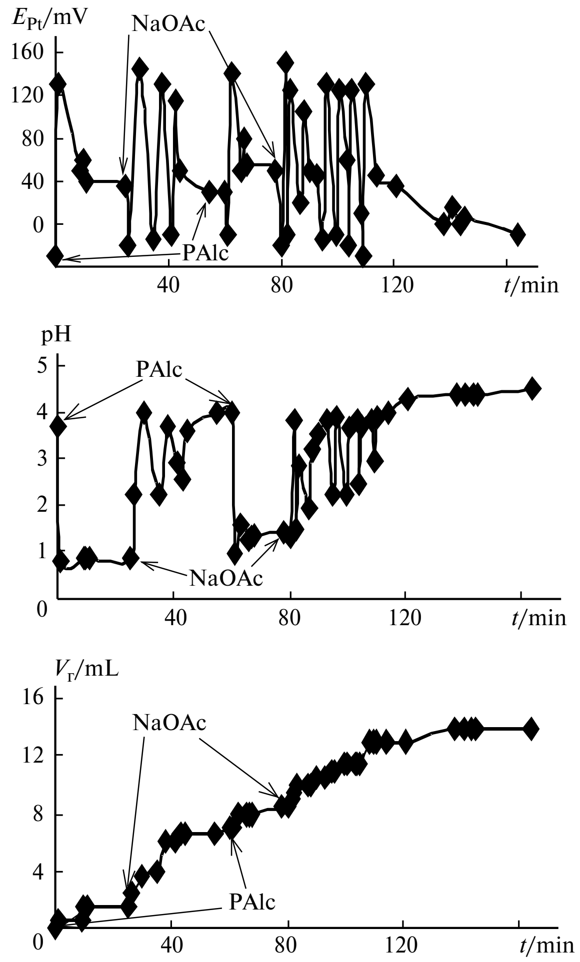

Fig. 4. Oxidative carbonylation of propargyl alcohol in methanol with the addition of fresh PAlc (0.1 mmol) and NaOAc (0.024 mmol) (shown by arrows). W = 700 rpm; $[KI]_0$ = 0.4 mol L^{-1}; $[PdI_2]_0$ = 0.01 mol L^{-1}; $[CO]_0 : [O_2]_0$ = 3 : 2.

In *n*-butanol, the oscillating carbonylation of PA soon damps (two or three oscillations), whereas analogous transformation of MA occurs for 3 h without a noticeable decrease in the oscillation amplitude or period (Fig. 7). It cannot be ruled out that the nature of the solvent influences the steps of generation of the active species that run the oscillating process.

The results we obtained provide the conclusion that the self-oscillations in the gas absorption rate, E_{Pt}, and pH in systems containing various alkynes and

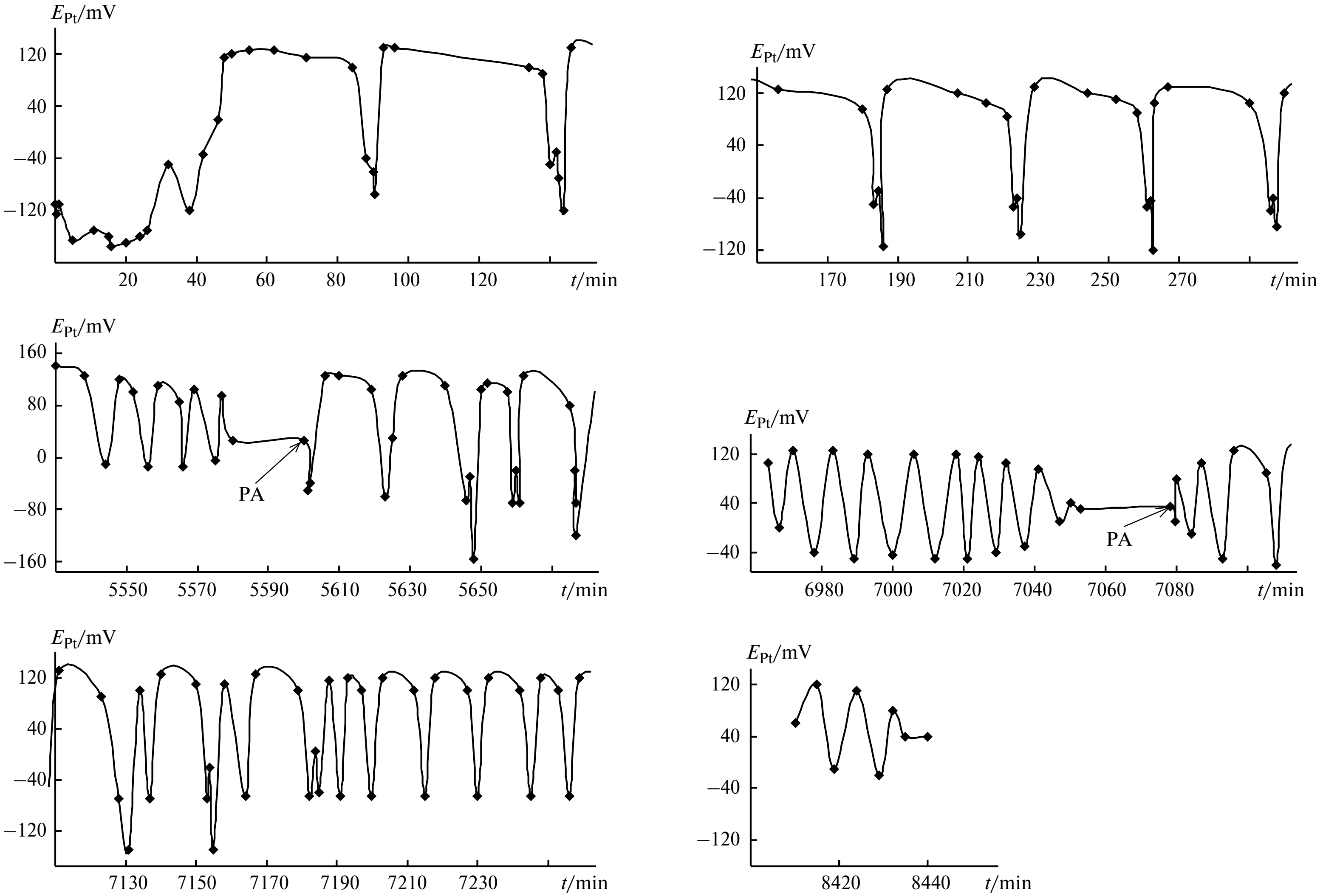

Fig. 5. Oxidative carbonylation of phenylacetylene in methanol with a decreased concentration of PdI_2 and introduction of 0.5 mmol of fresh PA (shown by an arrow). W = 700 rpm; $[KI]_0 = 0.4$ mol L^{-1}; $[PdI_2]_0 = 0.001$ mol L^{-1}; $[PA]_0 = 0.1$ mol L^{-1}; $[CO]_0 : [O_2]_0 = 3 : 2$.

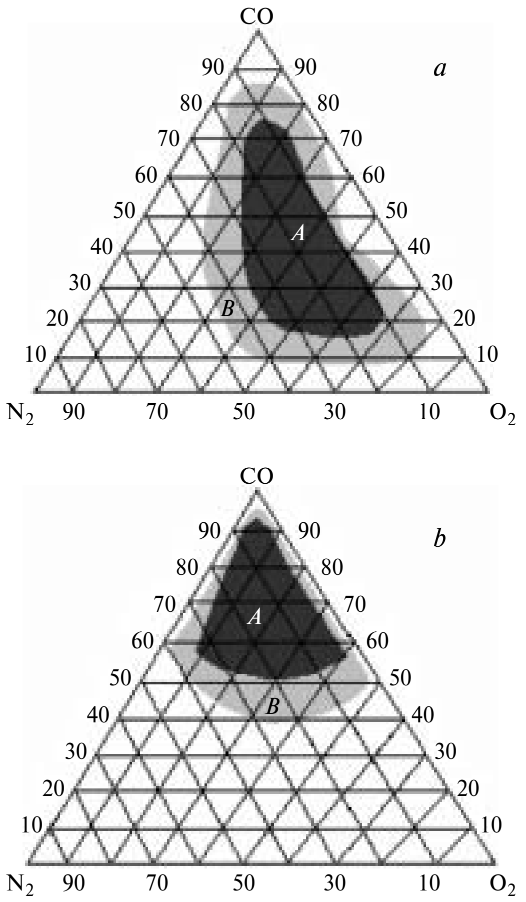

Fig. 6. Regions of existence of oscillations in the oxidative carbonylation of methylacetylene (*a*) and phenylacetylene (*b*): *A* is the region of stable oscillations; *B* is the region of rapidly damping oscillations.

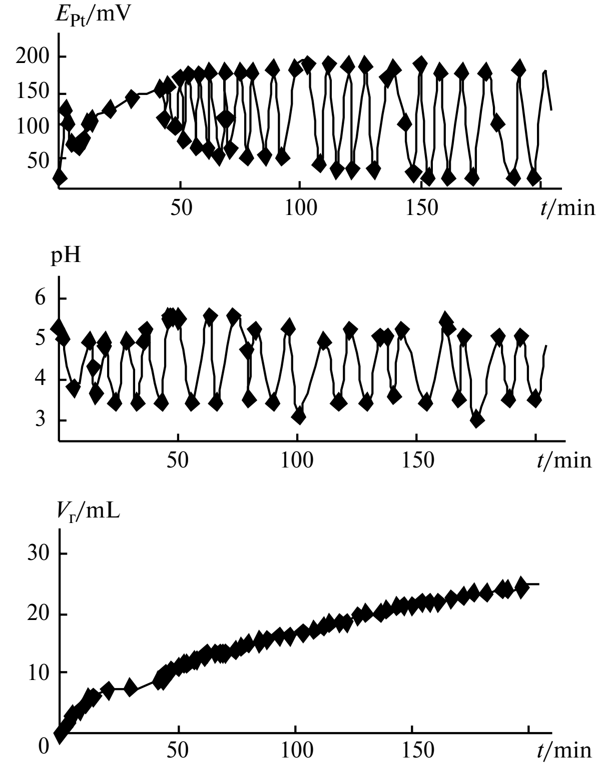

Fig. 7. Oxidative carbonylation of methylacetylene in *n*-butanol. $[KI]_0$ = 0.2 mol L^{-1}; $[PdI_2]_0$ = 0.00125 mol L^{-1}; $[MA]_0 : [CO]_0 : [O_2]_0$ = 5 : 3 : 2.

alcohols appear according to a general mechanism (see also Ref. 4).

We also studied the effect of oxidants, potential intermediates of the reaction (I_2 and H_2O_2), on the reaction pattern in the self-oscillating mode. The introduction of 0.0008 mmol of I_2 ($[I_2] : [PdI_2] = 8 \cdot 10^{-3}$) brings the system into an oxidized state and induces a delay of oscillations; after 3—5 min, the normal oscillations are resumed. The pH value decreases to 1—2 and in some cases, oscillations are resumed only after the addition of sodium acetate.

The introduction of hydrogen peroxide also results in oxidation of the system but the consequences differ somewhat from those observed with iodine. The addition of H_2O_2 (0.021 mmol; $[H_2O_2] : [PdI_2] = 2.1$) to the system before introduction of the alkyne (experiments with PA) increased the induction period, while the phase of steady-state oscillations remained unchanged. The addition of the same amount of H_2O_2 during the steady-state oscillations delayed the system transition to the reduced state; the period of oscillations increased 3—5-fold, while the amplitude increased toward positive potentials up to +200 mV. Upon repeated introduction of the peroxide, the same was observed once again (Figs. 8 and 9).

By taking samples during reaction (1) with their subsequent iodometric titration with a sodium thiosulfate solution (0.042 mol L^{-1}), it was shown that the reaction system contains an oxidant. The concentrations of the oxidant were different in the oxidized and reduced states of the system (0.1 and 0.008 mol L^{-1}, respectively).* Since the addition of 0.0008 mmol of I_2 interrupts the oscillations or, in some cases, completely terminates them, the oxidant present in the system in a quantity of 0.08 mmol but having no noticeable influence on the reaction is not molecular iodine. We assume that this is hydrogen peroxide.

To elucidate the possible transformation pathways of hydrogen peroxide under conditions of oxidative carbonylation of alkynes, we studied the kinetics of H_2O_2 decomposition at pH 7.5 and 2.0. The pH 2.0 was attained by adding methanol saturated with HCl. For comparison, a blank experiment without addition of H_2O_2 was carried out. The concentration of the peroxide solution added was 0.037 mol L^{-1}. The results of these experiments

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* The amounts of the oxidant in the system were 1.00 and 0.08 mmol, respectively.

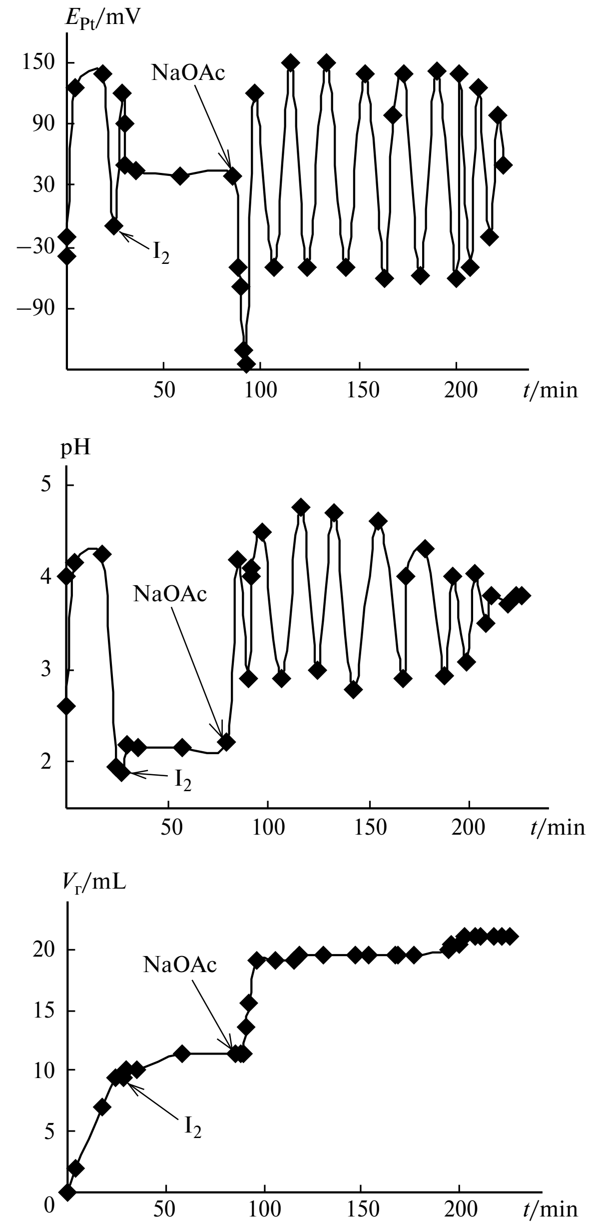

Fig. 8. Oxidative carbonylation of phenylacetylene in methanol with the addition of 0.0008 mmol of I_2 and 0.024 mmol of NaOAc (shown by arrows). $[KI]_0$ = 0.4 mol L^{-1}; $[PdI_2]_0$ = 0.01 mol L^{-1}; $[PA]_0$ = 0.1 mol L^{-1}; $[CO]_0 : [O_2]_0$ = 3 : 2.

(Fig. 10) showed that the decomposition kinetics of hydrogen peroxide at pH 7.5 and 2.0 are substantially dissimilar, which has to be taken into account in the simulation of reaction (1).

The results obtained were used to verify the mathematical model proposed previously for the oxidative carbonylation of alkynes.[4] A set of mechanisms capable potentially of exhibiting a complex dynamic behavior was formulated. The intention was to select, out of this set, the mechanisms describing adequately the experimental

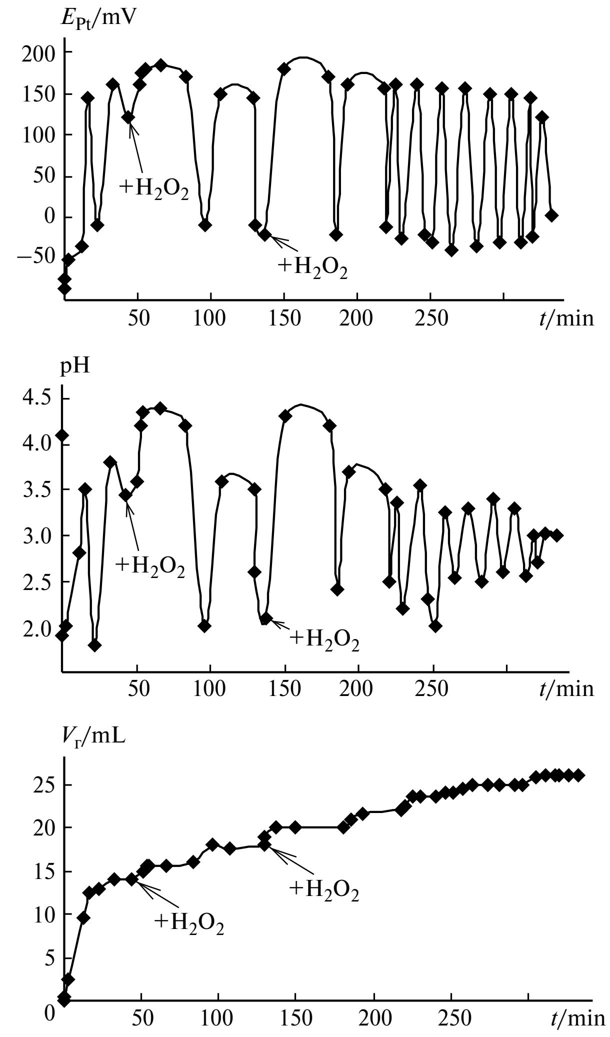

Fig. 9. Oxidative carbonylation of phenylacetylene in methanol with the addition of 0.021 mmol of H_2O_2 (the peroxide was introduced during the period of developed oscillations). $[KI]_0$ = 0.4 mol L^{-1}; $[PdI_2]_0$ = 0.01 mol L^{-1}; $[PA]_0$ = 0.1 mol L^{-1}; $[CO]_0 : [O_2]_0$ = 3 : 2.

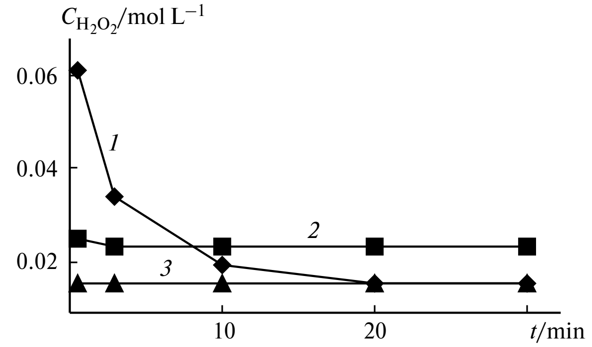

Fig. 10. Kinetics of decomposition of H_2O_2 introduced into the reaction system at pH 7.5 (*1*) and 2.0 (*2*); *3* is a blank experiment. $[KI]_0$ = 0.4 mol L^{-1}; $[PdI_2]_0$ = 0.01 mol L^{-1}.

Scheme 1

Reaction network for oxidative carbonylation of alkynes

Steps of formation of HPdI

1. $PdI_2 + CO + H_2O \rightarrow HPdI + CO_2 + HI$
2. $PdI_2 + CO + H_2O \rightleftharpoons IPdCOOH + HI$
3. $IPdCOOH \rightarrow HPdI + CO_2$
4. $PdI_2 + H_2O \rightleftharpoons PdI(OH) + HI$
5. $PdI(OH) + CO \rightarrow HPdI + CO_2$
6. $PdI(OH) + CO \rightarrow IPdCOOH$
7. $PdI_2 + 2\,CO + RC{\equiv}CH + 2\,MeOH \rightarrow$
$\rightarrow$ Products $+ HPdI + HI$

Steps of formation of Pd_2I_2

8. $PdI_2 + HPdI \rightarrow Pd_2I_2 + HI$
9. $PdI_2 + Pd^0 \rightarrow Pd_2I_2$

Steps of product synthesis

10. $Pd_2I_2 + 2\,CO + RC{\equiv}CH + 2\,MeOH \rightarrow$
$\rightarrow$ Products $+ 2\,HPdI$

Steps of oxidation of HPdI

11. $2\,HPdI + O_2 \rightarrow Pd_2I_2 + H_2O_2$
12. $HPdI + O_2 + HI \rightarrow PdI_2 + H_2O_2$
13. $HPdI + O_2 \rightarrow IPdOOH$
14. $IPdOOH \rightarrow HPdI + O_2$
15. $IPdOOH + HPdI \rightarrow H_2O_2 + Pd_2I_2$
16. $IPdOOH + HPdI \rightarrow H_2O_2 + Pd^0 + PdI_2$
17. $2\,HPdI + O_2 \rightarrow PdI_2 + Pd^0 + H_2O_2$
18. $2\,HPdI + 1/2\,O_2 \rightarrow PdI_2 + Pd^0 + H_2O$
19. $HPdI + I_2 \rightarrow PdI_2 + HI$
20. $HPdI + H_2O_2 + HI \rightarrow PdI_2 + 2\,H_2O$
21. $HPdI \rightarrow Pd^0 + HI$

Steps of oxidation and disproportionation of Pd_2I_2

22. $Pd_2I_2 + O_2 + 2\,HI \rightarrow 2\,PdI_2 + H_2O_2$
23. $Pd_2I_2 + I_2 \rightarrow 2\,PdI_2$
24. $Pd_2I_2 + H_2O_2 + 2\,HI \rightarrow 2\,PdI_2 + 2\,H_2O$
25. $Pd_2I_2 \rightarrow Pd^0 + PdI_2$

Steps of oxidation of Pd^0

26. $Pd^0 + I_2 \rightarrow PdI_2$
27. $Pd^0 + O_2 + 2\,HI \rightarrow PdI_2 + H_2O_2$

Steps of formation and consumption of oxidants

28. $2\,HI + O_2 \rightarrow H_2O_2 + I_2$
29. $I_2 + H_2O_2 \rightarrow 2\,HI + O_2$
30. $2\,HI + H_2O_2 \rightarrow I_2 + 2\,H_2O$
31. $2\,HI + 1/2\,O_2 \rightarrow I_2 + H_2O$
32. $2\,H_2O_2 \rightarrow 2\,H_2O + O_2$

data. The set of steps formulated on the basis of published and experimental data form the reaction network (RN) for the oxidative carbonylation of alkynes, which comprises 32 elementary and pseudo-elementary steps (Scheme 1).

The sets of the minimum two-route mechanisms (*viz.*, routes of oxidation of CO to CO_2 and oxidative carbonylation of alkynes) were cut out from the RN in such a way that each mechanism gave two final equations for the routes. According to our estimates, the full set of mechanisms that can be obtained in this way counts more than two thousands. To simplify the task of finding the mechanisms for this process, we resorted to the following procedure. Eight steps that ensure, in our opinion, an adequate description of the phenomena observed in the experiment were chosen out of the reaction network. These are the steps that make up the overall reaction (1). They can be divided into four groups.

1. Steps of formation of palladium hydride

$$PdI_2 + CO + H_2O \rightarrow CO_2 + HI + HPdI$$

$$PdI_2 + 2\,CO + RC{\equiv}CH + 2\,MeOH \rightarrow$$

$$\rightarrow \text{Products} + HI + HPdI$$

2. Step of formation of the active catalyst species (Pd^I complexes)

$PdI_2 + HPdI \rightarrow Pd_2I_2 + HI$

3. Step of synthesis of the alkyne carbonylation products

$Pd_2I_2 + 2\,CO + RC{\equiv}CH + 2\,MeOH \rightarrow$

$\rightarrow$ Products + 2 HPdI

4. Steps of oxidation of palladium hydride

$HPdI + O_2 + HI \rightarrow PdI_2 + H_2O_2$

$2\,HPdI + O_2 \rightarrow Pd_2I_2 + H_2O_2$

$HPdI + I_2 \rightarrow PdI_2 + HI$

$HPdI + H_2O_2 + HI \rightarrow PdI_2 + 2\,H_2O$

One step from each group was included in each mechanism. The sets of four steps thus produced were complemented with reaction network steps to attain balance for each of the intermediates involved. Such a combination of steps gave a set consisting of 350 mechanisms. Taking into account our results for the influence of oxidants (I_2 and H_2O_2) on the pattern of the oscillating mode of reaction (1), we selected for analysis ten mechanisms that included steps for iodine and hydrogen peroxide formation and conversion. By using the STEP program package,[10] which performs numerical integration of sets of differential equations, and the rate constants we selected, it was shown that four models have periodic solutions, which are in qualitative agreement with the experiment.

Mechanism 1

1. $PdI_2 + CO + H_2O \rightarrow HPdI + CO_2 + HI$
8. $PdI_2 + HPdI \rightarrow Pd_2I_2 + HI$
10. $Pd_2I_2 + 2\,CO + RC{\equiv}CH + 2\,MeOH \rightarrow$
$\rightarrow$ Products + 2 HPdI
18. $2\,HPdI + 1/2\,O_2 \rightarrow PdI_2 + Pd^0 + H_2O$
19. $HPdI + I_2 \rightarrow PdI_2 + HI$
26. $Pd^0 + I_2 \rightarrow PdI_2$
31. $2\,HI + 1/2\,O_2 \rightarrow I_2 + H_2O$

Mechanism 2

1. $PdI_2 + CO + H_2O \rightarrow HPdI + CO_2 + HI$
8. $PdI_2 + HPdI \rightarrow Pd_2I_2 + HI$
10. $Pd_2I_2 + 2\,CO + RC{\equiv}CH + 2\,MeOH \rightarrow$
$\rightarrow$ Products + 2 HPdI
17. $2\,HPdI + O_2 \rightarrow PdI_2 + Pd^0 + H_2O_2$
19. $HPdI + I_2 \rightarrow PdI_2 + HI$
26. $Pd^0 + I_2 \rightarrow PdI_2$
30. $2\,HI + H_2O_2 \rightarrow I_2 + 2\,H_2O$

Mechanism 3

1. $PdI_2 + CO + H_2O \rightarrow HPdI + CO_2 + HI$
8. $PdI_2 + HPdI \rightarrow Pd_2I_2 + HI$
10. $Pd_2I_2 + 2\,CO + RC{\equiv}CH + 2\,MeOH \rightarrow$
$\rightarrow$ Products + 2 HPdI
13. $HPdI + O_2 \rightarrow IPdOOH$
16. $IPdOOH + HPdI \rightarrow H_2O_2 + Pd^0 + PdI_2$
19. $HPdI + I_2 \rightarrow PdI_2 + HI$
26. $Pd^0 + I_2 \rightarrow PdI_2$
30. $2\,HI + H_2O_2 \rightarrow I_2 + 2\,H_2O$

Mechanism 4

1. $PdI_2 + CO + H_2O \rightarrow HPdI + CO_2 + HI$
8. $PdI_2 + HPdI \rightarrow Pd_2I_2 + HI$
10. $Pd_2I_2 + 2\,CO + RC{\equiv}CH + 2\,MeOH \rightarrow$
$\rightarrow$ Products + 2 HPdI
13. $HPdI + O_2 \rightarrow IPdOOH$
14. $IPdOOH \rightarrow HPdI + O_2$
16. $IPdOOH + HPdI \rightarrow H_2O_2 + Pd^0 + PdI_2$
19. $HPdI + I_2 \rightarrow PdI_2 + HI$
26. $Pd^0 + I_2 \rightarrow PdI_2$
30. $2\,HI + H_2O_2 \rightarrow I_2 + 2\,H_2O$

The simulation of mechanism 2 considered previously[4] implied a stepwise consumption of PA and H_2O_2 and oscillations of the concentration of I_2 during the process (Fig. 11).

As a first approximation, we can state the reasons for the appearance of self-oscillatory modes in the system in question. The oscillations of E_{Pt}, pH, and the gas absorption rate are, apparently, due to the presence of different palladium complexes (PdI_2, Pd^I, HPdI, and Pd^0), among which palladium is redistributed during the reaction. The reduction of palladium is associated with a decrease in pH. Transitions between different oxidation states of palladium are provided by nonlinear and, in particular, self-catalyzed steps, whose rate constants differ appreciably in magnitude (reduction of Pd^{II}, carbonylation of alkyne), and by nonlinear (self-catalyzed) oxidation steps of palladium hydride complexes. The nonlinear self-catalyzed pattern of these reactions ensures fast redistribution of palladium among different complexes and the mechanism of switching to other reactions. In our opinion, the steps where active species arise and decay are responsible for the appearance of oscillations. The block of steps describing the carbonylation of alkyne and the formation of two palladium hydride molecules is rather a necessary but not a sufficient condition for initiation of the oscillating mode in reaction (1).

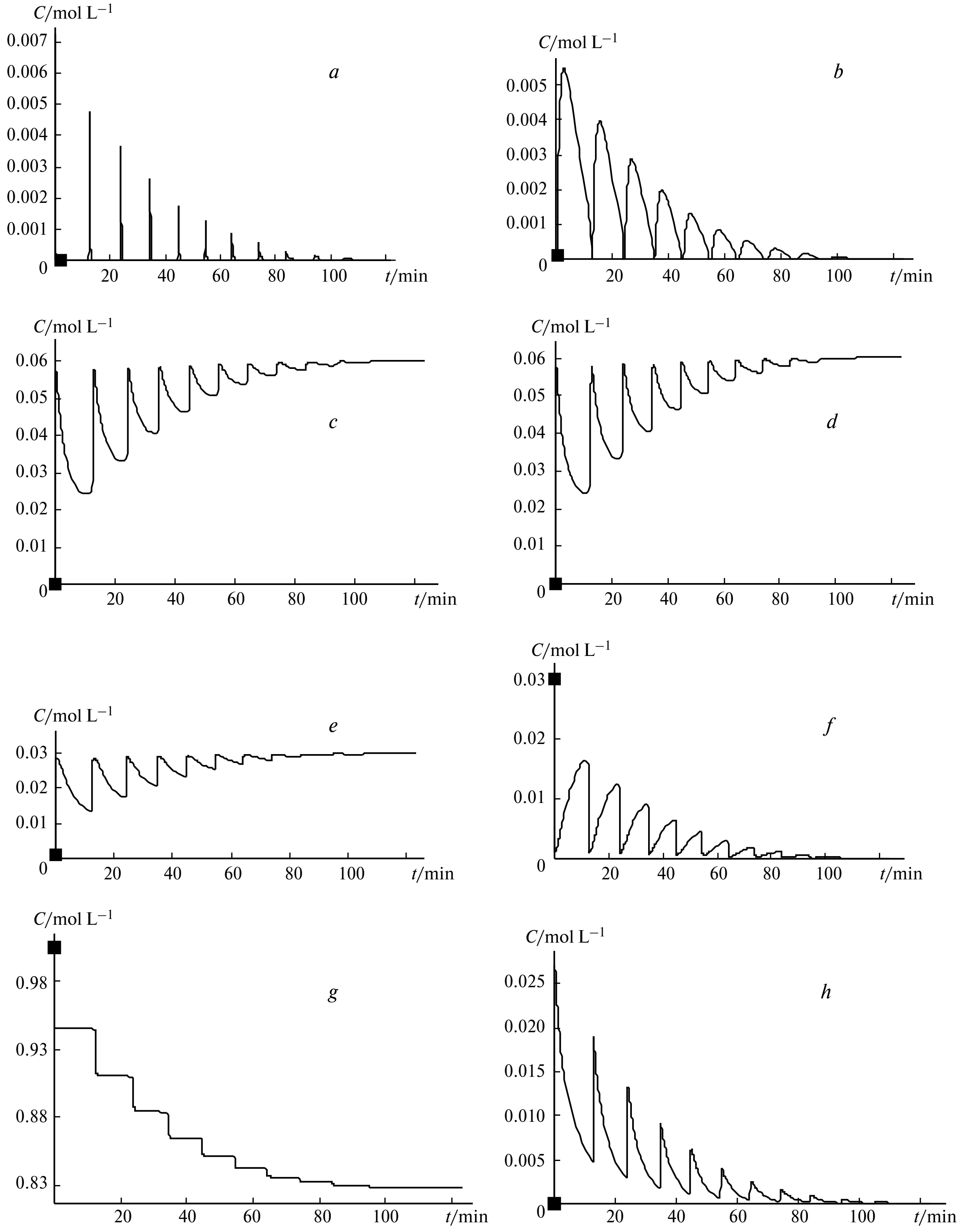

Fig. 11. Time dependence of the reactant concentrations calculated in terms of the model based on mechanism 2 (for rate constants for the steps and the initial conditions, see Ref. 4): (*a*) HPdI; (*b*) I_2; (*c*) HI; (*d*) Pd^0; (*e*) PdI_2; (*f*) Pd_2I_2; (*g*) PA; (*h*) H_2O_2.

A highly intricate problem not yet solved is the method for searching for the constants from experimental data. If an attempt to describe a process that occurs in a self-oscillating mode in terms of a kinetic model deduced from a hypothetical mechanism fails, this means that either the hypothetical mechanism does not contain the necessary steps or the "right" constants for the steps considered have not been found. Therefore, the approaches developed previously[11–13] for the qualitative analysis of complex mechanisms in order to identify multiple steady states and the possibility of oscillating reactions appear promising.

Generally, the results we obtained on oxidative carbonylation of various alkynes in various alcohols suggest that the probability of a complex dynamic behavior in the syntheses of complex molecules (self-oscillations and multiple steady states[4,14]) catalyzed by metal complexes is rather high. Investigation of particular blocks of the mechanism of oxidative carbonylation of alkynes and the problem of advancing and discrimination of hypotheses for self-oscillating processes would be considered in our subsequent studies.

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