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Oxidative Carbonylation of Alkynes in an Oscillation Mode: I. Concentration Limits for Oscillations in the Course of Phenylacetylene Carbonylation and Possible Mechanisms of the Process

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Abstract—An oscillating reaction of alkyne oxidative carbonylation is studied in a PdI_2–KI–CH_3OH catalytic system. Concentration limits for oscillations are found. A tentative kinetic model for the process is proposed. The mechanism of oscillations is discussed.

INTRODUCTION

Studies of oscillating chemical processes began in the second half of the 19th century [1, 2]. Oscillations are due to nonlinear relations (interactions) in a reaction system. The sources for these nonlinear relations are the processes of heat and mass transfer between a reaction system (catalyst) and a medium, as well as nonlinear steps (the reactions of intermediate species with each other) in a complex mechanism of the catalytic process [3]. The latter case is interesting from the standpoint of (a) predicting the complex behavior of chemical process in industry and (b) using oscillation phenomenology for elucidating the mechanisms of these unique processes [4].

Almost all well studied homogeneous catalytic reactions (e.g., Belousov–Zhabotinskii, Briggs–Rauscher, and Bray–Liebhafsky reactions) are the reactions of readily oxidizable organic or inorganic substrates with strong oxidants ($KBrO_3$, KIO_3, H_2O_2, or O_2) catalyzed by metal ions (Ce(IV)/Ce(III), Mn(III)/Mn(II), Fe(III)/Fe(II), Co(III)/Co(II), and others) [1]. Until recently, there was no information on oscillations associated with a complex mechanism in the processes of typical homogeneous catalysis by metal complexes where a complex organic molecule is synthesized from relatively simple reagents (cyclization, hydroformylation, carbonylation, polymerization metathesis, oxidative coupling, etc.). To the best of our knowledge, the first example of such a reaction was reported in 1985 by one of us [5]. That study was devoted to the oxidative carbonylation of acetylene in an oscillating mode in the $PdBr_2$–HBr–PPh_3–ROH–DMSO system. Recently, we published a preliminary communication on synchronous oscillations of pH, platinum electrode potential, and the rate of the oxidative carbonylation of alkynes in the PdI_2–KI–MeOH catalytic system [6]. This paper deals with the conditions under which these oscillations appear and a tentative mechanism of the reaction

$$\mathrm{PhC{\equiv}CH + CO + MeOH + O_2}$$
$$\longrightarrow \mathrm{MeOOCPh{=}CHCOOMe} \qquad \text{(I)}$$
$$(70\%\ \textit{cis-},\ 4\%\ \textit{trans-},\ 15\%\ \mathrm{A}),$$

whose products are methyl phenylmaleate, methyl phenylfumarate, and 2,2-dimethoxy-5-oxo-4-phenyl-2,5-dihydrofuran (A). Some portion of carbon monoxide is oxidized to CO_2.

EXPERIMENTAL

Experiments on the oxidative carbonylation of alkynes were carried out in a 200-ml glass reactor, which was maintained at a constant temperature of 40°C. This reactor was equipped by a reflux condenser, a sampler, necks for a stirrer, glass and platinum electrodes, an electrolytic bridge, and a calibrated gas burette. Liquid and gas phases were stirred with an efficient Teflon stirrer with a precessing shaft. The number of eccentric revolutions (100–900 rpm) that set the motion of the stirrer's shaft was controlled by the voltage of the engine. The voltage was adjusted with a laboratory autotransformer. The number of revolutions was measured by an ST-MEI stroboscopic tachometer.

The initial mixture of carbon monoxide, nitrogen, and oxygen was prepared in a gasometer and used for purging the reactor and filling the calibrated gas burette for the volumetric measurements of gas consumption. The composition of gases was determined by gas-adsorption chromatography using columns packed with activated carbon AR-3 (to analyze air, CO, and CO_2 at 160°C) and molecular sieves 13X (to analyze O_2, N_2, and CO at 40°C). The length of each column was 3 m, and the inner diameters were 3 mm. In both cases the fractions of packing were 0.25–0.5 mm in size. The thermal conductivity detector was used, and the carrier gas was argon.

The potential difference of glass (pH) and platinum (E_{Pt}) electrodes immersed in the catalytic solution relative to a standard silver-chloride electrode immersed in the saturated solution of KCl was recorded during experiments. A constant-temperature (40°C) cell filled with the saturated KCl solution was connected to the reactor via an electrolytic bridge filled with the colloidal (agar) solution of KI in methanol. To measure pH and E_{Pt}, millivoltmeters pH-121 and pH-673 were used. The concentration of phenylacetylene in the solution was determined by GLC. A 3 m × 3 mm column was filled with Porapak P. The concentration of carbonylation products was also determined by GLC (a 3 m × 3 mm column was filled with 10% Apiezon L on Inerton of the 0.25–0.3-mm fraction). The conditions for separation were the same in both cases: a thermal-conductivity detector was used, the carrier gas was helium, and the separation temperature was 230°C. Experiments were carried out as follows. A weighed portion of KI and methanol (8 ml) was loaded into the constant-temperature dried reactor with electrodes inserted beforehand. The mixture was stirred for 10 min, and then a weighed portion of PdI_2 was added to the solution. The number of stirrer revolutions was set to a desired value, and the solution was stirred for 10 min until the palladium salt dissolved. The reactor was purged with a mixture of CO, N_2, and O_2 (the overall volume of the mixture was at least 500 ml, and the composition was controlled as described above). Then, the reactor was connected to the gas burette filled with the same gas. The solution was stirred again for 10 min while monitoring pH and E_{Pt}. Then, 2 ml of the alkyne and ethylbenzoate (a GLC standard) solution in methanol was added to the contact solution via a syringe and a sampling inlet. The stirring was not interrupted during this operation. The volume of the contact solution became 10 ml. The instant alkyne was added to the solution was considered to be the onset of a run. The values of pH and E_{Pt} were recorded during the whole run using a KSP-4 logger. Changes in the gas volume inside the reactor were measured using the gas burette. The samples of gas and liquid phases were periodically analyzed by GLC.

RESULTS AND DISCUSSION

A detailed study of the catalytic PdI_2–KI–NaOAc–MeOH system [6] revealed that the number and characteristics of oscillations, as well as the fact of their appearance, are largely determined by the purity of phenylacetylene used in the experiments. Thus, when reagent-grade phenylacetylene was used without additional purification, we did not observe oscillations in ~25% of cases (of 70 runs carried out under the same conditions). Somewhat better results were observed when we used phenylacetylene that was stored after distillation at room temperature. However, in this case, the reproducibility of results was unsatisfactory. Also, in a series of experiments carried out in the PdI_2 (0.01 mol/l)–KI (0.4 mol/l)–MeOH system, we found a strong dependence of process characteristics on the stirring intensity and sodium acetate additives (Table 1). Oscillations in the system without sodium acetate occurred at 350–600 rpm. The sodium acetate additive (0.0024 mol/l) broadened the interval of stirring intensities at which oscillations were observed: it became 300–750 rpm (Table 1). Reproducibility was better when freshly prepared phenylacetylene was used that contained at least 98% of the main substance (Table 2). It was acceptable to keep distilled phenylacetylene in a freezer at 0°C for no longer than a month, in which case the characteristics of the process in the PdI_2–KI–MeOH system were independent of (a) the stirring intensity at 250–900 rpm [7], (b) exposure to daylight [8], and (c) the presence or absence of a platinum electrode in the reactor [9]. Factors a, b, and c were important for the above systems. The fact that the process characteristics were independent of the stirring intensity indicated that the reaction rates in the solution were independent of the gas diffusion of gases into the liquid phase and that the reaction was controlled by kinetics. Moreover, in the experiments with freshly distilled phenylacetylene, the addition of NaOAc for maintaining the initial value of pH was unnecessary.

After preparing the catalytic solution before purging the reactor with a mixture of CO and O_2, the value of pH becomes 7–8 and the value of E_{Pt} becomes 50–100 mV. After purging the reactor with the initial gas, the value of pH decreases to 5–6 and the value of E_{Pt} becomes ~0 mV. The typical temporal behavior of the process after adding phenylacetylene is described by three stages (Fig. 1):

(1) The first stage (2–3 min) is characterized by a decrease in E_{Pt} (from 0–20 to –(70–100) mV), pH (from 4.5–5.0 to 2.0–2.5), and the concentration of phenylacetylene by 20–30%. The consumption of CO and O_2 begins.

(2) At the second stage, which begins after 2–3 min and ends after 10–15 min, E_{Pt} remains constant or slowly increases and pH increases to 3.0–4.0. The mixture of gases is still consumed. Changes in pH and E_{Pt} do not seem to correlate somehow. During the first two stages, which we called the induction period, the oscillation regime is settled.

(3) Starting from 10–15 min, E_{Pt} increases drastically (by 150–200 mV), pH reaches 4.0–5.0 and the system proceeds to the mode of developed oscillations, which are accompanied by changes in E_{Pt} and pH and a stepwise consumption of gases during periods that corresponded to the minimal values of E_{Pt} and pH.

When phenylacetylene conversion is 80–90%, oscillations are damped and gas is not consumed. In some cases, oscillations are damped at lower phenylacetylene conversions (40–70%). In these cases, the process of oxidative carbonylation continues in the

Table 1. Effect of stirring intensity on the characteristics of oscillations*

W, rpm	Initial gas-phase composition				Final gas-phase composition				*t*, min	*V*, ml	*t*', min	*V*', ml	*n*	*F*, min	C_{in}, mmol/l	C_{fin}, mmol/l	Note
	O_2	N_2	CO	CO_2	O_2	N_2	CO	CO_2									
Without adding NaOAc																	
300	45	7	48	0	45	11	44	0	106	34	–	–	–	–	66 (6)	14	No oscillations
350	43	10	47	0	46	10	44	0	85	37	42	30	6	10	70 (4)	7	
400	40	13	46	1	40	14	45	1	74	32	23	24	6	9	49 (20)	4	
550	47	12	40	1	50	14	36	1	80	41	19	25	8	14	51 (14)	4	
600	47	9	44	0	50	17	32	1	150	30	60	18	6	18	40 (13)	4	
800	49	3	47	1	49	13	37	1	70	50	–	–	–	–	62 (2)	19	No oscillations; 20-ml solution
NaOAc added																	
225	44	10	46	0	47	13	39	1	35	21	–	–	–	–	44 (3)	38	No oscillations
300	46	11	43	0	47	9	44	0	100	36	22	26	8	15	52 (4)	5	
400	39	13	47	1	44	13	42	1	90	40	23	29	7	12	70 (3)	6	
550	41	9	50	0	46	11	42	1	90	45	30	36	7	15	30 (8)	3	
550	43	10	47	0	45	10	44	1	80	33	20	20	9	10	60 (3)	9	
600	45	4	51	0	47	11	51	1	100	42	20	28	8	20	52 (4)	5	
750	43	8	48	1	52	10	35	2	110	40	24	32	8	13	68 (3)	9	
800	49	9	42	0	40	10	49	1	70	40	–	–	–	–	43 (6)	14	No oscillations

* *W* is the number of stirrer revolutions; *t* is the duration of a run; *V* is the volume of consumed gas; *t*' is the induction period; *V*' is the amount of gas consumed for the time *t*'; C_{in} is the initial concentration of phenylacetylene by the time shown in parentheses; C_{fin} is the concentration of phenylacetylene at the end of a run; *n* is the number of oscillations; *F* is the average period over the first two or three oscillations ($[KI]_0$ = 0.4 mol/l; $[PdI_2]_0$ = 0.01 mol/l, and $[\text{phenylacetylene}]_0$ = 0.1 mol/l). Experiments were carried out with distilled phenylacetylene stored at 25°C. NaOAc was added in an amount of 0.024 mmol in 40 μl of methanol.

Table 2. Oxidative carbonylation of phenylacetylene in the KI–PdI_2–phenylacetylene–CH_3OH system*

W, rpm	Initial gas-phase composition				Final gas-phase composition				*t*, min	*V*, ml	*t*', min	*V*', ml	*n*	*F*, min	C_{in}, mmol/l	C_{fin}, mmol/l	Note
	O_2	CO	N_2	CO_2	O_2	CO	N_2	CO_2									
250	47	11	41	1	48	12	39	1	130	31	25	17	12	13	66 (3)	16	
250	49	6	44	1	54	10	35	1	116	38	20	24	7	13	–	–	The concentration of phenylacetylene was not measured; DR
400	46	14	39	1	46	19	34	1	85	19	18	12	8	12	79 (3)	18	
550	45	12	43	0	45	12	42	1	110	26	15	10	10	14	66 (3)	30	
700	48	9	42	1	48	9	42	1	48	17	33	16	3	6	–	–	The concentration of phenylacetylene was not measured
700	47	12	40	1	51	11	37	1	140	55	18	20	9	18	68 (5)	33	DR
850	43	23	34	0	47	18	34	1	130	21	18	12	6	12	71 (5)	42	DR
900	49	8	42	1	49	11	39	1	190	33	21	5	12	18	81 (3)	60	DR

* DR is for dark reaction (the reactor was isolated from the light). Experiments were carried out with distilled phenylacetylene stored in a freezer. Symbols are the same as in Table 1.

pseudo-steady-state mode: pH and E_{Pt} remain virtually constant (~4.0 and 50 mV, respectively). The rates of gas consumption and the formation of the products of oxidative carbonylation in the pseudo-steady-state mode are an order of magnitude lower than in the oscillating mode.

In addition to phenylacetylene, other alkynes were tested as substrates in reaction (I): methylacetylene, nonyne-1, dimethylethynyl carbinol, and propargyl alcohol. Experiments were carried out as described above (methylacetylene carbonylation was carried out in the system that was open with respect to the gas phase). It was shown that the carbonylation reactions of these alkynes in the oscillating mode were very similar and probably occurred via similar mechanisms, but some distinctions were also observed (see Fig. 2).

Tables 3 and 4 and Figs. 3–5 summarize the results obtained when studying the effect of PdI_2, KI, the initial concentration of phenylacetylene, and the partial pressures of CO and O_2 on the characteristics of phenylacetylene oxidative carbonylation.

Sustained oscillations are observed under the following conditions if the gas consists of 40% O_2 and 60% CO:

(a) $[KI]_0$ = 0.1–0.5 mol/l at $[PdI_2]_0$ = 0.01 mol/l, $[PhC{\equiv}CH]_0$ = 0.1 mol/l (Fig. 3, Table 3),

(b) $[PdI_2]_0$ = 0.00005–0.015 mol/l at $[KI]_0$ = 0.4 mol/l, $[PhC{\equiv}CH]_0$ = 0.1 mol/l (Fig. 4, Table 3), and

(c) $[PhC{\equiv}CH]_0$ = 0.01–0.2 mol/l at $[PdI_2]_0$ = 0.01 mol/l, $[KI]_0$ = 0.4 mol/l (Fig. 5, Table 3).

If the gas contains 40% O_2 and 60% CO or up to 6% O_2 and 94% CO, then sustained oscillations are observed at $[KI]_0$ = 0.4 mol/l at $[PdI_2]_0$ = 0.01 mol/l, $[PhC{\equiv}CH]_0$ = 0.1 mol/l (Table 4).

The period of oscillations in the above one-factor experiments (where one of the factors is the P_{O_2} : P_{CO} ratio) increases with an increase in [KI], a decrease in $[PdI_2]$, and an increase in the concentration of O_2. The dependence of the amplitude of oscillations on these factors is more complicated. The amplitude decreases as expected near the boundaries of the oscillation region. With a decrease in the PdI_2 concentration from 0.01 to 0.001 mol/l, the period of oscillations increases from 12–15 to 50 min. As this takes places, the total time during which oscillations are observed increases substantially (from 1.5 to 10 h). A decrease in the initial concentration of phenylacetylene is accompanied by a decrease in the period and the number of oscillations. The same behavior was observed in the course of each run as the concentration of phenylacetylene decreased. At $[PhC{\equiv}CH]_0$ = 0.01 mol/l, only one oscillation of E_{Pt} was observed with a decreased amplitude (from 90 to –50 mV). Near the boundaries of all concentration regions, similar phenomena were observed: the number of oscillations and their amplitudes reduced, and the shape of oscillations changed.

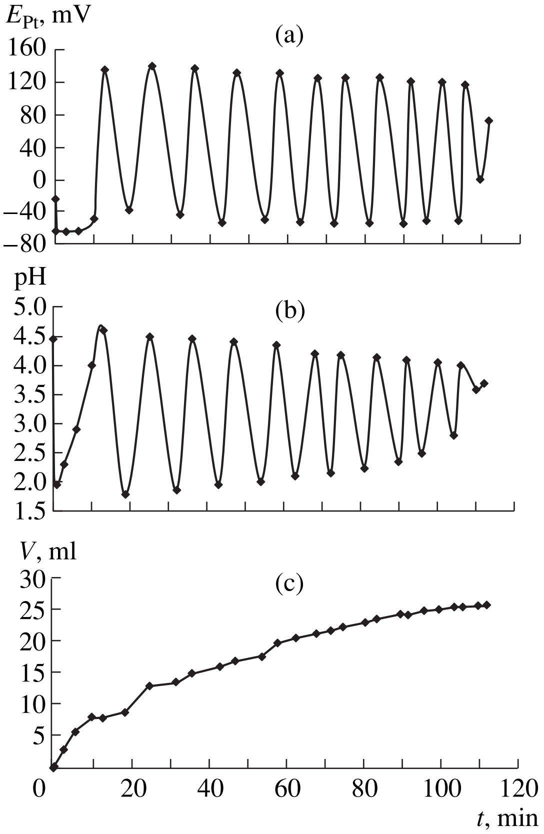

Fig. 1. Changes in (a) E_{Pt}, (b) pH, and (c) the volume of consumed gases in the standard run on the oxidative carbonylation of phenylacetylene (daylight, the intensity of stirring is 700 rpm, $[KI]_0$ = 0.4 mol/l; $[PdI_2]_0$ = 0.01 mol/l; $[\text{phenylacetylene}]_0$ = 0.1 mol/l; $[CO]_0 : [O_2]_0$ = 3 : 2).

Obviously, oscillations can damp if the concentration of phenylacetylene decreases substantially or if some other parameter falls outside the region that is optimal for oscillations. If oscillations prematurely damp, one can recommence them by adding a small amount of NaOAc or by purging the reactor with an initial gas. If the phenylacetylene conversion is high, the addition of this substrate also leads to recommencing oscillations while the first two stages are left out.

Based on the published data and the results obtained in this work, we propose a tentative mechanism of the processes occurring in the system. A decrease in E_{Pt} and pH when the reactor is purged with the CO–O_2 mixture is explainable by CO oxidation to CO_2 in the presence of water contained in methanol ($[H_2O]_0$ = 0.05 mol/l):

$$CO + H_2O + PdI_2 \longrightarrow CO_2 + HPdI + HI. \qquad (II)$$

The reduction of Pd(II) after adding phenylacetylene is even faster (stage 1):

$$\begin{aligned} &PdI_2 + CO + PhC{\equiv}CH + MeOH \\ &\longrightarrow \text{Products} + HPdI + HI. \end{aligned} \qquad (III)$$

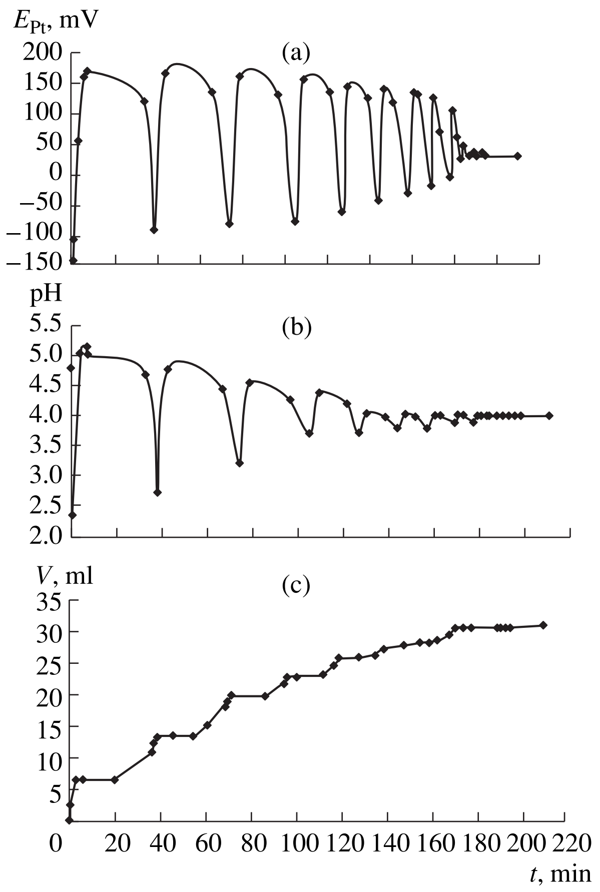

Fig. 2. Changes in (a) E_{Pt}, (b) pH, and (c) the volume of consumed gases in the oxidative carbonylation of dimethylethynyl carbinol (DMEC) ($W = 700$ rpm, $[KI]_0 = 0.4$ mol/l; $[PdI_2]_0 = 0.01$ mol/l; $[DMEC]_0 = 0.1$ mol/l; $[CO]_0 : [O_2]_0 = 3 : 2$).

According to the current understanding of alkyne oxidative carbonylation [10–12], the products are formed by the redox decomposition of acyl σ-organopalladium compounds that lead to hydride complexes (reaction (III)).

Palladium iodide complexes do not form stable carbonyls [11] and hydride–iodide complexes can hardly be stabilized by CO. The reaction of compounds like HPdI with alkynes most likely would eliminate the Pd–H bond. Therefore, the probability that the system would accumulate the HPdX compounds is low in the absence of phosphine ligands [13]. The most probable pathway for the transformation of hydride complexes is their decomposition to metallic palladium or their oxidation by various oxidants present in the system:

$$\mathrm{HPdI} \rightleftarrows \mathrm{HI} + \mathrm{Pd(0)}. \qquad \text{(IV)}$$

When the process occurs very intensively at the first stage (e.g., at high initial concentrations of phenylacetylene or PdI_2), a solid palladium residue is observed. In the initial mixture, the oxidants are O_2 and PdI_2 (PdI_4^{2-}). At the first stage (at relatively high concentrations of Pd(II)), nonlinear elementary reaction (V) dominates and leads to the appearance of Pd(I) complexes:

$$\mathrm{HPdI} + \mathrm{PdI_4^{2-}} \longrightarrow \mathrm{Pd_2I_4^{2-}} + \mathrm{HI}. \qquad \text{(V)}$$

Previous findings [10–12, 14] suggest that Pd(I) compounds are active in alkyne carbonylation.

To test this hypotheses in our system, we synthesized Pd(I) iodide complexes according to the method described in [14] (Table 5). If PdI_2 was replaced by the equivalent amount of Pd(I) in the initial solution, oscillations began immediately after adding phenylacetylene (stages 1 and 2 were bypassed, see Figs. 6 and 7). The results agree with the hypotheses that Pd(I) compounds are more active in the oxidative carbonylation of phenylacetylene than Pd(II) compounds:

$$\begin{gathered}\mathrm{Pd_2I_2} + \mathrm{CO} + \mathrm{PhC{\equiv}CH} + \mathrm{MeOH} \\ \longrightarrow \ \mathrm{Products} + 2\mathrm{HPdI}.\end{gathered} \qquad \text{(VI)}$$

Reactions (V) and (VI) are the steps of the autocatalytic reduction of Pd(II). Note that the reduced catalyst shows the maximal catalytic activity judging from the values of E_{Pt} (see Fig. 1).

The second stage begins when the concentration of Pd(II) decreases substantially. The concentration of Pd(I) complexes grows. This may lead to an increase in the rate of hydride oxidation by oxygen and other oxidants, which are formed in the system:

$$\mathrm{HPdI} + \mathrm{O_2} \rightleftarrows \mathrm{IPdOOH}, \qquad \text{(VII)}$$

$$\mathrm{IPdOOH} + \mathrm{HI} \longrightarrow \mathrm{PdI_2} + \mathrm{H_2O_2}, \qquad \text{(VIII)}$$

$$\mathrm{IPdOOH} + \mathrm{HPdI} \longrightarrow \mathrm{Pd_2I_2} + \mathrm{H_2O_2}. \qquad \text{(IX)}$$

These reactions explain an increase in the values of pH and E_{Pt} during the second stage. The oxidation of hydride complexes by molecular oxygen according to reactions (VII) and (VIII) was proposed earlier in [15], but we know of no experimental data that would support the formation of H_2O_2. In weakly acidic media, the I^- ion catalyzes the metathesis of H_2O_2 [16].

The oxidation of HI by oxygen

$$2\mathrm{HI} + 0.5\mathrm{O_2} \longrightarrow \mathrm{I_2} + \mathrm{H_2O}, \qquad \text{(X)}$$

can yield molecular iodine, which is capable of oxidizing hydride species (reaction (XI)), Pd(0) (reaction (XII)) [13], and Pd_2I_2 (reaction (XIII)):

$$\mathrm{HPdI} + \mathrm{I_2} \longrightarrow \mathrm{PdI_2} + \mathrm{HI}, \qquad \text{(XI)}$$

$$\mathrm{Pd} + \mathrm{I_2} \longrightarrow \mathrm{PdI_2}, \qquad \text{(XII)}$$

$$\mathrm{Pd_2I_2} + \mathrm{I_2} \longrightarrow 2\mathrm{PdI_2}. \qquad \text{(XIII)}$$

The oxidation of Pd(I) by iodine was studied in [10]. A buildup of oxidants leads to Pd(I) oxidation to Pd(II), an increase in pH and E_{Pt}, and probably to the complex dynamics of the oscillation process.

To a first approximation, we assumed that free radicals do not play an important role in the system under study and that oscillations are stipulated by the reactions of different palladium-containing intermediate

Table 3. Effect of reagent concentration on the oscillations characteristics*

Reagent	C, mol/l	t, min	V, ml	t', min	V', ml	n	F, min	Oscillations				W, rpm	C_{in}, mmol/l	C_{fin}, mmol/l	Note
								E_{Pt}, mV		pH					
								max	min	max	min				
KI	0.20	112	25	20	12	13	14	120	–25	4.85	1.90	700	65 (5)	20	
	0.40	110	26	26	13	8	18	145	–50	5.00	2.50	700	60 (8)	31	
	0.60	33	11	–	–	–	–	140	–	–	–	700	67 (10)	63	No oscillations
PdI_2	0.010	224	31	15	12	11	27	135	–40	5.30	2.60	700	66 (8)	33	E_{Pt} was not measured; DR
	0.010	68	21	32	15	6	14	100	–70	4.50	2.20	700	57 (14)	34	
	0.015	40	19	19	15	3	9	135	–50	4.85	2.20	700	49 (15)	41	
	0.020	50	18	28	16	2	25	50	–40	4.25	2.15	700	60 (3)	36	
Phenyl-acetylene	0.05	45	46	16	22	5	12	145	–30	5.15	3.00	700	32 (3)	26	
	0.05	60	14	16	7	7	10	140	–65	5.10	2.80	700	42 (10)	24	
	0.10	46	24	21	12	5	11	110	–70	4.25	1.80	700	90 (4)	49	
	0.15	132	49	20	23	2(9)	10	–150	–40	4.90	1.65	700	108 (3)	33	Two oscillations; after adding NaOAc, nine additional oscillations were observed
	0.20	57	30	26	26	2	7	–150	–130	5.45	5.40	700	99 (3)	39	Oscillations appear after adding NaOAc

* C is the concentration of reagents. Experiments were carried out with distilled phenylacetylene stored in a freezer. Other symbols are explained in Tables 1 and 2.

Table 4. Effect of gas composition on the oscillations characteristics*

Initial gas-phase composition**		Final gas-phase composition		*t*, min	*V*, ml	*t*', min	*V*', ml	*n*	*F*, min	Oscillations				*W*, rpm	C_{in}, mmol/l	C_{fin}, mmol/l	Note
										E_{Pt}, mV		pH					
O_2	CO	O_2	CO							max	min	max	min				
2	96	3	91	97	24	–	–	–	–	–	–	–	–	700	63 (5)	55	No oscillation
6	86	6	84	77	41	26	26	5	12	140	–110	3.45	0.30	700	57 (4)	4	
11	77	11	64	158	33	30	17	13	19	150	–50	3.70	0.85	700	65 (3)	13	
15	72	15	64	110	45	25	19	14	12	140	–60	3.85	1.10	700	74 (3)	20	
17	77	3	93	117	36	18	8	10	–	155	–20	3.80	1.10	700	75 (8)	14	The period of oscillations changed with a decrease in [O_2]
23	46	25	33	131	28	29	20	11	15	145	–35	3.60	0.75	700	47 (8)	17	
27	61	27	59	144	28	25	10	13	15	170	–30	3.85	1.10	700	57 (3)	30	
35	54	36	50	112	26	18	9	12	15	145	–65	4.60	1.75	700	65 (5)	37	
38	52	37	44	120	30	21	11	11	15	145	–80	4.80	2.00	700	62 (5)	30	
47	42	49	40	56	28	–	–	–	–	–	–	–	–	700	70 (5)	26	No oscillation
52	35	43	18	94	29	–	–	–	–	–	–	–	–	700	53 (3)	68	Phenylacetylene and NaOAc added; no oscillations
67	21	72	15	55	33	–	–	–	–	–	–	–	–	700	55 (6)	12	No oscillation

* Symbols are explained in Tables 1–3. Experiments were carried out with distilled phenylacetylene stored in a freezer.

** In addition to O_2 and CO, the gas phase may contain N_2 and CO_2.

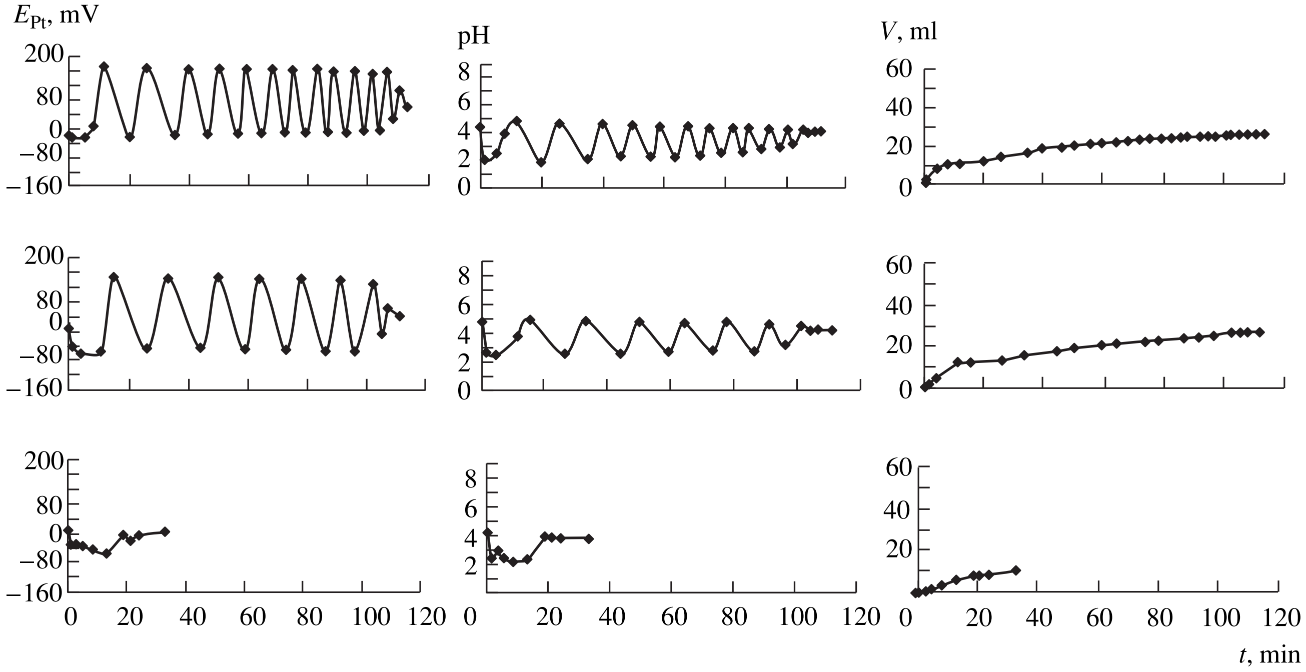

Fig. 3. The effect of KI concentration on phenylacetylene carbonylation: $[\mathrm{KI}]_0$ = 0.2 (top row), 0.4 (middle row), and 0.6 mol/l (bottom row); $[\mathrm{PdI}_2]_0$ = 0.01 mol/l; $[\mathrm{phenylacetylene}]_0$ = 0.1 mol/l; $[\mathrm{CO}]_0 : [\mathrm{O}_2]_0$ = 3 : 2.

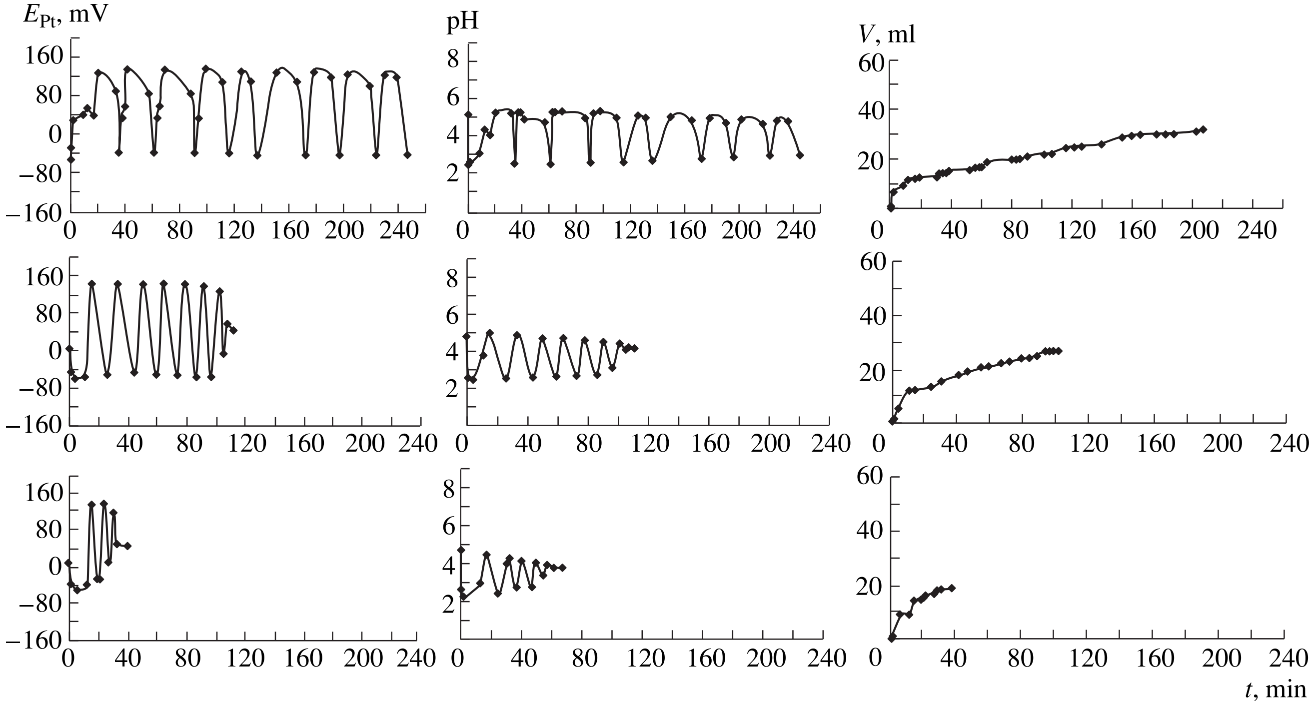

Fig. 4. The effect of PdI_2 concentration on phenylacetylene carbonylation: $[\mathrm{PdI}_2]_0$ = 0.005 (top row), 0.01 (middle row), and 0.015 mol/l (bottom row); $[\mathrm{KI}]_0$ = 0.4 mol/l; $[\mathrm{phenylacetylene}]_0$ = 0.1 mol/l; $[\mathrm{CO}]_0 : [\mathrm{O}_2]_0$ = 3 : 2.

species with each other and with oxidants rather than by the reactions of carbonylation product formation. The steps where HI is formed and consumed (IV), (V), (VIII), and (IX) can be another cause of oscillations.

The simplest variant of the mechanism that considers all the factors affecting the system behavior includes some of the above elementary steps and the blocks of steps (i.e., reactions combined of several ele-

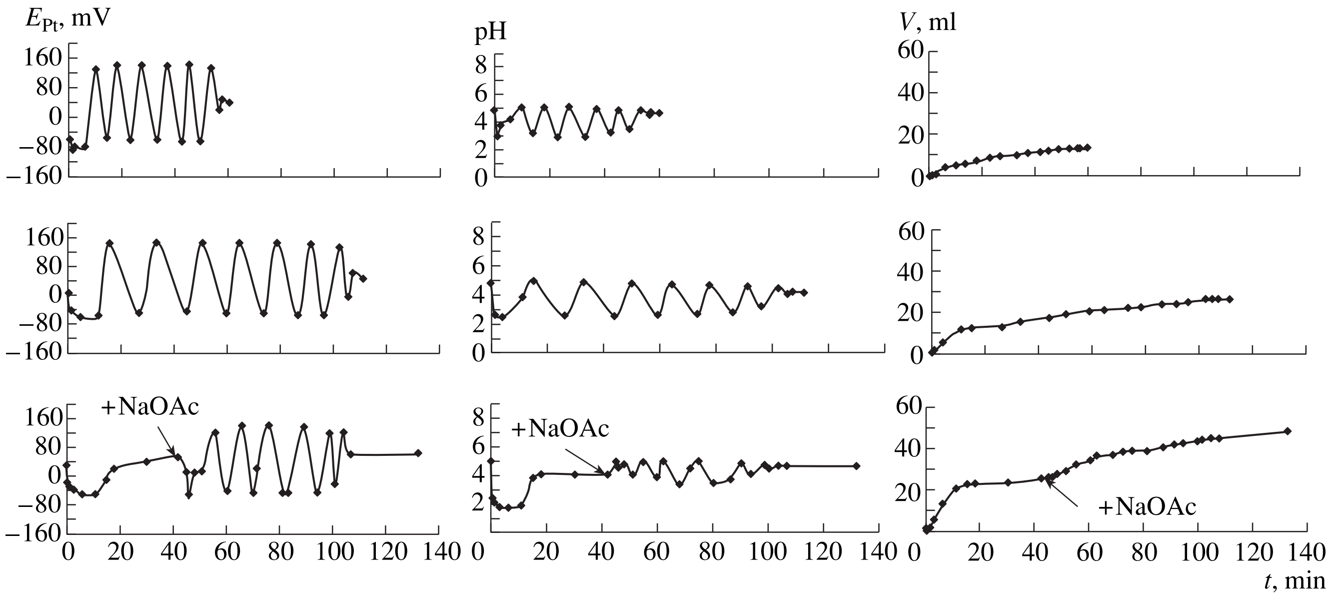

Fig. 5. The effect of phenylacetylene on phenylacetylene carbonylation: [phenylacetylene]$_0$ = 0.05 (top row), 0.1 (middle row), and 0.15 mol/l (bottom row); [KI]$_0$ = 0.4 mol/l; [PdI]$_0$ = 0.01 mol/l; [CO]$_0$: [O$_2$]$_0$ = 3 : 2.

mentary steps). The block of steps described by reaction (II) is the first source of HPdI and HI. It can be rewritten as follows:

$$PdI_2 + \{CO\} + \{H_2O\} \longrightarrow HPdI + \{CO_2\} + HI. \quad \text{(XIV)}$$

The concentrations of species in braces were not taken into account in the kinetic model. Nonlinear step (V) (the source of Pd(I), which is a carbonylation catalyst) can be written as

$$PdI_2 + HPdI \longrightarrow Pd_2I_2 + HI. \quad \text{(XV)}$$

The carbonylation process is described by the block of steps

$$\begin{gathered} Pd_2I_2 + PhC{\equiv}CH + \{2CO\} + \{2MeOH\} \\ \longrightarrow 2HPdI + \{MeOOCC(Ph){=}CHCOOMe\}, \end{gathered} \quad \text{(XVI)}$$

$$2HPdI + \{O_2\} \longrightarrow PdI_2 + Pd(0) + \{H_2O_2\}. \quad \text{(XVII)}$$

Step (XVII) combines reversible steps (IV) and (VII) and irreversible step (VIII).

Table 5. Elementary composition of Pd(I) complexes obtained according to the method described in [14]

Formula	Calculated		Found	
	Pd	I	Pd	I
KPd_4I_5	38.7	57.7	38.6	Undetermined
$CsPd_4I_5 \cdot 12H_2O$	30.2	45.0	29.8	45.6

For simplicity, we considered that the fast decomposition of peroxide by metathesis allows us to neglect changes in its concentration with time.

The formation of I_2 was taken into account by the reaction

$$2HI + \{0.5O_2\} \longrightarrow I_2 + \{H_2O\}, \quad \text{(XVIII)}$$

and I_2 consumption was taken into account by steps (XI) and (XII).

Overall, the simplest mechanism includes the following steps and blocks:

$$PdI_2 + \{CO\} + \{H_2O\} \longrightarrow HPdI + \{CO_2\} + HI, \quad \text{(XIV)}$$

$$PdI_2 + HPdI \longrightarrow Pd_2I_2 + HI. \quad \text{(XV)}$$

$$\begin{gathered} Pd_2I_2 + PhC{\equiv}CH + \{2CO\} + \{2MeOH\} \\ \longrightarrow 2HPdI + \{MeOOCC(Ph){=}CHCOOMe\}, \end{gathered} \quad \text{(XVI)}$$

$$2HPdI + \{O_2\} \longrightarrow PdI_2 + Pd(0) + \{H_2O_2\}, \quad \text{(XVII)}$$

$$HPdI + I_2 \longrightarrow PdI_2 + HI, \quad \text{(XI)}$$

$$Pd + I_2 \longrightarrow PdI_2, \quad \text{(XII)}$$

$$2HI + \{0.5O_2\} \longrightarrow I_2 + \{H_2O\}. \quad \text{(XVIII)}$$

The set of differential equations corresponding to this simplest mechanism is described below (Eqs. (1)–(7)). It was derived with one deviation from the mass action law: we considered the first order with respect to [HI] for block (XVIII) (see below for explanations):

$$\begin{gathered} d[HPdI]/dt = k_{14}[PdI_2] - k_{11}[HPdI][I_2] \\ - k_{15}[HPdI][PdI_2] - 2k_{17}[HPdI]^2 + 2k_{16}[Pd_2I_2], \end{gathered} \quad (1)$$

$$d[I_2]/dt = k_{18}[HI] - k_{11}[HPdI][I_2] - k_{12}[Pd][I_2], \quad (2)$$

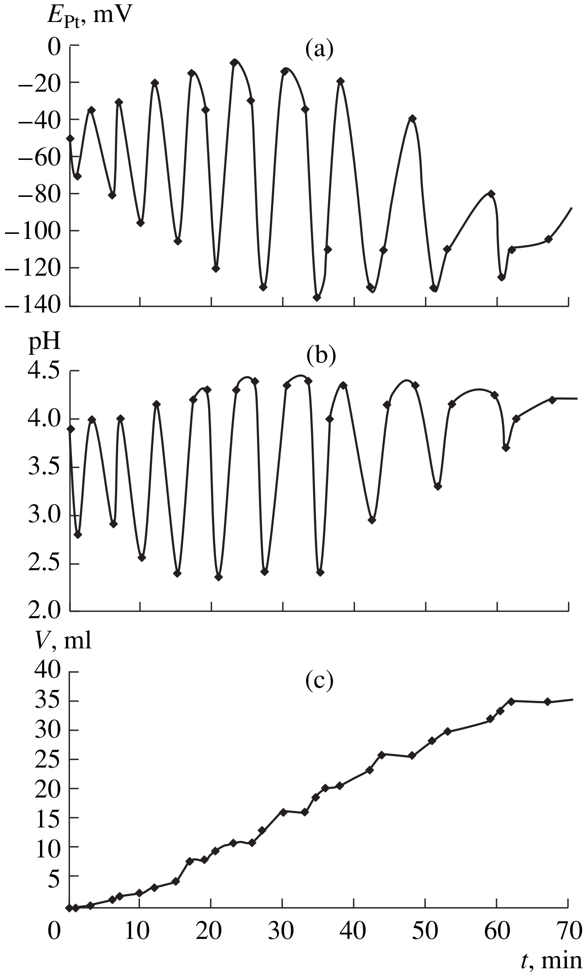

Fig. 6. Changes in (a) E_{Pt}, (b) pH, and (c) the volume of consumed gases in the standard run on the oxidative carbonylation of phenylacetylene system with the potassium complex of Pd(I) (W = 700 rpm, $[\mathrm{KI}]_0 = 0.4$ mol/l; $[\mathrm{Pd(I)}]_0 = 0.02$ mol/l; $[\text{phenylacetylene}]_0 = 0.1$ mol/l; $[\mathrm{CO}]_0 : [\mathrm{O}_2]_0 = 3 : 2$).

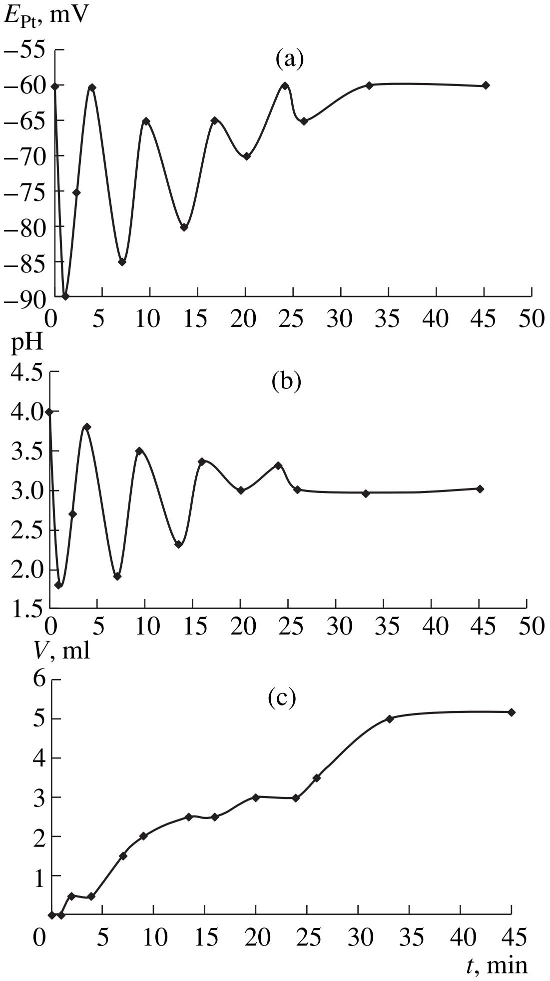

Fig. 7. Changes in (a) E_{Pt}, (b) pH, and (c) the volume of consumed gases in the standard run on the oxidative carbonylation of phenylacetylene system with the cesium complex of Pd(I) (W = 700 rpm, $[\mathrm{KI}]_0 = 0.4$ mol/l; $[\mathrm{Pd(I)}]_0 = 0.01$ mol/l; $[\text{phenylacetylene}]_0 = 0.1$ mol/l; $[\mathrm{CO}]_0 : [\mathrm{O}_2]_0 = 3 : 2$).

$$\begin{aligned} \mathrm{d[HI]}/\mathrm{d}t &= k_{14}[\mathrm{PdI_2}] + k_{11}[\mathrm{HPdI}][\mathrm{I_2}] \\ &+ k_{15}[\mathrm{HPdI}][\mathrm{PdI_2}] - 2k_{18}[\mathrm{HI}], \end{aligned} \tag{3}$$

$$\mathrm{d[Pd]}/\mathrm{d}t = k_{17}[\mathrm{HPdI}]^2 - k_{12}[\mathrm{Pd}][\mathrm{I_2}], \tag{4}$$

$$\begin{aligned} \mathrm{d[PdI_2]}/\mathrm{d}t &= -k_{14}[\mathrm{PdI_2}] + k_{11}[\mathrm{HPdI}][\mathrm{I_2}] \\ - k_{15}[\mathrm{HPdI}][\mathrm{PdI_2}] &+ k_{17}[\mathrm{HPdI}]^2 + k_{12}[\mathrm{Pd}][\mathrm{I_2}], \end{aligned} \tag{5}$$

$$\mathrm{d[Pd_2I_2]}/\mathrm{d}t = k_{15}[\mathrm{HPdI}][\mathrm{PdI_2}] - k_{16}[\mathrm{Pd_2I_2}], \tag{6}$$

$$\mathrm{d[PhC{\equiv}CH]}/\mathrm{d}t = -k_{16}[\mathrm{Pd_2I_2}][\mathrm{PhC{\equiv}CH}]. \tag{7}$$

Because there was no a computer program that would adequately estimate the kinetic parameters for the system that allows oscillatory solutions, we used an analogy between the simplest mechanism indicated above and the Oregonator model [8]. Our system was described by the following symbolic equations:

$$\mathrm{Y} \longrightarrow \mathrm{Z}, \tag{XIX}$$

$$\mathrm{Y} + \mathrm{Z} \longrightarrow, \tag{XX}$$

$$\mathrm{Z} \longrightarrow 2\mathrm{Z} + m, \tag{XXI}$$

$$2\mathrm{Z} \longrightarrow, \tag{XXII}$$

$$m \longrightarrow \mathrm{Y}. \tag{XXIII}$$

Here, $[\mathrm{HI}] \equiv m$, $[\mathrm{I_2}] \equiv \mathrm{Y}$, and $[\mathrm{HPdI}] \equiv \mathrm{Z}$. Then, steps (XVII), (XI), and (XVIII) correspond to steps (XXII), (XX), and (XXIII), respectively, assuming the first order with respect to [HI] in step (XVIII).

Steps (XV) and (XVI) taken together are autocatalytic with respect to HPdI and equivalent to step (XX) of the Oregonator model. Thus, the proposed mechanism contains steps and blocks that are analogous to four of five Oregonator steps. Therefore, to find the rate constants that allow an oscillatory solution within the framework of the mechanism, we used numeric values of the rate constants taken from the Oregonator model [8]: $k_{17} = 3 \times 10^3$ l mol^{-1} s^{-1}, $k_{18} = 0.02$ s^{-1}, and $k_{11} =$

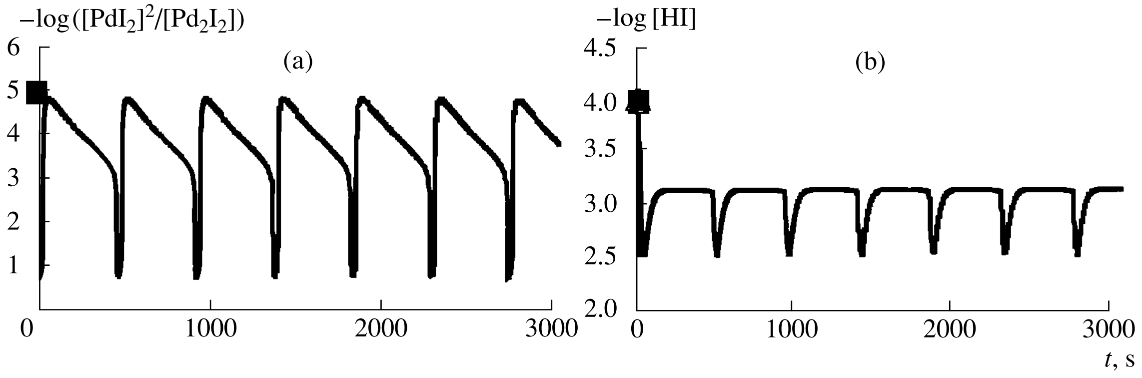

Fig. 8. Results of the mathematical modeling of the reaction of the oxidative carbonylation of phenylacetylene by solving the set of differential equations (1)–(7): (a) $-\log([PdI_2]^2/[Pd_2I_2])$ and (b) $-\log[HI]$, $[PdI]_0 = 0.01$ mol/l, $[\text{phenylacetylene}]_0 = 0.1$ mol/l.

2.4×10^6 l mol^{-1} s^{-1}. The rate constants for autocatalytic steps (XV) and (XVI) and steps (XII) and (XIV) were found by simple search.

The oscillatory solution to the system (1)–(7) was obtained using the STEP program [17] and the following values of the rate constants: $k_{11} = 2.4 \times 10^6$ l mol^{-1} s^{-1}, $k_{12} = 30$ l mol^{-1} s^{-1}, $k_{14} = 5 \times 10^{-4}$ s^{-1}, $k_{15} = 34$ l mol^{-1} s^{-1}, $k_{16} = 50$ s^{-1}, $k_{17} = 3 \times 10^3$ l mol^{-1} s^{-1}, and $k_{18} = 0.02$ s^{-1}. The oscillations of $-\log[H^+]$ were close to the experimentally observed oscillations of pH (Fig. 8).

Of course, the appearance of oscillations when the blocks of steps and some assumptions are used indicates that we identified only the principal stages of the process. The physical sense of the constants thus found cannot be considered at this point. Various interpretations are possible. Experimental tests of reaction (XVIII) showed that the direct oxidation of HI by oxygen at pH > 1 is too slow (probably because of the low HI concentration) compared to the rate of increasing pH during carbonylation and cannot be important.

Probably, the formation of I_2 and the transformation of hydrides occur with the assistance of a stronger oxidant, namely H_2O_2, formed by reaction (XVII). A more elaborate model should consider the formation of H_2O_2 by reaction (XVII) and its decomposition by the reactions

$$H_2O_2 + HI \longrightarrow HOI + H_2O, \qquad \text{(XXIV)}$$

$$HOI + HI \longrightarrow I_2 + H_2O. \qquad \text{(XXV)}$$

The oxidation of Pd(0) and Pd_2I_2 by hydrogen peroxide is also possible. With an increase in pH and a decrease in the H_2O_2 concentration, the disproportionation of H_2O_2 may begin [16].

The above arguments make it possible to reconstruct the qualitative picture of the oscillation process in the system. The most probable mechanism can be described as follows.

Palladium(II) is reduced in reactions (XIV) and (III) and forms HPdI. The latter reacts with PdI_2 in reaction (XV) and forms catalytically active Pd(I). Palladium(I) iodide carries the oxidative carbonylation of the alkyne, transforms in reaction (XVI) into hydride complexes, and causes autocatalytic steps (XV) and (XVI) that convert Pd(II) into HPdI. When the concentration of hydride complexes reaches some threshold value, they start to react with oxygen to form stronger oxidants IPdOOH and H_2O_2 in steps (VII)–(IX). Hydrogen peroxide oxidizes HI to form I_2 by reactions (XXIV) and (XXV). Both oxidants (H_2O_2 and I_2) oxidize HPdI and Pd_2I_2 to PdI_2 by reactions (XI) and (XIII) and prevent reactions (VII)–(IX), (XXIV), and (XXV) that produce oxidants themselves. As a result of these processes H_2O_2 and I_2 disappear and the system returns to the initial (oxidized) state, which is inactive toward carbonylation. In this state, palladium exists in the form of Pd(II). Then, all steps are repeated. Thus, the cycle begins with the autocatalytic reduction of palladium and ends with the autoinhibition of carbonylation by the oxidation of palladium hydride complexes and Pd(I) compounds formed during the process.

By now, the steps of maleate synthesis (block (XVI)) were considered within the framework of the linear mechanism. This assumption should probably be revised. Judging from the findings of this work and considering the hypotheses formulated for other carbonylation processes [18–23], we may assume that the reaction network of the oxidative carbonylation process in the oscillation mode is rather large. Unfortunately, the methods for advancing hypotheses of potentially oscillating processes have not been developed yet. A complicated, yet unsolved problem is parameter estimation from experimental data. If an attempt to describe the oscillation process based on a hypothetical mechanism is unsuccessful, it always remains uncertain whether the mechanism lacks the right steps or whether the right values of rate constants for the available steps are overlooked.

In our opinion, the results obtained in this work allow us to consider that the probability of a complex dynamic behavior (such as oscillations and multiple steady states [6, 24]) in the reactions of complex molecule synthesis is rather high in organometallic catalytic systems. Our further studies will be devoted to separate blocks of the mechanism of alkyne oxidative carbonylation and to the problem of advancing and discriminating mechanistic hypotheses relevant to the reasons why oscillations occur.

ACKNOWLEDGMENTS

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