Mechanism of synthesis of maleic and succinic anhydrides by carbonylation of acetylene in solutions of palladium complexes*

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The mechanism of synthesis of maleic and succinic anhydrides from acetylene and CO in the $PdBr_2$—LiBr—organic solvent catalytic system was studied using the procedure of advancement and discrimination of hypotheses. The hypotheses were obtained using the data bank on elementary steps and the Combl combinatorial program. The discrimination of the hypotheses was based on the data of NMR and IR spectroscopy, studies of isotope exchange, the role of potential organic intermediates, the kinetic isotope effect, and one-factor kinetic experiments. The most probable mechanism of synthesis of maleic anhydride includes insertion of acetylene and CO into the Pd—Pd bond of the Pd^{I} complex, which is formed from Pd^{II} at the initial step of the process. Succinic anhydride results from the intramolecular transformation of the hydride complex of palladium and maleic anhydride. The palladium hydride complexes detected in the contact solution apparently play the crucial role in the conjugation of oxidation, reduction, and addition type reactions.

Key words: reaction mechanisms, advancement and discrimination of hypotheses; alkynes, carbonylation, kinetics, isotope effect; succinic anhydride, maleic anhydride, synthesis from acetylene and CO.

Carbonylation of alkynes makes it possible to synthesize numerous oxygen-containing organic compounds (saturated and unsaturated acids, esters, amides, lactones, ketones, anhydrides) under mild conditions and presents both practical and theoretical interest.[1—4] Recently,[5] the most promising method for the synthesis of methyl methacrylate has been developed; the method is based on the carbonylation of methylacetylene in solutions of palladium complexes.

Palladium derivatives are the most active catalysts for the reactions of alkynes with carbon monoxide involving other reactants.[6] The catalytic methods for the synthesis of polyesters, succinic anhydride and products based on it, esters of alkynylcarboxylic acids, and citraconic anhydride developed in recent years are of practical interest.[6]

Cobalt- and palladium-based catalysts often promote simultaneous occurrence of oxidative, reductive, and "additive" (not redox) carbonylation of alkynes.[4,6] A number of studies have been devoted to the mechanism of conjugation of reactions of various redox types.[6,7] This study deals with the mechanism of the recently discovered synthesis of succinic anhydride[7] and also with the relationship between the mechanisms of formation of succinic and maleic anhydrides.

Experimental

Experiments were carried out in a gas-flow-type reactor maintained at a constant temperature (40 °C) with intense stirring of the gas and liquid phases under atmospheric pressure. The initial solution ($PdBr_2$—LiBr—organic solvent) was prepared directly in the reactor. A gas mixture (CO and C_2H_2) of the required composition was prepared beforehand in a gas meter and supplied to the reactor through columns with a drying agent at a velocity of ~2.2 L (L min)$^{-1}$. The velocity of the gas mixture supply was monitored by a calibrated rheometer. The gas velocity at the outlet was determined using a Mariotte's vessel and a graduated cylinder. The gas phase was analyzed by gas-adsorption chromatography on an LKhM-8MD instrument (using a 3-m-long column with a diameter of 3 mm packed with the AG-3 active carbon (0.25—0.50 mm fraction); the separation temperature was 140 °C; a katharometer was used as the detector; and argon was used as the carrier gas).

Water was supplied to the reactor using a microsyringe. The content of water was determined by GLC on an LKhM-8MD instrument (a 3-m-long column with a diameter of 3 mm packed with Polysorb (the 0.25—0.50 mm fraction); the temperature of separation was 140 °C, a katharometer was used as the detector; and helium was used as the carrier gas).

The composition of the contact solution was analyzed by GLC:

(a) succinic and maleic anhydrides (as well as citraconic anhydride and methylsuccinic anhydride) were determined on a Tsvet-110 instrument (a 3-m-long column with a diameter of 3 mm packed with 10% polyphenylmethylsiloxane PPMS-4 on Polychrom-1; the temperature of separation was 180 °C, a

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* Dedicated to the memory of Academician M. E. Vol'pin timed to his 75th birthday.

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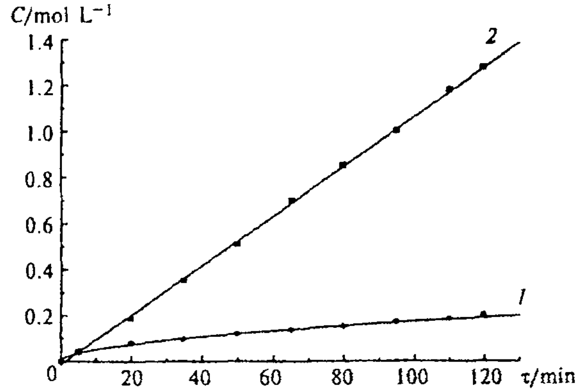


Fig. 1. Dependences of the concentrations (C) of succinic (*1*) and maleic (*2*) anhydrides on the duration of the experiment. Conditions: $[PdBr_2] = 0.05$ mol L^{-1}, $[LiBr] = 0.1$ mol L^{-1}, $p_{CO}/p_{C_2H_2} = 2.5$, $T = 40$ °C.

katharometer was used as the detector; and helium was used as the carrier gas);

(b) acrylic and propionic acids were analyzed on an LKhM-80 instrument (a 3-m-long column with a diameter of 3 mm packed with 10% poly(ethylene glycol) PEG 12000 on Inerton AW DMEC; the temperature of separation was 180 °C, a katharometer was used as the detector; and helium was used as the carrier gas).

The total amount of anhydrides and mono- and dicarboxylic acids was determined by potentiometric titration. Potentiometric titration of the solution and potentiometric measurements during the experiments were performed using a pH-673 instrument equipped with glass, platinum, and silver chloride electrodes (the latter was used as the reference electrode).

IR spectra of gases and solutions were recorded on an M-82 IR spectrometer, and the ^1H and ^{13}C NMR spectra were measured on a Bruker WP-200-SY instrument.

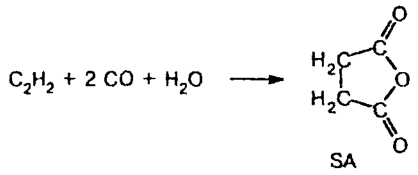
The "concentration—time" dependences obtained in kinetic experiments were processed by graphical differentiation at the quasi-steady-state section, after the period of formation of the active catalyst (Fig. 1). To ensure that the concentration of Br^- is constant ($[Br^-]$ = const) despite the variation of $[PdBr_2]$, the experiments were carried out at a high concentration of LiBr ($[LiBr] = 0.74$ mol L^{-1}). The variation of the partial pressures of acetylene and carbon monoxide was accomplished by their partial replacement by helium, the concentrations of the other reagents remaining the same.

Commercial reagents of "chemically pure" and "pure for analysis" grades were used in the experiments as received. Carbon monoxide was obtained by decomposition of formic acid in H_2SO_4, acetylene was additionally purified from phosphorus-and sulfur-containing compounds using solutions of $K_2Cr_2O_7$, $CuSO_4$, and $CuCl_2$. The purity of CO and C_2H_2 was no less than 99.6%.

Results and Discussion

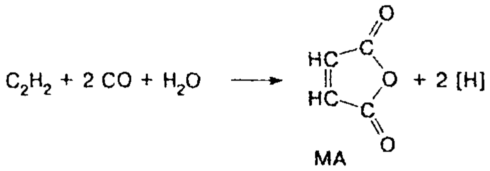
Results of preliminary experiments

It was shown previously[7] that in the catalytic system $PdBr_2$—LiBr—organic solvent (acetone, acetonitrile), reaction (1) occurs with a selectivity of ~70% with respect to acetylene (in the initial gas mixture, CO : C_2H_2 = 2.5, $[H_2O] = 0.3$ mol L^{-1}).

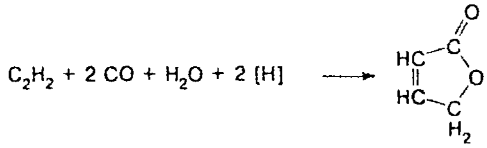


(1)

In addition to succinic anhydride (SA), other products are also formed in this system, namely, maleic anhydride (MA), ~7% (reaction (2)), dicarboxylic (succinic and maleic) acids (DA), ~12%, and acrylic acid (AA), ~7%. Propionic acid (PA) and 2(5*H*)-furanone (reaction (3)) are produced in substantially lower yields.



(2)



(3)

Some quantity of acetylene is converted into oligomers (there is unbalance). The hypothesis on the partial hydrogenation of oligomers makes it possible to bring together the redox balance of the process.

In the preliminary experiments, the question of the state of palladium in the catalytically active complexes was also addressed. The results of measurements of the voltage difference between the platinum and silver chloride (reference) electrodes (E_{Pt}) during the process (Fig. 2), the character of influence of added oxidants ($CuBr_2$, $Fe_2(SO_4)_3$, *p*-benzoquinone, chloranil), and the data of IR spectroscopy provide grounds for believing that compounds of Pd^I are responsible for the catalytic activity.[8]

The period of formation of the catalyst is matched in time by the decrease in the potential of the platinum electrode from ~240 to 60—80 mV and also by a decrease in the intensity of the absorption band at 2120 cm^{-1} (the terminal CO group) and an increase in the intensity of the bands at 1948 and 1935 cm^{-1} (bridging CO groups) in the IR spectrum of the sample. These facts are in good agreement with the assumption that during the period of catalyst formation, Pd^{II} is reduced to Pd^I.

The addition of oxidants ($CuBr_2$, $Fe_2(SO_4)_3$) to the initial catalytic solution results in an increase in the initial E_{Pt} value. Then, judging from the variation of E_{Pt}, the oxidant is rapidly reduced by the reaction gases. The addition of *p*-benzoquinone and chloranil results appar-

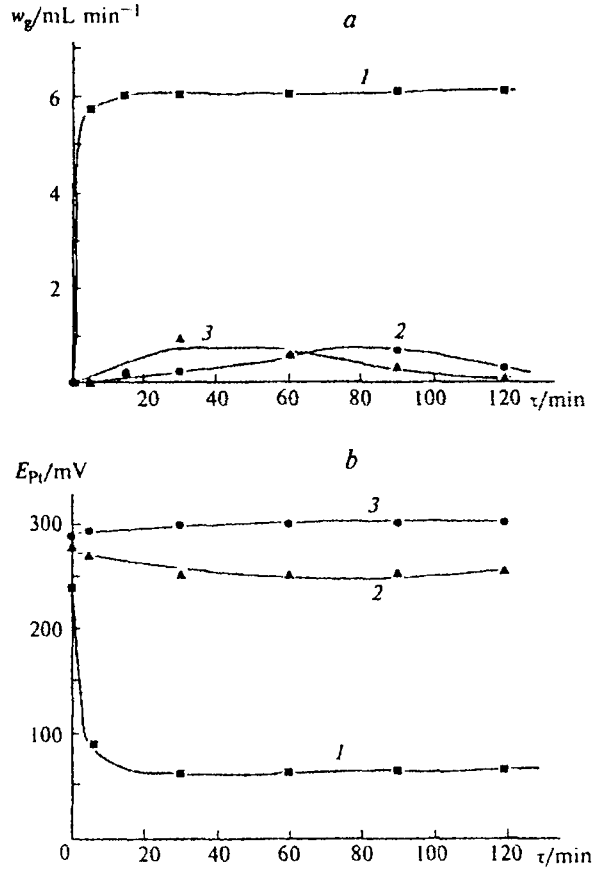


Fig. 2. Variation of the rate of gas absorption (w_g) (*a*) and redox potential (E_{Pt}) (*b*) during carbonylation of acetylene in the $PdBr_2$—LiBr—acetone system (*1*). The effect of quinone (*2*) and chloranil (*3*) on the rate of gas absorption and E_{Pt}. Conditions: $[PdBr_2]$ = 0.05 mol L^{-1}, [LiBr] = 0.1 mol L^{-1}, $p_{CO}/p_{C_2H_2}$ = 2.5, T = 40 °C.

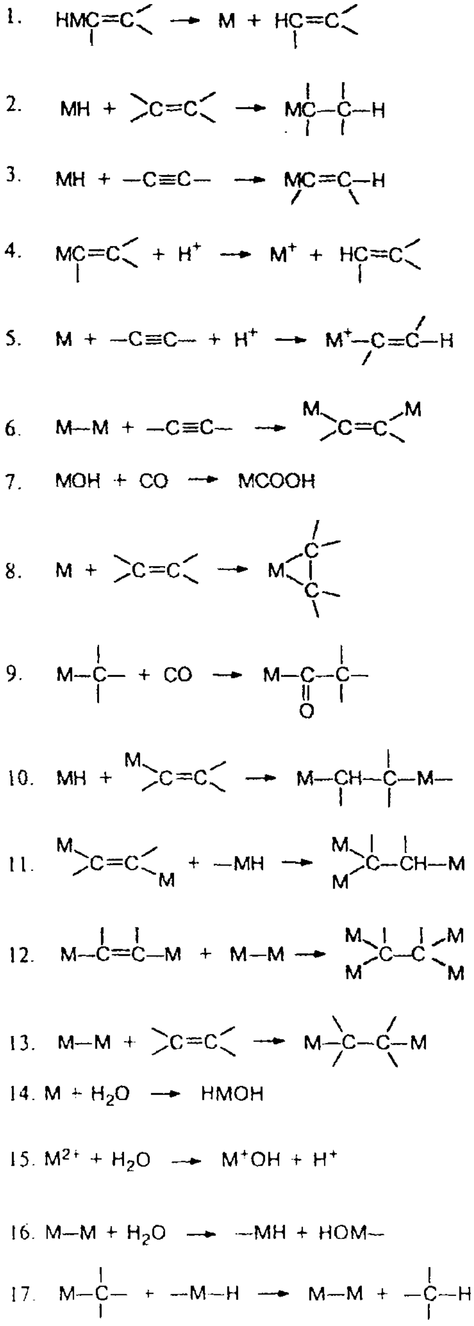
ently in the formation of stable and catalytically inactive complexes of Pd^{II} with these oxidants, which undergo practically no changes under the reaction conditions (see Fig. 2).

Advancement of hypotheses

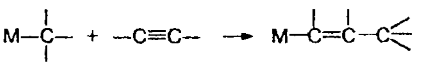
In the present study, we used the approach[9,10] that includes formal generation of hypothetical mechanisms and their subsequent selection (discrimination) based on the results of specially designed experiments. The procedure used here consisted of the following operations:

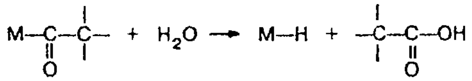
1. Identification of the set of bond transformations needed to obtain succinic anhydride from C_2H_2, CO, and H_2O (cleavage of one C≡C, two C≡O, and two OH bonds and formation of three C—C, two C—O, two C—H, and two C=O bonds).
2. Choosing the steps that include the above-mentioned transformations out of the bank of steps involving metal complexes and organometallic compounds.[11]
3. Combinatorial exhaustion of the resulting set of steps by virtue of the Comb 1 program for personal computer[12] aimed at obtaining combinations containing necessary bond transformations.
4. Analysis of the resulting combinations in order to choose "chemically sensible" sequences of steps on the way from the reactants to the succinic anhydride.

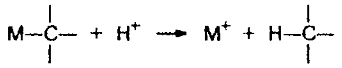
To advance hypotheses concerning the mechanism of the synthesis of succinic anhydride, we chose the following 20 steps (M is the metal atom incorporated in the complex or in the organometallic compound):



1. $\mathrm{HM\underset{|}{C}{=}C\!<} \longrightarrow \mathrm{M + H\underset{|}{C}{=}C\!<}$
2. $\mathrm{MH} + \mathrm{>C{=}C<} \longrightarrow \mathrm{M\underset{|}{\overset{|}{C}}{-}\underset{|}{\overset{|}{C}}{-}H}$
3. $\mathrm{MH} + \mathrm{-C{\equiv}C-} \longrightarrow \mathrm{M\underset{/}{C}{=}\underset{\backslash}{C}{-}H}$
4. $\mathrm{M\underset{|}{C}{=}C\!<} + \mathrm{H^+} \longrightarrow \mathrm{M^+} + \mathrm{H\underset{|}{C}{=}C\!<}$
5. $\mathrm{M} + \mathrm{-C{\equiv}C-} + \mathrm{H^+} \longrightarrow \mathrm{M^+{-}\underset{/}{C}{=}\overset{/}{C}{-}H}$
6. $\mathrm{M{-}M} + \mathrm{-C{\equiv}C-} \longrightarrow \mathrm{{}^{M}{>}C{=}C{<}^{M}}$
7. MOH + CO ⟶ MCOOH
8. $\mathrm{M} + \mathrm{>C{=}C<} \longrightarrow \mathrm{M{<}\begin{matrix}C\\|\\C\end{matrix}}$
9. $\mathrm{M{-}\underset{|}{\overset{|}{C}}{-}} + \mathrm{CO} \longrightarrow \mathrm{M{-}\underset{\underset{O}{\|}}{C}{-}\underset{|}{\overset{|}{C}}{-}}$
10. $\mathrm{MH} + \mathrm{{}^{M}{>}C{=}C{<}} \longrightarrow \mathrm{M{-}\underset{|}{C}H{-}\underset{|}{\overset{|}{C}}{-}M{-}}$
11. $\mathrm{{}^{M}{>}C{=}C{<}_{M}} + \mathrm{-MH} \longrightarrow \mathrm{{}^{M}_{M}{>}\overset{|}{C}{-}\overset{|}{C}H{-}M}$
12. $\mathrm{M{-}\overset{|}{C}{=}\overset{|}{C}{-}M} + \mathrm{M{-}M} \longrightarrow \mathrm{{}^{M}_{M}{>}\overset{|}{C}{-}\overset{|}{C}{<}^{M}_{M}}$
13. $\mathrm{M{-}M} + \mathrm{>C{=}C<} \longrightarrow \mathrm{M{-}\overset{\backslash}{\underset{/}{C}}{-}\overset{/}{\underset{\backslash}{C}}{-}M}$
14. $\mathrm{M + H_2O \longrightarrow HMOH}$
15. $\mathrm{M^{2+} + H_2O \longrightarrow M^+OH + H^+}$
16. $\mathrm{M{-}M + H_2O \longrightarrow -MH + HOM-}$
17. $\mathrm{M{-}\underset{|}{\overset{|}{C}}{-}} + \mathrm{-M{-}H} \longrightarrow \mathrm{M{-}M} + \mathrm{-\underset{|}{\overset{|}{C}}{-}H}$

18. 
$$M{-}C{-} + {-}C{\equiv}C{-} \longrightarrow M{-}C{=}C{-}C\lessgtr$$

19. 
$$M{-}C({=}O){-}C{-} + H_2O \longrightarrow M{-}H + {-}C{-}C({=}O){-}OH$$

20. 
$$M{-}C{-} + H^+ \longrightarrow M^+ + H{-}C{-}$$

The mechanism of formation of the catalyst, *i.e.*, Pd^I clusters, has not been specially studied. However, the currently available experimental and published data suggest that this occurs by a chain autocatalytic mechanism that includes three blocks of steps:

$$PdBr_2 + C_2H_2 + 2\,CO + H_2O \longrightarrow MA + HPdBr + HBr,$$

$$PdBr_2 + HPdBr \longrightarrow Pd_2Br_2 + HBr,$$

$$Pd_2Br_2 + C_2H_2 + 2\,CO + H_2O \longrightarrow MA + 2\,HPdBr.$$

The above reactions lead to fast reduction of Pd^{II} to Pd^I.

The advancement of hypotheses based on the twenty steps presented above, some of which might not be elementary steps, afforded ~500 combinations of steps. In our opinion, 46 of these combinations make sense from the chemical viewpoint.

The forty-six hypotheses can be divided into four groups according to the type of organic intermediate involved in the synthesis of succinic anhydride:

- group I — ethylene (6 mechanisms);
- group II — acrylic acid (22 mechanisms);
- group III — maleic anhydride (8 mechanisms);
- group IV — no organic intermediate (10 mechanisms).

Discrimination of the hypotheses

Based on the results of the preliminary experiments (catalytic activity of Pd^I derivatives) and also in view of the fact that the system contains no ligands capable of stabilizing Pd^0 derivatives, those mechanisms in which Pd^{II} and Pd^0 compounds act as the catalysts can be excluded from consideration.

The 23 hypotheses left after the first selection step, 3, 8, 4, and 8 hypotheses for groups I, II, III, and IV,

Group I

Mechanism 1

$C_2H_2 + Pd_2Br_2 \rightarrow \mathbf{1}$
$\mathbf{1} + 2\,HBr \rightarrow C_2H_4 + 2\,PdBr_2$
$C_2H_4 + Pd_2Br_2 \rightarrow \mathbf{2}$
$\mathbf{2} + 2\,CO \rightarrow \mathbf{3}$
$\mathbf{3} + H_2O \rightarrow HPdBr + \mathbf{4}$
$\mathbf{4} \rightarrow SA + HPdBr$

Mechanism 2

$C_2H_2 + HPdBr \rightarrow \mathbf{5}$
$\mathbf{5} + HBr \rightarrow C_2H_4$
$C_2H_4 + Pd_2Br_2 \rightarrow \mathbf{2}$
$\mathbf{2} + 2\,CO \rightarrow \mathbf{3}$
$\mathbf{3} + H_2O \rightarrow HPdBr + \mathbf{4}$
$\mathbf{4} \rightarrow SA + HPdBr$

Mechanism 3

$C_2H_2 + HPdBr \rightarrow \mathbf{5}$
$\mathbf{5} + HPdBr \rightarrow Pd_2Br_2 + C_2H_4$
$Pd_2Br_2 + H_2O \rightarrow HBr + \mathbf{6}$
$\mathbf{6} + CO \rightarrow \mathbf{7}$
$\mathbf{7} + C_2H_4 \rightarrow \mathbf{8}$
$\mathbf{8} + CO \rightarrow \mathbf{9}$
$\mathbf{9} \rightarrow SA + HPd_2Br$

Group II

Mechanism 4

$C_2H_2 + Pd_2Br_2 \rightarrow \mathbf{1}$
$\mathbf{1} + CO \rightarrow \mathbf{10}$
$\mathbf{10} + H_2O \rightarrow HPdBr + \mathbf{11}$
$\mathbf{11} + HBr \rightarrow AA + PdBr_2$
$AA + Pd_2Br_2 \rightarrow \mathbf{12}$
$\mathbf{12} + HBr \rightarrow PdBr_2 + \mathbf{13}$
$\mathbf{13} + CO \rightarrow \mathbf{4} \rightarrow SA + HPdBr$

Mechanism 5

$C_2H_2 + Pd_2Br_2 \rightarrow \mathbf{1}$
$\mathbf{1} + CO \rightarrow \mathbf{10}$
$\mathbf{10} + H_2O \rightarrow HPdBr + \mathbf{11}$
$\mathbf{11} + HBr \rightarrow AA + PdBr_2$
$AA + HPdBr \rightarrow \mathbf{13}$
$\mathbf{13} + CO \rightarrow \mathbf{4}$
$\mathbf{4} \rightarrow SA + HPdBr$

Mechanism 6

$H_2O + Pd_2Br_2 \rightarrow \mathbf{6} + HBr$
$\mathbf{6} + CO \rightarrow \mathbf{7}$
$\mathbf{7} + C_2H_2 \rightarrow \mathbf{14}$
$\mathbf{14} + HBr \rightarrow AA + Pd_2Br_2$
$AA + HPdBr \rightarrow \mathbf{13}$
$\mathbf{13} + CO \rightarrow \mathbf{4} \rightarrow SA + HPdBr$

Mechanism 7

$H_2O + Pd_2Br_2 \rightarrow \mathbf{6} + HBr$
$\mathbf{6} + CO \rightarrow \mathbf{7}$
$\mathbf{7} + C_2H_2 \rightarrow \mathbf{14}$
$\mathbf{14} + HBr \rightarrow AA + Pd_2Br_2$
$AA + Pd_2Br_2 \rightarrow \mathbf{12}$
$\mathbf{12} + HBr \rightarrow PdBr_2 + \mathbf{13}$
$\mathbf{13} + CO \rightarrow \mathbf{4} \rightarrow SA + HPdBr$

Mechanism 8

$C_2H_2 + HPdBr \rightarrow \mathbf{5}$
$\mathbf{5} + CO \rightarrow \mathbf{15}$
$\mathbf{15} + H_2O \rightarrow AA + HPdBr$
$AA + HPdBr \rightarrow \mathbf{13}$
$\mathbf{13} + CO \rightarrow \mathbf{4} \rightarrow SA + HPdBr$

Mechanism 9

$C_2H_2 + HPdBr \rightarrow \mathbf{5}$
$\mathbf{5} + CO \rightarrow \mathbf{15}$
$\mathbf{15} + H_2O \rightarrow AA + HPdBr$
$AA + Pd_2Br_2 \rightarrow \mathbf{12}$
$\mathbf{12} + HBr \rightarrow \mathbf{13} + PdBr_2$
$\mathbf{13} + CO \rightarrow \mathbf{4} \rightarrow SA + HPdBr$

Mechanism 10

$H_2O + Pd_2Br_2 \rightarrow BrPdOH + HPdBr$
$BrPdOH + CO \rightarrow \mathbf{16}$
$\mathbf{16} + C_2H_2 \rightarrow \mathbf{11}$
$\mathbf{11} + HBr \rightarrow AA + PdBr_2$
$AA + HPdBr \rightarrow \mathbf{13}$
$\mathbf{13} + CO \rightarrow \mathbf{4} \rightarrow SA + HPdBr$

Mechanism 11

$H_2O + Pd_2Br_2 \rightarrow BrPdOH + HPdBr$
$BrPdOH + CO \rightarrow \mathbf{16}$
$\mathbf{16} + C_2H_2 \rightarrow \mathbf{11}$
$\mathbf{11} + HBr \rightarrow AA + PdBr_2$
$AA + Pd_2Br_2 \rightarrow \mathbf{12}$
$\mathbf{12} + HBr \rightarrow \mathbf{13} + PdBr_2$
$\mathbf{13} + CO \rightarrow \mathbf{4} \rightarrow SA + HPdBr$

Group III

Mechanism 12

$C_2H_2 + Pd_2Br_2 \rightarrow \mathbf{1}$
$\mathbf{1} + CO \rightarrow \mathbf{10}$
$\mathbf{10} + CO \rightarrow \mathbf{17}$
$\mathbf{17} + H_2O \rightarrow HPdBr + \mathbf{18}$
$\mathbf{18} \rightarrow MA + HPdBr$
$MA + HPdBr \rightarrow \mathbf{19}$
$\mathbf{19} + HBr \rightarrow SA + PdBr_2$

Mechanism 13

$C_2H_2 + Pd_2Br_2 \rightarrow \mathbf{1}$
$\mathbf{1} + CO \rightarrow \mathbf{10}$
$\mathbf{10} + CO \rightarrow \mathbf{17}$
$\mathbf{17} + H_2O \rightarrow HPdBr + \mathbf{18}$
$\mathbf{18} \rightarrow MA + HPdBr$
$MA + HPdBr \rightarrow \mathbf{19}$
$\mathbf{19} + HPdBr \rightarrow SA + Pd_2Br_2$

Mechanism 14

$H_2O + Pd_2Br_2 \rightarrow \mathbf{6} + HBr$
$\mathbf{6} + CO \rightarrow \mathbf{7}$
$\mathbf{7} + C_2H_2 \rightarrow \mathbf{14}$
$\mathbf{14} + CO \rightarrow \mathbf{20}$
$\mathbf{20} \rightarrow MA + HPd_2Br$
$MA + HPd_2Br \rightarrow \mathbf{25}$
$\mathbf{25} + HBr \rightarrow SA + Pd_2Br_2$

Mechanism 15

$H_2O + Pd_2Br_2 \rightarrow \mathbf{6} + HBr$
$\mathbf{6} + CO \rightarrow \mathbf{7}$
$\mathbf{7} + C_2H_2 \rightarrow \mathbf{14}$
$\mathbf{14} + CO \rightarrow \mathbf{20}$
$\mathbf{20} \rightarrow MA + HPd_2Br$
$MA + HPd_2Br \rightarrow \mathbf{25}$
$\mathbf{25} + HPd_2Br \rightarrow SA + Pd_2Br_2 + 2\ Pd^0$

Group IV

Mechanism 16

$HPdBr + C_2H_2 \rightarrow \mathbf{5}$
$\mathbf{5} + HPdBr \rightarrow \mathbf{2}$
$\mathbf{2} + 2\ CO \rightarrow \mathbf{3}$
$\mathbf{3} + H_2O \rightarrow \mathbf{4} + HPdBr$
$\mathbf{4} \rightarrow HPdBr + SA$

Mechanism 17

$C_2H_2 + Pd_2Br_2 \rightarrow \mathbf{1}$
$\mathbf{1} + HBr \rightarrow \mathbf{5} + PdBr_2$
$\mathbf{5} + HPdBr \rightarrow \mathbf{2}$
$\mathbf{2} + 2\ CO \rightarrow \mathbf{3}$
$\mathbf{3} + H_2O \rightarrow \mathbf{4} + HPdBr$
$\mathbf{4} \rightarrow SA + HPdBr$

Mechanism 18

$C_2H_2 + Pd_2Br_2 \rightarrow \mathbf{1}$
$\mathbf{1} + HBr \rightarrow \mathbf{5} + PdBr_2$
$\mathbf{5} + Pd_2Br_2 \rightarrow \mathbf{21}$
$\mathbf{21} + 2\ CO \rightarrow \mathbf{22}$
$\mathbf{22} + HBr \rightarrow \mathbf{3} + PdBr_2$
$\mathbf{3} + H_2O \rightarrow \mathbf{4} + HPdBr$
$\mathbf{4} \rightarrow SA + HPdBr$

Mechanism 19

$C_2H_2 + Pd_2Br_2 \rightarrow \mathbf{1}$
$\mathbf{1} + CO \rightarrow \mathbf{10}$
$\mathbf{10} + H_2O \rightarrow \mathbf{11} + HPdBr$
$\mathbf{11} + HPdBr \rightarrow \mathbf{12}$
$\mathbf{12} + HBr \rightarrow \mathbf{13} + PdBr_2$
$\mathbf{13} + CO \rightarrow \mathbf{4} \rightarrow SA + HPdBr$

Mechanism 20

$C_2H_2 + Pd_2Br_2 \rightarrow \mathbf{1}$
$\mathbf{1} + HPdBr \rightarrow \mathbf{21}$
$\mathbf{21} + 2\ CO \rightarrow \mathbf{22}$
$\mathbf{22} + HBr \rightarrow \mathbf{3} + PdBr_2$
$\mathbf{3} + H_2O \rightarrow \mathbf{4} + HPdBr$
$\mathbf{4} \rightarrow SA + HPdBr$

Mechanism 21

$Pd_2Br_2 + H_2O \rightarrow \mathbf{6} + HBr$
$\mathbf{6} + CO \rightarrow \mathbf{7}$
$\mathbf{7} + C_2H_2 \rightarrow \mathbf{14}$
$\mathbf{14} + HPd_2Br \rightarrow \mathbf{23}$
$\mathbf{23} + HBr \rightarrow Pd_2Br_2 + \mathbf{8}$
$\mathbf{8} + CO \rightarrow \mathbf{9}$
$\mathbf{9} \rightarrow SA + HPd_2Br$

Mechanism 22

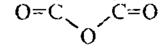
$Pd_2Br_2 + H_2O \rightarrow \mathbf{6} + HPdBr$
$BrPd_2OH + CO \rightarrow \mathbf{7}$
$\mathbf{7} + C_2H_2 \rightarrow \mathbf{14}$
$\mathbf{14} + HPd_2Br \rightarrow \mathbf{23}$
$\mathbf{23} + HBr \rightarrow Pd_2Br_2 + \mathbf{8}$
$\mathbf{8} + CO \rightarrow \mathbf{9}$
$\mathbf{9} \rightarrow SA + HPd_2Br$

Mechanism 23

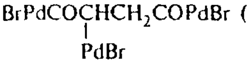
$C_2H_2 + Pd_2Br_2 \rightarrow \mathbf{1}$
$\mathbf{1} + HPdBr \rightarrow \mathbf{21}$
$\mathbf{21} + HBr \rightarrow \mathbf{2}$
$\mathbf{2} + 2\ CO \rightarrow \mathbf{3}$
$\mathbf{3} + H_2O \rightarrow HPdBr + \mathbf{4}$
$\mathbf{4} \rightarrow SA + HPdBr$

respectively, are listed below. We used the following designations:

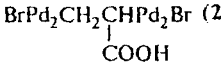
$BrPdCH{=}CHPdBr$ (**1**), $BrPdCH_2CH_2PdBr$ (**2**), $BrPdCOCH_2CH_2COPdBr$ (**3**), $BrPdCOCH_2CH_2COOH$ (**4**), $BrPdCH{=}CH_2$ (**5**), $BrPd_2OH$ (**6**), $BrPd_2COOH$ (**7**), $BrPd_2CH_2CH_2COOH$ (**8**), $BrPd_2COCH_2CH_2COOH$ (**9**), $BrPdCH{=}CHCOPdBr$ (**10**), $BrPdCH{=}CHCOOH$ (**11**), $BrPdCH_2CH(COOH)PdBr$ (**12**), $BrPdCH_2CH_2COOH$ (**13**), $BrPd_2CH{=}CHCOOH$ (**14**), $BrPdCOCH{=}CH_2$ (**15**), $BrPdCOOH$ (**16**), $BrPdCOCH{=}CHCOPdBr$ (**17**), $BrPdCOCH{=}CHCOOH$ (**18**),



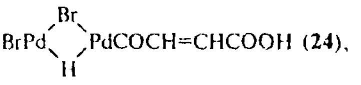
(**19**), $BrPd_2COCH{=}CHCOOH$ (**20**), $(BrPd)_2CHCH_2PdBr$ (**21**),



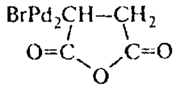
$BrPdCO\underset{PdBr}{\underset{|}{C}}HCH_2COPdBr$ (**22**),



$BrPd_2CH_2\underset{COOH}{\underset{|}{C}}HPd_2Br$ (**23**),



(**24**),



(**25**),

Pd_2Br_2 is a fragment of a Pd^I complex; HPd— is a fragment of a hydride Pd^{II} or Pd^I complex.

Not all the sequences of steps presented here include a closed catalytic cycle (resulting in the evolution of the initial form of the catalyst). However, at the stage of advancing hypotheses, this makes no difference. The necessary steps can be added during detailing of the mechanism and construction of the kinetic model.

The next stage of the selection involves elucidation of the roles of the potential organic intermediates, ethylene, acrylic acid, and maleic anhydride. Maleic anhydride and acrylic acid were identified among the products of carbonylation of acetylene. Ethylene was found in the exhaust gas only when the concentration of the catalyst was substantially increased.

To elucidate the influence of concentrations of the possible intermediates, we carried out a series of experiments in which the above-mentioned compounds were added to the reaction system. The concentration of the additive thus obtained was *a priori* larger than the highest concentration of the potential intermediate detected during the carbonylation (Table 1). The addition of ethylene does not influence significantly the rates of formation of the succinic and maleic anhydrides and acrylic acid (see Table 1). The slight decrease in the rates of formation of the products may be due to the decrease in the partial pressures of CO and C_2H_2. Ethylene does not undergo substantial conversion during the experiment, although the increase in the rate of formation of propionic acid might be due to its carbonylation. Thus, the mechanisms in which ethylene is proposed as the intermediate on the pathway to succinic anhydride (group I of hypotheses) can also be excluded from consideration.

The addition of acrylic acid also has no effect on the rates of formation of the anhydrides. The observed slight changes in the rates of formation of acrylic acid (decrease) and propionic acid (increase) suggest that acrylic acid might be converted into propionic acid. Therefore, the group of hypotheses in which the mechanism of the synthesis of succinic anhydride involves the intermediate formation of acrylic acid (group II) can also be excluded.

When maleic anhydride (0.33 mol L^{-1}; ~4%, w/w) is introduced into the system, the rate of formation of succinic anhydride increases, whereas the rate of formation of maleic anhydride decreases to approximately the same extent (Fig. 3). The introduction of a larger amount of maleic anhydride does not lead to further increase in the rate of formation of succinic anhydride. This finding is not at variance with the mechanisms assuming maleic anhydride as the intermediate of the synthesis of succinic anhydride. However, the observed change in the reaction rate exceeds only slightly the experimental error. Analysis of the hypotheses proposed makes it possible to interpret the limited increase in the rate of formation of succinic anhydride upon an increase in the concentration of maleic anhydride in the following way: apparently, the amount of hydride complexes of palladium in the reaction system becomes insufficient for the conversion of maleic anhydride into succinic anhydride.

Table 1. Effect of the concentration of ethylene and acrylic acid on the rates of formation of the acetylene carbonylation products[a]

Additive	Rates of formation/mol (L h)$^{-1}$			
(concentration)	SA	MA	AA	PA
None	0.64	0.075	0.072	No data
None	0.64	0.065	0.070	0.020
C_2H_4 (15%, v/v)	0.57	0.064	0.067	0.026
AA (0.15 mol L^{-1})	0.65	0.070	0.055	0.023

[a] Reaction conditions: $[PdBr_2]$ = 0.05 mol L^{-1}, [LiBr] = 0.1 mol L^{-1}, acetonitrile as the solvent, $p_{CO}/p_{C_2H_2} = 2.5$, T = 40 °C.

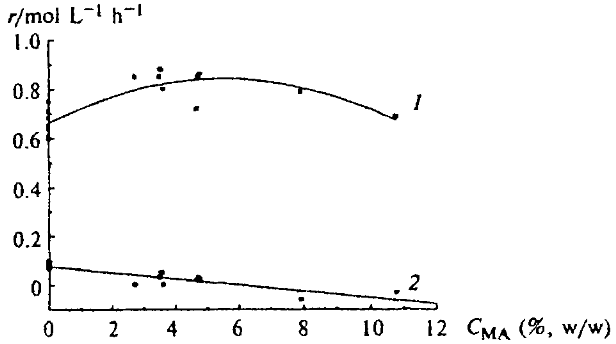


Fig. 3. The effect of the increase in the initial concentration of maleic anhydride on the rates (*r*) of formation of succinic (*1*) and maleic (*2*) anhydrides. Conditions: $[PdBr_2]$ = 0.05 mol L^{-1}, [LiBr] = 0.1 mol L^{-1}, $p_{CO}/p_{C_2H_2} = 2.5$, T = 40 °C.

Hydride complexes of palladium play an important role in all the hypotheses considered here; therefore, attempts were made to confirm the actual existence of these species under the conditions of acetylene carbonylation.

In the IR spectra of hydride complexes of transition metals, the absorption bands corresponding to H—M bonds occur in the same range as the bands for coordinated bridging carbon monoxide. Experiments with replacement of CH_3CN and H_2O by CD_3CN and D_2O showed that the absorption band at 1935 cm^{-1} observed in the quasi-steady-state carbonylation process remains unchanged; thus, the assignment of this band to a bridging carbonyl group can be considered to be correct. In the experiments with the addition of maleic anhydride, the IR spectra exhibited no band at 1948 cm^{-1}, which is apparently related to the bridging carbonyl group in a Pd^I complex containing acetylene in the coordination sphere. Thus, the band at 1935 cm^{-1} corresponds to a carbonyl complex of Pd^I containing maleic anhydride in the coordination sphere.

To identify the hydride complexes in the solution, in an experiment carried out in acetonitrile-d_3, after the period of catalyst formation (10 min), the sample was rapidly cooled to −40 °C, and its ^1H NMR spectrum was recorded.* By virtue of product accumulation pro-

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* The authors are grateful to E. V. Vorontsov (A. N. Nesmeyanov Institute of Organoelement Compounds of the RAS) for assistance in the spectral studies.

cedures, a weak broadened signal ($\nu_{1/2}$ = 70 Hz) at −1.88 ppm could be detected. Broadening might be due to exchange processes (even at this temperature) and to the relaxation effects caused by the quadrupole nucleus of palladium. When the solution was heated to 0 °C, the signal in question quickly disappeared. Since this region of the ^{1}H NMR spectrum does not contain characteristic signals of other groups (except those for hydroxyl complexes of Pd^{II}, which are formed in alkaline media[13]), this result makes it possible to regard the existence of hydride complexes of palladium in this system as authentic. The most probable pathway to the hydride complexes is oxidative carbonylation of acetylene to maleic anhydride and maleic and fumaric acid, for example,

$$Pd_2Br_2 + C_2H_2 + 2\ CO + H_2O \longrightarrow MA + 2\ HPdBr.$$

The next stage of the selection of hypotheses included investigation of kinetic isotope effects. Each of the remaining two groups of mechanisms (groups *III* and IV) can be divided into two parts:

1. Mechanisms in which water reacts either before the first irreversible step or at the first irreversible step.
2. Mechanisms in which water still participates in steps after irreversible transformations. In this case, the kinetic isotope effect (k_H/k_D) should be close to unity provided that the step involving H_2O is not a part of the conjugation node.

The first group comprises mechanisms *14*, *15*, *21*, and *22*, while the remaining mechanisms belong to the second group.

To verify the possibility for the above mechanisms to be realized in the system under consideration, we determined the kinetic isotope effect, which was defined as the ratio of the rates of product formation in protium- and deuterium-containing systems (r_H/r_D), all other factors being the same (Table 2).

Table 2. Kinetic isotope effects in the reactions of formation of succinic and maleic anhydrides[a]

System	r_H/r_D			
	SA	MA	AA	PA
$CD_3CN—C_2H_2—D_2O$[b]	1.13±0.05	0.9±0.1	1.8±0.15	2.5±0.3
$CD_3CN—C_2D_2—D_2O$[b]	1.10±0.05	0.9±0.1	1.7±0.15	2.2±0.3
$(CD_3)_2CO—C_2H_2—D_2O$	1.07±0.05	0.9±0.1	—	—

[a] Reaction conditions: $[PdBr_2]$ = 0.05 mol L^{-1}, [LiBr] = 0.1 mol L^{-1}, $p_{CO}/p_{C_2H_2}$ = 2.5, T = 40 °C.
[b] Reference system $MeCN—C_2H_2—H_2O$.

The fact that the kinetic isotope effects found for the rates of formation of maleic and succinic anhydrides are close to unity makes it possible to exclude mechanisms *14*, *15*, *21*, and *22* from consideration, because in these cases, cleavage of the H—OH (D—OD) bond occurs prior to the first irreversible step, and the rate constant for the rupture of the O—H bond depends substantially on which particular hydrogen isotope is involved. Apparently, cleavage of the H—OH bond before the first irreversible step is included in the mechanisms of formation of acrylic and propionic acids (see Table 2).

The results of studies of the distribution of deuterium in the carbonylation products and the isotope exchange following the addition of protium-containing maleic anhydride into a totally deuterated system (Table 3) provide grounds for claiming that the protium in maleic anhydride can rapidly exchange with deuterium and, hence, protium can get into succinic anhydride. These results are in good agreement with mechanisms *12* and *13* provided that the step of insertion of maleic anhydride into the Pd—H bond is reversible.

In most of the remaining mechanisms (*12*, *17*, *18*, *19*, *20*, *21*, *22*, *23*), an important role is played by protodemetallation. The initial catalytic system contains no hydrogen bromide; therefore, the catalytic solutions can become slightly acidic only as a result of hydrolysis of palladium(II) and palladium(I) bromides and the reduction of Pd^{II} to Pd^{I}. The maximum concentration of HBr created in the system by the above reactions cannot be higher than the concentration of palladium. Titration of samples withdrawn from the contact solution showed that the real concentration of HBr is close to zero. Hydrogen bromide rapidly reacts with acetonitrile yielding adducts of various compositions. The product $(MeCN)_2(HBr)_3$ was isolated from a MeCN—HBr solution; the structure of this compound was determined by X-ray diffraction analysis* and will be published elsewhere.

Based on the results outlined above, mechanisms including steps with the participation of HBr (*12*, *17*,

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* The X-ray diffraction study of $(MeCN)_2(HBr)_3$ was carried out by S. E. Nefedov and I. L. Eremenko (N. S. Kurnakov Institute of General and Inorganic Chemistry of the RAS).

Table 3. Distribution of H and D in the products of carbonylation in the $CD_3CN—C_2D_2—D_2O$ system[a]

[SA]/mol L^{-1}		$\frac{[(CHDCO)_2O]}{[(CD_2CO)_2O]}$	[MA]/mol L^{-1}		$\frac{[(CHCO)_2O]}{[(CDCO)_2O]}$
$(CHDCO)_2O$	$(CD_2CO)_2O$[b]		$(CHCO)_2O$[b]	$(CDCO)_2O$[b]	
0.15	0.87	0.17	0	0.20	0
0.38[c]	0.73	0.52	0.01	0.4	0.03

[a] Reaction conditions: $[PdBr_2]$ = 0.05 mol L^{-1}, [LiBr] = 0.1 mol L^{-1}, T = 40 °C, experiment duration 105 min.
[b] For convenience of the calculations, it was assumed that only symmetric molecules are formed in the system.
[c] Maleic anhydride $(CHCO)_2O$ (0.288 mol L^{-1}) was added to the initial solution.

18, *19*, *20*, *21*, *23*) are excluded from the subsequent discussion.

To distinguish between the remaining two mechanisms (*13* and *16*) and to construct an adequate kinetic model, the kinetic regularities of the process were studied by the method of one-factor experiment. Based on the analysis of the remaining hypotheses, the concentration of $PdBr_2$ and the partial pressures of C_2H_2 and CO were chosen as the variable parameters.

The dependence of the rate of product formation on the concentration of $PdBr_2$ is significant for estimating the role of non-linear steps (those including interaction of two intermediates). If such a step is included in the conjugation node,[9] then the ratio of the product formation rates would depend on the total concentration of palladium. If this step is not a part of the conjugation node but leads to the formation of palladium-containing compounds inactive in this process, then the dependences of the rates of formation of all the products on the concentration of the catalyst would follow identical nonlinear patterns. The dependences of the rates of formation of succinic and maleic anhydrides on the partial pressures of the reactants are significant for more precise determination of the structure of the conjugation node, *i.e.*, for the elucidation of the sequence of steps leading to these products.

In the preliminary experiments, it was found that in the range of stable operation of the catalytic system, the rates of product formation practically do not depend on the concentration of water. Since the catalyst operates steadily in a relatively narrow range of water concentrations, for each experiment with variation of other factors, a velocity of the water delivery was chosen in such a way as to ensure an approximately constant water concentration $[H_2O] = 0.1-0.2$ mol L^{-1}. The period of formation of the catalyst is associated with the reduction of the initial $PdBr_2$ to Pd^I derivatives. The content of water in the initial system is among the important factors influencing the characteristics of this process. Thus, in the system under study, water accomplishes a very complicated function; it participates in the steps of the catalyst formation and acts as both a reagent and the ligand determining the stability of the catalytic system. At $[H_2O] > 0.5$ mol L^{-1}, the system loses stability. The complex character of the influence of water concentration and the difficulty of maintaining it constant account for the not very good reproducibility of the kinetic data (±15 rel.%).

The dependences of the product formation rates on the concentration $[PdBr_2]_\Sigma$ are nearly linear up to $[PdBr_2]_\Sigma = 0.05$ mol L^{-1} (Fig. 4). The ratio of the formation rates r_{SA}/r_{MA} does not depend on $[PdBr_2]_\Sigma$ to within the experimental error. When the concentration of $PdBr_2$ becomes >0.05 mol L^{-1}, the order of the rate of formation of maleic anhydride with respect to $[PdBr_2]_\Sigma$ tends to increase, whereas that for the formation of succinic anhydride tends to decrease. The orders with respect to the partial pressures of CO and C_2H_2 for the rates of formation of the two anhydrides vary (Figs. 5, 6).

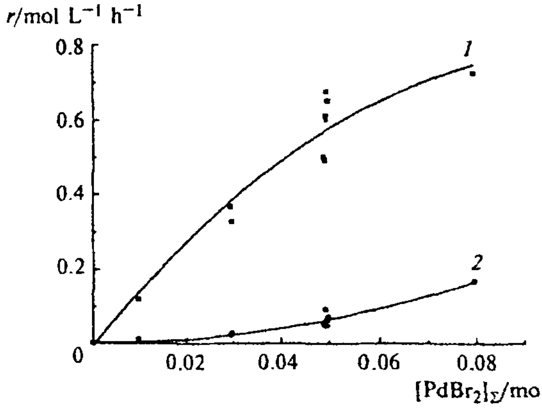


Fig. 4. Dependences of the rates of formation of succinic (*1*) and maleic (*2*) anhydrides on the total concentration of palladium bromide. Conditions: [LiBr] = 0.74 mol L^{-1}, acetonitrile as the solvent, $p_{C_2H_2}$ = 0.16 to 0.21 atm, p_{CO} = 0.73 to 0.78 atm, T = 40 °C.

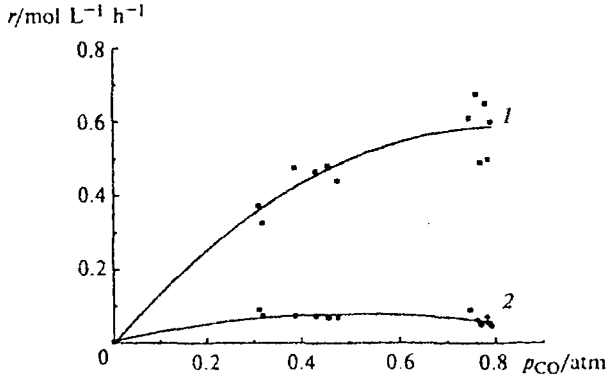


Fig. 5. Dependences of the rates of formation of succinic (*1*) and maleic (*2*) anhydrides on the partial pressure of carbon monoxide. Conditions: $[PdBr_2]$ = 0.05 mol L^{-1}, [LiBr] = 0.74 mol L^{-1}, acetonitrile as the solvent, $p_{C_2H_2}$ = 0.16 to 0.21 atm, T = 40 °C.

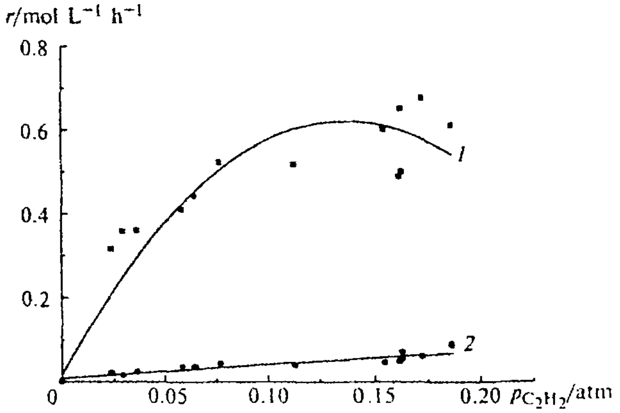
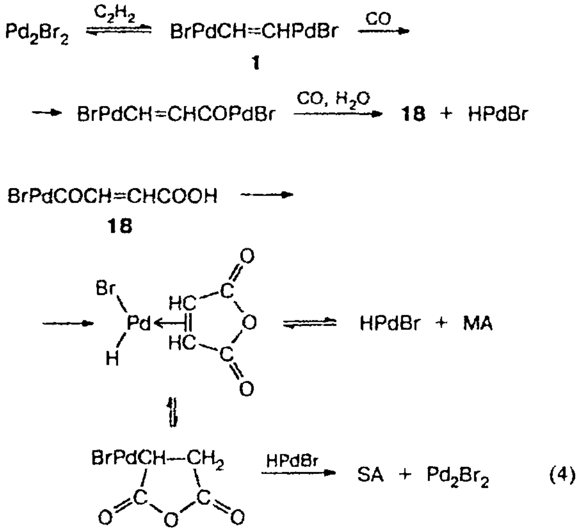
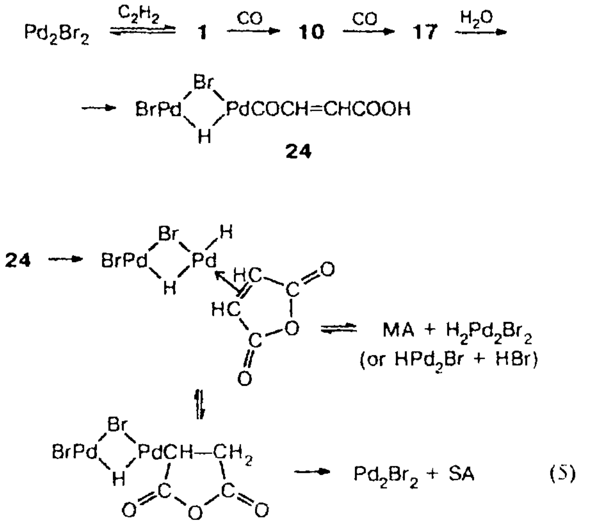


Fig. 6. Dependences of the rates of formation of succinic (*1*) and maleic (*2*) anhydrides on the partial pressure of acetylene. Conditions: $[PdBr_2]$ = 0.05 mol L^{-1}, [LiBr] = 0.74 mol L^{-1}, acetonitrile as the solvent, p_{CO} = 0.73 to 0.78 atm, T = 40 °C.

Let us discuss qualitatively the remaining hypotheses taking into account the kinetic data. In mechanism *13*, the step of formation of succinic anhydride is nonlinear and should be included in the conjugation node, since according to the data on isotope exchange, the step of insertion of maleic anhydride into the Pd—H bond is reversible (reaction (4)).



This mechanism is inconsistent with the experimental dependence $r_{SA}/r_{MA} = f([PdBr_2]_\Sigma)$. However, this disagreement can be eliminated by assuming that dimeric palladium complex $(HPdBr)_2$ acts in the system. In this case, mechanism *13* can be presented as follows:



In mechanism *16*, the second step is nonlinear. Provided that the first step is reversible, this should result in the order of the rate of formation of succinic anhydride with respect to the catalyst being greater than unity; this is at variance with the experimental results. This disagreement can be eliminated by assuming either that the first step is irreversible (to the best of our knowledge, there is no experimental evidence for β-elimination in σ-vinyl organometallic compounds) or that both HPdBr hydrides act as a single species $(H_2Pd_2Br_2)$.

$$H_2Pd_2Br_2 + C_2H_2 \rightleftharpoons H_2Pd_2Br_2(C_2H_2) \xrightarrow{CO}$$

$$\rightarrow BrPdCOCH_2CH_2PdBr \xrightarrow{CO}$$

$$\rightarrow BrPdCOCH_2CH_2COPdBr \xrightarrow{H_2O} SA + H_2Pd_2Br_2 \quad (6)$$

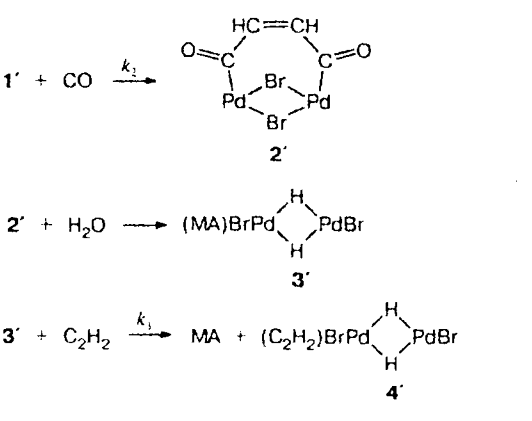
The dimeric hydride complex of Pd^{II} could be produced in this system upon oxidative carbonylation of acetylene to maleic anhydride. The "bottleneck" of this mechanism is the necessity for acetylene to displace the maleic anhydride from the coordination sphere of the palladium hydride (maleic anhydride and the hydride complex are formed apparently in the same step) when the concentrations of C_2H_2 and MA are commensurable.

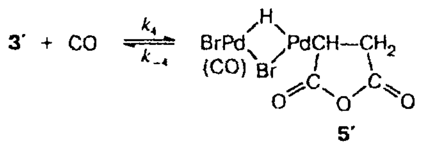
More detailed variants of mechanisms *13* and *16* (with more detailed specification of the coordination spheres of the intermediate compounds) were also developed. The structures of compounds **2'**—**8'** were proposed by analogy with known compounds and are hypothetical. All the vacant sites in the coordination spheres of Pd^I complexes and the intermediates are apparently occupied by acetonitrile molecules, which play a stabilizing role. In the mechanisms given below, some of the transformations occurring after the irreversible step are formulated as non-elementary steps (for example, *6'* → *7'*), because these steps are not reflected in the kinetic model.

As a result, mechanism *13* is presented as the following version:

Mechanism 13.1

$$Pd_2Br_2(CO)_2 + C_2H_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\mathbf{1'}}{Pd_2Br_2(CO)(C_2H_2)} + CO$$





$$\mathbf{5'} \xrightarrow[CO]{k_5} Pd_2Br_2(CO)_2 + SA$$

For this mechanism, kinetic equations (7) and (8) were derived.

$$r_{SA} = k_1k_2k_4k_5(p_{CO})^3p_{C_2H_2}[Pd]_{\Sigma}/D, \qquad (7)$$

$$r_{MA} = k_1k_2k_3(k_{-4} + k_5p_{CO})p_{CO}(p_{C_2H_2})^2[Pd]_{\Sigma}/D \qquad (8)$$

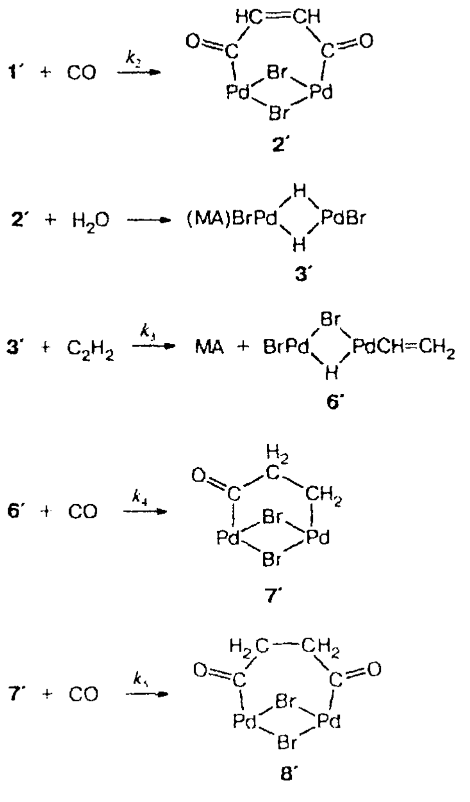
$$D = [(k_{-1} + k_2)p_{CO} + k_1p_{C_2H_2}][k_3k_{-4}p_{C_2H_2} +$$
$$+ k_3k_5p_{C_2H_2}p_{CO} + k_4k_5(p_{CO})^2].$$

The coordination vacancies in the intermediate compounds are apparently occupied by carbon monoxide or by solvent molecules. The material balance for the catalyst takes into account compounds $Pd_2Br_2(CO)_2$ and **1′**.

A more detailed version for mechanism *16* (mechanism *16.1*) and the corresponding kinetic equations were also obtained:

Mechanism 16.1

$$Pd_2Br_2(CO)_2 + C_2H_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\mathbf{1'}}{Pd_2Br_2(CO)(C_2H_2)} + CO$$



$$\mathbf{8'} + H_2O \xrightarrow{k_6} SA + \underset{\mathbf{9'}}{H_2Pd_2Br_2}$$

$$H_2Pd_2Br_2 + C_2H_2 \longrightarrow \mathbf{6'}$$

$$r_{SA} = \frac{k_1k_2k_4k_5(p_{CO})^3\,p_{C_2H_2}[Pd]_{\Sigma}}{[(k_{-1} + k_2)p_{CO} + k_1p_{C_2H_2}](k_{-4} + k_5p_{CO})k_6} \qquad (9)$$

$$r_{MA} = \frac{k_1k_2p_{CO}p_{C_2H_2}[Pd]_{\Sigma}}{(k_{-1} + k_2)p_{CO} + k_1p_{C_2H_2}} \qquad (10)$$

The rate constants for the kinetic models obtained were estimated using the coordinate-wise descent method. The minimum mean-square sum of deviations of the calculated values from the experimental values (f^2_{min}) was taken as the optimization criterion. The results of the calculation are presented in Table 4. According to the Fischer criterion, both mechanisms are adequate to experimental data. The fact that the magnitudes of the Fischer criterion obtained do not permit discrimination of models *13.1* and *16.1* is apparently due to the large experimental errors. Therefore, to perform further selection of mechanisms *13.1* and *16.1*, an additional series of experiments was carried out; in this case, the range of variation of the partial pressure of acetylene was increased to 0.4 atm. The rate constants were estimated and the values of the Fischer criterion were calculated for the whole set of experimental data (see Table 4). The results obtained make it possible to rule out mechanism *16.1*.

However, the kinetic model corresponding to mechanism *13.1* poorly describes the dependence of the rate of formation of succinic anhydride on the partial pressures of CO and acetylene (Fig. 7—9). (The dependences of r_{SA} on p_{C2H2} are presented in two plots (see Figs. 8 and 9), because these series of experiments were carried out at different partial pressures of CO; the increase in the partial pressure of acetylene in the additional series of experiments was accomplished by introducing an

Table 4. Results of calculation of the statistical criteria for the kinetic models describing mechanisms *13.1*, *13.2*, *16.1*, *16.2*

Mechanism	f^2_{min}	Fischer criterion	
		calculated	tabular[17]
13.1[a]	0.0949	1.03	4.60
13.1[b]	0.1921	1.27	3.14
13.2[b]	0.1345	0.97	3.15
16.1[a]	0.3869	4.18	4.60
16.1[b]	0.7496	4.99	3.14
16.2[b]	0.3867	2.78	3.15

[a] The first series of experiments.

[b] The calculation was carried out for the two series of experiments.

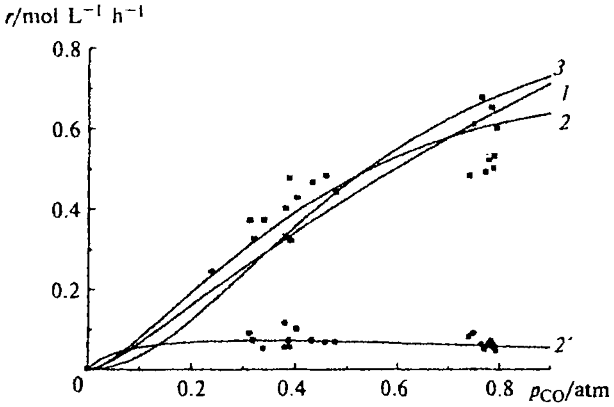


Fig. 7. Description of the experimental dependences of r on p_{CO} for succinic (*1—3*) and maleic (*2'*) anhydrides in terms of the equations corresponding to mechanisms *13.1* (*1*), *13.2* (*2, 2'*), and *16.2* (*3*). Conditions: $[PdBr_2]$ = 0.05 mol L^{-1}, [LiBr] = 0.74 mol L^{-1}, acetonitrile as the solvent, $p_{C_2H_2}$ = 0.16 to 0.21 atm, T = 40 °C.

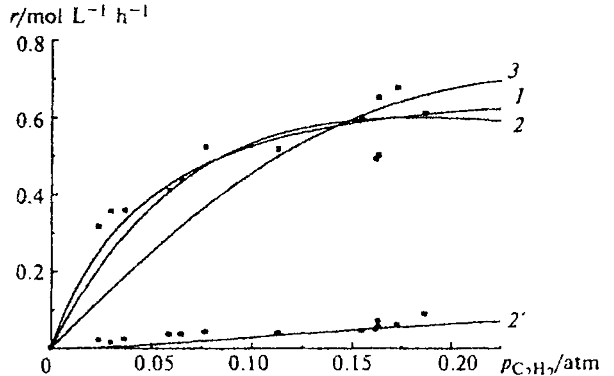


Fig. 8. Description of the experimental dependences of r on $p_{C_2H_2}$ for succinic (*1—3*) and maleic (*2'*) anhydrides in terms of the equations corresponding to mechanisms *13.1* (*1*), *13.2* (*2, 2'*), and *16.2* (*3*) (the first series of experiments). Conditions: $[PdBr_2]$ = 0.05 mol L^{-1}, [LiBr] = 0.74 mol L^{-1}, acetonitrile as the solvent, p_{CO} = 0.73 to 0.78 atm, T = 40 °C.

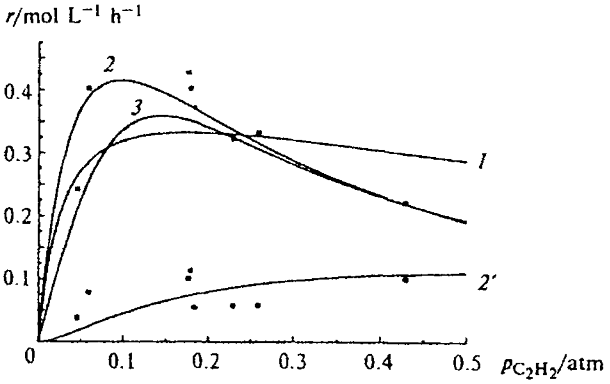


Fig. 9. Description of the experimental dependences of r on $p_{C_2H_2}$ for succinic (*1—3*) and maleic (*2'*) anhydrides in terms of the equations corresponding to mechanisms *13.1* (*1*), *13.2* (*2, 2'*), and *16.2* (*3*) (the additional series of experiments). Conditions: $[PdBr_2]$ = 0.05 mol L^{-1}, [LiBr] = 0.74 mol L^{-1}, acetonitrile as the solvent, p_{CO} = 0.38 to 0.40 atm, T = 40 °C.

inert gas into the system and, hence, by decreasing the partial pressure of CO.) Therefore, we attempted to improve the description by including the palladium complexes with acetylene and carbon monoxide, inactive in the carbonylation, which might form in the reaction system according to reactions (11) and (12), into the material balance for the catalyst.

$$Pd_2Br_2(CO)_2 + CO \xrightleftharpoons{K_{CO}} \underset{\mathbf{10'}}{Pd_2{}^{+}Br(CO)_3} + Br^- \quad (11)$$

$$Pd_2Br_2(CO)(C_2H_2) + C_2H_2 \xrightleftharpoons{K_{C_2H_2}} \underset{\mathbf{11'}}{Pd_2Br_2(CO)(C_2H_2)_2} \quad (12)$$

The rate constants for mechanism *13.2* (it is mechanism *13.1* supplemented by reactions (11) and (12)) were estimated using the following kinetic equations:

$$r_{SA} = k_1k_2k_4k_5(p_{CO})^3p_{C_2H_2}[Pd]_\Sigma/D, \qquad (13)$$

$$r_{MA} = k_1k_2k_3(k_{-4} + k_5p_{CO})p_{CO}(p_{C_2H_2})^2[Pd]_\Sigma/D, \qquad (14)$$

$$D = [(k_{-1} + k_2)(1 + K_{CO}p_{CO})p_{CO} + k_1p_{C_2H_2}(1 + \\ + K_{C_2H_2}p_{C_2H_2})][k_3k_{-4}p_{C_2H_2} + k_3k_5p_{C_2H_2}p_{CO} + k_4k_5(p_{CO})^2].$$

The $[Br^-]$ value does not appear in the kinetic equations, because all the experiments were carried out at a high concentration of LiBr.

The results of calculations are presented in Tables 4, 5 and in Figs. 7—9.

Table 5. Sets of rate constants obtained for kinetic model *13.2*

k_1	k_2	k_3	k_4	k_5	k_{-1}	k_{-4}	K_{CO}	$K_{C_2H_2}$	f_{min}
10000	45.61	3.28	8.15	264.99	495.21	0.0001	4.15	3.82	0.1346
3112.7	44.85	23.36	54.67	135.53	0.0001	0.0001	18.88	3.75	0.1345
6406.5	45.81	580.20	1476.0	934.87	297.25	0.0001	4.20	3.95	0.1350
49677.0	44.75	5.49	13.89	139.43	234.17	0.0001	50.06	3.83	0.1359
6984.2	46.23	44.70	113.60	8902.5	325.76	0.0001	4 30	4.02	0.1349
24246.0	38.48	3.73	9.52	280.22	177.12	0.0002	24 97	2.97	0.1356

The rate constants for mechanism *16.2* (mechanism *16.1* supplemented by reactions (11) and (12)) were estimated from the following kinetic equations:

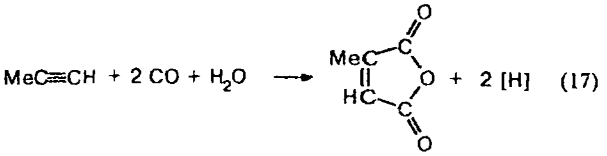
$$r_{SA} = k_1k_2k_4k_5(p_{CO})^3p_{C_2H_2}[Pd]_\Sigma/\{[(k_{-1} + k_2)(1 + K_{CO}p_{CO})p_{CO} + k_1p_{C_2H_2}(1 + K_{C_2H_2}p_{C_2H_2})](k_{-4} + k_5p_{CO})k_6\}, \qquad (15)$$

$$r_{MA} = k_1k_2p_{CO}p_{C_2H_2}[Pd]_\Sigma/[(k_{-1} + k_2)(1 + K_{CO}p_{CO})p_{CO} + k_1p_{C_2H_2}(1 + K_{C_2H_2}p_{C_2H_2})]. \qquad (16)$$

It should be noted that the assumed formation of inactive complexes of Pd with CO and C_2H_2 in the system does not again make it possible to rule out mechanism *16.2* resorting to the Fischer criterion (see Table 4). However, graphical comparison of the calculated curves and experimental points for mechanisms *13.2* and *16.2* (see Fig. 7—9) shows that mechanism *13.2* provides a better description of the experimental data. The adequacy of the description of the carbonylation of acetylene to succinic anhydride in terms of mechanism *13.2* can also be confirmed by looking at Fig. 10. The scatter of the points is apparently due to experimental errors.

Analysis of the numerical values for the rate constants in mechanism *13.2* (see Table 5) demonstrates that only k_2 and K_{C2H2} values can be determined with sufficient reliability. The magnitudes of other constants vary over wide limits. This is a trivial result for this class of problems of parameter identification in chemical kinetics.[14] To estimate the constants with smaller confidence intervals, it is necessary to analyze the identifiability of the constants[15] or to pass to processing of nonsteady-state kinetic data.

Additional evidence supporting mechanisms *13* (with allowance for their modifications) was obtained in the experiments on carbonylation of methylacetylene. When methylacetylene is carbonylated under the same conditions as C_2H_2, except for the concentration of water (~1 mol L^{-1}), citraconic anhydride is formed as the main product.



The material balance for alkyne can be brought together by no more than 50% (half of the alkyne is reduced in some form). When maleic anhydride is introduced into the system under the conditions of carbonylation of methylacetylene, succinic acid is formed. This implies that under the conditions of acetylene carbonylation, maleic anhydride could also be hydrogenated into succinic anhydride. All these data provide grounds for believing that the most probable mechanism of the synthesis of succinic anhydride involves intermediate formation of maleic anhydride. The main steps in the synthesis of the unsaturated anhydrides are insertion of the alkyne and carbon monoxide into the Pd—Pd bond of Pd^I complexes (see mechanism *13*).

If this mechanism is valid, the introduction of an oxidizing agent capable of competing with maleic anhydride for the hydride should increase the selectivity of

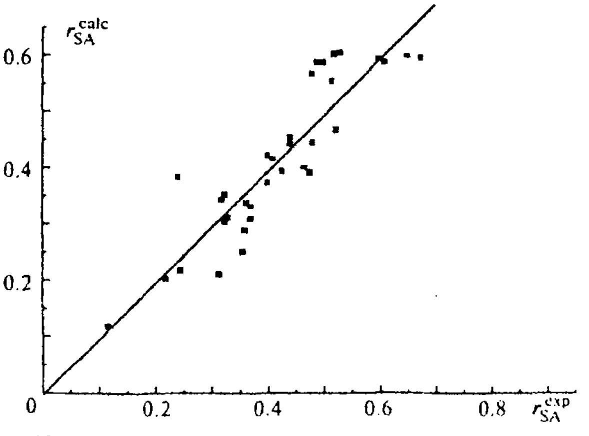


Fig. 10. Comparison of experimental (r_{SA}^{exp}) and calculated (r_{SA}^{calc}) rates of the formation of succinic anhydride for mechanism *13.2*.

Table 6. Effects of various oxidants on the characteristics of the process[a]

Oxidant (concentration or pressure)	r_{MA} mol (L h)$^{-1}$	r_{SA} mol (L h)$^{-1}$	r_{MA}/r_{SA}	Product yields based on C_2H_2 (%)
None	0.08	0.71	0.11	72.8
CCl_4 (10%, v/v)	0.10	0.79	0.13	73.8
CCl_4 (30%, v/v)	0.16	0.93	0.17	78.7
$K_3[Fe(CN)_6]$ (1.0 mol L^{-1})	0.02	0.15	0.13	74.7
$CuBr_2$ (1.0 mol L^{-1})	0.29	0.65	0.45	70.2
$CuCl_2$ (1.0 mol L^{-1})	0.45	0.33	1.36	48.9
CuO (1.0 mol L^{-1})	0.22	0.06	3.67	64.3
Fe_2O_3 (1.0 mol L^{-1})	0.17	0.03	5.67	63.2
V_2O_5 (1.0 mol L^{-1})	0.05	0.01	5.00	73.5
$C_6Cl_4O_2$ (1.0 mol L^{-1})	0.05	—	—	55.0
H_2MoO_4 (1.0 mol L^{-1})	0.10	—	—	56.4
MnO_2 (1.0 mol L^{-1})	0.20	—	—	33.5
$Co(Pc)O_2$ [b] (0.1 mol L^{-1})	0.04	0.004	10.0	68.8
O_2 (0.306 atm)	1.71	0.10	17.10	74.2
O_2 (0.277 atm)	1.62	0.15	10.80	77.8

Note: with $C_6H_4O_2$, $Cu(OAc)_2$, and CrO_3 (1.0 mol L^{-1}) as oxidants acetylene efficiently polymerizes, and only traces of carbonylation products are formed.

[a] Reaction conditions: $[PdBr_2]$ = 0.05 mol L^{-1}, [LiBr] = 0.1 mol L^{-1}, acetonitrile as the solvent, $p_{CO}/p_{C_2H_2}$ = 1.8 to 2.0. T = 40 °C. Most of the oxidants listed are insoluble in the contact solution.

[b] These concentrations of oxidants were calculated from the weighed portions used. $[PdBr_2]$ = 0.02 mol L^{-1}.

formation of MA. This assumption was confirmed in a series of experiments with various oxidants added to the system (Table 6). Most of the oxidants used were found to increase the selectivity of acetylene carbonylation into maleic anhydride. In the presence of oxygen, the yield of maleic anhydride reached ~60%.[16]

The effect of the total concentration of palladium bromide on the ratio of the rates of formation of the anhydrides at $[PdBr_2] > 0.05$ mol L^{-1} (see Fig. 4) must also be due to the reaction of $PdBr_2$ with the hydride complex of palladium.

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