

# Mechanistic study of acetylene carbonylation to anhydrides of dicarboxylic acids in solutions of palladium complexes

L.G. Bruk, I.V. Oshanina, A.P. Kozlova, E.V. Vorontsov, O.N. Temkin \*

*Lomonosov Academy of Fine Chemical Technology, Moscow, 117571, Russia*

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## Abstract

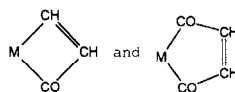
The mechanism of the reaction that produces maleic and succinic anhydrides from carbon monoxide and acetylene was studied in the catalytic  $\text{PdBr}_2\text{-LiBr-CH}_3\text{CN}$  system. The in situ study of reactivities of possible organic intermediates, the kinetic isotope effect study (for succinic and maleic anhydrides  $k_{\text{H}}/k_{\text{D}}$  was estimated to be  $1.05 \pm 0.05$  and  $0.9 \pm 0.1$ , respectively), the study of isotope exchange, and the oxygen effect on the process direction, revealed that maleic anhydride is most likely a key intermediate of the succinic anhydride formation. Maleic anhydride undergoes transformations through the mediation of a palladium hydride complex. This complex was detected in the catalytic solution at  $-40^\circ\text{C}$  with  $^1\text{H NMR}$  ( $\delta = -1.88$  ppm,  $\nu_{1/2} = 70$  Hz).

**Keywords:** Acetylene; Carbonylation; Maleic anhydride; Palladium; Succinic anhydride

## 1. Introduction

Alkyne carbonylation reactions, the subject of considerable investigation since the 1940s, are commercially used in the syntheses of acrylic acid and acrylates [1–3]. Reactions between alkynes and carbon monoxide, which involve various reagents, can produce saturated and unsaturated carboxylic and dicarboxylic acids, their derivatives (i.e., esters, amides, lactones, anhydrides, etc.), ketones, quinones, and hydroquinones [1,2]. Possible mechanisms of carbonylation reactions were studied in detail for reactions producing acids and esters [1,3,4]. There are three basic mechanisms for the synthesis of  $\alpha,\beta$ -unsaturated monocarboxylic and dicarboxylic acids, esters, and amides [3]. The first mechanism involves  $\text{M}(\text{CO})\text{X}$

( $\text{X} = \text{OH}, \text{OR}, \text{NR}_2$ ) as a key intermediate [3]. According to the second mechanism, catalytically active species are transition metal hydride complexes. The third mechanism implies the formation of cyclic intermediates with a metal atom in a cycle:

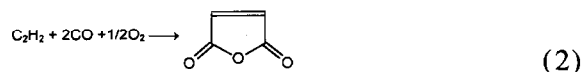
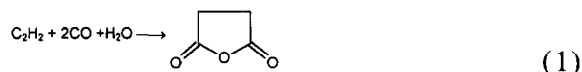


or insertion of alkynes and carbon monoxide into a metal–metal bond resulting in  $\text{M-CH=CH-M}$  and  $\text{M-CH=CH-CO-M}$ . Some mixed variants are also possible. In the alkyne carbonylation, unsaturated products can produce saturated monocarboxylic and dicarboxylic acids and their derivatives. For instance, acrylic and maleic acids can generate succinic acid [5]; acrylate can produce propionate [6].

\* Corresponding author.

Not much evidence on the mechanism for the syntheses of anhydrides of dicarboxylic acids can be found in the literature. It is remarkable that, unlike the synthesis of succinic anhydride, which is our recent finding [7], the synthesis of maleic anhydride has been known for more than 20 years [6]. However, mechanistic details of both reactions are poorly studied. Only our recent short communications were devoted to the synthesis of succinic anhydride [7,8].

This paper is devoted to the mechanistic study of syntheses of anhydrides of dicarboxylic acids in the catalytic  $\text{PdBr}_2\text{-LiBr-CH}_3\text{CN}$  system [7]:



## 2. Experimental

Experiments were performed in the gas-flow constant-temperature reactor with vigorous stirring of both gas and liquid phases at 1 atm. The gas phase was analyzed by gas-adsorption chromatography (phase, activated carbon AG-3 with a granule size of 0.25–0.5 mm; column 3 m long and 3 mm in diameter; temperature, 140°C; carrier gas, argon; thermal conductivity detector). The liquid phase was analyzed by the GLC method (column 3 m long and 3 mm in diameter, filled with 10% poly(methylphenylsiloxane) PFMS-4 on Polychrom-1; temperature, 180°C; thermal conductivity detector; carrier gas, helium). IR spectra of gases and solutions were recorded with an IR spectrometer M-82.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded with a Bruker WP-200SY instrument using a PRESAT14 pulse sequence. Potentiometric titration of solutions and potentiometric measurements during each run were conducted with the pH-673 potentiometer, glass and platinum electrodes. Silver chloride electrode was used as a reference electrode.

All reagents were of chemically pure grade and analytically pure according to the Russian

National Standards and were used without additional purification.  $\text{CO}$  and  $\text{C}_2\text{H}_2$  were purified to achieve a concentration of the main component of more than 99.5%.

## 3. Results and discussion

### 3.1. Results of preliminary experiments

In the  $\text{PdBr}_2\text{-LiBr-CH}_3\text{CN}$  system,  $\approx 70\%$  of acetylene consumed goes into the formation of succinic anhydride by reaction (1) at the initial  $\text{CO}:\text{C}_2\text{H}_2$  volume ratio of 2.5 and  $[\text{H}_2\text{O}] = 0.5$  mol/l. Besides succinic anhydride, the reacting system produces lesser amounts of maleic anhydride and succinic, maleic, fumaric, and acrylic acids, and even more limited amounts of propionic acid, 2(5H)-furanone, and ethylene. The balance of  $\text{C}_2\text{H}_2$  was  $90 \pm 5\%$  and the balance of  $\text{CO}$  was  $95 \pm 5\%$ . Fig. 1 shows the plots of concentration vs. time for succinic and maleic anhydrides.

The setting time of the steady-state reaction mode was 10–15 min during which palladium changed its oxidation state. In the initial solution saturated with  $\text{CO}$ , the characteristic adsorption band of terminal  $\text{CO}$  coordinated to  $\text{Pd(II)}$  was  $2120\text{ cm}^{-1}$ . The potential difference corresponding to  $\text{Pd(II)}/\text{Pd(I)}$  in the initial solution was  $\Delta\varepsilon = \varepsilon_{\text{Pt}} - \varepsilon_{\text{AgCl}} = 240\text{ mV}$ . Within 10–15 min of the beginning of the reaction, the band at  $2120\text{ cm}^{-1}$  almost completely disappeared and another less intense adsorption band appeared, which can be assigned to the bridging carbonyl group in



$1935\text{ cm}^{-1}$  [9]. The potential difference became  $\varepsilon_{\text{Pt}} - \varepsilon_{\text{AgCl}} = 60\text{--}80\text{ mV}$ . This points to the fact that, within the first 10–15 min,  $\text{Pd(II)}$  is reduced to yield diamagnetic  $\text{Pd(I)}$  dimer complexes.

Upon addition of oxidant ( $\text{CuBr}_2$ ,  $\text{Fe}_2(\text{SO}_4)_3$ , *p*-benzoquinone) to the initial reacting mixture, the period during which the reaction attained a steady-state mode increased. During this period, the initial gaseous mixture was consumed to a

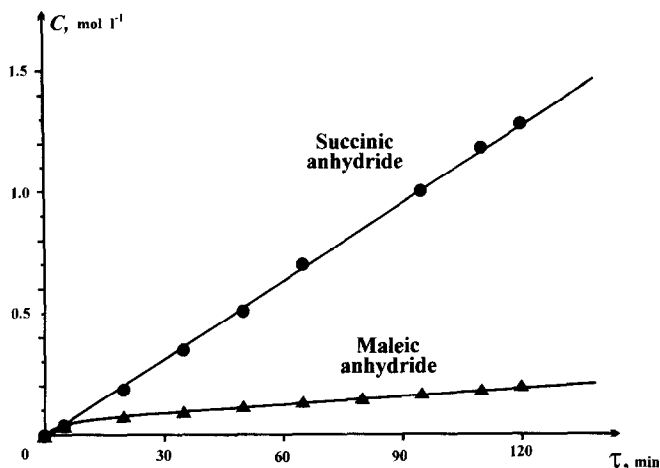


Fig. 1. The change in concentrations of succinic anhydride (1) and maleic anhydride (2) during the run in the PdBr<sub>2</sub>-LiBr-CH<sub>3</sub>CN system ([PdBr<sub>2</sub>] = 0.05 mol/l, [LiBr] = 0.1 mol/l,  $P_{CO}:P_{C_3H_2} = 2.5$ ,  $T = 40^\circ\text{C}$ ).

small extent, and the potential difference  $\varepsilon_{\text{Pt}} - \varepsilon_{\text{AgCl}}$  remained virtually constant.

These results suggest that, as in a number of palladium-based systems [10], palladium(I) carbonyl complexes are catalytically active components in the reacting mixtures.

### 3.2. Possible mechanisms for the formation of succinic and maleic anhydrides

In this study, we applied a hypothetico-deductive approach to mechanistic studies according to which the key stage of the study is the advancing of hypotheses followed by the discrimination between them [11].

Generation of hypothetical mechanisms can be conducted with the aid of a specially designed computer program [11] and the library of elementary reactions for the computer-assisted generation of the mechanisms. The program was used to generate mechanisms for the succinic anhydride formation [11]. Hypothetical mechanisms obtained were classified according to the type of organic intermediate: (i) ethylene, (ii) acrylic acid, (iii) maleic anhydride, and (iv) no organic intermediate [12].

The principle lines of discriminating experiments were as follows: (1) in situ study of the reactivity of possible organic intermediates, (2) the kinetic isotope effect study, and study of the

isotope exchange reactions to reveal the kinetic relationships between reactions that yield different products. According to the hypothetical mechanisms, the oxidative carbonylation reactions, which produce maleic anhydride and maleic and fumaric acids, should also yield palladium hydride complexes (*vide infra*). Because of this, it was important to elucidate the palladium hydride complexes under experimental conditions and to understand their role in the conjugation of various carbonylation reactions within the frame of the overall reaction mechanism.

### 3.3. Elucidation of hydride complexes

It should be noted that, in all instances, the mechanism of succinic anhydride formation should account for the transfer of the two hydrogen atoms from water to the acetylene carbon atoms to yield a  $-\text{CH}_2-\text{CH}_2-$  fragment. The most probable variant of the hydrogen transfer is the participation of palladium hydride complexes. In this connection, we attempted to detect palladium hydride complexes in solutions under the experimental conditions. Because Pd(I) hydride complexes with CO and Br<sup>-</sup> ligands are diamagnetic, <sup>1</sup>H NMR spectroscopy can be used for their elucidation. The reaction was conducted in acetonitrile-*d*<sub>3</sub>. <sup>1</sup>H chemical shift was referenced to the residual solvent (acetonitrile-*h*). Within 10 min

Table 1  
Effects of ethylene and acrylic acid on the characteristics of the carbonylation process in the  $\text{PdBr}_2\text{-LiBr-CH}_3\text{CN}$  system

Additive	Formation rates, $\text{mol l}^{-1} \text{h}^{-1}$			
	Succinic anhydride	Maleic anhydride	Acrylic acid	Propionic acid
None	0.64	0.065	0.070	0.020
Ethylene (15 vol%)	0.57	0.064	0.067	0.026
Acrylic acid (0.15 mol/l)	0.65	0.070	0.055	0.023

$[\text{PdBr}_2] = 0.05 \text{ mol/l}$ ,  $[\text{LiBr}] = 0.1 \text{ mol/l}$ ,  $P_{\text{CO}}/P_{\text{C}_2\text{H}_2} = 2.5$ ,  $T = 40^\circ\text{C}$ .

of the beginning of reaction, a sample of reacting mixture was rapidly cooled to  $-40^\circ\text{C}$ . Then, the  $^1\text{H}$  NMR spectrum of the sample was recorded. Using a PRESAT14 pulse sequence, a weak broadened ( $\nu_{1/2} = 70 \text{ Hz}$ ) signal at  $\delta = -1.88 \text{ ppm}$  was monitored. Line broadening is supposedly due to the exchange process, which occurs even at this temperature, and reveals relaxation effects, which are caused by the quadrupole palladium nucleus. Upon heating the solution to  $0^\circ\text{C}$ , this signal rapidly disappeared. A  $\delta = -1.88 \text{ ppm}$  signal belongs to the region of chemical shifts that is characteristic of transition metal hydride complexes. This value is close to those observed for other Pd(I) hydride complexes stabilized by phosphine ligands, dippp and  $\text{PPh}_3$  [dippp = 1,3-bis(diisopropylphosphino)propane]:  $[(\text{PPh}_3)_2\text{Pd}(\mu\text{-H})(\mu\text{-CO})\text{Pd}(\text{PPh}_3)_2]^+$  ( $\delta = -6.3 \text{ ppm}$ ) [13];  $[(\text{dippp})\text{Pd}(\mu\text{-H})(\mu\text{-CO})\text{Pd}(\text{dippp})]\text{Cl}$

( $\delta = -5.17 \text{ ppm}$ ) [14];  $[(\text{dippp})\text{Pd}(\mu\text{-H})_2\text{Pd}(\text{dippp})] \cdot \text{LiBEt}_4$  ( $\delta = -3.66 \text{ ppm}$ ) [15]; and  $[(\text{dippp})\text{Pd}(\mu\text{-H})_2\text{Pd}(\text{dippp})]$  ( $\delta = -2.52 \text{ ppm}$ ) [15]. Therefore, results of the  $^1\text{H}$  NMR spectroscopic study suggest the presence of palladium hydride complexes in the systems of acetylene carbonylation. The most probable route for the formation of hydride complexes is the oxidative carbonylation of acetylene to produce maleic anhydride or maleic and fumaric acids.

### 3.4. Study of the reactivity of possible intermediates under experimental conditions

The addition of ethylene to the gas phase or the addition of acrylic acid to the liquid phase in concentrations exceeding those observed in experiments negligibly affected the formation rate of succinic anhydride  $R_{\text{SA}}$  (Table 1). When ethylene substituted for the entire amount of acetylene in the initial gas mixture, the products of ethylene conversion were not observed. This result allowed us to exclude hypothetical mechanisms according to which ethylene and acrylic acid are reactive intermediates in the synthesis of succinic anhydride.

A plot of  $R_{\text{SA}}$  versus the initial concentration of maleic anhydride passes through a broad maximum (Fig. 2). The portion of the curve corresponding to the increase in  $R_{\text{SA}}$  with the concentration of maleic anhydride in the initial

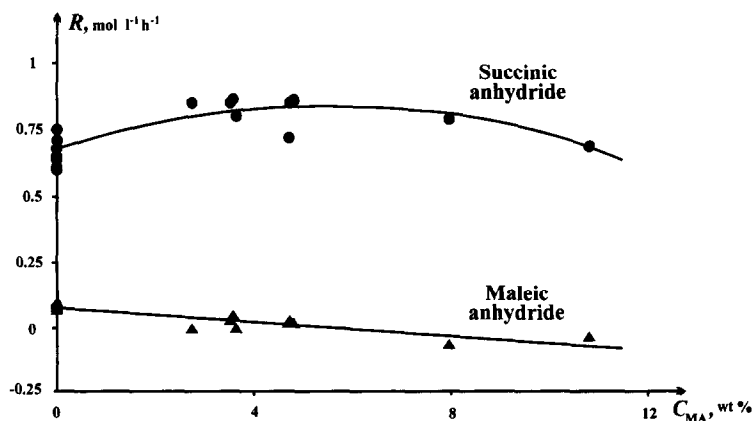
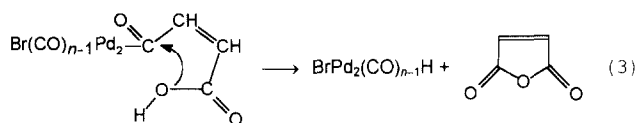
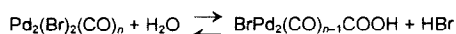
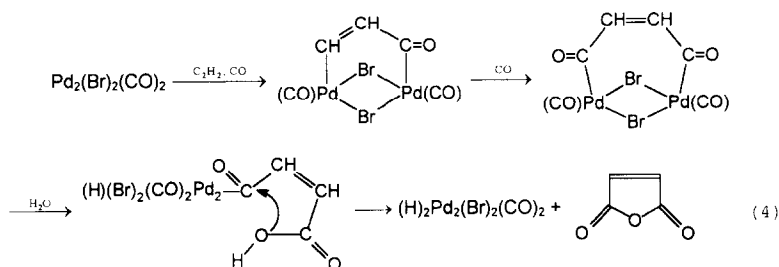


Fig. 2. The effect of maleic anhydride additives on the rate of succinic and maleic anhydride formation in the  $\text{PdBr}_2\text{-LiBr-CH}_3\text{CN}$  system ( $[\text{PdBr}_2] = 0.05 \text{ mol/l}$ ,  $[\text{LiBr}] = 0.1 \text{ mol/l}$ ,  $P_{\text{CO}}/P_{\text{C}_2\text{H}_2} = 2.5$ ,  $T = 40^\circ\text{C}$ ).



Scheme 1.



Scheme 2.

Table 2  
Kinetic isotope effects in the  $\text{PdBr}_2\text{-LiBr-CH}_3\text{CN}$  system

System	$k_{\text{H}}/k_{\text{D}}^a$			
	Succinic anhydride	Maleic anhydride	Acrylic acid	Propionic acid
Acetonitrile- $d_3$ - $\text{C}_2\text{H}_2$ - $\text{D}_2\text{O}$	$1.13 \pm 0.05$	$0.9 \pm 0.1$	$1.8 \pm 0.15$	$2.5 \pm 0.3$
Acetonitrile- $d_3$ - $\text{C}_2\text{D}_2$ - $\text{D}_2\text{O}$	$1.10 \pm 0.05$	$0.9 \pm 0.1$	$1.7 \pm 0.15$	$2.2 \pm 0.3$

$[\text{PdBr}_2] = 0.05 \text{ mol/l}$ ,  $[\text{LiBr}] = 0.1 \text{ mol/l}$ ,  $P_{\text{CO}}/P_{\text{C}_2\text{H}_2} = 2.5$ ,  $T = 40^\circ\text{C}$ .

<sup>a</sup>  $k_{\text{H}}/k_{\text{D}}$  was calculated as the ratio between the formation rate of a product in the standard system (Acetonitrile- $h_3$ - $\text{C}_2\text{H}_2$ - $\text{H}_2\text{O}$ ) and the formation rate of a product in the system, which is specified in the table (all other conditions being the same).

solution agrees well with the hypothesis that maleic anhydride is a key intermediate in the succinic anhydride formation. It is likely that the decrease in  $R_{\text{SA}}$  at high concentrations of maleic anhydride is due to the inhibition effect of maleic anhydride as a strong  $\pi$ -ligand undergoing the coordination on palladium centers. A characteristic of the process is that the rate of formation of maleic anhydride decreases with increase in the concentration of maleic anhydride. This fact is further evidence of the maleic anhydride consumption within the reacting system. Thus, after these experiments only two groups of mechanisms remain: (iii)

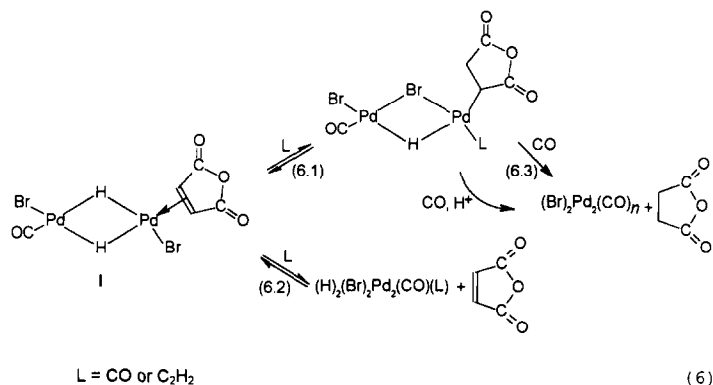
mechanisms involving a maleic anhydride as a reactive intermediate and (iv) the mechanism implying no organic intermediates.

At least two mechanisms, Scheme 1 and Scheme 2, for the formation of maleic anhydride and the palladium hydride complex are possible.

To test the possibility of these mechanisms of the formation of maleic anhydrides and palladium hydride complexes in the system under consideration, we conducted kinetic isotope effect studies using the deuterated solvent and reagents (Table 2).

Kinetic isotope effects of the formation rates of maleic and succinic anhydrides  $k_{\text{H}}/k_{\text{D}}$  are close to unity. This fact suggests that the mechanism 3 (Scheme 1) for the formation of maleic anhydride and all variants of the mechanism of succinic anhydride formation involving mechanism 3 as a part should be excluded from the consideration. Otherwise, the cleavage of the H–OH bond before the first irreversible step would result in the values  $k_{\text{H}}/k_{\text{D}} > 1$ .

From the formal standpoint, O–H bond breaking in the framework of mechanism 3 can occur after the irreversible step. There is the only variant of mechanism 3, which cannot be discarded on the basis of the experimental data: proton dissociates after the irreversible acetylene insertion,

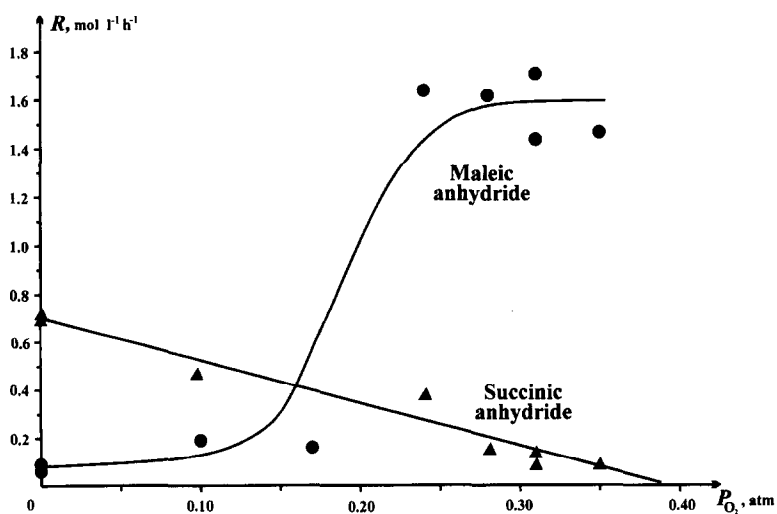


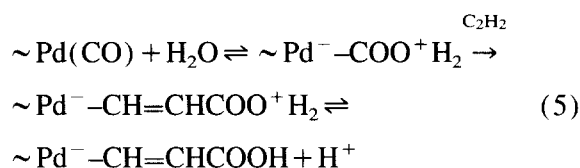
Scheme 3.

Table 3

The H–D distribution in carbonylation products in the acetonitrile-*d*<sub>3</sub>-C<sub>2</sub>D<sub>2</sub>-D<sub>2</sub>O system

No. of the run	Product concentration, mol/l		Concentration ratio
Succinic anhydride			
1	[(CHDCO) <sub>2</sub> O] <sup>a</sup> 0.15	[(CD <sub>2</sub> CO) <sub>2</sub> O] <sup>a</sup> 0.87	[(CHDCO) <sub>2</sub> O]/[(CD <sub>2</sub> CO) <sub>2</sub> O] 0.13
2 <sup>b</sup>	0.38	0.73	0.52
Maleic anhydride			
1	[(CHCO) <sub>2</sub> O] <sup>a</sup> 0.00	[(CDCO) <sub>2</sub> O] <sup>a</sup> 0.20	[(CHCO) <sub>2</sub> O]/[(CDCO) <sub>2</sub> O] 0.00
2 <sup>b</sup>	0.01	0.40	0.03

[PdBr<sub>2</sub>] = 0.05 mol/l, [LiBr] = 0.1 mol/l, time of each run was 105 min, T 40°C.<sup>a</sup> For the sake of simplicity, calculation was performed on the assumption that only symmetrical products are formed in the system.<sup>b</sup> In the second run, 0.288 mol/l (CHCO)<sub>2</sub>O was added to the solution.Fig. 3. The effect of oxygen partial pressure on the process direction in the PdBr<sub>2</sub>-LiBr-CH<sub>3</sub>CN-O<sub>2</sub> system ([PdBr<sub>2</sub>] = 0.05 mol/l, [LiBr] = 0.1 mol/l, T = 40°C).



However, because there is no direct evidence for mechanism 5, we consider it rather improbable.

It seems likely that mechanisms for the formation of acrylic and propionic acids involve the step of H–OH bond cleavage (before the first irreversible step). This assumption follows from values of kinetic isotope effects (Table 2).

We can summarize the above discussion by the statement that the most probable mechanism for the formation of maleic anhydride is that shown in Scheme 2 (Eq. 4). Then, reasonable questions arise whether maleic anhydride, which is presumably coordinated by the palladium hydride complexes, is capable of transforming to succinic anhydride and how this transformation occurs.

The simplest variant implies the insertion of maleic anhydride into a Pd–H bond followed by the reductive elimination of succinic anhydride (or the acidolysis resulting in the same product) as depicted in Eq. 6 (Scheme 3).

Complex I is the immediate product of the acetylene oxidative carbonylation and is a common intermediate on the pathways to succinic and maleic anhydrides. The reversibility of step (6.2) accounts for the effect of the maleic anhydride added on the direction of carbonylation process (Fig. 2).

The H–D exchange in the maleic anhydride added and the considerable increase in the content of H atoms in succinic anhydride upon this addition agree with the reversibility of steps 6.1 and 6.2 (Table 3).

If Eq. 6 (Scheme 3) is by and large true, the process direction can be controlled by the addition of a reactant, capable to react with the palladium hydride complexes and to be competitive with maleic anhydride. To test this conjecture, oxygen was selected to be this additive. Fig. 3 shows the effect of oxygen added to the gaseous mixture on

the direction of the carbonylation process at a fixed partial pressure ratio  $P_{\text{CO}}:P_{\text{C}_2\text{H}_2}$ .

It was reasonable to expect that the increase in the oxygen partial pressure would result in decreasing the formation rate of succinic anhydride and increasing the rate of formation of maleic anhydride. However, in the acetylene carbonylation, palladium(I) complexes showed an unexpectedly drastic increase in the catalytic activity toward maleic anhydride formation with increasing oxygen partial pressure above 0.15 atm. This effect is likely due to the modification of active centers, Pd(I) complexes, at the expense of oxygen coordination to Pd(I).

The above results are in complete agreement with Eq. 6 (Scheme 3), but they do not allow us to exclude the mechanisms that imply there is no organic intermediate participating in the reaction.

Further evaluation of mechanisms will be conducted with the aid of kinetic studies and reported elsewhere.

## Acknowledgements

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## References

- [1] P. Pino and G. Braca, in I. Wender and P. Pino (Eds.), *Organic Synthesis via Metal Carbonyls*, Vol. 2, Wiley, New York, 1977, p. 419.
- [2] A. Mullen, in J. Falbe (Ed.), *New Syntheses with Carbon Monoxide*, Springer, Berlin, 1980, p. 243.
- [3] O.N. Temkin, O.L. Kaliya, L.N. Zhir-Lebed', et al., *Homogeneous Oxidation*, Institute of Organic Catalysis and Electrochemistry, Alma-Ata, Vol. 17, 1978, p. 3.
- [4] O.N. Temkin, G.K. Shestakov and Yu. A. Treger, *Acetylene: Chemistry, Reaction Mechanisms, and Technology*, Khimiya, Moscow, 1991 (in Russian).
- [5] G.N. Freidlin, *Saturated Dicarboxylic Acids*, Khimiya, Moscow, 1978, p. 50 (in Russian).
- [6] O.N. Temkin, L.G. Bruk and G.M. Shulyakovskii, *Khim. Prom-st.*, 5 (1983) 22.
- [7] O.N. Temkin and L.G. Bruk, *Proc. 9th Soviet-Japanese Seminar on Catalysis*, Novosibirsk, 1990, p. 83.

- [8] L.G. Bruk, I.V. Oshanina, A.P. Kozlova and O.N. Temkin, Proc. of 9th Int. Symp. on Homogeneous Catalysis, Jerusalem, Israel, 1994, p. 68.
- [9] L.G. Bruk and O.N. Temkin, *Khim. Prom-st.*, 5 (1993) 57.
- [10] O.N. Temkin and L.G. Bruk, *Usp. Khim.*, 52 (1983) 206; *Russ. Chem. Rev.*, 52 (1983) 117.
- [11] O.N. Temkin, L.G. Bruk and A.V. Zeigarnik, *Kinet. Katal.*, 34 (1993) 445; *Kinet. Catal. Engl. Transl.*, 34 (1993) 389.
- [12] I.V. Oshanina, L.G. Bruk and O.N. Temkin, *Kinet. Katal.* (in press).
- [13] V.N. Zudin, V.D. Chinakov, V.M. Nekipelov, et al., *J. Mol. Catal.*, 52 (1989) 27.
- [14] M. Portnoy and D. Milstein, *Organometallics*, 13 (1994) 600.
- [15] M.D. Fryzuk, B.R. Lloyd, G.K.B. Clentsmith and S.J. Rettig, *J. Am. Chem. Soc.*, 113 (1991) 4332.