New catalytic systems for oxidative carbonylation of acetylene to maleic anhydride

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A classification of polyfunctional catalytic systems based on discrimination of the main component (the catalyst participating in all stages of the formation of the product of catalytic reaction) and elucidating the functions of additional components of a catalytic system is suggested. The role of additional components in a number of new palladium-based catalytic systems used in the synthesis of maleic anhydride by oxidative carbonylation of acetylene was studied. It was established that the functions of Co and Fe phthalocyanine complexes (PcCo and Pc*Fe, respectively) in the mechanism of the process are different.

Key words: polyfunctional catalytic systems, acetylene, carbonylation, palladium, maleic anhydride, succinic anhydride.

Many homogeneous and heterogeneous catalysts are multicomponent. Functions of individual components of catalytic systems in the mechanisms of catalytic reactions have been better understood in the case of homogeneous catalysis.¹⁻⁷ Two types of polyfunctionality of catalysts and catalytic systems are distinguished. If the components are united to form a common reaction catalytic center operating at all stages of the process and perform versatile chemical functions in the framework of this center, polyfunctionality is said to be determined by complex organization of the reaction center. Integration of acidic and basic groups to form active centers of hvdrolytic enzymes^{1-3,7} can serve as an example of this type of polyfunctionality. If no common center is formed while individual components of a catalytic system participate in the process (i.e., catalyze its different stages or groups of stages) and perform certain kinetic functions, such a polyfunctional catalytic system (PFCS) is characterized by kinetic polyfunctionality^{3,4,7} and is a system of catalysts. By changing the qualitative and quantitative composition of PFCS it is possible to control the rate and selectivity of reactions. Investigation of the role of components and the development of new PFCS has attracted the permanent interest of theoreticians and experimentalists beginning with the classical studies by I. I. Moiseev, M. N. Vargaftik, and Ya. K. Syrkin on the oxidation of olefins in the Pd¹¹-Cu¹¹ (socalled Wacker process) and Pd¹¹-p-benzoquinone⁵ systems. Several variants of PFCS classification have been suggested,^{2-4,6,7} in particular, classifications considering the topological structure of mechanism.^{3,4,7}

PFCS are particularly often used in oxidation processes.^{3,5,6,8,10} Ternary catalytic systems $PdCl_2--p$ -benzoquinone (Q) and PcFe complexes, CoSalophen,^{11,12} or $H_5PMo_{10}V_2O_{40}$ ¹³ are successfully used in aerobic oxidation of dienes and olefins. The CuCl-PdCl₂--CuCl₂ ternary system appeared to be active in oxidative carbonylation of alkynes at the \equiv C--H bond.¹⁴

In this work, we suggest one more classification which may be useful for those PFCS in which the main carrier of catalytic activity (e.g., a metal compound in the absence of which no reaction products are formed) and additional components can be distinguished. The latter can be different and perform different functions. The classification is based on the difference in the functions of additional components (catalysts). According to V. A. Golodov,⁶ the main carrier of catalytic activity is a first level catalyst. In the case of PFCS used in oxidation processes, additional components are most often intermediate oxidants (additional catalysts of oxidation). PFCS belonging to this type can be divided into the following groups.

1. Additional components do not participate in the stages of products formation and only favor regeneration of the active form of catalyst. For instance, palladium compounds are the main component in the Wacker process and analogous reactions,⁵ while the kinetic function of additional oxidant (CuCl₂, Q) is to catalyze oxidation of the reduced form of Pd¹¹ by dioxygen or a third intermediate oxidant.

2. Additional components participate in the stages of products formation by reacting with intermediate (e.g., σ -

Translated from Izvestiya Akademii Nauk. Seriya Khimicheskaya, No. 10, pp. 1899-1905, October, 1999. 1066-5285/99/4810-1875 \$22.00 © 1999 Kluwer Academic/Plenum Publishers or π -) organometallic compounds. In this case, the direction of intermediate decomposition and the character of products depends on the nature of the additional component. For instance, β -chloroethyl methyl ether instead of acetaldehyde acetal is formed from ethylene at high CuCl₂ concentrations in the CuCl₂--PdCl₂--MeOH system.^{15,16}

Oxidative demetallation of π -allyl complexes of Pd¹¹ in reactions with nucleophiles^{11-13,17,18} occurs with participation of Q (as a result of complexation with Q); therefore Q is an important intermediate oxidant in reactions of diene oxidation or allylic oxidation of olefins.¹¹⁻¹³ In this case the kinetic function of Q is to catalyze oxidation of π -allyl complexes of Pd¹¹ with oxygen.

3. An additional component participates in both formation and transformation stages of key intermediates into reaction products by interaction with the main catalytically active metal complex. Such a component (NO_2^-, Q) can change properties of the reaction center and, simultaneously, the mechanism and direction of the reaction.9,10,12 For instance, complexation with Q in solution of Pd¹ complex results in selective synthesis of dimethyl oxalate (DMO) in the course of oxidative carbonylation of methanol at atmospheric pressure and 40 °C,¹⁹ whereas dimethyl carbonate is formed in the system without Q. In the case of PdCl₂(CO)₂ complex, quinone changes the direction of decomposition of the intermediate compound CIPdCOOMe by forming a complex, which is transformed into DMO (a variant of the second type mechanism).¹⁹ The 3rd type of mechanisms is due to chemical polyfunctionality of the complex active center, whose components can perform various chemical functions at different stages of the process, rather than to kinetic polyfunctionality. The kinetic function in this process is to catalyze the overall process.

It is reasonable to consider the results of studying the mechanism of the action of different PFCS in the reactions of acetylene oxidative carbonylation to maleic anhydride (MA) as an example of the use of this classification.

Maleic anhydride is a widely used product. The known processes of its production have certain drawbacks (low selectivity, complex tecnology of isolation of desired product, *etc.*), which stimulate the search for alternatives.

The possibility of synthesizing MA from acetylene in $PdX_2-HY-Ox-O_2$ (X = Cl, Br; HY = H₂SO₄, HCl; Ox = FeCl₃, Fe₂(SO₄)₃) systems using the elegant reaction (1) was reported about 30 years ago.^{20,21}





Fig. 1. Dependence of concentration (C) of MA (I) and SA (2) on the duration of the experiment (I) in the $PdBr_2-LiBr-AN$ system.

We reported the synthesis of succinic anhydride (SA) in the $PdBr_2$ -LiBr-organic solvent (ketone or nitrile) catalytic system following the novel reaction (2).²²

$$C_2H_2 + 2 CO + H_2O \longrightarrow OC OC (2)$$

Maleic anhydride is formed as a side product (Fig. 1) under conditions of reaction (2). It was established that the plausible mechanism of reaction (2) is associated with intermediate formation of MA coordinated by a palladium hydride complex.^{22,23}

In this connection we conceived an idea of the possibility of changing the process selectivity in favor of MA formation by introduction of a reagent capable of oxidizing a palladium hydride complex and competing with MA in the reaction system. This assumption has been confirmed earlier.²³ The oxidants studied can be conventionally divided into three groups.

1. Reagents weakly affecting the reaction characteristics $(CCl_4, K_3[Fe(CN)_6])$.

2. Reagents inhibiting or destabilizing carbonylation of acetylene (*p*-benzoquinone, copper(1) acetate, chromium(v_1) oxide).

3. Oxidants changing the direction of the process in favor of MA formation. This group comprises O_2 , V_2O_5 , $CuCl_2$, $CuBr_2$, and dioxygen in the presence of cobalt and iron phthalocyanine complexes (PcCo and Pc*Fe, respectively). The maximum rate of MA formation was attained using O_2 . However, MA can be formed at a high rate only at high partial pressure of O_2 . Under certain conditions, a slight increase in the O_2 content in the initial mixture results in substantial increase in the rate of MA formation (critical phenomena)²⁴ (Fig. 2).

In this work, the behavior of a $PdBr_2$ -based PFCS in the oxidative carbonylation of acetylene to MA was studied in detail. It was found that characteristic features of the process of carbonylation of acetylene to MA and SA following reactions (1) and (2) change upon addition



Fig. 2. Dependence of the rate of formation (R) of MA (1) and SA (2) on the partial pressure (p) of oxygen in the PdBr₂-LiBr-AN system.

of PcCo or Pc*Fe into the $PdBr_2$ -LiBr-solvent (acetonitrile (AN), adiponitrile (ADN)) system. This change is likely associated with the natures of phthalocyanine, transition metal, and solvent.

Experimental

Experiments were carried out in a gas-flow-type thermostatted reactor with intense stirring of gaseous and liquid phases at 40 °C under atmospheric pressure. The catalytic solution was prepared in the reactor immediately before the experiment. The gas mixture supply was monitored by a calibrated rheometer. The reactor gases were cooled in a reflux condenser. The gas velocity at the outlet was determined using a Mariotte's vessel and a graduated cylinder. Water concentration in the initial solution before the experiment was determined by GLC on an LKhM-8MD chromatograph (with katharometer as detector, a 3 m × 3 mm column packed with Polysorb (a 0.25-0.5 mm fraction), analysis temperature 160 °C, with helium as carrier gas (0.8 L h⁻¹)). The moment of switching on stirring was taken as the beginning of the run. Samples of the contact solution and gas mixture at the reactor outlet taken in the course of experiment were analyzed by GLC (a Tsvet-110 chromatograph, with katharometer as detector, a glass 3 m × 5 mm column with 10% PPhMS-4 (polyphenylmethylsiloxane) on Polychrom-1; analysis conditions: separation temperature 180 °C, with helium as carrier gas (1.8 L h^{-1})). Gas samples were analyzed by gas adsorption chromatography (an LKhM-8MD chromatograph, with katharometer as detector, a 3 m × 3 mm column packed with AR-3 activated carbon (a 0.25-0.5 mm fraction), analysis temperature 140 °C, with argon as carrier gas (1.6 L h^{-1})). Water concentration in the course of experiments was maintained at -0.1 mol L⁻¹. The required velocity of the supply of water was determined by analyzing its content in the contact solution during the experimental run. The total volume of liquid samples did not exceed 0.5% of the total volume of the contact solution.

The total amount of the acidic products of acetylene carbonylation obtained in the course of experiment was determined using a potentiometric titration of the samples of contact solution (a pH-673 millivoltmeter, a glassy ESL-63-07 electrode, with an EVL 1M31 silver chloride electrode as

Steady-state rates of the formation of MA and SA were calculated from the slopes of linear segments of the dependences plotted in the "product concentration—time" coordinates. The average rate of the formation of dicarboxylic acids (DA) was determined from the results of potentiometric titration of the samples of contact solution.

Results and Discussion

Succinic anhydride is the main product of acetylene transformation in the $PdBr_2$ —LiBr—AN system (see Fig. 1). Previously,^{22,23} it has been shown that Pd^1 compounds are active in this system. Addition of strong oxidants (CuCl₂, CuBr₂, V₂O₅) to the initial catalytic solution changes the kinetic regularities of the formation of acetylene carbonylation products. Two different portions can be seen in the kinetic curves plotted in the "concentration of carbonylation products—time" coordinates (Fig. 3).

1. A period characterized by the absence of PFCS activity or very low rates of the formation of products among which MA predominates (from the beginning to the 30th min, see Fig. 3, a and c, or to the 50th min, see Fig. 3, b).

2. A period characterized by high activity of the PFCS. In the beginning of the second period, the rates of MA formation are higher than those of SA formation. Then, these rates become equal.

It is likely that in the first period almost all palladium exists in the form of Pd^{II} compounds and exhibits no catalytic properties in this state. As the added oxidant is consumed, some amount of Pd^{I} appears in the solution and the second period begins. The remaining amount of oxidant is sufficient to oxidize palladium hydride complexes. Therefore, in accordance with the proposed mechanism, MA is the main reaction product. A decrease in the concentrations of oxidant and Pd^{II} with time results in the change in selectivity in favor of SA. The decrease in the reaction rate in the experiment with $CuCl_2$ (see Fig. 3, *a*) is likely due to an inhibiting effect of this compound, the reasons for which have not been established as yet.

The activity of Pd¹ compounds is a feature common to all the above-mentioned systems. Strong oxidants, preventing the formation of Pd¹ compounds, inhibit carbonylation. At any stage, the process is only slightly selective with respect to MA. Development of an efficient PFCS requires an additional reagent capable of oxidizng palladium hydride complexes and simultaneously not favoring the transformation of Pd¹ into Pd¹¹. Such an oxidant must act continuously without appreciable change in its concentration and oxidation potential with time. Dioxygen can successfully perform this function; however, as has been shown previously,²⁴ this is possible only at high partial pressures (see Fig. 2). The use of transition-metal phthalocyanine complexes activating oxygen¹² enables substantial reduction of the partial



Fig. 3. Dependence of concentration (C) of MA (l) and SA (2) on the duration of the experiment (l) in the AN-PdBr₂-LiBr-CuCl₂ (a), AN-PdBr₂-LiBr-CuBr₂ (b), and AN-PdBr₂-LiBr-V₂O₅ (c) systems (1 mol L^{-1}).

pressure of O_2 , thus making the process more safe. The data on the formation rates of carbonylation products in different PdBr₂-based PFCS are shown in Table 1.

From these data it follows that the effect of the introduction of transition-metal phthalocyanine into PFCS is strongly dependent on the solvent used. In adipodinitrile, PcCo suppresses SA synthesis to only a small extent. Introduction of cobalt (in AN) and iron (in



Fig. 4. Dependence of the rate (R) of MA (1) and SA (2) formation: a, on [PcCo] at $p_{O_2} \equiv 0.1$ atm in the AN-PdBr₂--LiBr-PcCo system: b, on [Pc*Fe] at $p_{O_2} \equiv 0.1$ atm in the PdBr₂--LiBr-Pc*Fe-ADN system.

all solvents) phthalocyanine complexes provides a rather high rate of MA formation and appreciably inhibits the synthesis of SA at low partial pressures of O_2 , which indicates changes in the properties of the reaction center (Fig. 4, *a* and *b*). The reaction rate is strongly dependent on the partial pressure of O_2 (Fig. 5, *a* and *b*). In our opinion, this indicates the presence of oxygen activated with metal phthalocyanine in the palladium-containing reaction center and its participation in the stages of the synthesis of the products of acetylene carbonylation and gives reasons to consider these systems as PFCS of the third type:

To elucidate whether the oxidation state of palladium in active complexes is changed on introduction of PcCo into the PdBr₂—LiBr—AN system, admixtures of strong oxidants were used. Introduction of CuBr₂ instead of dioxygen into the PdBr₂—LiBr—PcCo—AN system leads to a picture (Fig. 6. *a*) which is very similar to the dependences for the PdBr₂—LiBr—CuBr₂—AN system (see Fig. 3, *b*). In this case a period characterized by very low activity of the catalyst is also observed, so that the

Solvent	No phthalocyanine			$[Pc(Co)]/[PdBr_2] = 0.97$			$[Pc^*(Fe)]/[PdBr_2] \approx 0.8$	
	RMA	R _{SA}	Sco	R _{MA}	R _{SA}	Sco	R _{MA}	Sco
	mol L ⁻¹ h ⁻¹		SC2H2	mol L ¹ h ¹		$\overline{S_{C_2H_2}}$	/mol L ⁻¹ h ⁻¹	$\overline{S_{C_2H_2}}$
AN	0.07	0.29	<u>91.8</u> 76.9	0.38	0.04	<u>87.9</u> 90.6	0.51	<u>88.8</u> 85.9
AN*	0.08	0.71	<u>89,8</u> 73.2	-		-	_	
BN	0.06	0.11	<u>40.5</u> 44.2	0.30	0.06	<u>73.6</u> 77.5	0.27	<u>65.7</u> 61.8
ADN	0.04	0.13	<u>84.8</u> 71.1	0.14	0.13	<u>79,5</u> 88.0	0.32	<u>91.3</u> 110.7
ADN*	0.05	0.16	<u>92.3</u> 76.2	-			-	

Table 1. Effect of intermediate oxidant on characteristics of the process in the $PdBr_2$ -LiBr-solvent system with admixture of phthalocyanine complexes

Nore. R is the rate of MA and SA formation: S is the overall selectivity toward CO (C_2H_2) with respect to carbonylation products. Reaction conditions: $p_{CO}/p_{C_2H_2} \equiv 10$; $p_{O_2} \equiv 10$ kPa; [LiBr] = 0.1 mol L⁻¹; [PdBr₂] = 0.05 mol L⁻¹; solid PcCo, and Pc*Fe in solution.

carbonylation products can be detected only at the 70th min of the experiment. Then, the rates of MA and



Fig. 5. Dependence of the rate (R) of MA (1) and SA (2) formation on p_{O_2} in the AN-PdBr₂-LiBr-PcCo (a) and ADN-Pc*Fe -PdBr₂-LiBr (b) systems.

especially SA formation are increased. It is likely that Pd¹ compounds are also more active in this system.

In the systems containing Pd¹ in active complexes, PcCo in the solid phase might perform two functions:

 affect the properties of the reaction center (suppression of the synthesis of SA);

 activate dioxygen for oxidation of the hydride ligands in palladium complexes.

The situation drastically changes when using the PdBr₂-LiBr-Pc*Fe-O₂-ADN system. Introduction of strong oxidants instead of O₂ into this system does not lead to decreasing the initial rate of MA formation. The systems are rather active from the beginning of experiment and no autocatalytic effect on the rates of the formation of MA is observed (see Fig. 6, b and c). In our opinion, the absence of an initial period characterized by a low rate of MA formation indicates the activity of Pd^{II} compound in this PFCS. What could lead to the change in the oxidation state of palladium in the active form of the catalyst? The fact is that Pd¹¹ compounds were inactive in all previously studied systems except for the PdBr₂-P(OPh)₃-HBr system.²⁵ The reason is most likely that iron phthalocyanine reacts with Pd^{II} complexes. The possibility of complexation between PdBr₂ and Pc*Fe needs special investigations.

If this assumption is true and iron phthalocyanine participates in the formation of a catalytically active center involving Pd¹¹ compounds, oxidation of hydride ligands formed as a result of oxidative carbonylation of acetylene to MA occurs in this case intramolecularly (as in the case of PcCo) and thus raher efficiently. No SA is contained among the carbonylation products at Pc*Fe concentrations higher than 0.04 mol L⁻¹ (see Fig. 4, b). Thus, unlike PcCo, Pc*Fe makes Pd¹¹ compounds active toward carbonylation.



Fig. 6. Dependence of concentration (C) of MA (I) and SA (2) on the duration of the experiment (I) in $AN-PdBr_2-LiBr-PcCo$ (0.04 mol L^{-1})-CuBr₂ (1 mol L^{-1}) (a); $ADN-PdBr_2-LiBr-Pc^*Fe$ (0.04 mol L^{-1})-CuBr₂ (1 mol L^{-1}) (b); and $ADN-PdBr_2-LiBr-Pc^*Fe$ (0.04 mol L^{-1})-CuCl₂ (1 mol L^{-1}) (c) systems.

Summing up the results obtained, we propose preliminary hypotheses for the mechanisms of function of the components in the PFCS studied.

In the system with PcCo:

$$PcCo(s) + Pd^{I} \implies PcCo(s)Pd^{I}(ads) \xrightarrow{C_{2}H_{2}, CO, H_{2}O, O_{2}}$$
$$\longrightarrow (O_{2})PcCo(s)[(HPdBr)_{2}(MA)] \implies$$
$$\longrightarrow PcCo(s) : Pd^{I}(ads) + MA + H_{2}O$$

Adsorption of Pd¹ complexes on the surface of PcCo increases the rate of MA formation and prevents Pd¹ oxidation to Pd¹¹. This is accompanied by a decrease in the rate of interaction between HPd and MA with the formation of SA.

In the system with Pc *Fe:

$$Pc^{*}Fe + Pd^{II} \implies Pc^{*}Fe \cdot Pd^{II} \xrightarrow{C_{2}H_{2}, CO,} H_{2}O, O_{2}$$

$$\rightarrow (O_{2})Pc^{*}Fe(HPdX)(MA) \implies Pc^{*}Fe \cdot Pd^{II} + MA + H_{2}O$$

In this case Pc*Fe inhibits the formation of Pd^I and completely suppresses the formation of SA. It is possible that transformations of reagents in this system never reach the stage in which hydride complexes are formed. As can be seen, in the framework of proposed schemes functions of additional oxidants appreciably differ from the functions reported earlier.¹¹⁻¹³

Using PFCS based on Pd¹ and PcCo, it is impossible to separate dioxygen and acetylene and organize the process of MA synthesis according to a scheme with two reactors (analogously to Wacker process), which would be desirable to make the process more safe. This is associated with difficulties in the choice of intermediate oxidant incapable of oxidizing Pd¹.

The two-reactor scheme can be realized in the system based on Pd^{II} and Pc*Fe. The PdBr₂-LiBr-Pc*Fe-V₂O₅ catalytic system can be used in the synthesis of MA in the absence of oxygen (Table 2). Finely dispersed vanadium pentoxide, whose function is to oxidize Pd^{II} hydride complexes or Pd⁰, was used as intermediate oxidant. In this three-component system, Pc*Fe performs the following functions:

a) formation of an active center with participation of Pd¹¹ in the stage of MA synthesis;

Table 2. Synthesis of MA in the $PdBr_2-LiBr-Pc^*Fe-V_2O_5$ system with intermediate reoxidation of vanadium with oxygen

1	Initial	Change in MA amount	R ⁰ MA	S _{MA} (%)	
/min	MA content	per run	/mol L ⁻¹ h ⁻¹	CO	C ₂ H ₂
		mmol			
180	0	2.11	0.50	47.1	41.2
140	2.11	0.78	0.29	55.9	53.1
200	2.89	1.67	0.30	68.0	94.9
135	4.56	0.65	0.68	82.8	90.3

Note. R^0_{MA} is the initial rate of formation; S_{MA} is the selectivity with respect to MA. Reaction conditions: $[PdBr_2] = 0.05 \text{ mol } L^{-1}$; $[LiBr] = 0.1 \text{ mol } L^{-1}$; $[Pc^*Fe] = 0.04 \text{ mol } L^{-1}$; $P_{CO}/P_{C_2H_2} = 2$; ADN as solvent; and $[V_2O_5] = 1 \text{ mol } L^{-1}$.

We demonstrated the possibility of repeated use of this catalyst with intermediate oxidation of regenerated vanadium oxide with oxygen (see Table 2).

* * *

Thus, the possibility of using cobalt and iron phthalocyanine complexes as additional components of PFCS which are active in the synthesis of MA via acetylene carbonylation is shown for the first time. It was established that PcCo affects catalytic properties of Pd¹ and activates dioxygen to oxidize hydride intermediates. In the course of MA synthesis, Pc*Fe activates Pd¹¹ compounds and dioxygen, in the latter case both to oxidize Pd¹¹ hydrides (one-reactor scheme) and to regenerate intermediate oxidant (two-reactor scheme). According to the suggested classification, the systems investigated can be considered as belonging to the third group of PFCS.

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