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LETTERS

New Oscillating Reaction in Catalysis by Metal Complexes: A Mechanism of Alkyne Oxidative Carbonylation

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The reaction of phenylacetylene carbonylation to phenyl maleate, phenyl fumarate, and dimethoxylactone in the homogeneous catalytic system $PdI_2-KI-O_2-NaOAc$ in methanol solution was found to exhibit oscillations in the redox potential, pH, and rate of gaseous $CO-O_2$ mixture consumption. This is the first example of an oscillating chemical reaction in typical metal-complex catalysis where a complex organic molecule is formed from simple reactants in solutions of metal complexes. Oscillations were observed for 3.5 h up to 95% conversion of alkyne. The oxidation of CO to CO_2 occurs in parallel with carbonylation. The products were analyzed by NMR spectroscopy and GLC coupled with mass spectrometry. The compositions of the gas and liquid phases were controlled by GC and GLC, respectively. The range of NaOAc concentrations within which oscillations were observed was found to be very narrow: from 0 to 0.01 mol/L. It was shown that oxygen transfer through the phase boundary is not a cause of oscillations. The run where PdI_2 was replaced by $K_2Pd_2I_4$ exhibited oscillations similar in shape and amplitude. A reaction scheme was proposed, which includes the processes of Pd(II) reduction to the active catalysts of carbonylation, Pd(I) complexes, followed by the oxidation of palladium(I) complexes by iodine.

Nearly all homogeneous oscillating reactions, like the Belousov−Zhabotinsky or Briggs−Rauscher systems, are facile oxidations of organic or inorganic substrates (malonic, citric, and oxalic acids, acetone, phenols, benzaldehyde, NADH, Br^-, I^-, SO_3^{2-}, $S_2O_3^{2-}$, Sn(II), and HS^-) by strong oxidants ($KBrO_3$, KIO_3, H_2O_2, and O_2) catalyzed by metal ions (Ce(IV)/Ce(III), Mn(III)/Mn(II), Fe(III)/Fe(II), Co(III)/Co(II)).[1] In these reactions, metal ions play the role of one-electron oxidants. Until recently, no oscillations were reported for typical reactions catalyzed by metal complexes (e.g., hydrogenation, cyclization, hydroformylation, carbonylation, polymerization, metathesis, etc.) where an organic molecule is built from simpler blocks (reactants) in solutions of metal complexes.[2]

Here we show that chemical oscillations in such reactions are possible. We report a new homogeneous oscillating reaction of alkyne carbonylation in the presence of palladium complexes and propose the mechanistic scheme that accounts for the complex dynamic behavior of this system.

Our study of oxidative alkyne carbonylation in the catalytic system PdI_2-KI-O_2-MeOH, which was described earlier by other researchers,[3] revealed the oscillating behavior of the system with $PhC\equiv CH$ in the presence of small amounts of NaOAc. The reaction occurs in a well-stirred batch reactor at 40 °C under atmospheric pressure of the $CO-O_2$ mixture (1:1).

In a typical run, PdI_2 (0.1 mmol), KI (4 mmol), and NaOAc (0.024 mmol) were dissolved in 8 mL of MeOH with vigorous stirring for 15 min. In due course of the reaction, the reactor was purged with the $CO-O_2$ mixture. Then, phenylacetylene

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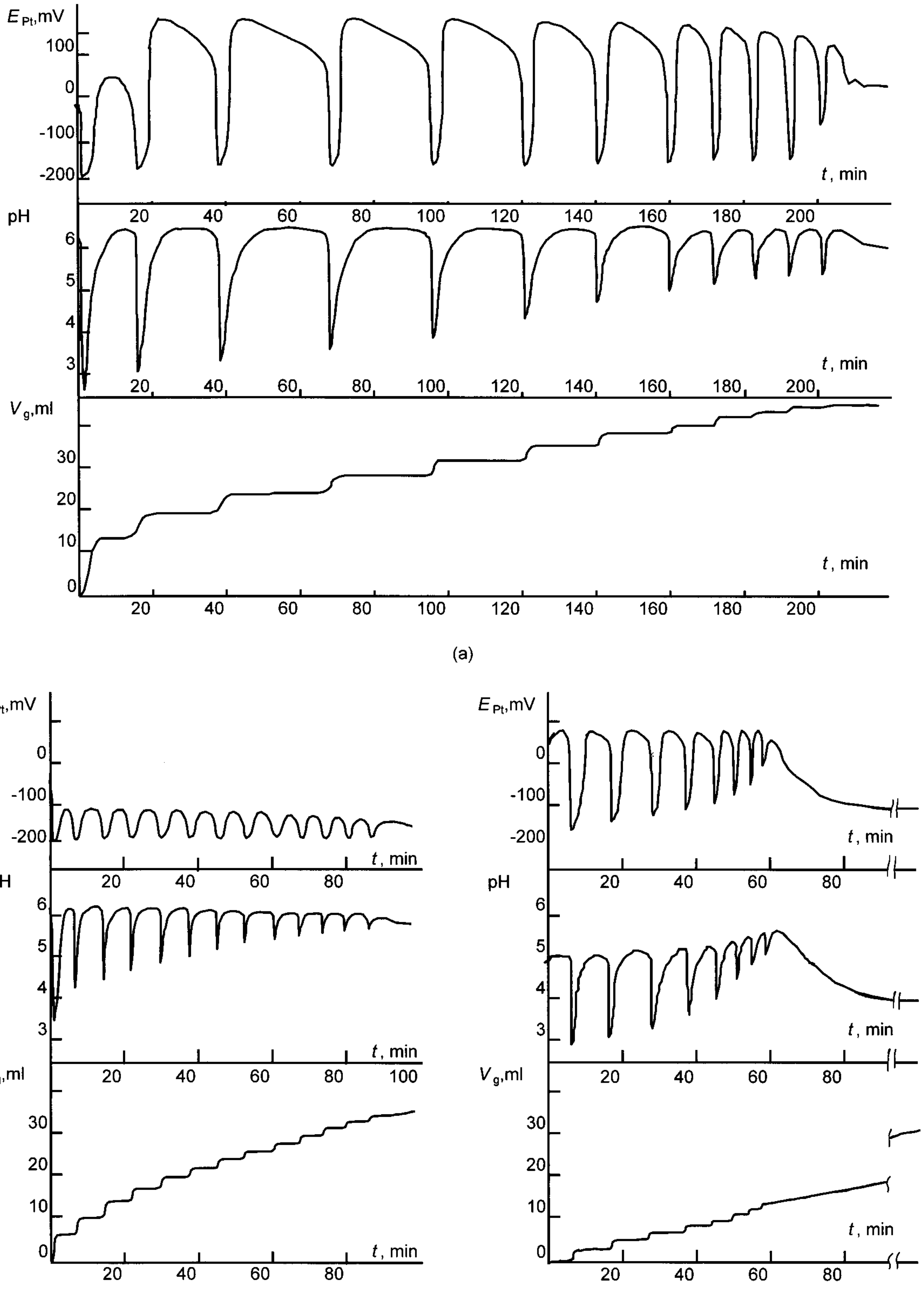


(a)

(b)

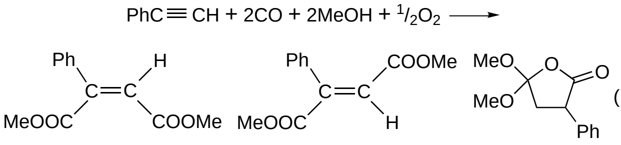
(c)

Figure 1. Oscillations of the platinum electrode potential (E_{Pt}), pH, and volume of the gas mixture $CO-O_2$ (V_g) consumed in the course of reaction: (a) initial concentrations are $[PdI_2]_0 = 0.01$ mol/L, $[KI]_0 = 0.4$ mol/L, $[PhC{\equiv}CH]_0 = 0.1$ mol/L, $[NaOAc]_0 = 0.0024$ mol/L; (b) initial concentrations of reagents are as in (a), but $[NaOAc]_0 = 0.01$ mol/L; (c) initial concentrations are the same as in (a), but NaOAc is absent.

dissolved in 2 mL of MeOH was added into the solution. The overall volume of the solution was 10 mL. Water (2 mmol) was added together with methanol to maintain the constant concentration of water at the initial level (~0.2 mol/L).

The products were analyzed by ^1H and ^{13}C NMR spectroscopy and coupled GLC/mass spectrometry. The compositions of the gas and liquid phases were controlled by GC and GLC, respectively. Reaction 1 produced phenyl maleate (**I**), phenyl fumarate (**II**), and dimethoxylactone (**III**). The oxidation of CO to CO_2 (2) occurs in parallel. The potentials of the platinum (E_{Pt}) and glass (pH) electrodes were measured with reference to the Ag/AgCl,KCl electrode, which contacted with the solution through the diffusive bridge.

Oscillations were observed for 3.5 h up to 95% conversion of alkyne. Figure 1 shows the behavior of the redox potential, pH, and volume of the gaseous mixture consumed. Water is



I (70%) **II** (4%) **III** (15%) (1)

$$CO + {}^{1}/_{2}O_2 \longrightarrow CO_2 \qquad (2)$$

formed in a 1:1 proportion to the products of phenylacetylene carbonylation by reaction 1 and catalyzes reaction 2. In due course of experiments, the concentration of water somewhat increases at the expense of reaction 1.

Sodium acetate determines the initial pH of the solution, which affects the oscillations. The range of NaOAc concentration within which oscillations were observed was found to be very narrow: from 0 to 0.01 mol/L. Higher concentrations of NaOAc caused the deep reduction of the system and appearance of metallic palladium. In the absence of NaOAc, one can see transition from the rapidly damped oscillations having a small amplitude to the pseudo-steady state (Figure 1c). The most prolonged oscillations with the largest amplitudes were attained at the NaOAc concentration of 0.0024 mol/L (Figure 1a). When the concentration of NaOAc was 0.01 mol/L, the solution became inhomogeneous because of palladium precipitation, and the amplitude of oscillations became smaller (Figure 1b).

Because changing the stirring intensity (stirring rate was varied from 300 to 600 rpm) had no influence on the magnitude, shape, or period of oscillations, we believed that oxygen transfer through the phase boundary is not a cause of oscillations; that is, the oscillator is of a purely chemical nature.

Oxygen is the oxidant in the system, while the iodide ion, carbon monoxide, phenylacetylene, and methanol are reductants.

Palladium(I) complexes of the $Pd_2X_4(CO)_2{}^{2-}$ composition (X = Br^-, I^-) have been shown to be active catalysts of alkyne carbonylation in PdX_2 solutions.[4-6] Therefore, a change in the value of the platinum electrode potential (E_{Pt}), which takes place when CO and PhC≡CH contact the solution PdI_2, were associated with the reduction of Pd(II) to Pd(I). The catalyst becomes active toward oxidative carbonylation of phenylacetylene only if part of Pd(II) is reduced to Pd(I) and E_{Pt} decreases by approximately 200 mV. The run where PdI_2 was replaced by $K_2Pd_2I_4$, synthesized by the known technique,[5] exhibited oscillations similar in shape and amplitude.

On the basis of the available data on the mechanism of oxidative carbonylation,[6-8] one may propose two reactions of Pd(II) reduction to Pd(I):

$$CO + H_2O + PdI_2 \rightarrow HPdI + HI + CO_2 \qquad (3)$$

$$HPdI + PdI_2 \rightarrow Pd_2I_2 + HI \qquad (4)$$

Reaction 3 is a key step of the water-gas shift reaction catalyzed by Pd(II)[9] and other metals.[10] Reaction 4 is considered as the main pathway to Pd(I) compounds.[4] Palladium(I) complex thus formed is active in oxidative carbonylation of phenylacetylene:

$$Pd_2I_2 + PhC{\equiv}CH + 2CO + 2MeOH \rightarrow 2HPdI + MeOOCC(Ph){=}CHCOOMe \qquad (5)$$

Palladium hydride complex formed by reaction 5 may further undergo reaction 4 to yield Pd(I) or reactions

$$HPdI + I_2 \rightarrow PdI_2 + HI \qquad (6)$$

$$HPdI + {}^{1}/_{2}O_2 + HI \rightarrow PdI_2 + H_2O \qquad (7)$$

We suggest reactions 6 and 7 in our system as the simplest plausible ones to oxidize HPdI. Iodine is formed by oxidation of HI by molecular oxygen:

$$2HI + {}^{1}/_{2}O_2 \rightarrow I_2 + H_2O \qquad (8)$$

Here, reactions 6−8 are responsible for the complete disappearance of HPdI and Pd_2I_2, after which phenylacetylene carbonylation stops. Reaction 3 corresponds to the "upper" oxidized state of the system, whereas process 5 is associated with the "lower" reduced state, which is active in oxidative carbonylation. Reactions 4 and 5 together are the autocatalytic process of Pd(II) reduction catalyzed by palladium hydride complex and controlled by the amount of I_2 in the system. Upon I_2 consumption, the concentrations of HPdI and HI begin to grow rapidly. This leads to the inhibition of reaction 3 and acceleration of reactions 6−8 that return the system to the "upper", inactive in carbonylation state.

We may propose a first-approximation mathematical model based on mechanism 3−8 in more detailed notation to describe the dynamic behavior of the system. The proposed model agrees with the experimental data: it correctly describes the period and shape of oscillations and the transition from oscillations to the pseudo-steady state, which is observed in the absence of a base (NaOAc). Discussion of the details of the model will be reported elsewhere.

Our results prove the possibility of complex dynamic behavior (such as chemical oscillations) in oxidative reactions of organic synthesis that are typical organometallic catalytic processes.

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