January, 1984] *Bull. Chem. Soc. Jpn., 57, 251—253 (1984)*

Oxidative Carbonylation of Piperidine in the Presence of Palladium(II)-Copper(II) Catalytic System

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(Received January 14, 1982)

A kinetic study on oxidative carbonylation of piperidine to give 1,1′-carbonyldipiperidine in the presence of Pd(II) and Cu(II) complexes at 40 °C has been investigated.

Carbonylation of amines depending on the conditions of the reaction and the catalyst nature produces various oxygen-containing derivatives.[1–4] Thermodynamic characteristics of the reaction are most favorable in case of the oxidative carbonylation.[3] A new catalytic system of the oxidative carbonylation of amines, based on Pd(II) and Cu(II) complexes in mild conditions, was reported previously.[5] Its high activity is due to the development of the synergistic effect of the mixed catalyst.

This paper is aimed at the elucidation of the reaction mechanism and causes of the synergistic effect by studying in detail the kinetics of the oxidative carbonylation of piperidine to give 1,1′-carbonyldipiperidine in the same catalytic system.

A static system under volumetric and potentiometric control was adopted. During the kinetic study, the reactor was energetically shaked up to provide good mixing of gas and liquid. In the study of the mechanism of separate stages, the solution of the complexes from the reactor was periodically fed to the cell of UR-20 spectrometer.

Results and Discussion

The rate of the reaction (1)

$$2C_5H_{10}NH + CO + 2Cu\,(II) \xrightarrow{Pd(II)} 2Cu(I) + (C_5H_{10}N)_2CO + 2H^+ \qquad (1)$$

increased linearly with both Pd(II) concentration and CO partial pressure (Fig. 1a, c) and nonlinearly with Cu(II) concentration (Fig. 1b). At the ratio of Cu(II) : Pd(II) = 2 the reaction order was 1, but it approached to zero at the ratio >40. It was found that the reaction rate was independent of the piperidine concentration in the 4.2×10^{-3}—1.4×10^{-1} mol l^{-1} range. The kinetic equation is thus represented in the following form:

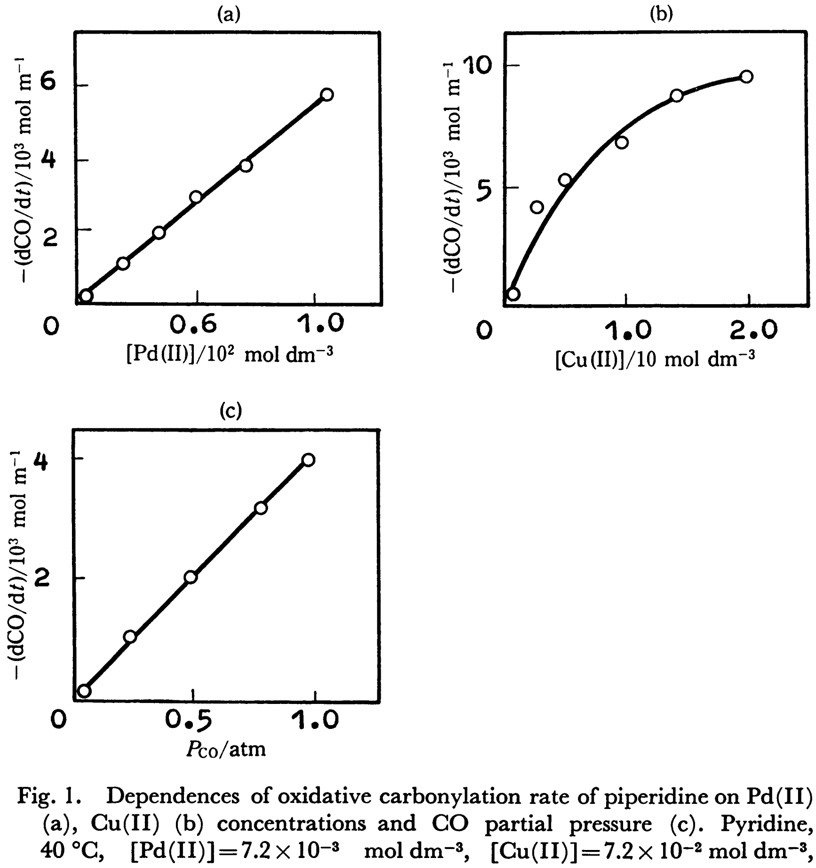

Fig. 1. Dependences of oxidative carbonylation rate of piperidine on Pd(II) (a), Cu(II) (b) concentrations and CO partial pressure (c). Pyridine, 40 °C, $[Pd(II)] = 7.2 \times 10^{-3}$ mol dm^{-3}, $[Cu(II)] = 7.2 \times 10^{-2}$ mol dm^{-3}, $P_{CO} = 1$ atm.

$$-\frac{\mathrm{dCO}}{\mathrm{d}t} = k_{\mathrm{ef}}\cdot[\mathrm{Cu(II)}]^n\cdot[\mathrm{Pd(II)}]\cdot[\mathrm{CO}], \qquad (2)$$

$$n = 0\text{—}1$$

Our data and those cited in the paper of Brakman[6] on piperidine carbonylation in the Cu(II)–Cu(I) catalyst system can be described by the kinetic Eq. 3:

$$-\frac{\mathrm{dCO}}{\mathrm{d}t} = k_{\mathrm{ef}}\cdot[\mathrm{Cu(I)CO}]\cdot[\mathrm{C_5H_{10}NH}], \qquad (3)$$

which shows that autocatalysis is carried out in the reaction till the complete consumption of Cu(II) with accumulation of 1,1′-carbonyldipiperidine and copper(I) carbonyl in the solution (bands in the IR spectrum at 1650 and 1970 $\mathrm{cm^{-1}}$).

In the absence of copper(II), $\mathrm{PdCl_2(C_5H_{10}NH)_2}$ in the excess of piperidine with CO gives a product having a number of bands in the "carbonyl" region, *i.e.* 1595, 1895, 2010, and 2045 $\mathrm{cm^{-1}}$.

If the excess of piperidine was replaced by two equivalents of triphenylphosphine, then the IR spectrum would show only one intensive band at 1590 $\mathrm{cm^{-1}}$ which, on the basis of literature data,[7] may be attributed to the carbamoyl complex. The band at 1595 $\mathrm{cm^{-1}}$ in the above-mentioned group is attributed to the same complex. The relation of other bands is not quite clear.

Literature[8] and our experimental data show that the key-complex of palladium in the catalytic reaction is represented by the carbamoyl complex which is stable to the action of the excess of amine and air oxygen at a room temperature but is easily decomposed by water forming metallic palladium and by piperidine complex of copper(II) forming 1,1′-carbonyldipiperidine (ν_{CO}= 1650 $\mathrm{cm^{-1}}$).

$$\mathrm{Pd(II)(CONC_5H_{10})} + 2\mathrm{Cu(II)} \xrightarrow{k_4} 2\mathrm{Cu(I)} + \mathrm{Pd(II)} + \mathrm{(C_5H_{10}N)_2CO} \qquad (4)$$

($\mathrm{Cl^-}$ and amine ligands are omited for Simplicity) Presynthesized carbamoyl complex of palladium(II) can be titrated potentiometrically by copper(II) chloride in the excess of piperidine and in the absence of CO (Fig. 2).

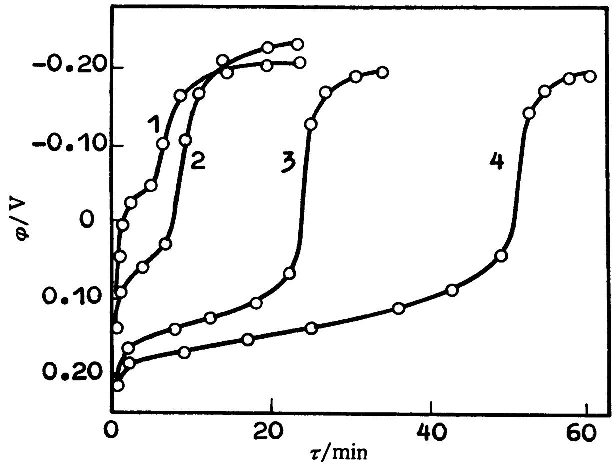

Fig. 2. Potentiometric curves of the interaction of carbamoyl complex of palladium with copper(II) amine complex. Pyridine, 25 °C, [Pd(II)]=4.0× 10^{-2} mol $\mathrm{dm^{-3}}$, [Cu(II)]=0.8× 10^{-2} (1), 1.6× 10^{-2} (2), 2.4× 10^{-2} (3), 4.0× 10^{-2} mol $\mathrm{dm^{-3}}$ (4).

According to the stoichiometric Eq. 4, 2 mol Cu(II) are necessary for the formation of 1,1′-carbonyldipiperidine. However, the first order for copper(II) obtained experimentally, indicates that the reaction (4) consists of minimum two stages where the interaction with the second complex of copper(II) proceeds, probably, fast and does not affect the rate of the process as a whole.

When the reaction is carried out directly in the IR spectrometer, palladium carbonyl preceding the carbamoyl complex is not observed. The formation of carbamoyl can be supposed to be carried out by CO incorporation into Pd–N bond despite the fact that in a similar Cu(I)–Cu(II) system the reaction proceeds through the stage of the formation of carbonyl; this reaction route is considered as a key reaction for the synthesis of carbamoyl complex.[9]

$$\mathrm{Pd(II)(C_5H_{10}NH)} + \mathrm{CO} \underset{k_5}{\overset{k_{-5}}{\rightleftarrows}} \mathrm{Pd(II)(CONC_5H_{10})} + \mathrm{H^+} \qquad (5)$$

The kinetic Eq. 6 corresponding to the stages (5) and (4) qualitatively agrees with the experimental one (2).

$$-\frac{\mathrm{dCO}}{\mathrm{d}t} = \frac{k_5\cdot k_4\cdot[\mathrm{Pd(II)}]\cdot[\mathrm{CO}]\cdot[\mathrm{Cu(II)}]}{k_{-5}[\mathrm{H^+}]+k_4\cdot[\mathrm{Cu(II)}]} \qquad (6)$$

By the graphic method the constants of the Eq. 6 have been determined as $k_5=117\ \mathrm{dm^3\,mol^{-1}\,min^{-1}}$ and $k_{-5}/k_4=1.82\times10^{-3}$. The k_4 can be determined independently by the initial rate of the reaction product of Pd(II) with carbon monoxide and copper(II). The constant k_4 thus obtained is 17 $\mathrm{dm^3\,mol^{-1}\,min^{-1}}$, which gives the value of $K_5=k_5/k_{-5}=3.8\times10^3$.

As the values of k_5 and k_4 are similar the change of the reaction order of Cu(II) from 0 to 1 in a relatively narrow range of copper(II) concentrations would be accounted for. In fact at low Cu(II) concentrations the reaction rate is limited by the reaction (4) and we find the first order for copper, while at high Cu(II) concentrations the products of Pd(II) and CO interaction are quickly transformed to urea derivatives and the process is limited by the reaction (5).

The synergistic effect in Pd(II)–Cu(II) system (Fig. 3) can be accounted for the fact that in the presence of Pd(II) the stage of the formation of the carbamoyl

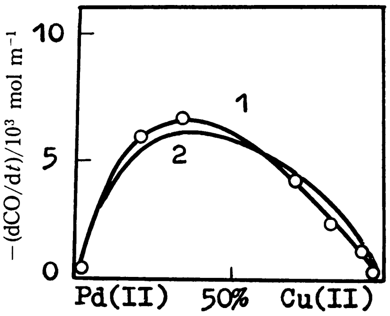

Fig. 3. Dependence of the initial rate of the oxidative carbonylation of piperidine on the ratio of palladium and copper complexes. Pd(II)+Cu(II)=5.0× 10^{-4} mol CO, $\mathrm{C_5H_{10}NH}$: (Pd(II)+Cu(II))=20. 1: Experimental points, 2: calculated curve.

complex is accelerated while Cu(II) additions accelerate its redox decomposition, *i.e.* an oxidizer is necessary for the stage of redox decomposition of the carbamoyl complex. In the classification offered,[10] this is a third type of synergism.

Hence, by the present study we managed to confirm the scheme of the process of piperidine carbonylation using a new mixed Pd(II)–Cu(II) catalyst for this reaction; to determine a key intermediate species *i.e.* the carbamoyl complex of palladium and to show that an oxidizer is necessary for the stage of redox decomposition of this complex which leads to the synergism in the system.

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