

## Oxidation of Butyraldehyde Initiated by Palladium (II) Ion-Pair Complexes

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Ion-pair complexes comprising a combination of  $\text{Bu}_4\text{NCl/Pd(OAc)}_2$  and  $\text{Bu}_4\text{PCl/Pd(OA)}_2$  were found to be highly active catalysts for the  $\text{O}_2$ -based autoxidation of butyraldehyde under mild conditions. Based on kinetic evidence, dimeric Pd complexes,  $\text{Pd}_2(\text{OAc})_4\text{Cl}_2^{2-}$ , are believed to be mainly responsible for the initiation process, although a catalytic contribution of monomeric species, e.g.,  $\text{Pd(OAc)}_2\text{Cl}_2^{2-}$ , cannot entirely be excluded. The oxidation of aldehyde to carboxylic acid and peracid follows a free radical mechanism.

Recently, we reported that ion-pair transition metal complexes comprising a combination of 18-crown-6 ether complexed potassium salts and palladium salts represent highly active catalysts for the oxidation of cyclohexanol<sup>1</sup> and the  $\text{O}_2$ -based autoxidation of aldehydes<sup>2</sup> in nonpolar solvents.

The present work demonstrates that the crown ether complexed alkali metal salt can be successfully substituted by quaternary N- and P-compounds, giving highly active new oxidation catalysts of the general type:  $\text{R}_4\text{NX/PdY}_2$  and  $\text{R}_4\text{PX/PdY}_2$  in which X and Y may be halides or carboxylic acid anions. In particular, the kinetics and mechanism of the  $\text{Bu}_4\text{Cl/Pd(OAc)}_2$  initiated oxidation of butyraldehyde in chlorobenzene is reported.

The oxidation of liquid aldehydes by molecular oxygen was reviewed by McNesby and Heller.<sup>3</sup> Transition metal salts of variable valence states are well known to initiate the oxidation,<sup>4-5</sup> and it is broadly agreed that redox processes producing

free radicals are involved in the initiation step. One exception, however, was reported by Hojo *et al.*,<sup>7</sup> who concluded, based on kinetic evidence, that the oxidation of benzaldehyde in benzene using noble metal oxygen complexes proceeded *via* a complex nonradical mechanism. The same system was reinvestigated by Sakamoto *et al.*,<sup>8</sup> using chlorobenzene as the solvent. These authors concluded that the oxidation of benzaldehyde initiated by the complex  $\text{PdO}_2(\text{PPh}_3)_2$ , followed a free radical mechanism.

Alkali metal and quaternary ammonium salts of  $\text{PdCl}_4^{2-}$  and  $\text{Pd}_2\text{Cl}_6^{2-}$  are well known.<sup>9-10</sup> Equilibrium studies related to such systems in polar solvents (e.g. water, acetic acid, acetonitrile and methanol) was recently reviewed by Henry.<sup>11</sup> However, little is known about ion-pair palladium(II) complexes in nonpolar organic solvents.

With respect to the catalytic behavior of Pd(II) solutions in oxidation reactions, the reader is reminded that cocatalysts of the Cu(II) or Fe(III) type often are used, (Wacker type systems). Such cocatalysts are, however, not necessary in the systems described here.

### EXPERIMENTAL

**Reagents.** The following reagents were used without further purifications:  $\text{PdCl}_2$  (Fluka A.G., *puriss*),  $\text{Pd(OAc)}_2$  (Fluka A.G., *puriss*), KOAc (Riedel-de Haën, *p.a.*), benzyltrimethylammonium chloride (Fluka A.G., *purum*), tetrabutylammonium chloride (Fluka A.G., *pract.*), tetrabutylphosphonium chloride (Ferak Berlin), 18-

crown-6 ether (A/S Borregaard, 98 %). Butyraldehyde (Merck, *zur Synthese*) and chlorobenzene (Merck, *p.a.*) were distilled in an inert atmosphere and stored under argon in the dark.

**Preparation of catalysts.** Concentrated catalyst solutions (50 ml,  $2 \times 10^{-3}$  M based on Pd) were prepared by mixing the salts and if desired the crown ether in chlorobenzene. The mixtures were homogenized by ultrasound treatment, normally for 0.5–2 h at 20 °C and diluted with chlorobenzene to 50 ml.

Catalyst solutions were stable at room temperature for days without any protection from light and air. However, prolonged standing resulted in precipitation of palladium(0).

**Oxidation experiments.** The oxidation experiments were carried out in a micro glass hydrogenation apparatus after Marhan (50 ml reactor and 50 ml thermostated gas burette, Otto Fritz GmbH) at atmospheric pressure. Prior to start the apparatus was filled with pure oxygen, and the reaction was monitored by measuring the O<sub>2</sub> uptake. The oxidation products were quantitatively analyzed by titrations, *i.e.* iodometric for the amount of peracid and neutralization for the total acid content using thymolphthalein indicator.

## RESULTS AND DISCUSSION

Within the experimental accuracy, the material balance of the O<sub>2</sub>-based oxidation of butyraldehyde at atmospheric pressure was found to be satisfied by the conversions (1) and (2),



Accordingly, the rate of the reaction can be monitored by measurement of O<sub>2</sub> absorbed and the amounts of acid and peracid formed. Using standardized reaction conditions in chlorobenzene solvent, the efficiency of Pd(II) catalysts containing quaternary ammonium or phosphonium salts were initially compared with previously reported catalysts containing 18-crown-6 ether complexes K salts.<sup>2</sup> Representative results comprising 1 h conversion/selectivity data and initial reaction rates as determined by O<sub>2</sub>-consumption are summarized in Table 1.

The data clearly demonstrate that combinations of quaternary N- and P-compounds and Pd(II) salts represent highly active oxidation catalysts and that the efficiency of such systems for the initiation of the O<sub>2</sub>-based autoxidation of butyraldehyde is comparable with Pd(II) catalyst systems containing crown ether complexed potassium salts as promotor. In particular, the catalytic activity was found to be extremely high in mixed chloride/acetate systems. In the case of the Bu<sub>4</sub>NCl/Pd(OAc)<sub>2</sub> system the activity was twice as high as the pure chloride system, and this system was therefore chosen for more detailed kinetic investigations.

**Kinetics.** Initiated by the catalyst system consisting of Bu<sub>4</sub>NCl and Pd(OAc)<sub>2</sub>, the experimental initial rate of butyraldehyde oxidation in chlorobenzene solvent based on the consumption of O<sub>2</sub> at atmospheric pressure, was found to obey eqn. (3).

$$r = -\frac{d|\text{O}_2|}{dt} = k_{\text{exp}} |\text{RCHO}|^x |\text{Pd(II)}|^y |\text{Bu}_4\text{NCl}|^z \quad (3)$$

Table 1. The O<sub>2</sub>-based oxidation of butyraldehyde at atmospheric pressure/10 °C in chlorobenzene (Pd(II) salt: 10<sup>-3</sup> M and butyraldehyde: 0.283 M).

Catalyst	Mol ratio	Conversion (1 h) %	Peracid selectivity, %	Initial rate mol O <sub>2</sub> l <sup>-1</sup> min <sup>-1</sup>
Pd(OAc) <sub>2</sub> (3 · 10 <sup>-3</sup> M)	—	<5	—	—
(18-crown-6) · KCl/Pd(OAc) <sub>2</sub>	4:1	58.3	61.2	6.7 · 10 <sup>-3</sup>
Bu <sub>4</sub> NCl/Pd(OAc) <sub>2</sub>	4:1	62.0	69.0	1.0 · 10 <sup>-2</sup>
Bu <sub>4</sub> NCl/Pd(OAc) <sub>2</sub>	2:1	60.8	70.4	1.0 · 10 <sup>-2</sup>
Bu <sub>4</sub> NCl/PdCl <sub>2</sub>	2:1	46.6	50.0	5.0 · 10 <sup>-3</sup>
Bu <sub>4</sub> PCl/Pd(OAc) <sub>2</sub>	2:1	68.9	59.5	1.3 · 10 <sup>-2</sup>
Bu <sub>4</sub> PCl/PdCl <sub>2</sub>	2:1	45.9	56.2	4.4 · 10 <sup>-3</sup>
Benzyl Me <sub>3</sub> NCl/Pd(OAc) <sub>2</sub>	2:1	26.2	40.5	1.0 · 10 <sup>-3</sup>

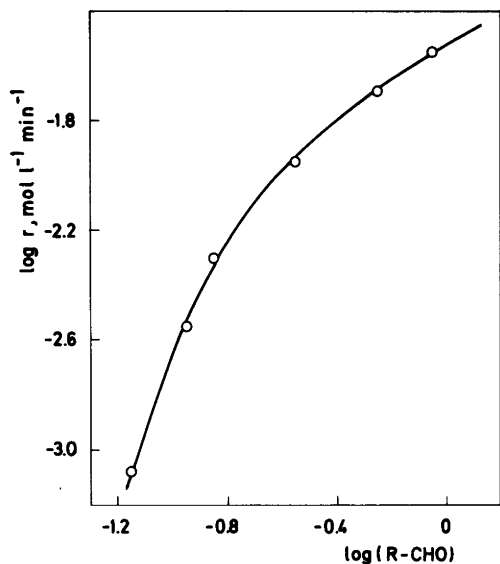


Fig. 1. The relationship between the initial rate of reaction in chlorobenzene at atmospheric pressure/10 °C and the concentration of butyraldehyde. ( $\text{Pd}(\text{OAc})_2$   $10^{-5}$  M, and  $\text{Bu}_4\text{NCl}$   $2 \times 10^{-5}$  M).

The orders of reaction,  $x$ ,  $y$ , and  $z$ , were dependent on the concentrations of aldehyde, Pd salt, and  $\text{Bu}_4\text{NCl}$ . At substrate concentrations lower than 0.15 M the rate of reaction is close to second order with respect to the concentration of butyraldehyde. Within the concentration range 0.15 M–0.6 M the order is close to one and at higher aldehyde concentrations the value of  $x$  drops to about 0.5, (Fig. 1).

At  $\text{Pd}(\text{OAc})_2$  concentrations lower than  $10^{-5}$  M ( $N/\text{Pd}=1$ ) the rate of reaction is second order with respect to the concentration of catalyst, but at Pd salt concentrations exceeding  $2 \times 10^{-5}$  M the order dropped to about 0.5. At intermediate Pd salt concentrations in the range  $10^{-5}$  M– $2 \times 10^{-5}$  M the order of reaction is about one (Fig. 2).

The rate of reaction is at maximum and independent of the  $\text{Bu}_4\text{NCl}$  concentration in systems in which the  $N/\text{Pd}(\text{II})$  ratio is 2–4 (Fig. 3). With a molar ratio less than 2 the order is approaching one while at  $N/\text{Pd}$  ratios  $>4$ , the order of reaction assumes a low negative value. Thus, for systems with a  $N/\text{Pd}$  ratio within the limits 2–4, the rate of oxidation can be expressed by the simple eq. (4).

$$r = k' [\text{RCHO}]^x [\text{Pd}(\text{II})]^y \quad (4)$$

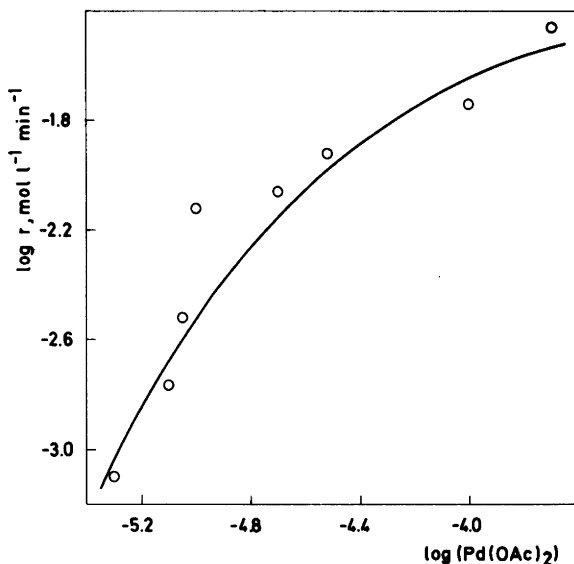


Fig. 2. The relationship between the initial rate of reaction in chlorobenzene at atmospheric pressure/10 °C and the concentration of  $\text{Pd}(\text{OAc})_2$ . (Butyraldehyde: 0.276 M, and  $\text{Bu}_4\text{NCl}/\text{Pd}(\text{OAc})_2=1$ ).

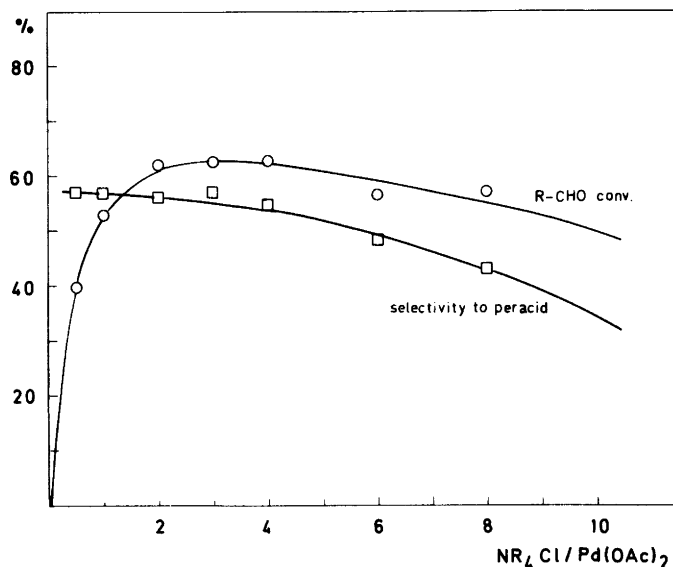


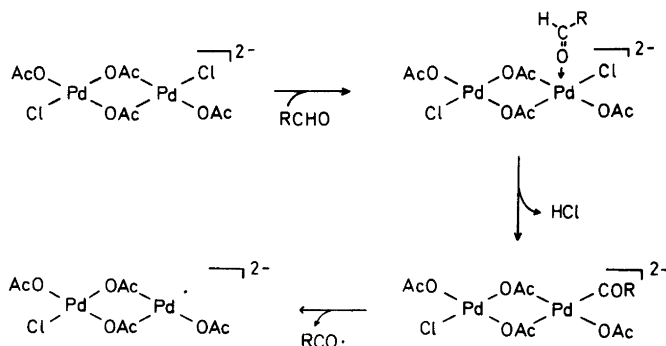
Fig. 3. The effect of  $\text{Bu}_4\text{NCl}/\text{Pd}(\text{OAc})_2$  molar ratio on the rate of conversion (42 min) and selectivity for the  $\text{O}_2$ -based oxidation of butyraldehyde in chlorobenzene at atmospheric pressure/ $10^\circ\text{C}$ . ( $\text{Pd}(\text{OAc})_2$   $10^{-5}$  M, and butyraldehyde: 0.276 M).

The values of  $x$  and  $y$  being as outlined in the text above.

The Arrhenius activation energy for such systems was determined to be,  $E_A = 70 \pm 3$  kJ  $\text{mol}^{-1}$  for the temperature range  $-5^\circ\text{C}$  to  $10^\circ\text{C}$  at  $\text{Pd}(\text{II}) = 10^{-5}$ ,  $\text{Bu}_4\text{NCl} = 2 \times 10^{-5}$  M, and butyraldehyde = 0.283 M. At these concentrations and  $10^\circ\text{C}$  the reaction orders  $x$  and  $y$  are both equal to one and  $k'$  is computed to be  $390 \pm 20$  l  $\text{x mol}^{-1} \text{min}^{-1}$ .

*The initiation process.* Using predissolved catalyst, no induction period is observed. In the

presence of free radical inhibitors, e.g. 2,6-di-*t*-butyl-*p*-cresol, the oxidation might easily be stopped completely for one hour or more. This observation supports the theory that the oxidation reaction proceeds *via* a free radical type mechanism. Since, it appears unlikely that the inhibiting effect of the sterically hindered inhibitor here used, is caused by blocking of free coordination sites on Pd, which would make a complex mechanism like the one proposed by Hojo *et al.*<sup>7</sup> possible. Based on kinetic evidence, and the complex relationship between the rate of



Scheme 1. The initiation process by dimeric Pd(II) ion-pair complexes.

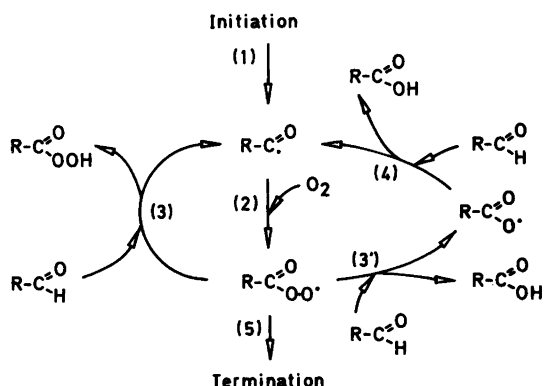
reaction and the concentration of palladium salt (Fig. 2), it appears reasonable to conclude that dimeric Pd species,  $\text{Pd}_2\text{X}_6^{2-}$ , as well as monomeric ion-pair complexes,  $\text{PdX}_4^{2-}$ , may initiate the oxidation reaction. The fundamental reaction steps leading to the formation of free RCO radicals are outlined in Scheme 1.

During the initiation process, the formation of a free RCO radical is coupled with the formal reduction of Pd(II) to Pd(I). In order to complete the initiation cycle, the Pd(I) complex has to be backoxidized to Pd(II). Initially, when the concentration of peracid is low, oxygen is most likely to be responsible for the backoxidation. As the oxidation reaction proceeds to a higher conversion, peracid as well may take part in this process.

*The chain propagation.* As previously reported for K-(18-crown-6)/Pd(II) initiated oxidation of aldehydes,<sup>2</sup> carboxylic acid as well as peracid were found to be primary reaction products in agreement with a reaction mechanism as outlined in Scheme 2.

Based on our experimental data reported in Fig. 3, it is clear that the selectivity to peracid is influenced by the content of  $\text{Bu}_4\text{NCl}$  in the reaction mixture. With increasing ratios of  $\text{Bu}_4\text{NCl}/\text{Pd}(\text{OAc})_2$  the selectivity to peracid is decreased. At the present, it is not clear whether this effect is due to changes in the relative rates of the reactions 3 and 3' (Scheme 2), or caused by secondary reaction of peracid formed.

*The chain termination.* As indicated on Scheme 2, we believe the peracid radical to be mainly responsible for the chain termination reaction:



Scheme 2. The chain propagation process.

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Assuming sufficiently long chains, it is an agreement with steady-state kinetics, to conclude that the termination reaction is a linear process in systems with low initial aldehyde concentrations ( $<0.15\text{M}$ ), while at higher substrate concentrations a bimolecular process, or termination via the RCO radical as well, may participate.

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