Mendeleev Commun., 1994, 4(2), 39–40

Pentane Carbonylation in the Photocatalytic System Bis(μ-chlorocarbonylrhodium)–Trimethylphosphine

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A new photocatalytic system for pentane carbonylation with efficiency 20-times higher than that for the systems already known has been found; it is formed by mixing bis(μ-chlorocarbonylrhodium) and trimethylphosphine solutions ([P]:[Rh] = 3).

Functionalization of alkanes by carbonylation is a promising method for the preparation of valuable organic compounds from paraffins.[1,2] Despite thermodynamic hindrances, this reaction can be performed in the presence of metallocomplexes either at high pressures[1] or using light energy.[3] The authors[4] had previously connected the small, limiting yields of benzaldehyde (1–2 cycles) obtained in the presence of $RhCl(CO)(PPh_3)_2$ in the photocatalytic carbonylation of benzene with the reversibility of the process and attainment of thermodynamic equilibrium. However, it has since turned out that exchange of the triphenylphosphine ligand for a more electron-donating trimethylphosphine ligand under the same conditions allows a 40-fold increase in the yield of benzaldehyde as well as the ability to perform carbonylation of saturated hydrocarbons. The reason for this limiting yield of aldehyde is found to be mainly the further photochemical decomposition of aldehyde and deactivation of the catalyst, rather than the reversibility of the process.[3,5,6] In this case there is the prospect of searching for more promising novel catalysts and conditions of alkane carbonylation in high yields.

We have shown[5] that carbonylation of pentane in the presence of $RhCl(CO)(PMe_3)_2$ **A** and carbon monoxide at pressures higher than 100 Torr[†] occurs with the participation of new active centres formed as a result of irradiation of the solution **A** in the presence of CO. The efficiency of the newly-formed complex is ten times higher than that for the generation of aldehyde with the participation of **A** under the same conditions. In this report we present the results of studies on the efficiency of the system containing $Rh_2Cl_2(CO)_4$ **B** and trimethylphosphine (PMe_3) in different ratios undergoing a pentane carbonylation reaction with an initial partial pressure of carbon oxide of 60 Torr. As already known,[7] when solutions of **B** and PMe_3 are mixed in alkanes in various proportions, monomeric and dimeric rhodium complexes of different structures are formed.

When the mixture **B** + PMe_3 in pentane is irradiated with light of $\lambda > 270$ nm for 1 h at CO pressure $P_{CO} = 60$ Torr and $[Rh] = 1$ mmol dm^{-3}, the maximum yield of hexanal ($Y_{max} = 5.9$ mmol dm^{-3}) is achieved at the ratio of phosphine concentration to rhodium concentration $n = [PMe_3]:[Rh] = 3$. At $n \leqslant 1$ no products are observed; at $n = 6$ the yield of hexanal is *ca.* 0.9 mmol dm^{-3}.

The efficiency of the system studied at $n = 3$ in the photocatalytic carbonylation of pentane is higher by more than one order of magnitude than the efficiency of the complex **A**. Fig. 1 presents the kinetic curve of accumulation of hexanal in the solution for the mixture of **B** + PMe_3 and, for comparison, a similar curve for catalytic carbonylation of pentane in the presence of **A** under the same conditions. The initial rate is higher by 20 times for the mixture **B** + PMe_3, and the plateau observed might be related to secondary reactions of hexanal decomposition.[3,5,6] The conservation of the plateau on the kinetic curve for a long period attests for the stability of the photocatalyst.

So, the high efficiency of the system indicates the participation of a new species different from those taking part in the photocatalytic process with **A**.[3] An investigation of UV and IR spectra shows that before CO is admitted into the system **B** + PMe_3 ($n = 3$), rhodium is mainly bonded in the complex **A**, but a minor part of the rhodium may be bonded in a complex without CO in the coordination sphere. The characteristic feature of the system is the large ($\cong 1$ mmol dm^{-3}) concentration of non-bonded phosphine in the solution.

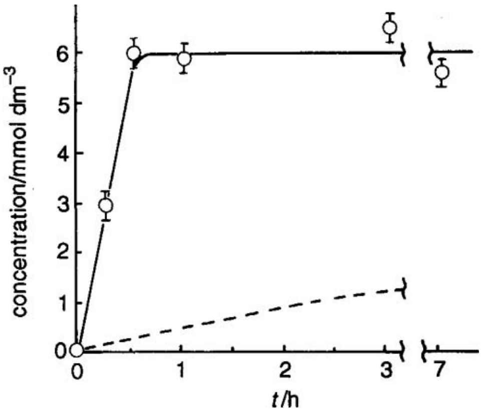

Fig. 1 Kinetic curve for the accumulation of hexanal on irradiation of mixture **B** + PMe_3 ($n = 3$) in pentane. Partial pressure of CO = 60 Torr, $[Rh] = 1$ mmol dm^{-3}, 1000 W high pressure mercury lamp, $\lambda > 270$ nm, 20 °C. Dotted line – kinetic curve obtained for the solution $[RhCl(CO)(PMe_3)_2] = 1$ mmol dm^{-3} under similar conditions[5].

When carbon monoxide is added to the system **B** + PMe_3 ($n = 3$), a band at 1996 cm^{-1} appears in the IR spectrum in addition to a band at 1962 cm^{-1} (characteristic for complex **A**). The intensity of the band 1996 cm^{-1} increases with CO pressure increase and the intensity of the band at 1962 cm^{-1} is practically unchanged at the same time. The irradiation results in a new shift of equilibrium between rhodium complexes in the system. For example, the irradiation of the system **B** + PMe_3 ($n = 3$, $P_{CO} = 60$ Torr) with monochromatic light 365 nm for 0.5 h leads to almost complete disappearance of complex **A** in the solution (bleaching of the band at 365 nm in the UV spectrum). The aldehyde is not recorded in this case. However, further irradiation of this solution with light $\lambda > 270$ nm gives a 12 mmol dm^{-3} yield of aldehyde (twice that for a comparable experiment without preliminary irradiation with monochromatic light).

To highlight the reasons for the high efficiency of the system, additional investigations are required. However, it is now clear that in the system **B** + PMe_3 + CO new species are formed which may be responsible for a more effective photocatalytic alkane carbonylation cycle simultaneously with the cycle involving participation of **A**. Non-bonded phosphine in the solution would stabilise both the initial species of a new photocatalytic cycle and intermediates. The stability of hydride[8] and acetylhydride[9] octahedral rhodium complexes with three phosphine ligands in the coordination sphere is, for example, well known.

The authors are grateful to I. P. Efimova for the help given in these experiments.

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[†] 1 Torr = (101 325/760) Pa ≈ 133.322 Pa.

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Received: Moscow, 15th November 1993
Cambridge, 14th December 1993; Com. 3/06955I