The effect of the conditions of the photocatalytic carbonylation of pentane catalyzed by the $Rh_2Cl_2(CO)_4$—PMe_3 system on the yield of C_6-aldehyde

N. K. Khannanov, G. N. Menchikova, and E. A. Grigoryan*

Institute of Structural Macrokinetics, Russian Academy of Sciences,
142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: +7 (095) 201 5795 (for ISMAN)

The yield of C_6-aldehyde in the photocatalytic system $Rh_2Cl_2(CO)_4$—PMe_3 passes through a maximum as the CO pressure and PMe_3 concentration increase. The increase in the yield of aldehydes with increasing CO pressure is related to the increase in the carbonylation rate and to the retardation of the photodecomposition of the aldehydes. The rate of the photocatalytic carbonylation of pentane in this system is 20 times higher than in the presence of $RhCl(PMe_3)_2(CO)$.

Key words: pentane carbonylation; photocatalysis; C_6-aldehyde, alkane activation; rhodium-phosphine system.

Alkane functionalization is a convenient method for the synthesis of valuable products from the natural gas and paraffins.[1] In recent years, remarkable results have been achieved in this field due to the use of light energy for the activation of homogeneous catalysts. In the case of alkane dehydrogenation, high quantum yields[2] and degrees of conversion of alkanes[3] have been obtained. On the other hand, in the carbonylation of alkanes, several new factors limiting these values have been elucidated.[4–8] It has been previously reported[4,5] that the limitation of the aldehyde yield in the carbonylation of hydrocarbons is caused by the attainment of thermodynamic equilibrium. However, subsequent studies[6] have shown that not only the initial rate of the process but also the aldehyde yield may be increased in the photocatalytic carbonylation of alkanes by modifying the catalyst.

In catalytic systems designed for the carbonylation of linear alkanes, the rate of aldehyde accumulation decreases in the course of the process due to the secondary reactions of the photoactive aldehyde molecule.[7]

If the stability of the catalytic system is high, the kinetic curve of aldehyde accumulation flattens out, *i.e.*, the aldehyde concentration reaches a steady-state value. The rate of alkane carbonylation, *i.e.*, the rate of aldehyde formation, also decreases in the course of deactivation reactions in the photocatalytic system, and the aldehyde concentration in the system begins to decrease after reaching a maximum. Thus, in photocatalytic systems for alkane carbonylation, the aldehyde concentration rather quickly reaches its limiting value, which is not directly related to the thermodynamics of the process.

It has been previously shown[8] that in the photocatalytic carbonylation of pentane at a CO pressure of 600 Torr in the presence of $RhCl(PMe_3)_2(CO)$ (**1**) the accumulation of aldehyde becomes sharply accelerated (by tens of times) after a half-hour induction period and then ceases in another half an hour. This increase in the activity of the system is caused by the formation of active complexes due to the displacement of phosphine from the coordination sphere of rhodium by carbon monoxide.

In this work, a combination of bis-μ-chlorodicarbonyl rhodium and trimethylphosphine (PMe_3) was studied with the purpose of finding more active systems for the photocatalytic carbonylation of pentane and to determine the factors that affect the rate of the process and the yield of the product. It is known that different rhodium complexes are formed in the system $Rh_2Cl_2(CO)_4$—PMe_3 (system **2**) at various ratios n = $[PMe_3]:[Rh]$.[9]

Experimental

Reagent grade pentane was purified and dried according to the known procedure.[10] Carbon monoxide was used without preliminary purification (admixture content was below 0.1 %). $Rh_2Cl_2(CO)_4$ (**3**) and $Rh_2Cl_2(PMe_3)_2(CO)_2$ were prepared according to the previously published procedure.[9] All operations with the complexes were performed *in vacuo* or under argon. Pure PMe_3 was prepared by decomposing the $AgI \cdot PMe_3$ complex *in vacuo* at 140 °C.

Mixture **2** was prepared in the following way. Solutions of **3** and PMe_3 (total volume 3 mL) were placed into different sections of a reactor (total volume 65 mL) separated from one

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another by a Teflon valve, and each of the parts was evacuated separately. The mixing was performed at room temperature, then the reactor was placed in a box where the mixture was sampled into a thermostatted quartz cuvette 2 mm thick for UV spectroscopy and irradiation, or into a cuvette made of KBr (0.541 mm thick) for IR spectroscopy. Before the irradiation, the solution in the cuvette was evacuated at the temperature of liquid nitrogen, then the solution was warmed up to −65 °C (pressure of the pentane vapor was 3 Torr), and carbon monoxide was let in.

The solution was irradiated with a DRSh high-pressure mercury lamp through a BS-3 light filter ($\lambda > 270$ nm). The aldehyde concentration was determined by GLC at 170 °C using a column (1 m×3 mm) filled with Silochrom C-80. Absorption spectra in the visible and UV spectral range were registered on a Specord M-40 spectrophotometer, and those in the IR range were registered on a Specord M-80 spectrophotometer.

Results and Discussion

During the preparation of system **2** the CO molecules are displaced from complex **3** by phosphine to form dimeric (and, at higher [PMe_3], also monomeric) rhodium complexes of various composition.[9] The equilibrium concentrations of these complexes depend on the concentrations of rhodium, CO, and PMe_3 in the solution. The following complexes were identified in the mixtures of **3** with PMe_3 in hydrocarbon media:[9,11] $Rh_2Cl_2(PMe_3)(CO)_3$, $Rh_2Cl_2(PMe_3)_2(CO)_2$ (**1**), and $Rh_2Cl(PMe_3)_3(CO)_2$. As has already been mentioned, complex **1** is active in the irradiation-induced reaction of alkane functionalization. The other complexes have not been previously studied in similar reactions. The activity of individual complexes of composition $Rh_2Cl_2(CO)_2(PMe_3)_2$, $Rh_2Cl_2(PMe_3)_4$, and $RhCl(PMe_3)_3$ has not been established for the photocatalytic carbonylation and dehydrogenation of pentane because their solubility in pentane is too low for these experiments.

The dependence of the yield of C_6-aldehyde ("hexanal") after 1 h of irradiation of system **2** is presented in Fig. 1 (curve *1*) for various ratios of $n([PMe_3]:[Rh])$ in the solution, at CO pressure 60 Torr. As can be seen from Fig. 1, the maximum yield is observed for $n = 3$. The curve of the dependence of the aldehyde yield on p_{CO} at fixed $[Rh]_0 = 10^{-3}$ *M* and $n = 3$ (Fig. 1, curve *2*) also passes through a maximum at $p_{CO} = 300$ Torr. In the case of $n = 3$ the IR spectrum of the solution after mixing **3** and PMe_3 shows a single absorption band (AB) at 1962 cm^{-1} in the range of carbonyl group valent vibrations. This AB almost disappears at $n = 6$. It should be mentioned that the IR spectrum of complex **1** also contains AB at 1962 cm^{-1} corresponding to the vibrations of terminal CO.

However, the activity of system **2** cannot be associated with the activity of complex **1** alone. First, the catalytic activity of system **2** calculated with respect to rhodium is significantly higher in the carbonylation of pentane than that of the solution of complex **1**. At $p_{CO} = 60$ Torr the initial rate of pentane carbonylation is 20 times higher for system **2**. The dependence of the hexanal yield on the CO pressure for system **2** at $n = 3$ (Fig. 1, curve *2*) and for the solution of complex **1** (Fig. 1, curve *3*) also significantly differ.

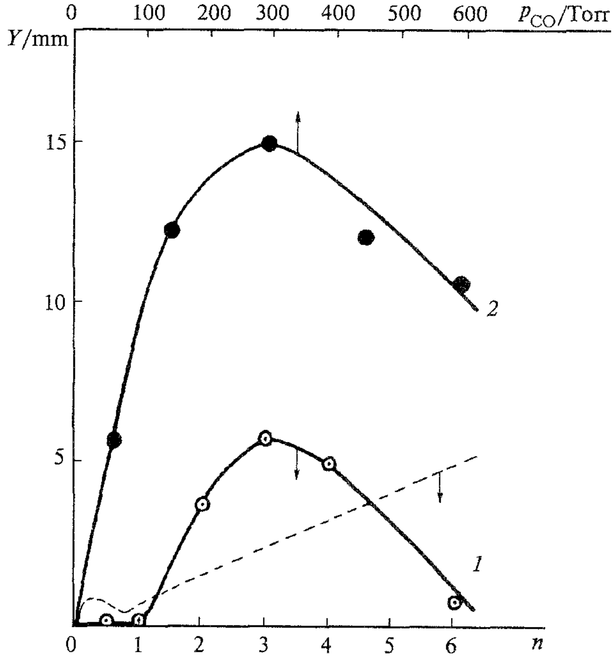


Fig. 1. The yield of the aldehyde after 1 h of irradiation (*Y*) in photocatalytic system **2** as a function of *n* (*1*) and CO pressure at $n = 3$ (*2*). The dependence of *Y* on the partial pressure of CO in solution **1** [8] is denoted by the dotted line (*3*). Reaction conditions: 20 °C, DRSh-1000 lamp, $\lambda > 270$ nm (filter BS-3), $[Rh]_0 = 10^{-3}$ mol L^{-1}. Taking into account the solubility of CO in heptane,[12] $[CO] \approx 10^{-3}$ mol L^{-1} at $p_{CO} = 60$ Torr.

Secondly (as will be shown below), in system **2** the conditions under which the band at 1962 cm^{-1} in the IR spectrum and that at 360 nm in the UV spectrum almost disappear (namely, $n = 3$, preliminary irradiation with monochromatic light with $\lambda = 365$ nm for 0.5 h) can be realized, and the activity of the system in the photocatalysis increases.

Finally, after letting CO in (60—300 Torr) the IR spectrum of the solution of system **3** has, in addition to the band at 1962 cm^{-1}, yet another AB at 1996 cm^{-1}, the intensity of which increases with increasing CO pressure.

Thus, some complex X must be formed in system **2** in the presence of CO, and it is likely to be one which is active in the photocatalytic carbonylation of pentane:

$$\mathbf{3} + PMe_3 + CO \rightleftharpoons X, \quad (1)$$

$$RH + CO \xrightarrow[X]{h\nu} RCHO. \quad (2)$$

The decrease in the aldehyde yield at CO pressures higher than 300 Torr (see Fig. 1, curve *2*) may be explained by the occurrence of a reaction deactivating the catalyst, because the irradiation of system **2** at 300 Torr for 5 h results in the appearance of a precipitate.

$$X + CO \xrightarrow{h\nu} \text{Deactivation products} \qquad (3)$$

In addition to the deactivation of the catalyst, the yield of C_6-aldehyde in the carbonylation of pentane may depend on the rate of the photochemical reactions resulting in the decomposition of aldehyde. Hexanal, like other alkanals, is a photoactive molecule and can undergo the following transformations:[7,13]

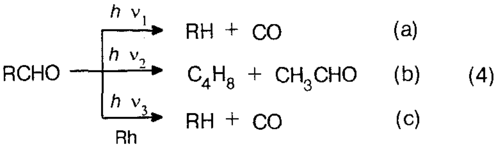
a) decarbonylation to give CO and the initial alkane;

b) radical reactions which give rise to hexanol, ethylcyclobutanol, decane, *etc.*;

c) Norrish type II cleavage with the formation of butene and acetaldehyde;

d) photocatalytic decarbonylation reactions involving the rhodium complexes.

Since only butene-1 and acetaldehyde have been observed in the irradiation of hexanal in solution (at λ > 270 nm),[8] one may assume that only reactions a, b, and c may occur in the system:



$$RCHO \begin{cases} \xrightarrow{h\nu_1} RH + CO & (a) \\ \xrightarrow{h\nu_2} C_4H_8 + CH_3CHO & (b) \\ \xrightarrow[Rh]{h\nu_3} RH + CO & (c) \end{cases} \qquad (4)$$

The kinetics of the accumulation of hexanal in system **2** (n = 3) at p_{CO} of 60 and 300 Torr were studied in order to decide which of the above processes predominate in the system. As can be seen from Fig. 2, at p_{CO} = 60 Torr the kinetic curve rapidly flattens, and the concentration of the aldehyde remains practically constant in the course of the experiment. At the same time, at p_{CO} = 300 Torr the aldehyde concentration after 2 h reaches a value which is 3.2 times higher than that at 60 Torr. Further irradiation results in a fast decrease in the hexanal concentration.

Let us estimate the ratio of the rates of the photodecomposition of aldehyde $W_{4a}:W_{4b}:W_{4c} = \gamma:\beta:\gamma$ (where α, β, and γ are the ratios of the corresponding reactions) to the total rate of aldehyde photodecomposition. Let us make use of the simplicity of the kinetic curve at p_{CO} = 60 Torr (see Fig. 2, curve *1*), taking into account that at the steady-state plateau the rate of aldehyde formation (W_{01}) is equal to the total rate of its photodecomposition.

$$W_{01} = W_{4a} + W_{4b} + W_{4c} \qquad (5)$$

Neglecting the concentration of butene formed during the period τ_1 = 0.5 h before reaching the plateau, one can estimate β:

$$\beta = W_{4b}/(W_{4a} + W_{4b} + W_{4c}) = W_{4b}/W_{01} \approx$$
$$\approx [C_4H_8]_{\tau_2}/(\tau_2 - \tau_1) \cdot W_{01}.$$

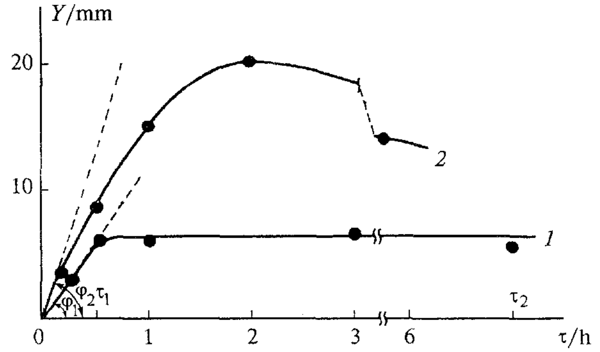


Fig. 2. Kinetic curves of aldehyde accumulation in system **2** (n = 3) at CO pressures of 60 (*1*) and 300 Torr (*2*). (For reaction conditions see Fig. 1).

Since after the period τ_2 = 7 h at p_{CO} = 60 Torr the concentration of butene in solution amounts to $(2.4\pm0.2) \cdot 10^{-2}$ mol L^{-1} and $W_{01} = 1.2 \cdot 10^{-2}$ mol L^{-1} h^{-1}, the value of β is 0.33±0.03.

In the absence of rhodium complexes in the solution, the photodecomposition of the aldehyde occurs only *via* reactions (4a) and (4b). By determining for any given moment the ratio of the concentrations of butene formed to aldehyde decomposed one obtains the value β = 0.27±0.04 and, hence, α = 0.73±0.10. These estimates lead to the conclusion that in the photocatalytic system **2** (n = 3) decomposition *via* reaction (4c) is insignificant, *i.e.*, γ = 0.

The increase in the yield of C_6-aldehyde with increasing partial pressure of CO could be related to the acceleration of reaction (2) due to high concentrations of CO and complex X in the solution. In order to fit the linear dependence of the rate of reaction (2) on p_{CO}, the initial rate of the process (W_0) has to increase fivefold as the p_{CO} increases from 60 to 300 Torr. However, as can be seen from Fig. 2, the initial rate of the process increases by only about 2 times. On the one hand, this may be related to the non-linear dependence of the quantum yield of the reaction (2) on the CO concentration.[8] On the other hand, it may be due to catalyst deactivation under the action of CO. The increase in the maximum concentration of aldehyde with the increase in CO pressure seems to be caused not only by the increase in the rate constant for the formation of aldehyde (reaction (2)), but also by the retardation of aldehyde photodecomposition (reaction (4)) .

The quantum yield of the photochemical decarbonylation of aldehyde (reaction (4a)) and that of the Norrish type II process (reaction (4b)) are independent of p_{CO}, and, therefore, these reactions should have no effect on the yield of aldehyde as p_{CO} increases. However, the action of CO and irradiation may generate rhodium complexes with higher extinction coefficients in the vicinity of λ = 300 nm (the maximum of aldehyde absorption) than those of the initial rhodium complexes. In this case, the intensity of the light absorbed by the

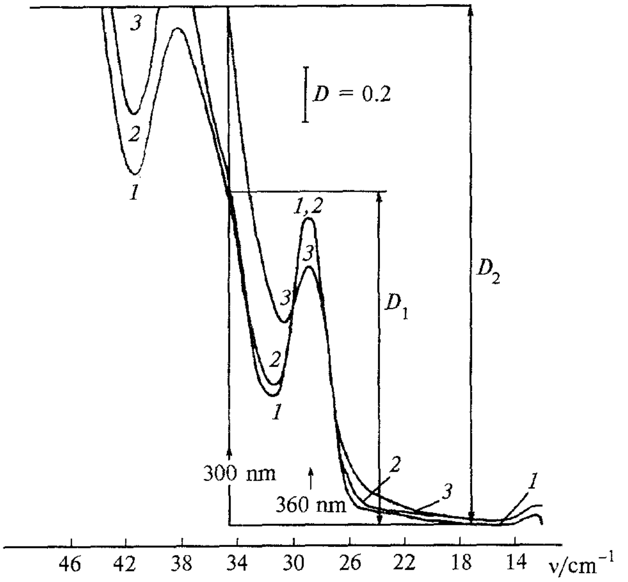


Fig. 3. Absorption spectra of solutions of system **2** (n = 3) before the introduction of CO (*1*), at p_{CO} = 300 Torr (*2*), and after 2 h of irradiation at p_{CO} = 300 Torr (*3*). (For reaction conditions see Fig. 1).

aldehyde in solution decreases (which implies the screening of decomposition), and thus reactions (4a) and (4b) may be retarded. We found that the screening effect of the photodecomposition does actually take place in this system.

Figure 3 shows the absorption spectra of system **2** (n = 3) recorded before irradiation in the absence of CO (curve *1*), at p_{CO} = 300 Torr (curve *2*), and after 2 h of irradiation at p_{CO} = 300 Torr (curve *3*). A comparison of these spectra shows that the introduction of CO produces only a slight increase in the absorption at λ = 300 nm. However, the absorption increases after the beginning of the irradiation (spectrum *3*) due to the formation of rhodium complexes. At p_{CO} = 60 Torr and further irradiation of this mixture for 1 h the optical density at λ = 300 nm remains practically unaffected.

Since the extinction coefficient of the aldehyde (ε_a = 22 L mol^{-1} cm^{-1}) is much lower than those of the rhodium complexes (10^4 L mol^{-1}cm^{-1}), the fraction of light absorbed by the aldehyde is proportional to its concentration:

$$I^{a}_{abs} = \frac{D_a}{D_a + \Sigma D_{Rh_i}} \cdot I^{0}_{abs} \approx \frac{\varepsilon_a \, l \, I^{0}_{abs}}{D} \cdot [\mathrm{RCHO}], \qquad (6)$$

where I^a_{abs} is the total intensity of the light absorbed by the aldehyde and the rhodium complexes in a cuvette, l is the width of the cuvette, D_a and D_{Rh_i} are the optical densities of aldehyde and rhodium complexes; and D is the optical density of the solution measured at λ = 300 nm.

At the maximum point of the kinetic curve (Fig. 2, curve *2*) and on the plateau (Fig. 2, curve *1*) the rate of aldehyde formation is equal to the overall rate of its photodecomposition. Therefore, $\gamma = 0$, *i.e.*, $W_{4c} = 0$.

$$W_{01} = W_{4a} + W_{4b} + W_{4c} = (\phi_{4a} + \phi_{4b}) \cdot I^{a}_{abs}, \qquad (7)$$

where ϕ_i and W_i are the quantum yields and reaction rates of the decomposition of aldehyde due to irradiation (see reaction (4)).

On the basis of Eqs. (6) and (7), one can easily obtain the ratio of the maximum aldehyde concentrations at p_{CO} = 60 Torr ([RCHO]$_1$) and 300 Torr ([RCHO]$_2$):

$$[\mathrm{RCHO}]_2/[\mathrm{RCHO}]_1 = (W_{02}/W_{01})(D_2/D_1), \qquad (8)$$

where W_{01} and D_1 are the initial rate of aldehyde formation and the optical density of the mixture at λ = 300 nm after its irradiation at p_{CO} = 60 Torr, and W_{02} and D_2 correspond to the analogous values at 300 Torr. From the data presented in Figs. 2 and 3 it follows that [RCHO]$_2$/[RCHO]$_1$ = 3.2, D_2/D_1 = 1.5, and W_{02}/W_{01} = 2.1.

It should be noted that the model considered here does not take into account the fact that the system was irradiated not by monochromatic light with λ = 300 nm, but by the set of lines with λ > 270 nm emitted by a high-pressure mercury lamp. However, since only three closely-spaced lines of the mercury lamp (298, 303, and 313 nm) overlap with the $n \rightarrow \pi^*$ absorption band of hexanal, one may assume that this heterogeneity only very slightly affects the result obtained. The decrease in the rate of the aldehyde formation due to the decomposition of the catalyst (reaction (3)) at the CO pressure of 300 Torr is more significant. Since the rate of aldehyde accumulation (Fig. 2, curve *2*) decreases after only 10 min of irradiation, the value of W_{02}/W_{01} = 2.1 found is related to the rate of aldehyde decomposition at the maximum point. Therefore, the initial rate of aldehyde formation at 300 Torr is greater than that calculated from Eq. (8): $W_{02} > 2.1 \cdot W_{01}$; $W_{02} = 2.5 \cdot 10^{-2}$ mol (L h)$^{-1}$. It should be mentioned that the experimental value corresponding to the first point of the kinetic curve is $2.3 \cdot 10^{-2}$ mol (L h)$^{-1}$, which attests to the noticeable deactivation of the catalytic system from the very beginning of the irradiation.

Thus, the increase in the maximum yield of the aldehyde with increasing CO pressure is related both to the enhancement of the initial rate of aldehyde formation and to the retardation of the rate of its photodecomposition. Norrish type II fragmentation and photodecarbonylation are the main directions of photodecomposition in the system. Photodecarbonylation involving the rhodium complexes (the reverse reaction (2)) is not observed. At pressures higher than 300 Torr the value of the maximum yield is largely due to the fast deactivation of the photocatalytic system.

The dependence of the maximum yield of the aldehyde on the concentrations of PMe_3 and CO is very complicated. The value of the maximum yield is determined by the rates of at least three processes, which may also depend non-linearly on the overall concentration of rhodium ($[Rh]_0$). Thus, decreasing in $[Rh]_0$ from 10^{-3} to $2 \cdot 10^{-4}$ mol L^{-1} (n = 3, p_{CO} = 300 Torr) brings about a 3.1-fold decrease in the aldehyde yield in 1 hour. Increasing $[Rh]_0$ beyond $1.5 \cdot 10^{-3}$ mol L^{-1} brings about the precipitation of a part of the rhodium (in the form of a white deposit) as the solution is subjected to freezing in the course of the degassing which proceeds the experiment, but does not increase the yield of the aldehyde. Increasing $[PMe_3]$ in the solution to $6 \cdot 10^{-3}$ mol L^{-1} also results in the formation of a precipitate when system **2** is stored in the dark under argon for several hours.

Since the rates of reactions (2)—(4) depend on the spectral composition of the absorbed light and its intensity, one may assume that changing these factors would increase the yield of the aldehyde. Actually, the irradiation of system **2** (n = 3, p_{CO} = 60 Torr) by monochromatic light at 365 nm for 0.5 h results in the complete disappearance of the band at 360 nm in the UV spectrum of the solution, and the aldehyde is not formed in this process. Further irradiation of this solution at $\lambda > 270$ nm results in a twofold increase in the yield of the aldehyde as compared with that in the control experiment without preliminary monochromatic irradiation. Approximately the same increase in the yield is observed when visible light with $\lambda > 400$ nm is excluded from the spectrum of the absorbed irradiation (using filters BS-3+UVS-5), although the initial mixture and solution almost do not absorb in this spectral range.

These data indicate that the equilibrium between various rhodium complexes is changed by irradiation. The absence of absorption at 400 nm in the spectra (see Fig. 3) may be caused by low concentrations of the complexes, low extinction coefficients, or dark processes. For example, it has been established by the method of flash photolysis[14] that the alkyl hydride intermediate $RhCl(PMe_3)_2(R)(H)$ has an absorption band with a maximum at ~ 500 nm.

Thus, by varying the components and the light intensity in photocatalytic system **2** one can increase the rate of aldehyde formation dozens of times compared with the most active catalyst based on complex **1** (see Refs. 6, 8). The yield of the aldehyde in the system studied is determined by the effect of these factors both on the rate of the carbonylation of pentane and on the catalyst deactivation as well as on the rate of photodecomposition of the C_6-aldehyde formed.

The elaboration of new systems for the photocatalytic carbonylation of alkanes to aldehydes, which would be very active and/or capable of performing the process under the action of visible light, seems feasible. However, these systems interact efficiently with the intermediate species of the photocatalytic cycle; for example, they can undergo the reaction of oxidative addition to give acyl complexes.[15] Therefore, the accumulating aldehyde can, on the one hand, interact with the photocatalyst transforming it to its inactive form and, on the other hand, decompose upon UV irradiation, which restricts the observed maximum concentration of aldehyde.

A significant increase in the yield of the oxygen-containing products in the photocatalytic carbonylation of alkanes may be expected when the carbonylation of alkanes is coupled with the hydrogenation of the aldehydes formed to the corresponding alcohols, which are photochemically inert at $\lambda > 200$ nm and less prone to interact with the photocatalyst. Some data (see Refs. 5, 16—18) point to the feasibility of the reduction of aldehydes to alcohols in the presence of the chlorocarbonylphosphine complexes of rhodium.

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