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Formation of acetaldehyde via photocarbonylation of methane with CO

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Abstract—Direct photocarbonylation of methane to give acetaldehyde occurred when a mixture of methane and CO dissolved in benzene was subjected to UV irradiation at $\lambda < 290$ nm. The reaction was accelerated by rhodium $RhCl(CO)(PR_3)_2$ complexes, where R = alkyl, Ph, or OPh.
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CO insertion into the C–H bonds of hydrocarbon chains is a very simple method for the synthesis of aldehydes. Investigation of this reaction in the presence of Vaska type rhodium complexes of general formula $RhCl(CO)(PR_3)_2$ (R = alkyl, aryl) resulted in aldehyde formation when benzene, long-chain alkanes and cyclic alkanes were irradiated with UV light of a wavelength greater than 300 nm.[1]

In the case of methane, direct carbonylation to acetaldehyde under normal pressure occurs as follows (reaction 1):

$$CH_4 + CO \rightarrow CH_3CHO \qquad (1)$$

It is thermodynamically unfavourable—the Gibbs free energy of the reaction is close to ~15 kcal/mol. As the calculation indicates, the reaction occurs efficiently under a pressure of about 4000 atm. Indeed, under these conditions, acetaldehyde was obtained in the presence of titanocene catalysts (6.5×10^{-3} mol/mol Ti).[2,3]

Herein, we report methane carbonylation with CO to give acetaldehyde, when a mixture of methane and CO dissolved in benzene was irradiated with UV light of a wavelength shorter than 290 nm at ambient temperature under atmospheric pressure. The reaction was acceler-

ated by the Vaska type rhodium complexes mentioned above.

The reaction was carried out in a Quartz reactor filled with a stirred benzene solution saturated with CO and CH_4 (10 ml) via irradiation through the reactor wall with a high pressure mercury lamp HOK 400 W—Phillips. In this way, UV light of the whole spectrum was introduced to the reaction mixture.

After running the reaction for 4 h, 0.014 mmol of acetaldehyde was obtained (Table 1). This establishes a 0.4% quantum yield, 0.4% methane conversion and 3.9% conversion of CO (27 mmol of CH_4 and 3.5 mmol of CO dissolved in 10 ml of benzene).[4] Beside acetaldehyde, a trace of benzaldehyde, as the product of benzene carbonylation, was present in the post reaction mixture.

To determine which UV light wavelength was responsible for methane carbonylation, the reaction was carried out in a Pyrex glass reactor transmitting only UV wavelengths longer than 290 nm.[1,5] No reaction occurred under these conditions.

To ascertain which irradiation wavelength supports the carbonylation in the presence of Vaska type rhodium complex catalysis, the reaction was carried out in Pyrex and Quartz wall reactors. In the former case, when the irradiation wavelength was longer than 290 nm, only benzaldehyde was formed. The largest yield was obtained for complexes containing alkylphosphines as

Table 1. The photocatalyzed carbonylation of methane and benzene in the presence of $RhCl(CO)(phosphine)_2$

Phosphine	PMe_3		$P(iPr)_3$		PBu_3		PCy_3		PPh_3		$P(OPh)_3$		—[a]
λ_{UV} (nm)	>290	OS[b]	>290	OS	>290	OS	>290	OS	>290	OS	>290	OS	OS
PhCHO (mmol)	0.08	0.16	0.04	0.13	0.03	0.12	0.02	0.09	0.002	0.02	—	0.01	Trace
MeCHO (mmol)	—	0.24	—	0.29	—	0.28	—	0.93	—	0.47	—	0.33	0.14
$MeCHO_{Rh}$[c] (mmol)	—	0.11	—	0.15	—	0.14	—	0.79	—	0.33	—	0.19	—
TON_{Rh}[d]	—	15	—	22	—	21	—	113	—	48	—	28	—

0.007 mmol Rh, $CO/CH_4 = 1:8$ (saturated solution in benzene); benzene—10 cm^3; 20 °C; 4 h; Mercury lamp: HOK-400 W—Phillips; Me = methyl, iPr = isopropyl, Bu—butyl, Cy—cyclohexyl; Ph—phenyl, PhCHO–benzaldehyde; MeCHO—acetaldehyde.
[a] Non-catalyzed reaction.
[b] OS—whole UV spectrum—reaction carried out in a Quartz reactor.
[c] Amount of MeCHO in the catalyzed reaction.
[d] Number of the catalytic acts at one Rh-atom in the catalyzed reaction.

ligands. From these complexes, the best result, 0.08 mmol of PhCHO, was obtained in the presence of $RhCl(CO)(PMe_3)_2$.

When the reactions were carried out in a Quartz reactor transmitting the whole UV light range, acetaldehyde and benzaldehyde were synthesized in higher yields than when the reaction was run in the absence of the Vaska type complexes or when the radiation wavelength was longer than 290 nm (Table 1).

The situation when carbonylations are running simultaneously is typical of photoactivation. Investigation of benzene and long-chain alkane carbonylations, indicated that they proceeded independently and that there was even a positive synergic effect on the yield.[1]

Again, the largest amount of benzaldehyde, 0.16 mmol, was obtained in the presence of $RhCl(CO)(PMe_3)_2$.

The largest quantities of acetaldehyde were obtained in the presence of complexes containing bulky phosphines: PCy_3, PPh_3 and $P(OPh)_3 = 0.93$, 0.47 and 0.33 mmol, respectively (Table 1). This indicates that the rhodium complexes accelerate methane carbonylation.

It is reasonable to state that the values mentioned above are sums resulting from both accelerated and non-accelerated reactions. Taking into consideration the latter, the greatest quantities of acetaldehyde obtained were:

0.79, 0.33 and 0.19 mmol, respectively. Since 0.007 mmol of the rhodium catalyst was used, the TON of the reaction accelerated by $RhCl(CO)(PCy_3)_2$ is greater than 100.

The efficiency of the acceleration resulted in a 1.2% quantum yield and methane and carbon oxide conversions equal to 3.7% and 21%, respectively.

As mentioned above, under normal pressure, methane cannot be carbonylated with CO directly to acetaldehyde. Here, the reactions investigated must proceed via formation of an unknown intermediate when methane and carbon monoxide are irradiated with UV light of a wavelength shorter than 290 nm. It is known that methane forms carbene–CH_2 and hydrogen radicals, when irradiated with UV light of a wavelength equal to 147 nm (reaction 2):[5]

$$\lambda = 147 \text{ nm}$$
$$CH_4 \rightarrow {:}CH_2 + 2H^{\cdot} \tag{2}$$

The UB3LYP/aug-cc-pVQZ and UMP2/aug-cc-pVTZ calculations on the possible transformation of $:CH_2$ to acetaldehyde (Table 2), show that the most probable reaction pathway involves a ketene which is subsequently hydrogenated by the hydrogen radicals liberated in reaction 2, to give acetaldehyde (Table 2, reactions 3 and 4):

Table 2. Free Gibbs energies (G_{298}, 298.15 K, 1 atm, Hartree) of the used substrates and free Gibbs energies (ΔG_{298}^R, 298.15 K, 1 atm, kcal/mol) of postulated reactions, calculated using different computational levels, respectively

Molecule/reaction	UB3LYP/aug-cc-pVQZ	UMP2/aug-cc-pVTZ
H(D)	−0.513046	−0.510475
H_2(S)	−1.181969	−1.166205
CO(S)	−113.381278	−113.156745
CH_2(T)	−39.173300	−39.058268
CH_4(S)	−40.514355	−40.386372
CH_2CO(T)	−152.588247	−152.133588
CH_3CHO(S)	−153.877413	−153.523295
$CH_4(S) + CO(S) \rightarrow CH_3CHO(S)$	11.4	12.4
$CH_4(S) \rightarrow (CH_2(T) + 2H(D))$	197.6	192.7
$(CO(S) + CH_2(T)) \rightarrow CH_2CO(T)$	−21.1	−11.7
$CH_2CO(T) + 2H(D) \rightarrow CH_3CHO(S)$	−165.1	−168.6
$(CH_2CO(S) + H_2(S)) \rightarrow CH_3CHO(S)$	−23.4	−19.1

S, D, T stand for singlet, doublet, and triplet states, respectively.

$$:CH_2 + CO \rightarrow CH_2{=}C{=}O \qquad (3)$$

$$CH_2{=}C{=}O + 2H^{\cdot} \rightarrow CH_3CHO \qquad (4)$$
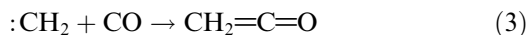
The negative values of the Gibbs free enthalpy calculated for reactions 2 and 3 (Table 2) indicate, that the reactions proceed spontaneously under the experimental conditions.

Since the Vaska type rhodium complexes absorb UV light at 365 nm,[6–8] they dissociate into unsaturated three-coordinated $RhCl(PR_3)_2$ complexes (reaction 5):

$$\lambda = 365 \text{ nm}$$
$$RhCl(CO)(PR_3)_2 \rightarrow RhCl(PR_3)_2 + CO \qquad (5)$$
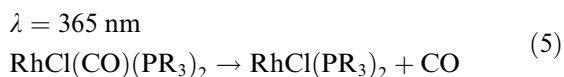
which are very active species and probably they also accelerate reactions 3 and 4.

The calculated energy for reaction 2 is ca. 190 kcal/mol, which corresponds to 145 nm wavelength energy. This is in very good agreement with the literature data. As we mentioned above, the UV light of this wavelength splits methane to methyl carbene and two hydrogen radicals.[5]

Thus we conclude that methane can be carbonylated to acetaldehyde when a CH_4 and CO saturated solution of benzene is irradiated with UV light of a wavelength of 145 nm. The reaction can be accelerated by $RhCl(CO)(PR_3)_2$ rhodium Vaska type complexes. The best result was obtained in the presence of the $RhCl(CO)(PCy_3)_2$ complex.

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