

# Oxidative carbonylation of methane in the presence of Rh complexes in aqueous acetic acid

Evgeniy G. Chepaikin, Grigoriy N. Boyko, Anna P. Bezruchenko, Alla A. Leshcheva, Eduard H. Grigoryan \*

*Institute of Structural Macrokinetics, Russian Academy of Sciences, Chernogolovka, Moscow Region, 142432, Russia*

Received 20 December 1996; accepted 21 June 1997

## Abstract

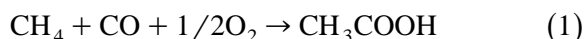
The formation of acetic acid by the oxidative carbonylation of methane in the presence of a  $\text{RhCl}_3\text{-DCl-KI}$  catalytic system is strongly accelerated when an aqueous medium is substituted by an aqueous–acetic one. © 1998 Elsevier Science B.V.

*Keywords:* Methane; Oxidative carbonylation; Rhodium complexes; Acetic acid; Methyl acetate

## 1. Introduction

Direct synthesis of oxygen containing organic products from methane with no reforming and methanol formation stages is a fundamental problem [1–3]. The most interesting is the functionalization of methane through carbonylation. A thermodynamic restriction for this reaction ( $\Delta G_{298}^0 = 13.1$  kcal/mol) can be eliminated by a few thousands atmospheres pressure increase [4], or by using light energy in a photocatalytic process [5,6], or by adding a third reagent into the reaction of methane addition to carbon monoxide [2,4]. This approach was first applied for preparing methylethylketone from  $\text{CH}_4$ ,  $\text{CO}$ ,

and  $\text{C}_2\text{H}_4$  [2,4]. The oxidative carbonylation of methane with the formation of acetic acid



is the most preferable in terms of thermodynamics.

Fujiwara et al. [7] prepared acetic acid according to Eq. (1) in the presence of Pd and Cu salts in a trifluoroacetic acid–perfluorohexane mixture with 4.1 mol/mol Pd yield for 40 h at 80°C and general pressure equal to 5 MPa. Lin and Sen developed a catalytic system for oxidative carbonylation of methane in aqueous medium which contained  $\text{RhCl}_3\text{-HCl-HI(KI)}$  [8]. However the activity of this system was also found to be rather low. The yield of the acid was 28 mol/mol Rh for 420 h at 95°C and

\* Corresponding author. Tel.: +7-95-9628006; fax: +7-95-9628040; e-mail: eduard@icp.ac.ru

CH<sub>4</sub>:CO:O<sub>2</sub> pressure equal to 7:1.05:0.35 (MPa). It was shown that methanol was not carbonylated under experimental conditions, but was oxidized to formic acid. Thus in spite of that the system resembles the catalytic one for methanol carbonylation (Monsanto process) [9], the mechanisms of their actions essentially differ from each other. One could suggest that the difference is caused by a specific effect of a solvent and the presence of oxygen in the system, however the role of HI being not clarified in oxidative carbonylation of methane.

Carbonylation is essentially accelerated when aqueous media are substituted by aqueous–organic ones, and in particular, by aqueous–acetic media [10–12]. Acetic acid is a specific solvent used in other homogeneous catalytic reactions [13]. The role of acetic acid as a specific solvent is the most clearly pronounced in carbonylation of ethylene when mechanisms of catalyst action are changed [12]. Acetic acid is also one of the most suitable solvents in reactions of alkanes with metal complexes. For example, the utilization of CH<sub>3</sub>COOD in H–D exchange of methane did not result in a noticeable reactivity of its methyl group [1].

This paper reports the study of the oxidative carbonylation of methane in the presence of the RhCl<sub>3</sub>–DCl–KI(DI) catalytic system in aqueous acetic acid.

## 2. Experimental

The use of deuterated reagents (CD<sub>3</sub>COOD, D<sub>2</sub>O, 99 at% D; DCl, DBr, 99.5 at% D) enabled us to analyze the products by <sup>1</sup>H NMR spectroscopy. The experiments were carried out in a stainless steel autoclave of 50 cm<sup>3</sup> volume. The components of the catalytic system were put together with the solvent (2.5 ml) into a glass liner which, in turn, was put into an autoclave. Then the autoclave was filled with gaseous reagents after air removal. The partial pressures were (MPa): CH<sub>4</sub> (6), CO (1.6), and O<sub>2</sub> (0.4). The autoclave was thermostatically controlled,

Table 1  
Dependence of the yields of products in the oxidative carbonylation of methane versus time

τ (h)	Products (M · 10 <sup>2</sup> )				
	CH <sub>3</sub> COOD	CD <sub>3</sub> COOCH <sub>3</sub>	HCOOD	CH <sub>3</sub> OH	Σ
4.5	1.1	0.4	—	—	1.5
7.0	3.5	1.2	—	—	4.7
12.0	6.3	2.0	1.0	0.1	9.4
16.0	9.0	3.2	2.8	0.3	15.3
20.0	12.0	3.2	2.7	0.3	18.2
24.0	15.0	3.3	2.8	0.3	21.4

95°C, P<sub>Σ</sub> = 8 MPa (20°C), CH<sub>4</sub>:CO:O<sub>2</sub> = 1.5:0.4:0.1, [RhCl<sub>3</sub>] = 1.5 · 10<sup>-2</sup> M, [KI] = 2.5 · 10 M, [DCl] = 0.12 M, 0.5 ml D<sub>2</sub>O, 2 ml CD<sub>3</sub>COOD.

the reaction mixture was stirred with a magnetic stirrer. After cooling and venting, the reaction mixture was examined by <sup>1</sup>H NMR spectroscopy. The data in Table 1 were generated by running a reaction for a certain time period, depressurizing, analyzing the reaction mixture, adding it back to the autoclave, and resuming the reaction for the next time period.

<sup>1</sup>H NMR spectra were recorded on a BS 587A (80 MHz) TESLA spectrometer using the signals from the residual protons of CD<sub>2</sub>H-groups of the solvent, namely, D<sub>4</sub>-acetic acid as internal standards for reading <sup>1</sup>H chemical shifts and the determination of concentrations of products in the reaction mixture. The application of such a method became possible after we confirmed that there is no noticeable H–D exchange in the methyl group of CH<sub>3</sub>COOD under the experimental conditions. The accuracy of the determination of concentrations is about 10%.

## 3. Results and discussion

Fig. 1 shows a typical <sup>1</sup>H NMR spectrum for the catalytic solution after the reaction. It is obvious that the method enables a quite reliable identification and quantitative determination of reaction products. Table 1 shows the data on the accumulation of the products of CH<sub>4</sub>, CO, and O<sub>2</sub> interaction in the RhCl<sub>3</sub>–DCl–KI system in

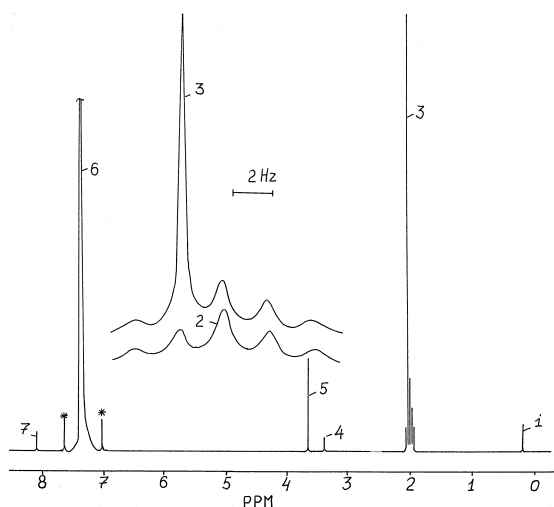


Fig. 1.  $^1\text{H}$  NMR spectra of the reaction solution (16 h, see Table 1) and acetic acid- $\text{D}_4$  as solvent.  $\delta$ , ppm: 1. 0.17 (s,  $\text{CH}_4$ ); 2. 2.05 (quin,  $\text{CHD}_2\text{COOD}$ , imp. in acetic acid- $\text{D}_4$ ); 3. 2.07 (s,  $\text{CH}_3\text{COOD}$ ) and 2; 4. 3.40 (s,  $\text{CH}_3\text{OD}$ ); 5. 3.66 (s,  $\text{CD}_3\text{COOCH}_3$ ); 6.  $\sim 7.36$  (s,  $\text{HOD}$ ,  $\text{HCl}$ ,  $\text{CD}_3\text{COOH}$ ); 7. 8.21 (s,  $\text{HCOOD}$ ).

$\text{CD}_3\text{COOD}-\text{D}_2\text{O}$  medium with time. In addition to the main product, acetic acid ( $\text{CH}_3\text{COOD}$ ), methyl acetate ( $\text{CD}_3\text{COOCH}_3$ ), methanol ( $\text{CH}_3\text{OD}$ ), and formic acid ( $\text{HCOOD}$ ) are formed. The yield of acetic acid is 10 mol/mol Rh, and the total yield of the useful products from methane amounts to 14 mol/mol Rh under these conditions. Therefore the activity of the  $\text{RhCl}_3-\text{DCI}-\text{KI}$  catalytic system is 5–6 times higher in aqueous acetic acid than in aqueous solution. It is seen in Table 2 that oxidative carbonylation of methane by Rh com-

plexes is observed only in the simultaneous presence of DCI and DI. One finds the traces of methyl acetate ( $\text{CD}_3\text{COOCH}_3$ ) in only DCI or DBr containing systems, and the presence of DI with the same concentration results in the traces of methyl iodide ( $\text{CH}_3\text{I}$ ). It is found that  $\text{Br}^-$  inhibits the reaction probably due to the stability of Rh bromocarbonyl complexes.

Special experiments were carried out which enabled the conclusion that the interaction of methanol (0.02 M) or methyl iodide (0.02 M) with the  $\text{RhCl}_3-\text{DCI}-\text{KI}$  system at  $95^\circ\text{C}$  in the presence of CO (1.6 MPa) does not result in the formation of acetic acid. Under these conditions methanol is converted to methyl acetate, and methyl iodide ( $\delta = 2.16$ , s) is converted to methyl chloride ( $\delta = 3.00$ , s). The presence of oxygen in the system does not affect the behaviour of methanol.

Therefore methanol, methyl iodide, and methyl acetate cannot be the intermediates in Eq. (1) and its mechanism strongly differs from that of the carbonylation of methanol in the Monsanto system [9]. In so doing, iodine compounds are very important, since no products of methane conversion are observed in their absence. It should be noted that an essential part of KI or DI introduced into the reaction, is converted to  $\text{I}_2$ . However, the substitution of oxygen for iodine (0.12 M) does not result in the formation of acetic acid. This is consistent with thermodynamic calculations. It is possible that oxidative carbonylation of methane in-

Table 2

Influence of the catalytic system composition on the oxidative carbonylation of methane

N	Components of the system (M)			Products ( $\text{M} \cdot 10^2$ )		
	DCI	DBr	KI(DI)	$\text{CH}_3\text{COOD}$	$\text{CD}_3\text{COOCH}_3$	$\text{CH}_3\text{I}$
1 <sup>a</sup>	0.24	—	0.025	0	0	0
2	0.24	—	—	0	< 0.01	
3 <sup>b</sup>	—	—	0.12	0	< 0.01	< 0.01
4	—	0.17	—	0	0	0
5	0.24	—	0.025	0.9	0.3	0
6	0.24	0.17	0.025	0.4	< 0.01	0

$95^\circ\text{C}$ ,  $P_{\Sigma} = 8$  MPa ( $20^\circ\text{C}$ ),  $\text{CH}_4:\text{CO}:\text{O}_2 = 1.5:0.4:0.1$ , 3 h,  $[\text{RhCl}_3] = 1.5 \cdot 10^{-2}$  M, 0.5 ml  $\text{D}_2\text{O}$ , 2 ml  $\text{CD}_3\text{COOD}$ .

<sup>a</sup>Without  $\text{RhCl}_3$ .

<sup>b</sup> $[\text{Rh}(\text{CO})_2\text{I}_2]^-$  instead of  $\text{RhCl}_3$ , DI instead of KI.

volves the products of oxygen, DI, and CO interaction, for example, DOI, according to a thermodynamically preferable reaction ( $\Delta G_{298}^0 \sim -5$  kcal/mol):



It should also be noted that the catalytic reaction of CO oxidation to  $\text{CO}_2$  proceeds intensely both in the presence and absence of methane. Since this process commonly proceeds with the intermediate formation of Rh(I) carbonyl complexes [14], one could easily suggest their formation with a certain concentration in the system under study. It is obvious that Rh(I) complexes activate the methane molecule which results in oxidative addition with the formation of the Rh– $\text{CH}_3$  bond. The Rh(III) methyl complex may be converted to the acyl one by the insertion of a CO molecule with following the isolation of acetic acid. Its interaction with the medium may result in the formation of methanol and formic acid.

Therefore the substitution of a certain share of  $\text{D}_2\text{O}$  by acetic acid in the  $\text{RhCl}_3$ – $\text{DCl}$ – $\text{KI}$ – $\text{D}_2\text{O}$  catalytic system results in a significant increase of the activity in the oxidative carbonylation of methane. A paper [15] which was published during the preparation of this paper for publication, reports that the perfluorobutyric acid– $\text{H}_2\text{O}$  mixture was used as a solvent. The results published by the authors [15] are in good agreement with the data reported in the present paper.

## Acknowledgements

The research described in this publication was made possible in part by Award No. RC2-146 U.S. Civilian Research and Development Foundation for the Independent States of the Former Soviet Union (CRDF) and Award No. 96-03-33950a from the Russian Foundation for Basic Research.

## References

- [1] A.E. Shilov, Activation of Saturated Hydrocarbons by Transition Metal Complexes, D. Reidel, Dordrecht, 1984, p. 203.
- [2] E.H. Grigoryan, Usp. Khim. (Russ.) 53 (1984) 347.
- [3] R.H. Crabtree, Chem. Rev. 95 (1995) 987.
- [4] N.S. Enikolopyan, G.N. Menchikova, E.H. Grigoryan, Dokl. Akad. Nauk. SSSR (Russ.) 291 (1986) 11.
- [5] T. Sakakura, T. Sodeyama, K. Sasaki, K. Wada, M. Tanaka, J. Am. Chem. Soc. 112 (1990) 7221.
- [6] N.K. Khannanov, G.N. Menchikova, E.H. Grigoryan, Mendeleev Commun., (1994) 39.
- [7] M. Kurioka, K. Nakata, T. Jintoku, Y. Taniguchi, K. Takaki, Y. Fujiwara, Chem. Lett., (1995) 244.
- [8] M. Lin, A. Sen, Nature 368 (1994) 613.
- [9] D. Forster, Ann. N.Y. Acad. Sci. 295 (1977) 79.
- [10] E.C. Baker, D.E. Hendriksen, R. Eisenberg, J. Am. Chem. Soc. 102 (1980) 1020.
- [11] T.C. Singleton, L.J. Prince, D. Forster, Prepr. Div. Pet. Chem. Am. Chem. Soc. 24 (1979) 329.
- [12] E.G. Chepaikin, A.P. Bezruchenko, A.A. Leshcheva, G.N. Boyko, Russ. Chem. Bull. 43 (1994) 360.
- [13] I.I. Moiseev,  $\pi$ -Compleksi v zhidkofaznom okislenii olefinov, ( $\pi$ -Complexes in the liquid phase oxidation of olefines), Nauka, Moscow, 1970, p. 240.
- [14] B.R. James, G.Z. Rempel, J. Chem. Soc. A 1 (1968) 78.
- [15] M. Lin, T.E. Hogan, A. Sen, J. Am. Chem. Soc. 118 (1996) 4574.