

# Mechanistic study on dehydrogenation of methanol with $[\text{RuCl}_2(\text{PR}_3)_3]$ -type catalyst in homogeneous solutions

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## Abstract

Catalytic dehydrogenation of methanol has been investigated in homogeneous solutions with a series of Ru(II) complexes,  $[\text{RuCl}_2(\text{P}(p\text{-C}_6\text{H}_4\text{X})_3)_3]$  ( $\text{X} = \text{H}$  (1), Me (2), F (3), OMe (4)) and  $[\text{RuCl}_2(\text{PMePh}_2)_3]$  (5). In the gas phase, hydrogen was formed selectively (> 99.5%), and formaldehyde, methylal (formaldehyde dimethyl acetal) and methyl formate were found in the liquid phase with satisfactory stoichiometry to the formed hydrogen. The reaction was retarded by the extra addition of free phosphine, suggesting the presence of pre-equilibrium dissociation of phosphine ligand. Kinetic analyses from this viewpoint explained well the dependence of rate on the concentration of catalyst (saturation curve). The order of evaluated pre-equilibrium constant ( $1 \approx 2 > 5$ ) is in accord with the general idea that the dissociation of phosphine ligand is controlled principally by steric bulk of ligands. The order of rate ( $3 > 1 > 2 > 4$ ) for 1–4, possessing the same cone angle of phosphine ligand, correlated clearly with basicity of phosphines. The results are interpreted in terms of the mechanism of rate-determining  $\beta$ -hydrogen abstraction via the Ru–OCH<sub>3</sub> intermediate.

**Keywords:** Ruthenium; Methanol; Dehydrogenation; Phosphine-derivative complexes; Ligand effect

## 1. Introduction

It is well known that Ru(II) complexes are particularly catalytically active for dehydrogenation of methanol to give H<sub>2</sub> and dehydrogenated product(s) (HCHO, H<sub>2</sub>C(OMe)<sub>2</sub>, HCO<sub>2</sub>Me) [1–4]. The catalysts include a very common  $[\text{RuCl}_2(\text{PPh}_3)_3]$  [1], and some complexes of other metal species are reported to be catalytically-active thermally [4] or under pho-

toirradiation [5–7]. In this reaction, formation of coordinatively unsaturated species is considered to be important. For example,  $[\text{RuH}_4(\text{PPh}_3)_3]$  and  $[\text{RuH}_2(\text{N}_2)(\text{PPh}_3)_3]$  are efficient catalysts, which have good leaving groups (H<sub>2</sub> and N<sub>2</sub>, respectively) [4]. For  $[\text{Ru}(\text{OCOME})\text{Cl}(\text{PR}_3)_3]$ , formation of a vacant site by bidentate to monodentate rearrangement of acetate ligand was suggested [3].

When Sn(II) ligand is introduced into Ru(II) complex, acetic acid (and/or methyl acetate) was found to be obtainable as a dehydrogenated product [8–11], which can formally be produced through the isomerization of methyl formate [12]. In this unique reaction, the first step to

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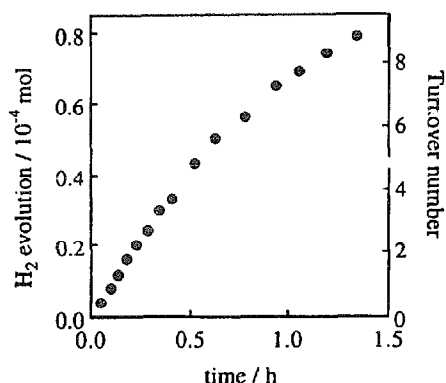


Fig. 1. Time course for the hydrogen evolution with **1** used as catalyst ( $[1] = 0.045$  mM).

dehydrogenate methanol to produce formaldehyde is considered to be slowest in the overall process [9].

Thus, in order to elucidate the factors affecting the methanol dehydrogenation in more detail, we studied here the kinetics and ligand effect using a series of Ru(II) complexes,  $[\text{RuCl}_2(\text{P}(p\text{-C}_6\text{H}_4\text{X})_3)_3]$  ( $\text{X} = \text{H}$  (**1**), Me (**2**), F (**3**), OMe (**4**)) and  $[\text{RuCl}_2(\text{PMePh}_2)_3]$  (**5**).

## 2. Results and discussion

Fig. 1 is a representative time course for the reaction with **1** as monitored by  $\text{H}_2$  evolution. The evolved gas was exclusively  $\text{H}_2$ , and the amounts of other gaseous products such as  $\text{CO}$ ,  $\text{CO}_2$  and  $\text{CH}_4$  were negligibly small ( $\text{CO} < 0.3\%$ ,  $\text{CO}_2 < 0.2\%$  and  $\text{CH}_4 < 0.004\%$ ). Turnover numbers are calculated from the amount (mole) of  $\text{H}_2$  formed divided by the charged amount (mole) of Ru(II) complex. Ini-

tial turnover rates were obtained from the initial linear slopes below a catalyst turnover number of 3.0. In the liquid phase, formaldehyde, methylal (formaldehyde dimethyl acetal) and methyl formate were found, which would be formed according the following reactions [9,13].

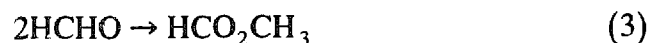
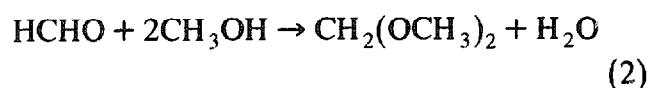
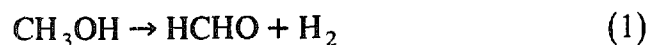


Table 1 shows the amounts of hydrogen and dehydrogenated products in the liquid phase, which were formed until catalyst deactivation became noticeable. Herein the concentrations of catalysts were chosen to be as high as possible to obtain greater amounts of products. It is obvious from Table 1 that in every case there is satisfactory stoichiometry between them.

### 2.1. Dependence of the rate on the concentration of added tertiary phosphines

It was found that the reactions with  $[\text{RuCl}_2(\text{P}(\text{C}_6\text{H}_5)_3)_3]$  (**1**),  $[\text{RuCl}_2(\text{P}(p\text{-C}_6\text{H}_4\text{Me})_3)_3]$  (**2**) and  $[\text{RuCl}_2(\text{PMePh}_2)_3]$  (**5**) were retarded by extra addition of  $\text{P}(\text{C}_6\text{H}_5)_3$ ,  $\text{P}(p\text{-C}_6\text{H}_4\text{Me})_3$  and  $\text{PMePh}_2$ , respectively. When the reciprocal of the initial rate ( $R$ ) was plotted as a function of the concentration of added phosphine, linear dependence was observed with a slight deviation in the region of low concentration (Fig. 2a, b and c).

Rate retardation by the extra addition of free ligand suggests that the catalytically active

Table 1  
Amounts of hydrogen and liquid-phase products formed in the dehydrogenation of methanol with catalysts 1–5

Catalyst	Concentration /mM	Reaction time /h	$\text{H}_2$ /mmol	Liquid-phase product/mmol			(I + II + 2 × III) /mmol
				HCHO (I)	$\text{CH}_2(\text{OCH}_3)_2$ (II)	$\text{HCO}_2\text{CH}_3$ (III)	
<b>1</b>	0.80	30	1.39	0.54	0.92	trace	1.46
<b>2</b>	0.65	99	1.42	0.48	0.40	0.22	1.32
<b>3</b>	0.35	72	0.72	trace	0.05	0.35	0.75
<b>4</b>	0.43	165	1.50	0.00	0.86	0.40	1.66
<b>5</b>	0.80	231	2.60	0.00	0.77	0.91	2.59

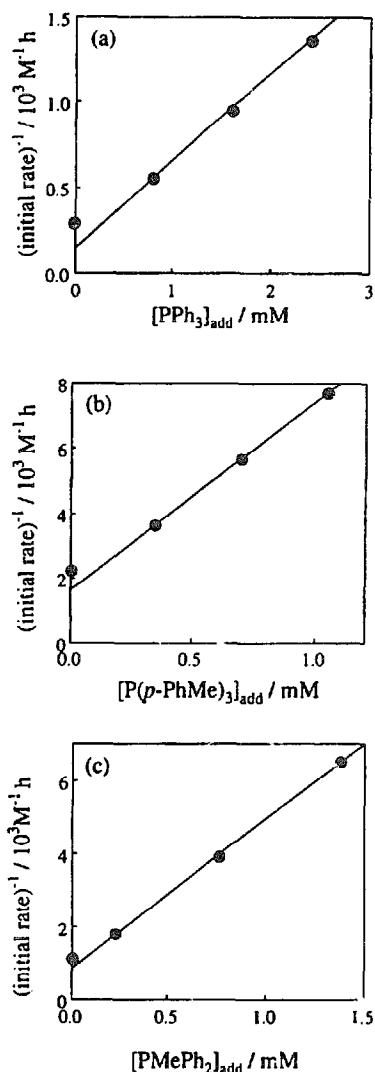
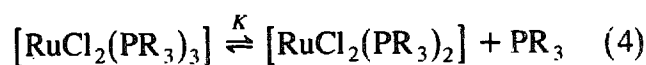


Fig. 2. Effect of the addition of free  $\text{PR}_3$  on the initial rate with (a) **1**, (b) **2** and (c) **5** used as catalysts.  $[\mathbf{1}] = 0.80$  mM,  $[\mathbf{2}] = 0.15$  mM,  $[\mathbf{5}] = 0.17$  mM.

species is formed by pre-equilibrium ligand dissociation (Eq. (4)).



If the rate of dehydrogenation is expressed as a second-order rate equation with respect to the  $[\text{RuCl}_2(\text{PR}_3)_2]$  formed and methanol, Eq. (5) is deduced.

$$R = k_2 [\text{RuCl}_2(\text{PR}_3)_2] [\text{MeOH}] = \frac{k_2 K [\text{Ru}]_0 [\text{MeOH}]}{K + [\text{PR}_3]} \quad (5)$$

where  $[\text{Ru}]_0$  is the concentration of the catalyst as charged ( $[\text{RuCl}_2(\text{PR}_3)_3] + [\text{RuCl}_2(\text{PR}_3)_2]$ ). Since the reactant methanol is present in excess (also acting as a solvent), a pseudo zero-order approximation would result for  $[\text{MeOH}]$  ( $k_2[\text{MeOH}] = k$ ). Hence Eq. (5) can be rearranged to give Eq. (6).

$$\frac{1}{R} = \frac{1}{k[\text{Ru}]_0} + \frac{[\text{PR}_3]}{kK[\text{Ru}]_0} \quad (6)$$

This equation accounts for the observed linear relationships between  $1/R$  and  $[\text{PR}_3]_{\text{added}}$  in the high-concentration region. The upward deviations in the low-concentration region would be due to the inherent contribution of the ligand dissociation to the total concentration of free ligand, which should become appreciable in this region. The values of  $k$  and  $K$  obtained by coupled use of intercepts and slopes in Fig. 2 are summarized in Table 2.

## 2.2. Dependence on the catalyst concentration

With **1**, **2** and **5** were used as catalyst, the catalyst concentration was varied between 0.045–0.80 mM (**1**), 0.022–0.285 mM (**2**) and 0.045–0.169 mM (**5**), respectively. The observed initial rate plotted as a function of the concentration of catalyst is given as circles in Fig. 3a, b and c. The observed tendency of saturation in the high concentration region seems to be in accord with the presence of equilibrium in Eq. (4), because the degree of dissociation would be lowered in this region.

The postulation above was verified quantitatively as follows. When no extra  $\text{PR}_3$  is added, the relation  $[[\text{RuCl}_2(\text{PR}_3)_2]] = [\text{PR}_3]$  results in

Table 2  
Evaluated values of equilibrium constant ( $K$ ) and rate constant ( $k$ )

Catalyst	$K/\text{M}$	$k/\text{h}^{-1}$
<b>1</b>	$2.9 \times 10^{-4}$	8.5
<b>2</b>	$2.8 \times 10^{-4}$	4.0
<b>5</b>	$2.0 \times 10^{-4}$	7.1

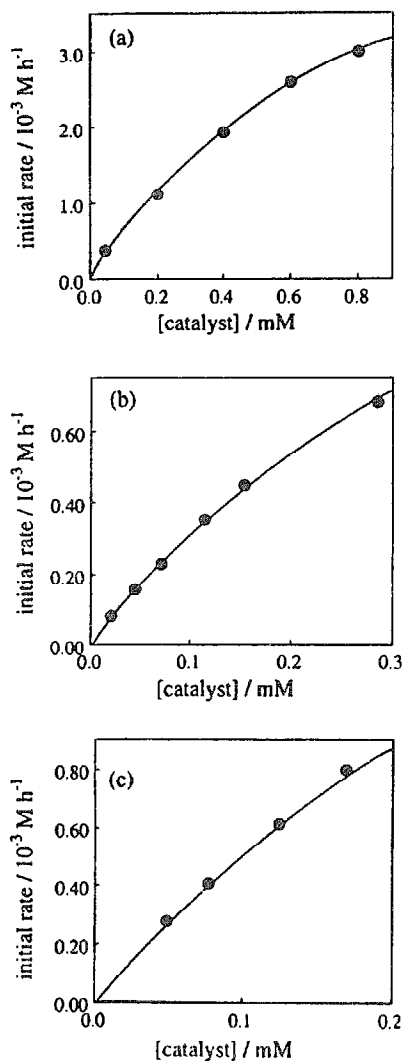


Fig. 3. Dependence of the initial rate on the concentration of catalyst. (a) 1, (b) 2, (c) 5.

Eq. (4). Hence, the concentration of  $[\text{RuCl}_2(\text{PR}_3)_2]$  is expressed as Eq. (7), and the rate as Eq. (8).

$$[\text{RuCl}_2(\text{PR}_3)_2] = \frac{1}{2} \left( \sqrt{K^2 + 4K[\text{Ru}]_0} - K \right) \quad (7)$$

$$R = \frac{k}{2} \left( \sqrt{K^2 + 4K[\text{Ru}]_0} - K \right) \quad (8)$$

By use of Eq. (8) together with the values of  $k$  and  $K$  in Table 2,  $R$  can be calculated as a function of  $[\text{Ru}]_0$ . In Fig. 3, the relationships based on this theoretical analysis are also given as solid lines. Coincidence of experimental and

theoretical values is evident, which supports the above postulation. A similar saturation curve was already pointed out for a different type of reaction with alcohols catalyzed by  $[\text{RuCl}_2(\text{PPh}_3)_3]$ , but was not analyzed quantitatively [14].

### 2.3. Mechanistic considerations

It has been recognized that an equilibrium for the dissociation of phosphine ligand from  $[\text{M}(\text{PR}_3)_n\text{L}_m]$  complex strongly depends on steric bulk of  $\text{PR}_3$  [15]. Taking into consideration this general trend, it seems reasonable that the values of  $K$  for 1 and 2 are close to each other (Table 2), because cone angle is common ( $\theta = 145^\circ$ ) for  $\text{P}(p\text{-C}_6\text{H}_5)_3$  and  $\text{P}(p\text{-C}_6\text{H}_4\text{Me})_3$ . The smaller cone angle of  $\text{PMePh}_2$  ( $\theta = 136^\circ$ ) would thus give a smaller value of  $K$  for 5.

Since 1–4 contain the phosphine ligand with the same cone angle ( $145^\circ$ ), the difference in the overall dehydrogenation rate may be caused by the process after the pre-equilibrium of Eq. (4). One of the plausible mechanisms for methanol dehydrogenation consists of three kinds of successive processes [16–19]: (1) coordination of methanol to the metal complex resulting in the formation of  $\text{M}-\text{OCH}_3$  intermediate, (2) formation of a hydride complex from the  $\text{M}-\text{OCH}_3$  intermediate via  $\beta$ -hydrogen abstraction, which liberates formaldehyde, and (3) decomposition of the hydride complex with  $\text{H}_2$  evolution, which regenerates the catalyst. Among the three, the second process seems to be rate-determining, because a lot of methoxy complexes are known [20] and stoichiometric formation of  $\text{H}_2$  by the reaction of hydride complex with protonic compound is common [21]. This view is supported by the deuterium isotope effect on the catalytic dehydrogenation of 2-propanol-2- $d_1$  with  $[\text{RuCl}(\text{SnCl}_3)_5]^{4-}$  [22], where the  $R_{\text{H}}/R_{\text{D}}$  value of 2.10 is claimed to be consistent with the rate-determining  $\beta$ -hydrogen abstraction.

Fig. 4 shows the plots of the common logarithm of initial rate ( $\log R$ ) for 1–4 vs.  $pK_a$

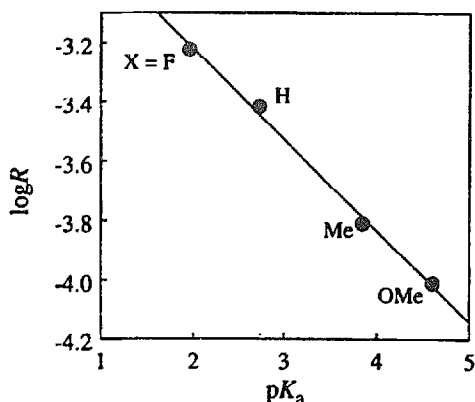


Fig. 4. Initial rate plotted as a function of  $pK_a$  of  $HP(p-C_6H_4X)_3^+$  for  $[RuCl_2(P(p-C_6H_4X)_3)_3]$  catalysts.

value of conjugated acid of phosphine ligand,  $HPR_3^+$ . Initial rates were determined here in the region of low catalyst concentration (0.045 mM), in which all the rates are approximately first-order with respect to the catalyst concentrations. It is obvious in Fig. 4 that the correlation is almost linear and the order of catalytic activity (3 (F) > 1 (H) > 2 (Me) > 4 (OMe)) is exactly the reverse of that for  $pK_a$  (OMe > Me > H > F), which is a good measure for the strength of  $\sigma$ -basicity of phosphine [23]. It is of interest that a similar plot against the Hammett  $\sigma_p$  value also gave a linear relationship (Fig. 5) [14,24].

The results in Figs. 4 and 5 indicate that the difference in the rate among 1–4 originates from the electronic effect of phosphine ligand, and that the rate-determining step could be analyzed in terms of the basicity (electron-donating

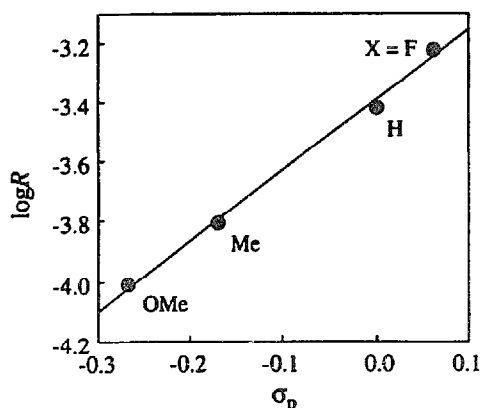


Fig. 5. Effect of substituent X in  $[RuCl_2(P(p-C_6H_4X)_3)_3]$  catalyst on the initial rate.

ability) of phosphine ligand. Thus, the least basic  $P(p-C_6H_4F)_3$  reduces most the electron density on Ru, which will facilitate the (electrophilic) interaction of Ru with  $\beta$ -hydrogen. The strength of this interaction is expected to decrease in the order of F (3) > H (1) > Me (2) > OMe (4). It is to be noted that the same order is also expected from the viewpoint of orbital interactions, since electron-withdrawing ligands are suggested to enhance the interaction between the vacant metal  $d$  orbital and the  $C-H^{\beta}$   $\sigma$  bond [25].

It may be possible to propose an alternative mechanism including a rate-determining oxidative addition of methanol [20]. However, this process would become more advantageous for the metal center with higher electron density [26–28]. For example, the second-order rate constant for oxidative addition of  $H_2$  to  $trans-[IrCl(CO)(P(p-C_6H_4X)_3)_2]$  (X = H, Me, OMe) was reported to increase in the order of H < Me < OMe [29], which is apparently opposite to the order observed here. In conclusion, the rate of methanol dehydrogenation would be accelerated by introducing (1) bulky ligand(s) to enhance the ligand dissociation, and (2) less electron-donating ligand(s) to promote the  $\beta$ -hydrogen abstraction.

### 3. Experimental

Preparations were made under an argon atmosphere using standard vacuum-manifold and Schlenk techniques. All reagents and solvents were of reagent grade. Light petroleum refers that fraction of b.p. 40–60°C.  $[RuCl_2(P(C_6H_5)_3)_3]$  was obtained according to the literature method [30].  $^{31}P\{^1H\}$  and  $^{19}F\{^1H\}$  NMR spectra were recorded on a JEOL JNM GX-270 spectrometer (109.3 MHz for  $^{31}P$  and 254.1 MHz for  $^{19}F$ ) at 25°C for saturated  $CH_2Cl_2$  solutions; chemical shifts are quoted relative to 85%  $H_3PO_4$  for  $^{31}P$  (0.0 ppm) and  $CF_3COOH$  for  $^{19}F$  (–78.5 ppm) as external

standards. Elemental analyses were conducted using a Yanaco MT-3 element analyzer.

### 3.1. Synthesis of $[RuCl_2(P(p-C_6H_4Me)_3)_3]$

$RuCl_3 \cdot 3H_2O$  (0.50 g, 1.91 mmol) was dissolved in methanol (100 ml), and heated under reflux for 5 min. After cooling to room temperature,  $P(p-C_6H_4Me)_3$  (3.54 g, 11.6 mmol) was added to the homogeneous solution, and then refluxed for 2 h. Upon cooling to room temperature, reddish brown crystals were formed, which were filtered, washed with diethyl ether (5 ml  $\times$  2), and dried under vacuum (1.59 g, 77% yield).  $^{31}P$  NMR:  $\delta(P) = 39.9$  ppm. Analyses found: C 69.69, H 5.95; calcd for  $C_{63}H_{63}P_3Cl_2Ru$ : C 69.73 and H 5.85%.

### 3.2. Synthesis of $[RuCl_2(P(p-C_6H_4OMe)_3)_3]$

$RuCl_3 \cdot 3H_2O$  (0.12 g, 0.46 mmol) was dissolved in methanol (30 ml), and heated under reflux for 5 min. After cooling to room temperature,  $P(p-C_6H_4OMe)_3$  (1.00 g, 2.84 mmol) was added to the homogeneous solution, and then refluxed for 3 h. Upon cooling to room temperature, brown crystals were formed, which were filtered, washed with diethyl ether (5 ml  $\times$  2), and dried under vacuum (0.32 g, 57% yield).  $^{31}P$  NMR:  $\delta(P) = 39.7$  ppm. Analyses found: C 61.16, H 5.13; calcd for  $C_{63}H_{63}O_9P_3Cl_2Ru$ : C 61.56 and H 5.17%.

### 3.3. Synthesis of $[RuCl_2(P(p-C_6H_4F)_3)_3]$

$RuCl_3 \cdot 3H_2O$  (0.15 g, 0.57 mmol) was dissolved in methanol (30 ml), and heated under reflux for 5 min. After cooling to room temperature,  $P(p-C_6H_4F)_3$  (1.09 g, 3.45 mmol) was added to the homogeneous solution, and then refluxed for 21 h. Upon cooling to room temperature and reducing the solution volume in vacuo, brown crystals were formed, which were filtered, washed with light petroleum (5 ml  $\times$  2) and light petroleum–diethyl ether (1:1 v/v, 5 ml  $\times$  2), and dried under vacuum (0.11 g, 17%

yield).  $^{31}P$  NMR:  $\delta(P) = 27.7$  ppm.  $^{19}F$  NMR:  $\delta(F) = -108.4$  ppm. Analyses found: C 57.83, H 3.59; calcd for  $C_{54}H_{36}F_9P_3Cl_2Ru$ : C 57.87 and H 3.24%.

### 3.4. Synthesis of $[RuCl_2(PMePh_2)_3]$

$RuCl_3 \cdot 3H_2O$  (0.50 g, 1.91 mmol) and  $PMePh_2$  (2.40 g, 12.0 mmol) were dissolved in methanol (100 ml), and heated under reflux for 14 h. Upon cooling to room temperature yellow crystals were formed, which were filtered, washed with diethyl ether (5 ml  $\times$  2), and dried under vacuum (1.07 g, 72% yield).  $^{31}P$  NMR:  $\delta(P) = 18.7$  ppm. Analyses found: C 60.46 H 5.09; calcd for  $C_{39}H_{39}P_3Cl_2Ru$ : C 60.62 and H 5.09%.

### 3.5. Catalytic reaction

The reaction solution was prepared by dissolving calculated amount of the Ru(II) complex in degassed methanol (200 ml). The reaction was performed at 64°C (refluxing) under a nitrogen atmosphere (1 atm) in a thermostated room (within  $\pm 1^\circ C$ ). The reactor was equipped with a reflux condenser ( $-20^\circ C$ ) to which a gas buret was attached. The volumetric measurement was started after refluxing became stationary. Products were analyzed by GC (TCEP, Porapak T and active carbon columns). For the sake of higher precision for analyzing formaldehyde, CO and  $CO_2$  (Porapak T), a methane convertor was used with a FI detector.

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