

# KINETIC STUDY OF CARBONYLATION OF METHANOL TO ACETIC ACID AND ACETIC ANHYDRIDE OVER A NOVEL COPOLYMER-BOUND *CIS*-DICARBONYLRHODIUM COMPLEX\*

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## ABSTRACT

The kinetic study of carbonylation of methanol-acetic acid mixture to acetic acid and acetic anhydride over a *cis*-dicarbonylrhodium complex ( $MVM'Rh$ ) coordinated with the ethylene diacrylate ( $M'$ ) crosslinked copolymer of methyl acrylate ( $M$ ) and 2-vinylpyridine ( $V$ ) shows that the rate of reaction is zero order with respect to both reactants methanol and carbon monoxide, but first order in the concentrations of promoter methyl iodide and rhodium in the complex. Polar solvents can accelerate the reaction. Activation parameters were calculated from the experimental results, being comparable to that of the homogeneous system. A mechanism similar to that of soluble rhodium catalyst was proposed.

In our previous paper we reported that the heterogenized *cis*-dicarbonylrhodium complex ( $MVM'Rh$ ) coordinated with ethylene diacrylate ( $M'$ ) crosslinked copolymer of methyl acrylate ( $M$ ) and 2-vinylpyridine ( $V$ ) was thermally stable and very reactive in the carbonylation of methanol to acetic acid<sup>[1]</sup>. We report the kinetic study of carbonylation of methanol-acetic acid mixture over this catalyst.

## EXPERIMENTAL

The heterogenized *cis*-dicarbonylrhodium complexes, the reagents, autoclaves, analytical instrument and procedures were identical with those described in previous paper<sup>[1]</sup>.

The data measured directly in this work were the changes of the pressure of carbon monoxide with the reaction time. The reaction conditions of this work are listed in Table 1.

## RESULTS AND DISCUSSION

As the carbonylation of methanol catalyzed by the ( $MVM'Rh$ ) complexes yielded methyl acetate, acetic acid and acetic anhydride, and no other byproducts derived from carbon monoxide, the rate of absorption of carbon monoxide was the rate of reaction, in  $\text{mols/L/h}$ . For the reproducibility of this study a minimum stirring speed above 400 rpm should be maintained.

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**Table 1** Reaction conditions of the kinetic study

Serial run	Temp. ( $\pm 1^\circ\text{C}$ )	$P_{\text{CO}}$ (initial) ( $\text{kg}/\text{cm}^2$ )	Methanol (m mol)	Methyl iodide (m mol)	Rh (mg atom)	Acetic acid (m mol)
1	140	30	494	80	0.14	350
2	140	30	494	80	0.14	
3	135	varied	494	80	0.14	
4	135	30	varied	80	0.14	
5	135	30	617	80	0.14	
6	135	30	494	80	varied	350
7	135	30	494	varied	0.14	350
8	varied	30	494	80	0.14	
9	135	30	494	80	0.14	varied
10	135	30	494	80	0.14	other solvent
11	135	30	494	80	0.14	
12	135	30	494	80	0.14	280

### 1. Effect of partial pressure of carbon monoxide on the rate of reaction

The partial pressure of carbon monoxide shown in Fig. 1 was the instantaneous one at the moment of measurement, not the initial one of the reaction. As shown in

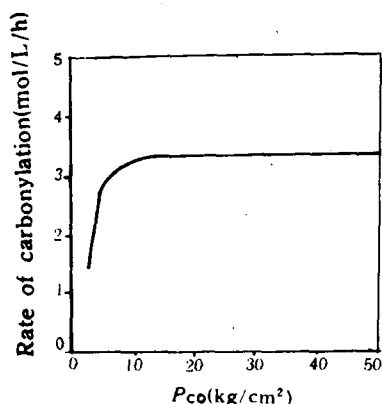


Fig. 1 Relation between rate of carbonylation and pressure of carbon monoxide \*

\*Reaction conditions: serial run 3 of Table 1

Fig. 1, when the reaction was carried out above a partial pressure of carbon monoxide of  $7 \text{ kg}/\text{cm}^2$ , the rate of reaction was independent of the pressure of carbon monoxide. This relationship happened in all experiments of this investigation, similar to that of homogeneous rhodium catalysts<sup>[2, 3]</sup>.

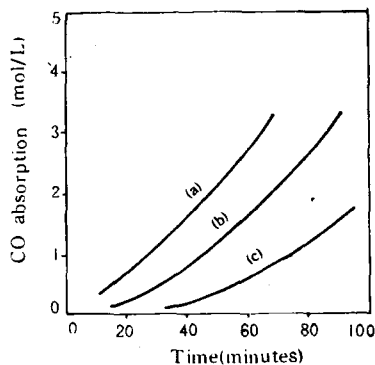
### 2. Effect of the concentration of methanol on the rate of reaction

The initial concentration of methanol did exercise some influence on the rate of reaction at the early stage as shown in Fig. 2 of the carbonylation of the methanol-benzene mixture. The higher the initial concentration of methanol was, the longer the time needed to reach a maximum rate of reaction. Furthermore, the rate of reaction decreased as the initial concentration of methanol increased. However, when the steady state was established, the rate no longer changed with the concentration of methanol in the ranges studied as shown in Fig. 3 for the carbonylation of methanol-benzene mixtures.

The concentration of methanol in Fig. 3 was that measured instantaneously during the reaction, and not the initial concentration of methanol. When the concentration of methanol was higher than  $0.5 \text{ mol}/\text{L}$ , the rate of reaction was independent of the concentration of methanol.

We also found that under the experimental conditions of Serial Run 5 methanol was nearly 100% converted at 120 minutes. However, the rate of carbonylation did not diminish but increased. This was due to the continuation of carbonylation

of methyl acetate formed to acetic anhydride<sup>[4]</sup>.



(a) 10.1 mol/L ; (b) 13.7 mol/L ; (c) 21.2 mol/L

Fig. 2 Relation between initial concentrations of methanol in methanol - benzene mixtures and time of carbonylation . \*

\* Reaction conditions : serial run 4 of Table 1 .

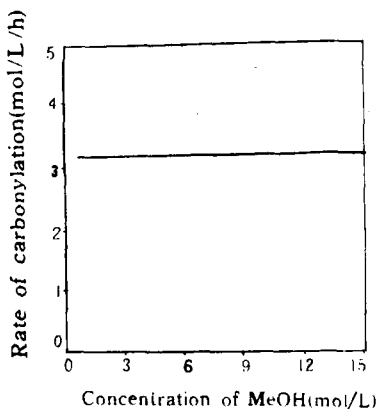


Fig. 3 Relation between rate of carbonylation and concentrations of methanol in methanol - benzene mixtures . \*

\* Reaction conditions : serial run 5 of Table 1

### 3. Effect of the concentration of rhodium complex on the rate of carbonylation

In this study we did vary the concentration of rhodium not by simple variation of the quantity of rhodium complex used , but by the synthesis of a series of complex with different rhodium contents (Table 2). Different quantities of solid rhodium complex in the reaction system consisted of gas - liquid - solid phases would make a

Table 2 Concentrations of rhodium active site in Serial Run 6 of Table 1

Catalyst	M <sub>2</sub>	M <sub>3</sub>	M <sub>5</sub>	M <sub>6</sub>
Rh content * in catalyst (%)	1.91	2.88	4.01	5.84
Quantity of catalyst used (g .)	0.5	0.5	0.5	0.5
Concentration of rhodium (m mol/l)	2.06	3.10	4.32	6.30

\* The rhodium contents in catalyst were determined by a method in literature<sup>[5]</sup>

heterogeneity in the mass transfer process and thus would introduce appreciable experimental error . The results are shown in Fig. 4. Under the reaction conditions of Serial Run 6 the rate of carbonylation was a linear function of rhodium concentration with a slope of  $0.15 \text{ sec}^{-1}$ .

### 4. Effect of the concentration of methyl iodide on the rate of carbonylation

A linear relationship between the concentration of methyl iodide and the rate of carbonylation with a slope  $2.7 \times 10^{-4} \text{ sec}^{-1}$  was found (Fig. 5).

As shown previously in the course of carbonylation the hydrogen iodide liberated instantaneously reacted immediately with methanol or methyl acetate to form methyl iodide<sup>[1]</sup>, so the constancy of iodine in form of

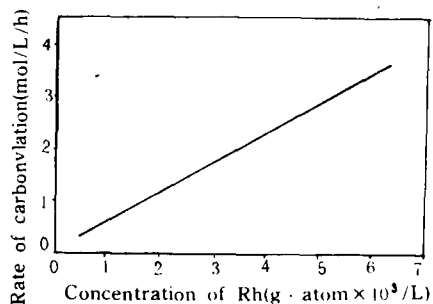


Fig. 4 Relation between rate of carbonylation and the concentration of rhodium complex . \*

\* Reaction conditions : serial run 6 of Table 1 .

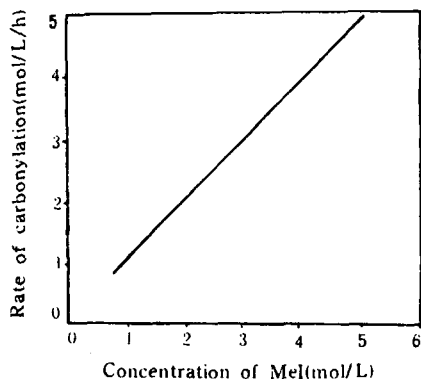


Fig. 5 Relation between rate of carbonylation and the concentration of methyl iodide . \*

\* Reaction conditions : serial run 7 of Table 1 .

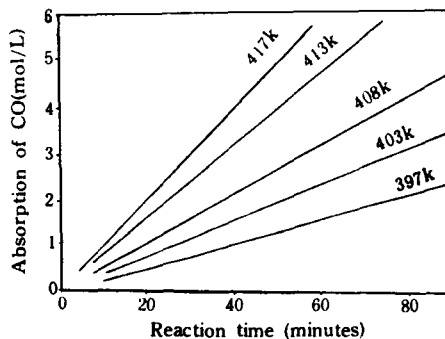


Fig. 6 Relation between absorption of carbon monoxide and reaction time at different temperatures . \*

\* Reaction conditions : serial run 8 of Table 1 .

methyl iodide is conceivable .

### 5. Effect of reaction temperature on the rate of carbonylation

All data in Fig. 6 were that at the steady state . The origin of reaction time was not that of the initiation of reaction but that of the steady state . The favorable effect of reaction temperature is apparent .

From these serial experiments at different temperatures the rate constants  $k$  can be determined and are listed in Table 3 .

Table 3 Rate constants at different reaction temperatures

Temperature (K)	397	403	406	408	413	417
Rate constant $k$ (l/mol/sec)	0.025	0.036	0.043	0.050	0.073	0.093

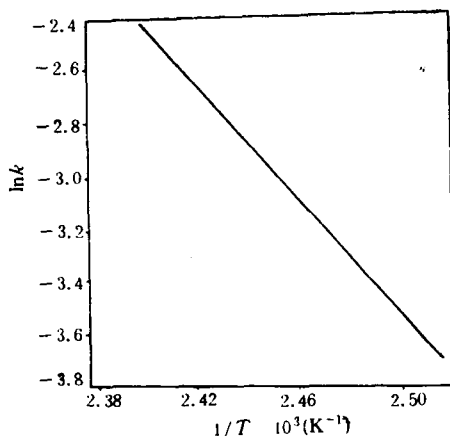


Fig. 7 The Arrhenius plot .

The Arrhenius plot is shown below .

According to the Arrhenius equation the activation energy  $E$  and the pre-exponential factor can be calculated .

$$E = 22.0 \text{ Kcal/mol}$$

$$k_0 = 2.57 \times 10^{10} \text{ L/mol/sec}$$

From these experimental results it can be ascertained that within the range studied with the concentration of methanol above 0.5 mol/L , partial pressure of carbon monoxide above 7 kg/cm<sup>2</sup> , the rate of carbonylation may be represented by the following equation .

$$r = k [Rh] [CH_3I]$$

where  $k = k_0 e^{-E/RT}$  , and  $k_0$  and  $E$  with the values shown above . Outside the range studied there might be other results .

The activation entropy and the enthalpy are readily calculated from the plot of  $\ln k/T$  vs.  $1/T$  to be

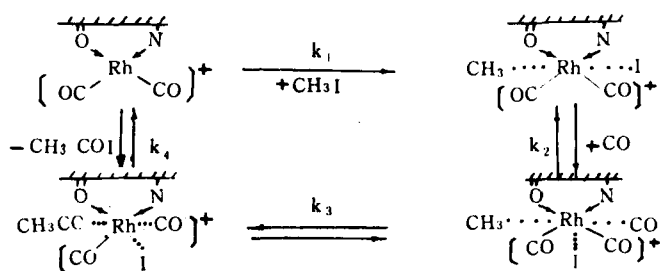
$$\Delta S^\ddagger = -13.1 \text{ cal/mol/K}$$

and

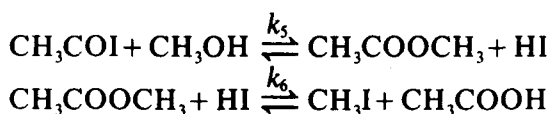
$$\Delta H^\ddagger = 21.2 \text{ Kcal/mol}$$

With the negative value of entropy and low enthalpy comparable to that of homogeneous system<sup>[2]</sup> it may be concluded that the oxidative addition of methyl iodide to the heterogenized *cis*-dicarbonylrhodium complex to form the transition state is the rate-determining step of this reaction. A reaction mechanism similar to that of homogeneous carbonylation<sup>[6]</sup> is proposed as shown in Scheme 1.

The acetyl iodide liberated by reductive elimination reacts with methanol to yield methyl acetate and hydrogen iodide, and methyl acetate is acidolyzed by hydrogen iodide to methyl iodide and acetic acid to complete the catalytic cycle.



Scheme 1



Hence, a theoretical rate equation may be deduced.

$$r = k_1 [\text{Rh}] [\text{CH}_3\text{I}] \left( 1 - K' \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{OH}][\text{CO}]} \right) \quad (\text{I})$$

where  $K' = 1/k_1 k_2 k_3 k_4 k_5 k_6$ .

If the insertion of carbon monoxide were the rate-determining step, the rate equation will be in the first order of the partial pressure of carbon monoxide. It is contradictory to the experimental results. The reduction of the theoretical rate equation (I) toward experimental equation gives

$$r = k_1 [\text{Rh}] [\text{CH}_3\text{I}] \quad (\text{II})$$

consistent with the experimental results.

#### 6. Effect of solvent on the rate of carbonylation

At the early stage of the carbonylation of methanol over (MVM' Rh) without

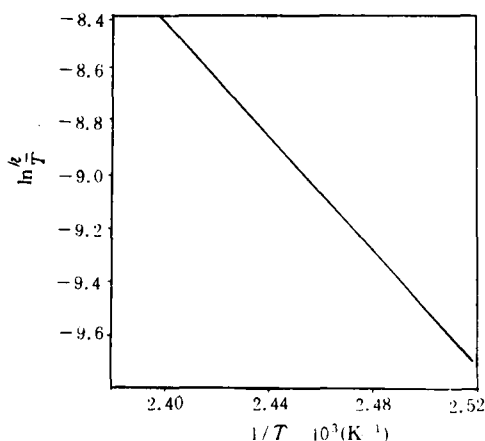


Fig 5 Plot for the calculation of activation entropy and enthalpy

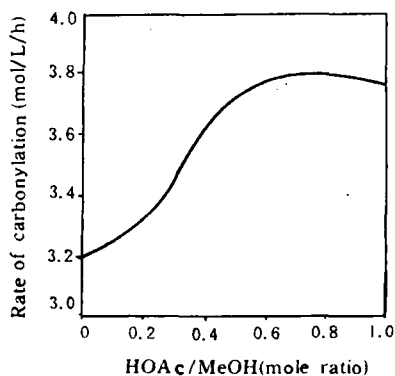


Fig.9 Relation between rate of carbonylation and initial quantity of acetic acid used.\*  
Reaction conditions: serial run 9 of Table 1.

other additives acetic acid was produced at a steady rate until all methanol was converted<sup>[1]</sup>. If an appreciable amount of glacial acetic acid was used as solvent, acetic acid and acetic anhydride were produced simultaneously at a still higher rate<sup>[1]</sup>. On the contrary, the homogeneous carbonylation of methanol will stop at a low conversion of methanol and resumes the reaction until another portion of new catalyst is added, or is carried out at a high speed to the complete conversion of methanol in a large amount of solvent and appreciable amount of water<sup>[7]</sup>.

In addition to acetic acid, methyl acetate is also a better solvent than benzene for this reaction.

As shown in Fig.9, when the quantity of solvent acetic acid increases, the rate of carbonylation is speeded up to a mole ratio of 0.7 between acetic acid and methanol, and then declines, but is still higher than that of methanol alone.

A comparison between the rates of carbonylation of methanol (curve I) and of methanol-acetic acid mixture (curve II) is shown in Fig. 10. From curve I it can be seen that the induction period takes about 20 minutes to start the absorption of carbon monoxide. However, for curve II the induction period is about 12 minutes and the steady rate is established about 20 minutes earlier than that of curve I.

In the course of this investigation it has been very often observed that the rate of carbonylation changed from the steady state to a higher one as the concentration of methanol diminished almost to zero. At this stage the reactions concerning methanol became less in importance but the carbonylation of methyl acetate to acetic anhydride still remained vividly. It has already been shown in many cases that the rate of carbonylation of methyl acetate to acetic anhydride catalyzed by homogeneous rhodium complexes is usually relatively low<sup>[8,9,10]</sup>. It is interesting to note that heterogenized rhodium complex (MVM/Rh) shows a high activity in carbonylation of methanol to acetic acid as well as in carbonylation of methanol-acetic acid to acetic acid and acetic anhydride.

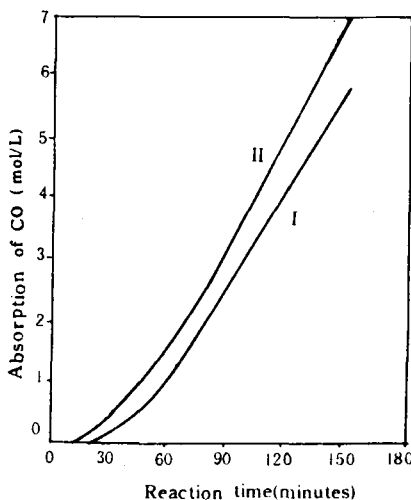


Fig.10 Comparison of the rate of carbonylation\*  
\*Reaction conditions:  
curve I, serial run 11 of Table 1.  
curve II, serial run 12 of Table 1.

#### Keywords :

Carbonylation of methanol; Copolymer-bound *cis*-dicarbonylrhodium complex; Kinetic study

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