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THE PHOTOCATALYTIC DEHYDROGENATION OF 2-PROPANOL BY USING $RhCl(PPh_3)_3$

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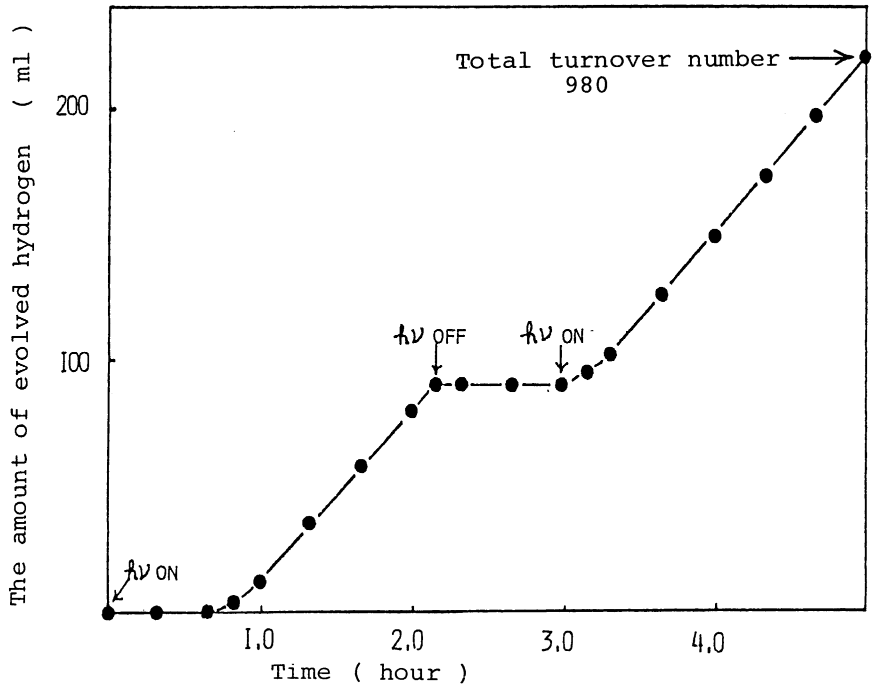
$RhCl(PPh_3)_3$(Wilkinson complex) catalyzes the dehydrogenation of 2-propanol under the photo-irradiation at room temperature. The catalytic activity of the reaction mixture including 2-propanol and this complex is very high, especially in the case of the preparation of this mixture under the oxygen atmosphere, and has the maximum value at the special concentration range of this complex.

Recently, photocatalytic reactions have been of interest to many workers. There are many reports about these, for example, decomposition of water, dehydrogenation of alcohol, oxidation of olefin, isomerization of olefin and so on. Saito and his group have found that the several types of rhodium compounds have the catalytic activity for the dehydrogenation of 2-propanol under the photo-irradiation[1)~5)]. We would like to report here $RhCl(PPh_3)_3$ has the photocatalytic activity for the dehydrogenation and its activity is higher than the other rhodium complexes.

The typical reaction procedure is as follows: 2-propanol(110 ml) and $RhCl(PPh_3)_3$ (9.2 mg) were introduced into the reaction vessel with the irradiation apparatus under the atmosphere control and mixed for 30 minutes at room temperature. After this procedure, irradiation was started. The reaction mixture was kept mixing by magnetic stirrer and its temperature was controled by water bath during the irradiation. High pressure mercury lamp (USHIO UM 102, 100 W) was used as the irradiation source. The evolved gas was determined as hydrogen by gaschromatography with MS-5A column. The electronic absorption spectra of the reaction mixtures were measured by SHIMADZU UV-202 Spectrometer at 1 hour later from the initiation of hydrogen evolution.



Catalyst : $RhCl(PPh_3)_3$ $1.0x10^{-2}$ mmol
Substrate : 2-propanol 110 ml
Reaction temperature 21 °C

Figure 1 Reaction time course

Figure 1 shows the typical reaction time course. The following characteristic feature was observed: 1). the induction period is present, 2). no reaction proceeds without irradiation, 3). hy-

Table 1 The catalytic property of various catalysts

Catalyst	(mmolx10^2)	Induction period (min.)	H_2 evolution rate (mmol/hr.)	Turnover number (/hr.)	
None	———	———	0	0	at 21°C
$RhCl_3 \cdot 3H_2O$	5.7	———	0	0	
$RhCl_3 \cdot 3H_2O$ *1	1.9	70	0.18	9	
$RhCl_3 \cdot 3H_2O$ *1	8.7	60	0.84	9	
$RhCl(PPh_3)_3$ *2	1.0	40	1.38	138	
$RhCl(PPh_3)_3$ *3	1.0	45	2.95	295	
$RhCl(PPh_3)_3$ *4	1.0	75	6.70	670	
Rhodium dinuclear complex (A-frame) *5				291	at 82.5°C
$Rh_2(OAc)_4$ + SIL-$CH_2CH_2PPh_2$ *6				12	
[$Rh(bpy)_2]Cl \cdot 2H_2O$ *7				6	

Reaction temperature : 21 °C, 2-propanol : 110 ml,

*1 : $SnCl_2 \cdot 2H_2O/RhCl_3 \cdot 3H_2O$ = 10, $LiCl/RhCl_3 \cdot 3H_2O$ = 3 see reference 2)

*2 : Reaction mixture was prepared under the nitrogen atmosphere.

*3 : Reaction mixture was prepared under the air atmosphere.

*4 : Reaction mixture was prepared under the oxygen atmosphere.

*5, *6, *7 : See references 3), 4), 5).

drogen evolution rate is constant with time, 4). total turnover number is 980 at the end of this run, 5). the reaction mixture is homogeneous.

Table 1 shows the comparison of the catalytic property between $RhCl(PPh_3)_3$ and the other rhodium compounds. Though the induction periods of these rhodium cmpounds are comparable, the catalytic activity of $RhCl(PPh_3)_3$ is extremely higher than that of $RhCl_3 \cdot 3H_2O$-$SnCl_2 \cdot 2H_2O$-LiCl system at the same reaction condition in this work. The maximum value of catalytic activity is 670/hour as the turnover number in the case of the reaction mixture which is prepared under the oxygen atmosphere. Even if compared with the other rhodium compounds reported such as rhodium dinuclear complexes $[Rh_2(CO)_2(PPh_2CH_2PPh_2)_2Cl]Cl$ (A-frame type)$^{3)}$, $Rh_2(OAc)_4$-PPh_3 system$^{6)}$, $Rh_2(OAc)_4$-SIL-$CH_2CH_2PPh_2$ system $^{4)}$, and $[Rh(bpy)_2]Cl \cdot 2H_2O^{5)}$, the activity of $RhCl(PPh_3)_3$ is best. It is interesting that the activity of reaction mixture which is prepared under the oxygen atmosphere is about five times as high as that under the nitrogen atmosphere. The small amount of oxygen accelerates this reaction but the role of oxygen is not clear.

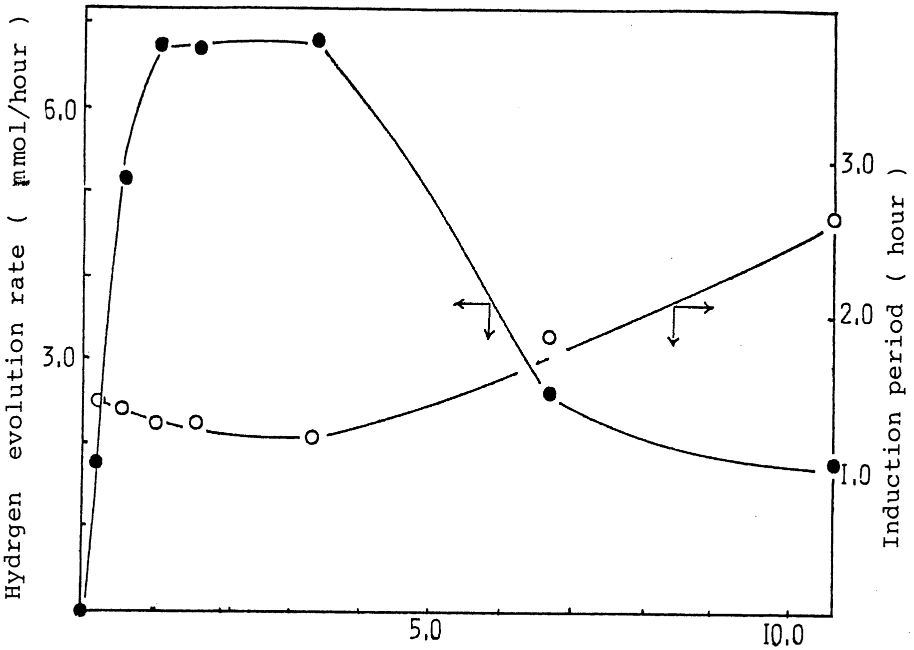
It seems that $RhCl(PPh_3)_3$ is the precursor of the real active species to this reaction and this species is formed under the irradiation. Because the induction period is observed in every case of this work even if the premixing time of this complex and 2-propanol is prolonged more than 30 minutes.

Figure 2 shows the catalyst concentration dependence of the hydrogen evolution rate and of the induction period. AS shown in Figure 2, both the hydrogen evolution rate and the induction period are not proportional to the concentration of $RhCl(PPh_3)_3$.

At the low concentration range of this complex, the hydrogen evolution rate increases with the increase of the concentration of this complex and amounts to the maximum value and then decreases gradually. On the other hand, the induction period decreases and amounts to the minimum value and then increases gradually with the increase of the concentration of this complex.

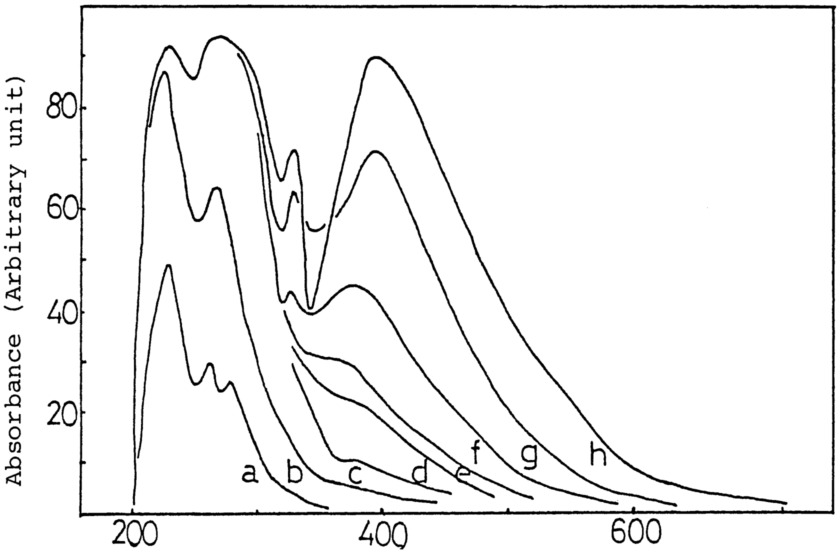
Figure 3 shows the electronic absorption spectra of several reaction mixtures. The absorbances of the 230 nm and the 265 nm increase and become the constant value with the increase of the concentration of this complex. By increasing the concentration furthermore, the new absorption appears at around the 396 nm and its absorbance increases continuously.

There is the good relationship between the results of Figure 2 and Figure 3,: the hydrogen evolution rate is enhanced with the increase of the 230 nm and the 265 nm and is retarded by the increase of the absorbance around the 396 nm. From these results, it is easy to speculate that the absorption around the 230 nm and the 265 nm belongs to the active species and the presence of much amount of $RhCl(PPh_3)_3$ changes the active species to the other.



Concentration of $RhCl(PPh_3)_3$ (x10^2 mmol)
2-propanol 110 ml
Reaction temperature 21 °C
Reaction mixture was prepared under the oxygen atmosphere.

Figure 2 Catalyst concentration dependence



Wave length (nm)
Concentration of $RhCl(PPh_3)_3$ complex (x10^2 m mol)
a : 0.2 , b : 0.4 , c : 0.6 , d : 0.9
e : 1.7 , f : 3.4 , g : 6.7 , h : 10.7
Reaction mixture was prepared under the oxygen atmosphere

Figure 3 Electronic absorption spectra of reaction mixtures

Figure 4 shows the Arrhenius plots of two cases, air atmosphere preparation and oxygen atmosphere preparation of the reaction mixture. Hydrogen evolution rate was measured at the temperature between 40 °C and 10 °C. The activation energies are 1.22 kcal/mol (air atmosphere preparation) and 1.27 kcal/mol (oxygen atmosphere preparation). These values are lower than that of $RhCl_3$ $3H_2O$-$SnCl_2$ $2H_2O$-LiCl system[2] and rhodium dinuclear complex(A-frame)[3].

Further investigation is in progress.

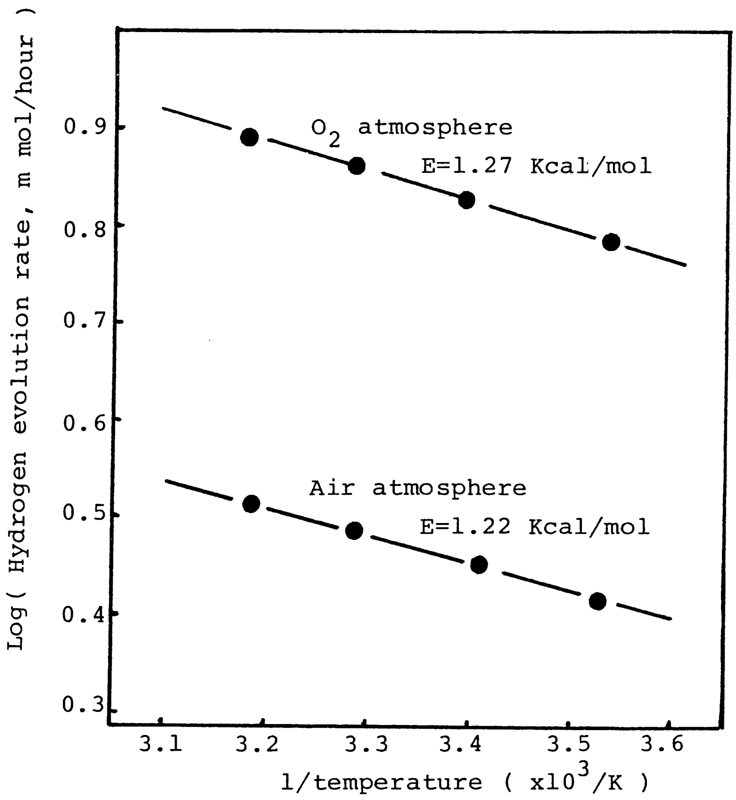


Figure 4 Arrhenius plot

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