

### Preliminary communication

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## SPECIFIC RATE ENHANCEMENT BY ALKYLPHOSPHINES IN A HOMOGENEOUS RHODIUM COMPLEX-CATALYZED HYDROGENATION OF CARBON MONOXIDE TO ETHYLENE GLYCOL

HIRO-O TANAKA, YOSHINORI HARA, EIICHI WATANABE, KEISUKE WADA\* and  
TAKERU ONODA

*Research Center, Mitsubishi Chemical Industries Limited, 1000 Kamoshida-chou, Midori-ku,  
Yokohama 227 (Japan)*

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### Summary

In the rhodium/alkylphosphine complex catalyzed hydrogenation of carbon monoxide the reaction rate and the productivity of ethylene glycol have been found to depend strongly on the steric as well as electronic properties of the phosphine ligand, and on the phosphine/rhodium ratio. Maximum productivities were attained with the P-*i*-Pr<sub>3</sub>/Rh and P-*n*-Pr<sub>3</sub>/Rh ratios being about unity and 165, respectively.

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Previously, we reported a novel and highly effective rhodium/tri-*n*-alkylphosphine catalyst system for the hydrogenation of carbon monoxide to ethylene glycol [1]. The striking feature of this catalyst system is a dramatic enhancement of the reaction rate by the addition of a tri-*n*-alkylphosphine, in large excess over rhodium, e.g., PR<sub>3</sub>/Rh = 40–300.

We thus extended the study to cover other trialkylphosphine ligands such as tri-cyclo- and tri-*sec*-alkyl-phosphines and others. Figure 1a illustrates the effect of varying the molar ratio of triisopropylphosphine (P-*i*-Pr<sub>3</sub>) to rhodium on the reaction rates, or the productivities, in terms of turn-over frequencies to ethylene glycol and methanol. The result with tri-*n*-propylphosphine (P-*n*-Pr<sub>3</sub>) is shown in Fig. 1b, for comparison. The reactions are very dependent on the amount of the phosphine ligand added. However, in contrast to P-*n*-Pr<sub>3</sub>, the productivity, with respect to ethylene glycol, increases to a maximum as the P-*i*-Pr<sub>3</sub>/Rh ratio approaches unity. The presence of a large excess of P-*i*-Pr<sub>3</sub> decreases the productivity markedly. Finding such contrasting behavior between P-*i*-Pr<sub>3</sub> and P-*n*-Pr<sub>3</sub> ligands, prompted us to examine the other phosphine ligands more closely. Thus, the productivities observed for 21 phosphines at PR<sub>3</sub>/Rh ratios of 1/1 and 40/1, were put into multiple regression analyses, by using  $\delta$  (chemical shift of the corresponding phosphine oxide [2]) and  $\theta$  (cone angle of the phosphine [3]), as variables, being electronic and steric parameters, respectively. Typical results of the analysis are

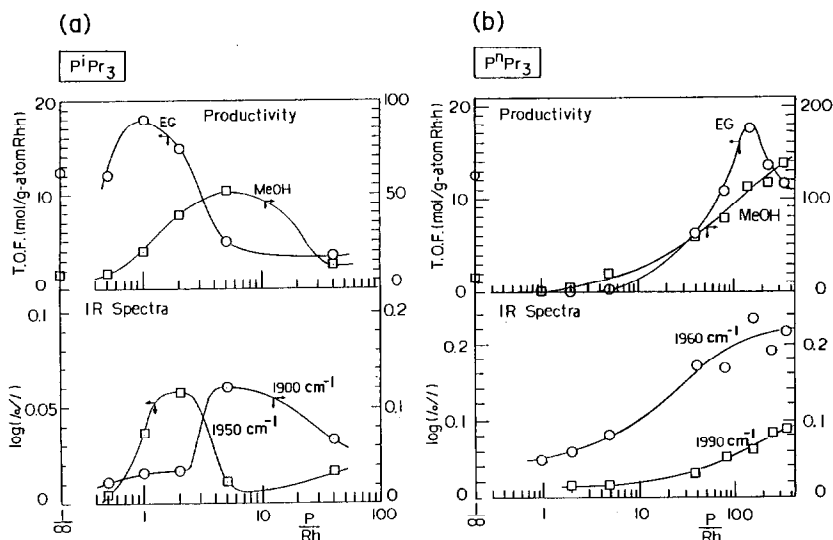


Fig. 1. Effect on ethylene glycol (EG) and methanol (MeOH) productivities, and IR intensities, by changing the phosphine to rhodium ratio. Reaction conditions: Rh(CO)<sub>2</sub>acac, 0.1 mmol; phosphines, variable; 1,3-dimethylimidazolidinone (DMI), 10 ml; 50 MPa, H<sub>2</sub>/CO 1/1; 240 °C, 2 h (a) Rh(CO)<sub>2</sub>-acac/P-*i*-Pr<sub>3</sub>/DMI; (b) Rh(CO)<sub>2</sub>acac/P-*n*-Pr<sub>3</sub>/DMI.

shown in Fig. 2a and 2b. Fairly good correlations, or *R* values, were achieved in both cases. It is evident that the reaction is not governed by simple factors e.g., bulkiness of phosphine ligand etc. In other words, not only the steric factor but also

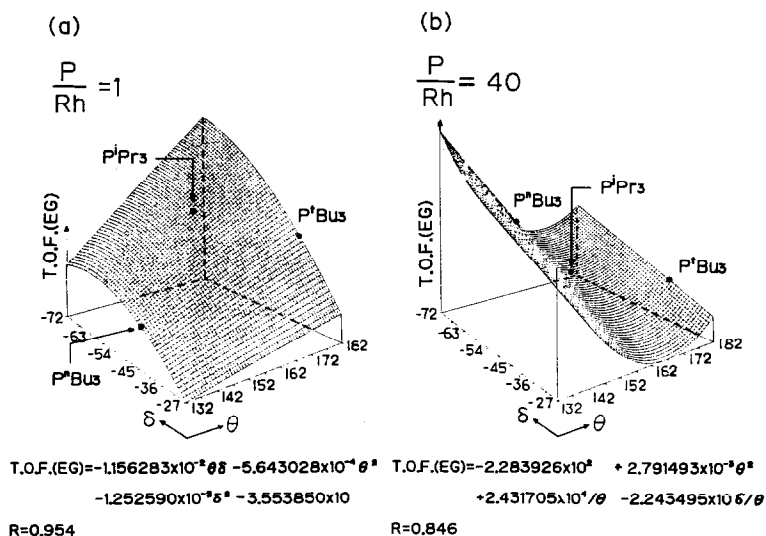


Fig. 2. Profiles of ethylene glycol productivity as functions of the electronic ( $\delta$ ) [2] and steric ( $\theta$ ) [3] ligand parameters for the system Rh(CO)<sub>2</sub>acac/PR<sub>3</sub>/DMI. Reaction conditions: Rh(CO)<sub>2</sub>acac, 0.1 mmol; DMI, 10 ml; 50 MPa, H<sub>2</sub>/CO 1/1; 240 °C, 2 h. Phosphines; (a) 0.1 mmol (PR<sub>3</sub>/Rh 1); (b) 4.0 mmol (PR<sub>3</sub>/Rh 40).

TABLE 1

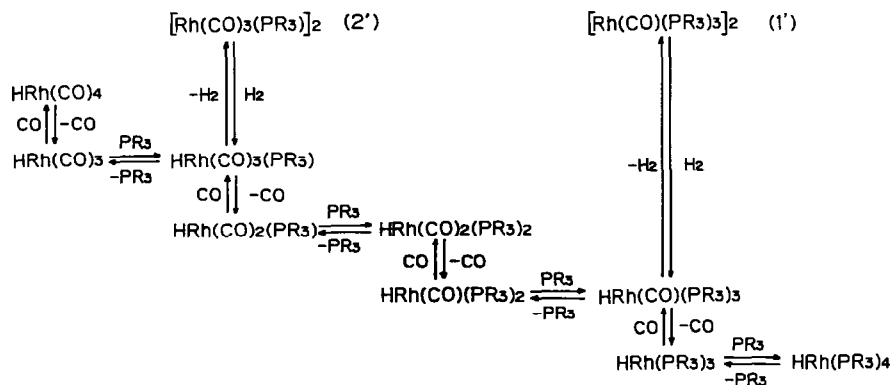
HYDROGENATION OF CARBON MONOXIDE BY Rh/P-n-Bu<sub>x</sub>-t-Bu<sub>3-x</sub> CATALYSTS<sup>a</sup>

Run	Promoter	<i>N</i> <sup>b</sup> (mol/g-atom·Rh·h)		<i>θ</i> <sup>c</sup> (°)	<i>δ</i> <sup>d</sup> (ppm)
		EG	MeOH		
1	P-n-Bu <sub>3</sub>	0.0	3.2	132	-43.0
2	P-n-Bu <sub>2</sub> -t-Bu	9.3	13.2	147	-53.0
3	P-n-Bu-t-Bu <sub>2</sub>	20.6	13.4	165	-59.3
4	P-t-Bu <sub>3</sub>	11.4	6.4	182	-41.0

<sup>a</sup> Reaction conditions: Rh(CO)<sub>2</sub>acac, 0.1 mmol; promoter, 0.1 mmol; 1,3-dimethylimidazolidinone (DMI), 10 ml; 50 MPa, H<sub>2</sub>/CO 1/1; 240°C, 2 h. <sup>b</sup> *N* = rate of turn-over. <sup>c</sup> Cone angle of the phosphine [3]. <sup>d</sup> Chemical shift of the phosphine oxide [2].

the electronic factor controls the rate of the hydrogenation. The situation is illustrated clearly by a series of experiments, using the mixed-alkylphosphines, P-n-Bu<sub>x</sub>-t-Bu<sub>3-x</sub> (*x* = 0–3), where P-n-Bu-t-Bu<sub>2</sub> shows the highest productivity provided PR<sub>3</sub>/Rh = 1 (Table 1). It should be noted that P-n-Bu-t-Bu<sub>2</sub> is the most electron donating (*δ* = -59.3 ppm), whereas its cone angle (*θ* = 165°) is rather low compared with that of tri-*t*-butylphosphine (*θ* = 182°). It is also noteworthy, that in order to attain a maximum ethylene glycol yield, completely different properties of the phosphine ligand are required for the two different PR<sub>3</sub>/Rh ratios, 1/1 and 40/1. We believe that the difference can be ascribed to the distinction in the chemistry of the active catalytic species involved in the respective reaction conditions.

The IR absorption at 1960 cm<sup>-1</sup>, observed in the P-n-Pr<sub>3</sub>-promoted hydrogenation, is assigned to that of the dimer [Rh(CO)(P-n-Pr<sub>3</sub>)<sub>3</sub>]<sub>2</sub> (**1**). It has been suggested that the intensity of the absorption correlates well with the productivity for ethylene glycol [1] (Fig. 1b). A similar, but intrinsically different chemistry was observed for the P-*i*-Pr<sub>3</sub>-promoted hydrogenation. During the course of the analytical study, we succeeded in isolating orange crystals formulated as Rh(CO)<sub>3</sub>(P-*i*-Pr<sub>3</sub>) from the reaction mixture. The single crystal X-ray analysis of the isolated complex established the non-bridged dimeric rhodium(0) structure, (P-*i*-Pr<sub>3</sub>)(CO)<sub>3</sub>Rh–Rh(CO)<sub>3</sub>(P-*i*-Pr<sub>3</sub>) (**2**) [4]. In solution, complex **2** gives an IR absorption at 1950 cm<sup>-1</sup>, which



SCHEME 1

correlates well with the productivity for ethylene glycol (Fig. 1a). Moreover, the use of complex **2**, as a catalyst precursor, shows essentially analogous productivity to that of the  $\text{Rh}(\text{CO})_2\text{acac-P-i-Pr}_3$  mixture. Therefore, the dimeric compounds of the general formula  $[\text{Rh}(\text{CO})_k(\text{PR}_3)_{4-k}]_2$ , ( $k = 1-3$ ) (**3**) are likely to be key precursors in the rhodium/alkylphosphine catalyzed hydrogenation of carbon monoxide. The dimers undergo hydrogenolysis readily and form mononuclear hydrido complexes of the type  $\text{HRh}(\text{CO})_m(\text{PR}_3)_n$ , ( $m, n \leq 3$ ) (**4**) [5]. Therefore, the strong dependence observed of reactivity on the  $\text{PR}_3/\text{Rh}$  ratio could be explained in the framework of the equilibria, as shown in Scheme 1.

The more crowded and more electron-donating P-i- $\text{Pr}_3$  seems to favor the left-hand side of the equilibrium. Hence, the hydrogenation proceeds mainly via a less phosphine-ligated hydrido intermediate,  $\text{HRh}(\text{CO})_3(\text{P-i-Pr}_3)$ . On the other hand, the highly phosphine-ligated intermediate,  $\text{HRh}(\text{CO})(\text{P-n-Pr}_3)_3$  on the right, seems to prefer the less crowded and less electron-donating P-n- $\text{Pr}_3$ .

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