

## Direct Determination of the Reaction Volume of an Organometallic Reaction at Very High Dilution

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## Abstract

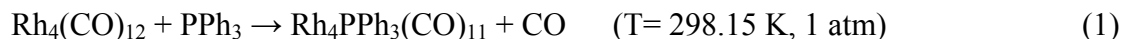
In n-hexane, under Ar (1atm) and 298.15 K,  $\text{Rh}_4(\text{CO})_{12}$  and  $\text{PPh}_3$  react to form a mono-substituted  $\text{Rh}_4(\text{CO})_{11}\text{PPh}_3$  and gaseous CO. This stoichiometric reaction was followed using in-situ FTIR. The concentrations of the organometallics were in the 10s of ppm range. Simultaneously, very precise online density measurements were made. Based on mass injection, partial molar volumes of reactive species were directly determined from multi-component reaction mixtures. These partial molar volumes were in good agreement compared to those of separate binary system study. Subsequently, the reaction volume was determined. From spectral analysis, not only the progress of reaction can be monitored, but also the pure component spectra of each existing species in the reaction can be recovered. The results from spectral analysis were used to confirm the reaction.

## 1.0 Introduction

It has been shown for some inorganic, organometallic, and organic reactions, application of pressure enable the control not only of the yield of the reaction but also selectivity for the competitive and consecutive reaction(s) which can lead to an improvement of chemo-, regio-, and stereo-selectivity.<sup>1</sup> While the sensitivity of the reaction rate dependency on pressure is characterized by activation volume, the volume of reaction is significant for the reaction equilibrium. Reactions accompanied by a decrease in volume are accelerated by pressure and the equilibria are shifted toward the side of products, while those accompanied by an increase of volume are retarded and the equilibria are shifted toward the side of reactants.

Typically, determinations of both parameters, namely activation volume and volumes of reactions are measured by kinetic studies at several pressures. Asano<sup>2</sup> and van Eldik<sup>1</sup> have reported the values of activation and reaction volumes of many reactions. In general, this method would require a wide pressure range (ca. 1~1000 bar). Alternatively, volume of reaction can also be determined by a relatively simple method by calculating the differences of partial molar volume at infinite dilution of products and reactants that are measured at atmospheric pressure. It had already been shown that both approaches are in agreement<sup>3 4</sup>.

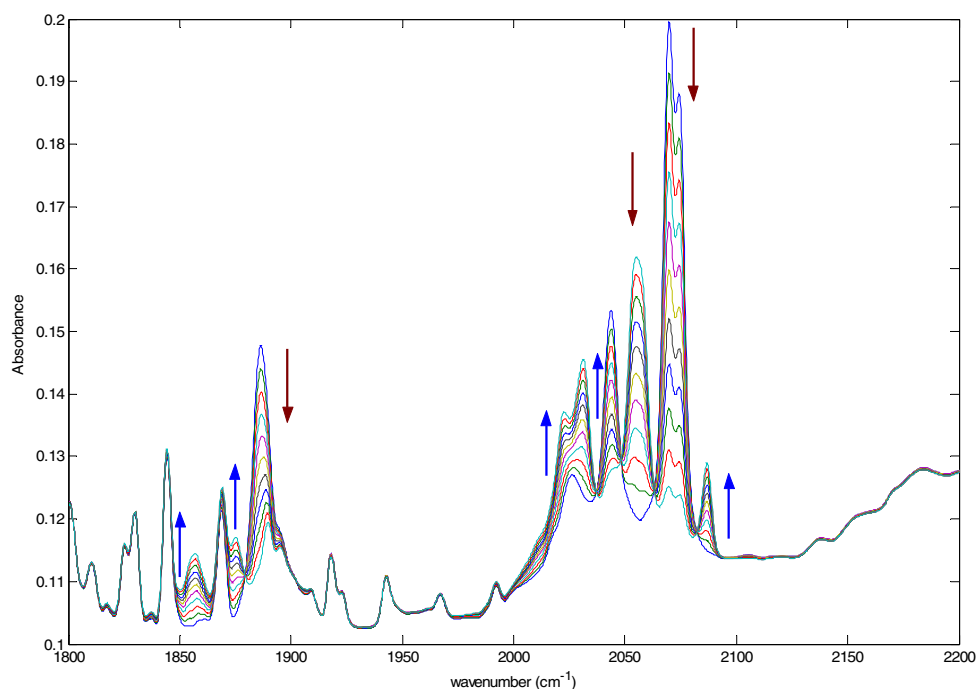
In this study, a well-known ligand substituted reaction in organometallics was selected and shown in Equation 1.



In n-hexane, under Ar (1 bar) and 298.15 K,  $\text{Rh}_4(\text{CO})_{12}$  and triphenylphosphine,  $\text{PPh}_3$  react to form a mono-substituted  $\text{Rh}_4(\text{CO})_{11}\text{PPh}_3$  and released gaseous CO.<sup>5</sup> This reaction was followed using in-situ FTIR. The concentrations of the organometallics were in the 10s of ppm range. Simultaneously, very precise online density measurements were made. In this work, the determination of partial molar volume at infinite dilution  $\bar{V}_i^\infty$  and hence reaction volume  $\Delta_r V^\infty$  were achieved using density measurements at very high dilution ( $x_i \approx 0.00001-0.0001$ ) of the multi-component reaction system.

## 2.0 Results and Discussion

The ligand substitution reaction of  $\text{Rh}_4(\text{CO})_{12}$  and  $\text{PPh}_3$  was done by adding several titration steps of  $\text{PPh}_3$  into the reactor containing the  $\text{Rh}_4(\text{CO})_{12}$  with n-hexane as a solvent medium. All concentrations were in 10s ppm level (mole fraction). While doing the reaction, both density and IR spectra of every step of injection were taken. The IR reaction spectra taken in the wavenumber range  $1800\text{-}2200\text{ cm}^{-1}$  are shown in Figure 1.



**Figure 1. Reaction spectra of ligand substituted of  $\text{Rh}_4(\text{CO})_{12}$  and  $\text{PPh}_3$  in the wavenumber range  $1800\text{-}2200\text{ cm}^{-1}$**

It can be noted from Figure 1 that while in every single  $\text{PPh}_3$  perturbation, some peaks at  $1886(\text{s})$ ,  $2044(\text{s})$ ,  $2070(\text{vs})$ ,  $2074(\text{vs})\text{ cm}^{-1}$  which belong to  $\text{Rh}_4(\text{CO})_{12}$  are decreasing and peaks at  $2087(\text{s})$ ,  $2057(\text{vs})$ ,  $2053(\text{vs})$ ,  $2031(\text{s})$ ,  $2020(\text{ms})$ ,  $2009(\text{w})$ ,  $1902(\text{vw})$ ,  $1871(\text{m})$ ,  $1851(\text{m})\text{ cm}^{-1}$  which belong to the product  $\text{Rh}_4(\text{CO})_{11}\text{PPh}_3$  are increasing. The reaction was stoichiometric. Any  $\text{PPh}_3$  introduced would immediately substitute one ligand CO and form the mono-substituted derivative

$\text{Rh}_4(\text{CO})_{11}\text{PPh}_3$  and release CO. The mono-substituted product  $\text{Rh}_4(\text{CO})_{11}\text{PPh}_3$  was totally soluble in n-hexane at the range of concentration applied. Di-substituted product of  $\text{Rh}_4(\text{CO})_{10}(\text{PPh}_3)_2$  wasn't formed since the  $\text{PPh}_3$  used was slightly less than (1:1 stoichiometric ratio). The reaction observed was in agreement with Whyman's (1972) work. The pure component spectra of  $\text{Rh}_4(\text{CO})_{12}$  and  $\text{Rh}_4(\text{CO})_{11}\text{PPh}_3$  were also reconstructed by using Band Target Entropy Minimization (BTEM)<sup>6 7 8 9</sup>.

While monitoring the reaction was done using IR, density of reaction mixtures (measured by densitometer DMA 5000) was also taken. Providing the known mass of solvent, and reactants ( $\text{Rh}_4(\text{CO})_{12}$  and  $\text{PPh}_3$ ), the mole number of each species in the reactive mixtures can be determined.

Based on these mole numbers of  $\text{Rh}_4(\text{CO})_{12}$  and  $\text{Rh}_4(\text{CO})_{11}\text{PPh}_3$ , the average apparent molar volumes of those components in n-hexane at the limit concentration go to zero were determined. In this study, the range mole numbers of  $\text{Rh}_4(\text{CO})_{12}$  and  $\text{Rh}_4(\text{CO})_{11}\text{PPh}_3$  used in this reaction system are in the level of 0-60 ppm and 0-54 ppm, respectively, was considered dilute enough to assume that apparent molar volume represents partial molar volume at infinite dilution. The values of partial molar volumes determined from multi-component system are tabulated in Table 1.

Table 1 Mole range and partial molar volume at infinite dilution of $\text{Rh}_4(\text{CO})_{12}$ and $\text{Rh}_4\text{PPh}_3(\text{CO})_{11}$			
Component- <i>i</i>	$\text{PPh}_3$	$\text{Rh}_4(\text{CO})_{12}$	$\text{Rh}_4\text{PPh}_3(\text{CO})_{11}$
Mole range (x $10^{-6}$ )	0-380	0 - 60	0 - 54
$\bar{V}_i^\infty$ (cm <sup>3</sup> /mole)	$221.65 \pm 1.04^b$	$315.06 \pm 2.58^a$	$471.09 \pm 2.15^a$
		$314.21 \pm 2.571^b$	

<sup>a</sup> from multi-component mixture; <sup>b</sup> from separate binary study

Subsequent reaction volume determination can be directly calculated using the differences of partial molar volumes of products and partial molar volumes of reactants as shown in Eq. 2. Partial molar volume of CO,  $\bar{V}_{\text{CO}}^\infty$  is equal to 52 (cm<sup>3</sup>/mole) had been already reported by Grigorien and Meilikhov.<sup>10</sup>

$$\Delta_r V^\infty = \bar{V}_{Rh_4PPH_3(CO)_{11}}^\infty + \bar{V}_{CO}^\infty - \bar{V}_{Rh_4(CO)_{12}}^\infty - \bar{V}_{PPH_3}^\infty \quad (2)$$

Thus, the reaction volumes determined by using partial molar volume differences of reactants and products is  $-13.62 \pm 3.52$  (cm<sup>3</sup>/mole).

### **3.0 Conclusion**

Successful simultaneous study of volumetric properties and spectroscopic analysis for a very high dilution ligand substituted organometallic reaction system was achieved, although no libraries nor no a priori information about the pure component spectra and volumetric properties of the components were available. IR reaction spectra and the reconstructed pure component spectra via BTEM algorithm, and mass balance provided information of the observable species and their moles in the reaction mixtures. Combined with the measured bulk property of the mixtures, direct determination of the partial molar volume of each observable reactive species from the multi-component reaction mixture can be determined. Thus the reaction volume can also be calculated.

The success of this study is very encouraging for further study into more complex systems i.e. determination of the volumetric properties of observable but non-isolatable intermediate species through simultaneous study of density and in-situ spectroscopy. In addition, the capability of measuring in the 10s ppm mole range is very crucial.

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