Journal of the Chinese Chemical Society, 1989, *36*, 57–62

KINETICS AND MECHANISM OF THE DECARBONYLATION OF BENZOYLFORMYL PALLADIUM(II) COMPLEX

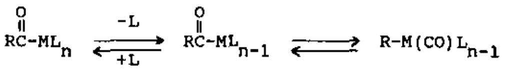
JWU-TING CHEN* (陳竹亭) and CHAU-IN LIU (劉昭吟)

Contribution from Department of Chemistry, National Taiwan University, Taipei, Taiwan, Republic of China.

The benzoylformyl Pd(II) complex, $Pd(PPh_3)_2(Cl)(COCOPh)$, thermally decomposes to the corresponding benzoyl complex by the loss of CO. The predominant route of decarbonylation is led by a reversible dissociation of a phosphine ligand. The disappearance of the benzoylformyl complex in solutions follows first order kinetics not only in the existence of excess PPh_3 but also in the absence of added PPh_3. Through the treatments of both preequilibrium and the steady state approximations to the kinetic data, the rate constants of the intramolecular acyl migration, k_1 and k_2; as well as the equilibrium constant and the individual rate constants of the reversible phosphine dissociation step, K, k_d and k_{-d}, were determined in $CHCl_3$. The activation parameters for k_d, being $\Delta H^{\ddagger} = 25.4$ Kcal Mol^{-1}, $\Delta S^{\ddagger} = 15.9$ eu, $\Delta G^{\ddagger} = 20.7$ Kcal Mol^{-1}; and for k_{-d}, being $\Delta H^{\ddagger} = 13.0$ Kcal Mol^{-1}, $\Delta S^{\ddagger} = -7.9$ eu, $\Delta G^{\ddagger} = 15.4$ Kcal Mol^{-1}, were evaluated.

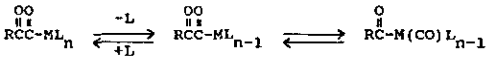
INTRODUCTION

Extensive studies and applications of the decarbonylation of the metal-acyl complexes have been reported.[1] From the mechanistic standing point, the intramolecular migration of an alkyl or an aryl group between an acyl carbon atom and a metal center, which is often accompanied by ligand substitution, has been well conducted as an essential process of the decarbonylation of metal-acyl complexes. However, detailed kinetic measurements are relatively scarce.



$$\overset{O}{\overset{\|}{RC}}\text{-}ML_n \underset{+L}{\overset{-L}{\rightleftarrows}} \overset{O}{\overset{\|}{RC}}\text{-}ML_{n-1} \rightleftarrows R\text{-}M(CO)L_{n-1} \quad (1)$$

The decarbonylation of α-ketoacyl metal complexes appears to be similar to Eq. 1, except that it contains a relatively uncommon intramolecular acyl migration. Nevertheless, this reaction is even rarer, mainly due to the paucity of well-characterized α-ketoacyl metal complexes[2].



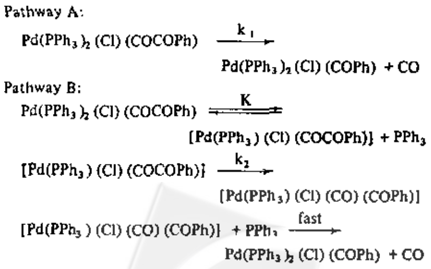
$$\overset{OO}{\overset{\|\|}{RCC}}\text{-}ML_n \underset{+L}{\overset{-L}{\rightleftarrows}} \overset{OO}{\overset{\|\|}{RCC}}\text{-}ML_{n-1} \rightleftarrows \overset{O}{\overset{\|}{RC}}\text{-}M(CO)L_{n-1} \quad (2)$$

The thermal decarbonylation of the benzoylformyl Pd(II) complex, $Pd(PPh_3)_2(Cl)(COCOPh)$, **1**, has been found to yield the corresponding benzoyl product.

$$\underset{\mathbf{1}}{trans\text{-}Pd(PPh_3)_2(Cl)(COCOPh)} \xrightarrow{solvent} trans\text{-}Pd(PPh_3)_2(Cl)(COPh) + CO \quad (3)$$

Its kinetic study clearly establishes a mechanism which comprises two parallel pathways.[3] One pathway undergoes an acyl migration in a satuated (d^8-four coordinate) Pd(II) species. The other pathway has an acyl migration in an unsatuated (d^8-three coordinate) Pd(II) species which results from a reversible dissociation of a phosphine ligand from **1**.

Scheme 1



Pathway A:

$$Pd(PPh_3)_2(Cl)(COCOPh) \xrightarrow{k_1} Pd(PPh_3)_2(Cl)(COPh) + CO$$

Pathway B:

$$Pd(PPh_3)_2(Cl)(COCOPh) \overset{K}{\rightleftarrows} [Pd(PPh_3)(Cl)(COCOPh)] + PPh_3$$

$$[Pd(PPh_3)(Cl)(COCOPh)] \xrightarrow{k_2} [Pd(PPh_3)(Cl)(CO)(COPh)]$$

$$[Pd(PPh_3)(Cl)(CO)(COPh)] + PPh_3 \xrightarrow{fast} Pd(PPh_3)_2(Cl)(COPh) + CO$$

The reversible dissociation of ligands in the organopalladium(II) species are considered to be essential in many stoichiometric and catalytic processes[4]. However, their equilibrium constants and rate constants are rarely known. In this paper, we report our work on the determination of the rate constants and their corresponding thermodynamic parameters for the forward as well as the backward reactions of the PPh_3 dissociation of **1**.

EXPERIMENTAL

Reagents and Compounds All reagents were used as purchased. Dry solvents, which were always distilled from CaH_2 or Na/benzophenone under dry nitrogen, were used when the moisture-free condition was necessary. The benzoylformyl Pd(II) complex and its starting materials were prepared by literature methods and references therein[3].

Kinetic Study The kinetic runs were conducted by conventional spectrophotometric methods on a Hitachi U-3410 model UV-VIS spectrophotometer. The reaction temperature was controlled to an accuracy of ± 0.2°C by a Julabo F10-VC water circulator. The temperatures of reaction solutions which were thermostated for at least 15 min. in the cuvette and placed in the cell compartment of the spectrophotometer, were recorded. The benzoylformyl Pd(II) complex was the limiting reagent. Its disappearance with time was followed by monitoring the absorption drop at 494nm. The pseudo-dirst-order rate constants were obtained directly from the build-in software of the Hitachi machine. All runs showed satisfactory linearity for $\ln(A_t - A_\infty)$ vs. time for five half lives. The kinetic data then were analyzed with a linear regression program.

RESULTS AND DISCUSSION

The kinetics for the title reaction with a variety of PPh_3 concentrations have been studied in CH_2Cl_2. The rate law in the form of Eq. 4 is in agreement with Scheme 1 when $[PPh_3] >> K$. Unlike other mechanistic systems, pseudo-first-order kinetics were observed not only under the conditions of using excess PPh_3, but also in the absence of any added PPh_3. Taking advantage of this extraodinary phenomenon, we have evaluated k_1, k_2, and K individually in the prior work. The K values are small. For example, at 25.4°C, in CH_2Cl_2, $K = 4.6 \times 10^{-5}$ M.[3] Therefore, the steady-state approximation for Scheme 1 will also be appropriate for $[Pd(PPh_3)(Cl)(COCOPh)]/[Pd\text{-}COCOPh]_0 < 0.05$, wherein the denominator represents the initial concentration of 1. Designating k_d and k_{-d} to stand for the rate constants of the forward and the backward reactions of the phosphine dissociation of complex **1** respectively, (i.e. $k_d/k_{-d} = K$), one may write the rate law into the following forms.

$$k_{obsd} = k_1 + \frac{k_2 K}{[PPh_3]} \tag{4}$$

$$\frac{-d[Pd(PPh_3)_2(Cl)(COCOPh)]}{dt} = \left(k_1 + \frac{k_2 k_d}{k_2 + k_{-d}[PPh_3]}\right)[Pd(PPh_3)_2(Cl)(COCOPh)] \tag{5}$$

$$\frac{1}{k_{obsd} - k_1} = \frac{1}{k_d} + \frac{k_{-d}[PPh_3]}{k_2 k_d} \tag{6}$$

With the known values of k_1 and K, Eq. 6 allows the determination of k_d and k_{-d}. The complete kinetic measurements for the title reaction thus provide an excellent opportunity to look at the insight of some fundamental, however hardly quantitatively approached organometallic transformations.

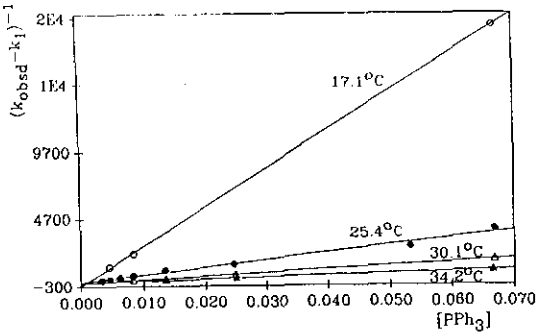


Fig. 1 The Kinetic Plot of $(k_{obsd}-k_1)^{-1}$ vs. $[PPh_3]$ for the Decarbonylation of $Pd(PPh_3)_2(Cl)(COCOPh)$ in CH_2Cl_2.

The plots of $(k_{obsd}-k_1)^{-1}$ vs. $[PPh_3]$ for the kinetic runs studied previously in CH_2Cl_2 indeed exhibit good linearity, as shown in Figure 1. The set of data at 25.4°C gives k_d, 7.0×10^{-2} s^{-1}, and k_{-d}, 1.5×10^3 $M^{-1} s^{-1}$. Unfortunately, the smaller-than-error values of k_d^{-1} for the lines of other temperatures result in negative intercepts which cause k_d, k_{-d}, and their respective thermodynamic parameters to be uncalculable.

The above rate constants are intriguing and worth some comments. The reversible phosphine dissociation in a Pd(II) complex is common and important. Surprisingly, very few comparable measurements of k_d for the Pd(II) system have been reported. The kinetic study of the thermolysis of cis-$Pd(PMePh_2)_2Me_2$ by Yamamoto et al. affords $k_d \leqslant 10^{-3}$ s^{-1}.[5] The larger value of our measurement is ascribed to the weaker PPh_3 and their trans arrangement, which both favor the dissociation step. Whiteside's study in the reductive elimination of cis-$Pt(PEt_3)_2R_2$, preceded by phosphine dissociation produced k_d ~ 10^{-6} s^{-1}.[6] Our result of a much larger k_d is consistent with the usually better substitution lability found in Pd(II) systems than in corresponding Pt(II) systems.

To our knowledge, the determination of k_{-d} for the Pd(II) systems is unprecedented. Direct investigation on these phosphine association steps is not feasible, because the coordinatively unsatuated intermediates are usually unavailable. The determination of k_d and k_{-d} is particularly significant, since these values may be general for various Pd(II) species,[3,5] which are often used as catalysts or employed for the promotion of organic transformations.

In order to acquire the thermodynamic data for k_d and k_{-d}, analogous kinetic study was done in chloroform. This solvent was chosen, because it is also considered to be non-coordinating; and its higher boiling point affords a wider temperature range which is more feasible for kinetic investigation than in CH_2Cl_2. The kinetic data are listed in Table 1. Figure 2 and Figure 3 illustrate the linear plots of k_{obsd} vs. $[PPh_3]^{-1}$ and $(k_{obsd}-k_1)^{-1}$ vs. $[PPh_3]$ respectively. Table 2 summarize the values of all of kinetic parameters which follow Eyring relationship as shown in Figure 4. Their corresponding activation parameters are collected in Table 3.

The values of k_1 and k_2 determined in chloroform show little change (less than five fold increase), compared with those obtained in CH_2Cl_2. This is not surprising, since the intramolecular processes of acyl migration are not expected to be greatly dependent on solvents. This argument is also supported by the close values of energetics for k_1 and for k_2 in

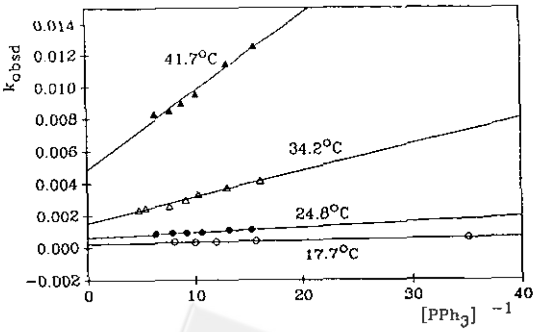


Fig. 2 The Kinetic Plot of k_{obsd} vs. $[PPh_3]^{-1}$ for the Decarbonylation of $Pd(PPh_3)_2(Cl)(COCOPh)$ in $CHCl_3$.

Table 1 The Kinetic Data for the Thermal Decarbonylation of $Pd(PPh_3)_2(Cl)(COCOPh)$ in $CHCl_3$.

T °C	$[Pd\text{-}COCOPh]_0$ 10^3M	$[PPh_3]_{add}$ 10^2M	k_{obsd} $10^3\ s^{-1}$
17.7	6.30	1.22	0.339
	6.25	9.95	0.309
	6.21	8.35	0.351
	6.38	6.38	0.381
	6.30	2.85	0.604
	6.34	1.42	0.966
24.8	6.30	6.54	1.12
	6.30	7.58	1.02
	6.38	9.38	0.937
	6.17	10.8	0.917
	6.30	12.6	0.897
	6.25	15.7	0.857
34.2	6.34	6.19	4.15
	6.30	7.65	3.72
	6.25	9.69	3.30
	6.25	10.9	2.95
	6.34	13.0	2.60
	6.34	18.5	2.50
	6.17	20.8	2.37
41.7	6.21	6.40	12.5
	6.25	7.65	11.4
	6.21	9.75	9.53
	6.25	11.2	8.94
	6.17	12.9	8.50
	6.30	15.8	8.28

Table 3 Thermodynamic Parameters for the Decarbonylation of $Pd(PPh_3)_2(Cl)(COCOPh)$

Solvent	Kinetic Parameter	$\Delta H^{\ddagger}(\Delta H^{\circ})$ Kcal Mol^{-1}	$\Delta S^{\ddagger}(\Delta S^{\circ})$ cal $Mol^{-1}K^{-1}$	$\Delta G^{\ddagger}(\Delta G^{\circ})$ Kcal Mol^{-1}
CH_2Cl_2	k_1	25.4	10.4	22.3
CH_2Cl_2	k_2	18.1	0.1	18.1
CH_2Cl_2	K	13.0	23.9	5.9
$CHCl_3$	k_1	22.7	3.1	21.8
$CHCl_3$	k_2	17.2^a	-2.7^a	18.0
$CHCl_3$	k_d	25.4	15.9	20.7
$CHCl_3$	k_{-d}	13.0	−7.9	15.4
$CHCl_3$	K	12.4	23.8	5.3

a). average value from preequilibrium and steady-state treatments.

two solvents. In contrast, k_d and k_{-d} are about 30 and 50 fold lower respectively in $CHCl_3$ than in CH_2Cl_2 at @ 25°C. The similar ΔG° values of the equilibrium of phosphine dissociation in two solvents indicate that the solvent offers little influence on the ground states. The above rate discrepencies, therefore, are attributted to the difference between the transition states, although its immediate reason is not explicit. Accordingly, $\Delta G^{\ddagger}$ for k_d and k_{-d} in CH_2Cl_2 may be estimated as 18.6 Kcal Mol^{-1} and 13.1 Kcal mol^{-1}. The positive $\Delta S^{\ddagger}$ for k_d and negative $\Delta S^{\ddagger}$ for k_{-d} support Scheme 1. The larger $\Delta G^{\ddagger}$ for k_d than that for k_{-d} and the positive $\Delta H^{\ddagger}$

Table 2 Kinetic Parameters for the Decarbonylation of $Pd(PPh_3)_2(Cl)(COCOPh)$ in $CHCl_3$

T °C	K_1 s^{-1}	k_2K^a $M\ s^{-1}$	K^a M	$(k_2K)^{-1}$ $M^{-1}\ s$	k_d s^{-1}	k_{-d} $M^{-1}s^{-1}$	k_2^a s^{-1}	k_2^b s^{-1}
17.7	2.25×10^{-4}	1.06×10^{-5}	9.7×10^{-5}	8.59×10^{4}	1.7×10^{-3}	1.7×10^{1}	1.1×10^{-1}	1.2×10^{-1}
24.8	6.62×10^{-4}	2.84×10^{-5}	6.3×10^{-5}	3.05×10^{4}	2.1×10^{-3}	3.3×10^{1}	4.5×10^{-1}	5.2×10^{-1}
34.2	1.54×10^{-3}	1.62×10^{-4}	2.5×10^{-4}	5.56×10^{3}	1.4×10^{-2}	5.7×10^{1}	6.4×10^{-1}	7.1×10^{-1}
41.7	4.84×10^{-3}	4.86×10^{-4}	3.8×10^{-4}	1.81×10^{3}	4.0×10^{-2}	1.0×10^{2}	1.3	1.4

a) determined by preequilibrium treatment. b) determined by steady-state treatment.

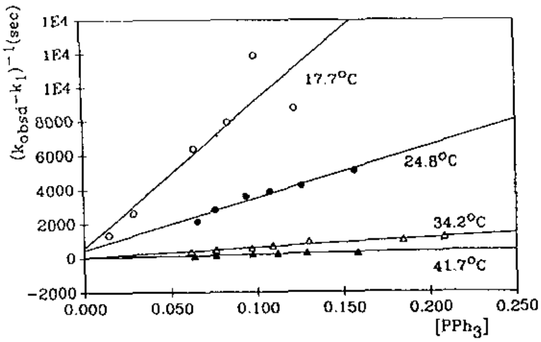


Fig. 3 The Kinetic Plot of $(k_{obsd}-k_1)^{-1}$ vs. $[PPh_3]$ for the Decarbonylation of $Pd(PPh_3)_2(Cl)(COCOPh)$ in $CHCl_3$.

for both parameters suggest that the transition state is a late-reaction type, of which the cleavage of the Pd-P bond is substantial. (or the formation of Pd-P is not important when the association step is considered.)

Reactions in a variety of solvents were briefly examined too, with data listed in Table 4. The coordinating ability of the solvent obviously overrides the polarity effect and slightly hinders the decarbonylation of 1. Detailed kinetic studies in various sovent systems are still in progress.

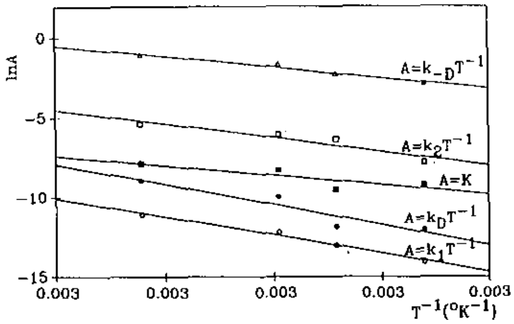


Fig. 4 The Eyring Plots for the Decarbonylation of $Pd(PPh_3)_2(Cl)(COCOPh)$ in $CHCl_3$.

Table 4 Kinetic Data for the Decarbonylation of $Pd(PPh_3)_2(Cl)(COCOPh)$ in Various Solvents[a]

solvent[b]	$[Pd\text{-}COCOPh]_0$	$[PPh_3]$	k_{obsd}
	M	M	s^{-1}
$CHCl_3$	7.99×10^{-3}	c	4.60×10^{-2}
CH_2Cl_2	6.98×10^{-3}	5.89×10^{-5}	3.05×10^{-2}
$CHCl_3/CH_2Cl_2$	6.70×10^{-3}	c	3.74×10^{-2}
acetone/CH_2Cl_2	6.75×10^{-3}	c	3.12×10^{-2}
benzene/CH_2Cl_2	6.66×10^{-3}	c	2.89×10^{-2}
CH_3NO_2/CH_2Cl_2	6.70×10^{-3}	c	2.07×10^{-2}
CH_3CN/CH_2Cl_2	6.78×10^{-3}	7.55×10^{-5}	1.05×10^{-2}
CH_3CN/CH_2Cl_2	6.64×10^{-3}	3.57×10^{-3}	2.69×10^{-3}
CH_3CN/CH_2Cl_2	6.59×10^{-3}	6.38×10^{-3}	1.62×10^{-3}
CH_3CN/CH_2Cl_2	6.73×10^{-3}	2.49×10^{-2}	5.94×10^{-4}

a) T = 25.3°C for all runs.
b) All solvent mixtures were in 1:1 volume ratio.
c) Concentration of dissociated PPh_3 was not determined.

ACKNOWLEDGEMENT

The kinetics studied in CH_2Cl_2 were done at Penn State University, USA. We are grateful to Professor C. T. Huang (黃青眞) of Department of Agricultural Chemistry, NTU for letting us use the UV-VIS spectrophotometer. We also thank National Science Council for the support of this work through Grant NSC77-0208-M002-48.

Received September 12, 1988.

Key Word Index– Decarbonylation, α-Ketoacyl complex, Kinetics and Mechanism.

REFERENCES

1. (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry;* University

Science Books: Mill Valley, CA, **1987**. Chapter 6 and references therein. (b) Specifically for Pd(II) system, Anderson, G. K.; Cross, R. J. *Acc. Chem. Res.* **1984**, *17*, 67.

2. (a) Dobrzynski, E. D.; Angelici, R. J. *Inorg. Chem.* **1975**, *14*, 59. (b) Casey, C. P.; Bunnell, C. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1976**, *98*, 1166. (c) Chen, J.-T.; Sen, A. *J. Am. Chem. Soc.* **1984**, *106*, 1506. (d) Ozawa, F.; Sugimoto, T.; Yamamoto, T.; Yamamoto, A. *Organometallics*, **1984**, *3*, 692.
3. Sen, A; Chen, J.-T.; Vetter, W. M.; Whittle, R. R.; *J. Am. Chem. Soc.* **1987**, *109*, 148.
4. (a) Twigg, M. V. Editor *Mechanisms of Inorganic and Organometallic Reactions;* Plenum Press, New York, **1987**. (b) Garrou, P. E.; Heck, R. F. *J. Am. Chem. Soc.* **1976**, *98*, 4115.
5. Ozawa, F.; Ito, T.; Nakamura, Y.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1868.
6. Foley, P.; DiCosimo, R.; Whitesides, G. M. *J. Am. Chem. Soc.* **1980**, *102*, 6713.