# Kinetics of the Reversible Formation of Alkoxycarbonyl–Platinum Complexes through Reactions of Alcohols with *trans*-Chlorocarbonylbis(triphenylphosphine)platinum(II)

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**Abstract:** The kinetics of the following reactions were examined for a variety of alcohols (ROH): $PtCl(PPh_3)_2(CO)^+ + ROH \rightleftarrows PtCl(PPh_3)_2(COOR) + H^+$. The reactions were found to be reversible and to obey the rate law $d[PtCl(PPh_3)_2(COOR)]/dt = k_1[PtCl(PPh_3)_2(CO)^+][ROH] - k_{-1}[PtCl(PPh_3)_2(COOR)][H^+]$. Values of $k_1$, determined at 25° in $CH_2Cl_2$ containing 8 vol % *N,N*-dimethylformamide, ranged from 11.1 $M^{-1}$ sec$^{-1}$ for methanol to 0.68 $M^{-1}$ sec$^{-1}$ for 2-propanol. The corresponding values of the equilibrium quotients, $K_{eq}$ $(=k_1/k_{-1})$, determined from kinetic measurements on both the forward and reverse reactions, ranged from $1.2 \times 10^{-3}$ to $6.8 \times 10^{-5}$, respectively. $k_{-1}$ proved to be relatively insensitive to variation of the alcohol.

The paper describes kinetic studies, for a series of alcohols (ROH), on both the forward and reverse reactions depicted by

$$\underset{\mathbf{1}}{PtCl(PPh_3)_2(CO)^+} + ROH \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \underset{\mathbf{2}}{PtCl(PPh_3)_2(COOR)} + H^+ \quad (1)$$

Salts of $PtCl(PPh_3)_2(CO)^+$ (**1**) were first prepared and characterized by Clark and his coworkers who also described the reaction of the cation **1** with alcohols to form the corresponding alkoxycarbonyl–platinum complexes **2**, as well as possibly related reactions of **1** and **2** with water to form $PtHCl(PPh_3)_2$.[1–4]

Other cationic metal carbonyls including $Mn(CO)_4(PPh_3)_2^+$,[5] $Ir(CO)_3(PPh_3)_2^+$,[6] $Ir(CO)_2(2,2'\text{-bipyridyl})I^+$,[7] and $Rh(CO)_2(SbPh_3)_3^+$ [8] have also been reported to react with alcohols to form the corresponding alkoxycarbonyl compounds, *e.g.*, $Mn(CO)_3(PPh_3)_2(COOR)$. Our kinetic studies on reaction 1 are thus of some general interest.

## Experimental Section

Materials. [*trans*-$PtCl(PPh_3)_2(CO)$]$BF_4$ (**1**) was prepared from *cis*-$PtCl_2(PPh_3)_2$ according to the method of Clark, Dixon, and Jacobs.[2] $PtCl(PPh_3)_2(COOCH_3)$ and $PtCl(PPh_3)_2(COOC_2H_5)$ were prepared by dissolving **1** in pure methanol or ethanol, respectively; the precipitated products which formed immediately were separated by filtration (*ca.* 90% yield) and dried for 24 hr *in vacuo*. *Anal.* Calcd for $PtCl(PPh_3)_2(COOCH_3)$: C, 56.0; H, 4.1. Found: C, 55.6; H, 4.2; $\nu_{C=O}$, 1661 cm$^{-1}$ (lit. 1664).[2] Calcd for $PtCl(PPh_3)_2(COOC_2H_5)$: C, 56.6; H, 4.2. Found: C, 56.8; H, 4.2; $\nu_{C=O}$, 1635 cm$^{-1}$ (lit. 1638).[2] The other products were obtained by adding a large excess of the appropriate alcohols to a $CH_2Cl_2$ solution of **1** containing *ca.* $10^{-1}$ *M* 2,4,6-tris(*tert*-butyl)pyridine to drive reaction 1 to the right. The resulting products, which precipitated within about 15 min, were separated in >90% yield by filtration, washed with $CH_2Cl_2$, and dried for 24 hr *in vacuo*. *Anal.* Calcd for $PtCl(PPh_3)_2(COOCH(CH_3)_2)$: C, 57.1; H, 4.4. Found: C, 57.5; H, 4.3; $\nu_{C=O}$, 1615 cm$^{-1}$. Calcd for $PtCl(PPh_3)_2(COOCH_2C_6H_5)$: C, 59.4; H, 4.2. Found: C, 59.1; H, 4.2; $\nu_{C=O}$ 1642 cm$^{-1}$.

Benzyl alcohol was purified by three successive recrystallizations using a Dry Ice–acetone bath; no volatile impurities could be detected by vpc. The other alcohols were dried with 4A molecular sieves and distilled under reduced pressure. Dichloromethane was redistilled after drying with $P_2O_5$. *N,N*-Dimethylformamide (Baker AR) was dried with 4A molecular sieves. Following the above treatments the alcohols and solvents were all stored under nitrogen.

Perchloric acid (70%) was Baker and Adamson reagent grade.

2,4,6-Tris(*tert*-butyl)pyridine (TTBP)[9] was recrystallized from petroleum ether (40–60°).

**Kinetic Measurements.** The rates of both the forward and reverse reactions were determined spectrophotometrically by following the spectral changes in the vicinity of 300 nm. In the case of the forward reactions the solution generally contained *ca.* $10^{-4}$ *M* [$PtCl(PPh_3)_2(CO)$]$BF_4$ and a substantial excess (typically $10^{-2}$–$10^{-1}$ *M*) of the alcohol. 2,4,6-Tris(*tert*-butyl)pyridine (*ca.* $10^{-3}$ *M*) was added to combine with the acid produced and thereby drive the reaction to completion. In the case of the reverse reactions, a substantial excess of $HClO_4$ (typically $1 \times 10^{-3}$–$5 \times 10^{-3}$ *M*) was added to a solution of $PtCl(PPh_3)_2(COOR)$ (typically $1 \times 10^{-4}$ *M*). The rates of reactions with half-lives of less than 5 sec were determined by the stopped-flow method using a Durrum-Gibson stopped-flow spectrophotometer equipped with a deuterium lamp. Slower reactions were followed conventionally in a Cary 14 spectrophotometer with a thermostated cell compartment. All kinetic measurements were made at 25.0 ± 0.2° in dichloromethane containing 8 vol % *N,N*-dimethylformamide as solvent.

## Results and Discussion

**Choice of Solvent.** The solubility limitations associated with the ionic reactant **1** restricted the choice of solvents to relatively polar organic liquids. Several solvents, notably pure dichloromethane, acetone, and chloroform, were tried but eliminated because they yielded irreproducible results which depended upon the order of addition of reactants (possibly because of complications associated with ion clustering). Pure *N,N*-dimethylformamide yielded satisfactory kinetic behavior but proved inconvenient because of the instability of the platinum carbonyl complex **1** in this medium. All of these complicating features were absent in the solvent medium finally selected for the kinetic studies, namely dichloromethane containing 8 vol % *N,N*-dimethylformamide (DMF). The kinetics of both the forward and reverse reactions in this medium were well behaved and unaffected by the addition of small amounts

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(2) H. C. Clark, K. R. Dixon, and W. J. Jacobs, *ibid.*, **90**, 2259 (1968); **91**, 1346 (1969).

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(9) Prepared and kindly supplied to us by Dr. E. A. Deutsch, Department of Chemistry, University of Chicago.

Table I. Kinetic Data for Forward Reactions[a]

| Alcohol | $10^2$[ROH], $M$ | $\overrightarrow{k}_{obsd}$, sec$^{-1}$ | $k_1$, $M^{-1}$ sec$^{-1}$ |
|---|---|---|---|
| $CH_3OH$ | 1.98 | 0.231 | 11.7 |
| $CH_3OH$ | 3.95 | 0.396 | 10.0 |
| $CH_3OH$ | 7.90 | 0.866 | 11.0 |
| $CH_3OH$ | 11.6 | 1.95 | 12.3 |
| $CH_3OH$ | 31.6 | 3.30 | 10.4 |
| $CH_3CH_2OH$ | 0.62 | 0.027 | 4.35 |
| $CH_3CH_2OH$ | 1.55 | 0.070 | 4.52 |
| $CH_3CH_2OH$ | 3.10 | 0.126 | 4.06 |
| $CH_3CH_2OH$ | 6.20 | 0.231 | 3.73 |
| $CH_3CH_2OH$ | 13.7 | 0.590 | 4.31 |
| $CH_3CH_2OH$ | 27.4 | 1.22 | 4.45 |
| $CH_3CH_2CH_2OH$ | 1.20 | 0.0343 | 2.86 |
| $CH_3CH_2CH_2OH$ | 2.20 | 0.0613 | 2.79 |
| $CH_3CH_2CH_2OH$ | 2.40 | 0.0693 | 2.89 |
| $CH_3CH_2CH_2OH$ | 4.40 | 0.121 | 2.75 |
| $CH_3CH_2CH_2OH$ | 8.60 | 0.220 | 2.56 |
| $CH_3CH_2CH_2OH$ | 17.2 | 0.403 | 2.34 |
| $(CH_3)_2CHOH$ | 2.34 | 0.0158 | 0.68 |
| $(CH_3)_2CHOH$ | 4.70 | 0.0315 | 0.67 |
| $(CH_3)_2CHOH$ | 9.40 | 0.0639 | 0.68 |
| $(CH_3)_2CHOH$ | 18.8 | 0.126 | 0.67 |
| $C_6H_5CH_2OH$ | 0.087 | 0.018 | 2.07 |
| $C_6H_5CH_2OH$ | 1.74 | 0.039 | 2.24 |
| $C_6H_5CH_2OH$ | 3.48 | 0.072 | 2.07 |
| $C_6H_5CH_2OH$ | 5.22 | 0.112 | 2.15 |
| $C_6H_5CH_2OH$ | 6.96 | 0.141 | 2.03 |
| $CH_2(OCH_3)CH_2OH$ | 0.90 | 0.053 | 5.89 |
| $CH_2(OCH_3)CH_2OH$ | 1.80 | 0.092 | 5.11 |
| $CH_2(OCH_3)CH_3OH$ | 2.70 | 0.139 | 5.15 |
| $CH_2(OCH_3)CH_2OH$ | 3.60 | 0.183 | 5.08 |
| $(CH_3)_3COH$[b] | 20 | | |

[a] In 8 vol % DMF–92 vol % $CH_2Cl_2$ at 25.0°. Initial [PtCl$(PPh_3)_2(CO)^+$] = *ca.* $1 \times 10^{-4}$ $M$. [TTBP] varied from $1 \times 10^{-3}$ to $2 \times 10^{-3}$ $M$. [b] Forward reaction either too slow or extent of reaction too small to be detected.

of water (up to 1% of the alcohol concentration in the case of the forward reactions).

**Stoichiometry.** The stoichiometries were established by the essentially quantitative isolation of the alkoxycarbonyl products of the reactions of **1** with the various alcohols as described earlier. The stoichiometries were confirmed, and the reversibility of the reactions demonstrated, by the quantitative matching of the observed spectral changes accompanying both the forward and reverse reactions with the spectral changes computed from the known spectra of the reactants and products. The results of such experiments, depicted in Figure 1 for the methanol reaction, are quantitatively in accord with the reversible stoichiometry described by eq 1.

**Kinetics.** The kinetics of each of the reactions conformed to the complete rate law described by eq 2, which is comprised of the expected second-order kinetic contributions from both the forward and reverse reactions.

$$d[PtCl(PPh_3)_2(COOR)]/dt = k_1[PtCl(PPh_3)_2(CO)^+][ROH] - k_{-1}[PtCl(PPh_3)_2(COOR)][H^+] \quad (2)$$

In each case the forward and reverse reactions were studied separately. Because of the relatively small equilibrium quotients it proved necessary to add a base to neutralize the acid generated in order to drive the reactions to completion in the forward direction. Bases such as pyridine were unsatisfactory apparently because of their tendency to coordinate to the platinum (probably with accompanying displacement of the chloride). However, 2,4,6-tris (*tert*-butyl) pyridine (TTBP), which is presumably constrained from such coordination by steric hindrance, proved quite satisfactory and was used for this purpose. No reaction between TTBP and **1** could be detected in the absence of alcohol, and the rate of reaction with alcohol was unaffected by variation of the concentration of added TTBP between $1 \times 10^{-3}$ and $2 \times 10^{-3}$ $M$. The addition of *ca.* $10^{-3}$ $M$ TTBP was sufficient to drive the forward reaction to completion except for the reactions of 2-propanol and 2-methoxyethanol whose equilibrium constants are

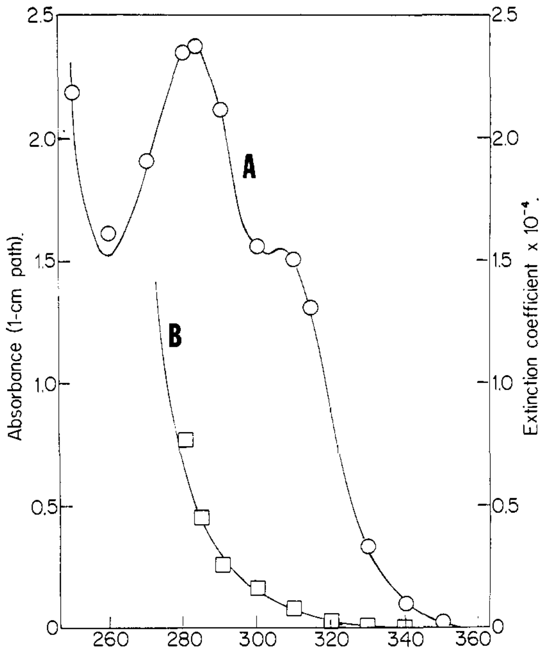


Figure 1. Spectral changes accompanying the reaction PtCl$(PPh_3)_2(CO)^+$ + $CH_3OH$ $\rightleftarrows$ $PtCl(PPh_3)_2(COOCH_3)$ + $H^+$: A, spectrum of $1.0 \times 10^{-4}$ $M$ $[PtCl(PPh_3)_2(CO)]BF_4$; B, spectrum of $1.0 \times 10^{-4}$ $M$ $PtCl(PPh_3)_2(COOCH_3)$; □, spectrum of solution following reaction of $1.0 \times 10^{-4}$ $M$ $PtCl(PPh_3)_2(CO)^+$ with excess $CH_3OH$ in presence of $1 \times 10^{-3}$ $M$ TTBP; ○, spectrum of solution following reaction of $1.0 \times 10^{-4}$ $M$ $PtCl(PPh_3)_2(COOCH_3)$ with excess $HClO_4$.

Table II. Kinetic Data for the Reverse Reactions[a]

| R | $10^3[HClO_4]$, $M$ | $\overleftarrow{k}_{obsd}$, sec$^{-1}$ | $10^{-3}k_{-1}$, $M^{-1}$ sec$^{-1}$ |
|---|---|---|---|
| $CH_3$ | 1.00 | 9.4 | 9.4 |
| $CH_3$ | 2.00 | 20.4 | 10.2 |
| $CH_3$ | 4.00 | 36.9 | 9.2 |
| $CH_2CH_3$ | 1.00 | 9.2 | 9.2 |
| $CH_2CH_3$ | 2.00 | 17.8 | 8.9 |
| $CH_2CH_3$ | 4.00 | 34.7 | 8.7 |
| $CH(CH_3)_2$ | 1.08 | 11.4 | 10.6 |
| $CH(CH_3)_2$ | 2.15 | 21.7 | 10.1 |
| $CH(CH_3)_2$ | 4.30 | 44.2 | 10.3 |
| $CH_2C_6H_5$ | 1.08 | 6.4 | 5.9 |
| $CH_2C_6H_5$ | 2.15 | 11.6 | 5.4 |
| $CH_2C_6H_5$ | 4.30 | 22.4 | 5.2 |
| $CH_2CH_2OCH_3$ | 1.00 | 25.7 | 25.7 |
| $CH_2CH_2OCH_3$ | 2.00 | 45.6 | 22.8 |
| $CH_2CH_2OCH_3$ | 4.00 | 92.5 | 23.1 |

[a] In 8 vol % DMF–92 vol % $CH_2Cl_2$ at 25.0°. Initial [PtCl$(PPh_3)_2(COOR)$] = *ca.* $1 \times 10^{-4}$ $M$.

**Table III.** Summary of Rate and Equilibrium Constants

| Alcohol | $k_1$, $M^{-1}$ sec$^{-1}$ | $k_{-1}$, $M^{-1}$ sec$^{-1}$ | $10^4K_{eq}$ |
|---|---|---|---|
| $CH_3OH$ | 11.1 ± 0.8 | (9.6 ± 0.4) × $10^3$ | 12 ± 1 |
| $CH_3CH_2OH$ | 4.2 ± 0.3 | (8.9 ± 0.3) × $10^3$ | 4.7 ± 0.3 |
| $CH_3CH_2CH_2OH$ | 2.7 ± 0.3 | | |
| $(CH_3)_2CHOH$ | 0.68 ± 0.12 | (10.3 ± 0.4) × $10^3$ | 0.63 ± 0.05 |
| $C_6H_5CH_2OH$ | 2.1 ± 0.1 | (5.5 ± 0.3) × $10^3$ | 3.8 ± 0.2 |
| $CH_2(OCH_3)CH_2OH$ | 5.3 ± 0.3 | (24 ± 2) × $10^3$ | 2.2 ± 0.2 |

rather unfavorable and for which the necessary small corrections for the reverse reactions were applied. The reverse reactions all went readily to completion.

Both the forward and reverse reactions were examined under conditions such that one of the reactants (*i.e.*, ROH or $HClO_4$) was present in substantial excess over the other ($PtCl(PPh_3)_2(CO)^+$ and $PtCl(PPh_3)_2(COOR)$, respectively) and the observed kinetic behavior was therefore pseudo first order, according to

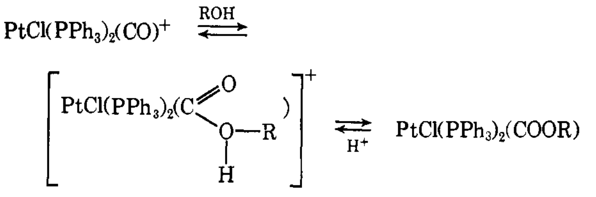
$$-\mathrm{d}\ln[PtCl(PPh_3)_2(CO)^+]/\mathrm{d}t = \overrightarrow{k}_{obsd} = k_1[ROH] \quad (3)$$

$$-\mathrm{d}\ln[PtCl(PPh_3)(COOR)/\mathrm{d}t = \overleftarrow{k}_{obsd} = k_{-1}[H^+] \quad (4)$$

Good first-order plots, extending over at least three half-lives, were obtained for each of the forward and reverse reactions. The results of the kinetic measurements are summarized in Tables I and II, and confirm the first-order dependencies of $\overrightarrow{k}_{obsd}$ and $\overleftarrow{k}_{obsd}$ on [ROH] and [$H^+$], respectively. The values of $k_1$ and $k_{-1}$ are summarized in Table III, together with the corresponding equilibrium quotients computed from the relation, $K_{eq} = k_1/k_{-1}$.

The representation of the ionic species, *i.e.*, $PtCl(PPh_3)_2(CO)^+$ and $H^+$, by eq 1 and 2, is clearly an oversimplification. In the absence of added TTBP the prevalent acid species in solution is presumably $HCON(CH_3)_2H^+$. Furthermore, in view of the relatively low dielectric constant of the medium, it is likely that the ionic species are actually present as ion pairs. It would, however, appear from the good second-order kinetic behavior observed for both the forward and reverse reaction that higher order ion clustering, if any, does not occur to a significant extent. This is also supported by the absence of any departures from Beers' law.

**Mechanism.** Following several earlier suggestions along related lines,[2,4,6] we interpret these reactions in terms of the mechanism depicted by eq 5, which involves nucleophilic attack of the alcohol on the carbon atom of the coordinated carbonyl ligand.



(5)

Analogous mechanisms have previously been proposed for the reactions of alcohols and water with other cationic metal carbonyls.[2,4,6] The hydrolysis of *cationic* tropolonates of silicon and of certain metals has also been interpreted in terms of nucleophilic attack of $OH^-$ on a carbon atom of the coordinated ligand.[10] Such reactions appear to have been observed, thus far, only for cationic complexes.

The absence of a base (*i.e.*, TTBP) dependence of the rate of the forward reaction (as well as the first-order acid dependence of the reverse reaction) implies that the alcohol molecules rather than the alkoxide ions are the nucleophiles in the present reactions. While reliable data on the relative basicity of alcohols are not available, there is no obvious basis for interpreting the observed trends of the rates or equilibrium quotients in terms of electronic properties. Instead, the order of $k_1$ value, *i.e.*, $CH_3OH > CH_2(OCH_3)CH_2OH \gtrsim CH_3CH_2OH > CH_3CH_2CH_2OH \gtrsim C_6H_5CH_2OH > (CH_3)_2CHOH > (CH_3)_3COH$, is probably more easily reconciled with a dependence on steric factors. The variation among the $k_{-1}$ values (particularly for the simple aliphatic alcohols) is relatively small and thus the equilibrium quotients $K_{eq}$ closely parallel the rate constants ($k_1$) for the forward reactions.

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[10] E. L. Muetterties and C. M. Wright, *J. Amer. Chem. Soc.*, **87**, 22 (1965).