plexes $[Pt(CH_3)Q_3]PF_6$ and $[Pt(CH_3)\{P(C_6H_5)_3\}Q_2]PF_6$ which do not undergo oxidative addition reactions, presumably because the positive charge causes contraction of the orbitals, also show the same nmr spectrum in sulfur dioxide as in chloroform.

The changes in chemical shift of the platinum-bonded methyl group in $Pt(CH_3)LQ_2^+$ as L is changed vary in the order $CH_3CN < (CH_3)_3C_5H_2N < C_5H_5N < C_6H_5CN \sim CO < P(OC_6H_5)_3 < P(CH_3)_2C_6H_5 < P(C_6H_5)_3 < As(C_6H_5)_3 < Sb(C_6H_5)_3$. A similar, but more limited, series was observed[2] for the cationic hydrides.

## Experimental Section

In the procedures described below $Q = P(CH_3)_2(C_6H_5)$. Percentage yields and analytical data are shown in Table I. The general instrumentation and methods have been described previously. Nmr spectra were recorded on a Varian A-60 spectrometer.

**$[PtClQ_3]PF_6$.**—To a suspension of *cis*-$PtCl_2Q_2$ (0.60 g) in methanol (15 ml) under nitrogen was added dimethylphenylphosphine (0.16 g) to give a clear solution. A saturated solution of $KPF_6$ in water was added to give a precipitate which was washed with water and recrystallized from methanol.

**$[PtQ_4](PF_6)_2$.**—To a suspension of *cis*-$PtCl_2Q_2$ (0.51 g) in methanol (15 ml) under nitrogen was added dimethylphenylphosphine (0.50 g) to give a yellow solution. A solution of $KPF_6$ (0.5 g) in water (5 ml) was added and the precipitate was washed with water then with cold methanol.

**Preparation of $[Pt(CH_3)LQ_2]Z$ {L = neutral ligand; Z = $PF_6$ or $B(C_6H_5)_4$}. Procedure a.**—To a suspension of *trans*-$PtCl(CH_3)Q_2$[6a] (*ca.* 0.15 g) in methanol (10 ml) under nitrogen was added 1 molar equivalent of L to give a clear solution. A saturated solution of $KPF_6$ in water was then added and the precipitate was filtered off, washed with cold water, and dried.

**Procedure b.**—A saturated solution of *trans*-$PtCl(CH_3)Q_2$ (*ca.* 0.15 g) in methanol under an atmosphere of the ligand L was treated with a solution of 1 molar equivalent of $AgBF_4$ in methanol (1 ml). The precipitate of silver chloride was filtered off and to the filtrate was added a saturated solution of $KPF_6$ in water. The resulting precipitate was washed well with cold water and dried.

**Procedure c.**—To a solution of *trans*-$PtCl(CH_3)Q_2$ (*ca.* 0.15 g) in the ligand L (8 ml) was added a solution of 1 molar equivalent of $AgBF_4$ in methanol (1 ml). The precipitate of silver chloride was filtered off and the filtrate was reduced to an oil which was dissolved in methanol (2 ml). A solution of $NaB(C_6H_5)_4$ (1 molar equivalent) in methanol (2 ml) was added and the resultant precipitate was washed with cold methanol.

**Solvates of $[P(CH_3)\{P(C_6H_5)_3\}Q_2]PF_6$ (I).**—Compound I was not obtained pure. The crude product from procedure a was dissolved in chloroform (0.5 ml), and after a few minutes the monosolvate crystallized out. A solution of the chloroform solvate in acetone was allowed to evaporate at room temperature and gave the monoacetone solvate. The chloroform solvate of the corresponding $As(C_6H_5)_3$ complex was obtained similarly. The nmr solution of $[PtQ_4](PF_6)_2$ in $CD_3COCD_3$ deposited crystals of a solvate after 5 min.

**$[Pt(CH_3)AQ_2]B(C_6H_5)_4$ (A = 2,4,6-Trimethylpyridine).**—A suspension of *trans*-$PtCl(CH_3)Q_2$ (0.195 g) in methanol (8 ml) containing A (0.200 ml) was warmed to give a clear solution. A solution of $NaB(C_6H_5)_4$ (0.128 g) in methanol (4 ml) was added and the mixture was set aside at room temperature for 20 hr. The resultant precipitate was recrystallized from chloroform–methanol.

***trans*-$[Pt(C_6H_5)_2Q_2]$.**—Attempts to prepare tetraphenylborate salts of cationic complexes containing a weakly coordinating ligand L, using procedures a, b, or c [substituting $NaB(C_6H_5)_4$ for $KPF_6$] gave *ca.* 80% yields of *trans*-$Pt(C_6H_5)_2Q_2$. The complex was also prepared (50% yield) from *cis*-$PtCl_2Q_2$ and phenyllithium. It formed colorless prisms, mp 220–222° dec, from pyridine. *Anal.* Calcd for $C_{28}H_{32}P_2Pt$: C, 53.76; H, 5.15. Found: C, 53.59; H, 5.16.

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# Chemistry of Metal Hydrides. VIII. The Hydrolysis of Transition Metal Alkoxycarbonyls and a Kinetic Study of the Hydrolysis of *trans*-$[PtCl(CO)(R_3P)_2]BF_4$

BY H. C. CLARK AND W. J. JACOBS

*Received October 22, 1969*

A kinetic study of the reaction of *trans*-$[PtCl(CO)\{P(C_2H_5)_3\}_2]BF_4$ with water to give the hydride $PtHCl\{P(C_2H_5)_3\}_2$ is consistent with a mechanism based on the reversible acid dissociation of the carbonyl cation to give a carboxylate species which undergoes further direct reaction with water to give the hydride. The transition metal alkoxycarbonyls $Fe(\pi\text{-}C_5H_5)(CO)_2(COOCH_3)$ and $Mn(CO)_5(COOC_2H_5)$ react with water under mild conditions to give the corresponding hydrido complexes $Fe(\pi\text{-}C_5H_5)H(CO)_2$ and $MnH(CO)_5$ or decomposition products of the latter.

## Introduction

Transition metal hydrides have been prepared by a variety of methods most of which require vigorous forcing conditions.[1] Direct hydrogenation at high pressure, reduction with hydride complexes of group III metals or hydrazine, and reductions with alkaline refluxing alcohols are all widely used. However, with the exception of protonation reactions in acidic aqueous media, few metal hydrides have been synthesized in aqueous media with water as the source of the hydride ligand. We previously reported[2,3] the reaction of the

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(1) M. L. H. Green and D. J. Jones, *Advan. Inorg. Chem. Radiochem.*, **7**, 115 (1965).

(2) H. C. Clark, K. R. Dixon, and W. J. Jacobs, *J. Am. Chem. Soc.*, **91**, 1346 (1969).

(3) H. C. Clark, K. R. Dixon, and W. J. Jacobs, *Chem. Commun.*, 548 (1968).

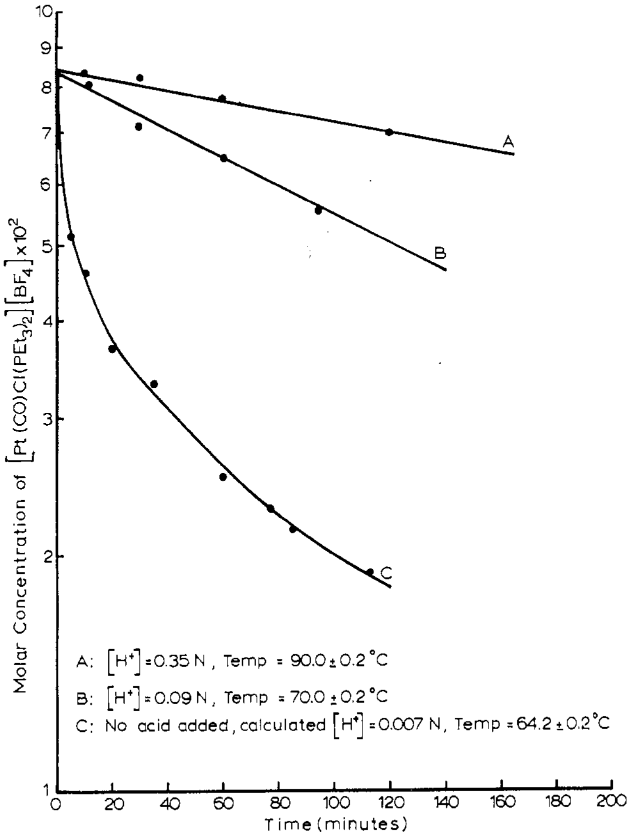


Figure 1.—Reaction of $[Pt(CO)Cl\{P(C_2H_5)_3\}_2][BF_4]$ with water at varying temperatures and hydrogen ion concentrations.

platinum carbonyl cation *trans*-$PtCl(CO)\{P(C_2H_5)_3\}_2^+$ with water to give the hydride *trans*-$PtHCl\{P(C_2H_5)_3\}_2$, and in this paper we present a more detailed study in an attempt to determine the mechanism of this reaction.

We also previously described[3] the reaction of water with platinum alkoxycarbonyl compounds, $PtCl(COOR)\{P(C_6H_5)_3\}_2$ ($R = C_2H_5$ or $CH_3$), to give the corresponding hydrido complex *trans*-$PtHCl\{P(C_6H_5)_3\}_2$ carbon dioxide, and alcohol.

We now extend such studies to alkoxycarbonyl complexes of iron and manganese to show the generality of this behavior.

## Results and Discussion

### 1. The Hydrolysis of *trans*-$[PtCl(CO)\{(P(C_2H_5)_3\}_2][BF_4]$.

—The salt *trans*-$[PtCl(CO)\{P(C_2H_5)_3\}_2][BF_4]$ is acidic in water–acetone solution. The products giving rise to this acidity have not been isolated, but the degree of dissociation has been estimated from pH measurements at different concentrations of the carbonyl salt in acetone–water solution (Table II). Since the original carbonyl salt can be recovered quantitatively by removal of the solvents, a reversible dissociation must be involved, and three possibilities can be suggested.

First, because of its position *trans* to the *trans*-labilizing carbon monoxide ligand, chloride might be replaced by hydroxide ion

$$trans\text{-}[PtCl(CO)\{P(C_2H_5)_3\}_2][BF_4] + H_2O \rightleftharpoons Pt(CO)(OH)\{P(C_2H_5)_3\}_2 + BF_4^- + HCl$$

Henry,[4] in his kinetics studies of the palladium-catalyzed oxidation of olefins, suggested a similar hydroxyl ion replacement of chloride ion in the square-planar palladium(II) anion $PdCl_3(C_2H_4)^-$

$$PdCl_3(C_2H_4)^- + H_2O \rightleftharpoons PdCl_2(H_2O)(C_2H_4) + Cl^-$$

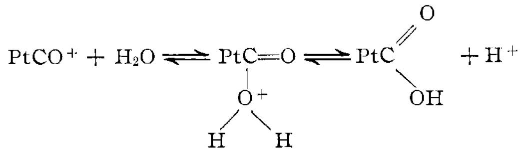
$$PdCl_2(H_2O)(C_2H_4) + H_2O \rightleftharpoons PdCl_2(OH)(C_2H_4)^- + H_3O^+$$

Second, there also exists the possibility of OH addition to the central atom giving a five-coordinate hydroxyplatinum species

$$[Pt(Cl)(CO)\{P(C_2H_5)_3\}_2][BF_4] + H_2O \rightleftharpoons PtCl(OH)(CO)\{P(C_2H_5)_3\}_2 + H^+ + BF_4^-$$

The empty $d_{z^2}$ orbital of platinum is available for bonding with nucleophiles and the cationic nature of the original complex may increase the chance of attack by a nucleophile.

Third, since the carbonyl carbon will be somewhat positive in nature because of the removal of electron density by the positively charged metal, attack by water or hydroxyl ion at the acyl carbon



$$PtCO^+ + H_2O \rightleftharpoons PtC(=O)(O^+H_2) \rightleftharpoons PtC(=O)OH + H^+$$

might be expected. No direct experimental evidence for such a carboxylate species could be obtained; characteristic infrared absorptions of this group are masked by the solvent. However, the close similarity of this equilibrium to the reaction of the triphenylphosphine analog of the carbonyl cation[3] with alcohols

$$trans\text{-}[PtCl(CO)\{P(C_6H_5)_3\}_2][BF_4] + ROH \rightleftharpoons PtCl(COOR)\{P(C_6H_5)_3\}_2 + H^+ + BF_4^-$$

can be stressed.

Furthermore, Deeming and Shaw[5] have recently isolated an iridium carboxylate complex as the product of reaction of water with an iridium carbonyl cation

$$IrCl_2(CO)_2\{P(CH_3)_2(C_6H_5)\}_2^+ + H_2O \longrightarrow IrCl_2(CO)(COOH)\{P(CH_3)_2(C_6H_5)\}_2 + H^+$$

This carboxylate underwent thermal decomposition to give the corresponding hydride, $IrHCl_2(CO)\{P(CH_3)_2(C_6H_5)\}_2$, and carbon dioxide. The formation of a platinum carboxylate and tetrafluoroboric acid leading to the observed acidity is therefore highly probable and is assumed in the subsequent discussion.

As the acidity of the solution was increased, the hydrolysis rate decreased (Figure 1). This retardation can be rationalized in terms of the initial equilibrium in water. If the mechanism involves further reaction of a platinum species, which we shall assume to be the carboxylate complex, then a rate equation may be set up in terms of the carbonyl cation concentration

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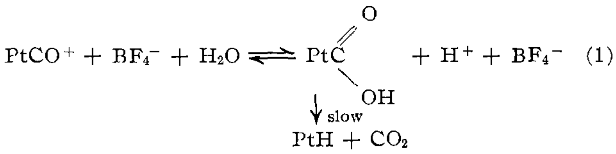
(4) P. M. Henry, *J. Am. Chem. Soc.*, **86**, 3246 (1964).

(5) A. J. Deeming and B. L. Shaw, *J. Chem. Soc., A*, 443 (1969).

and acid concentration, where the overall reaction may be represented as



$$\mathrm{PtCO^+ + BF_4^- + H_2O \rightleftharpoons PtC(=O)OH + H^+ + BF_4^-} \quad (1)$$

$$\mathrm{PtC(=O)OH \xrightarrow{\text{slow}} PtH + CO_2}$$

The rate of reaction can be written as

$$\text{rate} = \frac{-d[\mathrm{PtCOOH}]}{dt} = k[\mathrm{PtCOOH}]$$

Although $k$ may involve a term in water concentration, this can be assumed of constant value throughout the reaction. Using equilibrium 1, the carboxylate concentration may be expressed in terms of the concentration of carbonyl cation and acid: $[\mathrm{PtCOOH}]\cdot[\mathrm{H^+}] = K_{eq}[\mathrm{PtCO^+}][\mathrm{H_2O}]$ and $[\mathrm{PtCOOH}] = K'_{eq}\cdot[\mathrm{PtCO^+}]/[\mathrm{H^+}]$, where $K'_{eq} = K_{eq}[\mathrm{H_2O}]$. The rate of disappearance of the intermediate carboxylate can be approximated to the rate of reaction of the platinum carbonyl cation and the rate can be written as

$$\text{rate} = \frac{-d[\mathrm{PtCOOH}]}{dt} = \frac{-d[\mathrm{PtCO^+}]}{dt} = k[\mathrm{PtCOOH}]$$

and hence

$$\frac{-d[\mathrm{PtCO^+}]}{dt} = kK'_{eq}\frac{[\mathrm{PtCO^+}]}{[\mathrm{H^+}]} \quad (2)$$

As an approximation, the acid concentration can be written in terms of the amount of carbonyl complex consumed

$$[\mathrm{H^+}]^{t=t} = [\mathrm{PtCO^+}]^{t=0} - [\mathrm{PtCO^+}]^{t=t}$$

Hence the rate equation becomes

$$\frac{-d[\mathrm{PtCO^+}]}{dt} = k'[\mathrm{PtCO^+}]\{[\mathrm{PtCO^+}]^{t=0} - [\mathrm{PtCO^+}]\}^{-1}$$

where $k' = kK'_{eq}$. Integration gives the final rate equation

$$[\mathrm{PtCO^+}] - k^* \log [\mathrm{PtCO^+}] = k't + C \quad (3)$$

where $k^* = 2.3[\mathrm{PtCO^+}]^{t=0}$ and $C$ is an integration constant. This equation is entirely consistent with the chemistry involved. A simple first-order reaction of the intermediate carboxylate expressed in terms of the platinum carbonyl concentration gives the logarithmic term. However, as the reaction proceeds, the concentration of the acid increases and effectively acts to lower the concentration of the carboxylate by driving equilibrium 1 to the left. Hence the direct concentration term is an expression for the retarding effect of the acid produced.

Plots of $[\mathrm{PtCO^+}] - k^* \log [\mathrm{PtCO^+}]$ *vs.* time gave good straight lines for the first half-life of the hydrolysis reaction for temperatures ranging from 22.5 to 64° (see Figure 2). Observed values for the composite rate constant $k' = kK'_{eq}$ are given in Table I. Using these rate constants, the activation parameters $\Delta H^* = 20\ (\pm 3)$ kcal mol$^{-1}$ and $\Delta S^* = -21\ (\pm 3)$ eu were obtained. The rate equation was tested by addition of sufficient acid at the beginning of the reaction so that the acid concentration throughout the reaction could be assumed constant. Hence eq 2 simplifies to

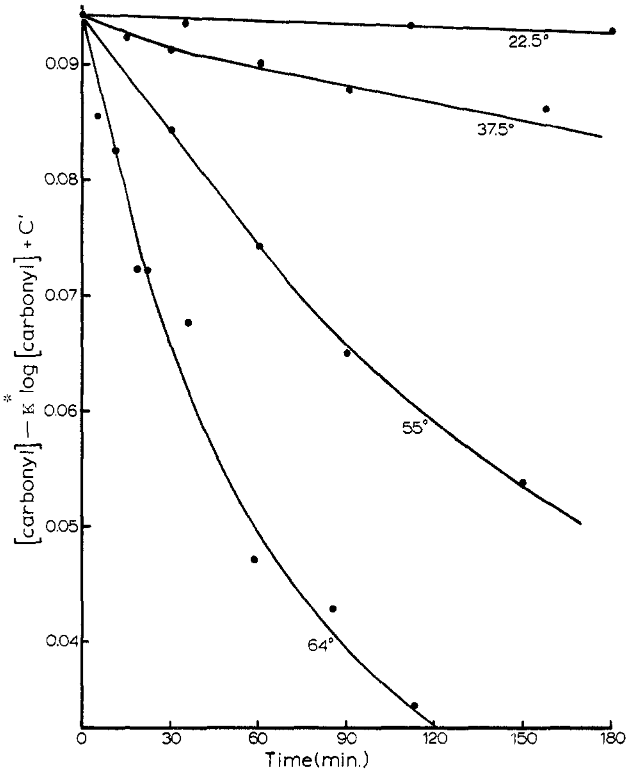


Figure 2.—Plots of $[\mathrm{PtCO^+}] - k^* \log [\mathrm{PtCO^+}]$ *vs.* time, where $C'$ is a constant to adjust the base line and $k^* = 2.303[\text{carbonyl}]^{t=0}$ and $[\text{carbonyl}]^{t=0} = 0.084\ M$.

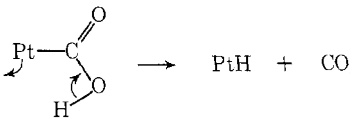
$$\frac{-d[\mathrm{PtCO^+}]}{dt} = k[\mathrm{PtCO^+}]$$

and pseudo-first-order kinetics should then be followed. Plots of $[\mathrm{PtCO^+}]$ *vs.* time at such high acid concentrations, using a logarithmic ordinate, gave good straight lines as expected (see Figure 1) and the rates were much slower than for the reactions with no added acid.

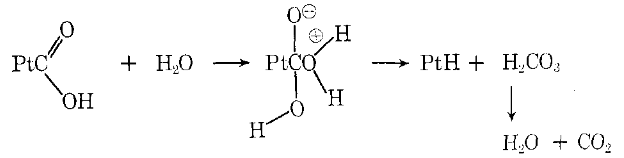
TABLE I

| Run | Temp, °C | $10^5k'$, $M$ sec$^{-1}$ |
|---|---|---|
| 1 | 22.5 | 0.02 |
| 2 | 37.5 | 0.11 |
| 3 | 55.0 | 0.53 |
| 4 | 55.0 | 0.50 |
| 5 | 64.0 | 1.7 |

The mechanism of the rate-determining step is unclear. Possibly the carboxylate intermediate undergoes direct decarboxylation to give the hydride



Such a mechanism is likely in the thermal decomposition of the iridium carboxylate previously mentioned.[5] However, the most likely mechanism in aqueous solution involves direct reaction with water to give carbonic acid



The high negative entropy of activation (−21 eu) measured for the reaction suggests that such a bimolecular reaction is more likely for a rate-determining step than is an intramolecular reaction for which much smaller $\Delta S^*$ values would be expected.

**2. The Hydrolysis of Transition Metal Alkoxycarbonyls.**—We previously reported the reactions of the compounds $PtCl(COOR)\{P(C_6H_5)_3\}_2$ (R = $CH_3$ or $C_2H_5$) with water to give the hydrido complex, *trans*-$PtHCl\{P(C_6H_5)_3\}_2$

$$PtCl(COOR)\{P(C_6H_5)_3\}_2 + H_2O \longrightarrow \textit{trans}\text{-}PtHCl\{P(C_6H_5)_3\}_2 + CO_2 + ROH$$

The reaction is catalyzed by halide salts, especially for R = $CH_3$, and the role of the catalyst is uncertain. We now report the reactions of alkoxycarbonyls of other transition metal complexes with water.

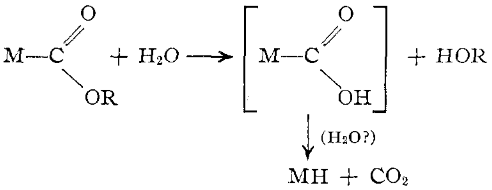
The iron alkoxycarbonyl $Fe(\pi\text{-}C_5H_5)(COOCH_3)(CO)_2$, first reported by King and coworkers,[6] reacts at 40° with shaking in water within 20 min to give a good yield of the hydride $Fe(\pi\text{-}C_5H_5)H(CO)_2$ and its decomposition product[7] $[Fe(\pi\text{-}C_5H_5)(CO)_2]_2$. Carbon dioxide was isolated nearly quantitatively and methanol was identified spectroscopically. Halide salts apparently had no effect on the reaction

$$Fe(\pi\text{-}C_5H_5)(CO)_2(COOCH_3) + H_2O \longrightarrow Fe(\pi\text{-}C_5H_5)(CO)_2H + CO_2 + CH_3OH$$
$$\downarrow \Delta$$
$$[Fe(\pi\text{-}C_5H_5)(CO)_2]_2 + H_2$$

Similar reactivity was observed for the manganese alkoxycarbonyl $Mn(CO)_5COOC_2H_5$.[8] Reaction with water took place at 80° within a few hours to give the manganese hydride $Mn(CO)_5H$ and its decomposition product $[Mn(CO)_5]_2$. Carbon dioxide was isolated in nearly quantitative yield and ethanol was identified as a product. Again halide salts had no apparent catalytic effect on the reaction

$$Mn(CO)_5COOC_2H_5 + H_2O \longrightarrow Mn(CO)_5H + CO_2 + C_2H_5OH$$
$$\downarrow \Delta$$
$$[Mn(CO)_5]_2 + H_2$$

The function of the halide salt remains uncertain and is required for hydrolysis of only the platinum alkoxycarbonyl compounds. It appears, however, that the reaction of transition metal alkoxycarbonyl compounds with water to give hydrides is quite general and does not appear to be particularly dependent on the transition metal or the nature of the surrounding ligands. The most likely position of attack by water is at the acyl carbon, to give a short-lived carboxylate which can then decarboxylate to give the metal hydride



A concerted reaction might also be involved, with water attack leading directly to the hydrido complex and carbon dioxide. In view of the high coordination number of both iron and manganese alkoxycarbonyls, a mechanism involving oxidative addition of water to the central metal appears unlikely.

## Experimental Section

Standard high-vacuum techniques were used for the reactions which were performed in thick-walled Pyrex glass tubing. Infrared spectra were recorded with a Beckman IR 10 spectrophotometer and samples were examined as Nujol mulls or gases. Proton nmr spectra were recorded on a Varian HA-100 spectrometer and chemical shifts were determined relative to tetramethylsilane.

All work with iron and manganese complexes was done under a nitrogen atmosphere. The iron alkoxycarbonyl complex $Fe(\pi\text{-}C_5H_5)(CO)_2(COOCH_3)$ was prepared by the method of King and coworkers.[6] The manganese alkoxycarbonyl complex $Mn(CO)_5(COOC_2H_5)$ was prepared by the method of Kruck and Noack.[8] Both these compounds were freshly sublimed prior to reaction with water. For the kinetic studies, spectra were recorded as chloroform solutions using Beckman Irtran-2 solution cells.

**(a) Calculation of Extent of Dissociation of $PtCl(CO)\{P(C_2H_5)_3\}_2^+$ in Water.**—The pH of acetone–water solutions of known added HCl concentrations was first measured to obtain a calibration for $[H^+]$ analysis in the solvent mixture.

The pH values of solutions of varying concentrations of the carbonyl salt in the water–acetone mixture were then measured, and, using the calibrations obtained from the known HCl solutions, $[H^+]$ and hence the percentage dissociation of the cation was calculated as shown in Table II.

Table II

| Initial concn of carbonyl salt, *M* | Calcd pH | $[H^+]$, *M* | % dissocn |
|---|---|---|---|
| 0.020 | 2.35 | 0.0045 | 23 |
| 0.040 | 2.30 | 0.0050 | 13 |
| 0.082 | 2.15 | 0.0071 | 9 |

**(b) Kinetic Study of Hydrolysis of *trans*-$[PtCl(CO)\{P(C_2H_5)_3\}_2][BF_4]$.**—The progress of the reaction of water with the carbonyl cation in acetone solution of 14 *N* water concentration was followed by infrared spectroscopy by observing the disappearance of the carbonyl peak, $\nu(C\equiv O)$, at 2100 $cm^{-1}$. Identical samples of 0.50 ml of the reacting stock solution were placed in Pyrex tubes of 1.0-ml capacity *via* a ground-glass syringe of 0.5-ml capacity. The tubes were evacuated, sealed, and heated in a constant-temperature oil bath. Tubes ready to be examined were cooled in liquid nitrogen to quench the reaction; then the volatile products were removed under vacuum at 0°. A 0.50-ml sample of chloroform was added to the solid residue and the solution was examined by infared spectroscopy with a 0.1-mm solution cell. A calibration of peak size *vs.* concentration of the carbonyl salt was made and this calibration allowed a direct translation of peak size in the spectra to concentration of the

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(6) R. B. King, M. B. Bisnette, and A. Fronzaglia, *J. Organometal. Chem.* (Amsterdam), **3**, 256 (1965).

(7) M. L. H. Green, C. N. Street, and G. Wilkinson, *Z. Naturforsch.*, **14b**, 738 (1959).

(8) T. Kruck and M. Noack, *Chem. Ber.*, **97**, 1693 (1964).

reactant carbonyl. The peak height to infinite time could be neglected from the calculations.

The two reactions that were run at specified starting acid concentrations had aqueous fluoroboric acid added to the stock solution at the beginning of the experiment.

(c) **Reaction of $Fe(\pi\text{-}C_5H_5)(CO)_2(COOCH_3)$ with Water.**—In an evacuated Pyrex tube, freshly sublimed[6] $Fe(\pi\text{-}C_5H_5)(CO)_2(COOCH_3)$ (0.25 g, 1.1 mmol) was shaken at 45° for 20 min in degassed water (1 ml) containing KCl (1.0 g). Effervescence was observed during the reaction and a deep red liquid, immiscible in water, and a black solid were obtained. The volatile products were distilled under vacuum through traps at $-25$, $-96$, and $-196°$ traps. The trap at $-196°$ contained carbon dioxide (0.036 g, 0.8 mmol) identified by infrared spectroscopy. Two less volatile products were isolated; one was characterized as methanol by infrared and nmr spectroscopy, and the other was tentatively identified by infrared spectroscopy as methyl formate.[9] The trap at $-25°$ contained water and a red liquid identified as $Fe(\pi\text{-}C_5H_5)(CO)_2H$ (0.09 g, 0.52 mmol) by infrared and $^1H$ nmr spectroscopy[10] (hydride chemical shift, $\tau$ 21 in $CHCl_3$). The nonvolatile products were extracted with chloroform and the chloroform extract contained the dimer $[Fe(\pi\text{-}C_5H_5)(CO)_2]_2$ (0.08 g, 0.44 mmol) identified by infrared spectroscopy. The residue, a white solid, was assumed to be KCl. On exposure of the hydrido compound to the atmosphere, reaction to the black dimer was complete within 1 min.

Identical results were obtained when the above reaction was repeated without the salt.

(d) **Reaction of $Mn(CO)_5(COOC_2H_5)$ with Water.**—In a Pyrex tube, freshly sublimed $Mn(CO)_5(COOC_2H_5)$[8] (0.28 g, 1.0 mmol) was shaken at 75° for 12 hr with KCl (1.0 g) and 4 ml of water. A viscous oil, immiscible in water, was left after reaction. The volatile products were distilled through traps at $-25$, $-96$, and $-196°$. The trap at $-196°$ contained carbon dioxide (0.039 g, 0.9 mmol) identified by infrared spectroscopy.

The other traps contained water and ethanol, characterized by infrared and proton nmr spectroscopy, and a yellow liquid characterized by infrared[11] and nmr spectroscopy[10] (hydride chemical shift, $\tau$ 18 in $CHCl_3$) as $Mn(CO)_5H$ (0.12 g, 0.6 mmol). The nonvolatile products contained a yellow solid, identified by infrared spectroscopy as the dimeric compound $Mn_2(CO)_{10}$ (0.06 g, 0.3 mmol), and a white water-soluble solid assumed to be KCl. Infrared spectrum of $HMn(CO)_5$ as gas: $\nu$(CO) 2035 (vs), 2030 (vs), 2025 (vs), 2015 (vs), 2130 (w), 2125 (w), 2120 (w), 2100 (w), 2050 (w) and 2045 (w) $cm^{-1}$.

The above reaction was repeated without potassium chloride and, although trace amounts of ethyl formate were isolated in the volatile products, the reaction was basically unchanged.

**Acknowledgments.**—The award of a Province of Ontario Graduate Fellowship and an NRC Bursary to W. J. Jacobs is greatly appreciated as well as research support from the National Research Council, Ottawa. We thank Dr. H. W. Baldwin for helpful discussions concerning the kinetic studies.

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[9] H. W. Thompson and P. Torkington, *J. Chem. Soc.*, 640 (1945).

[10] A. Davison, J. A. McCleverty, and G. Wilkinson, *ibid.*, 1133 (1963).

[11] F. A. Cotton, J. L. Down, and G. Wilkinson, *ibid.*, 833 (1959).

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# The Kinetic Chelate Effect. Chelation of Ethylenediamine on Platinum(II)

BY MARK J. CARTER AND JAMES K. BEATTIE

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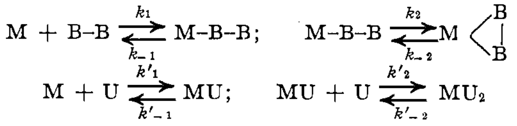
A kinetic explanation is offered for the chelate effect, based on observation of the rates of ethylenediamine ring closure in square-planar *trans*-dichlorobis(ethylenediamine)platinum(II). Stopped-flow spectrophotometry in basic solution gave rate constants at 25° in 1 *M* $LiClO_4$ of 10.4 ± 0.6 and 0.73 ± 0.06 $sec^{-1}$ for the first and second ring closures, respectively. By pH-stat titrimetry in acidic solution the acid dissociation constants of monodentate ethylenediamine were determined. These results are compared with analogous substitutions by ammonia to determine the kinetic origin of the chelate effect. Comparison with other observations on nickel(II)–ethylenediamine complexes provides an interesting distinction between the kinetic chelate effects in octahedral and square-planar complexes.

## Introduction

The increased thermodynamic stability of complexes of multidentate ligands relative to those of unidentate ligands is well known and has been extensively investigated.[1] This chelate effect must be reflected in the kinetics of complex formation as well as in stabilities. A further examination of the kinetic chelate effect is the subject of this paper. Consider the reactions



$$\mathrm{M} + \mathrm{B{-}B} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{M{-}B{-}B};\qquad \mathrm{M{-}B{-}B} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{M}\Big\langle\begin{matrix}\mathrm{B}\\ |\\ \mathrm{B}\end{matrix}$$

$$\mathrm{M} + \mathrm{U} \underset{k'_{-1}}{\overset{k'_1}{\rightleftharpoons}} \mathrm{MU};\qquad \mathrm{MU} + \mathrm{U} \underset{k'_{-2}}{\overset{k'_2}{\rightleftharpoons}} \mathrm{MU_2}$$

$$K_{\mathrm{B}} = \frac{\left[\mathrm{M}\Big\langle\begin{matrix}\mathrm{B}\\ |\\ \mathrm{B}\end{matrix}\right]}{[\mathrm{M}][\mathrm{B{-}B}]} = \frac{k_1k_2}{k_{-1}k_{-2}}$$

$$K_{\mathrm{U}} = \frac{[\mathrm{MU_2}]}{[\mathrm{M}][\mathrm{U}]^2} = \frac{k'_1k'_2}{k'_{-1}k'_{-2}}$$

in which B–B is a bidentate ligand and U is unidentate. The additional stability of the chelate complex means $K_{\mathrm{B}} > K_{\mathrm{U}}$ which requires

$$\frac{k_1k_2}{k_{-1}k_{-2}} > \frac{k'_1k'_2}{k'_{-1}k'_{-2}}$$

It is sometimes assumed that the first steps of these reactions are not sensitive to differences between otherwise similar unidentate and bidentate ligands, except

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[1] For a recent review see A. E. Martell, Advances in Chemistry Series, No. 62, American Chemical Society, Washington, D. C., 1967, p 272.