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Kinetics and Mechanism of the Oxidative Addition of Methyl Iodide to Tetrakis- and Tris(triphenylphosphine)platinum(0)

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The substitution and oxidative addition reactions of complexes of the type PtL_4 and PtL_3 ($L = P(C_6H_5)_3$) have received much recent attention.[1-4] Though the kinetics of the oxidative addition reactions of various alkyl halides and of triphenyl tin chloride to PtL_3 and $PtL_2(C_2H_4)$ complexes has been studied previously,[3,4] a detailed kinetic investigation of the reaction of CH_3I with PtL_3 and PtL_4 complexes has not been made. Consequently, we undertook a study on this reaction to elucidate the mechanism of the oxidative-addition and to throw more light on the possible reactive intermediates, the nature of which has been the subject of some controversy. Both PtL_2[3,4] and PtL_3[5,6] have been proposed, the former on experimental and the latter on theoretical and experimental grounds.

Experimental Section

$Pt[P(C_6H_5)_3]_3$ and $Pt[P(C_6H_5)_3]_4$ were prepared according to literature methods.[7] Reagent grade CH_3I was distilled under vacuum and degassed by freeze-thawing. All solvents were dried, distilled and deoxygenated with purified nitrogen.

All the kinetic measurements were made at 25°. The reactions were followed spectrophotometrically using a Cary 14 recording spectrophotometer with the cell compartment thermostated to ±0.3°. The rates of the reactions were measured by following the disappearance of the reactant platinum(0) complexes, usually at 410 nm where the extinction coefficient is $1.9 \times 10^3\ M^{-1}\ cm^{-1}$. The initial concentrations of the complexes were normally around $4 \times 10^{-4}\ M$, that of CH_3I ranged from 1.0 to 0.1 *M*, and that of $P(C_6H_5)_3$ from 10^{-2} to $10^{-3}\ M$. The data obtained yielded good linear plots by plotting $\ln (A - A_\infty)$ *vs. t*.

Triphenylphosphine and methyl iodide alone gave no change in the visible or near uv spectrum in times in excess of our kinetic studies. After longer times (factor of 2-3), a white precipitate of the phosphonium salt appeared. The solubility of this salt in benzene is very small (concentrations more than about $5 \times 10^{-5}\ M$ bring about precipitation). From data in the literature, we estimate the second order rate constant for triphenylphosphine and methyl iodide to be about $1 \times 10^{-5}\ M^{-1}\ sec^{-1}$. While this may be a midly competing reaction at the highest concentrations of phosphine used, it will have a negligible effect on our data since no spectral changes occur in the region of our measurement.

Results and Discussion

When k_{obsd} obtained for benzene as solvent was plotted against $[CH_3I]/[P(C_6H_5)_3]$, linear plots were obtained, but these had different slopes for different phosphine concentrations as shown for two cases in Figure 1. Rate constants obtained either from plots of this kind or by direct measurement for a fixed concentration of CH_3I equal to 0.546 *M* are given in Table I.

Table I. Kinetic Data in Benzene at 25°[a]

Initial $[P(C_6H_5)_3]$,[b] *M*	$10^3 \times k_{obsd}$, sec^{-1}	$10^3 \times (k_{obsd}/[CH_3I] = k')$, $M^{-1}\ sec^{-1}$
4×10^{-4} [c]	3.85	7.05
1×10^{-3}	3.19	5.8
2×10^{-3}	2.8	5.1
3×10^{-3}	2.6	4.8
5×10^{-3}	2.5	4.2
5.37×10^{-3}	2.15	4.0
7×10^{-3}	2.13	3.9
1×10^{-2}	1.9	3.7
No added $P(C_6H_5)_3$, *i.e.*, pure PtL_3	6.1	11.1

[a] All rate constants given are for $[CH_3I] = 0.546\ M$. [b] This refers to concentration of $P(C_6H_5)_3$ added, except for the first entry. [c] Reactant is $4.0 \times 10^{-4}\ M\ Pt[P(C_6H_5)_3]_4$.

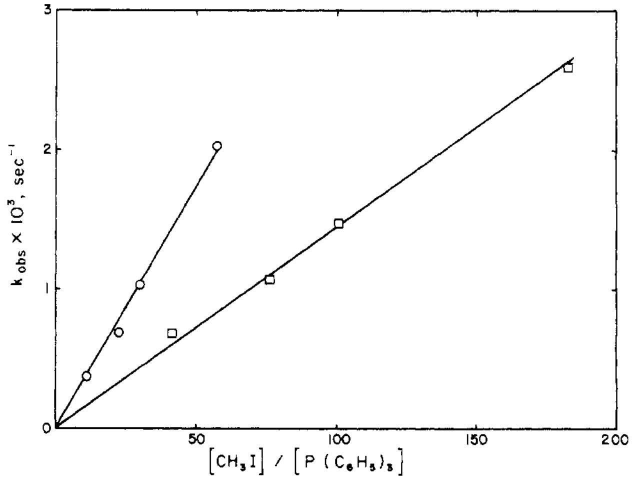

Figure 1. Plot of k_{obsd} *vs.* $[CH_3I]/[P(C_6H_5)_3]$ in benzene at 25°. Circles are for $1.0 \times 10^{-2}\ M\ P(C_6H_5)_3$ and squares are for $3.0 \times 10^{-3}\ M\ P(C_6H_5)_3$.

The kinetic behavior observed can be accommodated by the mechanism

$$PtL_3 \overset{K}{\rightleftharpoons} PtL_2 + L \tag{1}$$

$$PtL_3 + CH_3I \xrightarrow{k_1} Pt(CH_3)IL_2 + L \tag{2}$$

$$PtL_2 + CH_3I \xrightarrow{k_2} Pt(CH_3)IL_2 \tag{3}$$

It is assumed that $[PtL_3] + [PtL_2] = a - x$, where *a* is the initial concentration of the Pt(0) complex. The concentration of PtL_4 has been neglected since the equilibrium constant for the dissociation of this species is greater than 10 *M*.[5]

Reactions 1-3 give rise to the rate law

$$\frac{dx}{dt} = \frac{k_1[L] + k_2K}{K + [L]}[CH_3I](a - x) = k_{obsd}(a - x) \tag{4}$$

normalizing to a constant CH_3I concentration

$$k' = \frac{k_{obsd}}{[CH_3I]} = \frac{k_1[L] + k_2K}{K + [L]} \tag{5}$$

From this we get

$$\begin{aligned} k' &\to k_1 \quad (\text{as } [L] \to \infty) \\ k' &\to k_2 \quad (\text{as } [L] \to 0) \end{aligned} \tag{6}$$

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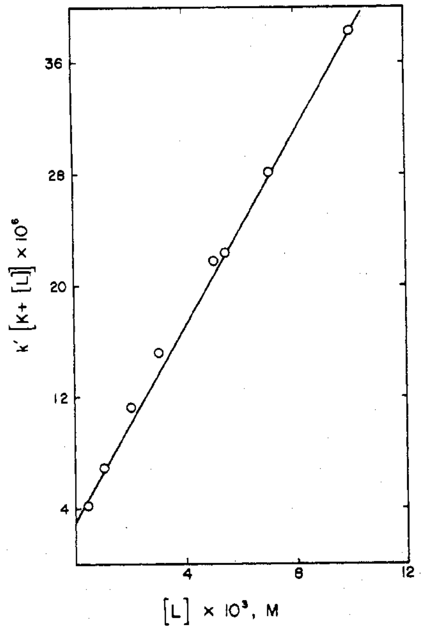

Figure 2. Plot of $k'(K + [L])$ *vs.* [L] in benzene at 25°. L is $P(C_6H_5)_3$, and $k' = k_{obsd}/[CH_3I]$.

Table II. Solvent Effect on Rates (25°)

Solvent	$k_{obsd}/[MeI]$, M^{-1} sec^{-1}	
	PtL_3	PtL_4
Dichloromethane	1.04×10^{-1}	8.2×10^{-2}
Benzene	1.1×10^{-2}	7.05×10^{-3}
Cyclohexane	4.0×10^{-3}	3.0×10^{-3}

The values of k' in Table I indicate this kind of behavior.

Rearranging eq 5 gives

$$k'(K + [L]) = k_1[L] + k_2K \tag{7}$$

From this, if K is known, the values of k_1 and k_2 can be computed. Using the value of 1.8×10^{-4} M for K obtained by Halpern,[4] a good linear plot is obtained when $k'(K + [L])$ is plotted against [L] (Figure 2). From this, the values of k_1 and k_2 obtained are 3.5×10^{-3} M^{-1} sec^{-1} and 2.0×10^{-2} M^{-1} sec^{-1}. The rate constant k_2 has been determined previously by Halpern by studying the reaction of $PtL_2(C_2H_4)$ with CH_3I.[3] His value of 1.3×10^{-2} M^{-1} sec^{-1} compares favorably with our value for k_2, considering the fact that the standard deviation of K is very large. Using values of K ranging from 1×10^{-4} to 3.4×10^{-4} M, a linear least-squares interpolation showed little change in k_1, but the k_2 values ranged from 3.5×10^{-2} to 1.5×10^{-2} M^{-1} sec^{-1}.

The last entry in Table I is for the reaction of 1.4×10^{-4} M PtL_3 (not shown in Figure 2). This should be about 50% dissociated into PtL_2, if $K = 1.8 \times 10^{-4}$ M. The value of k' is in good agreement with that expected for an equimolar mixture of reactants, PtL_2 and PtL_3.

It is disturbing that careful spectrophotometric study of such dilute solutions fails to give any evidence of PtL_2.[5] The only explanation seems to be that PtL_2 and PtL_3 have very similar absorption spectra.

The rates of reaction of CH_3I with both PtL_3 and PtL_4 were measured in dichloromethane and in cyclohexane as solvents. No excess phosphine was added. Table II shows the values of k' along with those in benzene for comparison. The rates increase as the polarity of the solvent increases. This indicates that a polar transition state is formed in the reaction.

The kinetics of the reaction of $Pt[P(CH_3)_2C_6H_5]_4$[8] with CH_3I could not be conveniently studied, since the use of excess CH_3I (necessary to attain pseudo-first-order conditions) gives good yields of the Pt(IV) complex, $Pt(CH_3)_2I_2(P(CH_3)_2C_6H_5)_2$. This was confirmed by elemental analysis of the isolated product and by its nmr spectrum, which agrees with that reported by Ruddick and Shaw.[9] *Anal.* Calcd: C, 28.6; H, 3.7. Found: C, 28.5; H, 3.6. This compound had been prepared earlier[9] by the reaction of CH_3I with $Pt(CH_3)I(PMe_2Ph)_2$ in a sealed tube for 4 weeks. The reaction with the Pt(0) species is complete within 1-2 hr. To ascertain the stereochemistry of the kinetic product of the addition of CH_3I to PtL_3 (L = triarylphosphine), an nmr experiment was attempted. To a CH_2Cl_2 solution of tris(tri-*p*-tolylphosphine)platinum(0) [this complex was used for solubility reasons] was added a slight excess of CH_3I in an nmr tube and the spectrum was recorded immediately. The signal obtained in the region of the coordinated methyl group was broad and unresolved due to exchange of free and coordinated phosphines. To circumvent this problem, the experiment was repeated with bis(tri-*p*-tolylphosphine)ethyleneplatinum(0). A well-resolved triplet for the coordinated methyl group was observed at δ −0.05 with J_{P-H} of 6.6 Hz and J_{Pt-H} of 77 Hz immediately after addition. This signal grew in intensity as the reaction proceeded, along with the growth of the signal for free ethylene. This indicates that the kinetic product is *trans*-$Pt(CH_3)IL_2$, at least when PtL_2 is the reactant.

An X-ray crystallographic study has been made of the finally isolated product in the reaction of PtL_4 with CH_3I. This also is *trans*-$Pt(CH_3)IL_2$ (structure determined as SO_2 adduct).[10]

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Registry No. CH_3I, 74-88-4; $Pt[P(C_6H_5)_3]_3$, 13517-35-6; $Pt[P(C_6H_5)_3]_4$, 14221-02-4; $Pt[P(CH_3)_2C_6H_5]_4$, 33361-89-6; $Pt(CH_3)_2I_2[P(CH_3)_2C_6H_5]_2$, 42402-13-1.

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