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A Kinetic and Mechanistic Study of the Formation of Sulfinato Iridium(III) Complexes by Oxidative Addition Reactions

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The kinetics of oxidative addition of sulfonyl chloride (RSO_2Cl) to trans-*$Ir(CO)XL_2$ is given by the second order rate law: rate = $k_2[Ir(CO)XL_2][RSO_2Cl]$. The rates increase with increasing basicity of ligands L and X in the order $Cl < Br < I$ and $P(OPh)_3 < PPh_3 < P(\text{p-}CH_3C_6H_4)_3 < P(CH_3)Ph_2$. The dependence of the rate on R in RSO_2Cl is $\text{p-}ClC_6H_4 < C_6H_5 < \text{p-}CH_3C_6H_4 < \text{n-}C_3H_7$. The activation parameters for the reaction of $Ir(CO)Cl(PPh_3)_2$ with $PhSO_2Cl$ in benzene are $\Delta H^* = 16$ kcal/mol and $\Delta S^* = -14$ cal/deg mol. This reaction is not inhibited by radical scavengers galvinoxyl or duroquinone and not promoted by benzoyl peroxide. The mechanistic implications of these results are discussed.*

Introduction

Since the first report of the oxidative addition of alkyl and aryl sulfonyl chlorides to *trans*-[Ir(CO)Cl(PPh$_3$)$_2$] [1], the synthesis of sulfinato-metal complexes by oxidative addition to complexes of d^8 and d^{10} metal ions has become a well established reactivity pattern [2]. The increasing involvement of sulfinato-metal complexes in industrial processes has been noted [3]. The oxidative addition of aryl sulfonyl chloride is one of the most significant steps in the homogeneously catalyzed desulfonylation of aryl sulfonyl chlorides [4]. Previous reports of sulfinato-metal complexes have been concerned primarily with the mode of the coordination of the RSO_2 ligand, and no kinetic studies have been reported. Investigations of the kinetics and mechanisms of oxidative addition reactions of complexes of metals with d^8 electronic configuration are of continuing interest because of their relevance to fundamental processes in homogeneous catalysis. We report here the results of an investigation of the kinetics of reaction (1):

$$\textit{trans-}Ir(CO)XL_2 + RSO_2Cl \rightarrow Ir(CO)XClL_2(RSO_2) \qquad (1)$$

Experimental

Materials

Reagent grade benzene was distilled under nitrogen and stored over molecular sieves. The sulfonyl chlorides were vacuum distilled or sublimed and stored under nitrogen. All solvents were de-oxygenated with dry argon or nitrogen which was passed through Alfa dioxo-catalyst. The iridium(I) complexes were prepared and characterized as previously described [5], and the purity of the iridium(I) complexes was checked by noting the absence of extraneous bands in the 2000–2200 cm^{-1} region.

Kinetic Measurements

The rates of reactions in dichloromethane were determined by recording the intensity of the C═O infrared stretching bands in the 1960 cm^{-1} region with a Perkin–Elmer Model 621 Spectrophotometer. The samples were thermostatted in a Barnes Engineering Company variable temperature control accessory. A Cary Model 16K spectrophotometer outfitted with a thermostatted cell holder was used to record the visible spectra which were used to follow the kinetics in benzene solutions. The disappearance of absorption at the following wavelengths was monitored. Ir[P(OPh)$_3$]$_2$(CO)Cl, 466 nm; Ir(PPh$_3$)$_2$(CO)Cl, 440 nm; Ir[P(*p*-tolyl)$_3$]$_2$(CO)Cl, 442 nm; Ir(PMePh$_2$)$_2$(CO)Cl, 434 nm; Ir(PPh$_3$)$_2$(CO)NCS, 450 nm; Ir(PPh$_3$)$_2$(CO)Br, 445 nm; Ir(PPh$_3$)$_2$(CO)I, 452 nm. The initial concentrations of the iridium(I) complexes were generally in the range 0.5 to 5.0×10^{-3} *M* and the concentration of RSO_2Cl was in at least 20-fold excess. Precautions were taken to exclude oxygen by using an argon purge and serum cap techniques.

Results and Discussion

The course of reaction (1) can be readily followed by the infrared spectra which shows a decay of the 1962 ν(C═O) band in *trans*-Ir(CO)Cl(PPh$_3$)$_2$ and a concomitant growth of a band at 2080 cm^{-1}. The

TABLE I. Second-Order Rate Constants for the Reaction *trans*-$IrX(CO)L_2 + RSO_2Cl \rightarrow Ir(SO_2R)ClX(CO)L_2$ in Benzene.

L	X	R	°C	$10^3 k_2\ M^{-1}\ sec^{-1}$
PPh_3	Cl	C_6H_5	25	14.4
			30	19.7
			35	32.8
			40	52.9
PPh_3	Cl	p-$CH_3C_6H_4$	25	25.8
PPh_3	Cl	p-ClC_6H_4	25	6.31
PPh_3	Cl	n-C_3H_7	30	113.
$P(OPh)_3$	Cl	p-$CH_3OC_6H_4$	25	0.153[a]
$P(OPh)_3$	Cl	C_6H_5	25	0.050[a]
PPh_3	Br	C_6H_5	25	36.
PPh_3	I	C_6H_5	20	121.
PPh_3	I	C_6H_5	25	256.
$PMePh_2$	Cl	C_6H_5	25	340.
PPh_3	NCS	C_6H_5	25	24.7[a]
$(p$-$CH_3C_6H_4)_3P$	Cl	C_6H_5	25	37.[a]

[a] In dichloromethane; kinetics by ir method.

rates of the reactions were also determined by monitoring the disappearance of the visible absorption bands in the 430–470 nm region which are characteristic of the iridium(I) carbonyl complexes. Plots of $\ln(A_t - A_\infty)$ *vs.* time where A_t is the absorbance time t and A_∞ is the absorbance at infinite time, were linear up to 75% completion of the reaction; thereafter there was evidence for a second slower reaction in which the sulfinato complex gave the species $[Ir(CO)Cl_3(PPh_3)_2]$. Pseudo-first order constants were thus obtained by the slopes of the plots over the initial 75% reaction. Treatment of the data by the Guggenheim method [6] gave good agreement with the results obtained above. Second order rate constants calculated from five solutions of various concentrations which had relative standard deviations of ±12% or better are given in Table I.

The rate law for the reaction is given by (2):

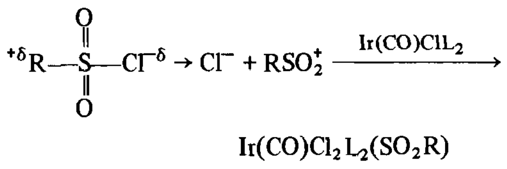
$$-d[Ir(CO)X(PR_3)_2]/dt = k_2[Ir(CO)X(PR_3)_2][RSO_2Cl] \qquad (2)$$

This second order kinetic law is observed in the oxidative addition of various substrates such as H_2, O_2, CH_3I [7], PhSH [8], and RN_3 [9] to $Ir(CO)Cl(PPh_3)_2$. The activation parameters for the reaction of $Ir(CO)Cl(PPh_3)_2$ and $PhSO_2Cl$ in benzene, $\Delta H^* = 15.7 \pm 1.3$ Kcal/mol and $\Delta S^* = -14.1 \pm 2$ cal/deg mol, are in the range commonly observed for oxidative addition of molecules such as H_2, O_2, and $PhSSC_6H_3(NO)_2$ [10] to $[Ir(CO)Cl(PPh_3)_2]$. The effect of addition of PPh_3 on the rate of reaction could not be determined because of its rapid reaction with RSO_2Cl.

The dependence of rates of reaction on L in *trans*-$Ir(CO)XL_2$ is: $P(OPh)_3 \ll PPh_3 < P(p\text{-}CH_3C_6H_4)_3 < PPh_2(CH_3)$, which is in the order of increasing ligand basicity. The variation of rates on X is Cl < Br < I, which is also the order of increasing ligand basicity. These observations are in accord with the kinetic trends observed for the reactions of $IrCOL_2X$ with H_2 and O_2 [7] and further support the proposal [11] that oxidative addition reactions can be mechanistically viewed as acid–base reactions.

Interestingly, however, increasing acidity of the substrate reactive center, the sulfonyl sulfur, does not appear to lead to increasing rates. Electron withdrawing substituents on the sulfonyl group gave slight decreases instead of the expected increases in rates. The observed decreasing trend is $n\text{-}C_3H_7SO_2Cl > p\text{-}CH_3C_6H_4SO_2Cl > C_6H_5SO_2Cl > p\text{-}ClC_6H_4SO_2Cl$. This rate trend is directly opposite to the trend observed in the reactions of $Ir(CO)Cl(PPh_3)_2$ with aryl azides [9] and with aryl thiols [8], *e.g.* $p\text{-}CH_3OC_6H_4SH < C_6H_5SH < p\text{-}O_2NC_6H_4SH$. A mechanism which primarily involves Ir–S bond formation in the rate determining step by direct nucleophilic attack on the sulfonyl sulfur, a process which would be enhanced by electron withdrawing substituents, is not fully in accord with our observations.

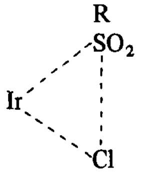
A transition state which would primarily involve Ir–Cl bond formation would be in accord with the rate dependence on RSO_2Cl, but not with the dependence on X and L. A mechanistic pathway (3) which might be consistent with the trend observed



$$^{+\delta}R-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-Cl^{-\delta} \rightarrow Cl^- + RSO_2^+ \xrightarrow{Ir(CO)ClL_2} Ir(CO)Cl_2L_2(SO_2R) \qquad (3)$$

for the RSO_2Cl variation would be the heterolysis of the S–Cl bond in the rate determining step followed by rapid nucleophilic attack by $Ir(CO)ClL_2$. This type of mechanism has been proposed for reactions of RSO_2Cl with $[Mn(CO)_5]^-$ and $[Co(CO)_3(PPh_3)]^{-3}$. But again this mechanism is not fully in accord with the dependence of rates on L and Y.

The transition state which is in accord with our observations is the species "A",



(A)

in which Ir–S and Ir–Cl bond making, as well as S–Cl bond cleavage contribute to the energy of the activated complex. This type of transition state has been proposed for reactions of $Ir(CO)ClL_2$ with methyl iodide [12] and benzene thiols [8].

Spin trapping experiments with nitrosodurene on the oxidative addition reaction of (*p*-tolyl)SO_2Br and *cis*-$PtMe_2(PMe_2Ph)_2$ provide evidence for the involvement of radicals [14]. The rate of formation of sulfinato complex from the reaction of $Ir(CO)Cl(PPh_3)_2$ and $PhSO_2Cl$ was not greatly enhanced by the presence of molecular oxygen or radical initiator benzoyl peroxide. Radical scavengers such as galvinoxyl and duroquinone did not inhibit the rate of formation of sulfinato–iridium complex. Slow reactions of $Ir(CO)Cl(PPh_3)_2$ with the radical initiators and scavengers was observed, and the reactions of hydroperoxides with $Ir(CO)Cl(PPh_3)_2$ have been previously noted [13]. It is thus not likely that the reaction of RSO_2Cl with $Ir(CO)Cl(PPh_3)_2$ proceeds by a free-radical mechanism [15].

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