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THE KINETICS OF OXIDATIVE ADDITION OF METHYL FLUOROSULPHONATE TO *trans*-CHLORO- AND TO *trans*-BROMO-CARBONYLBIS(TRIPHENYLPHOSPHINE)IRIDIUM(I)

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Summary

Kinetic parameters are reported for the reactions of *trans*-chloro- and of *trans*-bromo-carbonylbis(triphenylphosphine)iridium(I) with methyl fluorosulphonate in a range of solvents. These kinetic results are compared with those for similar oxidative addition to iridium(I) complexes.

Introduction

A large number of reactions have been described in which a small organic or inorganic molecule reacts with a square-planar iridium(I) compound to produce an octahedral iridium(III) species. Kinetic studies have been reported for several such oxidative addition reactions [1]. Examples of reactions involving Vaska's compound, *trans*-chlorocarbonylbis(triphenylphosphine)iridium(I) (*trans*-[$IrCl(CO)(PPh_3)_2$]), include those with methyl iodide [2, 3], hydrogen [2], oxygen [2, 3], bis(trifluoromethyl)dicyanoethylene [4], and a series of substituted thiophenols [5]. Whilst the majority of kinetic investigations have been concerned with Vaska's compound itself, there have been studies on closely related compounds as well, for instance on a series of complexes *trans*-[$IrCl(CO)(L)_2$] where L = one of a variety of phosphine ligands [6].

Methyl fluorosulphonate undergoes oxidative addition to iridium(I) compounds, e.g. [7]:

$$trans\text{-}[Ir^{I}Cl(CO)(PPh_3)_2] + MeOSO_2F \rightarrow Ir^{III}Cl(Me)(OSO_2F)(CO)(PPh_3)_2$$

We have investigated the kinetics of oxidative addition of methyl fluorosulphonate to *trans*-chloro- and to *trans*-bromo-carbonylbis(triphenylphosphine)-iridium(I) in several solvents. In this paper we describe our results, and compare them with those from kinetic studies of analogous oxidative additions.

Results

The reaction of methyl fluorosulphonate with *trans*-$[IrX(CO)(PPh_3)_2]$, where X = Cl or Br, in aromatic solvents goes to completion, and follows, when the methyl fluorosulphonate is present in large excess, first-order kinetics up to 95% of complete reaction. This indicates a rate law:

$$-\mathrm{d}[\mathrm{Ir}^{\mathrm{I}}]/\mathrm{d}t = k\cdot[\mathrm{Ir}^{\mathrm{I}}]$$

Repetitive scan monitoring of the reactions shows an isosbestic point, at 405 nm for the reaction with the chloro-complex in benzene solution. Plots of experimentally determined first-order rate constants (k) against concentration of (excess) methyl fluorosulphonate are linear and pass through the origin. Thus the complete rate law is:

$$-\mathrm{d}[\mathrm{Ir}^{\mathrm{I}}]/\mathrm{d}t = k_2\cdot[\mathrm{Ir}^{\mathrm{I}}]\cdot[\mathrm{MeOSO_2F}]$$

which is of the usual form for oxidative additions to iridium(I) complexes. We have been careful to avoid the presence of oxygen (cf. Experimental section), both so that there is no oxygen adduct present in the iridium(I) complex solutions and to avoid any initiation of radical pathways [8] by oxygen.

Observed first-order rate constants for oxidative addition of methyl fluorosulphonate to *trans*-$[IrCl(CO)(PPh_3)_2]$ in benzene are shown in Table 1, and values for toluene, chlorobenzene, and bromobenzene solutions appear in Table 2. Results for the analogous bromo-complex are given in Table 3. Values for the respective second-order rate constants are collected together in Table 4.

From the variation of the second-order rate constants with temperature, the activation parameters for the reaction of the chloro-complex with methyl fluorosulphonate in benzene solution have been calculated as $\Delta H^{\ddagger} = 17.0$ kcal·mol^{-1} and $\Delta S^{\ddagger} = -11$ cal·deg^{-1}·mol^{-1}. The standard errors of these values are 0.45 kcal·mol^{-1} and 2 cal·deg^{-1}·mol^{-1} respectively.

TABLE 1

OBSERVED FIRST-ORDER RATE CONSTANTS (k) FOR THE REACTION OF CHLOROCARBONYLBIS(TRIPHENYLPHOSPHINE)IRIDIUM(I) WITH METHYL FLUOROSULPHONATE IN BENZENE

19.2°				
$[MeOSO_2F]$ (M)	0.049	0.212	0.238	
$10^4 \times k$ (s^{-1})	3.9	11.6	13.1	
24.5°				
$[MeOSO_2F]$ (M)	0.076	0.145	0.215	0.283
$10^4 \times k$ (s^{-1})	10.4	18.4	24.3	28.7
29.3°				
$[MeOSO_2F]$ (M)	0.047	0.090	0.133	0.175
$10^4 \times k$ (s^{-1})	7.5	14.8	21.6	26.0
34.7°				
$[MeOSO_2F]$ (M)	0.053	0.101	0.149	0.197
$10^4 \times k$ (s^{-1})	10.7	23.4	33.3	44.8
38.4°				
$[MeOSO_2F]$ (M)	0.018	0.035	0.051	0.068
$10^4 \times k$ (s^{-1})	6.3	11.5	16.0	21.8
40.6°				
$[MeOSO_2F]$ (M)	0.018	0.035	0.051	0.067
$10^4 \times k$ (s^{-1})	8.0	14.3	20.5	27.2

TABLE 2

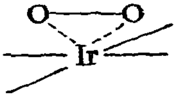
OBSERVED FIRST-ORDER RATE CONSTANTS (k) FOR THE REACTION OF CHLOROCARBONYLBIS(TRIPHENYLPHOSPHINE)IRIDIUM(I) WITH METHYL FLUOROSULPHONATE IN SUBSTITUTED BENZENES, AT 25.0°

Toluene								
$[\mathrm{MeOSO_2F}]$ (M)	0.029	0.043	0.056	0.069	0.083	0.096	0.110	0.123
$10^4 \times k$ (s^{-1})	2.6	4.3	4.9	7.3	7.7	10.7	11.5	13.7
Chlorobenzene								
$[\mathrm{MeOSO_2F}]$ (M)	0.022	0.042	0.060	0.079	0.098	0.117	0.136	0.155
$10^4 \times k$ (s^{-1})	4.4	12.0	12.4	21.0	21.9	28.4	29.4	32.7
Bromobenzene								
$[\mathrm{MeOSO_2F}]$ (M)	0.023	0.042	0.061	0.080	0.099	0.118	0.137	0.156
$10^4 \times k$ (s^{-1})	5.8	10.1	19.4	20.1	31.0	31.3	41.6	41.7

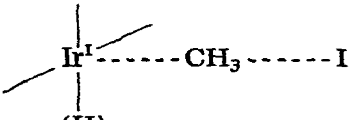
Discussion

Rate trends

For the reactions of the complexes *trans*-$[\mathrm{IrX(CO)(PPh_3)_2}]$ with hydrogen and with oxygen, where the transition state is thought [2] to be three centred, as in I, the order of reactivities is X = I > Br > Cl. For the reactions of this series of complexes with methyl iodide [2], and other alkyl halides [9], which are thought to proceed by S_N2 attack by the $\mathrm{Ir^I}$ at carbon as in II, the order of reactivities is the reverse, viz. Cl > Br > I. The reactions with methyl fluorosulphonate exhibit the reactivity sequence Cl > Br, which thus suggests that the mechanism is that which operates with methyl iodide. However, it must be admitted that the reactivity difference towards methyl fluorosulphonate is rather small. *trans*-$[\mathrm{IrCl(CO)(PPh_3)_2}]$ reacts more rapidly with methyl fluorosulphonate than with methyl iodide. The respective second-order rate constants are 0.024 and 0.0043 $\mathrm{l \cdot mol^{-1} \cdot s^{-1}}$, in benzene solution at 35°. This is consistent with a transition state II, with fluorosulphonate a better leaving group [10] than iodide from the carbon.



(I)



(II)

Activation parameters

Early workers [2] noted the marked difference between the activation parameters for the reaction of *trans*-$[\mathrm{IrCl(CO)(PPh_3)_2}]$ with hydrogen and with oxygen (transition state I) on the one hand, and with methyl iodide (transition state II) on the other. Later results [3, 4] on reactions of this iridium(I) complex

TABLE 3

OBSERVED FIRST-ORDER RATE CONSTANTS (k) FOR THE REACTION OF BROMOCARBONYLBIS(TRIPHENYLPHOSPHINE)IRIDIUM(I) WITH METHYL FLUOROSULPHONATE IN BENZENE AT 25.0°

$[\mathrm{MeOSO_2F}]$ (M)	0.027	0.056	0.080	0.110	0.133	0.156	0.186	0.210
$10^4 \times k$ (s^{-1})	2.5	4.3	6.1	8.7	10.1	12.6	13.4	17.1

TABLE 4

CALCULATED SECOND-ORDER RATE CONSTANTS (k_2), WITH THEIR RESPECTIVE STANDARD ERRORS (SE), FOR THE REACTION OF CHLORO- AND OF BROMO-CARBONYLBIS(TRIPHENYLPHOSPHINE)IRIDIUM(I) WITH METHYL FLUOROSULPHONATE

Compound	Solvent	Temp. (°C)	$10^3\ k_2$ ($l \cdot mol^{-1} \cdot s^{-1}$)	$10^3 \times$ SE (k_2) ($l \cdot mol^{-1} \cdot s^{-1}$)
$IrCl(CO)(PPh_3)_2$	Benzene	19.2	4.8	0.1
		24.5	8.8	0.3
		29.3	14.7	0.4
		34.7	23.4	0.8
		38.4	30.8	1.0
		40.6	38.3	0.4
	Toluene	25.0	11.7	0.7
	Chlorobenzene	25.0	20.8	2.2
	Bromobenzene	25.0	28.4	2.2
$IrBr(CO)(PPh_3)_2$	Benzene	25.0	7.7	0.3

with other molecules have tended to blur this apparent distinction. Indeed, when one plots activation enthalpies against activation entropies for reactions of *trans*-[$IrCl(CO)(PPh_3)_2$] in benzene solution, all the points fall on or close to a slightly curved line (Fig. 1). It is apparent that activation parameter values are not diagnostic of mechanism for these oxidative additions. In view of the relative leaving group properties of iodide and of fluorosulphonate, it is surprising that the activation enthalpy for the addition of methylfluorosulphonate to *trans*-[$IrCl(CO)(PPh_3)_2$] is so much larger than that for the addition of methyl iodide.

From Fig. 1 it is possible to determine the isokinetic temperature (β) [11]

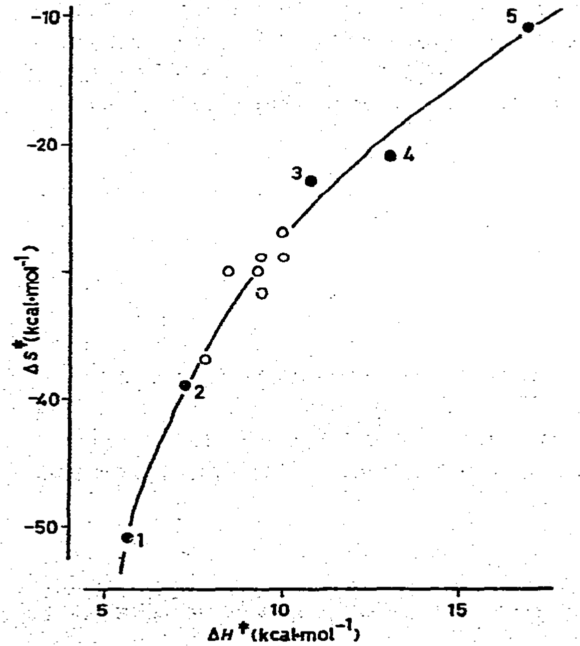


Fig. 1. Plot of activation entropies ($\Delta S^{\ddagger}$) against activation enthalpies ($\Delta H^{\ddagger}$) for oxidative addition to *trans*-[$IrCl(CO)(PPh_3)_2$] in benzene solution. Compounds added: ● 1 MeI; ● 2 $CF_3C(CN)=C(CN)CF_3$; ● 3 H_2; ● 4 O_2; ● 5 $MeOSO_2F$; ○ YC_6H_4SH.

TABLE 5

ACTIVATION PARAMETERS FOR OXIDATIVE ADDITION REACTIONS OF CHLOROCARBONYLBIS(TRIPHENYLPHOSPHINE)IRIDIUM(I), IN BENZENE SOLUTION

Compound	$\Delta H^{\ddagger}$ (kcal·mol^{-1})	$\Delta S^{\ddagger}$ (cal · deg^{-1} · mol^{-1})	Ref.
H_2	10.8	—23	2
O_2	13.1	—21	2
CH_3I	5.6	—51	2
$CF_3C(CN)=C(CN)CF_3$	7.2	—39	4
YC_6H_4SH [a]	7.8 to 10	—27 to —37	5
CH_3OSO_2F	17.0	—11	[b]

[a] Y = 4-H, 4-F, 4-Cl, 4-Br, 4-CH_3, 4-OCH_3, 4-NO_2. [b] This work.

for this series of reactions, from the definition $\delta\Delta H^{\ddagger} = \beta \cdot \delta\Delta S^{\ddagger}$. For oxidative addition to this iridium(I) complex in benzene solution β is approximately 10°. This is within the normal range of values of β for organic systems; reports of isokinetic temperatures for inorganic systems are rare. The closeness of this value of β to room temperature indicates that caution should be observed when interpreting rate trends [11].

Solvent effects

Logarithms of rate constants for the reactions of *trans*-[IrCl(CO)(PPh$_3$)$_2$] with methyl iodide and with oxygen in a wide range of solvents correlate [3] with the dielectric constant (D) function $(D-1)/(2D+1)$ and with solvent E_T values [12]. The slopes of the $(D-1)/(2D+1)$ plots are 4.0 for the reaction with methyl iodide and 2.1 for the reaction with oxygen. Complicating side reactions have prevented us from monitoring the kinetics of oxidative addition of methyl fluorosulphonate to *trans*-[IrCl(CO)(PPh$_3$)$_2$] in solvents other than aromatic compounds. In a restricted range of these solvents (Table 6) a similar plot of logarithms of rate constants for the addition of methyl fluorosulphonate against $(D-1)/(2D+1)$ has a slope of approximately 2.7. This intermediate value suggests that such plots may not prove of general use in mechanism diagnosis for oxidative additions.

Experimental

Kinetic runs were carried out in 1 cm cells in the thermostatted cell com-

TABLE 6

SECOND-ORDER RATE CONSTANTS, k_2, AT 25°, FOR THE REACTION OF *trans*-CHLOROCARBONYLBIS(TRIPHENYLPHOSPHINE)IRIDIUM(I) WITH METHYL FLUOROSULPHONATE IN AROMATIC SOLVENTS, AND THE RESPECTIVE VALUES OF THE DIELECTRIC CONSTANT FUNCTION $(D-1)/(2D+1)$ [a] AND OF SOLVENT E_T VALUES [b]

Solvent	$(D-1)/(2D+1)$	E_T	$10^3 \times k_2$ (s^{-1})
Benzene	0.229	34.5	8.8
Toluene	0.239	33.9	11.7
Bromobenzene	0.372	37.5	20.8
Chlorobenzene	0.377	37.5	28.4

[a] From ref. 14. [b] From ref. 15.

partment of a Unicam SP800A recording spectrophotometer. The temperature of the cell contents was monitored by a copper-constantin thermocouple. Solutions of the reagents were thermostatted and mixed in a nitrogen atmosphere. Reagent concentrations are cited in the Table captions. The progress of the oxidative addition reactions was monitored at 488 nm, at which wavelength the iridium(I) complexes have large extinction coefficients but the iridium(III) products absorb very little. Rate constants were computed using a standard least-mean-squares program [13] (ICL 4130 computer); activation parameters were computed from the temperature variation of second-order rate constants using the same program.

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