Trialkyloxonium salts are known to be strong alkylating agents toward substances possessing a lone pair of electrons.[9,17] Thus the reaction of $(CH_3)_3O^+PF_6^-$ with polar solvents used here was not unexpected. The alkylation reaction which occurs with acetonitrile was slow, however, so that useful spectral data using this solvent could be obtained. Our nmr data on approximately 40% solutions of $(CH_3)_3O^+PF_5^-$ in acetonitrile suggest that over a 15-min period reaction to give the methylnitrilium ion $CH_3C{\equiv}NCH_3^+$ occurs to the extent of about 90%. Similar results were obtained from the infrared spectra taken in this solvents.

Trimethylsulfonium hexafluorophosphate did not react with acetonitrile. However, a slow reaction of $(CH_3)_2SSCH_3^+PF_6^-$ was observed in this solvent. No product was characterized from this reaction.

Acknowledgment. We are pleased to acknowledge the partial support for this work provided by the Wisconsin Alumni Research Foundation. We are indebted to Miss P. Carney for assistance in running the proton nmr spectra.

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Kinetics of the Addition of Hydrogen, Oxygen, and Methyl Iodide to Some Square-Planar Iridium(I) Complexes[1]

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Abstract: A study is described of the kinetics of the following series of reactions in benzene and dimethylformamide, *trans*-$IrX(CO)(PPh_3)_2 + YZ \rightarrow IrXYZ(CO)(PPh_3)_2$, where X = Cl, Br, and I and YZ = H_2, O_2, and CH_3I. The kinetics, in each case, were found to obey the second-order rate law, rate = $k_2[IrX(CO)(PPh_3)_2][YZ]$. The kinetic patterns of the reactions with H_2 and O_2 were very similar. The activation parameters for these reactions, in benzene, were all in the range $\Delta H^* = 10.8$ to 13.1 kcal/mole and $\Delta S^* = -14$ to -24 eu. In each case the dependence of rate on the halogen followed the order I > Br > Cl. The reactions with CH_3I exhibited a somewhat different reactivity pattern, the dependence of the rate on the halogen following the reverse order, Cl > Br > I. The activation parameters for these reactions (in benzene) were in the range $\Delta H^* = 5.6$ to 8.8 kcal/mole and $\Delta S^* = -43$ to -51 eu and exhibited a marked solvent dependence. The mechanistic implications of these results are discussed.

Complexes of group VIII metals of d^8 configuration, notably square-planar complexes of platinum(II),[2–4] iridium(I),[5–7] and rhodium(I)[7,8] (as well as certain pentacoordinated ruthenium(0) complexes[9,10]) are well known to add a variety of covalent molecules such as hydrogen,[5] halogens,[5,9] hydrogen halides,[3–9] methyl iodide,[2,7] and oxygen[6] to form (generally hexacoordinated) complexes of d^6 configuration. In recent years such oxidative addition reactions have attracted widespread interest and have been studied extensively from the standpoint of their novel stoichiometry and products and also of their significance in homogeneous catalytic reactions such as hydrogenation and hydroformylation.[11–13] However, the study of the kinetics and mechanisms of these reactions has hitherto received virtually no attention. We report here the results of the first such systematic investigation of the kinetics of the series of reactions

$$trans\text{-}IrX(CO)(PPh_3)_2 + YX \longrightarrow IrXYZ(CO)(PPh_3)_2$$

where Ph = C_6H_5, X = Cl, Br, and I and YZ = H_2, O_2, and CH_3I.

Experimental Section

Materials. *trans*-$IrCl(CO)(PPh_3)_2$ was prepared by the method described by Johnson.[14] $H_3IrCl_6 \cdot 6H_2O$ was dissolved in 2-methoxyethanol and neutralized with sodium carbonate. The solution was refluxed for about 5 hr, while CO was continuously bubbled through, until reduction to iridium(I) (presumably $IrCl(CO)_3$) was achieved, the solution at this stage being light yellowish brown in color. The mixture was then cooled and the stoichiometric equivalent of triphenylphosphine added. The yellow product which separated out was recrystallized from toluene. *Anal.* Calcd for $IrCl(CO)[P(C_6H_5)_3]_2$: C, 56.96; H, 3.88; P, 7.94. Found: C, 56.7; H, 4.1; P, 7.64.

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[14] N. P. Johnson, Ph.D. Thesis, University of London, 1964. The preparation of *trans*-$IrBr(CO)(PPh_3)_2$ from $Ir(CO)_3Br$ was first reported by M. Angoletta, *Gazz. Chim. Ital.*, **89**, 2359 (1959).

trans-$IrBr(CO)(PPh_3)_2$ was prepared by dissolving $IrCl(CO)(PPh_3)_2$ in tetrahydrofuran and adding a tenfold excess of LiBr. After standing for 1 hr, the solution was evaporated to dryness, the residue extracted with water (to remove LiCl and excess LiBr), and the water-insoluble product recrystallized from benzene. *Anal.* Calcd for $IrBr(CO)[P(C_6H_5)_3]_2$: C, 53.89; H, 3.67; Br, 9.69; P, 7.51. Found: C, 53.75; H, 3.80; Br, 9.52; Cl, 0.0.

trans-$IrI(CO)(PPh_3)_2$ was prepared by dissolving $IrCl(CO)(PPh_3)_2$ in benzene, adding a tenfold excess of NaI in ethanol, shaking the mixture for 1 hr in the dark, and then evaporating to dryness. The residue was taken up with a benzene-water mixture. The benzene layer was separated and evaporated to dryness; the product was recrystallized from benzene. *Anal.* Calcd for $IrI(CO)[P(C_6H_5)_3]_2$: C, 50.98; H, 3.47; I, 14.56. Found: C, 50.75; H, 3.39; I, 14.74.

All of the above preparations were performed under a nitrogen atmosphere.

Reagent grade methyl iodide was extracted with aqueous sodium thiosulfate (to remove iodine), dried over 5A molecular sieve, distilled (bp 43°), and stored over clean mercury. Benzene and dimethylformamide (DMF) were redistilled and dried over 5A molecular sieve. Prior to use, the solvents were deoxygenated with purified nitrogen.

Kinetic Measurements. The kinetics of the reactions with O_2 and H_2 were studied by measuring the rate of uptake of the gas at constant pressure using the apparatus and procedure described earlier.[15] The initial concentration of $IrX(CO)(PPh_3)_2$ in these experiments was generally in the range 5×10^{-4} to 5×10^{-3} *M*. The partial pressures of H_2 and O_2 were varied from approximately 200 to 700 mm and the corresponding concentrations in solution computed from solubility data in the literature.[16] The reactions with CH_3I were followed spectrophotometrically using the following absorption peaks to measure the rate of disappearance of $IrX(CO)(PPh_3)_2$: $IrCl(CO)(PPh_3)_2$, λ_{max} 387 mμ (ϵ_{max} 3.89×10^3); $IrBr(CO)(PPh_3)_2$, λ_{max} 389 mμ (ϵ_{max} 3.65×10^3); $IrI(CO)(PPh_3)_2$, λ_{max} 397 mμ (ϵ_{max} 1.87×10^3). These experiments were made using either a Cary 14 or Beckman DB recording spectrophotometer with a thermostated cell compartment. The initial concentration of $IrX(CO)(PPh_3)_2$ in these experiments was generally in the range 5×10^{-4} to 5×10^{-3} *M* and the concentration of CH_3I in at least 20-fold excess (0.1 to 0.8 *M*). Oxygen was rigorously excluded.

A Cary Model 14 spectrophotometer was used to record the visible and ultraviolet spectra and a Beckman IR-7 spectrophotometer to record the infrared spectra. Microanalyses were performed by Mr. W. Saschek of the Department of Chemistry, University of Chicago.

Results and Discussion

The reactions whose kinetics were examined (in each case for X = Cl, Br, and I) are

$$trans\text{-}IrX(CO)(PPh_3)_2 + H_2 \longrightarrow IrXH_2(CO)(PPh_3)_2 \quad (1)$$

$$trans\text{-}IrX(CO)(PPh_3)_2 + O_2 \longrightarrow IrX(O_2)(CO)(PPh_3)_2 \quad (2)$$

$$trans\text{-}IrX(CO)(PPh_3)_2 + CH_3I \longrightarrow IrXI(CH_3)(CO)(PPH_3)_2 \quad (3)$$

Under the conditions of the kinetic measurements all the reactions went essentially to completion. At lower H_2 partial pressures (<200 mm) the reaction of $IrCl(CO)(PPh_3)_2$ with H_2 was readily reversible and preliminary measurements yielded a value of approximately 1.5×10^4 M^{-1} for the equilibrium constant $K (= [IrClH_2(CO)(PPh_3)_2]/[IrCl(CO)(PPh_3)_2][H_2])$ in benzene at 30°.

The infrared spectra of all the reactants and products are summarized in Table I. The spectra determined for $IrCl(CO)(PPh_3)_2$ and its adducts, all of which have previously been characterized, are in satisfactory agreement with those reported earlier.[5-7] Apart from small shifts, the spectra of the bromo and iodo compounds all resembled those of the corresponding chloro compounds suggesting that they are isostructural. The structure of $IrCl(O_2)(CO)(PPh_3)_2$ has been determined,[17] and it has been claimed[13] that infrared and nmr evidence favors a *cis*-dihydride *trans*-diphosphine configuration for $IrClH_2(CO)(PPh_3)_2$. The configuration of the $IrXI(CH_3)(CO)(PPh_3)_2$ compounds are, at present, unknown and X-ray determinations of these are planned.

Table I. Infrared Spectra of Reactants and Products[a]

Compound	ν_{CO}, cm^{-1}	ν_{IrH_2}, cm^{-1}	ν_{OO}, cm^{-1}
$IrCl(CO)(PPh_3)_2$	1950		
$IrBr(CO)(PPh_3)_2$	1955		
$IrI(CO)(PPh_3)_2$	1975		
$IrClO_2(CO)(PPh_3)_2$	2000		858
$IrBrO_2(CO)(PPh_3)_2$	1996		862
$IrIO_2(CO)(PPh_3)_2$	1995		862
$IrClH_2(CO)(PPh_3)_2$	1975	2100, 2190	
$IrBrH_2(CO)(PPh_3)_2$	1982	2105, 2200	
$IrIH_2(CO)(PPh_3)_2$	1995	2100, 2225	
$IrClD_2(CO)(PPh_3)_2$	1995	1460, 1573[c]	
$IrClICH_3(CO)(PPh_3)_2$	2048 (2047)[b]		
$IrBrICH_3(CO)(PPh_3)_2$	2046[b]		
$IrI_2CH_3(CO)(PPh_3)_2$	2045[b]		

[a] In Nujol mull unless otherwise noted. [b] In tetrahydrofuran solution. [c] ν_{IrD_2} in chloroform. In Nujol only one peak at 1572 cm^{-1} was detected in agreement with earlier observations.[5]

The general trend of increasing CO stretching frequencies, in agreement with that reported earlier[5-7] for the chloro compounds, is $IrX(CO)(PPh_3)_2 < IrX(O_2)(CO)(PPh_3)_2 \approx IrXH_2(CO)(PPh_3)_2 < IrXI(CH_3)(CO)(PPh_3)_2$. This presumably reflects the decreasing extent of π back donation from Ir to CO and hence the increasing effective oxidation state of the Ir.[18,19] The only marked halogen dependence noted was in the case of the CO stretching frequencies of $IrX(CO)(PPh_3)_2$ which increased in the order X = Cl < Br < I. For all the other compounds ν_{CO} (as well as ν_{IrH_2} and ν_{OO}) were essentially independent of the nature of the halogen.

Kinetics. All the reactions studied exhibited second-order kinetics, *i.e.*

$$-d[IrX(CO)(PPh_3)_2]/dt = k_2[IrX(CO)(PPh_3)_2][YZ] \quad (4)$$

Since the concentration of YZ was always either constant throughout each experiment (for H_2 and O_2) or in sufficiently large excess (for CH_3I) to remain essentially constant, the observed disappearance of $IrX(CO)(PPh_3)_2$ in every case obeyed a pseudo-first-order rate law. For each reaction it was established at least at one temperature that the pseudo-first-order rate constant (k_1) was proportional to the concentration of YZ (typical data in Table II) in accord with eq 4. Second-order rate constants for the other temperatures were generally computed from kinetic experiments at a single YZ concentration assuming the second-order rate law to be valid. The kinetic data are summarized in Tables III and IV.

The kinetic patterns for the additions of H_2 and of O_2 to $IrX(CO)(PPh_3)_2$ exhibited many similarities. In both cases the reactivity sequence was found to be $IrI(CO)(PPh_3)_2 > IrBr(CO)(PPh_3)_2 > IrCl(CO)(PPh_3)_2$.

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Table II. Typical Kinetic Data for the Addition of Various Molecules to $IrCl(CO)(PPh_3)_2$ in Benzene

Addend	Temp, °C	Partial pressure of addend, mm	Concn of addend, M	k_1, sec^{-1}	k_2, M^{-1} sec^{-1}
H_2	30	255	1.00×10^{-3}	0.94×10^{-3}	0.94
		415	1.63×10^{-3}	1.50×10^{-3}	0.92
		613	2.42×10^{-3}	2.24×10^{-3}	0.93
O_2	30	242	3.24×10^{-3}	1.21×10^{-4}	3.74×10^{-2}
		371	4.97×10^{-3}	1.93×10^{-4}	3.91×10^{-2}
		473	6.25×10^{-3}	2.48×10^{-4}	3.98×10^{-2}
		630	8.45×10^{-3}	3.25×10^{-4}	3.85×10^{-2}
CH_3I	25	...	0.20	7.8×10^{-4}	3.9×10^{-3}
		...	0.40	1.28×10^{-3}	3.2×10^{-3}
		...	0.60	1.98×10^{-3}	3.3×10^{-3}
		...	0.80	2.90×10^{-3}	3.6×10^{-3}

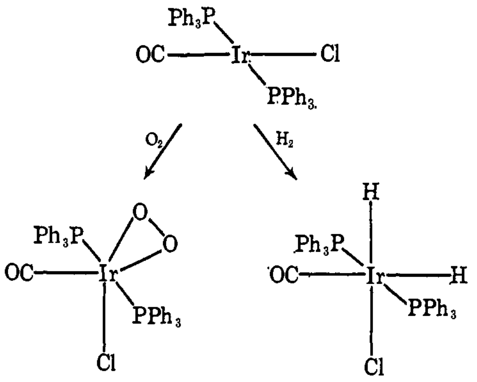
Table III. Summary of Kinetic Data for the Reactions $IrX(CO)(PPh_3)_2 + YZ \rightarrow IrXYZ(CO)(PPh_3)_2$

X	YZ	Solvent	Temp, °C	k_2, M^{-1} sec^{-1}
Cl	H_2	Benzene	20	0.50
			25	0.67
			30	0.93
			35	1.30
Cl	H_2	Toluene	20	0.34
Cl	H_2	DMF	30	1.86
Cl	D_2	Benzene	30	0.76
Br	H_2	Benzene	20	7.1
			25	10.5
			30	14.3
I	H_2	Benzene	30	$>10^2$
Cl	O_2	Benzene	20	2.07×10^{-2}
			25	3.36×10^{-2}
			30	3.9×10^{-2}
			35	6.4×10^{-2}
Cl	O_2	DMF	30	1.75×10^{-1}
Br	O_2	Benzene	20	0.62×10^{-1}
			25	0.74×10^{-1}
			30	1.07×10^{-1}
			35	1.49×10^{-1}
I	O_2	Benzene	20	0.21
			25	0.30
			30	0.41
			35	0.54
Cl	CH_3I	Benzene	20	2.6×10^{-3}
			25	3.5×10^{-3}
			30	3.9×10^{-3}
			35	4.3×10^{-3}
Cl	CH_3I	DMF	25	2.8×10^{-2}
			30	4.1×10^{-2}
			35	7.2×10^{-2}
Br	CH_3I	Benzene	20	1.2×10^{-3}
			25	1.6×10^{-3}
			30	1.8×10^{-3}
			35	2.3×10^{-3}
I	CH_3I	Benzene	20	0.64×10^{-3}
			25	0.91×10^{-3}
			30	1.05×10^{-3}
			35	1.37×10^{-3}

Table IV. Activation Parameters

X	YZ	Solvent	ΔH^*, kcal/mole	ΔS^*, eu
Cl	H_2	Benzene	10.8	−23
Br	H_2	Benzene	12.0	−14
Cl	O_2	Benzene	13.1	−21
Br	O_2	Benzene	11.8	−24
I	O_2	Benzene	10.9	−24
Cl	CH_3I	Benzene	5.6	−51
Br	CH_3I	Benzene	7.6	−46
I	CH_3I	Benzene	8.8	−43
Cl	CH_3I	DMF	16.4	−10

The ΔH^* values for these reactions were all in the range 10.8 to 13.1 kcal/mole, and the ΔS^* values in the vicinity of −20 eu. These entropies of activation (which are, however, of the same order as those commonly observed[20,21] for substitution reactions of square-planar complexes) are unexpectedly negative for reactions involving uncharged reactants and products and suggest either a marked increase in polarity, or unusually stringent stereochemical restrictions, in going from reactants to the transition state. The suggestion of a polar transition state also derives some support from the appreciable increases in rate observed on going from benzene to the more polar solvent dimethylformamide. The significance of this in terms of the detailed mechanisms of the apparently simple addition reactions, whose stereochemistry is depicted below, is, however, not clear.



The reaction of $IrCl(CO)(PPh_3)_2$ with H_2 exhibited only a small deuterium isotope effect (k_{H_2}/k_{D_2} = 1.22).

The reactions of $IrX(CO)(PPh_3)_2$ with CH_3I exhibited a markedly different kinetic pattern. Thus the reactivities of $IrX(CO)(PPh_3)_2$ toward CH_3I followed the opposite order of dependence on the nature of the halogen, namely $IrCl(CO)(PPh_3)_2$ > $IrBr(CO)(PPh_3)_2$ > $IrI(CO)(PPh_3)_2$. The rate constants in each case were markedly lower than the corresponding rate constants for reaction with H_2, despite the much lower dissociation energy of CH_3I and the apparently greater thermodynamic driving force for the formation of

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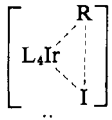
$IrXI(CH_3)(CO)(PPh_3)_2$ (as judged from the smaller tendency of the latter, as compared with $IrXH_2(CO)(PPh_3)_2$, to dissociate). Furthermore, the reactions of $IrX(CO)(PPh_3)_2$ with CH_3I in benzene exhibited lower activation enthalpies (~5 to 9 kcal/mole) and more negative activation entropies (~−50 eu) than the corresponding reactions with H_2 and O_2. The increase in rate in going from benzene to dimethylformamide solution was also somewhat greater as a result of a markedly less negative ΔS^* compensated only in part by an increase in ΔH^*. The activation parameters and their solvent dependence are rather reminiscent of those reported for the Menschutkin reactions, $R_3N + RX \rightarrow R_4N^+X^-$ and interpreted in terms of the highly polar transition state $[R_3N^{\delta+}\cdots R\cdots X^{\delta-}]$ approaching that of the products.[22,23] The extension of this interpretation to the present case is a reasonable one and would perhaps favor a transition-state configuration of the type i rather than ii.

$$[L_4Ir^{\delta+}\cdots R\cdots I^{\delta-}]$$

i



ii

We hope to explore this theme more fully through studies on other alkyl halides and other solvents.

Other Reactions. The rates of the reactions of $IrCl(CO)(PPh_3)_2$ with HCl, HBr, Cl_2, Br_2, and I_2 all were found to be too high for measurement by conventional methods, but we hope to study these reactions using a stopped-flow apparatus. The reaction with CH_3Br proved too slow for measurement. $IrCl(CO)(PPh_3)_2$ was found to react with CH_2ICH_2I to yield $IrClI_2(CO)(PPh_3)_2$ and ethylene, but no kinetic measurements were made. In addition, $IrCl(CO)(PPh_3)_2$ in benzene was observed to react with CH_2I_2, CCl_4, $SOCl_2$, and acetyl halides but the products of these reactions have not yet been characterized.

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