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Kinetics and Mechanism of the Oxidative Addition of Iodomethane to β-Diketonatobis(triphenylphosphite)rhodium(I) Complexes

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Abstract

The kinetics and mechanism of the oxidative addition of CH_3I to $[Rh(\beta\text{-diketone})(P(OPh)_3)_2]$ complexes was studied in acetone medium at various temperatures. The experimental rate law is $R = k[Rh(\beta\text{-diketone})(P(OPh)_3)_2][CH_3I]$. The order of the effect of the β-diketone on the reactivity of the complexes is acac > BA > DBM > TFAA > TFBA > HFAA indicating that electronegative substituents of the β-diketone decrease the reactivity of the complexes towards oxidative addition reactions. The volume of activation for some of the reactions was determined in various solvents. The large negative values of the volume and entropy of the activation indicated a mechanism which occurs via a polar transition state.

Introduction

The kinetics of the oxidative addition reactions of transition metal complexes with d^8 or d^{10} electron configurations with alkyl halides have been extensively reported in recent years. The impetus for these investigations has been to gain a greater understanding of the electronic and steric factors influencing these reactions, which is a vital step in the functioning of many of these compounds as homogeneous catalysts.

In these reports various factors, which have a large influence on the rate of the oxidative addition reactions, have been investigated. The inhibitory effect of electron withdrawing ligands on the reactions rates has been reported by several authors [1–4]. The electronic effect of different substituents on the β-diketone on the rate of the oxidative addition reaction has been determined [3] for the reaction:

$$[Rh(\beta\text{-diketone})(CO)(PPh_3)] + CH_3I \longrightarrow [Rh(\beta\text{-diketone})(CO)(PPh_3)(CH_3)(I)]$$

The inhibiting effect of the strong electronegative CF_3 groups on the reactivity of the metal complex is explained by the fact that electron density is removed from the metal, making the complex a stronger Lewis acid and thus less reactive in an associative mechanism [3].

Ugo *et al.* [5] showed that steric effects are also an important factor in controlling the rate of the oxidative addition reaction. The influence of the solvent on the reaction rate has also been extensively investigated [1, 3, 4, 5]. These electronic and steric effects, as well as the solvent effects, support the idea of a polar transition state [3–6]. The concept of a polar transition state is also supported by large negative values of the entropy of activation [3, 5, 7], as well as large negative values of the volume of activation [7]. All these above-mentioned factors indicate that the oxidative addition reactions of Ir(I) and Rh(I) complexes with alkyl halides occur via an associative (S_N2) addition mechanism [3, 6, 7].

The majority of the complexes studied contained at least one carbonyl ligand [1–5, 7] and it is found that many of these oxidative addition reactions are complicated by an alkyl–acyl conversion reaction [1, 3, 8–10]. This paper reports the oxidative addition reaction of $[Rh(\beta\text{-diketone})(P(OPh)_3)_2]$ complexes with CH_3I and without the presence of a carbonyl ligand a less complex mechanism is thus expected. In the present study the β-diketones: acetylacetone (acac), dibenzoylmethane (DBM), benzoylacetone (BA), trifluoroacetylacetone (TFAA), trifluorobenzoylacetone (TFBA) and hexafluoroacetylacetone (HFAA) were used to determine the effect of the substituents on the reaction rate.

Experimental

The $[Rh(\beta\text{-diketone})(P(OPh)_3)_2]$ complexes were prepared by methods described earlier [11]. Iodomethane (Merck) was always used as freshly distilled samples, while the solvents used were reagent grade.

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One of the oxidative addition products, [Rh(acac)(P(OPh)$_3$)$_2$(CH$_3$)(I)] was prepared as follows. A large excess CH$_3$I (~3 cm^3) was added to [Rh(acac)(P(OPh)$_3$)$_2$] in 5 cm^3 acetone. The reaction mixture was sealed and set aside for *ca.* 24 h. The yellow solution was evaporated under reduced pressure to remove the solvent and excess methyliodide. The resulting yellow precipitate was dissolved in about 3 cm^3 acetone. The solution was filtered and the reaction product was reprecipitated by the dropwise addition of water. Analysis for RhC$_{42}$H$_{40}$O$_8$IP$_2$ (calculated values in parentheses) Rh, 10.7 (10.7); C, 52.77 (52.3); H, 4.48 (4.2); O, 13.5 (13.3); P, 6.46 (6.4); I, 13.6 (13.2%).

The stereochemistry of [Rh(acac)(P(OPh)$_3$)$_2$(CH$_3$)(I)] was determined by ^{1}H NMR spectra, recorded on a Bruker WN300 spectrometer. The ^{1}H NMR spectrum of [Rh(acac)(P(OPh)$_3$)$_2$(CH$_3$)(I)] shows two methyl signals, a singlet (δ = 1.43 ppm (CD$_3$)$_2$CO) for the bidentate ligand acac-methyl protons, suggesting that the two CH$_3$ groups of the β-diketone, acac, are magnetically equivalent. The methyl signal of the addend appear as a double doublet (δ = 1.78 ppm, J(P–CH$_3$) = 3.1 Hz and J(Rh–CH$_3$) = 1.2 Hz), suggesting ^{105}Rh–CH$_3$ and ^{31}P–CH$_3$ coupling. The observed chemical shift and coupling constants compare favourably with other compounds where a methyl group is directly attached to the rhodium atom, such as [Rh(Cl)$_2$(CH$_3$)(CO)(PPh$_3$)$_2$] [12, 13] where δ = 0.85 ppm, J(P–CH$_3$) = 5.0 Hz and J(Rh–CH$_3$) = 2.1 Hz. The values of J(P–CH$_3$) and J(Rh–CH$_3$) in the current complex are smaller, but this is expected since J(P–CH$_3$) decreases along the series of chloro-, bromo- and iodorhodium(III) derivatives [12]. Another interesting phenomenon in the ^{1}H NMR spectrum of [Rh(acac)(P(OPh)$_3$)$_2$(CH$_3$)(I)] is the fact that the methine protons of acetylacetone appear as a triplet (J = 0.9 Hz). This triplet could be ascribed to long range coupling with the methyl protons of the addend. Steric interactions between the methyl and triphenylphosphite groups force the methyl group towards the methine proton, thus leading to long range coupling between these protons. This type of steric interaction is clearly seen in the value of the I–Rh–I bond angle of *ca.* 170° in a similar complex, [Rh(TFAA)(P(OPh)$_3$)$_2$(I)$_2$] [14], where the slightly distorted octahedral arrangement is attributed to steric interaction between the iodide and triphenylphosphite ligands. It is expected that the steric interaction between a methyl and triphenylphosphite group is to be much bigger.

The product of the oxidative addition reaction, [Rh(β-diketone)(P(OPh)$_3$)$_2$(CH$_3$)(I)] [15], thus assumes an octahedral geometry, in which the β-diketone ligand and two triphenylphosphite groups are located in an equatorial plane with the methyl and iodide ligands in axial positions. The *trans* addition of CH$_3$I to [Rh(β-diketone)(P(OPh)$_3$)$_2$] is also

TABLE I. Second Order Rate Constants at Various Temperatures of the Reaction of [Rh(β-diketone)(P(OPh)$_3$)$_2$] with CH$_3$I in Acetone Medium. The pK_a Values of the β-Diketone Wavelength where the Reaction was Followed and Activation Parameters are also Listed

β-Diketone	Substituents on β-diketone		pK_a [17]	λ (nm)	T (°C)	k (mol^{-1} dm^3 s^{-1})	T (°C)	k (mol^{-1} dm^3 s^{-1})	T (°C)	k (mol^{-1} dm^3 s^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J mol^{-1} K^{-1})
	R$_1$	R$_2$										
acac	CH$_3$	CH$_3$	8.94	340	30.4	$1.26(3) \times 10^{-1}$	25.0	$9.6(2) \times 10^{-2}$	17.8	$5.9(2) \times 10^{-2}$	40(3)	−128(9)
BA	CH$_3$	C$_6$H$_5$	8.70	388	33.7	$4.5(2) \times 10^{-2}$	25.0	$3.42(5) \times 10^{-2}$	15.8	$1.93(5) \times 10^{-2}$	30(6)	−172(20)
DBM	C$_6$H$_5$	C$_6$H$_5$	9.35	373	29.8	$2.12(7) \times 10^{-2}$	25.0	$1.49(3) \times 10^{-2}$	16.5	$8.4(2) \times 10^{-3}$	49(2)	−115(7)
TFAA	CH$_3$	CF$_3$	6.30	400	34.2	$1.03(2) \times 10^{-2}$	25.0	$5.6(1) \times 10^{-3}$	14.8	$2.75(6) \times 10^{-3}$	47(3)	−129(8)
TFBA	CF$_3$	C$_6$H$_5$	6.30	360	34.4	$5.2(1) \times 10^{-3}$	25.0	$2.63(5) \times 10^{-3}$	14.7	$1.31(1) \times 10^{-3}$	51(2)	−123(8)
HFAA	CF$_3$	CF$_3$	4.35	370	32.5	4.3×10^{-4}	25.0	2.4×10^{-4}	20.1	1.6×10^{-4}	56(3)	−126(10)

confirmed by the structure determination of a similar complex, *trans*-[Rh(BPHA)P(OPh)$_3$)$_2$(CH$_3$)(I)] [15], where BPHA = *N*-phenyl-*N*-hydroxylamine, in which *trans* addition occurred.

Kinetic Measurements

The oxidative addition reactions were followed spectrophotometrically on a Hitachi 150-20 spectrophotometer. The formation of [Rh(β-diketone)(P-OPh)$_3$)$_2$(CH$_3$)(I)] were measured at the wavelengths indicated in Table I, for the different β-diketones complexes. All kinetic runs were performed in acetone as solvent except where the solvent effect was investigated. An excess of CH$_3$I was used for all kinetic runs in order to achieve pseudo-first order reaction conditions. Under these conditions the pseudo-first order rate constants, k_{obs}, were calculated from the slopes of linear $\ln(A_\infty - A_t)$ *versus* time plots at three different temperatures. Plots of iodomethane concentration *versus* k_{obs} were linear with a zero intercept. The values of the second order constants (k) at various temperatures, as well as the enthalpy and enthropy of activation and pK_a values of the β-diketones are listed in Table I. The effect of different solvents on the rate of oxidative addition reactions of [Rh(acac)(P(OPh)$_3$)$_2$] are listed in Table II. Kinetic measurements at elevated pressures were performed by a method described previously [16]. The volumes of activation in different solvents were derived from a non-linear least-squares treatment of the ln k *versus* pressure data and are listed in Table III.

TABLE II. Second Order Rate Constants of the Reaction of [Rh(acac)(P(OPh)$_3$)$_2$] with CH$_3$I in Various Solvents (T = 25.0 °C)

Solvent	Dielectrical constant [18]	k (mol^{-1} dm^3 s^{-1})
Acetone	20.7	9.6×10^{-2}
1,2-dichloroethane	10.36	9.2×10^{-2}
Chlorobenzene	5.62	4.4×10^{-2}
Benzene	2.28	5.0×10^{-3}

TABLE III. Second Order Rate Constant (k)[a] as a Function of Pressure for the Oxidative Addition of [Rh(β-diketone)(P(OPh)$_3$)$_2$] with CH$_3$I (T = 21 °C)

β-Diketone	Solvent	P (bar)	k (mol^{-1} dm^3 s^{-1})	$\Delta V^{\neq}$ (cm^3 mol^{-1})
acac	acetone	1	0.0821	−18.7(10)
		400	0.1092	
		550	0.1354	
		700	0.1358	
		850	0.1584	
		1000	0.1686	
		1400	0.2455	
TFBA	acetone	150	2.8516×10^{-3}	−19.3(6)
		400	3.551×10^{-3}	
		700	4.598×10^{-3}	
		1000	5.716×10^{-3}	
		1300	7.05×10^{-3}	
TFBA	1,2-dichloroethane	310	5.424×10^{-3}	−9.1(3)
		613	6.067×10^{-3}	
		907	6.687×10^{-3}	
		1210	7.615×10^{-3}	
TFBA	dichloromethane	205	4.921×10^{-3}	−17.7(5)
		495	5.939×10^{-3}	
		705	6.727×10^{-3}	
		1035	8.659×10^{-3}	
		1315	10.99×10^{-3}	
TFBA	chloroform	1	7.358×10^{-3}	−22.7(4)
		200	8.91×10^{-3}	
		500	11.46×10^{-3}	
		800	15.21×10^{-3}	
		1100	20.53×10^{-3}	

[a] Mean value of between two and three kinetic runs.

Results and Discussion

The investigated reactions are such that in the range of concentrations covered, k_{obs} depends linearly on the concentration of iodomethane. The experimental data can thus be expressed as in (1)

$$k_{obs} = k_1 [CH_3I] \qquad (1)$$

The effect of the substituents of the β-diketone on the reaction rate is shown in Table I. It is clear from these results that the reactivity of the β-diketone complexes of rhodium(I) towards oxidative addition of iodomethane is in the order acac > BA > DBM > TFAA > TFBA > HFAA. This order reveals the following effect of the substituents R_1 and R_2 of the β-diketone (the electronegativities of CH_3, phenyl and CF_3 are 2.3, 3.0 and 3.35 respectively [19]) on the reactivity of these complexes towards oxidative addition reactions. (i) If a CH_3 group is replaced by a more electronegative phenyl group, the value of k decreases by a factor of about 2 to 3 ($k^{acac} > k^{BA} > k^{DBM}$). (ii) The effect of the more electronegative CF_3 group is significant: if a CH_3 group is replaced by a CF_3 group the value of k decreases by a factor of about 20 ($k^{acac} \gg k^{TFAA} \gg k^{HFAA}$).

This electronic effect of the more electronegative substituents on the reaction rate can be explained by the fact that electron density is removed from the metal, making it a weaker Lewis base. The rhodium atom thus becomes a weaker nucleophile and therefore less reactive towards oxidative addition. The effect of the pK_a values of the various β-diketones on the reaction rate is also shown in the linear free energy relationship, Fig. 1. The slope of the plot of log k *versus* pK_a values of the β-diketone is 0.42.

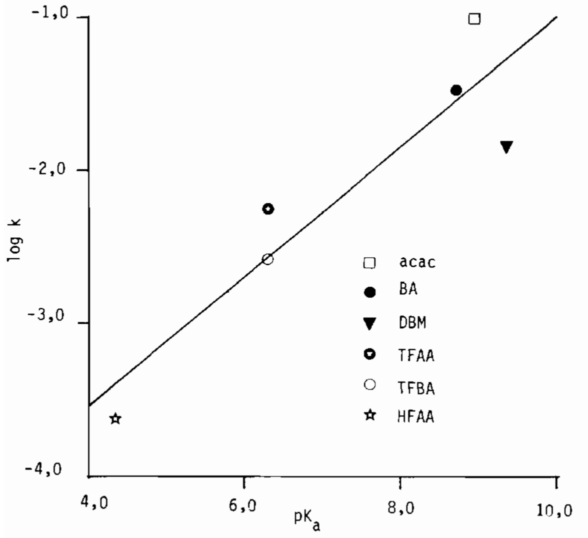


Fig. 1. Graph of log k *vs.* pK_a of the β-diketone in the oxidative addition reaction of $[Rh(\beta\text{-diketone})(P(OPh)_3)_2]$ with CH_3I in acetone at 25.0 °C.

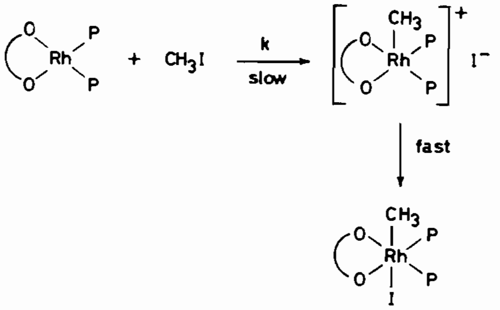
A similar effect of electron-withdrawing substituents of the β-diketone was also found for the oxidative addition of iodomethane to $[Rh(\beta\text{-diketone})(CO)(PPh_3)]$ complexes [3]. A similar electronic effect of various phosphine ligands with different basicities was also observed for the oxidative addition of CH_3I to $[Ir(Cl)(CO)(L)_2]$ [5]. It was found that an increase in the electron density on the iridium atom resulted in an increase of the rate of the oxidative addition reaction.

The reaction between $[Rh(\beta\text{-diketone})(P(OPh)_3)_2]$ and CH_3I could only be studied in a limited range of solvents due to the insolubility of the Rh(I) complexes in many solvents. It was found (see Table II) that the reaction rate is enhanced by more polar solvents. Similar solvent effects were also found for various other oxidative addition reactions [1, 3, 4, 5]. The significant solvent effect is indicative of a mechanism in which a polar transition state is stabilized by more polar solvents and can be taken as evidence that the function of the solvent is to ease the charge separation during the rearrangement and formation of a 5-coordinate intermediate.

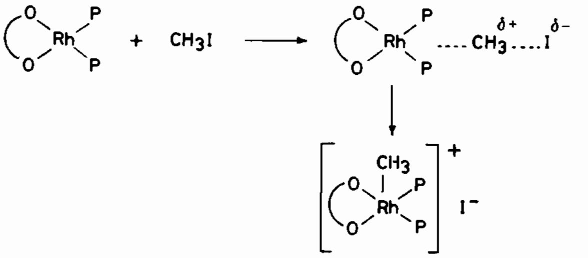
The conventional activation parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ (see Table I) show no worked variation with the character of the β-diketone. The $\Delta H^{\neq}$ values, are relatively small, compensating by highly negative $\Delta S^{\neq}$ values, both of which may be considered as characteristic of an associative mechanism. The large negative $\Delta S^{\neq}$ values indicate an increase in the coordination number during the formation of the transition state.

The volumes of activation, $\Delta V^{\neq}_{exp}$, for the oxidative addition of CH_3I to $[Rh(TFBA)(P(OPh)_3)_2]$ were determined in four solvents, see Table III. Volumes of activation are generally discussed in terms of intrinsic ($\Delta V^{\neq}_{intr}$) and solvational ($\Delta V^{\neq}_{solv}$) volume changes, *i.e.* volume changes due to changes in bond lengths, bond angles and coordination number and changes in the electrostriction parameter [20] respectively. During oxidative addition a volume decrease is expected because of bond formation ($\Delta V^{\neq}_{intr}$) and increasing electrostriction ($\Delta V^{\neq}_{solv}$) due to a polar transition state involving heterolytic cleavage of the CH_3–I bond. The value of $\Delta V^{\neq}_{intr}$ may be obtained from the intercept of the plot of $\Delta V^{\neq}_{exp}$ *versus* the solvent parameter q_p, *i.e.* the volume change in a hypothetical non-solvating medium. Unfortunately a plot of $\Delta V^{\neq}_{exp}$ *versus* q_p gave a non-linear relationship with the result that a value of $\Delta V^{\neq}_{intr}$ could not be determined. Although we were unable to estimate the value of $\Delta V^{\neq}_{intr}$ it is expected that $\Delta V^{\neq}_{solv}$ would make a significant contribution to the value of $\Delta V^{\neq}_{expt}$ with the result that $|\Delta V^{\neq}_{intr}|$ would be significantly smaller than $|\Delta V^{\neq}_{expt}|$. The value of $|\Delta V^{\neq}_{intr}|$ thus appears rather small for the simultaneous formation of two bonds between the rhodium atom and the methyl group and iodine atom in a concerted three-centre mechanism. The volume of activation for the dimerization reaction of cyclopentadiene (for which a three-centre transition state has been proposed) shows a $\Delta V^{\neq}{}_{\text{intr}}$ value of -31 cm^3 mol^{-1} [20, 21].

With the structures of the reactant [22–24] and final product known, the kinetic data (the effect of the substituents of the β-diketone and solvent on the reaction rate as well as the $\Delta S^{\neq}$ and $\Delta V^{\neq}$ values) suggest the following reaction mechanism.



The proposed first step may be represented as



i.e. a linear transition state.

References

1 A. J. Hart-Davis and W. A. G. Graham, *Inorg. Chem., 9,* 2658 (1970).

2 W. H. Thomson and C. T. Sears, *Inorg. Chem., 16,* 769 (1977).

3 S. S. Basson, J. G. Leipoldt and J. T. Nel, *Inorg. Chim. Acta, 84,* 167 (1984).

4 M. Kubota, G. W. Kiefer, R. M. Ishikawa and K. E. Bencala, *Inorg. Chim. Acta, 7,* 195 (1973).

5 R. Ugo, A. Pasini, A. Fusi and S. Cerini, *J. Am. Chem. Soc., 94,* 7364 (1972).

6 J. K. Stille and K. S. Y. Lau, *Acc. Chem. Res., 10,* 434 (1977).

7 H. Stieger and H. Kelm, *J. Phys. Chem., 77,* 290 (1973).

8 A. J. Hart-Davis and W. A. G. Graham, *Inorg. Chem., 10,* 1653 (1971).

9 S. S. Basson, J. G. Leipoldt, A. Roodt, J. A. Venter and T. J. van der Walt, *Inorg. Chim. Acta, 119,* 35 (1986).

10 S. S. Basson, J. G. Leipoldt, A. Roodt and J. A. Venter, *Inorg. Chim. Acta, 128,* 31 (1987).

11 A. M. Trzeciak and J. J. Ziólkowski, *Inorg. Chim. Acta, 64,* L267 (1982).

12 A. J. Oliver and W. A. G. Graham, *Inorg. Chem., 9,* 243 (1970).

13 M. C. Baird, J. T. Mague, J. A. Osborn and G. Wilkinson, *J. Chem. Soc. A,* 1347 (1967).

14 G. J. van Zyl, G. J. Lamprecht and J. G. Leipoldt, *Inorg. Chim. Acta, 122,* 75 (1986).

15 G. J. Lamprecht, G. J. van Zyl and J. G. Leipoldt, to be published.

16 G. J. Lamprecht, J. G. Leipoldt and T. W. Swaddle, *Inorg. Chim. Acta, 129,* 21 (1987).

17 J. Stary, 'The Solvent Extraction of Metal Chelates', Pergamon, Oxford, 1964).

18 R. C. Weast (ed.), 'C.R.C. Handbook of Chemistry and Physics', C.R.C. Press, Boca Raton, Fla., 1980.

19 J. E. Huheey, 'Inorganic Chemistry Principles of Structure and Reactivity', Harper and Row, New York, 1972.

20 M. Kotowski, D. A. Palmer and H. Kelm, *Inorg. Chem., 18,* 2555 (1979).

21 B. Rainstrich, R. H. Sapiro and D. M. Newitt, *J. Chem. Soc.,* 1761 (1939).

22 J. G. Leipoldt, G. J. Lamprecht and G. J. van Zyl, *Inorg. Chim. Acta, 96,* L31 (1985).

23 G. J. van Zyl, G. J. Lamprecht and J. G. Leipoldt, *Inorg. Chim. Acta, 102,* L1 (1985).

24 G. J. Lamprecht, J. G. Leipoldt and G. J. van Zyl, *Inorg. Chim. Acta, 97,* 31 (1985).