

The Oxidative Addition of Methyl Iodide to β -Diketonecarbonyl-triphenylphosphinerhodium(I) Complexes

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The kinetics and mechanism of the reaction $[Rh(\beta\text{-diketone})(CO)(PPh_3)] + CH_3I \rightarrow [Rh(\beta\text{-diketone})(CH_3)(I)(CO)(PPh_3)]$ where $\beta\text{-diketone} = \text{acac}$, TFDMAA, TFAA and HFAA, were studied with the aid of i.r. and visible spectrophotometry. The reaction proceeds by two consecutive steps through a postulated ionic intermediate. The influence of phosphine dissociation, solvent polarity, alkyl group variation and different electronegative $\beta\text{-diketone}$ substituents on the reaction rate were investigated. The rate constant for a metal–acyl \rightarrow metal–alkyl conversion (CH_3 migration) was determined.

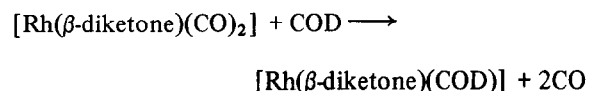
Introduction

It is well-known that homogenous catalysis of processes such as carbonylation, olefin hydrogenation *etc.* can often be effected by d^8 and d^{10} complexes of the group VIII transition metals. An important part of these catalytic cycles is the oxidative addition of a covalent molecule to the low-valent metal complex [1].

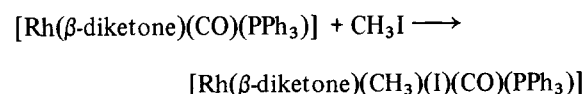
The oxidative addition of alkyl halides (RX) to Vaska-type compounds, *trans*- $M(CO)(X)(L)_2$ ($M = Ir(I)$ and $Rh(I)$; $X = \text{halide}$ and $L = \text{tertiary phosphine or arsine}$), has been studied extensively with regard to aspects such as mechanism [2–5], as well as steric and electronic effects [6–9]. The presence of a carbonyl ligand offers in addition the interesting possibility of giving either the *trans*-substituted alkyl $M(CO)(X)_2(R)(L)_2$, or via isomerization acyl $M(COR)(X)_2(L)_2$ compound as final products.

Oxidative addition reactions can proceed by different reaction pathways [10] and one of the factors influencing the preferred choice is the nucleophilicity

of the metal in the complex. Apart from the general increasing Lewis basicity on descending in a periodic group for a given type of complex [11], it is also the σ - and π -bonding framework of metal–ligand interactions which plays a major role. The substitution reaction



where COD = cyclooctadiene, showed a 2000-fold increase in the ligand-dependent rate constants of the order benzoylacetone (BA) < dibenzoylmethane (DBM) < trifluoroacetylacetone (TFAA) < trifluorobenzoylacetone (TFBA) < hexafluoroacetylacetone (HFAA) [12]. HFAA, with two powerful electrophilic CF_3 groups, is thus a far better *trans* labilizer than for example BA or DBM containing the less electrophilic phenyl or CH_3 groups. The effect of the CF_3 groups on the reactivity was explained by their ability to decrease the electron density on the metal making the complex a stronger Lewis acid and thus more reactive in an associative mechanism. This reasoning, if applied to oxidative addition, predicts expected opposite rate trends with regard to Lewis basicity for the metal in the above $\beta\text{-diketone}$ complexes. Replacement of one CO by a less capable π -acid such as triphenylphosphine (PPh_3) could enhance still further the rate of oxidative addition. With this in mind we studied the kinetics and mechanism of the reaction



where $\beta\text{-diketone} = \text{acetylacetone (acac)}$, trifluorodimethylacetylacetone (TFDMAA), TFAA and HFAA.

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TABLE I. IR Carbonyl Frequencies (cm^{-1}) of Rhodium Complexes.

β -diketone pK_a^* type	substituents	$[\text{Rh}(\beta\text{-dik})(\text{CO})(\text{PPh}_3)]$ (I)	$[\text{Rh}(\beta\text{-dik})(\text{COCH}_3)(\text{I})(\text{PPh}_3)]$ (II)	$[\text{Rh}(\beta\text{-dik})(\text{CH}_3)(\text{I})(\text{CO})(\text{PPh}_3)]$ (III)
8.9 acac	CH_3, CH_3	1988	1735	2045
6.3 TFAA	CF_3, CH_3	1996	1740	2062
6.8** TFDMAA	$\text{CF}_3, \text{CH}(\text{CH}_3)_2$	1998	1740	2058
4.4 HFAA	CF_3, CF_3	2000	—	2070

*From ref. 14. **Present work, spectrophotometric determination, 25 °C, $\mu = 0.1 \text{ mol dm}^{-3} \text{ NaClO}_4$.

Experimental

Materials

The different β -diketone complexes, $[\text{Rh}(\beta\text{-diketone})(\text{CO})_2]$, were prepared from $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (Engelhardt) by literature methods [12, 13]. Complexes of the type $[\text{Rh}(\beta\text{-diketone})(\text{CO})(\text{PPh}_3)]$ were prepared as follows: to a solution of $[\text{Rh}(\beta\text{-diketone})(\text{CO})_2]$ (0.2 g) in 20 cm^3 petroleumbenzene (Merck, B.P. 50–70 °C) was added an equimolar amount of PPh_3 . The mixture was briefly boiled with *ca.* 1 g activated charcoal and the filtrate slowly evaporated (6 hr) to yield a yellow crystalline product.

Freshly prepared N-methylpyridinium iodide was recrystallized from benzene prior to use. Methyl iodide (Merck) was always used as freshly distilled samples. The oxidative addition products were difficult to isolate due to their oily nature in excess methyl iodide. Pure $[\text{Rh}(\text{TFAA})(\text{CO})(\text{CH}_3)(\text{I})(\text{PPh}_3)]$ could however be isolated as follows: to $[\text{Rh}(\text{TFAA})(\text{CO})(\text{PPh}_3)]$ (0.2 g) in 1,2-dichloroethane (20 cm^3) was added excess methyl iodide (2 cm^3). The yellow solution was covered with a transparent film and set aside for 24 hr, the time for complete reaction as monitored by i.r. spectra. The now dark red solution was evaporated under reduced pressure to remove solvent and the excess CH_3I . The red-brown oil was dissolved in acetone (20 cm^3). Crystallization was effected within 30 min by dropwise addition of water. The mother liquor precipitated a dark brown oil on longer standing, possibly due to decomposition which may also be responsible for the low yield (20 mg) of the yellow crystalline product. *Anal.* calcd. (%) for $\text{RhPF}_3\text{IC}_{24}\text{H}_{19}\text{O}_3$: P, 4.39; F, 8.52; I, 18.60; C, 43.54; H, 3.37. Found: P, 4.49; F, 8.27; I, 18.41; C, 41.82; H, 2.76.

Kinetic Measurements

The reactions were followed spectrophotometrically with a Pye Unicam SP 1700 double-beam spectrophotometer equipped with a thermostatted (0.1 K) cell compartment, as well as recorder and line printer facilities. The formation of $[\text{Rh}(\beta\text{-diketone})(\text{CO})(\text{CH}_3)(\text{I})(\text{PPh}_3)]$ products were measured

at wavelengths of 450, 400, 450 and 430 nm where β -diketone = acac, TFDMAA, TFAA and HFAA respectively. All kinetic runs were performed in 1,2-dichloroethane as solvent unless stated otherwise. Initial concentrations of $[\text{Rh}(\beta\text{-diketone})(\text{CO})(\text{PPh}_3)]$ were generally in the $1.25\text{--}5.0 \times 10^{-3} \text{ M}$ range whilst the concentration of CH_3I was in at least a 40-fold excess (0.2–2.0 M). Under these pseudo-first-order conditions the first-order rate constants, k_{obs} , were calculated from the slopes of linear $\ln(A_\infty - A_t)$ vs. time plots. A_∞ measurements were made after about ten half-lives, except for $[\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)]$ where biphasic plots of $\ln(A_\infty - A_t)$ vs. time data necessitated computerized least-squares curve fitting for the first stage of each reaction run.

Infrared spectra (625–3800 cm^{-1} region) were recorded with a Pye-Unicam SP1000 spectrophotometer using either the KBr disc technique for solids or cells with NaCl windows for 1,2-dichloroethane solutions of complexes. Reaction progress involving the transmittance change in carbonyl frequencies at the early stages were recorded for solutions (0.04 M in rhodium complex and 0.5 M in CH_3I) at the shortest possible scan cycles of approx. 2 min. Temperature fluctuations were $\pm 2^\circ \text{C}$ for the duration of the reaction.

Results and Discussion

Infrared analysis of the reaction progress in terms of the Rh(I) carbonyl starting complex (I) and the formation of either or both of the Rh(III) acetyl-(II) or carbonylmethyl(III) complexes, all having different identifiable carbonyl frequencies (Table I), provides a powerful method in elucidating the main reaction pathway [2, 5]. Repeated time scanning of 1,2-dichloroethane solutions of (I) containing excess CH_3I showed an immediate intensity decrease in its CO peak and a simultaneous growth of two new CO peaks corresponding to II and III respectively. The peak of III developed at a faster rate compared to that of II. The only exception to this pattern is the

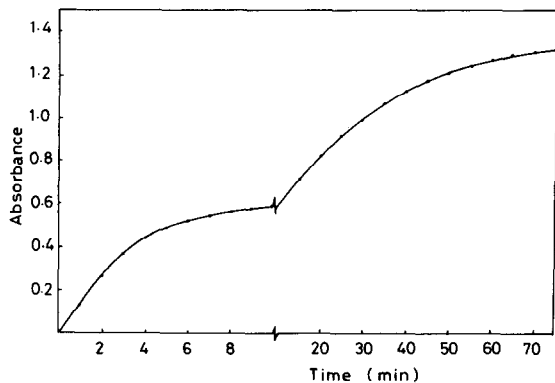


Fig. 1. Biphasic absorbance-time plot for CH_3I addition to $[\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)]$. The first curve corresponds to the K_1 and k_2 paths and the second to the acyl-alkyl conversion (k_4) in Scheme 2. $[\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)] = 5 \times 10^{-3} \text{ M}$; $[\text{CH}_3\text{I}] = 0.4 \text{ M}$; Temp. = 29.8°C .

HFAA complex of I which has the slowest rate and gave only one new CO peak growth corresponding to III. Comparison of the relative intensities of the CO peaks of II and III also showed that the amount of II formed during the reaction decreased in the sequence $\text{acac} > \text{TFAA} \sim \text{TFDMAA} > \text{HFAA}$, and that the highest yield of II (acac complex) was less than one third that of III at this stage of the reaction if the same ratio of molar absorptivities, as found for $[\text{RhCl}(\text{CO})(\text{PPh}_3)_2]$ [5], is assumed.

The i.r. spectra also showed that only one final product (III) was formed at infinite times (Scheme 1). The much slower $\text{II} \rightarrow \text{III}$ conversion was confirmed by successive i.r. spectra of a solution of $[\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)]$ containing less than the stoichiometric amount of CH_3I .

These spectra clearly showed that after the initial $\text{I} \rightarrow \text{II}$ and $\text{I} \rightarrow \text{III}$ conversions, the peak of unreacted I remained constant and that of III increased further at the cost of II. This can be accounted for by a much slower acyl-alkyl conversion, similar to the case of $[\text{Ir}(\text{Cl})_2(\text{COCH}_2\text{Ph})(\text{PPh}_3)_2]$ [15]. The reversibility of this step seems to be solvent-dependent, since a change of solvent to CH_3I gave an equilibrium mixture of approximate equal quantities of II and III at infinite time.

Since the visible spectra of II were unobtainable, it was decided to check on the possibility that absorb-

ance data for each run was in fact a composite of the $\text{I} \rightarrow \text{III}$ and $\text{I} \rightarrow \text{II}$ conversions or of the former alone. The visible spectrum of the isolated $[\text{Rh}(\text{TFAA})(\text{CO})(\text{CH}_3)(\text{I})(\text{PPh}_3)]$ was the same as found for the reaction between the starting complex and CH_3I at the completion of each kinetic run. The slow $\text{II} \rightarrow \text{III}$ conversion, as shown in the second increase of Fig. 1, was detected for $[\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)]$ only. The monophasic absorbance-time plots for the other complexes, together with the i.r. results on the low yield of II, indicated a negligible contribution of II to the absorbance measurements.

The reactions followed pseudo-first-order kinetics with

$$k_{\text{obs}} = \frac{k_2 K_1 [\text{CH}_3\text{I}]}{1 + K_1 [\text{CH}_3\text{I}]} \quad (1)$$

where the constants are interpreted in terms of Scheme 2. The linear forms of eqn. (1) are shown in Fig. 2 from which K_1 and k_2 values were determined as given in Table II. Activation parameters are given in Table III.

The proposed mechanism (Scheme 2) shows the reacting complex, $[\text{Rh}(\beta\text{-diketone})(\text{CO})(\text{PPh}_3)]$, to be partly dissociated (according to the results of Fig. 3) to a coordinatively unsaturated compound. The vacated site on the rhodium may now be occupied by a solvent molecule or it may even dimerize to $[\text{Rh}(\beta\text{-diketone})(\text{CO})]_2$, similar to the case of CH_3I addition to Wilkinson's complex, $[\text{RhCl}(\text{PPh}_3)_3]$

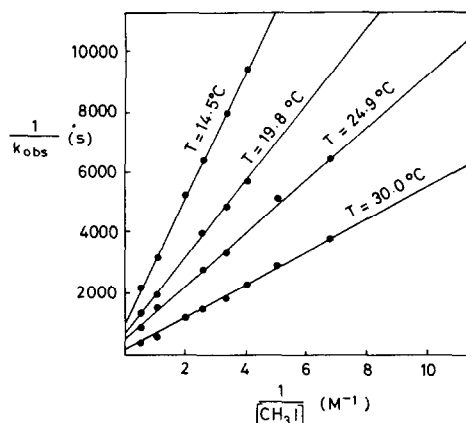
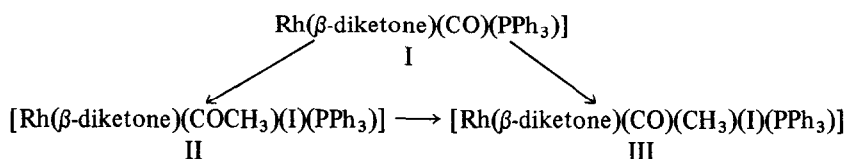
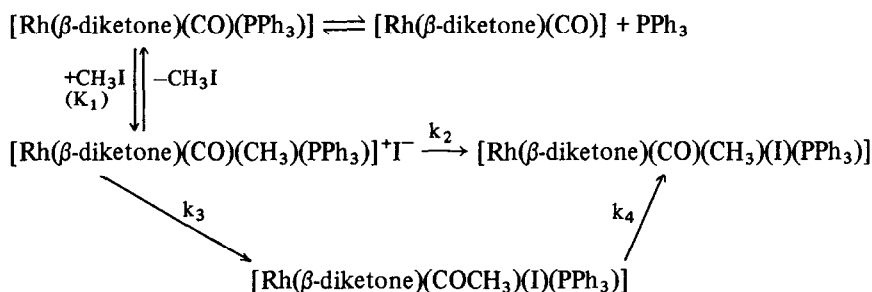


Fig. 2. Concentration and temperature dependence of k_{obs} with methyl iodide. $[\text{Rh}(\text{TFAA})(\text{CO})(\text{PPh}_3)] = 5 \times 10^{-3} \text{ M}$.



Scheme 1



Scheme 2

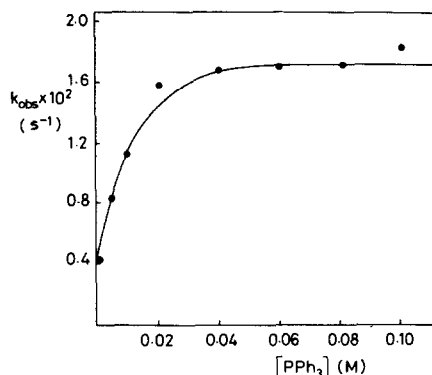
TABLE II. K_1 and k_2 Values for the Oxidative Addition of CH_3I to Various $[\text{Rh}(\beta\text{-diketone})(\text{CO})(\text{PPh}_3)]$ Complexes (Standard Deviations in Parentheses).

β -diketone	Temp. (°C)	$k_2 \times 10^4$ (s ⁻¹)	K_1 (M ⁻¹)
acac	15.6	36.3(3.0)	2.22(0.26)
	20.5	50.1(3.2)	3.23(0.30)
	25.1	65.4(4.4)	3.30(0.27)
	29.8	97.7(1.8)	6.20(0.22)
TFAA	14.5	9.1(0.7)	0.53(0.05)
	19.8	11.9(0.1)	0.66(0.02)
	24.9	15.7(0.4)	0.72(0.05)
	30.0	17.8(1.2)	0.99(0.08)
TFDMAA	20.0	6.1(0.4)	2.74(0.27)
	25.0	14.5(1.2)	2.49(0.31)
	30.2	23.3(1.3)	2.55(0.29)
	35.2	38.8(2.1)	2.35(0.20)
HFAA	24.6	1.29(0.12)	0.35(0.05)
	29.7	1.72(0.20)	0.28(0.04)
	34.7	3.30(1.70)	0.21(0.07)

TABLE III. Activation Parameters for the k_2 -path (Standard Deviations in Parentheses).

Complex	ΔH^* (kJ mol ⁻¹)	ΔS_{298}^* (J K ⁻¹ mol ⁻¹)
$[\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)]$	50.1(4.0)	-118(10)
$[\text{Rh}(\text{TFAA})(\text{CO})(\text{PPh}_3)]$	28.2(3.7)	-204(12)
$[\text{Rh}(\text{TFDMAA})(\text{CO})(\text{PPh}_3)]$	78.2(5.9)	-38(10)
$[\text{Rh}(\text{HFAA})(\text{CO})(\text{PPh}_3)]$	120.1(3.3)	-82(9)

[16]. The constancy of k_{obs} values for various initial $[\text{Rh}(\beta\text{-diketone})(\text{CO})(\text{PPh}_3)]$ concentrations excludes a dimer participation. The undissociated $[\text{Rh}(\beta\text{-diketone})(\text{CO})(\text{PPh}_3)]$ is the more (and presumably, sole) reactive form if for no other

Fig. 3. Variation of k_{obs} with added PPh_3 at 25.0 °C. $[\text{CH}_3\text{I}] = 0.5 \text{ M}$; $[\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)] = 5 \times 10^{-3} \text{ M}$.

reason than being a better Lewis base compared to the dissociated form. This complements the conclusion (*vide supra*) that substitution lability is of lesser importance than the polarity on the central metal in the complex.

Iodide ion catalysis of CH_3I oxidative additions to $[(\text{cod})\text{Ir}(\text{phen})]^+$ [17] and $[\text{Rh}(\text{L})_2(\text{CO})(\text{I})]$ [18] proceed via a five coordinate complex in the former or through substitution of a labile ligand ($\text{L} = \text{tertiary phosphine}$) in the latter. We did not observe enhancement in reaction rates even at a fivefold excess of N-methylpyridiniumiodide over rhodium complex concentrations, but a substitution reaction about 400X slower than the oxidative addition reaction did take place. I.r. spectra revealed a complete absence of the carbonyl ligand at infinite times. This was not pursued further.

A pronounced solvent effect is perceptible in Table IV. Decreasing solvent polarity has a pronounced effect on the equilibrium constant since plots similar to those of Fig. 2 gave zero intercepts for chlorobenzene and toluene. This will result as a special case for eqn. (1), with K_1 being small giving $k_{\text{obs}} = k_2 K_1 [\text{CH}_3\text{I}]$. The net relative solvent efficiency in promoting oxidative addition, as judged by $K_1 k_2$ values, thus decreases in the order acetone-(1.0) > 1,2-dichloroethane(0.66) > chlorobenzene-(0.05) > toluene(0.02).

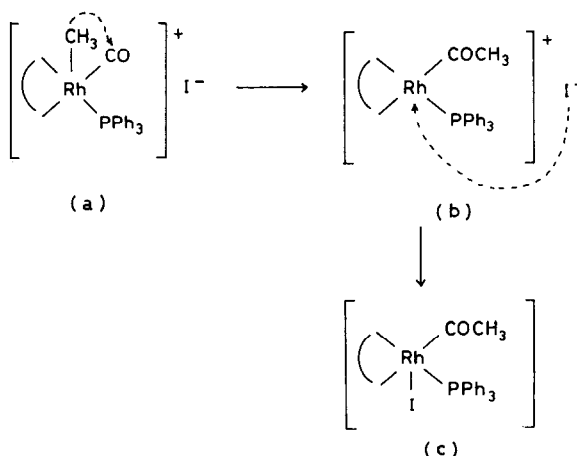
TABLE IV. Solvent Effect for the Addition of CH_3I to $1.25 \times 10^{-3} M$ $[Rh(TFAA)(CO)(PPh_3)]$ at $25.0^\circ C$ (Standard Deviations in Parentheses).

Solvent	Diel. const.	$k_2 \times 10^4$ (s^{-1})	K_1 (M^{-1})	$k_2 K_1 \times 10^4$ ($M^{-1} s^{-1}$)
acetone	20.70	16.7(0.4)	1.03(0.1)	17.2(0.67)
1,2-dichloroethane	10.36	15.7(0.4)	0.72(0.05)	11.33(0.55)
chlorobenzene	5.71	—	—	0.91(0.07)
toluene	2.44	—	—	0.32(0.04)

This solvent effect, together with the large negative ΔS^\ddagger values for the k_2 -path (Table III), lends strong support for a polar transition state during the rapid initial set-up of the equilibrium leading to the ionic intermediate. Similar solvent effects were found for iridium [6] and other rhodium [19] complexes. We also found that $[Rh(acac)(CO)(PPh_3)]$ reacted 120X slower with C_2H_5I compared to CH_3I . The different slopes but similar k_2 -values in Fig. 4 indicate a pronounced reduction in the K_1 value in using C_2H_5I instead of CH_3I . This would be true if the nucleophilic attacks of the rhodium atom on the α -carbon of the alkyl halide are hampered by the greater steric demand of the ethyl in comparison to the methyl group.

The postulate for the existence of the ionic intermediate, $[Rh(\beta\text{-diketone})(CO)(CH_3)(PPh_3)]^+I^-$, is based on studies [19, 20] which led to the isolation of the more insoluble tetraphenylborate salts from for example $[Rh(C_5H_5)(CO)(CH_3)(P(CH_3)_2C_6H_5)]^+Br^-$. The charge separation in these ionic intermediates is also solvent-dependent. The transformations along the k_3 path are assumed to be a

rate-determining methyl group migration, followed by a fast nucleophilic attack by I^- on the acyl cation:



The cations in (a) and (b) are presumably in the square pyramidal form which is more stable than the trigonal bipyramid for a d^6 ion. This was also confirmed in structure determinations of $[Rh(I)_2(CH_3)(PPh_3)_2] \cdot C_6H_6$ [21] and $[AsPh_4][Rh(I)(COEt)(mnt)(PPh_3)]$ (mnt = maleonitriledithiolate anion) [22] where the respective CH_3 and $COEt$ groups occupy the apical position of the square pyramid. The I^- in the latter compound can also be reversibly removed with Ag^+ which, in the presence of a strong coordinating solvent, led to the isolation of neutral solvated acyl complexes, $[Rh(COR)(PPh_3)(mnt)(solv)_x]$. A similar formulation is envisaged in (b) with the solvent molecule in the apical position resulting in a subsequent fast substitution by the halide ion.

The k_2 path involves direct substitution of I^- *trans* to the CH_3 group in the apical position of (a). This step is believed to be rate determining, due to the strong labilizing effect of a CH_3 ligand. While the above reasoning for the k_2 and k_3 paths relies strongly on the assumption of square pyramidal geometry for the ionic intermediate in solution, it is also known that fluxional behaviour of non-rigid ML_5 stereochemical forms does occur. The chosen model only serves the purpose of explaining a proposed mechanism for the present case.

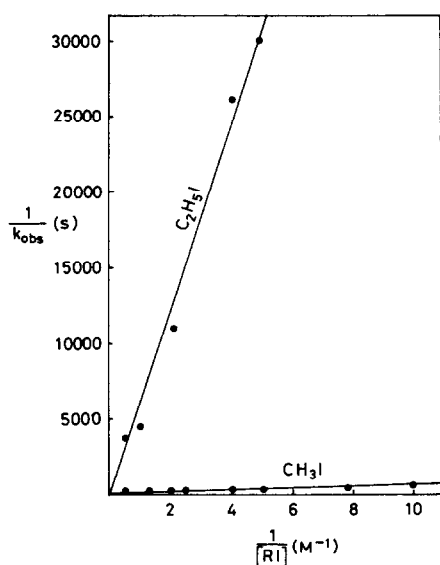


Fig. 4. Variation of k_{obs} with different alkyl iodide concentrations at $25.0^\circ C$ for $[Rh(acac)(CO)(PPh_3)]$.

The acyl-alkyl conversion (k_4 path) proceeds with $k_{\text{obs}} = 1.8 \times 10^{-4} \text{ s}^{-1}$ for $[\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)]$ at 25°C and is independent of CH_3I concentrations in the range $0.1\text{--}2.0 \text{ M}$. This rate constant compares favourably with a value of $2.8 \times 10^{-4} \text{ s}^{-1}$ obtained from i.r. measurements and is approximately 36X smaller than the corresponding k_2 value (Table II). It is also of the same magnitude compared with $k = 4.4 \times 10^{-4} \text{ s}^{-1}$ for the benzyl migration in $[\text{IrCl}_2(\text{COCH}_2\text{Ph})(\text{PPh}_3)_2]$ [15] using benzene as solvent. The latter study reported mild solvent effects. This remains to be explored in our case since strong coordinating solvents should be competitive with the migratory alkyl group for the vacant site of structure (c) (*vide supra*).

The relative nucleophilicity of the β -diketone complexes employed in this study follow a reactivity order of $\text{acac}(1.0) > \text{TFAA}(0.24) \sim \text{TFDMAA}(0.22) \gg \text{HFAA}(0.02)$. The decrease in this sequence parallels the increase in the number of electronegative substituents on the β -diketone and thus also the decreasing pK_a values of the series of β -diketones (Table I). The carbonyl frequency, which is a linear function of the electron density at the rhodium, will increase with lower electron density on the metal. This expectation is fulfilled for each type of complex in Table I. The enhancement in reactivity of these complexes for oxidative addition, based only on the series of β -diketones employed, can be considered as a mild effect. The above decreasing order of reactivity of the β -diketone complexes is also the expected trend since the Lewis basicity decreases in the same direction.

Acknowledgement

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