Journal of Organometallic Chemistry, 366 (1989) 369–375
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 09680

Kinetics of the substitution of β-Diketones in β-diketonato(1,5-cyclooctadiene)rhodium(I) complexes by benzoyl-1,1,1-trifluoroacetone

J.H. Potgieter

Department of Chemistry, University of Pretoria, Pretoria (Republic of South Africa)

(Received November 16th, 1988)

Abstract

The kinetics and mechanism of the reactions between [Rh(β-diketone)(COD)] and trifluorobenzoylacetone (TFBA) to give [Rh(TFBA)(COD)] have been studied in a petroleum-ether medium at various temperatures with UV spectroscopy. The rate law is $-\mathrm{d}[\mathrm{Rh}(\beta\text{-diketone})(\mathrm{COD})]/\mathrm{d}t = (k_s + k_y[\mathrm{TFBA}])[\mathrm{Rh}(\beta\text{-diketone})(\mathrm{COD})]$ and the reaction is shown to proceed via an associative mechanism. The value of k_s and k_y were determined for various β-diketone complexes with β-diketone = acac, BA, DBM, TFAA and HFAA. The reactivities of the complexes fall as the β-diketone is varied in the sequence BA > acac > DBM > TFAA > HFAA, indicating that electronegative substituents in the β-diketone increase the *trans*-effect and therefore the strength of the Rh–O bonds. Since the ring opening is the rate-determining step in the reaction, It can be concluded that the complex containing the β-diketone with the largest *trans*-effect, which gives rise to the strongest Rh–O bonds, will undergo the slowest substitution. The effect of the substituents of the β-diketone (CF_3, phenyl and CH_3) on the *trans*-effect is discussed.

Introduction

It is well known that the carbonyl groups in complexes of the type [Rh(β-diketone)$(CO)_2$] can be completely replaced by olefins or partly replaced by ligands such as triphenylphosphine (PPh_3) or triphenylarsine ($AsPh_3$) [1,2], according to the reaction

$$[\mathrm{Rh}(\beta\text{-diketone})(\mathrm{CO})_2] + \mathrm{PPh}_3 \rightarrow [\mathrm{Rh}(\beta\text{-diketone})(\mathrm{CO})(\mathrm{PPh}_3)] + \mathrm{CO} \qquad (1)$$

This property has been successfully used to determine the relative *trans*-influence of the two oxygen atoms of non-symmetrical β-diketones, and thus the effect of different substituents R^1 and R^2 in the β-diketones $R^1.CO.CH_2.CO.R_2$ on the relative *trans*-influence of the oxygen atoms. It has been found that the oxygen atom nearest to an electron attracting group (such as a CF_3 group) has the smallest *trans*-influence [3,4]. This is in agreement with the polarization theory [5] and the σ-*trans*-effect [6], since the oxygen atom nearest to the CF_3 group will be the least polarizable and a weaker σ-donor as a result of the electron attraction by the CF_3 group.

Both carbonyl groups in complexes of the type [Rh(β-diketone)$(CO)_2$] are replaced by 1,5-cyclooctadiene (COD) [1]:

$$[\mathrm{Rh}(\beta\text{-diketone})(\mathrm{CO})_2] + \mathrm{COD} \rightarrow [\mathrm{Rh}(\beta\text{-diketone})(\mathrm{COD})] + 2\mathrm{CO} \qquad (2)$$

[Rh(β-diketone)(COD)] complexes can in turn undergo substitution reactions with other β-diketones according to the reaction:

$$[\mathrm{Rh}(\beta\text{-diketone})(\mathrm{COD})] + \beta\text{-diketone}' \rightarrow [\mathrm{Rh}(\beta\text{-diketone}')(\mathrm{COD})] + \beta\text{-diketone} \qquad (3)$$

The kinetics of these reactions were studied to determine the effects of the substituents R^1 and R^2 in the different β-diketones in the [Rh(β-diketone)(COD)] complexes on the *trans*-effect of the oxygen atoms in the β-diketones. Because the relative magnitudes of these *trans*-effects will influence the strength of the Rh–O bonds, the effect of the substituents R^1 and R^2 in the various β-diketones on the ring opening (breaking of the Rh–O bonds), which is the rate-determining step in the reaction, can be evaluated.

Experimental

The various β-diketone complexes [Rh(β-diketone)(COD)] were prepared from $[Rh_2Cl_2(COD)_2]$, which was made by refluxing 1.00 g of $RhCl_3 \cdot 3H_2O$ in 25 cm^3 of ethanol and 3 cm^3 of 1,5-cyclooctadiene (COD) for 45 min until an orange-yellow precipitate separated out [7]. This precipitate was washed with methanol, dried at 80 °C for 30 min, and then recrystallized from petroleum ether (Merck, b.p. 60–80 °C). An 0.10 g sample of the $[Rh_2Cl_2(CO)_2]$ was dissolved in the minimum volume of petroleum-ether and an equivalent amount of β-diketone was added [8] and 10 cm^3 of a 30% KOH solution was added dropwise with vigorous stirring. 30 min after the addition of the KOH solution the two phases of the mixture were separated. The [Rh(β-diketone)(COD)] complexes were obtained from the organic phase and recrystallized from petroleum-ether. The following β-diketone complexes were made in this way: β-diketone = acetylacetone (acac), benzoylacetone (BA), dibenzoylmethane (DBM), trifluoroacetylacetone (TFAA), hexafluoroacetylacetone (HFAA) and trifluorobenzoylacetone (TFBA).

The rate constants were determine by monitoring the formation of [Rh(TFBA)(COD)] with a Cecil CE 595 double-beam spectrophotometer equipped with a thermostated (±0.1 K) cell compartment and a recorder. The wavelength used was that at which there was the maximum difference in absorbance between reactant and product. All kinetic runs were performed with petroleum ether (Merck, b.p. 60–80 °C) as solvent, and was monitored under pseudo-first order conditions. At least a 10-fold excess of TFBA was used. The absorbance spectra of the complexes were recorded with a Cecil CE 595 spectrophotometer. The position of

Table 1

Values of λ_{max} for the reactants and product of the reaction between [Rh(β-diketone)(COD)] and TFBA, and the wavelength λ_{exp}, at which the reaction was monitored

β-Diketone	Reactant λ_{max} (nm)	Product	
		λ_{max} (nm)	λ_{exp} (nm)
acac	340	365	380
BA	350	365	388
DBM	363	365	385
TFAA	350	365	384
HFAA	350	365	380

λ_{max} of the reactants and the product, as well as the wavelength at which the reaction was monitored, are given in Table 1.

Results

The pseudo-first order rate constants, k_{obs}, were calculated from the slopes of linear plots of $(A_\infty - A_t)$ versus time for various TFBA concentrations. The plots were linear for at least 60% conversion and A_∞ values were determined after at least 8 half-lives. The effect of the concentration of trifluorobenzoylacetone (TFBA) on the pseudo-first order rate constants in the case of the reaction with [Rh(acac)(COD)] is shown in Fig. 1.

The rate law in all cases is given by:

$$\frac{-\mathrm{d}[\mathrm{Rh}(\beta\text{-diketone})(\mathrm{COD})]}{\mathrm{d}t} = \left(k_s + k_y[\mathrm{TFBA}]\right)[\mathrm{Rh}(\beta\text{-diketone})(\mathrm{COD})] \tag{4}$$

Since the reactions were carried out under pseudo-first order conditions:

$$k_{obs} = k_s + k_y[\mathrm{TFBA}] \tag{5}$$

The rate constants k_s and k_y at various temperatures for the various complexes were determined from the least-squares fits of the data to eq. 5 by use of a non-linear least squares programme [9]. The values of k_s and k_y as well as the activation parameters $\Delta H_y^\star$ and $\Delta S_y^\star$ for the various complexes are given in Tables 2 and 3.

The kinetic data and the large negative values of $\Delta S_y^\star$ indicate that the substitution reactions proceed via an associative mechanism. The following mechanism is proposed:

$$[\mathrm{Rh}(\beta\text{-diketone})(\mathrm{COD})] + \mathrm{Solv.} \underset{k_4}{\overset{k_{-s}}{\rightleftarrows}} [\mathrm{Rh}(\beta\text{-diketone})(\mathrm{COD})(\mathrm{Solv.})] \tag{6}$$

$$[\mathrm{Rh}(\beta\text{-diketone})(\mathrm{COD})(\mathrm{Solv.})] + \mathrm{TFBA} \xrightarrow{k_f} [\mathrm{Rh}(\mathrm{TFBA})(\mathrm{COD})] + \mathrm{Solv.} + \beta\text{-diketone} \tag{7}$$

$$[\mathrm{Rh}(\beta\text{-diketone})(\mathrm{COD})] + \mathrm{TFBA} \xrightarrow{k_y} [\mathrm{Rh}(\mathrm{TFBA})(\mathrm{COD})] + \beta\text{-diketone} \tag{8}$$

(where Solv. = solvent)

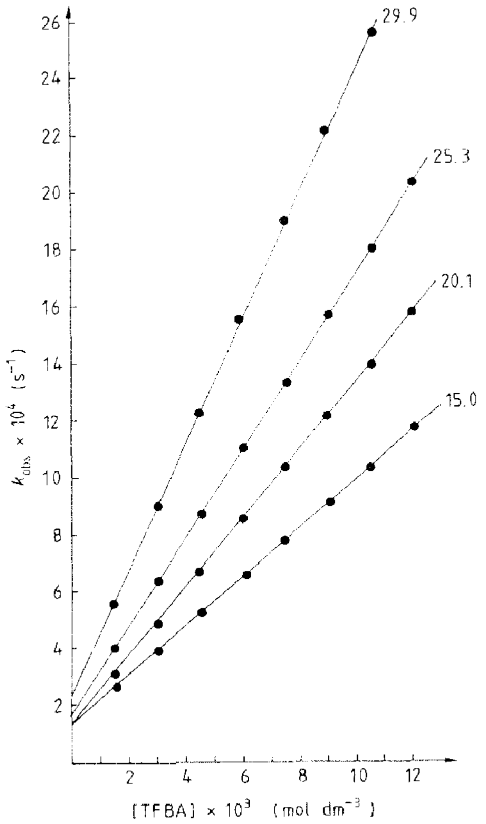

Fig. 1. Plot of k_{obs} vs. [TFBA] at various temperatures for the reaction between [Rh(acac)(COD)] and TFBA. [Rh(acac)(COD)] = 1.2×10^{-4} mol dm^{-3}.

Table 2

Values of k_s and k_y for the reactions between various [Rh(β-diketone)(COD)] complexes and TFBA

Complex	Temp. (°C)	k_s ($\times 10^4$) (s^{-1})	k_y ($\times 10^2$) (mol^{-1} dm^3 s^{-1})
[Rh(acac)(COD)]	15.0	1.37	8.61
	20.1	1.26	12.13
	25.3	1.65	15.61
	29.9	2.39	22.07
[Rh(BA)(COD)]	10.1	2.63	6.79
	15.1	2.78	9.87
	20.2	4.28	15.32
	25.0	6.44	19.94
[Rh(DBM)(COD)]	15.3	1.70	5.35
	20.1	1.86	6.11
	25.2	1.00	7.50
	29.9	3.68	9.06
[Rh(TFAA)(COD)]	15.1	9.69	2.39
	20.1	7.21	3.21
	24.9	6.79	4.12
[Rh(HFAA)(COD)]	14.8	1.84	2.71
	24.8	0.41	3.58

Table 3

Activation parameters derived from the k_y values

Complex	ΔH_y^* (kJ mol^{-1})	ΔS_y^* (J K^{-1} mol^{-1})
[Rh(acac)(COD)]	42.1	−119
[Rh(BA)(COD)]	49.3	−93
[Rh(DBM)(COD)]	27.1	−176
[Rh(TFAA)(COD)]	37.0	−147
[Rh(HFAA)(COD)]	17.0	−214

Literature reports for similar reactions [10,11] indicate that the intermediate complex in reaction (6) is not present as [Rh(COD)(Solv.)$_2$] but as [Rh(β-diketone)(COD)(Solv.)].

Discussion

The results (especially the values of k_y in Table 2) indicate that the reactivities of the β-diketone complexes fall in the order BA > acac > DBM > TFAA > HFAA. This order can therefore be considered as the order of the *trans*-effect of the various β-diketones. This points to the following effects of the substituents R^1 and R^2 of the β-diketone on the reactivities of the complexes:

(a) The replacement of a CH_3 group by the more electronegative phenyl group causes a decrease in the value of k_y by a factor of 2.66; $k_y^{BA} > k_y^{DBM}$.

(b) The effect of the more electronegative CF_3 group (the electronegativities of CH_3, phenyl and CF_3 are 2.3, 3.0 and 3.35 respectively [12]) is even more marked; when a CH_3 group is replaced by a CF_3 group the value of k_y falls by a factor of 4.36; $k_y^{acac} > k_y^{TFAA} > k_y^{HFAA}$.

(c) When a phenyl group is replaced by a CF_3 group the value of k_y also decreases; $k_y^{BA} > k_y^{TFAA}$ and $k_y^{DBM} > k_y^{HFAA}$.

In terms of the values of the rate constants the complexes can therefore be divided into two groups: β-diketones with phenyl groups as substituents and β-diketones with CF_3 groups as substituents.

The kinetic data reveal that an increase in the electron-attracting power of one of (and more so that of both) the substituents R^1 and R^2 of the β-diketone results in a decrease in the kinetic *trans*-effect. These findings are supported by those of other workers [13], who found that an increase in the electron attracting power of the substituents R^1 and R^2 caused an increase in the kinetic *trans*-effect observed in the substitution reactions of the type [Rh(β-diketone)(CO)$_2$] + COD → [Rh(β-diketone)(COD)] + 2CO. They are also in agreement with the thermodynamic *trans*-influence, which depends on the strength of the chemical bonds in the ground state. The crystal structures of [RhQ(CO)(PPh$_3$)], [Rh(BPHA)(CO)(PPh$_3$)] and [Rh(TTA)(CO)(PPh$_3$)] (made by the reaction between the dicarbonyl complex and PPh$_3$; Q = 8-hydroxyquinoline, BPHA = *N*-benzoyl-*N*-phenylhydroxylamine and TTA = thenoyltrifluoroacetone) revealed that the carbonyl group *trans* to the most electronegative atom of the chelate ring (in the case of [RhQ(CO)$_2$]) and *trans* to the oxygen atom nearest to the most electronegative group of the bidentate ligands (in the case of [Rh(BPHA)(CO)$_2$] and [Rh(TTA)(CO)$_2$]) was not replaced during the reaction [3,14,15], thus the most electronegative atom of the chelate ring has the smallest *trans*-influence [4]. These results and conclusions based on the structure determinations are in agreement with the polarization theory and the σ-*trans*-effect, since the oxygen atom nearest to the CF_3 group will be the least polarizable and a weaker σ-donor as a result of the electron-attracting power of the CF_3 group [5,6]. It is therefore clear that one can distinguish between a thermodynamic *trans*-influence, which determines the specific isomer that will be formed during reaction (1), and a kinetic *trans*-effect, which determines the rate at the substitution reaction.

Conclusions

The β-diketone with the largest number of, and the strongest electronegative groups, has the largest *trans*-effect on the substitution of carbonyl groups from a [Rh(β-diketone)(CO)$_2$] complex. Therefore, this β-diketone also has the strongest Rh–O bonds. The rate at which the reaction proceeds depends on:

(a) which bond between the leaving β-diketone and the rhodium atom will be cleaved first,
(b) which bond between the incoming β-diketone and the rhodium atom is formed first, and
(c) whether the cleavage of the bond or the formation of the bond is rate determining.

The product from all the reactions is the same and so the rate of the reaction is determined by the ring-opening step, which in turn depends on the nature of the substituents R^1 and R^2 of the β-diketone. The β-diketone with the largest *trans*-effect (HFAA) [13] undergoes the slowest (most difficult) bond cleavage when replaced by another β-diketone. This explains why the rates of the substitution reactions investigated decrease in the order BA > acac > DBM > TFAA > HFAA.

Acknowledgements

Thanks are expressed to the South African C.S.I.R. for financial assistance.

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