Kinetics of the substitution of acetylacetone in acetylactonato-1,5-cyclooctadienerhodium(I) by derivatives of 1,10-phenanthroline and 2,2'-dipyridyl

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Abstract

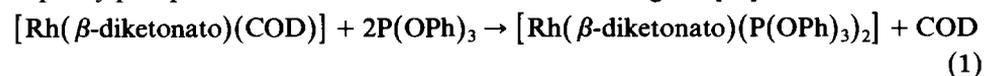The reaction between [Rh(acac)(COD)] and various derivatives of 1,10-phenanthroline and 2,2'-dipyridyl in MeOH to give [Rh(NN)(COD)]$^+$ has been studied. The observed rate law is $T = k$[Rh(acac)(COD)][NN]. The large negative values for the entropy of activation suggest an associative mechanism. The values of the second-order rate constants vary only from 12.4 to 29.0 M^{-1} s^{-1} at 25°C for a pK_a range of the derivatives of phenanthroline from 3.57 to 6.31, indicating that the basicity of the incoming ligand plays a minor role. The much higher value of k for the reaction with 2,2'-dipyridyl (124 M^{-1} s^{-1} at 25°C) is attributed to the lower rigidity of 2,2'-dipyridyl in an associative mechanism.

Introduction

It has been shown that complexes of the type [Rh(LL')(CO)$_2$], where LL' = mono-charged bidentate ligands like β-diketones, 8-hydroxyquinoline and 2-picolinate, are very suitable for studies of the relative *trans*-influence of the donor atoms of the bidentate ligand [1–7] since only one of the carbonyl groups can be substituted by certain neutral ligands such as triphenylphosphine [8]. This phenomenon was sucessfully used to establish the factors that determine the thermodynamic *trans*-influence of the donor atoms for a number of bidentate ligands [1–7]. A kinetic study of the substitution of the carbonyl groups in these complexes showed that there must be distinguished between a thermodynamic *trans*-influence and a kinetic *trans*-effect [9]. The former determines the specific isomer that will be formed during the substitution of only one of the CO groups and the latter determines the reactivity of these complexes towards substitution reactions.

We also established that β-diketonatocyclooctadiene complexes of rhodium(I), [Rh(β-diketonato)(COD)], are very suitable for studies of the mechanism of the substitution reactions of rhodium(I) complexes for the following reasons:

i. The [Rh(β-diketonato)(COD)] complexes react with π-bonding ligands such as triphenylphosphite with the substitution of the COD ligand [10]:

$$\left[\text{Rh}(\beta\text{-diketonato})(\text{COD})\right] + 2\text{P(OPh)}_3 \rightarrow \left[\text{Rh}(\beta\text{-diketonato})(\text{P(OPh)}_3)_2\right] + \text{COD}$$

$$(1)$$

This allowed the study of the effect of the substituents R_1 and R_2 of the β-diketone, $R_1COCH_2COR_2$, on the *trans*-effect of the β-diketone since COD is the leaving ligand [10]. The term *trans*-effect is used although the β-diketone is a bidentate ligand, since one of the oxygen atoms of the β-diketone ligand is *trans* to the Rh–ligand bond which is broken during the first and rate-determining step and the *trans*-effect is usually much more important than the *cis*-effect [11].

ii. The [Rh(β-diketonato)(COD)] complexes react with strong σ-donor (and weak π-bonding) ligands such as 1,10-phenanthroline with substitution of the β-diketone. This allowed the study of the effect of substituents of the β-diketone (and thus the basicity of the β-diketone) on the β-diketone as a leaving ligand [12].

The substituents of the β-diketone have a very large influence on the reactivity of the [Rh(β-diketonato)(COD)] complexes towards both types of the above-mentioned substitution reactions. The reactivities of these complexes rise in the order acac < BA < DBM $\ll$ TFAA < TFBA $\ll$ HFAA irrespective of whether the β-diketone is the leaving or non-labile ligand, where Hacac = acetylacetone, HBA = benzoylacetone, HDBM = dibenzoylmethane, HTFAA = trifluoroacetylacetone, HTFBA = trifluorobenzoylacetone and HHFAA = hexafluoroacetylacetone. The plot of log k versus the pK_a of the β-diketone has a slope of -0.8 for the reaction of these complexes with phenanthroline [12] and -0.45 for the reaction with triphenylphosphite [10], illustrating the large influence of electronegative substituents on the reactivity of these complexes. The rate constants for the first-mentioned type of reaction, for example, increase from 2.90×10^1 for the acac complex to 2.76×10^5 dm^3 mol^{-1} s^{-1} for the HFAA complex at 25°C [12].

To complement the studies outlined above we decided to study the effect of the basicity of the incoming ligand for the reaction between [Rh(acac)(COD)] and 1,10-phenanthroline derivatives. The following ligands were used for the study: phenanthroline (phen), 5-nitrophenanthroline (5-nitrophen), 5,6-dimethylphenanthroline (5,6-dimephen), 4,7-dimethylphenanthroline (4,7-dimephen), 3,4,7,8-tetramethylphenanthroline (3,4,7,8-tmephen) and 2,2'-dipyridyl (dipyr). The pK_a-values of these ligands are listed in Table 1.

Table 1

Rate constants and activation parameters for the reaction [Rh(acac)(COD)] + NN $\rightarrow$ [Rh(NN)(COD)]$^+$ + acac$^-$, where NN = various derivatives of 1,10-phenanthroline and dipyridyl, in methanol at 25°C; [Rh(acac)(COD)] = 5×10^{-4} mol dm^{-3}

Incoming ligand	pK_a [a]	λ_{exp} (nm)	k (dm^3 mol^{-1} s^{-1})	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})
5-nitrophen	3.57	480	12.4	30.8	-121
phen	4.86	480	29.0	32.6	-108
5,6-dimephen	5.20	485	19.9	38.7	-90
4,7-dimephen	5.97	470	18.8	36.7	-97
3,4,7,8-tmephen	6.31	460	19.6	40.7	-84
dipyr	4.30	480	124	26.8	-115

[a] Ref. 19.

Experimental

[Rh(acac)(COD)] was synthesized as described before [12] and recrystallized from acetone. The various derivatives of 1,10-phenanthroline were obtained from Pfaltz and Bauer and used without further purification. It was previously shown that phenanthroline reacts with [Rh(β-diketonato)(COD)] complexes with the substitution of the β-diketone and formation of the orange cation [Rh(phen)(COD)]$^+$, with λ_{max} at 480 nm [12]. The values of λ_{max} for all the derivates of phenanthroline are between 460 and 480 nm.

The rate constants for all the reactions were obtained by monitoring the formation of [Rh(NN)(COD)]$^+$ (NN = the various incoming ligands) at the wavelengths listed in Table 1 with a Durrum stopped-flow model D-110 spectrophotometer. All the kinetic runs were performed in methanol at three different temperatures (17, 25 and 35°C). An excess of the incoming ligand was used for all runs to give pseudo-first-order kinetics.

Good linear first-order plots were obtained for at least two half-lives. The pseudo-first-order rate constants were determined for various concentrations of the incoming ligand (over a ten-fold range). For all the reactions studied, the plots of k_{obs} versus [NN] were linear and passed through the origin. The values of the second-order rate constants for the various incoming ligands were obtained from these plots and are listed in Table 1. The value of the activation parameters ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) were calculated by means of a non-linear least-squares fit of the rate constant versus temperature data to the Eyring–Polanyi equation, and are also listed in Table 1.

Discussion

The reaction between [Rh(acac)(COD)] and the incoming ligand may be represented by reaction (2)

$$[Rh(acac)(COD)] + NN \rightarrow [Rh(NN)(COD)]^+ + acac^- \qquad (2)$$

Since plots of k_{obs} versus [NN] pass through the origin the rate law is given by eq. 3:

$$rate = k[Rh(acac)(COD)][NN] \qquad (3)$$

The observed zero intercept ($k_s \simeq 0$ in the general rate law for square planar substitution reactions; rate = $(k_s + k_y[Y])$[substrate], [13]) was to be expected since the displacement of a chelate by a solvent would be much more difficult than the displacement of a monodentate ligand.

A high-pressure kinetic study of the reaction between [Rh(acac)(COD)] and phen clearly indicated an associative mechanism [14]. The high negative values for the entropy of activation for all the incoming ligands (see Table 1) also point to an associative mechanism for these reactions. Since it may thus be assumed that these reactions proceed via an associative mechanism the incoming ligand would be expected to have a large influence of the reaction rate, but over a pK_a-range of the derivatives of phenanthroline of 3.57 to 6.31 the rate increased only from 12.4 to

29.0 M^{-1} s^{-1} (see Table 1). Similar results were obtained for a number of other substitution reactions with an amine as entering ligand. For the reaction

$$[Pt(dipyr)Cl_2] + am \rightarrow [Pt(dipyr)(am)(Cl)]^+ + Cl^-$$
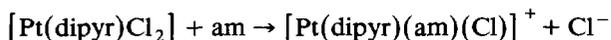
the values of the rate constants increase only from 4.0×10^{-3} to 6.75×10^{-3} M^{-1} s^{-1} for an increase in the pK_a of the incoming ligand from 1.9 to 6.34. The slope of the plot of log k versus the pK_a of the amine was only 0.057 [15]. Similarly the slope of the plot of log k versus the pK_a of the entering amine for the reaction

$$[Rh(COD)(Cl)(Pip)] + am \rightarrow [Rh(COD)(am)(Cl)] + pip$$
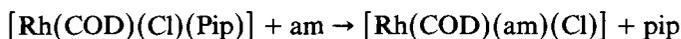
was only 0.17 [16], where pip = piperidine. These studies [15,16] also showed that although the basicity of the incoming amine plays a minor role, the steric effect of methyl groups in the α-position of pyridine caused a large decrease in the reaction rate.

Since no *ortho*-substituted derivative of phenanthroline was used in this study, the steric influence of the various derivatives of phenanthroline should be much the same. The small effect of the pK_a of the incoming ligand (see Table 1) might indicate that bond making in the transition state is not very important, suggesting that the transition state has a substantial S_N1 character. However, the observed $\Delta S^{\ddagger}$ values as well as the volume of activation for the reaction between [Rh(acac)(COD)] and phenanthroline [12,14] and the very large effect of electronegative substituents of the β-diketone on the reaction rates [12] clearly point to an associative mechanism. The small effect of the pK_a of the entering ligands does not necessarily mean that bond-breaking rather than bond-making supplies the driving force for the reaction. It simply means that the basicity of the entering group plays a minor role in the formation of the five-coordinate transition state and that the nucleophilicity of the different derivates of phenanthroline are about the same.

The stucture of [Rh(β-diketonato)(COD)] complexes is such that the molecule deviates significantly from a planar geometry [17]. The two oxygen atoms and the centres of the two double bonds of the COD ligand form a planar arrangement. The two C=C double bonds (bond length about 1.40 Å) are perpendicular to the coordination polyhedron, and so there will be a significant steric effect of the COD ligand. The crystal structure of [Ir(acac)(COD)(CH$_3$)(I)] illustrates this steric effect [18]. The H$_3$C–Ir–I bond angle is only 156.6(7)°, substantially below the expected 180°. Both the carbon and iodine atoms are displaced towards the acac ring atom plane away from the COD ligand, reflecting the steric effect of the COD ligand. It may be this steric effect of the COD ligand which causes the slightly lower rate constants for the methyl-substituted phenanthroline ligands (although we did not use an *ortho*-substituted phenantholine) compared with those for the reaction with phenanthroline. It is notable that the reaction with 2,2'-dipyridyl is much faster than the reaction with phenanthroline. This may be attributed to the fact that 2,2'-dipyridyl is much less rigid than phenanthroline. The rigidity of phenanthroline together with the steric hindrance caused by the COD ligand will result in a slower reaction than that with 2,2'-dipyridyl. The lower rigidity of the dipyr ligand will stabilize the five-coordinate intermediate in an associated mechanism, resulting in a faster reaction. The much lower value of $\Delta H^{\ddagger}$ for the reaction with 2,2'-dipyridyl (see Table 1) is consistent with this suggestion.

Acknowledgements

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