Kinetics of the Substitution of Carbonyl Ligands in β-Diketonatodicarbonylrhodium(I) Complexes by Cyclo-octadiene

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The reactions between [Rh(β-diketone)(CO)₂] and cyclo-octadiene in a methanol medium to give [Rh(β-diketone)(COD)] were studied for various β-diketones at different temperatures. The rate law is $-d[Rh(\beta\text{-diketone})(CO)_2]/dt = (k_s + k_y[COD])[Rh(\beta\text{-diketone})(CO)_2]$. *The values of* k_s *and* k_y *were determined for different β-diketone complexes with β-diketone = BA, DBM, TFAA, TFBA and HFAA. The order of the effect of the β-diketone on the reactivity of the complexes is BA < DBM < TFAA < TFBA < HFAA, indicating that electronegative substituents of the β-diketone increase the kinetic* trans *effect of the β-diketone. The effect of the substituents of the β-diketone (*CF_3*, phenyl and* CH_3*) on the kinetic and thermodynamic* trans *effect is discussed.*

Introduction

It is well known that one of the carbonyl groups in complexes of the type $[Rh(\beta\text{-diketone})(CO)_2]$ can be substituted by neutral ligands like triphenylphosphine (PPh_3) or triphenylarsine ($AsPh_3$) [1, 2]:

$$[Rh(\beta\text{-diketone})(CO)_2] + AsPh_3 \longrightarrow [Rh(\beta\text{-diketone})(CO)(AsPh_3)] + CO \qquad (1)$$

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 $R_1\cdot CO\cdot CH_2\cdot CO\cdot R_2$ on the relative *trans* influence of the oxygen atoms. It has been found that the oxygen atom nearest to an electron-attracting group (like 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 least polarizable and a weaker σ-donor as a result of the electron-attracting power of the CF_3 group.

Both CO-groups in complexes of the type $[Rh(\beta\text{-diketone})(CO)_2]$ are substituted by cyclo-octadiene (COD) [1]:

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

The kinetics of this reaction were studied to determine the effect of the substituents R_1 and R_2 of the different β-diketones on the *trans* effect of the oxygen atoms of the β-diketones.

Experimental

The different β-diketone complexes, $[Rh(\beta\text{-diketone})(CO)_2]$, were synthesized by refluxing approximately 0.2 g $RhCl_3\cdot 3H_2O$ in 20 cm^3 dimethylformamide for about 30 minutes until the colour changed from red to yellow. A slight excess of the β-diketone was added to the resulting yellow solution. The complexes were precipitated by adding an excess of water to the solution. The following β-diketone complexes were synthesized: β-diketone = benzoylacetone (BA), dibenzoylmethane (DBM), trifluoroacetylacetone (TFAA), trifluorobenzoylacetone (TFBA) and hexafluoroacetylacetone (HFAA). The complexes were purified by recrystallization from methyl alcohol. $[Rh(HFAA)(CO)_2]$ was purified by sublimation under reduced pressure at room temperature. The volatile crystals were kept in a refrigerator.

The reaction rate constants were determined by following the formation of $[Rh(\beta\text{-diketone})(COD)]$ using a Durrum (Model 110) stopped flow spectrophotometer. The reactions were followed at a wavelength where the maximum difference in absorbance between reactant and product occurred. The reaction progress was monitored under pseudo first order conditions, using an excess of COD. The absorbance spectra of the various complexes were obtained on a Pye-Unicam Sp 1700 spectrophotometer. The positions of λ_{max} of the products and reactants as well as the wavelength at which the reaction progress was monitored are given in Table I.

Results

The plots of log $(A - A_t)$ *versus* time were linear for at least two half-lives. The pseudo first order rate

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TABLE I. λ_{max} of the Reactants and Products of the Reaction between $[Rh(\beta\text{-diketone})(CO)_2]$ and COD and the Wavelength at which the Reaction was Monitored, λ_{exp}.

β-diketone	Reactant λ_{max}, nm	Product λ_{max}, nm	λ_{exp}, nm
BA	333	333	390
DBM	360	360	400
TFAA	320	300	325
TFBA	332	332	380
HFAA	308	306	360

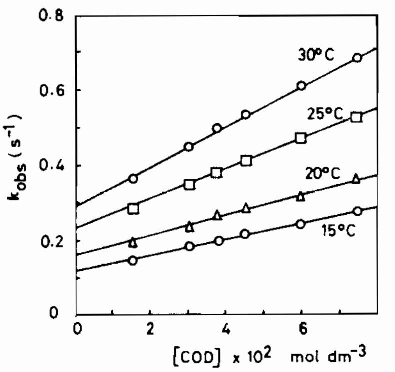

Fig. 1. The plot of k_{obs} *vs.* [COD] at the various temperatures for the reaction between $[Rh(TFBA)(CO)_2]$ and COD. $[Rh(TFBA)(CO)_2]$ = 7.5 × 10^{-4} mol dm^{-3}.

constants were determined at various cyclo-octadiene concentrations. The effect of the concentration of cyclo-octadiene on the pseudo first order rate constants in the case of the reaction with $Rh(TFBA)(CO)_2$ is shown in Fig. 1. In all cases the rate laws are given by:

$$\frac{d[Rh(\beta\text{-diketone})(COD)]}{dt} = (k_s + k_y[COD])[Rh(\beta\text{-diketone})(CO)_2] \qquad (3)$$

Since the reactions were done under pseudo first order conditions

$$k_{obs} = k_s + k_y[COD] \qquad (4)$$

The reaction rate constants k_s and k_y at the different temperatures for the various complexes were determined from the least squares fit of the data to eqn. 4 by using a nonlinear least squares program [7]. The values of k_s and k_y at 25 °C, as well as the values of $\Delta H_y^{\ddagger}$, $\Delta S_y^{\ddagger}$, $\Delta H_s^{\ddagger}$ and $\Delta S_s^{\ddagger}$ for the various complexes, are given in Table II.

Discussion

It is clear from the results (see especially the values of k_y in Table II) that the reactivity of the β-diketone complexes is in the order BA < DBM ≪ TFAA < TFBA ≪ HFAA. This order can thus be considered as the order of the *trans* effect of the various β-diketones. This revealed the following effects of the substituents R_1 and R_2 of the β-diketone on the reactivity of the complexes: (i) If a CH_3 group is replaced by the more electronegative phenyl group the value of k_y increased by a factor of 2 to 4; $k_y^{DBM} > k_y^{BA}$ and $k_y^{TFBA} > k_y^{TFAA}$. (ii) The effect of the more electronegative CF_3 group (electronegativities of $-CH_3$, phenyl and $-CF_3$ are 2.3, 3.0 and 3.35 respectively [8]) is however much more significant; the reaction rate constants (especially the k_y values) increase very much when a CH_3 or phenyl group is replaced by a CF_3 group. According to the reaction rate constants the complexes can thus be devided into three groups: β-diketones with no CF_3 group, those with one CF_3 group, and hexafluoroacetylacetone.

The kinetic results thus revealed that an increase in the electron attracting power of one of (but more so of both) the substituents R_1 and R_2 of the β-diketone has an increase in the kinetic *trans* effect. This is the opposite of that observed in the case of the thermo dynamic *trans* influence which depends on the strength of the chemical bonds in the ground state. The crystal structure determinations of $[Rh(TTA)(CO)(PPh_3)]$, $[RhQ(CO)(PPh_3)]$ and $[Rh(BPHA)(CO)(PPh_3)]$ (synthesized by the reaction between the dicarbonyl complex and PPh_3; TTA = thenoyltrifluoroacetone, Q = 8-hydroxyquinoline and BPHA = N-benzoyl-N-phenylhydroxylamine) 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 $[Rh(TTA)(CO)_2]$ and $[Rh(BPHA)(CO)_2]$),

TABLE II. Reaction Rate Constants k_s and k_y at 25 °C and the Activation Parameters.

β-diketone	pK_a	k_s(s^{-1})	k_y(M^{-1} s^{-1})	$\Delta H_y^{\ddagger}$(KJ mol^{-1})	$\Delta S_y^{\ddagger}$(JK^{-1} mol^{-1})	$\Delta H_s^{\ddagger}$(KJ mol^{-1})	$\Delta S_s^{\ddagger}$(JK^{-1} mol^{-1})
BA	8.7	0.17	0.10	67	−36	46	−107
DBM		0.10	0.36	51	−83	48	−102
TFAA	6.3	0.43	2.30	34	−124	44	−105
TFBA	6.3	0.22	4.10	44	−86	44	−111
HFAA	4.3		200	46	−44		

was not substituted during the reaction [4, 9, 10]. According to this the most electronegative atom of the chelate ring has the smallest *trans* influence. The rhodium–ligand bond lengths in [Rh(TFBA)(COD)] also revealed that the oxygen atom nearest to the electronegative CF_3 group has the smallest *trans* influence [3]. These results and conclusions based on the results of 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 would 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 thus clear that we can distinguish between a thermodynamic *trans* effect, which determines the specific isomer that will be formed during reaction (1), and a kinetic *trans* effect, which will determine the reaction rate of the substitution reaction. The specific isomer that will be formed during reaction (1) will depend on the relative strengths of the two Rh–C bonds in the dicarbonyl complexes and thus on the relative thermodynamic *trans* influence of the two atoms of the chelate ring *trans* to the two carbonyl groups.

The kinetic *trans* effect is however related to the nature of the transition state and determines the reaction rate. The large kinetic *trans* effect caused by the electronegative groups can be explained by their ability to withdraw electron-density from the metal ion and thus stabilize the five co-ordinated transition state in an associative mechanism. Electron-attracting substituents (R_1 and R_2) of the β-diketone will thus increase the reaction rate. The effect of the pK_a values of the various β-diketones on the reaction rate constants is shown in Fig. 2. The large negative entropy values (See Table II) are also in agreement with an associative mechanism.

This approach is in agreement with the general experience that the formation of a chelate ring with strong metal–ligand bonds leads to a greater thermodynamic stability, while the ability of the metal ion to form compounds with a larger coordination number increases with a decrease in the strength of metal–ligand (chelate ring) bonds [11]. The stability of the compounds Cu(β-diketone)$_2$ for example decrease in the order $Cu(BA)_2 > Cu(TTA)_2 > Cu(HFAA)_2$, showing that an increase in the acidic strength of the β-diketone leads to a decrease in the thermodynamic stability of the complexes. The stability of the adducts of the copper β-diketonates with phosphorous esters and with pyridine however increases in the opposite sequence [12].

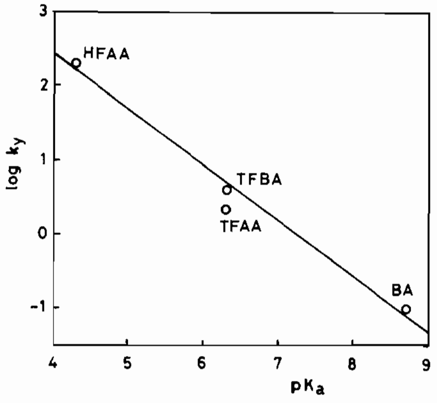

Fig. 2. A plot of log k_y *vs.* pK_a of the β-diketone.

It is thus clear that an increase in the acidic strength of the β-diketone leads to a) an increased tendency of the metal ion to form compounds with an increased coordination number, and b) increased stability of the formed adducts.

The strong electron-attracting power of the substituents R_1 and R_2 of the β-diketone (especially if $R = CF_3$) will decrease the electron density on the metal ion making the complex thus a stronger Lewis acid. The five coordinated transition state is thus stabilized when R is an electronegative group. This will lead to an increase in the reactivity of the dicarbonyl complex, see Table II and Fig. 2.

Acknowledgements

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