Kinetic and mechanistic studies of metal complexes of β – diketones - a review

ADEWUMI IDOWU ADEAGBO. PhD
Department of Chemistry, Emmanuel Alayande College of Education, Oyo, Oyo State. Nigeria

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Abstract

Metal complexes of β – diketones: pentane – 1, 3 – diketones (Hpd), 1, 1, 1 – trifluoropentane – 1 ,3 – dione(Htfpd), 4, 4, 4 – trifluoro(2 - thienyl)butane – 1, 3 –dione (Htftbd), and 2 - thenoyltrifluoroacetone (Htta) in the studies examined have rate constants (k_{MHE}) values lower than the rate of water exchange by several orders of magnitude, However, the Eigen Wilkinson trend: $Cu^{2+} \gg Co^{2+} > Ni^{2+} > Fe^{3+}$ was identified with some of the β – diketonates. Substituents effects were not important in the rate determining steps as the rate constant k_{ME-} of most metal ions do not change significantly on varying the ligands. However, in mono, di and tri-metallic β – diketonates complexes of the type [M(RCOCHCOR), varying R have significant effect on the reaction rate and labile β – diketones were found to significantly influence reaction rates compared to reactions where the β – diketones are non – labile.

Key words: Eigen Wilkinson constant, protonated ligands, labile and non – labile β - diketone

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I. Introduction

Transition metals form complexes with organic ligands readily, most especially multidentate ligands, this is mainly due to the chelate effect, although the ready formation of complexes could be kinetically or thermodynamically driven.

Organic multidentate ligands abound in nature, in industrial wastes and effluents, medicine, pharmaceuticals and synthetic chemistry byproducts etc. The Complexes formed by the aforementioned ligands and metals, especially transition metals have found applications in almost all human endeavors, which include but not limited to physiological, industrial, and environmental fields.

βeta-diketones are excellent chelating, protonated ligands, which form compounds with transition metals, rare earths and actinide ions [1,2]. βeta-diketonates possess a wide range of applications [3] catalyst, biological models, plant growth regulators, dyes and polymers. The keto – enol properties of β – diketones gave their reactions with metals a potential for kinetic and mechanistic diversity not found in other ligands.

Kinetic investigations applies in various chemical processes [4,5]. Many aspects of biochemistry, pharmaceutical, biological activities and industrial processes can be explained by kinetics [6]. Conduct of kinetic studies of complex formation between metal complexes and various ligands led to a proposal of bonding mechanism. The mechanism could then be applied to complexes containing other metal ions and other multidentate ligands, and hence provide a means of solving problems encountered in diverse fields. [7]

The need for Mechanistic information and knowledge, cannot be overemphasized. They are applied for the design of new drugs: Pt(II) anticancer drugs [8], determining stability of nutrients in plants [9]. The formation of metal complexes of certain ligands investigated [10] showed that the metal ions demonstrated probable catalytic effects and in order to understand the catalytic function of metals or coordination compounds in processes carried out on an industrial scale, it is necessary to learn the exact mechanisms of such reactions [11].

The major determinant of the mechanism of complexation for metal ions of the first transition series was found to involve loss of a water molecule from the metal ions at the rate determining step, however, the reactions of metal species with β – diketones were found to be quite different from those of other similar ligands. The aim of this work is to examine in detail the kinetic and mechanistic deductions from kinetic data and findings of studies involving β – diketonate metal complexes. The specific objectives are:

(i) To study the prevalent path of reactions involving β – diketones, in which the ligand is either labile or inert

(ii) To ascertain variation in reactivity of metal ions in such reactions stated in (i) above

(iii) To verify probable predictable trends in structure and reactivity of the ligands

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II. Deductions from kinetic and mechanistic studies of metal complexes of β − diketones

A perusal of literature show kinetic studies involving $β − diketonate$ metal complexes spanned over decades. The earlier investigations were targeted at deducing the mechanisms involved when $β − diketones$ form metal complexes. Metal**s** of interest in those studies are mainly the first transition metal series: Chromium (III), Iron(III), Cobalt(II), Nickel(II), Copper(II), and oxoion: Vanadyl $(VO_2)^{2+}$ and Uranyl $(UO_2)^{2+}$ complexes of β-diketones: pentane-2,4-dione (Hpd), 1,1,1- trifluoro − 2,4 − pentanedione (Htfpd), 4,4,4 − trifluorothienylbutanedione (Htftbd), thenoyltrifluoroacetone (Htta) and heptane -3, 5 − dione (Hhptd) [12, 10, 13, 14, 15, 16, 17]. The reactions were carried out mainly in aqueous solutions, except in few cases which were conducted in 90% methanol medium [18, 19] The ionic strength of 1.0, 0.5, and 0.2M was maintained with lithium or sodium perchlorate. These studies investigated formation of mono complexes, and at temperature 25 ± 0.1 ^{o}C, the resulting kinetic data shows the following:

(i) There is no direct reaction between the metal ion and the keto tautomer of the β- diketone.

(ii) The formation of the complexes occurred exclusively through the reaction of the metal ion with the enol (HE) and enolate (E^{-}) forms of the β - diketone although the keto (HK) tautomer was dominant in solution.

The formation or dissociation (when reverse reaction was monitored) of the complexes was characterized by one or two consecutive reactions, depending on the metal ion. Other variables obtained in those studies are showed in table 1.0. The metal - ligand reactions was found to follow a general scheme (Scheme 1.0), accompanied by slight variations in very few cases. Having established the relative inactivity of the keto tautomer of the β − diketones [14] the postulated scheme is an attempt to rationalize the path(s) through which each metal ion proceeds in reacting with the keto (where it obtains), enol and or enolate ion of the ligands.

Examining the outcome of the reactions, the simplest of the β − diketone series, pentanedione $CH_3COCH_2COCH_3$(Hpd), have rates (In bracket) of reaction of its enol tautomer with the metal ions,: Cr^{3+}(0.011), Fe^{3+}(5.2), Ni^{2+}(19.3), Cu^{2+} (3.4×10^3) indicating values that are not comparable (Quantitatively) but are appreciably lower than the rate of water exchange (Table 1.0), although, a probable trend was identified $Cu^{2+} \gg Ni^{2+} > Fe^{3+} > Cr^{3+}$. However, the rate obtained for $[UO_2]^{2+}$ (4.9×10^3) and $Fe(OH)^{2+}$ (4.4×10^3) was adjudged normal, literatures on the rate of water exchange for uranium ions are scarce. The rates obtained for the enol tautomer of $CF_3COCH_2COCH_3$, an 'homologue' of Hpd: 1, 1, 1 − trifluoropentanedione (Htfpd): Fe^{3+}(19.6), Ni^{2+}(1.7), Cu^{2+} (NR) VO^{2+}(3.5), a trend could not be ascertained as copper(II) ions gave kinetic data not consistent with any of the multistep relaxation kinetics of the type HK ⇌ HE ⇌ ME, recorded for the other metal ions. Similarly the enol form of 4, 4, 4 − trifluorothienylbutanedione (Htftbd): Fe^{3+}(1.4), Ni^{2+}(2.3) Co^{2+}(≥300), Cu^{2+} (≥3.0×10^4), gave observation similar to pentanedione: $Cu^{2+} \gg Co^{2+} > Ni^{2+} > Fe^{3+}$. The rate of reactions of the metal ions with enolate ions are approximately normal, and the available data is due to metal complexes of 4, 4, 4 − trifluorothienylbutanedione (Htftbd): VO^{2+} (3.6×10^3), Fe^{3+}(2.4×10^4), Ni^{2+}(1.0×10^4) Co^{2+}(≥3.0×10^4), Cu^{2+} (≥3.0×10^6), these proffer a trend $Cu^{2+} > Co^{2+} \approx Ni^{2+} \approx Fe^{3+} > VO^{2+}$. The reactivity trend of the enol form of the ligands observed for metals show trend for Cu^{2+} (Hpd ≈ tta ≈ Htftbd), and for Ni^{2+} (Hpd > Htfpd > Htftpd ≈ tta)

Reasons proposed for the behavior of metals when reacted with β − diketones in these studies include hard/soft acid/ base factor in which variation based on the classification in the hard acid - Cr^{3+}, Fe^{3+}, VO^{2+} and intermediate acid ions: $Cu^{2+}Ni^{2+}$and Co^{2+} are so observed. Strong intra - molecular hydrogen bonds which makes the protonated ligand (enol tautomer) a poor entering group, hence reduced rate of reaction. The enolate tautomer constitute a form of nucleophile which probably enhance its reactivity. The energetics involved in translating unidentate intermediate through ring closure (proton controlled ring closure) and strain associated with the formation of a chelated ring.
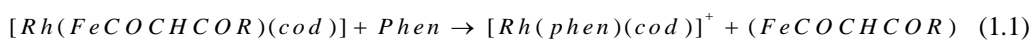
Table 1.0: Observed Variables in the Formation/Hydrolysis Reactions of Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, $(VO_2)^{2+}$ and $[UO^{2+}]_2$ monoβ − diketonate complexes.

Metal ion (d^n)	Eigen − Wilkinson formation constant (K_{E-W})	Ligand	Reacting Ligand Specie Reaction Rate $(dm^3\ mol^-\ s^-)$		
			MHE(k_1) formation constant via Enol tautomer	HK − Keto tautomer	ME^-(k_4) −formation constant via enolate tautomer
$Cr^{3+}$$d^1$		Hpd	1.05×10^{-2}	-	-
		Hhptd	6.60×10^{-2}	-	-
Fe^{3+}(d^5)	3.6×10^1	Htfpd	19.6	-	2.6×10^4
		Htftbd	1.4	-	2.4×10^4
		Hpd	5.2	0.29	-
		Htta	1.4		2.4×10^4

$Co^{2+}(d^7)$	7.2×10^5	Htfpd	>76	-	$\geq 3.0 \times 10^4$
		Htftbd	≥ 300	-	$\geq 3.0 \times 10^4$ $\geq 3 \times 10^4$
		Htta	-	-	
$Ni^{2+}(d^8)$	7.2×10^3	Htfpd	1.7	-	3.4×10^3
		Htftbd	2.3	-	1.0×10^4
		Hpd	19.3	-	-
		Htta	2.3	-	1.0×10^4
$Cu^{2+}(d^9)$	1.0×10^9	Htfpd	-	-	-
		Htftbd	$\geq 3.0 \times 10^4$	slow	$\geq 3.0 \times 10^6$
		Hpd	2.0×10^4	15	$\leq 2 \times 10^8$
		Htta	2.0×10^4	15	$\geq 3 \times 10^6$
$VO^{2+}(d^1)$	1.1×10^2	Htfpd	3.5	-	2.0×10^2
		Htftbd	7.6	-	3.6×10^3
		Hpd	-	4.4	-
$UO_2^{2+}(d^1)$		Htfpd	≥ 1000	-	-
		Htftbd	≥ 1000	-	-
			4928 ± 727		
		Hpd	1×10^4	-	-
		Htta		18.1 ± 0.5	3×10^5
				-	

$M^{2+} + HE \leftrightharpoons MHE^{*2+} \leftrightharpoons ME^+ + H^+$ (i)   metal – enol intermediate forms (k_1, k_{-1}), enol intermediates rearranges, monocomplex forms (k_2, k_{-2})

$M^{2+} + HE \leftrightharpoons M^{2+} + E^- \leftrightharpoons ME^{+*} \leftrightharpoons ME^+$ (ii)   β – diketone deprotonates (K_{HE}), metal – enolate intermediate forms (k_4, k_{-4}), monocomplex forms (k_3, k_{-3}),

Scheme 1.0: Observed scheme for the substitution kinetics of β-diketones: Hpd, Htftbd, Htfpd, Htta and Metal ions (M^{n+}): Co^{2+}, Ni^{2+}, Cu^{2+}, VO^{2+}, and UO^{2+} In these reactions, the β-diketones are labile,

The reactions between [Rh(β-diketonate)(COD)] and phenanthroline in methanol medium which gave [Rh(phen)- (COD)]$^+$ (β – diketone was a leaving ligand) was studied [20] for various β-diketones at different temperatures with rate law: R = k[Phen][Rh([β-diketonate)-(COD)]. The order of the effect of the β- diketonate on the reactivity of the complexes was found to be dependent on the electronegativity of the substituents on the β-diketone. The values of the second-order rate constants at 25°C are 2.90 x 10^1, 5.12 x 10^1, 6.14 x 10^1, 1.33 x 10^3, 2.42 x 10^3 and 2.76 x 10^5 dm^3 mol^{-1} s $^{-1}$ for the acac, bza, dbm, tfaa, tfbza and hfaa complexes, respectively implying hfaa>tfbza>tfaa >dbm >bza. [21] substituted cyclooctadiene (cod) ligand in β - diketonatocyclooctadienerhodium(I) complexes by triphenylphosphite, the reaction was found to follow a rate law: R = k[Rh β - diketonato)(COD)][P(OPh)$_3$]. Although the β – diketonate specie was non – labile, the reaction rate was dependent on the electronic structure of the β – diketones and increases in an order indicating a direct dependence on the substituents of the β – diketone, such that the more the electronegativity of the substituents, the larger the reactivity of these complexes towards substitution reactions. In the study conducted by [22], the substitution of ferrocenyl- containing β-diketo-nato–1,5-Cyclooctadienerhoudiunn(I)complexes [Rh(cod) (Fc(COCHCOR)], the reaction proceeded according to equation 1.1.

$$[Rh(FeCOCHCOR)(cod)] + Phen \rightarrow [Rh(phen)(cod)]^+ + (FeCOCHCOR) \quad (1.1)$$
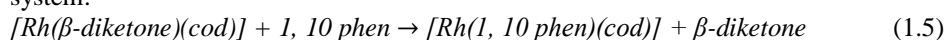
Where R = CF$_3$, CCl$_3$, CH$_3$, Ph, and Fc = Ferrocene, cod = 1,5 – cyclooctadiene, phen = 1, 10 – phenanthroline. The general rate law applicable to the substitution reaction was found to be:

$$\text{Rate} = \{k_s + k_2[phen]\}[Rh(FcCOCHCOR)(cod)] \quad (1.2)$$

$$= k_{obs}[Rh(FcCOCHCOR)(cod)] \quad (1.3)$$

$$k_{obs} = k_s + k_2[phen] \quad (1.4)$$

The second order rate constant k_2 at the rate determining step was deduced to be the breaking of the bond between the metal (Rhodium) and the oxygen atom of the β – diketone, thus the stronger the electron withdrawing capacity of the substituent R of the diketone, the weaker the Rh – O bond and the higher the second order rate constant. Similar study conducted [23] where 1, 10 – phenanthroline replaced β-diketones in the system:
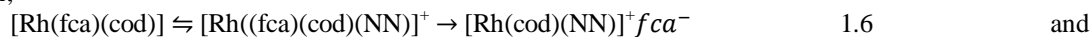
[Rh(β-diketone)(cod)] + 1, 10 phen → [Rh(1, 10 phen)(cod)] + β-diketone   (1.5)

[Rh(β-diketone)(cod)] = [Rh(RcCOCHCOR)(cod)], Rc = Ruthenocene

R = CF$_3$, CH$_3$, C$_6$H$_5$.

The values of second order rate constants (k_2) for the substitution reactions between the [Rh(β-diketonato)(cod)] complexes and 1,10- phenanthroline was found to vary with the β-diketones.
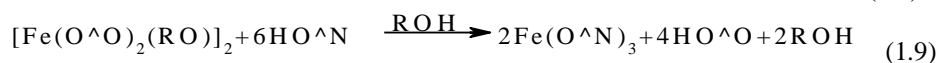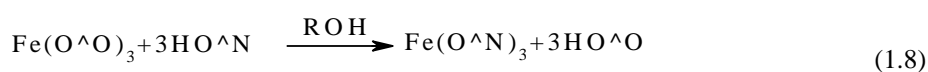[24] investigated the displacement of ferocenoylacetato (fca) from (1, 5 – cyclooctadiene)(ferrocenoylacetateto)rhodium(I) which resulted in second order rate constants varying with the incoming ligands: 2, 2 – dipyridyl and derivatives of 1, 10 – phenanthroline, the reaction is described by the equation;
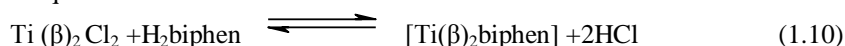
$$[Rh(fca)(cod)] \leftrightharpoons [Rh((fca)(cod)(NN)]^+ \rightarrow [Rh(cod)(NN)]^+ fca^- \qquad 1.6 \qquad \text{and}$$

rate law that govern the reaction;

$$Rate = k[Rh(fca)(cod)(NN)] \qquad\qquad 1.7$$

The rate determining step was ascribed to be the breakage of the metal – Oxygen bond of diketonato moiety. Hence on varying the incoming ligands, slight variations in k_2 (5.5 – 26 dm^{3}mol^{-1}s^{-1}) is implied and observed since the β - diketone is constant, the only outlier value in the study was 118 dm^{3}mol^{-1}s^{-1} (2, 2 - dipyridyl). [25] studied the kinetics of substitution of neutral octahedral chelate complexes of iron (III) represented by equation 1.8 and 1.9.

$$Fe(O^\wedge O)_3 + 3 HO^\wedge N \xrightarrow{ROH} Fe(O^\wedge N)_3 + 3 HO^\wedge O \qquad (1.8)$$

$$[Fe(O^\wedge O)_2(RO)]_2 + 6 HO^\wedge N \xrightarrow{ROH} 2 Fe(O^\wedge N)_3 + 4 HO^\wedge O + 2 ROH \qquad (1.9)$$

The tris β-diketone complexes: Fe (O̅O)$_3$, (O˅O) = acac, bza, dbm and ttfa), reacted with excess of 8-hydroxyquinoline (= HO˅N) in alcohol to form the complex Fe (O˅N)$_3$. The starting complex was subjected to solvolytic dissociation, producing Fe(O˅O)$_2$(ROH)$_2^+$, Fe(O˅O)$_2$(ROH)(RO) and binuclear complex [Fe(O˅O)$_2$(RO)]$_2$. No direct second order reaction was observed between the entering ligand HO˅N and the intact complexes Fe(O˅O)$_3$. The reaction kinetics was denoted triphasic, that is the substitution process was controlled by three first order rate constants in the order $k_1 > k_2 > k_3$, non is dependent on the concentration of entering ligand HO˅N and each describe different step of the reaction. The effect of the nature of the coordinated β-diketone in the complexes Fe (O˅O)$_3$ on the size of k_1, k_2 and k_3 was found to be minor.
[26] conducted a substitution kinetics of [Rh((Cp-R^2)Fe(R^1-Cp-COCHCOCH$_3$))(cod)] (R = C$_9$H$_{19}$ – C$_{18}$H$_{37}$) with 1,10-phenanthroline. The displacement of the β-diketonato ligand from [Rh(β-diketonato)(cod)] exhibited saturation kinetics, which was not inter alia detected for simple β-diketonato substitution, hence ascribed to the long chain alkyl substituents on the complexes. It was concluded that the R-substituents with chain length varying from C$_9$H$_{19}$ – C$_{18}$H$_{37}$, and with one or more than one R-group substituent, had very little effect on the reaction rate. Study of O, O' chelated titanium (IV) complexes conducted by [27] was summarized by the reaction in equation 1.10.

$$Ti (\beta)_2 Cl_2 + H_2biphen \rightleftharpoons [Ti(\beta)_2biphen] + 2HCl \qquad (1.10)$$

In the study, the β-diketonates (β) are non-labile ligands, the series; Ti (dbm)$_2$Cl$_2$ and Ti (ba)$_2$Cl$_2$ have similar electron-withdrawing tendencies and identical k_s values, while Ti (tfba)$_2$Cl$_2$ with R = CF$_3$ have larger k_s value. The graphs of k_{obs} against the incoming H$_2$biphen concentration are straight lines with a non - zero intercept which signified a first order dependence on [H$_2$biphen], with the general rate law;

$$Rate = \{k_s + k_2 [H_2biphen]\} [Ti(\beta)_2Cl_2] \qquad (1.11)$$
$$= k_{obs} [Ti (\beta)_2 Cl_2] \qquad (1.12)$$

The second order rate constant, k_2 was larger than k_s in all cases, although k_2 values were of similar order, for the series β = acac, tfba, ba and dbm, ranging from 0.153 to 0.485 mol^{-1}dm^{3}s^{-1}, and in the order acac <tfba < ba <dbm, T = 25°C, the authors interpreted these outcome in terms of the β-diketonato ligands being non-labile in the reaction hence not significantly influencing the rate of substitution in Ti(β)$_2$Cl$_2$. However, the influence on the reactivity is by indirectly affecting the electron-density around the titanium centre. Greater solvent interaction was observed with Ti(tfba)$_2$Cl$_2$ containing the highly electron-withdrawing group CF$_3$.
[28] substituted tetrathiafulvalene (TTF) on β – diketone and studied the effect of the β – diketonato substitution position on the kinetics of substitution of the TTF – containing β – diketonato ligand with 1, 10 – phenanthroline. The substitution position had slight influence on the second order rate constant, a higher rate was observed where a positioning of the TTF moiety is connected with the pseudo - aromatic core of β – diketonato ligand.
The formation of copper(II) complex of dibenzoymethane investigated by [29] was found to follow a rapid pre-equilibrium mechanism leading to the formation of an intermediate at rate k_1 of the order 10^5 while the rate of complex formation, k_2 (5.0×10^{-2}s^{-1}) obtained is constant at all copper concentrations and several orders of magnitude lower than the expected value for Cu^{2+} exchange rate ($10^5 < 10^8$ M^{-1}s^{-1}), the authors suspected that the

formation of the complex was not governed by the loss of water from the Cu(II) ions, but some metal – ligand bond formation takes place before the Cu- OH_2 bond is completely broken. A probable substituent influence on the kinetics of formation of copper(II) and nickel(II) complexes of β – diketones: benzoylacetone (bza), dibenzoylmethane (dbm), trifluorothienylacetone (tta), and trifluoropentanebutanedione (tfbpd) was investigated [30], it was observed that k_1, ascribed to the rate of formation of outer copper(II) complexes vary for the β - diketones in the order $Cu(dbm)_2 2H_2O > Cu(bza)_2 2H_2O > Cu(tfpbd)_2 2H_2O > Cu(tta)_3$, and Nickel(II) complexes: $Ni(tfpbd)_2 2H_2O > Ni(dbm)_2 > Ni(bza)_2 2H_2O > Ni(tta)_3$, while the second order rate constant k_2 was found constant on formation of the copper(II) complexes which was probable rate determining and ascribed to ring closure, but on formation of the nickel(II) complexes k_2 varies with each complex and was ascribed to a probable entering of a second ligand.

III. Conclusions

The review showed reactions involving β – diketones could be categorized into: (i) formation of the metal – diketonate complexes, where the enol/enolate factors were prominently displayed and (ii) substitution in β – diketonates which followed similar paths, whether β – diketonate moiety is labile or not. The involvement of the O – H bond from water molecules are relatively dormant in such reactions. This is probably due to the presence of more active oxygen atoms on the diketonate moiety and more electronegative atoms or groups (−OR), where R = substituents on β-diketonates or metal, M. Hence the dependence of β – diketonate substitution reaction rates on the enol/enolate/keto specie of the ligands and or breakage of the M – O bond, which is not comparable with the rate of water exchange (Eigen constant).

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