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THERMOCHEMISTRY OF METAL XANTHATO COMPLEXES. A REVIEW

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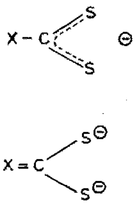
ABSTRACT

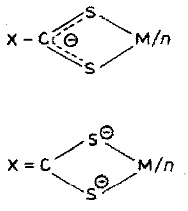
In the present review, the work done on thermal studies of metal xanthato complexes is presented. The thermal studies include thermogravimetry, differential thermogravimetry, differential thermal analysis, differential scanning calorimetry and mass spectrometry. Thirty-two references are included.

INTRODUCTION

The reactions of carbon disulphide with a variety of nucleophiles X^- or X^{2-} give rise, respectively, to compounds known as dithioacids or dithiols [1]. The deprotonated forms of these compounds (A) interact strongly with metal ions (or metalloids) to form compounds where, with a few exceptions, both of the sulphur atoms are bound to the metal ion (B).



(A)



(B)

Major types of ligand that have been studied, which show exciting coordination properties, are the dithiocarbamates ($X = NR_2$), the xanthates ($X = OR$) and dithioaromatic acid anions ($X = CR_3$, aryl).

A number of metal xanthates have been synthesized and characterized in recent years [2–9]. Special interest in the study of metal xanthates was aroused because of the striking structural features presented by this class of

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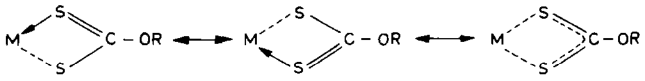
compounds and also because of diversified applications, such as accelerators in vulcanization, high-pressure lubricants in industry and also as fungicides and pesticides [10–13]. Xanthate ligands have been known to stabilize the higher coordination states of metals due to their low charge and relatively small bites (~ 3 Å). The special features associated with complexes containing sulphur donor ligands are attributed to the ability of sulphur to form multiple bonds (π bonds) caused by the presence of a vacant $d\pi$ orbital in sulphur.

The σ-donation and π-back donation of the sulphur atoms are assumed to be of the same order of magnitude as found in the case of 1,1-dithioates. An additional π-electron flow from the oxygen atom to the sulphur atom via a planar delocalized π-orbital system contributes to the special features of the xanthate ligands. Several canonical forms may be written for the structure of the xanthate group in $M(S_2COR_2)_n$, where M is the metal ion and n is the valency. Thus, in the xanthate, the type of R group is expected to influence



the stability and other physicochemical properties of a metal complex, depending on the inductive effect of the group(s) attached to the oxygen atom. The general chemistry and analytical chemistry of metal xanthates has been comprehensively reviewed by Ramachandra Rao [2].

HISTORICAL REVIEW

During the past decade, the thermal properties of metal xanthato complexes have been extensively investigated as one of the most interesting topics in the field of coordination chemistry. A number of papers appeared dealing with the applications of thermogravimetry, differential thermal analysis, differential scanning calorimetry and mass spectrometry to metal xanthates. Two reviews have appeared on the volatility and thermochemistry of metal complexes with sulphur ligands [14,15]. The present review incorporates some interesting papers on the thermal behaviour of metal xanthates.

In metal xanthates, thermal analysis data have been utilized to:

(a) investigate the limit of the horizontal stretch between which the complex retains the assigned formula;

(b) study the mode of thermal transformation of metal complexes;

(c) determine the correct temperature range for the rèsulting product to attain constant weight, thereby affording standardization of the conditions for gravimetric evaluation of metal ions;

(d) confirm the purity of metal complexes, in conformity with their stoichiometries;

(e) evaluate the activation energy and order of reaction for the decomposition reaction of the complex;

(f) determine the enthalpies of fusion and sublimation.

Volatility of metal xanthates

In 1960, Drawert et al. [16] first of all reported that nickel(II) alkylxanthates sublime at 10^{-3} J. In 1976, Larionov and Kosareva [17] separated mixtures of nickel(II) ethylxanthates and cobalt(III) ethylxanthates by sublimation at reduced pressure. Cavell et al. [18] reported the volatility characteristics of eleven nickel(II) alkylxanthates, $Ni(S_2COR)_2$; R = ethyl, methyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, *t*-butyl, *n*-amyl, isoamyl, *n*-hexyl, cyclohexyl. The order of volatility depends on the nature of the terminal R group of the xanthate moiety and follows the sequence

ethyl > *t*-butyl > isopropyl > *n*-propyl > methyl ≈ isobutyl > isoamyl,
cyclohexyl > *n*-butyl > *n*-amyl > *n*-hexyl

TABLE 1

Volatility data for nickel alkylxanthates

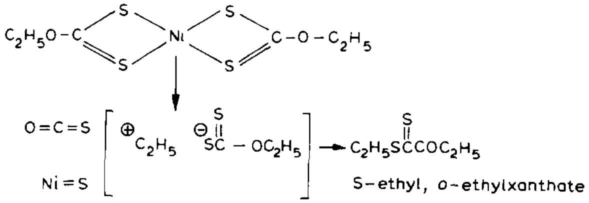
Nickel xanthato complex	M.p. (°C)	Volatility characteristics
Methyl	> 200	Completely volatile in range 80–150°C, no decomposition
Ethyl	137	Completely volatile in range 80–130°C, no decomposition
n-Propyl	108–109	Volatile in range 80–110°C, above this range decomposition occurs. Less volatile and less thermally stable than ethyl derivative
n-Butyl	97–98	Volatile in range 80–95°C. Very little decomposition in this range. Complex decomposes above m.p.
n-Amyl	65–67	Volatile in range 90–115°C, with some decomposition
n-Hexyl	61–62	Not very volatile. Low volatility around 90°C, but at higher temperatures decomposition occurs
Isopropyl	116–118	Volatility started at 60°C. In range 60–110°C, rapid volatility. Above 110°C, some decomposition
Isobutyl	110–111	Volatile in the range 80–125°C with no decomposition
t-Butyl	139–140	Volatile in range 100–120°C with no decomposition
Isoamyl	91–95	Volatile in range 90–195°C. Complex decomposes slightly above m.p.
Cyclohexyl	Melts over wide range of temp.	Volatile in range 100–150°C. Completely volatile with only slight decomposition below 120°C

This sequence indicates that as the R group chain-length increases beyond *n*-propyl, the volatility decreases. In other words, volatility increases with the introduction of branched chains in R groups (Table 1).

In 1973, Sceney et al. [19] reported volatility properties of palladium(II) alkylxanthato complexes, $Pd(S_2COR)_2$; R = methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, *t*-butyl, *n*-amyl, isoamyl, *n*-hexyl, cyclohexyl. They reported that the degree of volatility depends on the nature of the R group of the xanthate moiety. The most volatile complexes are the *n*-propyl, isopropyl, *n*-butyl and isobutyl derivatives. In the same year, Khwaja et al. [20] studied the volatility characteristics of a series of group VB metal xanthato complexes, $M(S_2COR)_3$ (M = As, Sb, Bi; R = methyl, ethyl, isopropyl, *n*-butyl, cyclohexyl, benzyl). They reported that only arsenic(III) complexes were volatile without decomposition at 10^{-1} J. The melting points of a number of metal xanthates were determined by differential thermal analysis. The melting points of complexes of type $M(S_2COC_2H_5)_n$ ($n = 2, 3$; M = Cr(III), Co(III), Ni(II), Zn(II), Cd(II), Pb(II)) were determined by Larionov and Kosareva in 1975 [21] and they observed that the lead complex has the lowest melting point, i.e., 132°C. Baudis and Wieber [22] determined the melting points of thallium xanthate complexes, namely, phenylthallium bis(*o*-methylxanthate); m.p. 107–109°C and *p*-tolylthallium bis(*o*-methylxanthate); m.p. 99–102°C. Until now, no paper has appeared dealing with the enthalpy of fusion.

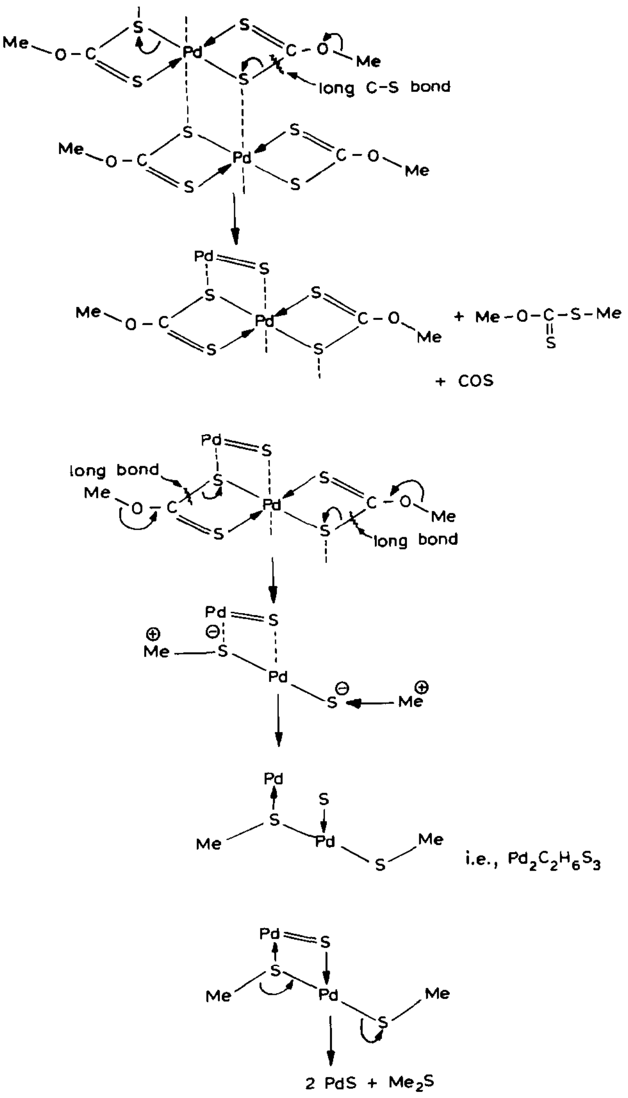
Thermal decomposition mechanisms of metal xanthato complexes

Among the earliest work on the thermal decomposition mechanisms of sulphur ligated complexes is that of Cavell et al. [18] in 1973, which reported thermogravimetric data in both air and nitrogen atmospheres for eleven nickel(II) alkylxanthato complexes, $Ni(S_2COR)_2$ (R = ethyl, methyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, *t*-butyl, *n*-amyl, isoamyl, *n*-hexyl, cyclohexyl). In these cases, the volatile decomposition products were collected, condensed and analysed by mass spectrometry. The following mechanism has been proposed for thermal decomposition of nickel(II) ethylxanthato



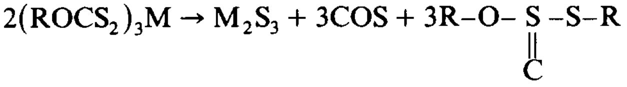
complexes. It has been reported that the thermal stability of these complexes decreases as the R group chain-length increases. On the other hand, the thermal stability increases with the introduction of branched chains in R groups.

In the same year, Sceney et al. [19] extensively studied the thermal decomposition of eleven palladium(II) alkylxanthates, $Pd(S_2COR)_2$ (R = methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, *t*-butyl, *n*-amyl, isoamyl, *n*-hexyl, cyclohexyl). The bimolecular thermal decomposition mechanism, as given below, is proposed for the methyl derivative. The volatile decomposition products were characterized by mass spectrometry and the solid intermediate, $Pd_2C_2H_6S_3$, was isolated and characterized by elemental analysis. The thermogravimetric (TG) data (air and nitrogen atmospheres)



for these complexes are consistent with the following trends: the *n*-propyl derivative exhibits the greatest thermal stability; as the chain length of the terminal R group of the xanthate moiety increases, the thermal stability of the complex also increases and the rate of thermal decomposition decreases; as branching within the terminal R group increases, the thermal stability of the complex decreases and the rate of thermal decomposition increases.

Khwaja et al. [20] in 1973, studied a series of Group VB metal xanthato complexes by thermogravimetry. The complexes have the general formula $M(S_2COR)_3$ ($M = As, Sb, Bi$; $R =$ methyl, ethyl, isopropyl, *n*-butyl, cyclohexyl, benzyl). The volatile decomposition products were characterized by mass spectrometry. The TG data (air atmosphere) for these complexes and mass spectral data for the volatile products of thermal decomposition are consistent with two possible thermal decomposition mechanisms



$$2(ROCS_2)_3M \rightarrow M_2S_3 + 3COS + 3R{-}O{-}\underset{\overset{\|}{C}}{S}{-}S{-}R$$

$$2(ROCS_2)_3M \rightarrow M_2S_3 + 3COS + 3CS_2 + 3\,H_2O + \underset{\text{olefin}}{6(R{-}H)}$$

The TG data for these complexes indicate that, in general, thermal stability of the complexes increases as the chain length of the terminal R group of the xanthate moiety increases.

Larionov and Kosareva [21] have reported a thermal stability sequence for a series of transition metal xanthato complexes, $M(S_2COC_2H_5)_n$, $n = 2$ or 3 and for three Group IIIB metal ethylxanthato complexes, $TlS_2COC_2H_5$, $M(S_2COC_2H_5)_3$ ($M = Sb, Bi$). The TG data for these complexes are consistent with the following thermal stability sequence

$$\mathrm{Sb(III)} < \mathrm{Bi(III)} \sim \mathrm{Tl(I)} < \mathrm{Zn(II)} < \mathrm{Pb(II)} \approx \mathrm{Cd(II)} <$$
$$\mathrm{Cr(III)} < \mathrm{Ni(II)} < \mathrm{CO(III)}$$

Thermogravimetric data for these complexes in argon atmosphere are also reported. The solid residues obtained from thermal decompositions are characterized by elemental analysis and correspond in each case to the "normal" sulphide.

Thermogravimetric data were also reported for the pyridine adduct complexes, $(C_2H_5OCS_2)_2Ni \cdot py_2$ and $(C_2H_5OCS_2)_2Zn \cdot py_2$. It has been observed that the thermal stabilities of these base adducts are less than those of the corresponding parent complexes.

In 1984, from our laboratory, we reported [23] the chemistry and mechanisms of thermal degradation reactions of zirconium(IV) alkylxanthate derivatives of type $ZrO(S_2COR)_2 \cdot 2\,H_2O$ ($R = CH_3, C_2H_5, C_3H_7$). The thermal behaviour of these compounds under non-isothermal conditions was investigated by thermogravimetric, derivative thermogravimetric and differential scanning calorimetric techniques. All these complexes in nitrogen atmosphere showed a two-stepped weight loss. The first weight loss occurred

TABLE 2

Thermal degradation data for zirconium(IV) alkylxanthate derivatives

Complex	1st Step weight loss range (°C)	Product	2nd Decomposition range (°C)	Product	Activation energy (kcal mol^{-1})	Heat of reaction (kcal mol^{-1})
$ZrO(S_2COCH_3)_2 \cdot 2\,H_2O$	80	$ZrO(S_2COCH_3)_2$	200–265	ZrS_2	40.24	21.62
$ZrO(S_2COC_2H_5)_2 \cdot 2\,H_2O$	108	$ZrO(S_2COC_2H_5)_2$	280–350	ZrS_2	35.80	20.50
$ZrO(S_2COC_3H_7)_2 \cdot 2\,H_2O$	130	$ZrO(S_2COC_3H_7)_2$	340–400	ZrS_2	15.20	16.32

in the temperature range 80–130°C and corresponded to loss of water molecules. The second weight loss occurred in the temperature range 200–400°C and zirconium sulphide was ultimately formed. The residue obtained after the endothermic decomposition in the second step has been assigned, on the basis of weight loss, for infrared spectral studies and elemental analysis. The volatile decomposition products were condensed and analysed by mass spectrometry and found to be exactly similar to those reported by Cavell et al. [18] and Khwaja et al. [20]. The apparent activation energy and order of reaction were evaluated by the graphical methods of Coats and Redfern, and the heat of reaction from differential scanning calorimetric curves. It was observed that the thermal stability increases as the chain length of the terminal R group in the xanthate moiety increases (Table 2). The second step decomposition reactions in all cases followed first-order kinetics.

Recently, we have also reported [24] the thermogravimetric study of ruthenium(III), rhodium(III), osmium(IV) and iridium(III) complexes of methyl- and ethylxanthates under nitrogen atmosphere. These complexes yielded the respective metal sulphides at the end of the first decomposition step, i.e., at 400, 530, 250 and 350°C, respectively. Beyond these temperatures, the TG curves showed a small arrest followed by continuous weight loss in each case. Except for osmium sulphide, which is completely volatile in the range 300–540°C, all the sulphides lost sulphur, but even at 1000°C the pure metals were not obtained. This was attributed either to incomplete decomposition of these sulphides or to the probability of formation of non-stoichiometric sulphides of these metals.

The TG studies of $M(S_2COR)_2$ ($M = Zn$, Cd, Hg; $R = CH_3$, C_2H_5, C_3H_7) complexes in nitrogen and oxygen atmospheres have also been reported [25] (Table 3). The products were identified by analyses, infrared spectral studies and mass spectrometry. With the same ligand, it was found

TABLE 3

Thermal decomposition ranges and end products for zinc, cadmium and mercury alkylxanthates

Complex	Decomp. range (K)	End product
$Zn(S_2COR)_2$ in N_2	453–553	ZnS
$Zn(S_2COR)_2$ in O_2	443–570	ZnS
	650–820	ZnS → ZnO
$Cd(S_2COR)_2$ in N_2	548–613	CdS
$Cd(S_2COR)_2$ in O_2	523–628	CdS
	778–880	CdS → CdO
$Hg(S_2COR)_2$ in N_2	570–650	HgS
$Hg(S_2COR)_2$ in O_2	550–620	HgS
	630–720	Volatilization

that zinc, cadmium and mercury exhibit an increasing trend of thermal stability from zinc to mercury.

Solution thermochemistry of metal xanthato complexes

In 1974, Annuar et al. [26,27] calculated enthalpies for complexation reactions of nickel(II) with a series of alkylxanthate ions, $ROCS_2^-$ (R = methyl, ethyl, *n*-butyl, isobutyl) by solution calorimetry. The complexation reaction in dioxane/water solvent is given below

$$Ni(NO_3)_2 \cdot 6\,H_2O(soln) + 2\,KRX_n(soln) \xrightarrow{\Delta H_{RL}^{303}} Ni(RX_n)_2(soln) + 2\,KNO_3(soln) + 6\,H_2O$$

$$\Delta H_{RL}^{303} = \Delta H_{FC}^{303} + 2\Delta H_{FS}^{303} - 2\Delta H_{FL}^{303} - \Delta H_{FN}^{303}$$

where ΔH_{FC}^{303} = heat of formation of solvated complex; ΔH_{FS}^{303} = heat of formation of solvated $K^+NO_3^-$ ion pair; ΔH_{FL}^{303} = heat of formation of solvated $K^+RX_n^-$ ion pair; ΔH_{FN}^{303} = heat of formation of solvated $Ni^{2+}2\,NO_3^-$ ion pair system. Since, for all five systems studied, ΔH_{FS}^{303} and ΔH_{FN}^{303} are constant, $\Delta H_{FL}^{303} \propto \Delta H_{FC}^{303} - 2\,\Delta H_{FL}^{303}$ and hence, variation of ΔH_{RL}^{303} as the terminal alkyl group R on the xanthate moiety changes, indirectly reflects the "influence" of that group on the heat of formation of the solvated nickel alkylxanthato complex, if it is assumed that the heat of mixing and dilution of nickel nitrate and potassium alkylxanthate solutions is negligible. The concentrations of all components in all the various systems studied was within the range 10^{-2}–10^{-4} M (Table 4).

A much simplified representation of the formation of a nickel alkylxanthate in the solvent system, i.e., the reaction whereby solvent molecules associated with solvated nickel ion in the first solvation sphere are displaced by two xanthate ions to form the nickel alkylxanthato complex. Due to the release of solvent molecules, the entropy change (ΔS_{RL}^{303}) is positive and the complexation reaction is spontaneous. Further, the total change in the number of species constituting the complexation reaction is probably not dramatically affected by relatively minor changes in the overall

TABLE 4

Heats of formation of solvated nickel alkylxanthate ion pairs by solution calorimetry in dioxane/water at 303 K

Complex	Mean ΔH_{RL}^{303} (kJ mol^{-1} of complex)
$Ni(CH_3OCS_2)_2$	10.62 ± 0.56
$Ni(C_2H_5OCS_2)_2$	4.80 ± 0.18
$Ni(C_3H_7OCS_2)_2$	4.88 ± 0.32
$Ni(n\text{-}C_4H_9OCS_2)_2$	3.52 ± 0.28
$Ni(iso\text{-}C_4H_9OCS_2)_2$	5.72 ± 0.50

TABLE 5

Thermodynamic data for the addition of two molecules of various bases to nickel alkylxanthates in benzene solution at 303 K

R	Base [a]	10^3[Ni] (mol^{-1})	K (mol^{-1})	$-\Delta H^0$ (kJ mol^{-1})	$-\Delta G^0$ (kJ mol^{-1})	$-\Delta S^0$ (kJ^{-1} mol^{-1})	$\Delta H^0/\Delta S^0$
Methyl	mpy	1.0–4.0	2.6×10^4	79.4±3.6	25.6±0.5	178±14	446
Methyl	py	1.0–6.0	5500±2000	79.2±0.8	21.7±1.1	190±6	416
Ethyl	py	3.9–9.4	1690±260	75.0±4.0	18.7±0.5	186±15	404
Propyl	py	1.0–8.0	1090±173	81.4±3.1	17.6±0.4	210±12	387
Hexyl	py	1.0–8.0	1300±370	76.8±1.5	18.1±0.8	194±8	396
Isobutyl	py	4.0–6.0	1200±120	77.4±1.2	17.8±0.1	197±5	394
Benzyl	py	1.0–2.0	4200±800	80.8±1.1	21.0±0.6	197±6	410
Isopropyl	mpy	1.0–6.0	1630±390	70.6±1.7	18.6±0.7	171±8	415
Isopropyl	py	1.0–8.0	324±44	62.4±3.1	14.6±0.4	158±12	395
Cyclohexyl	py	1.0–4.0	283±35	72.8±1.7	14.2±0.3	193±7	377
2-Methyl-cyclohexyl	py	1.0–4.0	183±18	74.9±0.7	13.1±0.2	204±3	367
Methyl	bpy	1.0–4.0		73.7±0.4			
Hexyl	bpy	1.0–4.0		75.5±0.6			
Isopropyl	bpy	1.0–6.0		70.2±0.7			

[a] py = pyridine, mpy = methyl pyridine, bpy = 2,2′-bipyridyl.

system, such as progressive variation of the terminal alkyl group of the xanthate moiety, and hence $\Delta S^{303}_{\mathrm{RL}}$ may be assumed to be the same for all five complexation reactions studied. Thus, the change in the free energy of the reaction $(-\Delta G^{303}_{\mathrm{RL}})$ increases as the chain length of the terminal alkyl group of the xanthate ligand increases, and decreases as chain branching within the same alkyl group increases. It appears that the thermodynamic stability of complexes of the type $\mathrm{Ni(RX}_n)_2$, where R is a linear chain alkyl group, is strongly influenced by the inductive effect of R. However, if R is a branched-chain alkyl group, the steric effect of R is greater than the corresponding inductive effect and the former is the predominating influence on the stability of the complex.

In 1971, Dakternieks and Graddon [28] determined the total enthalpy change at 303 K for the adduct formation of nickel(II) ethylxanthate with pyridine in benzene by thermometric titrimetry. The standard free energy change ΔH^0 was found to be -75 kJ mol^{-1} and the standard entropy change ΔS^0 was found to be -186 J K^{-1} mol^{-1}.

Graddon and Prakash [29] have reported thermodynamic data for the addition of two molecules of various bases to nickel(II) alkylxanthato complexes in benzene solution at 303 K. The data are given in Table 5.

Boyd [30] determined the thermodynamic data at 298 K for the addition of two molecules of base to nickel(II) alkylxanthato complexes in *t*-butanol as solvent, according to the reaction

$$\mathrm{Ni(S_2COR)_2 + 2\ B \rightleftharpoons Ni(S_2COR)_2B_2}$$

where R = ethyl, *n*-propyl or *n*-butyl, and B = pyridine or picoline. Volume magnetic susceptibility of the base adduct product as a function of temperature was determined by NMR spectroscopy and the enthalpy of adduct formation was calculated using Evans' method [31]. The standard enthalpies for adduct formation ($-\Delta H^0$) were found to be 14.56, 17.03 and 14.64 kJ mol^{-1} for R = ethyl, *n*-propyl and *n*-butyl, respectively. Thus, base adduct formation is favoured and the magnitude of ΔH^0 reflects the nickel–pyridine bond strength.

Mellgren [32] has reported the heat of formation at 298 K of lead(II) ethylxanthate from the potassium salt of ethylxanthate and from a variety of lead salts. The heat of adsorption of potassium ethylxanthate on a series of sulphate-treated galena surfaces is also reported. For the simplest of these surfaces, referred to as "galena · SO_4", ΔH (adsorption of $KS_2COC_2H_5$) = -94.56 kJ mol^{-1} (Pb^{2+}). For adsorption of potassium ethylxanthate on carbonate-treated galena, "galena · CO_3", $\Delta H = -69.04$ kJ mol^{-1} (Pb^{2+}) and for adsorption of potassium ethylxanthate on thiosulphate-treated galena, "galena · S_2O_3", $\Delta H = -82.42$ kJ mol^{-1} (Pb^{2+}). These data have considerable significance in the context of froth flotation thermodynamics.

CONCLUSIONS

Studies on the thermal behaviour of the majority of the transition metal xanthates along with some non-transition metal xanthato complexes have been discussed in this review. But the insufficient data available made it difficult to establish any straightforward relation between the thermal behaviour of the complexes and the nature of the metal ion.

Although only a few metal xanthates have been reported to be volatile, it has given scope for the use of gas chromatography for the separation of metals as the corresponding xanthate complexes. However, it is surprising that no use has been made of gas chromatographic techniques for the separations. It was observed that volatility increases as the oxidation state of the metal decreases and, further, that volatility increases as branching of the alkyl group of the xanthate ligand increases. As a result of insufficient data being available, it is premature to establish any correlation between the volatility of metal xanthates and the structure of the complexes, although volatility may increase as the degree of association in the solid state increases.

Perhaps one of the most interesting and important aspects of the work reviewed is the thermal decomposition mechanism. Apart from the work of Sceney et al. [19] on palladium xanthates, Cavell et al. [18] on nickel xanthates, Khwaja et al. [20] on Group VB metal xanthates and Pandey et al. [23–25] on zirconium(IV) xanthates, platinum xanthates, zinc(II), cadmium(II) and mercury(II) xanthates, data on the thermal decomposition mechanisms of these species are sparse. Among the majority of the recently studied metal xanthates, the common feature observed is that during thermal decomposition of these complexes, S-alkyl-, *o*-alkylxanthates and COS are evolved and metal sulphides are the end products formed. Of interest is the fact that the Group VB metal xanthates show a rather different mechanism of thermal breakdown to those of nickel, palladium, etc. In such complexes, olefins are formed. A point worth noting is that the decomposition reside in the majority of platinum xanthates up to 1000°C did not correspond to either metal or pure sulphide, which may be attributed to the possibility of the formation of non-stoichiometric platinum sulphides at that temperature [25]. A differential thermal analysis study of metal xanthates has been made to obtain data on melting points and phase changes. Enthalpies of fusion are not known for xanthate complexes. It would appear, therefore, that there is considerable need for investigation of metal xanthato complexes to determine melting points by differential thermal analysis and enthalpies of fusion using differential scanning calorimetry.

In the area of thermal decomposition kinetics, it is somewhat surprising to find so little published work. For the period reviewed, the literature revealed only one reference [23]. In zirconyl complexes, the decomposition reaction followed first-order kinetics.

For a limited number of metal xanthato complexes, solution calorimetry has been used to determine the standard enthalpy of formation. An interesting aspect of solution thermochemistry is reflected in the works of Graddon et al. [28,29] who determined the enthalpy of base adduct formation in benzene with different bases. It has been found that changes in the free energy and enthalpy of adduct formation are related to the inductive effect of the R-substituent group of the ligand. Thermodynamic data were derived for the addition of base to a metal alkylxanthate using NMR spectroscopy to determine volume magnetic susceptibility of the base adduct system and the Evans method to calculate the enthalpy of adduct formation. This type of work needs considerable extension.

Thus, it is obvious from the work reviewed here that there is great scope for further interesting and valuable investigations in all aspects of thermal studies of metal xanthato complexes such as determination of the thermal decomposition mechanism, decomposition kinetics, volatility, etc. Further, a wide range of possible investigations can be made in this field, such as the investigation of the thermal behaviour of metal complexes with one metal and the ligand with a series of different substituent R groups or the complexes of a particular ligand with different metal atoms, so as to obtain a close insight into the significance of factors such as inductive effect, structures, etc., of the ligand and the thermal behaviour. Similarly, the effect of cationic size of the metal on the thermal behaviour of the complexes may be studied to derive useful information for group classification. Such studies may open up more interesting areas of investigation which may be related to the effect of the above parameters on the mechanism of thermal decomposition reactions and their kinetics.

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