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SOLUTION THERMOCHEMISTRY OF SOME NICKEL ALKYL XANTHATES

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ABSTRACT

Complexation enthalpies for nickel ion and a series of alkyl xanthate ions, RXn^- (R = methyl, ethyl, n-propyl, n-butyl and iso-butyl) are reported. The data are interpreted in terms of inductive and steric influence of R on the thermodynamic stability of the nickel alkyl xanthate.

INTRODUCTION

Thermochemical data for metal complexes of alkyl derivatives of xanthic acid are sparse. Cavell et al.[1] have reported the volatility characteristics and detailed TG data for eleven nickel alkyl xanthate complexes. Such complexes were found to be completely volatile in the temperature range 80–150 °C (0.01 Torr). A general thermal decomposition mechanism for these complexes involving carbonyl sulphide, nickel sulphide and S-ethyl O-ethyl xanthate as stable intermediates was proposed and it was apparent both from the TG data and the volatilisation characteristics that the "nature" of the terminal alkyl group attached to the xanthate moiety considerably influences the thermal stability of nickel alkyl xanthates.

Khwaja et al.[2] have reported detailed TG data for six arsenic(III), antimony(III) and bismuth(III) alkyl xanthates, $[ROCS_2]_3M$ where R = methyl, ethyl, isopropyl, n-butyl, cyclohexyl and benzyl and proposed a general thermal decomposition mechanism for these complexes involving carbonyl sulphide, carbon disulphide, olefins and the metal sulphide as stable intermediates. In sharp contrast to the nickel alkyl xanthate complexes, mass spectral analysis of the volatile fragments evolved from the thermal degradation of the arsenic, antimony and bismuth complexes revealed the absence of stable intermediates of the general type ROCSSR. Hence, the thermal decomposition mechanism of a particular metal alkyl xanthate appears to depend upon both the nature of the R-group and the coordinated metal. No calorimetric data for metal xanthates exist. This paper reports a detailed solution calorimetric study for the derivation of the enthalpy of formation at infinite dilution in dioxane/water solvent (85% (volume) dioxane/15% water) of five nickel alkyl xanthates $(R{-}O{-}CS_2)_2Ni$: R = methyl, ethyl, n-propyl, n-butyl and iso-butyl. The characteristic endothermic complex formation reactions and the magnitude of the corresponding standard enthalpy increments are explained in terms of the influence exerted by the terminal alkyl group of the xanthate moiety on the Ni–S coordinate bond strength.

EXPERIMENTAL

Calorimeter

The Tronac, Model 450, Isoperibol solution calorimeter was used in the investigation. The calorimeter was tested using the "THAM" reaction. Found: Mean $\Delta H^{\ominus}_{\mathrm{THAM}} = -29.068 \pm 0.022$ KJ mol^{-1} (303 K) (5 determinations); Literature: $\Delta H^{\ominus}_{\mathrm{THAM}} = -28.875 \pm 0.008$ KJ mol^{-1} (303 K)[3]. "THAM" sample: NBS Standard reference material No. 724, dried by the recommended procedure[4]. Heats of formation of nickel alkyl xanthates in 85% volume dioxane/water solvent at infinite dilution are quoted with a total uncertainty equal to twice the standard deviation of a set of at least six determinations.

Potassium alkyl xanthates

The potassium salts of the xanthate ligands (KS_2COR, where R = methyl, ethyl, n-propyl, n-butyl, iso-butyl) were prepared according to the method of Vogel[5]. The salts were purified by several recrystallisations, from acetone/ether solvent, followed by washing with ether. Micro-analytical analyses were obtained (Australian Microanalytical Service) and typical results are recorded in Table 1.

TABLE 1

MICROANALYTICAL DATA FOR THE POTASSIUM ALKYL XANTHATES

Potassium ligand	*C*		*H*		*S*	
	Calculated	*Found*	*Calculated*	*Found*	*Calculated*	*Found*
KS_2COCH_3	16.5	16.8	2.1	2.3	43.8	43.9
$KS_2COCH_2CH_2CH_3$	27.6	27.6	4.0	4.1	36.8	36.6

Nickel alkyl xanthates

The nickel xanthate complexes were prepared by adding an aqueous solution of "A.R. grade" nickel nitrate [$Ni(NO_3)_2 \cdot 6H_2O$] to an aqueous solution containing a slight excess of the recrystallised potassium xanthate salt. The complexes were filtered and washed thoroughly with water and thoroughly dried in a vacuum desiccator. Each complex was recrystallised several times from chloroform and subsequently dried in a vacuum desiccator. The complexes were ultimately purified by sublimation. Micro-analytical analyses were obtained (Australian Microanalytical Service) for the purified complexes, typical results are recorded in Table 2.

TABLE 2

MICROANALYTICAL DATA FOR THE NICKEL ALKYL XANTHATES

Nickel alkyl xanthate	*C*		*H*		*S*	
	Calculated	*Found*	*Calculated*	*Found*	*Calculated*	*Found*
$Ni(CH_3OCS_2)_2$	17.6	17.4	2.2	2.4	46.9	46.4
$Ni(n\text{-}C_3H_7OCS_2)_2$	29.9	30.2	4.4	4.4	39.8	39.6

Melting points of all the nickel alkyl xanthates prepared, were measured on a Mettler FP2 melting point apparatus and are collected in Table 3.

TABLE 3

MELTING POINTS OF NICKEL ALKYL XANTHATES

Nickel alkyl xanthate	*Melting point (°C)*	*Literature value (°C)*	*Reference*
$Ni(CH_3OCS_2)_2$	>250	>220, 158–160	6, 7
$Ni\ (C_2H_5OCS_2)_2$	136.5–137.5	148, 137, 134–135	6, 7
$Ni(n\text{-}C_3H_7OCS_2)_2$	108–109	117, 103	6
$Ni(n\text{-}C_4H_9OCS_2)_2$	97–98	103, 88–89	6, 7
$Ni(i\text{-}C_4H_9OCS_2)_2$	110–111	108, 118–119	6, 7

p-Dioxane

"Analar" grade dioxane (May and Baker) was dried over potassium hydroxide pellets for 24 h and subsequently refluxed for 6 h with sodium, nitrogen being passed continuously through the mixture, which was fractionally distilled and the fraction o boiling point 101–102 °C collected. The dioxane was passed down a column of finely divided chromatographic alumina to remove traces of organic peroxides, and was stored in a dark glass Winchester fitted with a drying tube. As required, 85% dioxane/15% distilled water solvent was accurately prepared.

Nickel nitrate hexahydrate

"Analar" grade $Ni(NO_3)_2 \cdot 6H_2O$ (B.D.H.) was stored under vacuum in a desiccator, using calcium sulphate as the desiccant. A stock solution of nickel nitrate (1.0748×10^{-2} M) in the dioxane/water solvent was accurately prepared for use as the calorimetric solution.

RESULTS AND DISCUSSION

The following thermochemical equation stoichiometrically describes the formation of a nickel alkyl xanthate in the dioxane/water solvent.

$$\mathrm{Ni(NO_3)_2\cdot 6H_2O(soln)+2KRXn(soln)} \xrightarrow{\Delta H_{\mathrm{RL}}^{303}} \mathrm{Ni(RXn)_2(soln)+2KNO_3(soln)+6H_2O(soln)}$$

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

$\Delta H_{\mathrm{FC}}^{303}$ = heat of formation of solvated complex;

$\Delta H_{\mathrm{FS}}^{303}$ = heat of formation of solvated $\mathrm{K^+NO_3^-}$ ion pair;

$\Delta H_{\mathrm{FL}}^{303}$ = heat of formation of solvated $\mathrm{K^+RXn^-}$ ion pair;

$\Delta H_{\mathrm{FN}}^{303}$ = heat of formation of solvated $\mathrm{Ni^{2+}2NO_3^-}$ ion pair system.

Since, for all five systems studied, $\Delta H_{\mathrm{FS}}^{303}$ and $\Delta H_{\mathrm{FN}}^{303}$ are constant $\Delta H_{\mathrm{RL}}^{303} \propto \Delta H_{\mathrm{FC}}^{303} - 2\Delta H_{\mathrm{FL}}^{303}$ and hence, variation of $\Delta H_{\mathrm{RL}}^{303}$ 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 alkyl xanthate complex, if it is assumed that the heat of mixing and dilution of the nickel nitrate and potassium alkyl xanthate solutions is negligible. The concentration of all components in the various systems studied was within the range 10^{-2} to 10^{-4} molar; thus all measured heats of reaction refer to the standard state of infinite dilution. For each system, at least two different concentrations of KRXn solution were used to verify the validity of this assumption.

Measurement of $\Delta H_{\mathrm{RL}}^{303}$

Nickel nitrate solution (1.0748×10^{-2} M; 40.0 ml; i.e. 0.4299 mmoles) was transferred to the reaction vessel, via a calibrated delivery pipette. Ampoules were loaded with potassium alkyl xanthate solution of at least two different concentrations delivered from a calibrated microsyringe. All the complexation reactions were endothermic. (This nickel nitrate solution was used in all the calorimetric experiments and an excess of nickel $\mathrm{Ni^{II}}$ was present in all cases.)

All the relevant heat capacity data and $\Delta H_{\mathrm{RL}}^{303}$ values for the five nickel alkyl xanthates studied are given in Table 4 and summarised in Table 5.

From the derived enthalpy data for the nickel alkyl xanthate complexes two definite trends emerge. For a series of nickel alkyl xanthates with isomeric alkyl groups (R = n-butyl and iso-butyl), increased branching of the alkyl group is manifested as a greater amount of energy being required to initiate complex formation, i.e. as branching increases, nickel alkyl xanthate formation becomes more endothermic, and when the straight chain-length of the alkyl group, attached to the xanthate moiety, is increased, less energy is required to bring about complex formation, i.e. the formation reactions become less endothermic.

If the present enthalpy data obtained for the formation of the nickel alkyl xanthates in solution is considered in conjunction with our other thermochemical data, i.e. the volatilization data[1], TG data[1] and melting points (Table 3), the nickel alkyl xanthates are thermodynamically stable complexes even though they are

TABLE 4

ΔH_{RL}^{303} VALUES: NICKEL ALKYL XANTHATES

Terminal R group on xanthate moiety	*KCS_2OR (moles) 10^{-4}*	*Corrected temp. change (mV)*	*Heat capacity ε (Amp. sec)*	*ΔH_{RL}^{303} (kJ mol^{-1})*	*Mean ΔH_{RL}^{303} (kJ mol^{-1} KCS_2OR)*
CH_3	3.240	0.2870		5.65	5.30 ± 0.28
	3.260	0.2583	6379.2	5.05	
	3.323	0.2922		5.61	
	4.094	0.3245		5.00	
	3.944	0.3434	6308.8	5.47	
	4.146	0.3146		4.74	
	2.425	0.2155	6309.8	5.61	
C_2H_5	5.6664	0.2137	6417.3	2.42	2.40 ± 0.09
	5.6664	0.2208		2.50	
	3.5299	0.1383	6382.9	2.50	
	3.5299	0.1228		2.22	
	1.8090	0.0659	6367.0	2.32	
	1.8090	0.0690		2.43	
C_3H_7	3.7525	0.1385		2.34	2.44 ± 0.16
	3.7526	0.1462	6338.0	2.47	
	3.6377	0.1485		2.59	
	4.4924	0.1550		2.19	
	4.4924	0.1816	6349.0	2.57	
	4.4924	0.1275		1.80	
	5.9043	0.2350		2.51	
	5.9043	0.2520	6306.2	2.69	
	2.7435	0.1120	6285.5	2.57	
	2.7435	0.1160		2.66	
nC_4H_9	4.1787	0.1000	6425.8	1.54	1.76 ± 0.14
	4.1237	0.1047		1.63	
	4.8407	0.1415	6351.9	1.86	
	4.8407	0.1395		1.83	
	3.0726	0.0980	6320.0	2.01	
	3.29206	0.0868		1.67	
iC_4H_9	5.0424	0.282	6474.2	3.62	2.86 ± 0.25
	5.0390	0.200		2.57	
	8.0012	0.330	6400.7	2.64	
	8.0012	0.324		2.59	

TABLE 5

SUMMARY: ENTHALPY OF FORMATION AT INFINITE DILUTION OF FIVE NICKEL ALKYL XANTHATES

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
$Ni(i\text{-}C_4H_9OCS_2)_2$	5.72±0.50

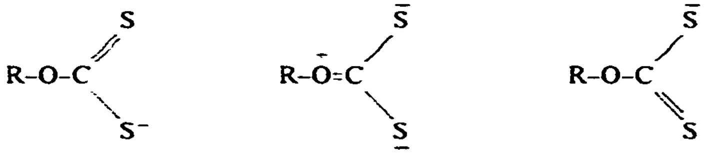
endothermically formed in solution. From the volatilisation and TG data the following thermodynamic stability sequences emerge.

Methyl$\gg$ethyl $\simeq$ n-propyl$\gg$n-butyl — R = straight-chain alkyl group
$\longrightarrow$ decreasing stability

i-Butyl$>$n-butyl — R = branched-chain alkyl group
$\longrightarrow$ decreasing stability

The enthalpy data herein obtained for the nickel alkyl xanthates may be partially explained by a consideration of the "nature" of the terminal R-group attached to the xanthate moiety. Two effects are evident: (1) the inductive electronic effect of the alkyl group[8] and (2) the steric effect caused by the presence of bulky alkyl groups. It is expected that (1) and (2) are very important factors influencing the thermal stability of the xanthate complexes.

With reference to the three basic canonical forms proposed to represent the xanthate moiety:



(a) (b) (c)

It has been shown[8] that (b) constitutes an almost negligible part of the overall structure of the xanthates, thus explaining the relatively lower thermal stability of the metal xanthates compared to the related metal dithiocarbamates, where a (b) type structure for the dithiocarbamate moiety is more probable. However, it is evident that an alkyl group that has an electron-donating inductive effect is able to reduce the positive charge on the highly electronegative oxygen in structure (b) thus increasing the overall contribution of this canonical form to the xanthate resonance hybrid and thereby increasing the stability of the resulting complex. It is known[9] that increase of the linear chain-length of an alkyl group progressively increases the electron-donating capacity of that group. Also, an increase in branching within the alkyl group, leads to a significant increase in the electron-donating capacity of that group[9]. Thus the following electron-donor capacity sequence of alkyl groups is

$iC_4H_9 > nC_4H_9 > nC_3H_7 > C_2H_5 > CH_3$

The quantitative increase in the inductive effect of an alkyl group as the number of carbon atoms in the chain exceeds three is small. For branched xanthate ligands, a steric effect operates to oppose the formation of the xanthate metal complex. This effect is clearly reflected in the higher positive enthalpy of formation of nickel isobutyl xanthate compared to nickel butyl xanthate. However, TG data obtained in this laboratory for these two complexes verify that the thermal stability of the nickel isobutyl xanthate exceeds that of nickel butyl xanthate, and hence the branched alkyl group of the xanthate moiety exerts a "protecting" influence on the complex rendering it less susceptible to thermal degradation. Such a "protecting" influence adds credence to the mechanism proposed by the authors[1] for the thermal decomposition of nickel alkyl xanthate complexes. Thus, as the degree of branching in the terminal alkyl group of the xanthate moiety increases, the thermodynamic stability of the corresponding metal complexes decreases and the thermal stability increases.

A much simplified representation of the formation of a nickel alkyl xanthate in the solvent system adopted is the reaction, whereby solvent molecules associated with the solvated nickel ion in the first solvation sphere are displaced by two xanthate ions to form the nickel alkyl xanthate complex. Due to the release of solvent molecules from the solvated nickel ion and xanthate ion upon mutual combination, ΔS^{303}_{RL} is positive and $T\Delta S^{303}_{RL}$ exceeds ΔH^{303}_{RL}. Thus ΔG^{303}_{RL} is negative and the complex formation reaction is spontaneous. Further, the total change in the number of species constituting the complexation reaction is most probably not dramatically effected by relatively minor changes in the overall system such as progressive variation of the terminal alkyl group of the xanthate moiety and hence ΔS^{303}_{RL} may be assumed to be the same for all five formation reactions studied. Thus $-\Delta G^{303}_{RL}$ increases as the linear 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 $Ni(RXn)_2$ where R is a linear-chain alkyl group is strongly influenced by the inductive effect of R, whereas 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.

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