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THERMAL STUDIES ON NICKEL ALKYL XANTHATE COMPLEXES:

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ABSTRACT

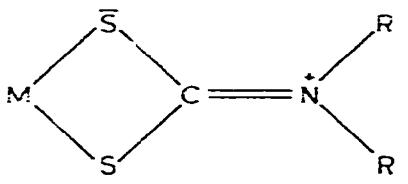
This paper is the first of a series reporting the results of a comprehensive thermogravimetric and calorimetric analysis of netel complexes of various alkyl derivatives of xanthic acid and dithiocarbamic acid.

Eleven nickel alkyl xanthates have been prepared and analysed thermogravimetrically. Detailed volatilisation characteristics of these complexes are also reported. The thermal stability of nickel alkyl xanthates is best described as moderate since all decompose initially to NiS at relatively low temperatures (140–180°C). A thermal decomposition mechanism for the nickel alkyl xanthates involving carbonyl sulphide, nickel sulphide and S-ethyl O-ethyl xanthate as stable intermediates has been confirmed by mass spectrometric techniques. It is apparent from the thermogravimetric analysis data and volatilisation characteristics that the "nature" of the terminal alkyl group attached to the xanthate moiety considerably influences the thermal stability of nickel alkyl xanthates.

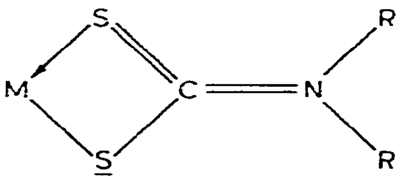
INTRODUCTION

In recent years, there has been a considerable increase in interest in the chemistry of metal dithiocarbamates and xanthates. Much of the early work is of analytical interest and major contributions have been made by Cambi, Malatesta, Delépine and others[1–6]. Recently, reviews on the more fundamental aspects of the chemistry of metal dithiocarbamates and xanthates by Coucouvanis[7] and Eisenberg[8] have appeared.

For the dithiocarbamates, Chatt *et al.*[9], suggested that the three canonical forms below (A, B, C) contributed equally to the electronic behaviour, while Nakamoto[10] and Van der Kerk and coworkers[11,12] suggest that (A) is more important than (B) and (C). The latter, however, agrees that (C) becomes less important and (A) and (B) more important as the R-groups attached to nitrogen become more electron donating. Other workers[13,14] agree that the nature of the R-groups determine the preference of one canonical form over another. Vigee and Selbin[15] suggest that Chatt *et al.*[9] could be essentially correct, as the combination of wave functions for the three forms would be equivalent to the wave function of a conjugated structure (D), which these authors favour. It appears therefore, that the two



(A)



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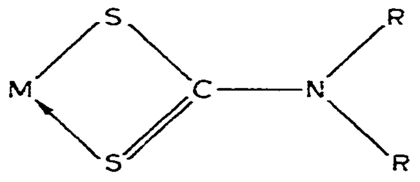

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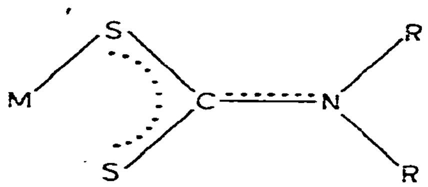


(D)

sulphur donor atoms of the dialkyldithiocarbamate moiety are essentially equivalent. For the xanthates, the situation is much more uncertain. Chatt *et al.*[9] suggest that there is little contribution from canonical forms, the difference between the dithiocarbamates and xanthates arises primarily from the greater mesomeric electron releasing tendency of the $-NR_2$ grouping of the dithiocarbamates compared to the $-OR$ grouping of the xanthates. Many different types of analytical investigations have been carried out on both dithiocarbamates and xanthates, but few on the thermal behaviour of either.

D'Ascenzo and Wendlandt[16] examined a number of metal diethyldithiocarbamate complexes by thermogravimetric (TG), differential thermal analytical (DTA) and high temperature reflectance spectroscopy, and the same authors[17] also reported iron(III) diethyldithiocarbamate as a new volatile metal chelate. Bernard and Bosel[18] studied the thermal behaviour of lead, zinc and cadmium dithiocarbamates by TG and DTA but the effects resulting from the variation of the R-group have not been determined. No thermal data is available for xanthate complexes. This paper reports the volatility characteristics and thermogravimetric analysis data for eleven nickel alkyl xanthates $Ni(CS_2OR)_2$ [R = ethyl, n-propyl-, i-propyl-, n-butyl-, i-butyl-, t-butyl-, n-amyl-, i-amyl-, n-hexyl-, and cyclohexyl]. A thermal decomposition mechanism for these complexes is proposed.

EXPERIMENTAL

Preparation of nickel alkyl xanthates, $Ni(ROCS_2)_2$

The potassium salts of the appropriate xanthate ligand were prepared as described by Vogel[19]. They were recrystallised from acetone/ether and washed with ether.

The nickel alkyl xanthate complexes were prepared by adding an aqueous solution of AR grade $Ni(NO_3)_2 \cdot 6H_2O$ to an aqueous solution containing a slight excess of ligand. The complexes were filtered and washed several times with water and then dried in air. They were recrystallised from chloroform and dried in a vacuum desiccator for several days. Finally, where possible, they were sublimed and the sublimed material collected and used in further experimental work. Micro-analyses were carried out on the sublimed complexes by the Australian Microanalytical Service.

The nickel complexes prepared in this way were: methyl-, ethyl-, n-propyl-, iso-propyl-, n-butyl-, iso-butyl-, t-butyl-, n-amyl-, iso-amyl-, n-hexyl-, and cyclohexyl-xanthate. The micro-analytical results for the nickel methyl n-propyl, amyl- and hexyl-xanthates reported in Table I are typical of the others and show satisfactory agreement with predicted values. The thermogravimetric curves were obtained on a Stanton Thermobalance (Model TR-01) using air and nitrogen furnace atmospheres. Sample sizes of 90–95 mg were used at the conventional furnace heating rate of 4°C per minute.

TABLE I

MICRO-ANALYTICAL RESULTS FOR THE NICKEL METHYL n-PROPYL, n-AMYL- AND n-HEXYL-XANTHATES

	C	*H*	*S*	*Ni*
$Ni(CS_2OCH_3)_2$				
found	17.4	2.4	46.4	21.4
calculated	17.6	2.2	46.9	21.5
$Ni(CS_2OC_3H_7)_2$				
found	30.2	4.4	39.6	—
calculated	29.9	4.4	39.9	—
$Ni(CS_2OC_5H_{11})_2$				
found	37.9	5.8	32.4	15.3
calculated	37.4	5.7	33.3	15.3
$Ni(CS_2OC_6H_{13})_2$				
found	41.0	6.3	32.0	13.6
calculated	40.7	6.3	31.0	14.2

Volatility studies

Volatilisations were carried out in all cases in a vacuum of better than 0.01 mm Hg. The vacuum was measured approximately on an Edwards Vacustat.

TABLE II

THERMOGRAVIMETRIC ANALYSIS OF SOME NICKEL ALKYL XANTHATE COMPLEXES

Nickel alkyl xanthate derivative	*Molecular weight*	*Start of major decomposition (°C)*	*End of major decomposition (°C)*	*Weight loss (mg)*	*Final residue (mg)*	*Theoretical NiO mass (mg)*
methyl	273	150	180	56.55	23.70	24.6
methyl (N_2)	273	150	190	55.55	24.15	24.7
ethyl	301	180	280	61.00	20.85	22.6
ethyl (N_2)	301	180	250	60.35	21.85	22.4
n-propyl	329	150	230	61.55	19.55	20.5
i-propyl	329	150	220	61.55	19.90	20.5
n-butyl	357	150	230	65.70	17.80	19.0
i-butyl	357	180	260	61.00	20.25	19.0
t-butyl	357	140	260	56.50	21.20	19.0
n-amyl	385	160	230	66.80	17.55	17.6
i-amyl	385	160	250	60.00	16.45	17.5
n-hexyl	413	170	270	69.00	16.15	17.0
cyclohexyl	409	180	260	66.60	15.70	16.6

RESULTS AND DISCUSSION

In Fig. 1, the thermograms for each complex are reproduced. In Table II the decomposition characteristics of all the complexes investigated are reported. The TG thermograms obtained for nickel alkyl xanthate complexes were very similar, whether the decomposition took place in an air or nitrogen atmosphere. In general, decomposition begins between 140 and 180°C followed by a rapid loss in weight in which over 60% of the molecule is lost. A long plateau then results for which there is evidence of NiS formation, which is followed by a short loss of weight to NiO around 700°C.

All the thermograms show a rapid major weight loss step in the temperature range 140–180°C (Table II) (region A–B, Fig. 1). This section of the profile represents the major breakdown of all the nickel alkyl xanthates and, from the similarity of the

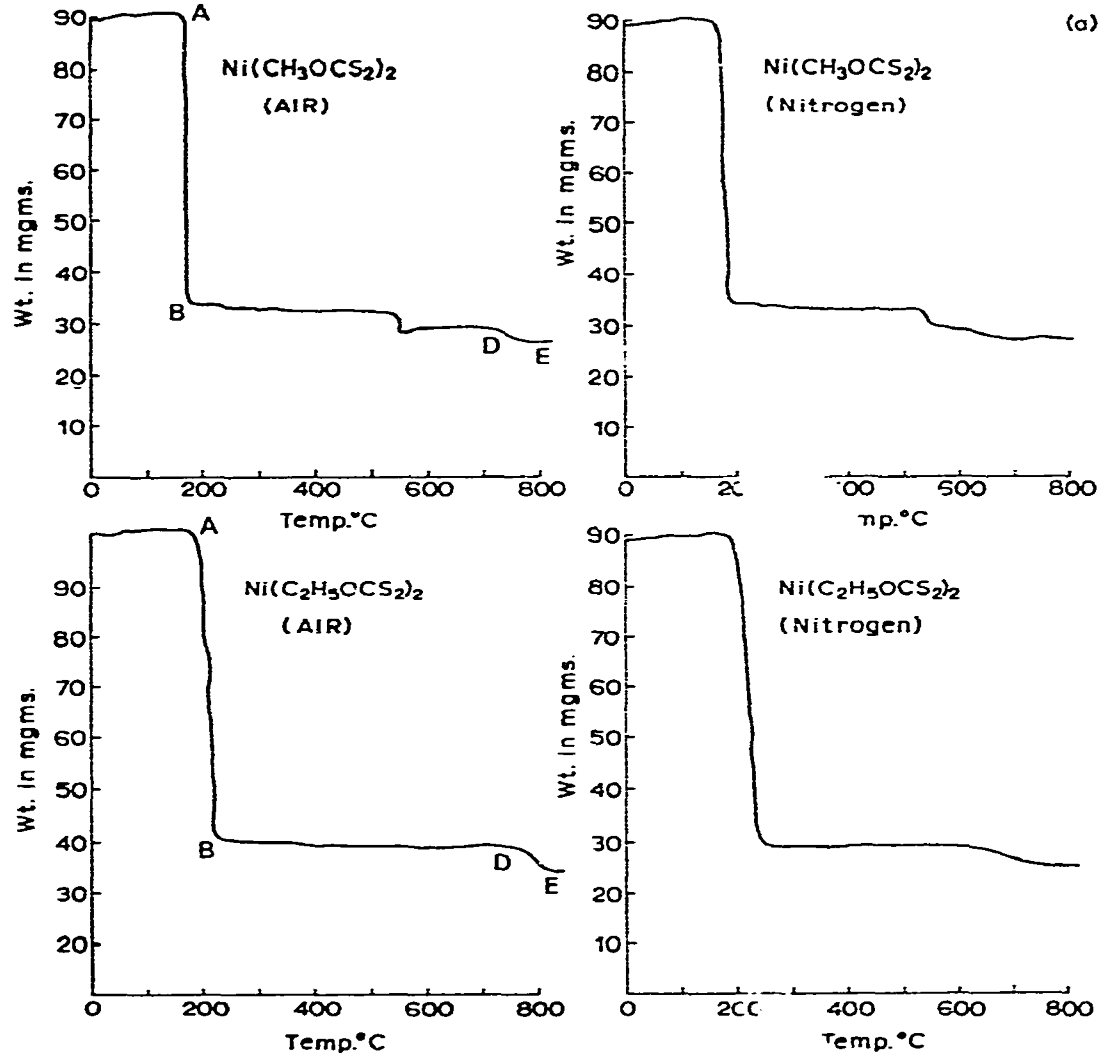


Fig. 1A

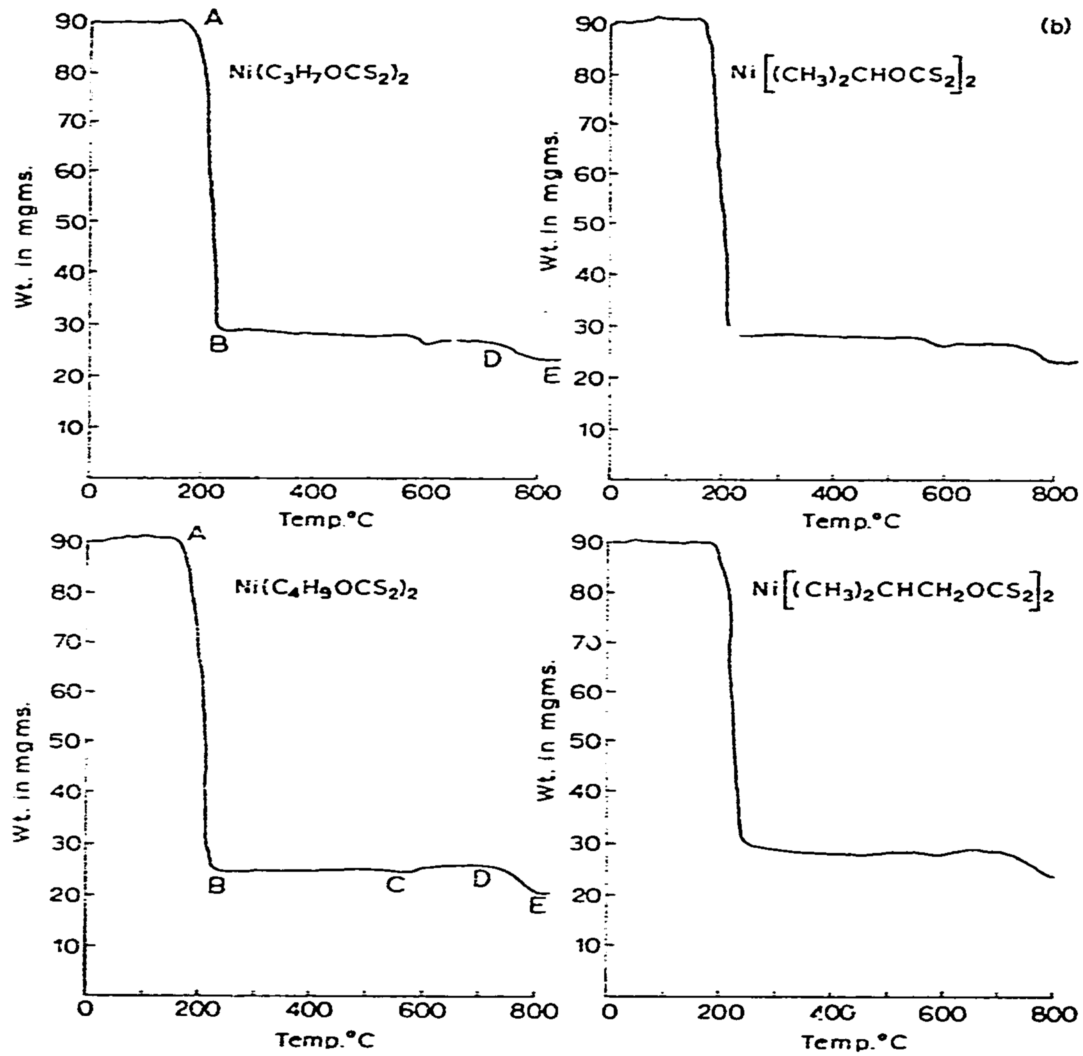


Fig. 1B

thermograms, it is apparent that differences in complex thermal stability are small but that the least stable is the n-hexyl derivative with the i-butyl- and cyclohexyl derivatives among the most stable. The magnitude of the initial weight loss increases progressively from the methyl through to the hexyl derivative with interesting variations among the isomers of a particular derivative. The t-butyl and iso-amyl-derivatives show TG characteristics which distinguish them from all the others. A decomposition step, separate from the major decomposition step occurs, (Fig. 1C, region B–C) being more evident in the iso-amyl-derivative than in the t-butyl derivative. For all thermograms, except those for the ethyl derivative (air and nitrogen atmosphere) and the normal and iso-butyl derivatives, a small weight loss step is observed at a temperature between approximately 520–600 °C and in the region around 750 °C a weight loss step is obtained corresponding to the production of NiO as the final product of thermal decomposition.

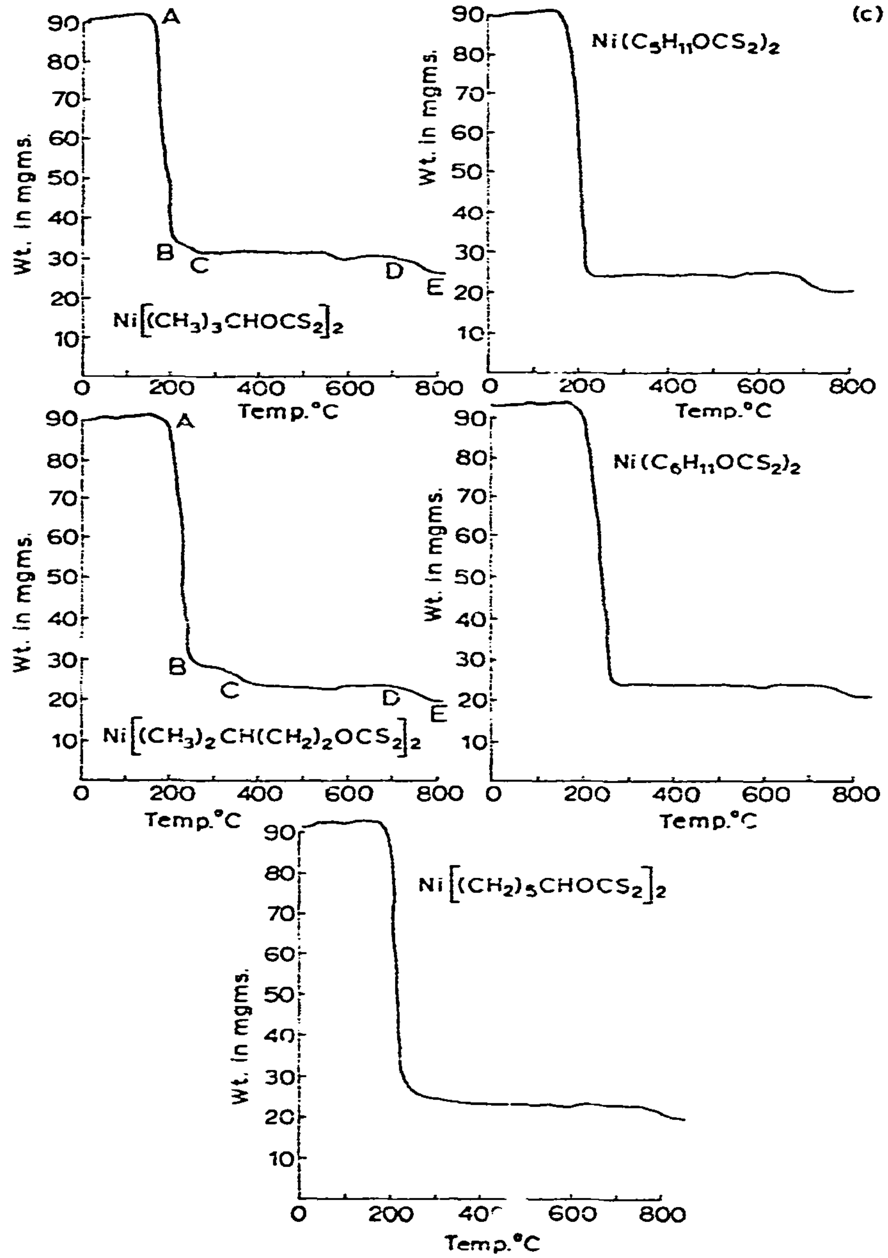


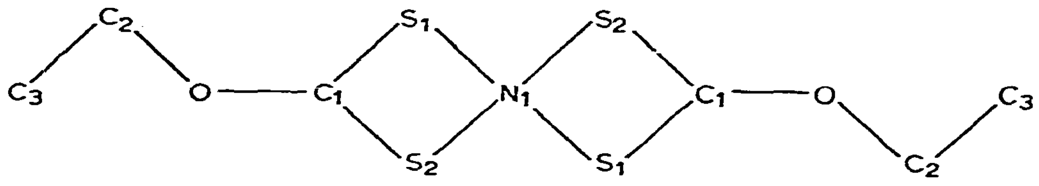
Fig. 1C. Thermogravimetric curves for several nickel alkyl xanthates.

If it is assumed that the major decomposition step results in the formation at B of NiS, then for a mass of nickel ethyl xanthate of 89.85 mg (Fig. 1A), the expected mass of NiS is 27.1 mg. The experimental value obtained is 29.5 mg. From B–D, a gently sloping plateau is present, which is followed by the weight loss step D–E. If it is accepted that the final product is NiO, then the mass of approximately 24.5 mg NiO corresponds to a mass of NiS of approximately 29.5 mg, which agrees with the plateau in the region B–D.

In the case of nickel n-butyl xanthate (Fig. 1B), the final product NiO (E) has a mass of 20.5 mg, which would correspond to a predicted value for NiS of 25.0 mg. The experimental value (D) is 25.0 mg. In the region C–D, there is an increase of weight which is considered to be due to surface oxidation of NiS to $NiSO_4$ in the presence of air; when the temperature of about 750°C is reached; decomposition to NiO then begins to occur.

It is presumed that the variations in the region B–C for the t-butyl and iso-amyl complexes, and the small weight loss step which occurs around 520–600°C are due to the rate of decomposition or the temporary retention of decomposition products by the matrix of the sample.

Such thermal data can be rationalised if all the available crystal structural data for nickel xanthate complexes is considered. Franzini[20] has determined the structure of nickel ethyl xanthate and shown that the whole molecule is planar.



The C_1–S_2 bond length is given as 1.65 Å and the C_1–S_1 as 1.73 Å. The author indicates that the "nature" of these bonds, while not clear in relation to only one molecule, is perfectly understandable when the interactions between different molecules in the crystal lattice are considered. S_1 is weakly attracted by the Ni in another molecule, but while S_2 does not interact with its nearest neighbour O in another molecule, there may be a very weak repulsion between them. Consequently, the two sulphur atoms are not equivalent. On the basis of this argument, it is suggested that the mechanism of thermal decomposition of nickel alkyl xanthates involves S-ethyl, O-ethyl xanthate as a stable intermediate, with NiS and carbonyl sulphide emerging as the stable fragments from the primary decomposition step (Fig. 2).

In each case examined, the experimental weight losses are to within reasonable

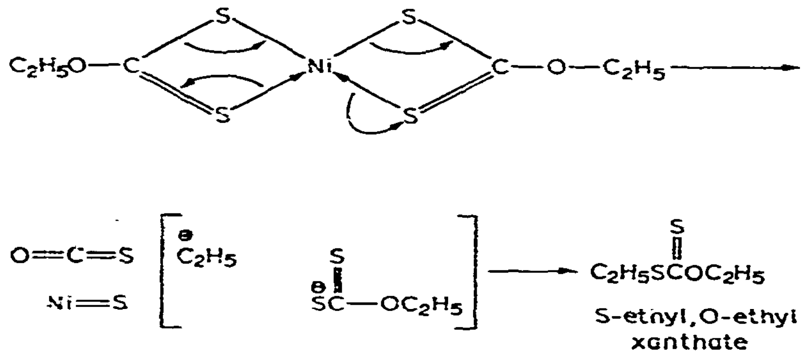
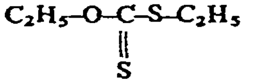


Fig. 2. Thermal decomposition mechanism for nickel alkyl xanthates.

approximations to those predicted on the basis of the proposed thermal decomposition mechanism.

Several thermal decomposition mechanisms are possible theoretically. Bulmer and Mann[21] studied the thermal decomposition of dialkyl- and diaryl- disulphurdicarbothionates $(R\cdot O\cdot CS\cdot S)_2$ and for the dibenzyl compound they suggest a thermal decomposition mode which might involve $(RCH_2\cdot S)_2+COS$ as intermediates. Fackler *et al.*[22] however, observed R–O cleavage in some metal xanthates, the thermal decomposition producing olefins, *e.g.*, iso-butene. In the present work the thermal decomposition mechanism proposed has been confirmed by mass spectral analysis of the decomposition products. When the xanthate decomposes at 180°C, a gas is given off and a clear liquid condenses on the cooler part of the glass tube. Both of these were analysed using the mass spectrometer. The gas gave a strong parent peak at *m/e* of 60, indicative of carbonyl sulphide. No other compound was indicated from the mass spectrum. The clear liquid gave a parent peak of *m/e* 150. This confirmed the presence of S-ethyl, O-ethyl xanthate.



$$C_2H_5{-}O{-}\underset{\underset{S}{\|}}{C}{-}S{-}C_2H_5$$

Consequently, it is concluded that nickel ethyl xanthate decomposes according to the above mechanism and as all of the nickel xanthates investigated show similar TG profiles their decomposition mode is probably identical.

TABLE III
VOLATILITY CHARACTERISTICS OF SOME NICKEL ALKYL XANTHATE COMPLEXES

Nickel xanthate derivative	*M.pt. (°C)*	*Volatility characteristics*
methyl	>220	completely volatile 80–150 °C. No decomposition.
ethyl	137	completely volatile 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.pt.
n-amyl	65–67	not as volatile as previous complexes. Complex volatile 90–115 °C with some decomposition.
n-hexyl	61–62	not very volatile. Low volatility around 90°, but at higher temperatures decomposition occurs.
iso-propyl	116–118	volatility started at 60 °C. In temperature range 60–110 °C, volatility rapid no decomposition. Above 110 °C, some decomposition. More volatile than n-isomer.
iso-butyl	110–111	volatile in temperature range 80–125 °C. No decomposition.
t-butyl	139–140	volatile in range 100–120 °C with no decomposition. More volatile than iso- and n-isomers.
iso-amyl	91–95	volatility evident in temperature range 90–105 °C. Complex decomposes slightly above m.pt. More volatile than n-isomer.
cyclohexyl	melts over wide range of temperature	volatile in temperature range 100–150 °C. Completely volatile with only slight decomposition below 120 °C.

Volatility studies

All of the nickel complexes investigated were volatile to some extent. The order of volatility was found to be ethyl > t-butyl > i-propyl > n-propyl > methyl $\simeq$ i-butyl > i-amyl, cyclohexyl > n-butyl > n-amyl > n-hexyl. The volatility characteristics for the various nickel alkyl xanthate complexes are summarised in Table III.

From these volatility studies, it would appear that as the chain length in the R-group increases beyond n-propyl, the complex becomes less thermally stable and less volatile. Conversely, where branching occurs within a particular R-grouping, thermal stability and volatility increases.

While the complexes are all volatile at low pressure and at normal pressure, there was no evidence that volatility was a special feature of these complexes: decomposition was the principle characteristic exhibited. This appears to be in contrast to the behaviour of iron(III) diethyldithiocarbamate, reported as a new volatile metal chelate by D'Ascenzo and Wendlandt[17].

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