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THERMAL AND KINETIC STUDIES OF SOME METAL COMPLEXES OF 2,4-PENTANEDIONE

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ABSTRACT

The heats of fusion, vaporisation, and decomposition have been measured for a number of 2,4-pentanedione complexes by differential scanning calorimetry. Kinetic parameters have been derived from the calorimetric results.

Mass spectrometric studies are reported over a range of temperatures and comparisons are made with earlier work where appropriate. Possible structures of dichlorobis(2,4-pentanedionato)titanium(IV) are proposed on the basis of the physical measurements.

INTRODUCTION

The chemical and physical properties of transition metal complexes of 2,4-pentanedione (acac) are well documented[1] but there have been few systematic studies of their thermal properties. This is surprising since the complexes have potential technological usefulness.

The isothermal decompositions of some 2,4-pentanedione complexes were reported by Charles and his coworkers[2-4]. Differential thermal analysis and thermogravimetric data were obtained by Glavas and Ribar[5]. The air atmosphere used by these workers resulted in oxidation at moderate temperatures and no quantitative thermochemical results were obtained. Heats of sublimation have been obtained by Wood and Jones[6] and Berg and Truemper[7] although these are contradicted by more recent measurements[8-10].

The inadequacy or absence of quantitative thermal data has prompted us to reinvestigate some of these complexes.

Differential scanning calorimetry (DSC) was used to measure the quantitative thermal properties in a nitrogen atmosphere, thus avoiding premature oxidation[5].

We have also studied the temperature dependence of the mass spectra of the compounds with a direct insertion probe in order to facilitate our interpretation of the thermal data.

EXPERIMENTAL

Compounds

The crystalline complexes were prepared by literature methods. Satisfactory microanalyses were obtained (Table I) with the exception of those for the dihydrates. We were not able to obtain the stoichiometric water contents to a sufficient accuracy although such stoichiometries have been reported[2].

TABLE I

MICROANALYTICAL DATA OF METAL COMPLEXES
acac = 2,4-pentanedionato.

Compound	*Found* (%)		*Theoretical* (%)	
	C	H	C	H
$Al(acac)_3$	55.7	6.85	55.5	6.53
$Sc(acac)_3$	52.9	5.91	52.6	6.18
$Ti(acac)_2Cl_2$	37.5	4.55	37.9	4.45
$V(acac)_3$	51.7	6.35	51.7	6.08
$VO(acac)_2$	45.6	5.50	45.3	5.32
$Cr(acac)_3$	51.5	6.07	51.6	6.06
$Mn(acac)_2\cdot 2H_2O$	41.3	6.07	41.5	6.23
$Mn(acac)_3$	50.9	6.23	51.1	6.01
$Fe(acac)_3$	51.0	6.00	51.3	6.13
$Co(acac)_3$	51.1	6.11	50.6	5.94
$Cu(acac)_2$	46.2	5.54	45.9	5.39
$Zn(acac)_2\cdot H_2O$	43.7	5.76	42.7	5.73

Calorimetry

A Perkin–Elmer Differential Scanning Calorimeter (DSC-1B) was used with a modified method of sample encapsulation. The empty space in the sample pan was filled with aluminium powder, thus creating an internal heat sink and yielding more accurate heats of sublimation[11]. This method did not affect the instrument calibration and was used for both the volatile and involatile complexes. The calorimetric procedure has been described elsewhere[12].

Kinetic parameters were obtained from the DSC curves by means of a least-squares fit to

$$\frac{d\alpha}{dt} = A\cdot\exp(-E_A/RT)\cdot(1-\alpha)^n$$

where α = fractional extent of reaction at temperature T, A = Arrhenius pre-exponential factor, E_A = activation energy, n = apparent order of reaction[13], $d\alpha/dt$ = rate of reaction.

The original computer program[14] has been revised and a subroutine added to display graphically the calculated and observed rates of reaction. An ICL 1903A computer and an ICL digital plotter were used for this work.

Mass spectrometry

The complexes and their decomposition products were studied at temperatures up to 673°K with a Hitachi Perkin–Elmer RMU-5 mass spectrometer using a direct insertion probe.

IR spectroscopy

A Perkin–Elmer 457 spectrophotometer was used to compare the IR spectra of the volatile complexes, their sublimates and dichlorobis(2.4-pentanedionato)-titanium(IV) as nujol mulls.

NMR spectroscopy

NMR spectra of the titanium(IV) compound dissolved in deuterobenzene were recorded with a JEOL C6OHL spectrometer using TMS as an internal reference.

RESULTS AND DISCUSSION

Mass spectrometry

The mass spectra of a number of pentanedionates were recorded over the range 300–700°K in order that any temperature dependence might be correlated with their thermal behaviour. The spectra obtained were compared with those in the literature[15–17]. Sasaki *et al.*[15] related their results, obtained at 523°K, to the electronegativities of the central atoms while Shannon *et al.*[16,17] related the absence of a peak due to $Macac^+$ in some cases to the electron acceptor properties of the central atom.

We have found that the correlation between thermal behaviour and mass spectra was quite marked, compounds which sublimed unchanged gave spectra in which the major peaks corresponded to $M(acac)_2^+$ and $M(acac)_3^+$ while those which decomposed on heating gave spectra whose major peaks corresponded to fragments of the pentanedione ligand such as CH_3CO^+ and CO^+. A similar correlation was also observed with variation in temperature, those compounds which decomposed showed no metal-containing fragments at the higher temperatures while those which volatilised only showed changes in intensities associated with increased rates of volatilisation. Comparison of the mass spectra with that of the ligand indicated that the volatile decomposition products were derived from 2,4-pentanedione rather than smaller molecules such as acetone or methane as was reported previously[4]. The patterns of $Mn(acac)_3$ and $Mn(acac)_2$ showed the expected similarities resulting from the quantitative loss of acac from the Mn^{III} compound.

Thus, our studies together with the earlier work imply that the ease of decomposition of pentanedionates is dependent on the ease of reduction of the central metal atom.

The spectrum of $V(acac)_3$ shows (Fig. 1) strong peaks for $VO(acac)_2^+$, VO^+, $V(acac)_2^+$, and $V(acac)^+$ indicating that there are two fragmentation mechanisms operating in this case.

The spectrum of $Ti(acac)_2Cl_2$ (Fig. 1) shows peaks for both $Ti(acac)_3^+$ and $Ti(acac)_2Cl^+$ and no peak for $Ti(acac)_2Cl_2$. This is not consistent with a simple monomeric formulation and polymeric structures such as those shown in Fig. 2 may be a better representation.

We were unable to detect any differences in the mass spectra above or below the transition temperature noted in the following section. The intensities of the lines

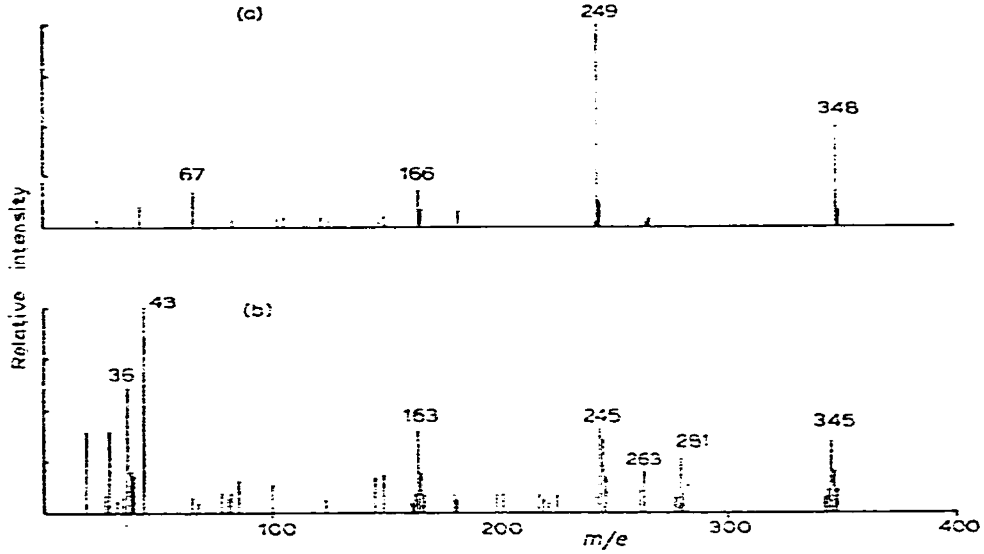

Fig. 1. Mass spectra: a, $V(acac)_3$; b, $Ti(acac)_2Cl_2$.

in the spectra were low due to the involatility of the compound, which also contradicts a simple monomeric structure.

Thermal and kinetic measurements

The results of our DSC measurements were dissimilar from the DTA results of Glavas and Ribar[5] in that we were able to differentiate between two distinct types of

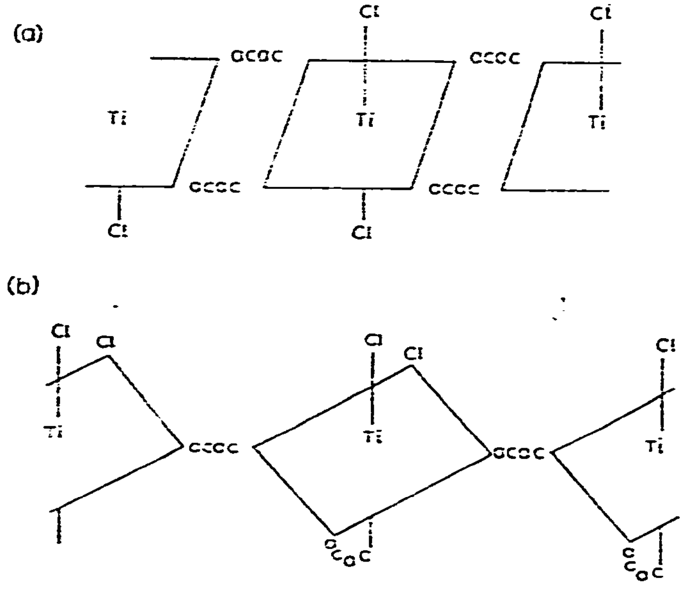

Fig. 2. Polymeric structures of $Ti(acac)_2Cl_2$. a, *Trans* configuration; b, *cis* configuration.

thermal behaviour without the complication of oxidation reactions. The complexes of Al^{III}, Sc^{III}, V^{III}, Cr^{III}, and Zn^{II} each vaporised completely. Their heats of fusion, vaporisation and the heat of dehydration of the zinc complex are shown in Table II. These values refer to the peak temperature, T_p, of the reaction occurring over the range T_i–T_f °K. No attempt was made to correct these to 298 °K since the heat capacities of the gaseous complexes were not available.

TABLE II

HEATS OF FUSION (ΔH_f), VAPORISATION (ΔH_v) AND DECOMPOSITION (ΔH_{dec}) OF SOME COMPLEXES OF 2,4-PENTANEDIONE

Metal	*Wt. loss* (%)	*Scan* (°K·min⁻¹)	ΔH_f (kJ·mol⁻¹)	ΔH_v	ΔH_{dec}	T_i^a (°K)	T_p^a	T_f^a	*Refs.*
Al^{III}	100	16, 32	35±2			460	469	475	8, 9, 10
				94±6		460	540	548	
			32.7±0.3			458	460	462	
Sc^{III}	100	16, 32		169±7		445	550	555	6, 10
Ti^{IV}	0	16, 32			15.2±0.7	460	472	483	
V^{III}	100	16, 32	30±1			460	475	485	6, 10
				197±6		450	580	595	
$V^{IV}O$		16, 32	34±1			505	545	550	
	88.5				20.0±0.3	555	580	595	
Cr^{III}	100	32	35.2±0.2			490	494	498	8, 9, 10
				90±3		490	580	595	
Mn^{II}	12.6	16	(Dehydration)		102.1±0.9	315	365	380	
(Dihydrate)	33.7				11.8±0.8	545	550	552	
					−21.7±0.9	552	557	570	
Mn^{III}	23.1				19.4±0.7	430	445	447	
					−26.2±0.9	447	450	455	
	59.0				13.3±1.0	520	540	542	
					−21.5±1.5	542	545	565	
Fe^{III}		16	34.1±0.9			455	461	463	
	91.2			82±1	82±1	452	520	535	
Co^{III}	71.0	8, 16, 32			57±2	475	490 492	498	
Cu^{II}	90.0	16, 32		57.3	(Sublimation)	475	550	560	7
Zn^{II}	100	16, 32	(Dehydration)		25.1±0.6	325	360 385 400	375	
	(Overall)		25.9±0.3			380	405	415	
				48±2		435	505 515	520	

T_i^a, T_p, T_f at the lower scan, where applicable.

The vapour pressure studies of Wood and Jones[6] and of Berg and Truemper[7] are at variance with our own and other recent measurements of heats of sublimation of the chelates. These latter yielded results similar to our own for the aluminium and chromium complexes[8–10]. There are large discrepancies between our results and those of Melia[10] for the scandium and vanadium(III) complexes. The acceptable precision of both sets of results suggests that some anomalous temperature dependence may account for the observed differences. If these complexes associate in the vapour phase, as do the lanthanide chelates[18], then an increase in temperature would result in dissociation of the aggregates with a correspondingly higher heat of vaporisation. This increase is apparent on comparing our own, higher temperature results with those of Melia[10]. The DSC curve of the zinc complex showed two small peaks in the region of the major fusion peak. The higher temperature peak was close to the melting point of the monohydrate[19] while the lower temperature peak probably corresponded to a phase transition.

Sublimation was the major reaction observed for the Fe^{III} and Cu^{II} complexes. The observed weight losses were less than 100% and a small amount of residue was produced. The IR spectra of the sublimates were identical to those of the original materials and in the case of the Fe^{III} complex the sum of the two heats of reaction, 116 $kJ \cdot mol^{-1}$, was found to be similar to the reported value, 99 $kJ \cdot mol^{-1}$ of the heat of sublimation[10].

Each of the other complexes decomposed to unidentifiable charred products rather than to the oxide as was observed for decompositions in air[5]. There were two peaks in the DSC curve of $VO(acac)_2$ which we were unable to resolve. The first peak sharpened when no aluminium powder was present in the sample pan and was identified with fusion by comparison of the heat of reaction with the other heats of fusion. A sublimate was then evolved with an IR spectrum identical to that of $VO(acac)_2$ but, at higher temperatures, a lighter green sublimate was evolved during extensive decomposition of the complex.

Dichlorobis(2,4-pentanedionato)titanium(IV) is said[20,21] to be a monomeric compound. Our mass spectrometric results (see above) contradict this structural assignment as does the extreme insolubility of the complex in organic solvents. The complex did not melt or vaporise on heating, as did the volatile chelates described previously, but gave two peaks in the DSC curve, the second of which was caused by charring of the complex.

During the first peak there was no weight loss, but a colour change from orange to yellow. The n.m.r. spectrum of the orange form, in benzene-d_6, had two methyl peaks centred at $\delta = 1.59$ p.p.m. with a methine peak at $\delta = 5.20$ p.p.m. while the yellow form had singlets at $\delta = 1.72$ and 5.38 p.p.m. This is consistent with stereochemistries of *cis* and *trans*, respectively, in benzene solution. The changes in the IR spectra of the solid during the transition were not consistent with a simple solid-state *cis–trans* isomerisation. The heat of the phase change may, therefore, be due to a structural reorganisation within a polymeric species involving the movement of chlorine atoms from *cis* to *trans* positions.

There were three peaks in the DSC curve of the Mn^{II} complex the first of which was associated with dehydration. The heats of reaction derived from the second two peaks were equal (within experimental error) to those calculated for the Mn^{III} complex beyond 455 °K. The first endothermic peak in the DSC curve of the Mn^{III} complex was sharp and characteristic of fusion. After the second, exothermic peak a brown solid was formed which analysed for $Mn(acac)_2$ (*Anal.* Calc. (%) for $Mn(acac)_2$: C, 47.4; H, 5.57. Found (%): C, 47.7; H, 5.9).

The following reactions probably occurred

$$Mn(acac)_3(cryst) \rightarrow Mn(acac)_3(l)$$

$$Mn(acac)_3(l) \rightarrow Mn(acac)_2(cryst) + acac(g)$$

with the transient existence of the 2,4-pentanedionyl radical, requiring a weight loss of 28.1%.

The cobalt compound decomposed, yielding a black charred product and some pink sublimate. The analysis of the latter (C, 44.1%; H, 5.62%) was closer to that required for the cobalt(II)chelate (C, 46.7%, H, 5.49%) and probably contained the Co(III)chelate as impurity. Thus a similar but less facile reduction to that of the Mn^{III} compound may have occurred.

We have only obtained kinetic parameters for the compounds which yielded simple DSC peaks without shoulders or discontinuities. The variations in the kinetic parameters with heating rate were investigated for some representative compounds since the validity of dynamic methods, such as DSC, has been questioned[22–24].

The magnitudes of the kinetic parameters A, E_A, and n (see Experimental) are shown in Table III.

TABLE III

PRE-EXPONENTIAL FACTORS (A), ACTIVATION ENERGIES (E_A), AND APPARENT ORDERS OF REACTION (n) FOR THE THERMAL DECOMPOSITION OF SOME COMPLEXES OF 2,4-PENTANEDIONE

Metal	*Scan* (°*K*·*min*$^{-1}$)	*Range of* α	A *sec*$^{-1}$	E_A (*kJ*·*mol*$^{-1}$)	n
Fe^{III}	8	0.10–0.93	1.4×10^{11}	131	0.64
	32	0.08–0.73	9.3×10^{14}	169	0.99
	32	0.06–0.87	1.2×10^{13}	151	0.68
Cu^{II}	8	0.07–0.91	3.6×10^{7}	94	0.95
	16	0.05–0.84	1.2×10^{9}	115	0.21
	32	0.03–0.81	8.2×10^{8}	114	0.30
Co^{III}	8	0.04–0.65	3.8×10^{42}	416	−0.50
	16	0.05–0.65	1.1×10^{45}	445	−0.60
Al^{III}	16	0.04–0.78	1.1×10^{1}	33	0.11
	32	0.03–0.92	5.7×10^{2}	50	0.20
Sc^{III}	8	0.06–0.82	5.2×10^{2}	51	0.30
	16	0.03–0.78	1.9×10^{3}	56	0.22
V^{III}	16	0.10–0.77	1.5×10^{2}	48	0.15
	32	0.08–0.81	4.3×10^{3}	63	0.43
Cr^{III}	8	0.05–0.90	2.7×10^{5}	78	0.34
	16	0.04–0.98	1.8×10^{5}	77	0.24
	32	0.04–0.71	3.6×10^{5}	79	0.42

The results were diagnostic of the thermal behaviour of the complexes. The activation energy E_A was always greater than a heat of decomposition but smaller than a heat of sublimation. The large values of A and E_A found for the decomposition of $Co(acac)_3$ were associated with the electron-transfer mechanism which results in partial reduction of Co^{III}. Similar high values of A and E_A were obtained for the decomposition of pyridine perchromate which yielded Cr^{III} by an electron transfer mechanism[25]. The unusual, negative values of n indicate that the general equation which we have used may not be strictly applicable when metal–ligand bond cleavage is not the rate-controlling mechanism. Electron transfer or vaporisation kinetics require different equations but, nevertheless, our equation can be generally applied to a reaction of unknown mechanisms to yield characteristic solutions. For the volatile chelates[6], E_A was always less than the heats of vaporisation or sublimation and A was less than 10. Diffusion, rather than bond-cleavage was expected to be the rate-determining step in these cases. The variations in the values of A, E_A, and n with heating rate (Table II) were found to be no greater than the variation in successive runs at constant heating rates. This would seem to support the views of Hill[24] who suggested that there may be no fundamental error in dynamic methods of determination of kinetic parameters. An example of the agreements between calculated and experimental rates is shown in Fig. 3 for $Co(acac)_3$.

The methods used in this paper may provide a means of characterising the thermal behaviour of solids by differential scanning calorimetry.

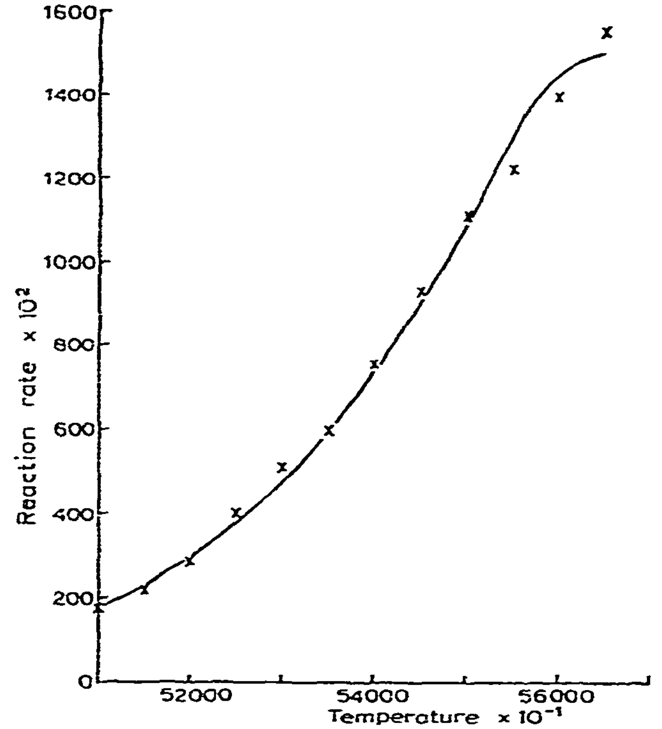

Fig. 3. Computed (——) and experimental (×) rates of decomposition of $Co(acac)_3$.

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