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CALORIMETRIC AND KINETIC STUDIES OF THE OXYGEN, PYRIDINE AND 3-METHYLPYRIDINE ADDUCTS OF *N,N'*-ETHYLENEBIS(SALICYLIDENEIMINATO) COBALT(II)

GRAHAM BEECH
Department of Physical Sciences, The Polytechnic, Wolverhampton WV1 1LY (Great Britain)

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ABSTRACT

Calorimetric data for the compounds listed in the title have been obtained from differential scanning calorimetry (DSC) studies. Comparison is made where possible, with earlier work and comment is made on the magnitudes of the heats of decomposition in relation to the properties of the compounds. Kinetic data were derived from the calorimetric results and these data are combined with other, previously published results, in order to confirm the heat of decomposition of the oxygen adduct derived from the direct calorimetric measurements. The pyrolysis behaviour of the parent complex has been studied by pyrolysis, gas–liquid chromatography and DSC.

INTRODUCTION

Calvin and his coworkers have described the preparation of *N,N'*-ethylenebis(salicylidineiminato)cobalt(II) (Co Salen) and related compounds[1]. Co Salen forms a 1:1 solid complex with pyridine[1] and removal of the latter yields an activated form of the complex which possesses oxygen-carrying properties. The fully oxygenated complex has the stoicheiometry $(\text{Co Salen})_2O_2$. Calvin and coworkers have also reported kinetic[2], magnetic[3], and solid–vapour equilibrium[4] properties of Co Salen and its derivatives.

The oxygenation reaction of Co Salen is reversible and deoxygenation takes place on increasing the temperature of the sample or on evacuation. The oxygenation–deoxygenation cycle may be repeated many times and the efficiency of oxygen production was found to fall to only 50% of theoretical for reaction 1 after more than

$$(\text{Co Salen})_2O_2\ (\text{cryst.}) \rightarrow 2(\text{Co Salen})\ (\text{cryst.}) + O_2\ (\text{g}) \qquad (1)$$

300 cycles[5].

The physical properties of Co Salen and its derivatives have been extensively investigated. Magnetic measurements[3,6] suggested that the inactive form has a structure in which adjacent molecules are bonded to each other, thus preventing the access of oxygen molecules. Martell and Calvin suggested[7], on the basis of X-ray and magnetic measurements, that the layer spacing in the crystal structure of Co Salen is wide enough to permit access of oxygen molecules. The latter then each bridge two Co Salen units and the diamagnetism of the compound is accounted for by the interaction of electron spins through the oxygen molecule.

Vogt *et al.*[8] have proposed a formulation $(\text{Co Salen})_2O_2 \cdot H_2O$ for the oxygenated complex and maintained the presence of water to be essential to the activity of Co Salen.

Recent X-ray studies have shown the inactive Co Salen to have a dimeric structure with pentacoordinate cobalt atoms[9], and the pyridine adduct to have a square-pyramidal structure[10]. The inactivity of each of these compounds towards oxygen uptake was ascribed to the close packing of molecules rather than electronic causes.

In order to attempt to understand the energetics of oxygen uptake and adduct formation by Co Salen, a thermochemical investigation was undertaken and the results are reported here. There has been one previous thermochemical study of oxygen uptake[11] and the kinetics of this process have also been obtained[2].

EXPERIMENTAL

The Perkin–Elmer differential scanning calorimeter (DSC-1B) was used, as previously described[12]. All decompositions were carried out in dry nitrogen at a heating rate of 8 or 16°K·min^{-1}. The curves obtained from the calorimeter were subjected to a least-squares analysis, as previously described[13], for the pre-exponential factor (A), the activation energy (E_A) and the "order of reaction" (n)[14] in the equation

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

where α is the extent of decomposition and $d\alpha/dt$ the rate of decomposition, at temperature T.

The ICL 1903A computer at this Polytechnic was used for the least-squares analysis and the ICL digital plotter was used to display the results.

Pyrolysis–gas–liquid chromatography

A Pye 104 Model 24 gas–liquid chromatograph was used equipped with a Curie-point pyrolyser. Pyrolysis time was 15 sec at 753°K with nitrogen as the carrier gas. A carbowax column was used at an oven temperature of 323°K.

Preparation of compounds

The preparations of the oxygen and pyridine adducts have been previously described[1]. The 3-methyl pyridine complex was prepared by the method used for the pyridine adduct. Satisfactory microanalyses were obtained for each of the compounds and stoicheiometries were checked by weight loss measurements.

RESULTS AND DISCUSSION

Calorimetric measurements

The results of these measurements are shown in Table I.

TABLE I

HEATS OF DECOMPOSITION[a] OF (Co Salen)$_n$L

Compound	$\Delta H(1)$ (*kJ/mol*)	$\Delta H(2)$ (*kJ/mol*)	T_i (°K)	T_p (°K)	T_f (°K)	*Weight loss (%)* *Found*	*Weight loss (%)* *Calc.*
(Co Salen)$_2$O$_2$	84±4		295	330	350	4.2	4.9
Co Salen.py		60.6±0.5	350	395	400	19.9	19.6
Co Salen (3-Mepy)		66.7±0.2	385	432	445	20.5	22.2

[a] $\Delta H(i)$ refers to the peak temperature, T_p of the decomposition (i) which occurred over the range T_i to T_f (°K).

Each of the adducts decomposed in a single step to Co Salen. The heat of the deoxygenation reaction (reaction (1)) was found to be 84±4 kJ/mole of oxygen. This is in excellent agreement with the previous value obtained by Miller[11] of 80.1 kJ/mole. The latter was derived for the reverse of reaction (1) from more conventional direct calorimetric measurements at 273°K. The magnitude of this ΔH supports the concept of chemical bonding (or chemisorption), rather than physical absorption, of the oxygen molecule.

Simultaneous gas evolution analysis (GEA) during the DSC experiments detected only oxygen during the decomposition. Even at relatively elevated temperatures no evolution of water vapour was detected which would be expected if the formulation of Vogt[8] were correct.

The 1:1 adducts decomposed according to reaction 2,

$$\text{Co Salen}\cdot\text{L (cryst.)} \rightleftharpoons \text{Co Salen (cryst.)} + \text{L (g)}, \qquad (2)$$

where L is pyridine (py), or 3-methyl pyridine (3-Mepy). The ligands are bonded *via* the ring nitrogen atom to Co^{II} to complete an essentially square-pyramidal structure[10]. Each decomposition yielded the active Co Salen. Since the structures of the reactants and products are so similar then the difference in $\Delta H(2)$ must reflect differences in Co^{II}–N bond energies. The difference is primarily due to the greater basicity of 3-methylpyridine compared with that of pyridine[15]. The smallness of the difference indicates that the 3-methyl group may inhibit back donation of electron density by a π-mechanism from the metal to the ligand and hence partially cancel out the increased σ-bond strength. This effect has been observed previously in octahedral cobalt(II) and nickel(II) complexes of pyridine bases by Nelson[16] and Beech[12].

It would be interesting to obtain results for the 2-methyl- and 4-methylpyridine adducts but it was not possible, in this investigation, to obtain products of well-defined stoicheiometries.

Further heating of Co Salen in the inactive or active forms to elevated temperatures resulted in a complex decomposition. The compound began to melt, showing an endothermic peak in the DSC curve, at 620°K. At the temperture corresponding to the maximum rate of melting, 625°K, decomposition commenced and became exothermic. The peak maximum of this exotherm was at 632°K and the reaction was completed by 640°K. The weight loss accompanying the decomposition was 15.6± 0.6%. Effluent gases were monitored continuously with the gas-evolution detector of the calorimeter and the evolution of a gas with a higher conductivity than that of nitrogen was detected from 625°K. In order to identify the gases evolved, the pyrolysis behaviour of the compound was studied and two major gaseous products were detected by gas–liquid chromatography. The retention times of several of the most likely decomposition products were measured under identical experimental conditions as used for the pyrolysis. In no case, however, was it possible to unambiguously identify the two major gaseous products. The dissimilarity of the pyrolysis–GLC curves for Co Salen and the pure ligand is shown in Fig. 1.

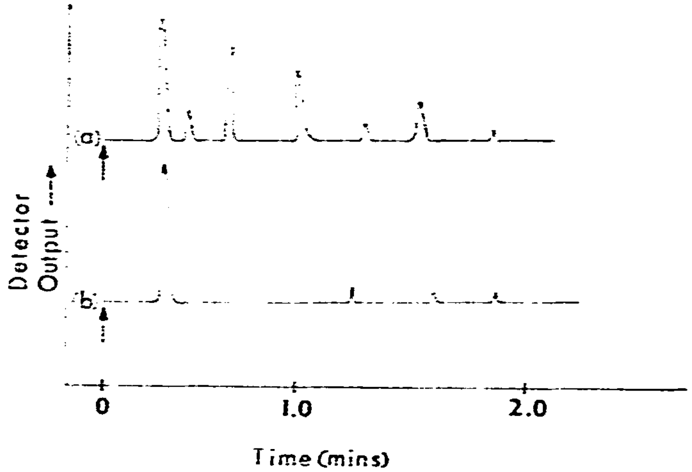

Fig. 1. Pyrolysis GLC curves of Co Salen (a) and of the pure ligand, Salen (b).

It is possible that the cobalt(II) is oxidised to cobalt(III) with concurrent ligand breakdown. Certainly the appearance of the DSC curve at these higher temperatures is very similar to that of bis(acetylacetonato)manganese(III). This compound decomposed to the manganese(II) complex with loss of acetylacetone and a change in valency state[17].

Kinetic measurements

Kinetic parameters for the deoxygenation reaction were obtained from the DSC curves by a least-squares fit to the equation

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

as described in the experimental section. The results for reaction (1) are shown in Table (I) and an example of the fit of experimental and computed results plotted by the computer program is shown in Fig. 2. The value of *A* is of the expected magnitude for a vibration-initiated decomposition[18]. The value of *n* may indicate a first order decomposition which is the same as that found for the oxygenation of Co Salen by

TABLE II

MEAN VALUES OF KINETIC PARAMETERS FOR THE REMOVAL OF OXYGEN FROM (Co Salen)$_2$O$_2$ (REACTION 1)

Range of α	*A*	*E*$_A$ *(kJ/mol)*	*n*
0.06–0.71	2.2×10^{15}	113	1.35
0.08–0.71	4.7×10^{14}	102	1.61
0.03–0.50	7.1×10^{15}	113	1.62
Average values	11×10^{14}	109	1.5

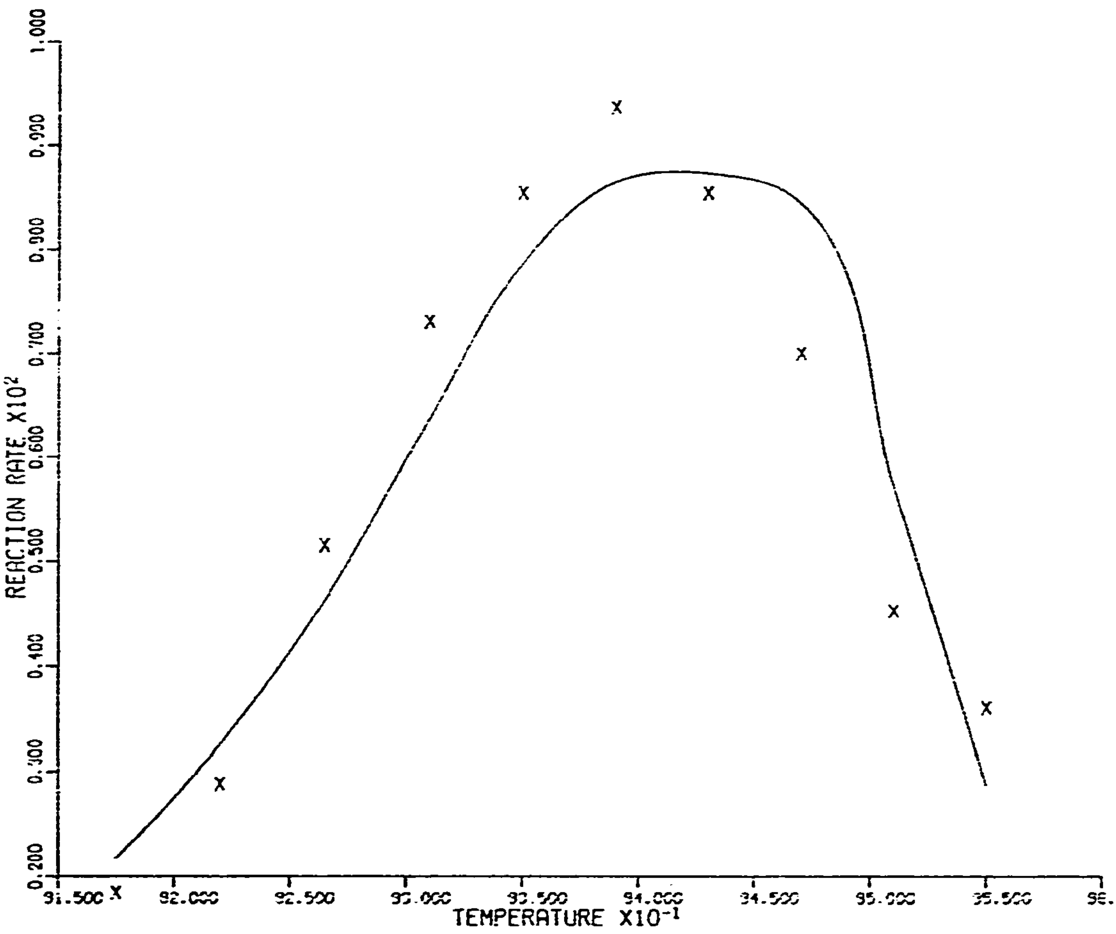

Fig. 2. Experimental (×) and computed (—) rates of decomposition of (Co Salen)$_2$O$_2$ as a function of temperature.

Barkelew and Calvin[2]. These workers found the activation energy for oxygenation to be 29.3 kJ/mole of oxygen. Combining this value (E_A^f) with that reported here for deoxygenation (E_A^r), the heat of reaction, $\Delta H(1)$, for reaction 1 is given by

$$\Delta H(1) = E_A^r - E_A^f$$

From which $\Delta H(1)$ is 80 ± 4 kJ/mole of oxygen.

It is interesting that this value of $\Delta H(1)$, derived kinetically, is in excellent agreement with the direct calorimetric values discussed previously.

CONCLUSION

The calorimetric results support the presently accepted view that the oxygen molecule in $(\text{Co Salen})_2O_2$ is covalently bonded to cobalt atoms but no evidence was obtained to support the water-bonded structure due to Vogt[8]. The kinetic results suggest that the rate-controlling step involves the breaking of cobalt–oxygen molecule bonds rather than the diffusion of oxygen through the activated crystal. The lattice spacing in the crystal must, therefore, be considerably larger than the radius of the oxygen molecule.

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