

# Thermal Decomposition of the Hydrogen-bonded Complexes Quinol-bis(1,8-epoxymen-thane) and Quinol-1,4-dioxan

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## Introduction

Cyclic ethers are often excellent Lewis bases. The ring structure exposes the oxygen lone pairs of electrons to approaching acceptors. Tetrahydrofuran is used very widely in organo-metallic chemistry both as solvent and as a ligand readily replacible by thermal or chemical process [1]. 1,4-Dioxan gives complexes which are more thermally stable than those of tetrahydrofuran because the chair configured ring invariably bonds at both oxygen and to separate acceptors. Crystal structures have been reported for dioxan complexed to metals, for example  $(\text{CuCl}_2)_3 \cdot 2\text{dx}$  [2] and  $\text{CdCl}_2 \cdot \text{dx}$  [3], or hydrogen bonded as in  $\text{H}_2\text{SO}_4 \cdot \text{dx}$  [4].  $\text{NiBr}_2 \cdot 4\text{H}_2\text{O} \cdot 3\text{dx}$  [5] and  $\text{SmBr}_3 \cdot 9\text{H}_2\text{O} \cdot 2\text{dx}$  [6]. In the last two examples the dioxan is hydrogen-bonded to coordinated water molecules. Complexes of dioxan with phenols had not been reported until the recent determination [7] of the crystal structure of quinol-dioxan (1:1).

1,8-epoxymen-thane(1,8-cineole,  $\text{C}_{10}\text{H}_{18}\text{O}$ ) is a widely occuring terpene ether found in for example, cajeput oil and oil of eucalyptus. The lone pairs on the oxygen atom are well exposed in spite of the bulk of the molecule. Crystalline complexes are known [8,9] in which cineole is bonded to metal atoms such as  $\text{Sn}^{\text{IV}}$ ,  $\text{Sn}^{\text{II}}$ ,  $\text{Fe}^{\text{III}}$  and  $\text{Ag}^{\text{I}}$ . The crystals are of poor quality and low thermal stability so that few crystal structures have been reported. Another important class of crystalline cineole complexes are the hydrogen-bonded products obtained with many phenols [10]. The structure of quinol-bis(cineole) has been reported recently [9].

In the present paper we report thermal decomposition studies on the chain polymer quinol-dioxan and the trimolecular complex quinol-bis(cineole) using vapour pressure measurements,

differential scanning calorimetry and gravimetric studies.

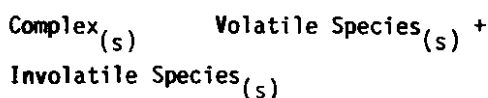
## Experimental

Vapour pressure measurements were made using the apparatus described previously [11,12], using a calibrated, electronic manometer. Large crystals were taken from mother liquor, blotted dry, transferred rapidly to the cell and traces of solvent removed by careful evacuation.

Differential scanning calorimetry used a Perkin Elmer DSC1b instrument as described in earlier papers [12,13]. Experiments were carried out at atmospheric pressure under nitrogen flowing at  $30 \text{ cm}^3 \text{ min}^{-1}$ , heating at  $8.33 \text{ K min}^{-1}$ . Care was taken to avoid build-up of pressure in the d.s.c. capsules, which can produced misleading results when a component is vaporising rapidly. 1-10 mg of dried crystals (as above) were loaded into aluminium pans, crushed and weighed before transfer to the furnace.

## Results and Discussion

The results of vapour pressure measurements and differential scanning calorimetry are given in Tables-1 and 2. Although both these techniques measure the enthalpy of thermal decomposition reaction such as:



it is not unusual for different reactions to occur. Vapour pressures are measured at equilibrium, in a closed system. In the d.s.c. experiment

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Table-1: Vapour Pressure Experiments

	$\Delta H/\text{kJmol}^{-1}$	$\Delta S/\text{JK}^{-1}$	$-\Delta G/\text{kJmol}^{-1}$
Quinol-1,4-dioxan [1:1]			
Low T reaction	$129.2 \pm 0.5$	$430 \pm 10$	$17.7 \pm 0.3$
High T reaction	$69.0 \pm 0.6$	$283 \pm 11$	$15.4 \pm 0.3$
Quinol-bis(cineole)	$33.2 \pm 0.5$	$167 \pm 10$	$16.6 \pm 0.4$
1,8-cineole (liquid)	$47.8 \pm 0.5$		

the temperature is changing, typically at  $8$  or  $16^\circ\text{min}^{-1}$ , the volatile product is vented and equilibrium is never established. Different decomposition processes are most likely to occur for systems where alternative structures and stoichiometries are readily available. For any one process the measured enthalpy is the difference in lattice enthalpy between *Complex* and *Involatile Species*. This difference includes changes in packing energy, hydrogen bonding and other interactions and the volatilisation of the *Volatile Species*.

Thermal decomposition of the quinol-bis(1,8-cineol) and quinol-1,4-dioxan complexes gave different results from the two techniques in each case. For quinol-bis(1,8-cineol) the d.s.c. experiment showed cineol to be completely released during two broad overlapping endotherms with maxima about  $338$  and  $363$  K. The enthalpy for these processes combined was  $47.9$  kJ per mole of cineol released. This is very close to the enthalpy of vaporisation of cineol,  $47.8$   $\text{kJmol}^{-1}$ . The boiling point of cineol is  $449.4$  K at atmospheric pressure, with a vapour pressure at  $334$  K of  $14.0$  Torr. The vapour pressure of quinol-bis(1,8-cineol) at this temperature is  $4.0$  Torr. The complex gave a linear  $\log p$  vs.  $1/T$  relationship over the range  $329 - 345$  K, giving an enthalpy of  $33.2$  kJ per mole of cineol lost.

Table-2: Differential Scanning Calorimetry

	$\Delta W_{\text{expt}}$ %	$\Delta W_{\text{Th}}$ %	D.S.C. T1/K	Experiments T2/K	$\Delta H/\text{KJmol}^{-1}$
Quinol-1,4-dioxan[1:1]	$43.0 \pm 0.6$	$44.44$	$308$	$346$	$35.4 \pm 0.9$
Quinol-bis(cieole)	$74.0 \pm 0.9$	$73.7$	$323$	$338.363$	$47.9 \pm 0.8^*$

T1 was minimum temperature at which decomposition was detected.

T2 was the peak temperature of the endotherm.

$\Delta H$  is quote "per mole of donor released"

$\Delta W$  represents weight loss to quinol.

$\Delta H$  for the overlapping endotherms combined.

In the d.s.c. the first feature of the quinol-(1,4-dioxan) system was an endotherm with a maximum at  $346$  K, corresponding to the loss of all the dioxan, with an enthalpy of  $35.4$   $\text{kJmol}^{-1}$ . The remaining quinol gave a sharp endotherm of fusion with a maximum at  $448$  K, in good agreement with the literature melting point of  $443.5$  K. (The maximum rate of fusion in d.s.c. measurements always occurs slightly above the conventional "melting point"). If the d.s.c. experiment was carried out in a cell which was not freely vented the complex melted in a sharp endotherm at  $358$  K. Loss of dioxan then occurred gradually between  $370$  and  $435$  K.

However the vapour pressure data showed two processes occurring at low temperature. As each fresh sample was heated the slope of the  $\log \lambda$  vs.  $1/T$  graph fell to about half its previous value with a transition temperature of  $315$  K (Fig. 1). If the temperature was then reduced and equilibrium re-established, points were obtained extrapolating the high-temperature line down from  $315$  K. Data were obtained to  $304$  K. The stability of this equilibrium was indicated by re-heating the cooled samples and obtaining further points lying on the same line. The transition at  $315$  K appears to represent a change of structure and not a change of stoichiometry. Weight loss experiments confirmed that the dry, crystalline material above  $315$  K is still quinol-dioxan (1:1). In the initial run on a fresh sample there was no evidence of sudden loss of dioxan at the transition temperature. Dioxan which had been released was not re-absorbed rapidly on cooling.

The interpretation of these observations is not simple. The enthalpy change from starting material to product must be independent of route. The d.s.c.

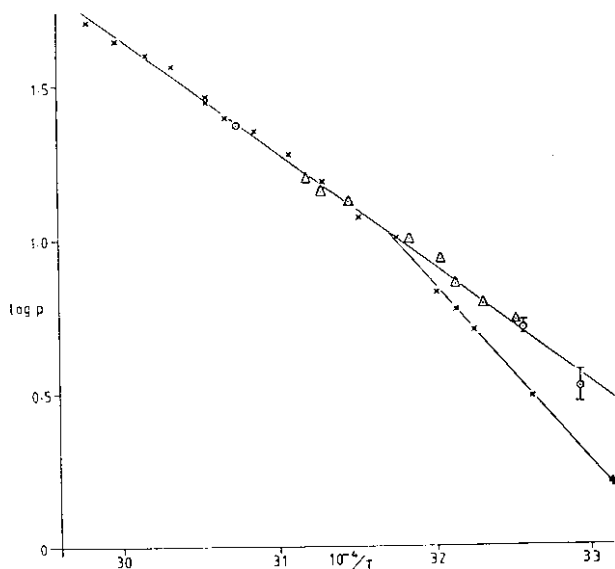
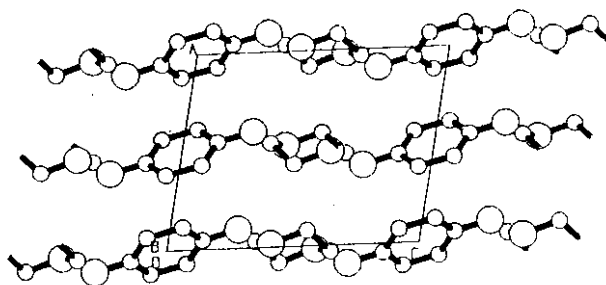


Fig.1: Log vapour pressure as a function of  $1/T$  for the quinol-1,4-dioxan system. All data points refer to one experiment. Points during the initial heating are shown as crosses, circles indicate points obtained on cooling and triangles mark points observed during a second heating of the sample.

experiment has the drawback that it will underestimate  $\Delta H$  for a gradual process difficult to separate from the baseline and also for a sample which has partially decomposed as the experiment is assembled, whereas vapour pressure measurements are valid as long as sufficient starting material remains to establish equilibrium. This explanation cannot be correct for quinol-bis (1,8-cineole) because the higher  $\Delta H$  was observed from the d.s.c. Probably the reaction seen in the vapour pressure experiment involves the formation of the (1:1) complex which decomposes at higher temperature under equilibrium conditions to leave quinol. In the d.s.c. the two processes occur at similar temperature, giving the overlapping endotherms which were observed.

It is not uncommon to find a process of low  $\Delta H$  replaced by one of higher  $\Delta H$  on raising the temperature (see, for example,  $\text{NaI} \cdot 3\text{dx}$  [12]) but quinol-dioxan shows the converse, which is most unusual. The transition at 315 K is a structural rather than a stoichiometric change since no sudden change in composition was detected. It could be that the chains with two hydrogen-bonds per dioxan (Fig. 2a) are replaced by isolated (1:1) units (Fig. 2b) with a single hydrogen-bond. This structure could well pack less efficiently than the chains so producing the lower  $\Delta H$ .

QUINOL - DIOXAN



QUINOL - DIOXAN

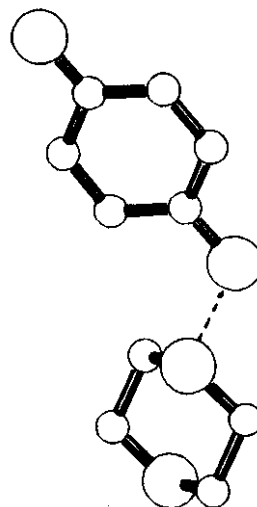


Fig. 2: a. Quinol-1,4-dioxan chains in the crystal structure [7].

b. Possible isolated quinol-1,4-dioxan complex in the high temperature form.

There is no obvious explanation of why the  $\Delta H$  from the d.s.c. experiment should be so much lower than the vapour pressure value. As with the cineole complex, the d.s.c. value is very close to the  $\Delta H$  of vaporisation of dioxan,  $37.5 \text{ kJmol}^{-1}$  [11].

Following Drago [14], enthalpies of liquid-phase reactions of Lewis acids with Lewis bases can be estimated as sums of electrostatic and covalent terms. Applying tabulated values of the parameters we obtained  $\Delta H$  for the reaction of dioxan and phenol as  $23.3 \text{ kJmol}^{-1}$  and for phenol with tetrahydropyran  $25.3 \text{ kJmol}^{-1}$ . No data are available for quinol. These values cannot be compared directly with the lattice enthalpy changes discussed in this paper except to serve as minimum values.

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