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Desolvation of *trans*-9,10-Dihydroxy-9,10-diphenyl-9,10-dihydroanthracene · Cyclohexanone: Kinetic Compensation Effect

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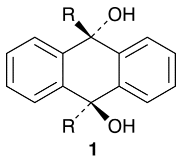
The crystal structure and thermal analysis of the inclusion compound with host:guest ratio of 1:2 formed between *trans*-9,10-dihydroxy-9,10-diphenyl-9,10-dihydroanthracene and cyclohexanone are reported; the kinetics were investigated for various particle sizes and experimental conditions and it was shown that a compensation effect exists between the Arrhenius parameters.

Diol host compounds based on the substituted *trans*-9,10-dihydroxy-9,10-dihydroanthracene moiety (**1**) form a variety of inclusion compounds with both aromatic and aliphatic guest molecules.[1–4] We now present the results of the crystal structure, thermal analysis and kinetics of the decomposition of the inclusion compound formed between *trans*-9,10-dihydroxy-9,10-diphenyl-9,10-dihydroanthracene and cyclohexanone (DACH). The kinetics were analysed by isothermal decomposition runs at selected temperatures, and curve fitting techniques allowed us to select suitable models to describe the desolvation mechanism and derive the appropriate Arrhenius parameters. In general the kinetics of decomposition of organic inclusion compounds have not received a great deal of attention. This may be owing to the fact that the decomposition often involves multiple steps, with the formation of new intermediate host–guest phases, whose composition and structure are not readily established. Recently we discussed the relationship between the crystal structure and desolvation kinetics of a series of related inclusion compounds.[5]



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Scheme 1

Single crystal diffraction data were measured on an Enraf-Nonius CAD4 diffractometer. The structure was solved using direct methods with SHELXS-86[6] and refined using least-squares refinement on F^2 with SHELXL-93.[7] The inclusion compound crystallises in the triclinic space group $P\bar{1}$, with $Z = 1$. A host:guest ratio of 1:2 was obtained from thermal analysis. This required the host molecule to be located in a special position, with its molecular centre at a centre of inversion. The guest was located in a general position, with the carbonyl oxygen disordered over two positions, with site occupancies of 60 and 40% respectively. The packing of host molecules results in the formation of channels running parallel to [001], along which the guest molecules reside. The topologies of the channels can be seen in Fig. 4, where the area occupied by the host is represented by a hatched area, and the guest atoms are presented with van der Waals radii. These channels, running along [001], vary in diameter between ~5.5 and ~4.5 Å. The crystal data and refinement parameters are summarised in Table 1.

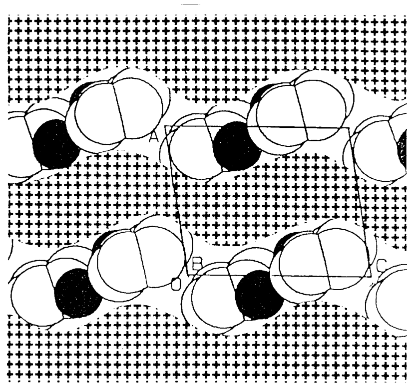

Fig. 4 A cross section of the host molecules of DACH, viewed along [010], cut at $y = 0$, showing channels parallel along [001]. The hatched area represents that occupied by the host, while the guest is presented with van der Waals radii with oxygen atoms shaded

The kinetics of desolvation of the inclusion compound DACH were investigated using three different instruments under isothermal conditions, namely a quartz microbalance (QMB), a levitation balance and TG. The resultant extent of reaction (α) *versus* time curves all showed markedly long induction periods, followed by the main section. The reaction coefficient (k) for the induction period was assumed to be $1/t_i$, where t_i is the length of the induction period, and hence the Arrhenius parameters for the induction periods could be evaluated for all three of the experimental setups. The activation energy for the induction period varied between 97 and 117 kJ mol^{-1}. The main

Table 1 Crystal data, experimental and refinement parameters

Molecular formula	$C_{26}H_{20}O_2 \cdot 2C_6H_{10}O$
Relative molecular mass	560.70
Space group	$P\bar{1}$
a (Å)	8.741(3)
b (Å)	9.008(3)
c (Å)	10.863(7)
α (°)	112.30(6)
β (°)	93.290(6)
γ (°)	101.14(3)
Z	1
Volume (Å^3)	768.5(4)
Density (calc.) (g cm^{-3})	1.212
$F(000)$	300
μ(Mo-Kα) (cm^{-1})	0.77
Crystal dimensions (mm)	0.2 × 0.3 × 0.3
Range scanned θ(°)	2.05–24.97
Range of indices h, k, l	−10,10; −10,9; 0, 12
No. of reflections collected	2855
Reflections observed [$I_{rel} > 2\sigma(I_{rel})$]	1469
No. of restraints/parameters	3/206
$R1/wR2$ [$I_{rel} > 2\sigma(I_{rel})$]	0.0797/0.2374
Extinction coefficient	0.09(2)
Max. and min height in electron density map (e Å^{-3})	0.459, −0.191
GOF S	1.053

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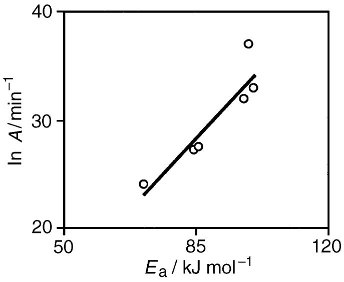

Fig. 10 Compensation behaviour for the desolvation of DACH

section of the reaction was found to be sigmoidal in the QMB experiments, following the Avrami–Erofe'ev model (A4), but deceleratory in all other cases, following the contracting area model (R2). The activation energies obtained from the main section ranged between 71 and 100 kJ mol^{-1}.

In the studies of the thermal desolvation of DACH, three powdered samples of different particle size and pretreatment were studied by means of isothermal TG (with N_2 gas flow). These isothermal TG experiments, unlike those carried out without purge gas, did not show the existence of an induction period, and also followed the R2 reaction mechanism. The activation energies obtained for these reactions varied from 85 to 98 kJ mol^{-1}, depending on particle size and pre-treatment.

In the kinetic studies of the desolvation of inclusion compound DACH, the apparent values of E_a and ln A were found to change with sample preparation and different experimental conditions, showing the mutual interdependence between the two Arrhenius parameters. A plot of ln A *versus* E_a, obtained for the main section of the reaction from all the kinetic experiments performed is shown in Fig. 10. it is clear that an approximately linear relationship exists between the Arrhenius parameters. From the plot the values of the isokinetic temperature (T_{iso}) and rate coefficient (k_{iso}) were found to be 331.4 K and 0.069 min^{-1} respectively. We have observed that the presence of N_2 purge gas reduced the induction period of the reactions. This would imply that the presence of N_2 gas accelerates nucleation, giving rise to deceleratory desolvation curves. The variation in both the experimental and physicochemical factors, *e.g.* the experimental conditions, sample pretreatment and size distribution, influence the kinetics of the process. This is detected as a change in the shape of the α-time curves. Such changes in the α–time curves result in distortion of the kinetic parameters and their subsequent interdependence. The establishment of the kinetic compensation effect illustrates that, irrespective of experimental technique and conditions, a temperature (T_{iso}) exists at which the rate coefficients of all the different reactions are equal.

Techniques used: Differential scanning calorimetry, thermogravimetric analysis, single crystal X-ray diffraction

References: 20

Table 2: Atomic co-ordinates and equivalent isotropic displacement parameters (Å^2) for DACH

Table 3: Bond lengths (Å) and angles (°) for DACH

Table 4: Kinetic parameters for the isothermal desolution of DACH obtained by means of different methods

Table 5: Kinetic parameters for the desolvation of DACH by means of conventional TG, using samples prepared by different methods

Fig. 1: TG and DSC curves of compound DACH

Fig. 2: Disorder modelled in cyclohexanone

Fig. 3: Projection down [010]. The guest molecules are only shown with O(1GA)

Fig. 5: α–time curves obtained at 25, 30, 35, 40 and 45 °C for the desolvation of DACH on the quartz microbalance

Fig. 6: The least-square plot of (a) ln $1/t_i$ *versus* $1/T$, (b) ln k *versus* $1/T$

Fig. 7: Arrhenius plot for the desolvation of DACH on the levitation balance

Fig. 8: Arrhenius plots for the desolvation of DACH on the TG without nitrogen purge gas

Fig. 9: The weight loss (%) *versus* time curves for the desolvation of DACH by means of isothermal TG using different samples at 40 °C

Fig. 11: Schematic representation of the procedure of the desolvation of DACH kinetics

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