

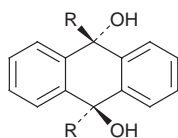
Thermal Stabilities and Kinetics of Desolvation of Related Inclusion Compounds of *trans*-9,10-Dihydroxy-9,10-diphenyl-9,10-dihydroanthracene†

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The kinetics of desolvation of the inclusion compounds formed between the diol host and 2-, 3- and 4-methylcyclohexanones show a compensation effect in their Arrhenius parameters.

Organic molecules that form crystalline host–guest inclusion compounds have been studied extensively.¹ Hosts containing the hydroxy moiety often form remarkably stable inclusion compounds with guests capable of participating in hydrogen bonding. One such diol host compound is *trans*-9,10-dihydroxy-9,10-diphenyl-9,10-dihydroanthracene (DDDA), as shown in Scheme 1, which forms a variety of inclusion compounds with both aromatic and aliphatic guest molecules.^{2–5} The enclathration and desolvation kinetics of this host have been studied with acetone,⁶ 1,3-dioxolane⁷ and cyclohexanone.⁸ The crystal structures of the inclusion compounds of DDDA with 2-methylcyclohexanone (DA2M), 4-methylcyclohexanone (DA4M)² and cyclohexanone (DACH)⁸ have been elucidated. Lattice enclathration has been successfully used in the separation of close isomers.^{9,10}



Scheme 1 R = phenyl(DDDA)

We now report the thermal analysis and kinetics of desolvation of the inclusion compounds with the three methylcyclohexanone isomers. We also present the results of competition experiments carried out between mixtures of cyclohexanone and the methylcyclohexanone isomers.

Experimental

All the samples were obtained by exposing pre-sieved samples of the unsolvated host to the vapour of the chosen guest. X-Ray powder diffraction was used to confirm that the inclusion compound was formed, since a phase change takes place upon formation of the inclusion compound. Thermal analysis and competition experiments were carried out as previously described.¹⁰

Results and Discussion

Thermal Analysis.—The thermal analysis results are summarised in Table 1. From the analysis of the thermogravimetric results it was established that inclusion compounds with host:guest ratios of 1:2 were formed which desolvated in a single step. In the DSC traces the guest loss reaction corresponds to a single endothermic peak at onset temperatures well below the melting point of the host. It has been suggested¹ that the relative stability of an inclusion compound can be measured as the difference between the onset temperature of guest release (T_{on}) and the boiling point of the guest (T_b). All four inclusion compounds desolvate at temperatures below the boiling point of the solvent. From the values of $T_{on} - T_b$ the inclusion compounds formed with DACH and DA4M appear to be more stable than those with DA2M and 3-methylcyclohexanone (DA3M). A sharp endothermic peak at 256–262 °C was attributed to the melt of the host compound. In all cases, upon guest desorption, the host compound reverts to the same structure, the α -phase. Therefore the ΔH values of guest release were standardised based on their melting point enthalpies. The standardised enthalpy values are shown in Table 1.

Kinetics of Desolvation.—The kinetics of desolvation of the three inclusion compounds were studied by means of conventional isothermal TG. Series of isothermal TG experiments were carried out over appropriate temperature ranges. Plots were obtained for the extent of reaction, α , versus time [$\alpha = (m_0 - m)/(m_0 - m_f)$, where m_0 is the initial mass and m_f the mass of the sample when the reaction is complete]. All the curves were deceleratory and uniquely described by the contracting area kinetic model (R2): $1 - (1 - \alpha)^{1/2} = kt$.¹¹ The Arrhenius parameters were obtained over an α range of 0 to 0.95 with correlation coefficients between 0.991 and 0.999. All the plots of $\ln k$ versus $1/T$ and kinetic results are shown in Fig. 1 and Table 2 respectively.

Table 1 Thermal analysis results

Code	Guest	$T_{on}/^{\circ}\text{C}$	$(T_{on} - T_b)/^{\circ}\text{C}$	$\Delta H/\text{kJ mol}^{-1}$	Mass loss(%)	
					exp.	calc.
DACH ⁸	Cyclohexanone	128.5	–27.1	35.5	34.3	35.0
DA2M	2-Methylcyclohexanone	81.4	–81.1	39.1	37.7	38.1
DA3M	3-Methylcyclohexanone	80.3	–88.2	53.5	37.8	38.1
DA4M	4-Methylcyclohexanone	108.9	–61.1	51.1	37.9	38.1

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The activation energies obtained for the different desolvation reactions were in the range of 79–101 kJ mol^{–1}, with the desolvation of DA4M showing the lowest activation energy and DA3M the highest.

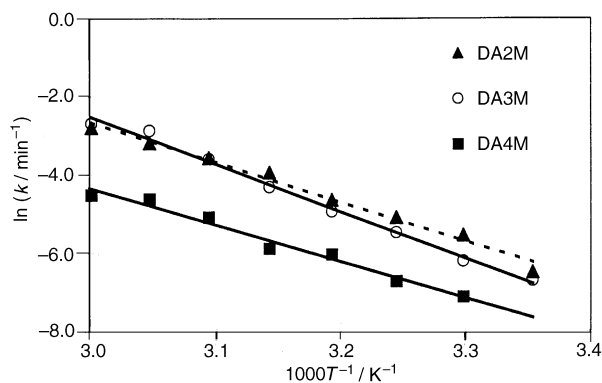


Fig. 1 Arrhenius plots of $\ln k$ versus $1/T$ for the desolvation of DA2M, DA3M, DA4M

Table 2 Kinetic parameters of isothermal desolvation investigated by means of isothermal TG

Code	Temp. range/°C	E_a /kJ mol ⁻¹	$\ln A$
DACH ⁸	25–60	86 (3)	27.5 (1)
DA2M	25–60	85 (4)	28.1 (2)
DA3M	25–60	101 (3)	33.9 (1)
DA4M	30–60	79 (5)	24.1 (2)

It is a well known phenomenon that, for a group of related reactions, a linear relationship exists between E_a and $\ln A$. This is called the kinetic compensation effect¹² and is expressed in general as follows:

$$\ln A = bE_a + c$$

where b and c are constants (for the reaction with DACH⁸, $b = 0.36 \text{ mol kJ}^{-1}$, $c = -2.67$). This effect has been observed both for heterogeneous and homogeneous reactions. Zsako *et al.*¹² have suggested that the parameter b characterises the strength of the bond to be broken, and c is related to the structure of, and defects in, the starting reactant.

For the desolvation of all four inclusion compounds the Arrhenius parameters show an approximately linear relationship, as illustrated in Fig. 2. Hence the compensation behaviour exists between the Arrhenius parameters for these four related reactions.

Competition Results.—Competition experiments were conducted between two-component guest mixtures. The results for the competition experiment between mixtures of cyclohexanone and 2-methylcyclohexanone, 3-methylcyclohexanone and 4-methylcyclohexanone are shown in Fig. 3.

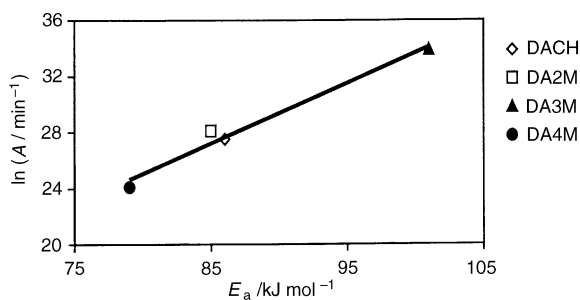


Fig. 2 Compensation behaviour observed for the desolvation of all four inclusion compounds

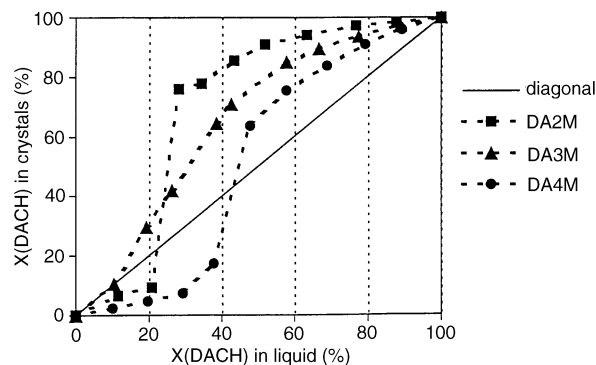


Fig. 3 Results of the competition experiments carried out between two-component mixtures of cyclohexanone and the methylcyclohexanones

Conclusion

Previous kinetic studies on channel type organic inclusion compounds formed by related hosts showed that the activation energies of desolvation fall between 58 and 151 kJ mol⁻¹.¹³ The activation energies of desolvation obtained in this study fall in the range observed for inclusion compounds where the guests are located in channels with no physical barriers to their diffusion out of the host lattice.

The same reaction mechanism, that of the contracting area geometrical model (R2), was observed for all four desolvation reactions. It comprises a phase-boundary controlled reaction, of which the rate is determined by two-dimensional growth of the product interface at a constant velocity on cylindrical particles. Compensation behaviour was observed for the kinetics of desolvation of the four different inclusion compounds, using the same apparatus and experimental conditions. In this case a linear relationship exists between the Arrhenius parameters. The existence of the compensation effect confirms that these four desolvation reactions are similar with respect to the types of bonds to be broken.

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