Kinetics of Inclusion

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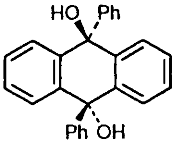
The kinetics of inclusion of acetone vapour by an organic diol host have been measured as a function of temperature and vapour pressure of acetone.

Studies on the kinetics of inclusion have concentrated mainly on inorganic hosts.[1] Recently a new experimental technique has been described which allows the measurement of the velocity of intercalation reactions in systems of layered host and liquid guest.[2] However, the kinetics of inclusion between solid organic hosts and vapour guest molecules has received little attention, because the measurements are experimentally difficult and the inclusion compounds formed are often unstable under ambient conditions.

We have constructed an automated balance system which allows measurement of mass change with time under controlled conditions of pressure and temperature.[3] The apparatus is particularly suitable for the study of reactions of the kind shown in Scheme 1 where H is a solid organic host and G is a volatile guest. The host–guest compound (β-phase) is often unstable at room temperature and decomposes with loss of guest molecules, usually with concomitant rearrangement of the host compound to the non-porous α-phase. We have studied a number of such systems, elucidated their crystal structures and measured their thermal properties.[4–6] We now present the results of the kinetics of formation between the organic host *trans*-9,10-dihydroxy-9,10-diphenyl-9,10-dihydroanthracene **1** and acetone vapour.

$$\mathrm{H(s,\alpha)} + n\mathrm{G(g)} \rightleftharpoons \mathrm{HG}_n\mathrm{(s,\beta)}$$

Scheme 1



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Kinetic measurements were carried out by exposing finely powdered host compound (sieved fraction 63–125 μm) to acetone vapour at various pressures and recording the mass increase with time. Typical isothermal kinetic curves are shown in Fig. 1. The interesting feature of the kinetics is that for a given pressure of acetone vapour, the rate of reaction decreases with increasing temperature. This is illustrated in Fig. 2 which shows the kinetic results at an acetone pressure of 91 mmHg at 293 and 303 K. We fitted the kinetic results to the first order equation and derived values for the rate constants k_{obs}. We noted that in order for the host in the α-phase to combine with acetone, a threshold vapour pressure P_0 of the guest was required. Values of $P_0(T)$ at different temperatures were derived by plotting the rate constant k_{obs} against the vapour pressure of the guest. This is shown in Fig. 3. The experimental results are consistent with the rate law $\ln(1 - \alpha) = k_f[(P - P_0)/P_0]t$ from which we derived values of the rate constants k_f for the forward reaction. A plot of $\ln k_f$ *versus* T^{-1} yielded a value of 26.8 kJ mol^{-1} for the activation energy. We interpret the threshold pressures $P_0(T)$ as the equilibrium pressures for the reaction shown in Scheme 2, for which $K_p = P_0^{-2}$. A plot of $2\ln P_0$ *vs.* T^{-1} yielded a straight line with $\Delta H = -94.1$ kJ mol^{-1}, the enthalpy of the reaction for guest inclusion.

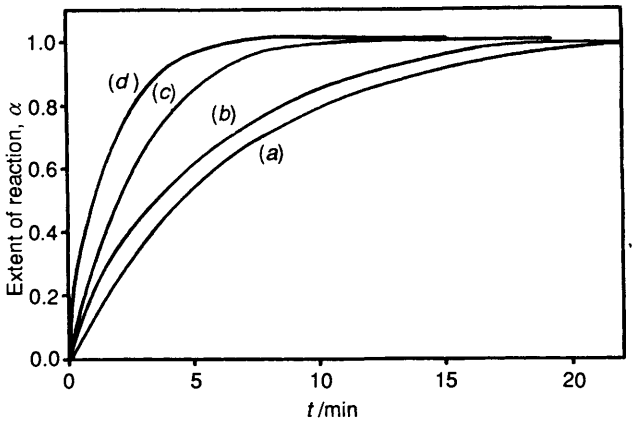

Fig. 1 Kinetic curves of extent of reaction (α) *versus* time (*t*) at 248 K, under pressures of (*a*) 44, (*b*) 48, (*c*) 69 and (*d*) 122 mmHg, acetone

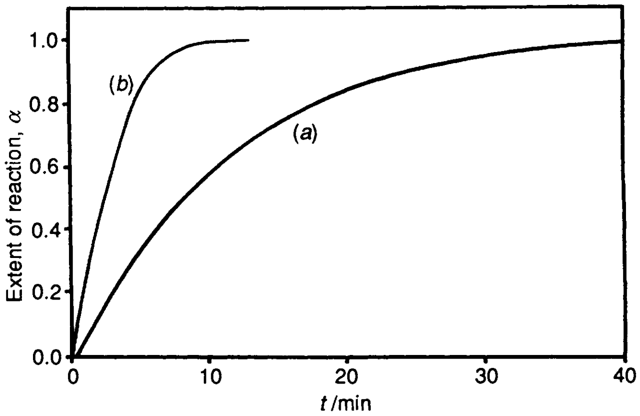

Fig. 2 Kinetic curves at guest vapour pressure 91 mmHg, at (*a*) 293 and (*b*) 303 K

$$\mathrm{H(s,\alpha)} + 2\mathrm{Acetone(g)} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \mathrm{H{\cdot}Acetone_2(s,\beta)}$$

Scheme 2

The crystal structure of the non-porous α-phase of the host has been elucidated[7] and does not exhibit hydrogen bonding. We have determined the crystal structure of the host·acetone$_2$ inclusion compound by diffraction methods using single crystals grown from a solution of the host in acetone. This structure shows that the acetone guest molecules lie in channels. There is a hydrogen bond between the hydroxy moieties of the host and the carbonyl oxygens of the acetone, with an O··· O distance of 2.79 Å. A projection of the structure is shown in Fig. 4.

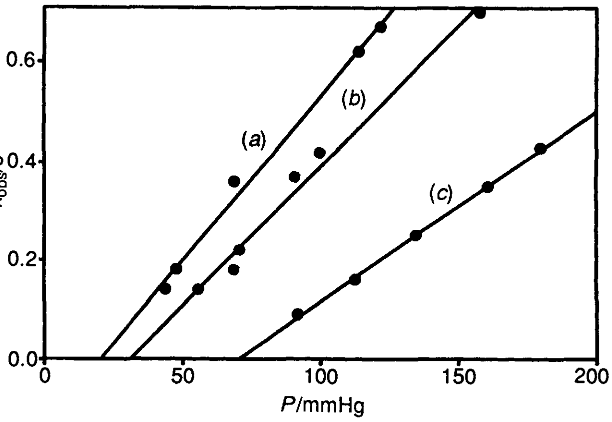

Fig. 3 Plot of observed rate constant *versus* guest vapour pressure, yielding $P_0(T)$ values at (*a*) 284, (*b*) 293 and (*c*) 303 K

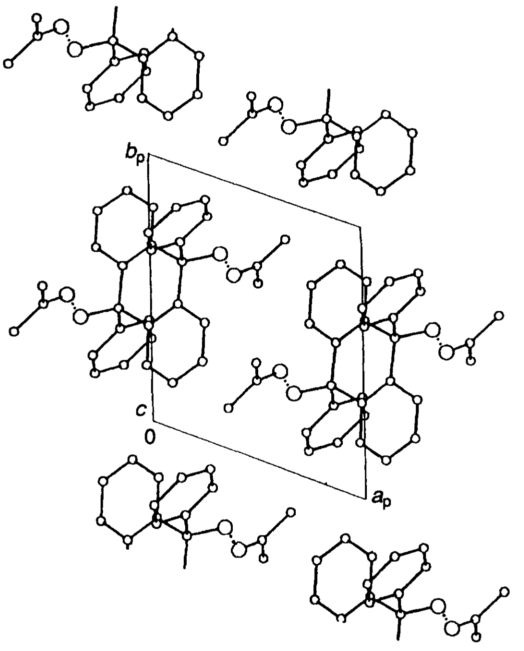

Fig. 4 Projection along [001] for the structure of the inclusion compound

We measured the X-ray powder diffraction patterns of both the α- and β-phases and matched them successfully with those calculated from the coordinates obtained from the crystal structures using the computer program LAZY PULVERIX.[8]

We have observed this apparent anti-Arrhenius behaviour with other organic host compounds which include guests from the pure vapour phase and suggest that this may be a general phenomenon when the process of inclusion is associated with a phase change to a new crystal structure.

Crystal data.—$C_{26}H_{20}O_2{\cdot}2C_3H_6O$, M_r = 480.60, triclinic, space group $P\bar{1}$, a = 8.689(14), b = 9.466(6), c = 9.448(6) Å, α = 92.60(5), β = 114.85(9), γ = 107.46(9)°, V = 659(1) Å^3, $Z = 1$, $D_m = 1.20$, $D_c = 1.21$ g cm^{-3}, crystal size = 0.28 × 0.28 × 0.56 mm. Intensity data were collected at room temperature on an Enraf–Nonius CAD4 diffractometer using Mo-Kα (λ = 0.7107 Å) radiation to θ_{max} = 23°; 2055 unique reflections were collected. The structure was solved and refined using the SHELX-76 program.[9] The least squares refinement converged to a final R = 0.085 for 1673 reflections with $I > 2\sigma(I)$; R_w = 0.098 with $w = (\sigma^2F + 7.4 \times 10^{-4} F^2)^{-1}$. Residual electron density (max, min) = 0.36, −0.34 e Å^{-3}. All heavy atoms were treated anisotropically and hydrogen atoms were refined with geometrical constraints. The hydroxy hydrogen was located unambiguously in a difference electron density map and refined with a constrained bond length. The guest atoms were located routinely, and they refined uneventfully, yielding acceptable bond lengths and angles.

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