

Activation Energy for the Dehydration of Nickel Oxalate Dihydrate

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Summary Extrapolation of rate data for the dehydration of nickel oxalate dihydrate to conditions of zero mass of sample yields data uninhibited by water vapour and an energy of activation of $31.0 \text{ kcal mol}^{-1}$ which is significantly greater than existing values.

EXPERIMENTAL difficulties such as self-cooling^{1,2} and effects due to water vapour^{1,3-5} complicate the determination of kinetic parameters for the dehydration of solid hydrates. Early workers, such as Smith and Topley,¹ corrected their data for an effect due to water vapour by accounting for the lack of free flow of water through the anhydride produced. A more prevalent type of water inhibition which occurs at or near the hydrate-anhydride interface causes rate decreases when small water vapour pressures are introduced into the reaction vessel.⁴ It has been tacitly

assumed that this inhibition does not occur "*in vacuo*"^{6,7} *i.e.*, under conditions where the water vapour from dehydration is continually removed. We report that for the dehydration of nickel oxalate dihydrate this assumption is invalid.

Small samples of finely powdered nickel oxalate dihydrate (NOD) were spread on to an aluminium pan which was suspended on to a quartz helix balance in a vessel connected to vacuum pumps through wide-bore tubing. During dehydration the reaction vessel was opened directly to the pumps and a McLeod gauge (*ca.* 100 cm from the sample) normally indicated 10^{-6} Torr. The curves of α *vs.* time obtained (α is the fraction of dehydration) were linear from $\alpha = 0$ to $\alpha = 0.45$. This linear region may be taken to be proportional to the fundamental rate constant for interfacial penetration.⁸

The rate of dehydration *in vacuo* was a function of the mass of sample employed (Figure). A Pirani gauge, calibrated for water vapour, was then placed adjacent to the sample. During dehydration *in vacuo*, small water vapour pressures were measured, e.g., a pressure of 1.1 Torr was noted for a 2 mg sample (110 °C). For samples of ≤ 3 mg, the steady-state, maximum water vapour pressure observed was proportional to the mass. A plot of $1/k$ against mass, m , was linear for small values of mass and gave a value of $k_{m \rightarrow 0}$, where $k = (d\alpha/dt) \times 100$ (inset in Figure). Complete kinetic runs were performed with samples as small as 0.2 mg, and extrapolations to zero mass, (Figure) were made at a series of temperatures between 85 and 124 °C. Below 85 °C, rate was independent of sample size (≤ 3 mg). Self-cooling^{1,3} is unimportant below 85 °C because of the slow rates of dehydration, e.g., at 60 °C, 50% dehydration took 5,000 min. The mass-extrapolated data and the low temperature data (< 85 °C) fell approximately on to the same Arrhenius line, i.e., the energies of activation, E_a , were 31.6 and 30.4 kcal mol⁻¹ respectively. The average value of 31.0 kcal mol⁻¹ taken as E_a for this reaction. Danes and Ponec⁹ found an E_a of 10 kcal mol⁻¹ for dehydration of NOD "in vacuo" (152°–177 °C). Jacobs and Kureishy¹⁰ determined E_a from the initial rates without removal of water vapour and obtained 18.4 kcal mol⁻¹ (172°–223°). Shkarin and his co-workers¹¹ used both DTA (240°–360 °C) and isothermal techniques (180°–240 °C) and got in each case a value for E_a of 23 kcal mol⁻¹ in air and nitrogen. The increased value of E_a obtained by us is significant because the dehydration process is now clearly anomalous,^{8,12} i.e., the pre-exponential factor does not agree with that predicted by the Polanyi–Wigner equation.^{13,14}

The initial rates of dehydration observed in the previous studies are all at least a factor of 10^{-3} smaller than those obtained by extrapolation of the Arrhenius plot from our results. Fine powder was used in all cases. Differences in the rates of dehydration caused by topographical variations amongst the samples cannot be estimated from available data on NOD, but can be obtained from rate data for the interfacial dehydration of manganous formate dihydrate.^{8,15} Individual single crystals (ca. 1 mm³) dehydrate about 18 times more slowly than fine powder. The rates of dehydration of the dihydrate powder prepared in different laboratories are different by a factor of five.^{8,15} These comparisons suggest that the maximum variation in

rates of dehydration of different preparations of NOD powder is ca. 10. Therefore the rates of the previous investigations^{9–11} are too small by a factor of at least 100.

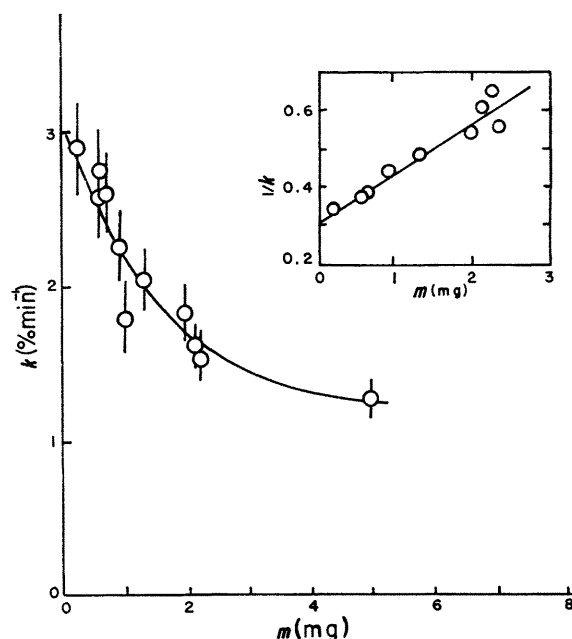


FIGURE Dependence of the rate of dehydration of nickel oxalate dihydrate (fine powder) upon the mass of sample employed (110 °C) in vacuo. $k = (d\alpha/dt) \times 100$; $m =$ mass of sample. Inset. Data of the Figure plotted as $1/k$ vs. m , with extrapolation to zero mass.

The severity of the inhibition is shown by the fact that the rate (110 °C) was reduced by a factor of 24 (compared to the mass-extrapolated value) in an ambient water vapour pressure of only 0.04 Torr; at 110 °C the equilibrium pressure is 1.0 Torr.¹⁶ Inhibition can be a factor in either isothermal or thermoanalytical techniques, and may be particularly significant in the latter, where the ambient water vapour is often ill-defined owing to the rapid evolution of water in a relatively poor vacuum or owing, in the presence of air or inert gas, to the hindrance of the free diffusion of water vapour away from the sample.

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