

The Hydration of Indane-1,2,3-triones and Related Triones

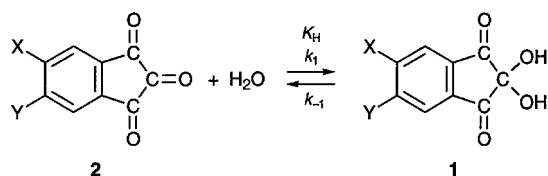
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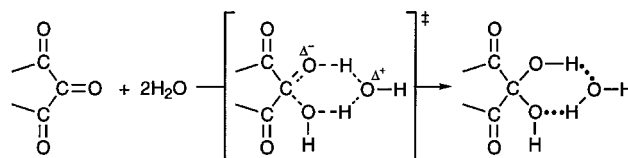
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A series of 5-mono- and 5,6-di-substituted indane-1,2,3-triones, phenalene-1,2,3-trione and 1,3-diphenylpropane-1,2,3-trione form 2,2-dihydroxy-1,3-dione hydrates; the rates for the uncatalysed hydrations were measured and the structure of the transition state is elucidated from activation parameters, the kinetic role of water, and solvent isotope and substituent effects.

The hydration of mono- and di-substituted indane-1,2,3-triones (**2**), as well as of phenalene-1,2,3-trione and 1,3-diphenylpropane-1,2,3-trione, was investigated. The equilibrium constants and rate coefficients for mono-hydration, K_H and k_1 , respectively, to form the substituted 2,2-dihydroxyindane-1,3-diones (**1**) were estimated or measured. The results from ^1H NMR and UV–VIS spectroscopic studies indicate that, in 0.7–96.7% (v/v) dioxane–water, the triones are almost completely (*i.e.* >98%) hydrated, *cf.* ref. 2.



The rate coefficients, k_1 , for the uncatalysed hydration in dioxane–water (96.7%, v/v) were measured at 25.0, 35.0 and 45.0 °C. The activation parameters were evaluated with ΔH^\ddagger between 4.0 and 6.6 kcal mol $^{-1}$ and ΔS^\ddagger between –54 and –46 cal mol $^{-1}$ K $^{-1}$. The effect of water content on the hydration rates in aqueous dioxane at 25.0 °C was studied. A plot of $\log k_1$ against $\log [\text{H}_2\text{O}]$ was linear with a slope of 2.06. The kinetic solvent isotope effect, $k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}}$, in dioxane–water (96.7%, v/v) was found to be 1.65 for **2a** (X = Y = H). These results indicate two strongly hydrogen-bonded water molecules in the transition state and are very similar to the results found for dialdehydes.⁵ The application of a modified Hammett equation to the hydration of **2** gave a Hammett reaction constant (ρ) of *ca.* 1.05 in 96.7% aqueous dioxane at 25.0 °C. The latter indicates a significant extent of negative charge development at the reaction site in the transition state, relative to the initial state. A pathway is shown in the Scheme for the hydration of the triones with the transition state having one water molecule attacking the carbonyl group as a nucleophile and a second water molecule acting as a general acid–base catalyst transferring protons.



Scheme

Techniques used: UV–VIS, ^{13}C NMR

References: 25

Scheme: 1

Table 1: ^{13}C NMR chemical shifts for the substituted indane-1,2,3-triones and hydrates in $[\text{D}_6]\text{Me}_2\text{SO}$

Table 2: Rate coefficients (k_1) for the hydration of substituted indane-1,2,3-triones in dioxane–water (96.7%, v/v)

Table 3: Activation parameters for the hydration of substituted indane-1,2,3-triones in dioxane–water (96.7%, v/v) at 30.0 °C

Table 4: Rate coefficients (k_2) for the hydration of indane-1,2,3-trione in aqueous dioxane at 25.0 °C

Table 5: Hammett reaction constants (ρ) for the uncatalysed hydration of indane-1,2,3-triones in dioxane–water (96.7%, v/v) at 25.0 °C

Table 6: The physical constants of the previously unreported substituted 2,2-dihydroxyindane-1,3-diones

Table 7: The physical constants of the previously unreported substituted indane-1,2,3-diones

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