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An isothermal microcalorimetric study of the imidazole catalysed hydrolysis of triacetin and the observed rate constant dependence of triacetin concentration

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Abstract

The imidazole catalysed hydrolysis of triacetin reaction is being used as a standard test method for isothermal microcalorimeters where the reaction parameters, rate constant and enthalpy change are used as the reaction specification. To increase the robustness of the test method and to expand on our intellectual enquiry for the study of reactions by calorimetry, this paper improves upon the previous mathematical model for the reaction. Our findings are that the rate constant determined from the model used in previous studies has a linear dependency on the reciprocal concentration of triacetin. To account for this dependence on triacetin and for the dependence on imidazol, demonstrated by others using the same model, this paper presents a more general mathematical model that can be used to obtain reaction parameters in a broader context. At a fixed concentration of imidazol, a triacetin independent rate constant was determined as $1.91 \times 10^{-7} \pm 1.68 \times 10^{-8}$ dm^3 mol^{-1} s^{-1}.

Keywords: Isothermal microcalorimetry; Triacetin; Kinetic; Rate constant; Order

1. Introduction

The previous publications, detailed below [1–5], on the calorimetric investigations into the solution phase imidazole catalysed hydrolysis of triacetin have focussed on, initially, qualitative then quantitative analysis. In 1982 Chen and Wadsö [1] presented a qualitative method of reaction analysis where the magnitude of the calorimetric signal was correlated to quantities of reactants. In 1995 Willson et al. [2] showed that the calorimetric output (power versus time) could be quantified in terms of kinetic and thermodynamic properties of the reaction. For this general approach, the kinetics and thermodynamic parameters associated with a reaction can be determined by selecting an appropriate mathematical model that describes the calorimetric output [3].

In 2001, Beezer et al. [4] set out a protocol describing an experimental method to harmonise the experimental procedures for running a triacetin experiment in an isothermal microcalorimeter. Hills et al. [5] were the first to challenge the reaction model proposed by Willson et al. [2] when they showed that the rate constant had a dependency on imidazole concentration. It is the aim of this paper to add to the observations of Hills et al. [5] by showing that the rate constant is also dependent on the concentration of triacetin. For both the Hills et al. [5] and this study, it can be shown that the dependency of the rate constant on imidazole and triacetin is minimal at the concentrations stated in the Beezer protocol and insensitive to small variations in concentrations about this concentration. Building upon findings from the previous studies, above, this paper defines the mathematical model in more general terms. The purpose of which is two fold: Firstly this reaction is being used as a standard test method for isothermal microcalorimeters and so the reaction parameters calculated from such studies are required as specifications. As such, variations in reaction concentrations may affect the robustness of the method. Secondly, we wish to show that by using the methods described in this and related publications, such parameters are accessible by calorimetry.

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No mechanistic interpretations of the observations are attempted in this paper except that a more general mathematical model for calorimetric data analysis is proposed.

Where the analytical approach is to apply a mathematical model describing a reaction, it is necessary that the model selected for the analysis is an acceptable representation of the reaction mechanism. The robustness of the model is proven only in the fullness of time where extensive examination shows consistency over a wide range of conditions such as temperature, concentration, pressure, etc. This study illustrates the fact that a model with a limited or unknown scope of application can still be useful providing the context in which it is applied is carefully specified. For previous publications [2,4,5], the concentrations of triacetin use in the studies are 0.259 mol dm^{-3} [2], 0.245 mol dm^{-3} [3] and a range of 0.237–0.240 mol dm^{-3} [5].

2. Interpretation of calorimetric data

In this study, imidazole concentration is kept constant and the concentration of triacetin is varied.

A second order solution phase model was used to analyse the data and is the same model as used in previous publications [2,4,5], Eq. (1) shows the general form of the mathematical model:

$$P = [kt\Delta H^{1-n} V^{1-n}(n-1) + Q^{1-n}]^{n/(1-n)} k\Delta H^{1-n} V^{1-n} \quad (1)$$

where P is power, V is the volume of the reaction solution, n is the reaction order, k is the rate constant and Q and ΔH are the enthalpy change and specific enthalpy change for the reaction. Where $n = 2$ (i.e. a second order reaction), Eq. (1) can be simplified to Eq. (2):

$$P = \Delta HVQ^2 \frac{k}{(ktQ + \Delta HV)^2} \quad (2)$$

Substituting $A \times \Delta H$ for Q in Eq. (2) gives Eq. (3) (where A is the quantity of triacetin used).

$$P = \Delta HVA^2 \frac{k}{(ktA + V)^2} \quad (3)$$

Eq. (3) is the mathematical model used to derive the reaction parameters from the calorimetric data and is the same model used in previous publications [2,4,5]. All calorimetric data generated for this publication were checked for order by applying the mathematical procedure detailed by Willson et al. [2] and by a graphical means [6] specific to second order reactions. The graphical method is to plot the calorimetric signal, power, raised to the power of −0.5 against time where a linear plot indicates a second order reaction. The advantage of this method is this is a rapid test for a second order reaction compared to the relatively laborious method for the determination of reaction order [7]. From Eq. (1), it can be seen that by writing $n = 2$ and solving for time, power (P) is linearly proportional to time in the following way:

$$-\Delta H \frac{V}{Qk} + \frac{(P\Delta HVk)^{1/2}}{kP} = t \quad (4)$$

Therefore,

$$\frac{P^{1/2}}{P} = P^{-0.5} \equiv t \quad (5)$$

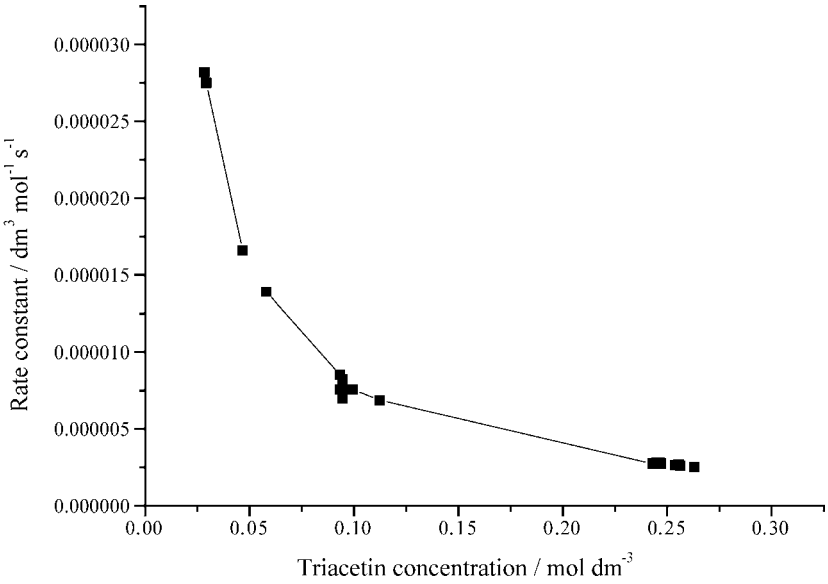

Fig. 1. A plot showing observed rate constants calculated from Eq. (3) as a function of triacetin concentration. For each data set, calculations were made using $n = 2$ and fitting for rate constant and enthalpy change. The differences in enthalpy change across the data set were no greater than ±3 kJ mol^{-1}.

Table 1
This shows the resulting observed rate constants derived from triacetin concentrations ranging from 0.0284 to 0.263 mol dm^{-3}

Triacetin concentration (mol dm^{-3})	Rate constant (dm^3 mol^{-1} s^{-1})	Enthalpy change (kJ mol^{-1})
0.0284	2.82×10^{-5}	−95.8
0.0293	2.75×10^{-5}	−95.9
0.0467	1.66×10^{-5}	−95.0
0.05	1.74×10^{-5}	−88.1
0.0581	1.39×10^{-5}	−91.5
0.0933	8.52×10^{-6}	−90.8
0.0933	7.56×10^{-6}	−90.8
0.0946	8.24×10^{-6}	−92.0
0.0946	7.59×10^{-6}	−92.0
0.0946	6.99×10^{-6}	−92.0
0.0993	7.56×10^{-6}	−94.3
0.1123	6.87×10^{-6}	−90.9
0.243	2.73×10^{-6}	−91.6
0.2431	2.73×10^{-6}	−95.4
0.2448	2.83×10^{-6}	−89.9
0.2465	2.82×10^{-6}	−90.1
0.2471	2.73×10^{-6}	−89.9
0.2537	2.62×10^{-6}	−96.1
0.2555	2.68×10^{-6}	−96.7
0.2561	2.59×10^{-6}	−90.2
0.263	2.50×10^{-6}	−97.3

These values were determined using the mathematical model as described by Willson et al. [2]. The associated enthalpy change was, within ±1.5%, the same as the published value [4].

3. Materials and methods

Experiments were run in an isothermal microcalorimeter (TAM, Thermometric AB, Järfälla, Sweden) and were set up according to the manufacturer's manual. The studies were performed at 298.15 K with an amplification setting of 300 μW and in 3 cm^3 glass ampoules. Baseline and electrical calibration checks were performed at the start of each series of experiments. Approximately 50 h of power–time data were collected for each experiment with data collection every 10 s.

The test protocol detailed by Beezer et al. [4] was followed to prepare reaction samples. The range of triacetin concentrations used was 0.0284–0.263 mol dm^{-3} with a fixed imidazol concentration of 3.82 mol dm^{-3}. A 30-min equilibrium time in the calorimeter was allowed before data collection commenced.

At the conclusion of the experiment, the calorimetric data were imported into a graphics-fitting programme, Origin^{TM} and the data analysed using Eq. (3), above. V (solution volume, 3 ml) and A (triacetin quantity) are known and are entered as constants. The program then iterates for both k and ΔH. Refer to Willson et al. [8] for a discussion on the validity of this type of iterative analysis.

4. Results and discussion

At all concentrations of triacetin, the derived enthalpy change was found to be consistent with literature value [4].

A plot of the rate constant versus triacetin concentration (Fig. 1) shows that the observed rate constant has a small dependency on triacetin concentration at the triacetin concentration used in previous publications [2,4,5] detailed in the introduction to this paper. However, it was found that the rate constant has a high dependency on triacetin concentration at concentrations less than 0.2 mol dm^{-3} (Table 1). The relationship between the rate constant and the triacetin concentration can be seen in Fig. 2 when the rate constant

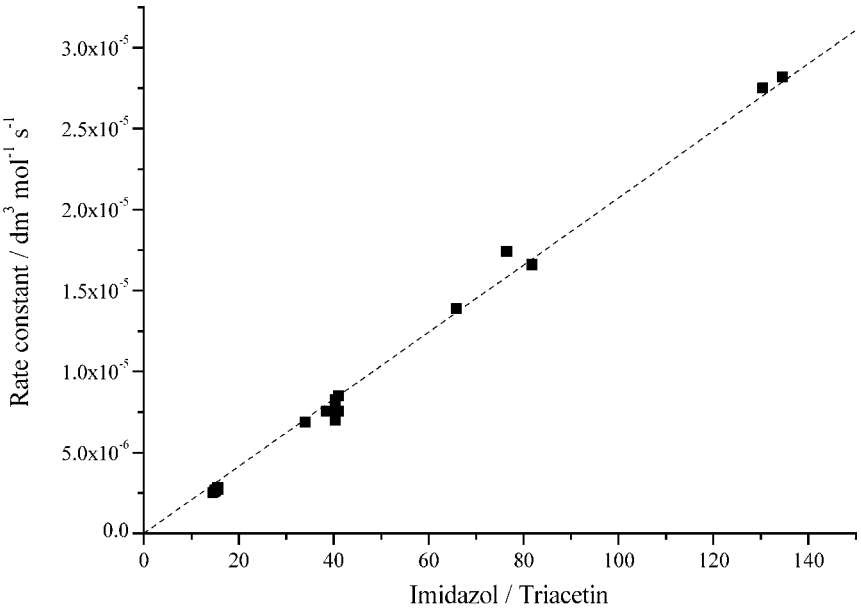

Fig. 2. A linear relationship was found when the observed rate constant was plotted against imidazol concentration divided by the triacetin concentration. The slope of this line is $1.91 \times 10^{-7} \pm 1.68 \times 10^{-8}$ dm^3 mol^{-1} s^{-1}.

is plotted against the reciprocal of the triacetin concentration resulting in a linear plot, the slope of which is a constant. From the study by Hills et al. [5], the rate constant is also proportional to the concentration of imidazol. Combining these two observations results in the rate constant being related to both imidazol and triacetin as shown in Eq. (6):

$$k_{\text{obs}} = \text{Slope}\frac{\text{Imidazol}}{\text{Triacetin}} \tag{6}$$

Note that the slope has the value of $1.91 \times 10^{-7}\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$. Substituting the right hand side of Eq. (6) for k_{obs} in Eq. (3) gives:

$$P = \Delta HV\text{Triac slope}\frac{\text{Imid}}{(\text{Slope Imid}\,t + V)^2} \tag{7}$$

The slope is a constant that is independent of triacetin concentration and may be regarded as a true rate constant (from the point of view of triacetin concentration) and provides for a more general mathematical model.

5. Conclusion

No attempt was made to derive mechanistic information by spectroscopic or related studies as it was the intention of this study to focus on developing the robustness of the test reaction for the purpose of calibration. However, in this study the observed rate constant has been shown to have a dependency on the triacetin concentration, the dependency increasing as concentration is reduced. Having shown the dependency is the reciprocal of triacetin concentration and that other studies [5] have shown the rate constant to be proportional to imidazol concentration, it was then possible to re-write the initial mathematical model resulting in Eq. (7). The slope is the triacetin independent rate constant and has the value of $1.91 \times 10^{-7} \pm 1.68 \times 10^{-8}\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$.

Using the data published by Hills et al. [5] where the concentration of triacetin is held constant and the concentration of imidazol varied, a similar calculation of a rate constant could be made. A plot of rate constant versus imidazole/triacetin gave a slope of $1.65 \times 10^{-7} \pm 5.01 \times 10^{-9}\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$. The Hills et al. [5] study did not follow the protocol detailed by Beezer et al. [2] as the sample volume used was $3.1\,\text{cm}^3$ and that the extrapolation of the plot rate constant versus imidazole/triacetin concentrations does not go through the origin. Forcing a linear regression through the origin gives a slope of $1.73 \times 10^{-7} \pm 1.53 \times 10^{-8}\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$. However, our conclusions are that the rate constant 1.91×10^{-7} and 1.73×10^{-7} are, with in experimental error, the same.

Even though the calorimeter can not directly return mechanistic information, by selection of an appropriate model that describes the reaction, some mechanistic information can be obtained indirectly. This and other calorimetric studies of the triacetin reaction bring us yet another step closer to the true mechanism describing the hydrolytic pathway.

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