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Thermochimica Acta 386 (2002) 139–142

thermochimica
acta

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Microcalorimetric study of a proposed test reaction—the imidazole catalysed hydrolysis of triacetin
Temperature and imidazole concentration dependence

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Received 24 April 2001; received in revised form 3 September 2001; accepted 25 September 2001

Abstract

The imidazole catalysed hydrolysis of triacetin has recently [1] been proposed as a test reaction for isothermal heat conduction microcalorimeters affording validation and traceability for results derived from these instruments. The published values for $\Delta_R H$, $-91.7 + 3.0$ kJ mol^{-1} and for the rate constant at 298 K, k, $2.8 \times 10^{-6} \pm 9.7 \times 10^{-8}$ dm^3 mol^{-1} s^{-1}, were the results from an international inter- and intra-laboratory study. The protocol [1] for the conduct of the reaction specifies the reaction composition and a temperature of 298 K. Here, we report the temperature and imidazole concentration dependence of the rate constant for this reaction and the derived value of the activation energy; $E_a = 64.30 \pm 2.00$ kJ mol^{-1}. The value of $\Delta_R H$ is independent of temperature and a test for completeness of reaction (i.e. the reaction goes to completion at all temperatures and no effective equilibrium constant is determinable) is described.

Keywords: Microcalorimetric; Imidazole; Hydrolysis of triacetin

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1. Introduction

In a recent paper [1], we proposed the use of the imidazole catalysed hydrolysis of triacetin as a test reaction for isothermal heat conduction microcalorimeters. This reference [1], also describes the background to the selection of this reaction as a suitable test reaction for isothermal heat conduction microcalorimetry. The results of an international inter- and intra-laboratory study were: $\Delta_R H = -91.7 \pm 3.0$ kJ mol^{-1} and $k = 2.8 \times 10^{-6} \pm 9.7 \times 10^{-8}$ dm^3 mol^{-1} s^{-1}. The protocol for conduct of the reaction [1] specified the reaction composition and the temperature as 298 K. During the course of the study conducted in our laboratory it was noted that the reaction shows a dependence on the imidazole concentration used. Naturally the rate constant depends on temperature and two laboratories have cooperated in establishing appropriate data. A recent paper [2] has described the use of isothermal heat conduction calorimetry in not only allowing determination of enthalpy and rate constant data, but also in permitting evaluation of equilibrium constants for reaction systems that do not go to completion. The paper describes how to calculate Q, the total number of joules involved in the reaction system. It is not necessary to observe the reaction over its whole lifetime for this

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0040-6031/02/$ – see front matter
PII: S0040-6031(01)00773-0

quantity to be evaluated. It can be determined for a reaction of constant kinetic order observed over 50 h or so [2]. Thus, a test for completeness of reaction is that *Q* should remain constant (mol^{-1}, g^{-1}) over a modest temperature range (assuming no change in reaction mechanism nor dependence of enthalpy on temperature). Clearly the test for the existence of an equilibrium in the reaction system is that the value of *Q* should vary with temperature.

The imidazole catalysed hydrolysis of triacetin goes to completion, i.e. *Q* is constant as a *f*(*T*). This is an important criterion in establishing a test reaction's utility—it should have simple application over a range of conditions—in this case temperature. Furthermore, the reaction will be perceived to be robust if there are predictable consequences for small variations in reaction conditions. Hence, we report here both the temperature and imidazole concentration dependence of this reaction.

2. Experimental

All the experiments were conducted according to the published protocol [1] except that temperatures and imidazole concentrations were as specified in the tables of results. The calorimeters used were a TAM (Thermal Activity Monitor Jarfalla, Sweden at University of Greenwich) and a MicroDSC III (Setaram, Caluire, France at Technical University Freiberg). Both Instruments were operated according to the manufacturer's instructions.

3. Results and discussion

3.1. Temperature studies

The results of the University of Greenwich study are displayed in Table 1 and those of the Technical University Freiberg study in Table 2. Typical thermal–power time curves obtained (University of Greenwich) are shown in Fig. 1. All the values for $\Delta_R H$ are within the range described in the previous paper [1]. Moreover, the more extensive study from Freiberg shows no systematic trend in $\Delta_R H$ values with temperature. Both sets of data show linear Arrhenius plots of $\ln k$ versus $1/T$ with derived values for the activation energy which differ by only 1.4 kJ mol^{-1}. The combined data (regression coefficient for the $\ln k$ versus $1/T$ plot is 0.9997) results in a derived value for E_a of 64.30 ± 2.00 kJ mol^{-1}. The conformity of the data to the Arrhenius equation over the range 298–353 K together with the constancy of the value of $\Delta_R H$ (although note that the value of $\Delta_R H$ at 80 °C lies just outside the determined error limits suggesting that at around this temperature the reaction behaviour differs from that at lower temperatures) indicates that the reaction mechanism remains the same over this range and that there is no observed dependence of enthalpy on temperature.

Table 2
Results (Technical University Freiberg) for temperature studies

Temperature (T, °C)	$\Delta_R H$ (kJ mol^{-1})	k ($\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$)
25	−88.75	2.95×10^{-6}
30	−88.98	4.47×10^{-6}
35	−89.63	6.50×10^{-6}
40	−89.33	9.75×10^{-6}
50	−89.65	20.54×10^{-6}
60	−88.69	42.39×10^{-6}
70	−88.68	83.20×10^{-6}
80	−88.47	161.33×10^{-6}

3.2. Imidazole concentration dependence

In a limited series of experiments, it was noted that the derived rates of reaction at 298 K exhibited a dependence on the imidazole concentration in the

Table 1
Results (University of Greenwich) for temperature studies

Temperature (T, °C)	$\Delta_R H$ (kJ mol^{-1})	k ($\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$)	[Triacetin] (mol dm^{-3})	Volume (V, dm^3)
25	−93.15	2.68×10^{-6}	0.24	0.0031
30	−93.76	4.12×10^{-6}	0.238	0.0031
35	−94.53	6.16×10^{-6}	0.237	0.0031

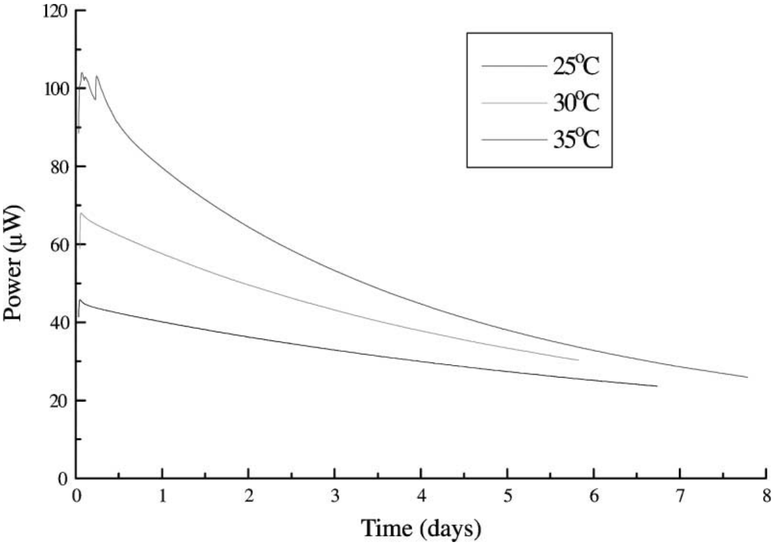

Fig. 1. Typical plots for experiments performed (plots in ascending order) at 25, 30 and 35 °C.

Table 3
Dependence of the rate constant on the imidazole concentration

[Imidazole] (mol dm^{-3})	$\Delta_R H$ (kJ mol^{-1})	k (dm^3 mol^{-1} s^{-1})	[Triacetin](mol dm^{-3})	Volume (V, cm^3)
3.53	ND	2.40×10^{-6}	0.237	3.1
3.67	−90.57	2.52×10^{-6}	0.236	3.1
3.82	−90.29	2.72×10^{-6}	0.236	3.1
4.0	−90.14	2.9×10^{-6}	0.237	3.1

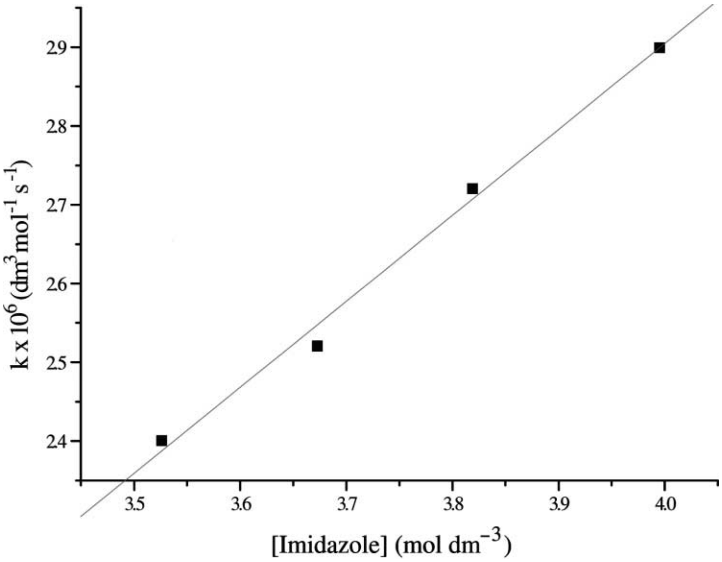

Fig. 2. The dependence of the rate constant at 298 K on the concentration of imidazole.

reaction system. The results of this limited variation study (four different concentrations of imidazole) are displayed in Table 3. The data suggests that the dependence of the rate constant on the imidazole concentration is linear, Fig. 2. Thus, at least over the study range of concentration, it is possible to write

$$k_{\mathrm{obs}} = k[\mathrm{imidazole}].$$

The triacetin reaction is analysed [1] as overall a second order reaction and the result presented here is a clear indication of the role of imidazole as both a buffer component and a catalyst. No attempt was made to explore the role of pH variation in this reaction system. The result does, however, indicate that the protocol requirement with respect to imidazole concentration is now less demanding. Solutions can be made within the study range of imidazole concentrations and the rate constant predicted from these data. Note, however, that this is a limited data set and results from other workers in establishing the validity of these data would be very welcome.

4. Conclusion

The imidazole catalysed hydrolysis of triacetin would appear to be a very useful and robust test reaction for isothermal heat conduction microcalorimeters. It appears to be well behaved over a wide range of temperature and to have a simple dependence upon the imidazole concentration. It should, therefore, be of wide application in systems for which both thermochemical and kinetic information is important. These situations will, perhaps, be most significant for slow reactions where conventional studies may have more limited application (such as shelf-life determination, long term stability data, studies of complex heterogeneous systems, etc.). This reaction, studied according to the published protocol has, at 298 K, a half-life of around 18 days. Thus, the reaction is essentially complete in around 100 days. We have studied the reaction for this time period and note that analysis of data drawn at any time throughout this period always results in data that conforms to the recommended values cited above. Thus, this reaction will allow short time examination, $t \sim 12$ h, that will permit the test to be performed successfully. In the event that the outcomes do not correspond with the recommended values it is possible to suggest reasons from comparison of the recovered values with the recommended values [3], i.e. to trouble-shoot.

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