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THE INTEGRATION OF AN ULTRAVIOLET-VISIBLE SPECTROMETER AND A REACTION CALORIMETER

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Abstract

A small ultraviolet-visible absorption spectrometer which uses fibre optic coupled immersion probes has been incorporated into a laboratory scale reaction calorimeter. The combined instrument has been tried out using the hydrolysis of acetic anhydride as a test reaction. With the calorimeter operating in the isoperibolic mode good agreement is found for the pseudo-first order reaction rate constant as determined from spectroscopic and calorimetric measurements. Experiments have been made in order to follow the reaction indirectly using optical pH measurements with acid-base indicators. The possibility of determining the temperature dependence of the rate constant in a single experiment has also been investigated.

Keywords: reaction calorimetry, reaction kinetics, ultraviolet-visible spectrophotometry

Introduction

The quality and quantity of information that can be obtained from laboratory scale reaction calorimetry can be increased by incorporating sensors, other than thermometers, into the calorimeter. Ultraviolet-visible absorption spectroscopy, or spectrophotometry, is often used in mechanistic studies in inorganic [1] and organic chemistry [2] to follow reactions where the half-life is of the order of several minutes or more. Many process studied using reaction calorimetry have a similar half-life. Advances in electronics, fibre optic technology and personal computers have led to the introduction of small, rapid, low cost spectrometers. In this work the combination of an Ocean Optics USB 2000 ultraviolet-visible spectrometer with a laboratory scale calorimeter is described.

The spectrometer was chosen because of its small size (9×6×3 cm), radiation is coupled into the spectrometer using fibre optic cables fitted with SMA connectors, the spectrometer takes its power from the computer's USB and the comprehensive operating software. The spectrometer system is completed with an Analytical Instruments Systems DT 1000 combined tungsten halide-deuterium source and a small diameter Ocean Optics T300-RT-UV-VIS transflection (transmission-reflection) immersion probe.

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The combined calorimeter-spectrometer system has been tried out using the hydrolysis of acetic anhydride

$$\mathrm{Ac_2O{+}H_2O \rightarrow 2HOAc} \tag{1}$$

as a test reaction.

Under the experimental conditions used here the reaction may be considered to follow pseudo-first order kinetics [3] with rate constant *k*. In an initial series of experiments the calorimeter has been operated in the isoperibolic mode and the reaction has been followed by monitoring the ultraviolet absorption of acetic anhydride between 250 and 280 nm.

Ocean Optics has developed a method of optical pH measurement using acid-base indicators [4]. Each indicator covers a range of 3–4 pH units and under favourable conditions differences of 0.001 unit can be determined. A second series of experiments was made in order to investigate the possibility of following the reaction using this kind of measurement and the reaction scheme

$$\mathrm{Ac_2O{+}H_2O{\rightarrow}2HOAc} \qquad \text{(slow)} \tag{2}$$
$$\mathrm{HOAc{=}H^{+}{+}OAc^{-}} \qquad \text{(fast)} \tag{3}$$

The temperature dependence of the reaction rate constant can be obtained in a single experiment in differential scanning calorimetry using the approach of Borchardt and Daniels [5] and in adiabatic calorimetry [6]. A similar method using spectrophotometry to follow the reaction has been applied to inorganic reactions [7]. A series of experiments was made in which a temperature ramp was applied to the reactor jacket in order to determine the temperature dependence of the reaction rate constant from both calorimetric and spectroscopic measurements.

Theory

The differential heat balance equation for a heat transfer calorimeter is [8]

$$C_\mathrm{p}\,(\mathrm{d}^\mathrm{R}T/\mathrm{d}t)=UA(^\mathrm{J}T-{}^\mathrm{R}T)+\dot{Q}_\mathrm{chem}+\dot{Q}_\mathrm{loss}+P_\mathrm{stirrer} \tag{4}$$

where $^\mathrm{R}T$ is the reactor temperature, $^\mathrm{J}T$ the mean jacket temperature, C_p the heat capacity of the reactor contents, UA the global heat transfer constant, $\dot{Q}_\mathrm{chem}$ the chemical heat flow, $\dot{Q}_\mathrm{loss}$ the rate of heat loss and P_stirrer the power dissipated by the stirrer. For a calorimeter operating in the isoperibolic mode with constant heat loss and stirrer power dissipation the chemical heat flow is [9]

$$\dot{Q}_\mathrm{chem}=UA(^\mathrm{R}T-{}^\mathrm{R}T_0)+C_\mathrm{p}\,(\mathrm{d}^\mathrm{R}T/\mathrm{d}t) \tag{5}$$

where $^\mathrm{R}T_0$ is the steady state reactor temperature before the start of the reaction.

For a reaction with first order reaction kinetics the chemical heat flow is:

$$\dot{Q}_\mathrm{chem}=\dot{Q}^0_\mathrm{chem}\exp^{(-\mathrm{k}t)} \tag{6}$$

where $\dot{Q}^0_\mathrm{chem}$ is the chemical heat flow at t=0.

The concentration of a substance is related to the optical absorption by Beer's law [2].

$$A_{\lambda} = -\log(I/I_0) = \varepsilon_{\lambda} cl = \varepsilon'_{\lambda} c \qquad (7)$$

where A_{λ} is the absorbance at the wavelength λ, I and I_0 are the radiation intensity at the detector with and without the absorbing substance, ε_{λ} is the molar extinction coefficient, c is the concentration of the absorbing substance and l is the optical path length. If the optical path length is constant then it can be incorporated into ε_{λ} to give ε'_{λ} . By analogy with Eq. (6) the absorbance of the acetic anhydride can be expressed as

$$A_{\lambda} = A_{\lambda}^{0} \exp^{(-\mathrm{kt})} \qquad (8)$$

A modified form of Eq. (8) has been used to determine k as it was observed that sometimes the intensity did not return to its value before the start of the reaction. The best results were obtained using

$$-\log(I) = A_{\lambda}^{0} \exp^{(-\mathrm{kt})} + a + bt \qquad (t>0) \qquad (9)$$

$$-\log(I) = a \qquad (t<0) \qquad (10)$$

Equations (6), (9) and (10) have been used with non-linear least squares fitting routines of the ΣPlot graphical program [10] to determine the reaction rate constant.

Calculations show that for a solution which is initially 1 M with respect to acetic anhydride, assuming ideal behaviour, the pH changes from an initial value of 7 to 2.2 at the end of the reaction. For conversions (X) above 0.01 the hydrogen ion concentration is given quite accurately by

$$[\mathrm{H}^{+}] = \sqrt{2K_{\mathrm{a}} X [\mathrm{Ac_2O}]_0} \qquad (11)$$

where K_{a} is the acid dissociation constant and $\left[\mathrm{Ac_2O}\right]_0$ is the initial acetic anhydride concentration. By expressing the conversion in terms of the rate constant Eq. (11) can be rewritten as

$$[\mathrm{H}^{+}] = \sqrt{2K_{\mathrm{a}} [\mathrm{Ac_2O}]_0 (1-\exp^{(-\mathrm{kt})})} \qquad (12)$$

Acid-base indicators are weak water soluble acids in which the acid (HIn) and its conjugate base (In^{-}) absorb in different regions of the visible part of the spectrum [11]. The degree of ionization of the indicator is determined by its dissociation constant (K_{In}) and the pH of the solution. If A_{HIn} and $A_{\mathrm{In}^{-}}$ are the absorbances of HIn and In^{-} and $[\mathrm{HIn}]_0$ is the total indicator concentration then with the use of Eq. (12)

$$A_{\mathrm{In}^{-}} / A_{\mathrm{In}^{-}}^{0} = K_{\mathrm{HIn}} / (K_{\mathrm{HIn}} + \sqrt{2K_{a} [\mathrm{Ac}_2]_0 (1-\exp^{(-\mathrm{kt})})}) \qquad (13)$$

$$A_{\mathrm{HIn}} / A_{\mathrm{HIn}}^{0} = \sqrt{2K_{\mathrm{a}} [\mathrm{Ac_2O}]_0 (1-\exp^{(-\mathrm{kt})})} / (K_{\mathrm{HIn}} + \sqrt{2K_{\mathrm{a}} [\mathrm{Ac_2O}]_0 (1-\exp^{(-\mathrm{kt})})}) \qquad (14)$$

where A_{In^-} and A_{HIn} are the peak absorbances of In^- and HIn and $A^0_{\mathrm{In}^-}$ and A^0_{HIn} are their absorbances when the indicator is present completely as In^- or HIn .

The reaction rate constant can be written as

$$k=-(\mathrm{d}[\mathrm{Ac}_2\mathrm{O}]/\mathrm{d}t)/[\mathrm{Ac}_2\mathrm{O}] \tag{15}$$

and Eq. (15) can be expressed in terms of the chemical heat flow, the heat of reaction (Q_{chem}) and the enthalpy of reaction ($\Delta_\mathrm{r}H$) as

$$k=-\dot{Q}_{\mathrm{chem}}/(n_0\Delta_\mathrm{r}H+Q_{\mathrm{chem}}) \tag{16}$$

where n_0 is the initial number of moles of acetic anhydride and $\Delta_\mathrm{r}H$ is the enthalpy of reaction. The heat of reaction is obtained by integrating the chemical heat flow with respect to time. The rate constant can be expressed in terms of the absorbance and its time derivative as

$$k=-(\mathrm{d}A_\lambda/\mathrm{d}t)/A_\lambda \tag{17}$$

Equations (16) and (17) have been used to determine the rate constant in the experiments in which a temperature ramp was applied to the reactor jacket.

Experimental

The main features of the combined calorimeter-spectrometer are shown schematically in Fig. 1. The calorimeter, the method of on-line calibration (determination of C_p and UA) and the determination of $\dot{Q}_{\mathrm{chem}}$ and Q_{chem} has been described previously [9]. Two personal computers are used in the combined instrument, the first is to con-

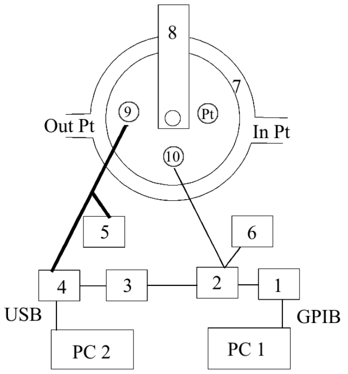

Fig. 1 Schematic diagram of the combined reaction calorimeter-spectrophotometer. 1 – Keithlye 2000 multimeter and scanner card, 2 – Hewlett Packard HP E3631 E programmable power supply, 3 – relay, 4 – Ocean Optics USB 2000 spectrometer, 5 – Analytical Instruments Systems DT 1000 light source, 6 – Haake F3 circulating thermostat, 7 – 0.5 L jacketed pyrex reactor, 8 – IKAVISC MR D1 stirrer, 9 – Ocean Optics T300 RT UV-VIS transflection probe, 10 – 25 ohm calibration resistor, Pt 100 ohm four-wire platinum resistance thermometer. Electrical and interface connections are shown as narrow lines and fibre optic connections as broad lines

trol the calorimeter and acquire the calorimetric data and the second is to control the spectrometer and acquire the spectroscopic data. This increases the flexibility of the system and makes it possible to set up the calorimetric and spectroscopic parts of an experiment separately. The Keithley 2000 multimeter and scanner card are used to measure the resistance of 100 ohm four-wire platinum resistance thermometers and voltages related to the stirrer speed and torque. The Hewlett Packard HP E3631 A programmable power supply is used (a) to supply and measure the power supplied to the calibration heater (b) to control the Haake F3 circulating thermostat and (c) to activate the relay. This closes the spectrometer's external software trigger and starts its data acquisition thus synchronising it to that of the calorimeter.

A feature of the USB 2000 spectrometer, because it uses a linear CCD array detector, is that a complete spectrum is obtained on each data acquisition. This data can be streamed to the computer's hard disk and used to generate three dimensional diagrams such as that shown in Fig. 2. These diagrams are a useful guide to the how a reaction develops. The spectrometer software can extract the intensity at up to six preset wavelengths on each acquisition and save this data for an off-line quantitative analysis of the reaction. The spectrometer operating software makes intense use of the computer especially when complete spectra are being streamed to disk.

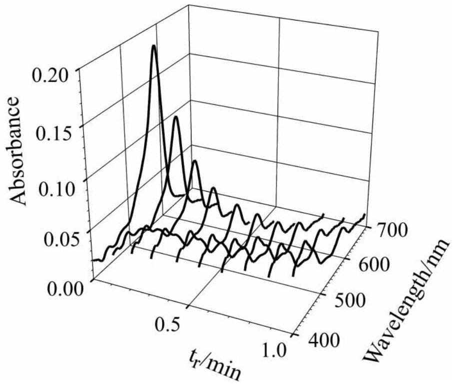

Fig. 2 Time evolution of the visible spectrum for the hydrolysis of an initially 1 M solution of acetic anhydride to which a small quantity of bromophenol blue indicator had been added

A typical experiment consists of filling the reactor with ~370 mL of distilled water, starting the calorimeter control software and setting the reaction temperature. Approximately 25 g of acetic anhydride (99% pure, Aldrich) is poured into a conical flask fitted with a stopper. The flask and its contents are weighed and then placed in the bath of the Haake F3 thermostat. The UV lamp is switched on and allowed to stabilise. The spectrometer data acquisition parameters, integration time, number of acquisitions to average, acquisition frequency and wavelengths are set and then the detector dark signal is measured by closing a shutter to interrupt the light beam. After this the spectrometer is put into the external software trigger mode. Meanwhile when the calorimeter is stable the first calibration is made. When the reactor temperature is again stable the spectrometer's external trigger is closed from the calorimeter software and the averaging of the reactor and jacket temperatures is started. After approximately 10 min the flask containing the acetic anhydride is removed from the bath of the thermostat, wiped dry and its contents poured quickly into the reactor. At the same time the on-line determination of the chemical heat flow and heat of reaction is started. At the end of the reaction the spectrometer software is closed and a second calorimeter calibration is made.

The optical pH measurements were made in the same way except that at about half way through the initial temperature averaging period a small quantity of indicator was added to the water in the reactor. At the end of the reaction, if necessary a small quantity of a strong acid was added to the reaction mixture in order to convert all the indicator to its acid form. The variable temperature experiments were made in the same way as the isoperibolic experiments except that 5 min after the start of the reaction a voltage ramp was applied to the analog input of the thermostat.

Results

Figure 3 shows the time variation of –log(*I*) for three of the six wavelengths for which data was taken and the on-line calculated chemical heat flow for the hydrolysis of an initially 0.7 M solution of acetic anhydride at 40°C. The value of $k = 5.12(2)\ 10^{-3}\ s^{-1}$ was obtained by fitting $\dot{Q}_{chem}$ using Eq. (6) for reaction times greater than 5 min. Table 1 summarises the results of fitting the spectroscopic data using Eqs (9) and (10). The mean value of k=4.3(2) $10^{-3}\ s^{-1}$ is in good agreement with that derived from the calorimetric data. It is necessary to start fitting the spectroscopic after the start of the reaction when the curve starts to decay exponentially. The reason for the apparent deviation from Beer's law will be discussed below. The results of experiments conducted at 10, 25 and 40°C are summarised in the modified Arrhenius diagram, Fig. 4, in which *k* is plotted *vs.* the thermodynamic temperature with both variables being displayed on a logarithmic scale. The values of the rate constant determined from the spectroscopic data are consistently slightly smaller than those obtained from the calorimetric data.

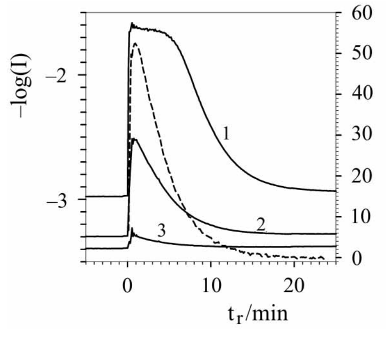

Fig. 3 Time dependence of –log(*I*) for three wavelengths (1 – λ=255 nm, 2 – λ=265 nm and 3 – λ=280 nm) and $\dot{Q}_{chem}$ (dashed curve) for the hydrolysis of acetic anhydride at 40°C

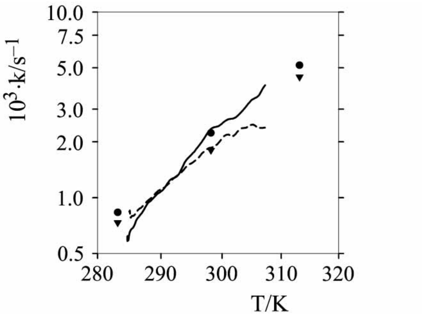

Fig. 4 Modified Arrhenius diagram for the hydrolysis of acetic anhydride. ● – calorimetric data, ▼ – spectroscopic data. The results of the temperature ramp experiment are shown as spectroscopic data solid curve (λ=270 nm) and calorimetric data dashed curve

Table 1 Parameters obtained by fitting the values of –log(I) shown in Fig. 3 using Eqs (9) and (10). Standard errors in units of the least significant digit are shown in parentheses, t_{start} is the reaction time at which the least squares fitting was started

λ/nm	A^0	$10^3 \cdot k/s^{-1}$	a	$10^5 \cdot b/s^{-1}$	t_{start}/min
255	7.93(5)	4.462(10)	–2.9762(3)	2.14(3)	9.0
260	4.89(2)	4.455(10)	–3.1113(3)	1.48(3)	7.0
265	2.531(9)	4.357(10)	–3.2177(4)	1.23(4)	4.0
270	1.212(4)	4.420(10)	–3.2976(2)	1.23(2)	4.0
275	0.445(2)	4.19(3)	–3.3585(9)	1.5(7)	2.0
280	0.1284(4)	4.06(3)	–3.3941(1)	1.11(9)	2.0

Figure 2 shows the time evolution of the visible spectrum for the hydrolysis of an initially 0.7 M solution of acetic anhydride to which a small quantity of bromophenol blue indicator ($pK_{In} \approx 4$) was added. Initially the pH of the solution is 7 and the indicator is present almost completely as In^- which absorbs with λ_{max}=690 nm and the solution is pale blue. After the start of the reaction the In^- is converted to HIn with λ_{max}=440 nm and the solution becomes a pale yellow colour. Experiments were made with indicators with smaller values of pK_{In} but it was difficult to analyse the results because of overlapping of the absorption bands of the indicator (e. g. colour changes of yellow to orange).

The results of a temperature ramp experiment are also shown in Fig. 4. The evaluation of the calorimetric data required some attention as the heat loss, the heat exchange coefficient and less importantly the heat capacity vary during the course of the experiment. It was assumed that these quantities varied linearly with time between the start and end of the ramp and that their initial and final values were those given by the two calibrations. A value of –61.4 kJ mol^{-1} [12] was used for the enthalpy of reaction in Eq. (16). The spectroscopic data was analysed using Eq. (17) and for both the calorimetric and spectroscopic data the Savitzky–Golay algorithms

[13] were used for smoothing and differentiating the experimental data. There is reasonably good agreement between the results obtained with the calorimeter operating in the isoperibolic and temperature ramp modes.

Conclusions

This work shows that a spectrophotometer using fibre optic coupled immersion probes can be readily incorporated into a laboratory scale reaction calorimeter and that useful results can be obtained. However some problems have been encountered. The transflection probe used in these experiments has rather a small aperture and it was found that there was a tendency for air bubbles to accumulate inside the light path. This could be ameliorated by reducing the stirrer speed but this can only be done to a certain extent because it is necessary to keep the reaction mixture well mixed. In the case of the hydrolysis of acetic anhydride, because of the limited miscibility of the two components, a certain stirrer speed is necessary to disperse the acetic anhydride and to prevent drops of it accumulating inside the probe. The large value of A^0 for λ=255 nm given in Table 1 shows that the signal at the detector should be immeasurably small at the start of the reaction. The observed value is believed to be due to stray light which is worst at the shortest wavelengths. This can distort the shape of absorption bands as well as leading to departures from Beer's law. The majority of mechanistic work is done in very dilute solutions in order to avoid thermal effects. In a calorimetric study this is not possible and very high values of the peak absorbance are encountered. This problem can be overcome by making measurements at the side of the absorption band as illustrated in this work.

The indirect method of following the reaction using optical pH measurements has the potential advantage of having absorption bands in the visible part of the spectrum where stray light is not a problem. Also, since only a small quantity of indicator is used and the absorbances are not very large it is possible to use the peaks of the absorption bands. A disadvantage of this method is that even for a reaction with simple kinetics the rate constant depends on the observed data in a very complicated way.

In conclusion the following suggestions can be made. The majority of calorimetric experiments where spectrophotometry can also be applied involve organic compounds which absorb in the ultraviolet. It would therefore be useful to have a spectrometer optimised for this region of the spectrum. It is also desirable to be able to detect rather small intensity changes and a spectrometer with a photodiode array detector may be preferable to one that uses a CCD array detector.

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