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Thermal behavior of Landolt reactions in comparatively dilute aqueous solutions followed by heat exchange calorimetry of batch type

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Abstract

In batch-type Landolt reactions composed of potassium iodate and sodium hydrogen sulfite, the color of the solution changes suddenly at a time interval after mixing the component substances. This is often presented as chemical magic with the nickname "clock reaction". The thermal behavior of more dilute solutions than in the demonstration is studied by heat exchange calorimetry of batch type. Sample and reference vessels are fixed differentially in a precision water bath. Heat evolved in the vessel is exchanged freely with the surrounding water. Crystalline sodium hydrogen sulfite is added to an aqueous solution of potassium iodate to start the reaction. The temperature change in the vessels is detected by a thermistor, and treated by an analogue computation to obtain the rate of heat evolution and total heat effect. The heat of reaction Q_{reac} is estimated after correction for the negative heat of solution of sodium hydrogen sulfite. Free iodine may be produced after the consumption of sodium hydrogen sulfite, if $[\mathrm{NaHSO_3}]_{\mathrm{init}}$ is not larger than three times $[\mathrm{KIO_3}]_{\mathrm{init}}$. Q_{reac} increases in direct proportion to $[\mathrm{NaHSO_3}]_{\mathrm{init}}$ in the region of excess $[\mathrm{KIO_3}]_{\mathrm{init}}$. However, as expected, constant values of Q_{reac} were observed in the region of excess $[\mathrm{NaHSO_3}]_{\mathrm{init}}$ when it is more than 3.6 times larger than $[\mathrm{KIO_3}]_{\mathrm{init}}$. The reaction enthalpy at infinite dilution was estimated to be −228.4 kJ per 1 mole of $[\mathrm{NaHSO_3}]_{\mathrm{init}}$.

INTRODUCTION

The Landolt reaction [1] is composed of redox reactions involving iodate ions and hydrogen sulfite ions [2], i.e.

$$\mathrm{IO_3^- + 3HSO_3^- \rightarrow I^- + 3SO_4^{2-} + 3H^+} \qquad (1)$$

$$\mathrm{5I^- + IO_3^- + 6H^+ \rightarrow 3I_2 + 3H_2O} \qquad (2)$$

$$\mathrm{I_2 + HSO_3^- + H_2O \rightarrow 2I^- + SO_4^{2-} + 3H^+} \qquad (3)$$

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As a result of studies on the rate constants [3, 4] and a computer simulation [5] of these reactions, reaction (1) proceeds at the lowest speed and is the rate-determining step. However, reaction (3) is extremely fast. With excess iodate ions, the iodine produced by reaction (2) is consumed immediately by reaction (3). When $[HSO_3^-]$ becomes zero in the system, the residual iodide ions and iodate ions react by reaction (2) to produce free iodine and the color of the solution changes suddenly in the presence of starch. The Landolt reaction is also called the "iodine clock reaction". No calorimetric study (in contrast to spectrophotometric studies) has been found in a recent CAS on-line search.

The thermal behavior of the Landolt reaction [6] was followed by heat exchange calorimetry [7] of batch type. In the calorimeter, the sample and reference vessels are fixed differentially in a temperature-controlled water bath. The heat evolved in the sample vessel is exchanged freely with the surrounding water. The temperature in the vessel is expressed by the Newtonian cooling equation. The total heat effect Q and the rate of heat evolution q are obtained from the electric signals detected via a thermistor and processed by analogue computation circuits.

In our previous report [6], using excess initial concentration of potassium iodate ($[KIO_3]_{init}$), the total heat effect in the Landolt reaction (Q_{reac}) depended only on $[NaHSO_3]_{int}$. However, the relative reaction rate (estimated as the reciprocal of reaction time t_{reac} obtained from the observed q vs. t curve) depended linearly on both $[KIO_3]_{init}$ and $[NaHSO_3]_{init}$. The calorimetric t_{reac}^{-1} was on the same extrapolated line as that observed visually from the color change of the sample. However, the detection of the color change in dilute solutions is probably impossible visually. Fortunately, calorimetry makes the detailed study of the Landolt reaction possible even in dilute solutions for which the color change may not be detected visually.

In the present report, heat exchange calorimetry of batch type was applied to estimate the heat evolution in the Landolt reaction between dilute solutions of KIO_3 and $NaHSO_3$ at 25.0°C. To simplify the analysis of the effects on the thermal phenomena of reducing concentrations of the relevant chemical species in the system, the addition of starch was omitted. The thermal behavior was also discussed in relation to pH values.

EXPERIMENTAL

Reagents

All KIO_3 and $NaHSO_3$ used were of guaranteed grade and used without further purification. Deionized water was used after distillation. The initial concentration of KIO_3 was 1.000 mM, and that of $NaHSO_3$ was within the range 1.94–7.72 mM. The pH value was also measured for $[KIO_3]_{init} = 5.000$ mM.

Apparatus

Our basic apparatus for heat exchange calorimetry was almost the same as previously reported [8]. A glass box $21 \times 30 \times 27$ cm^3 in size with all surfaces covered by insulating boards was used for the water bath and filled with water (12 dm^3). Two 100 cm^3 glass bottles (one to hold the sample and the other to serve as a reference vessel) were fixed in the water bath with an aluminium frame. In each vessel, a small bead thermistor (MB type, Takara Kogyo Co., Tokyo) was installed as temperature sensor. A magnetic stirrer of submarine type (M-3, Iuchi Seieido, Tokyo) was directly fixed to the bottle. The temperature of the water bath was controlled within ± 3–4×10^{-4} K by a method previously reported [9]. The temperature signals observed were processed by analogue circuits, from which Q and q were obtained as output voltages [8]. Traces of Q and q were obtained by a 2-pen Y–t recorder (R-02, Rika Denki Kogyo Co., Tokyo). The pH was also observed by a pH meter between a glass electrode and an Ag/AgCl electrode via a KNO_3 salt bridge, from which the output voltage was also recorded against time.

Procedure

Each aliquot of 50.0 g of KIO_3 solution was weighed and placed in both sample and reference vessels. After the two vessels were fixed in the water bath, the temperature control system operated by the small microcomputer (M5, SORD Co., Tokyo) was started, keeping the temperature at 25.0 ± 0.1°C. Thermal equilibrium between the water bath and the measuring devices was attained after a time lapse of 30–40 min in typical runs. The time constants of the analogue circuit were adjusted to those of the calorimeter by adjusting variable resistors. Heat calibration of the apparatus was then carried out by electrical heating, applying almost the same amount of heat as the practical experiments.

Weighed crystalline $NaHSO_3$ was put directly into the sample vessel from outside the calorimeter without removing the insulating boards, and at the same time the reaction started. Alternatively, almost the same amount of $NaHSO_3$ was added to water, and the heat of solution of $NaHSO_3$ was observed separately. The Q_{reac} was estimated as the difference between the two observations.

RESULTS AND DISCUSSION

In a previous paper [6], the thermal behavior of the Landolt reaction was studied in the range of $[KIO_3]_{init}$ from 2.699 to 20.00 mM and $[NaHSO_3]_{init}$ from 1.92 to 7.67 mM. The reciprocal of t_{reac} showed a linear relationship with the product of $[NaHSO_3]_{init}$ and $[KIO_3]_{init}$ in the previous concentration range. The empirical expression $t_{reac}^{-1} = 365.6([KIO_3]_{init} \times [NaHSO_3]_{init}) + 7.20 \times 10^{-4}$ was obtained by the method of least squares (after Church and Dreskin [10]). However, $[KIO_3]_{init}$ studied in the present report was only 1.000 mM and $[NaHSO_3]_{init}$ was between 1.94 and 7.72 mM. The value of t_{reac} was also reduced by the same order as the increase in $[NaHSO_3]_{init}$. Strictly speaking, the observed t_{reac} was 1.4–2.2 times longer than expected from the empirical expression; the latter was, therefore, not applied to the low $[KIO_3]_{init}$ systems used in this work.

A typical record of Q vs. t for the Landolt reaction is shown in Fig. 1. The sample solution was $[KIO_3]_{init} = 1.000$ mM and $[NaHSO_3]_{init} = 3.24$ mM; the observed Q was 38.2 ± 0.74 J. The reaction was started by adding solid $NaHSO_3$, which dissolved easily. In Fig. 1, an endothermic heat of solution was detected soon after the addition of $NaHSO_3$. The heat of solution of crystalline $NaHSO_3$ in water was found as the mean from several runs; the standard deviation was -1.623 ± 0.020 J; ΔH was estimated to be 9.99 ± 0.12 kJ mol^{-1} at 25.0 ± 0.1°C. The value of Q_{reac} for the Landolt reaction was estimated from the observed Q and the heat of solution of $NaHSO_3$.

Plots of Q_{reac} vs. $[NaHSO_3]_{init}$ are shown in Fig. 2. For values of $[NaHSO_3]_{init}$ of 1.94, 3.24, 3.85, 4.20, 5.76 and 7.72 mM, Q_{reac} was 23.2 ± 0.28, 39.8 ± 0.76, 43.7 ± 0.80, 44.1 ± 0.63, 44.5 ± 0.79 and 44.6 ± 0.36 J, respectively. Each standard deviation is shown by error bars on each plot in Fig. 2. In the region of low $[NaHSO_3]_{init}$ or in the region of excess $[KIO_3]$, plots of Q_{reac} (J) vs. $[NaHSO_3]_{init}$ (mM) were almost linear. The

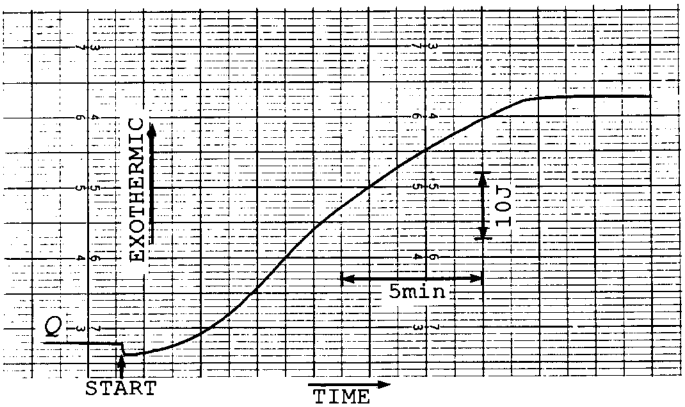

Fig. 1. Typical observed graph of Q vs. t.

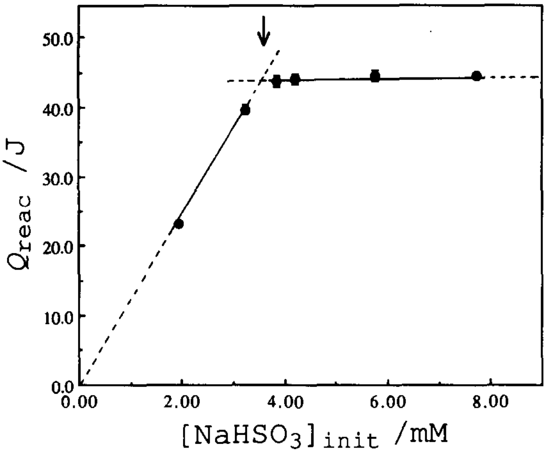

Fig. 2. Plots of Q_{reac} vs. $[NaHSO_3]_{init}$ observed for $[KIO_3]_{init} = 1.000$ mM.

empirical relation was calculated to be $Q_{reac} = 12.21[NaHSO_3]_{init} - 0.17$ by the method of least squares. However, in the region of high $[NaHSO_3]_{init}$, the same plots were almost horizontal. The empirical relation was calculated to be $Q_{reac} = 0.13[NaHSO_3]_{init} + 43.61$ by the method of least squares. In the measured range of $[KIO_3]_{init}$ values, q was not observed in a good signal-to-noise ratio, owing to small q values continuing for a long time. The first three sample solutions were colored yellow after the reaction, whereas for high $[NaHSO_3]_{init}$, no color change was found, as expected. When $[KIO_3]_{init} < [NaHSO_3]_{init}$ in the system, Q_{reac} was considered to be a constant value, determined by $[KIO_3]_{init}$. The intersection of two lines each indicating a region of excess $[KIO_3]_{init}$ and excess $[NaHSO_3]_{init}$ (Fig. 2) was at $[NaHSO_3]_{init} = 3.6$ mM (shown by an arrow in Fig. 2). The $NaHSO_3$ was consumed by oxygen dissolved in the solution [10]. The result shown in Fig. 2 was significantly larger than both the theoretical value and the 3.1 of the literature value [10]. In this work, oxygen in water or sample solutions was not eliminated, so its effect may be more significant.

For the same concentration region as reported previously [6], the pH behavior of the Landolt reaction for $[KIO_3]_{init} = 5.000$ mM, $[NaHSO_3]_{init} = 3.856$ mM, $[KIO_3]_{int} = 1.000$ mM and $[NaHSO_3]_{init} = 2.880$ mM was observed and shown in Figs. 3A and 3B, respectively. Each downward arrow in Fig. 3 corresponds to a visual change in color. However, the record of the pH change in the reaction for which $[KIO_3]_{init} = 1.000$ mM and $[NaHSO_3]_{init} = 7.676$ mM is shown in Fig. 3C; this is essentially different from A and B. The pH value in the aqueous KIO_3 solution changed from 6.1 to 2.6 after addition of crystalline $NaHSO_3$. The pH range was a little larger than in Fig. 3A or 3B, and, moreover, the minimum point indicated by a downward arrow in Figs. 3A and 3B is not

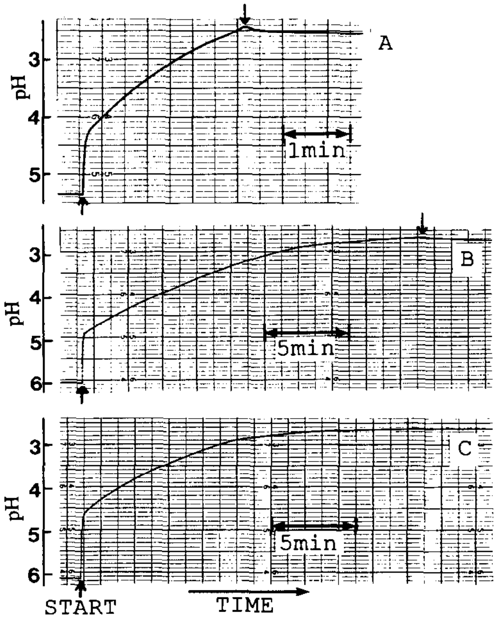

Fig. 3. Graphs of pH against time: A, $[KIO_3]_{init} = 5.000$ mM, $[NaHSO_3]_{init} = 3.856$ mM; B, $[KIO_3]_{init} = 1.000$ mM, $[NaHSO_3]_{init} = 2.880$ mM; C, $[KIO_3]_{init} = 1.000$ mM, $[NaHSO_3]_{init} = 7.676$ mM.

found in Fig. 3C. In this pH region, HSO_3^- may be considered as the only chemical species.

Reaction enthalpies calculated from Q_{reac} were plotted against ionic strength in the range from 3–29 mM and extrapolated to infinite dilution. $\Delta H^{\ominus}_{reac}$ was estimated to be −228.4 kJ per 1 mole of $[NaHSO_3]_{init}$. However, the overall reaction is also expressed by reaction (1). Ions included in reaction (1) are IO_3^-, HSO_3^-, I^-, SO_4^{2-} and H^+, and their standard formation enthalpies $\Delta H_f^{\ominus}$ in aqueous solution [11] are −221, −626.2, −55.2, −909.3 and 0 kJ mol^{-1}, respectively. The values of $\Delta H_f^{\ominus}$ for HSO_3^- was calculated to be −227.8 kJ per 1 mole of $[NaHSO_3]_{init}$, which agrees fairly well with that from experiments.

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