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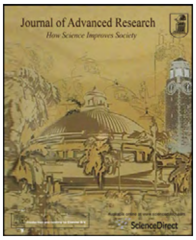

ORIGINAL ARTICLE

Study of the autocatalytic chlorate–triiodide reaction in acidic and neutral media

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Abstract The oxidation reaction of triiodide, I_3^-, by chlorate is investigated in a slightly acidic and neutral media. The reaction was verified and monitored both potentiometrically and spectrophotometrically. Generally, a slow linear decay preceded by an induction period was observed for the triiodide concentration following the addition of chlorate. The induction period is likely to be related to the time required for the generation of suitable concentrations of plausible intermediates (HIO and HIO_2), which are assumed to auto-catalyse the reaction. We examined the effect of acidity and concentrations of both chlorate and triiodide on the induction time for this reaction. The acidity of the medium influenced the induction period, while the oxidation of iodide by chlorate competed with that of iodine as the medium acidity increased, making the reaction more complicated. Therefore, a suitable pH is highly recommended for studying the chlorate–triiodide reaction. A plausible mechanism involving the HIO, HIO_2, and I_2O species is proposed.

Introduction

Since the pioneering work of Bray and Liebhafsky (BL) on the oscillation reaction of iodine and hydrogen peroxide, the oxidation reaction of iodine to iodate has received significant attention [1–5]. Several other oscillation reactions have since been proposed; these include the Briggs–Rauscher reaction, in which the acidic oxidation of malonic acid by a mixture of hydrogen peroxide and iodate is catalysed by manganous ion [6], and those based on chlorite [7] and bromite [8] – iodide reactions. Many of these reactions have also shown a clock behaviour, in which an abrupt change in the concentration of some chemical species occurs after an induction period. Recently, a clock behaviour has been observed in a highly acidic medium for a reaction involving chlorate, which suggests the possibility of new chlorate-based oscillation reactions [9]. Although they exhibit a complicated dynamic behaviour, oscillation reactions are still attracting considerable interest due to their unique importance throughout the entire spectrum of science and engineering [10–12].

Our group has for some time investigated the oxidation reactions of iodide by several important oxidants, including ozone, hydrogen peroxide, hypochlorite ions and peroxyacetic acid [13–15]. Indeed, the oxidation of iodide has served as the basis for the analysis of several oxidants [16,17]. In this paper, a clock reaction based on

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the oxidation of triiodide, I_3^-, by chlorate in slightly acidic and neutral media is presented. Iodine oxidation by hydrogen peroxide has been previously studied, but this has mainly been in a highly acidic media and in the presence of IO_3^- [18,19]. The absence of high acidity resulted in no oxidation, as previously stated by Bray [1]. Without iodate the reaction could start, but an induction period long enough to permit some iodate formation preceded it [3]. In the current study, we found that chlorate could oxidise triiodide not only in a slightly acidic media but also in a neutral media. The effect of pH and the concentrations of both chlorate and triiodide on the reaction behaviour were also investigated. A plausible mechanism explaining the nature and steps of this reaction is proposed.

Experimental

All solutions were prepared in deionised water (Milli-Q, Millipore, Japan) and all chemicals were of analytical grade. Sodium chlorate (99.0%) was purchased from Kanto Chemicals Co., Inc., Japan. To prepare a potential buffer solution, iodine was generated electrochemically in a buffered solution containing excess amount of I^-. Based on the high I^- concentration used in this investigation, iodine existed mainly as I_3^-. However, there would still have been a small amount of I_2 according to the following equilibrium:

$$I^- + I_2 \leftrightarrow I_3^-. \quad (1)$$

In the electrochemical measurements, a platinum electrode (1.6 mm in diameter) was used as the indicator electrode. The surface of the indicator electrode was polished with a fine emery paper and then with aqueous slurries of successively fine alumina powder (down to 0.06 μm) and then sonicated in an ultrasonic bath for 10 min. The electrode potential was measured versus Ag/AgCl/Cl$^-$ (KCl sat.) and a Pt spiral was used as a counter-electrode. The electrochemical measurements were performed using a 100 B/W electrochemical analyser (Bioanalytical Systems, Inc.). In the spectrophotometric measurements, a UV–vis spectrophotometer V-550 (JASCO, Co.) was used.

Results and discussion

Potentiometric investigation

A preliminary investigation of the chlorate–triiodide reaction was carried out using a potentiometric method in which a Pt electrode was used as an indicator electrode and the I_3^-/I^- redox couple was used as a potential buffer at a pH of 3.2. The reaction progress was estimated based on the change in the open circuit potential of the indicator electrode that resulted when chlorate reacted with the I_3^-/I^- potential buffer. It is worth mentioning here that the reaction of chlorate and iodide should be excluded under this condition of low acidity, since a highly acidic medium (which sometimes reaches to 12 M) is required for this reaction to proceed [20–27]. Interestingly, the potentiometric approach we used is capable of distinguishing between the reactions that consume and/or produce iodine. The following Nernstian equation was developed to estimate the change in potential, ΔE, when an oxidant, Ox, gains two electrons in the oxidation of I^- at 25 °C under the condition of the initial concentration of iodide, $[I^-]_o$, being much greater than that of the oxidant [Ox]:

$$\Delta E \text{ mV} = 29.6 \log\{(1 + [\mathrm{Ox}]/[I_3^-]_o)\}, \quad (2)$$

where $[I_3^-]_o$ is the initial concentration of I_3^-.

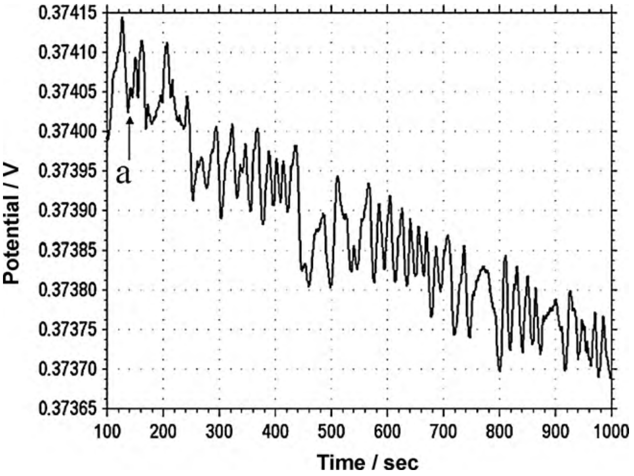

Fig. 1 The potential change due to the reaction of 10 mM $NaClO_3$ to 0.05 M acetate buffer (pH 3.2) containing 10 mM KI and 12 μM I_2. The arrow indicates the addition of $NaClO_3$ solution to the acetate buffer.

The positive change in the open circuit potential, ΔE, of the indicator electrode is direct evidence for iodide consumption or iodine production; a negative ΔE is evidence of iodine consumption or iodide production. Since a high concentration of iodide was used in this study, the change in the iodide concentration would be negligible and the change in ΔE would simply be related to the change in the iodine concentration. Fig. 1 shows the potential change which occurred when $NaClO_3$ (10 mM) was added to 0.05 M acetate buffer (pH 3.2) containing 10 mM KI and 12 μM I_2. A potential increase of 7.7 mV is expected by Eq. (1) if the reaction between $NaClO_3$ and I^- is completed. Surprisingly, instead of increasing, the potential remained constant for a period of ∼100 s and then decreased slowly. It worth mentioning that similar but shorter induction periods for the reaction of chlorate and iodine in highly acidic solutions have previously been observed [9]. The decrease in potential sustains the consumption of I_2 (in other words iodine oxidation) as inferred from Eq. (1). Following this result, we sought another technique to investigate the oxidation reaction of iodine by chlorate.

Spectrophotometric investigation

Spectrophotometric techniques have proven ideal for studying the reactions of iodine. We decided to keep the iodide in the spectrophotometric measurements in a high concentration so as to compare with the aforementioned potentiometric results and later potentiometric applications. Henceforth, we will talk about the spectrum of I_3^- not I_2. Fig. 2 depicts the immediate change in the spectrum of I_3^- after the addition of chlorate ions. In agreement with the results of Nowack and Von Gunten [23], two peaks at 288 and 352 nm were identified for I_3^- in a 0.1 M phosphate buffer (PB) (pH 7) containing 10 mM KI and 0.1 mM I_3^- (Fig. 2a). The intensity of these peaks decreased significantly, as shown in Fig. 2b, after the addition of 1.36 ml of 0.5 M $NaClO_3$ to 5 ml of 0.1 M PB containing 10 mM KI and 0.1 mM I_3^-. The large decrease in the peak intensities is likely due to the high concentration of ClO_3^- added. This confirms the existence of a reaction between I_3^- and chlorate under the described conditions. Interestingly, the intensity of the peaks decreased gradually with the concentration of chlorate, which is very useful for chlorate analysis. A similar approach – but based on the oxidation of indigo carmine by chlorate ions in an acidic solution – has recently been reported for chlorate determination [28]. The change