

5.02 Kinetics of the Persulfate-iodide Clock Reaction (4 points)

In this experiment you will investigate the kinetics of the reaction between persulfate and iodide ions



The rate of reaction may be measured by adding a small, known quantity of thiosulfate. The iodine produced in this reaction (R1) is, as it is formed, reduced back to iodide by the thiosulfate:



thiosulfate

tetrathionate

This continues until all the thiosulfate has been consumed, whereupon any further iodine formed in reaction (R1) has nothing to react with, so begins to appear in the solution. Iodine of course is coloured, so by determining when iodine first becomes visible, it is possible to measure the speed of reaction (R1). To make the measurement more precise, the colour of the iodine is enhanced by the addition of starch solution.

Self-indicating reactions of this type, in which nothing seems to happen for while and then a change suddenly becomes visible, are known as clock reactions. Clock reactions often appear in chemistry shows, and many involve iodine, since the colour change resulting from the generation of iodine is particularly marked. However, other chemical systems, such as the ceric/cerous/bromide reactions involved in the Belousov-Zhabotinskii reaction [1] show similar behaviour.

A few clock reactions are cyclic, so that the abrupt change of colour repeats; these are known as "oscillating clocks", for obvious reasons. In an oscillating clock reaction multiple stationary states exist; the system is repeatedly switched between those states. For this to happen, chemical feedback is essential - this is typically the result of autocatalysis. Limitation of the reaction rate by diffusion through the solution is also required. Further details of oscillating reactions are given in reference [2].

Background information

You should be able to fully understand the theory behind this experiment on the basis of your knowledge of 1st year kinetics.

Relevant lecture courses: Introduction to Kinetics (Hilary term, 1st year); Electrochemistry (Trinity term, 1st year); States of matter (Trinity term, 1st year); Reaction Kinetics (Michaelmas term, 2nd year).

Safety

The chemicals that you need for this experiment present a negligible risk to health, apart from ammonium persulfate, which, in rare cases, may act as a sensitizer.

For further information, see the safety details at the end of these instructions, and <http://ptcl.chem.ox.ac.uk/~hmc/tlab/experiments/502.html>.

Theory

In Part 1 of the experiment you will investigate the effect of reactant concentration on the rate of reaction, and thereby obtain the rate equation. The effect of temperature is studied in Part 2, and the results used to find the activation energy for the reaction. Finally, in Part 3 the effect of the ionic strength of the solution on the rate is measured, from which a possible structure of the reaction intermediate may be deduced.

Rate equation

At constant temperature and ionic strength, the rate equation for reaction (R1) is

$$\text{Rate} = - \frac{d[S_2O_8^{2-}]}{dt} = k [S_2O_8^{2-}]^m [I^-]^n \quad (1)$$

In this experiment you will use the initial rate method to find the orders m and n . The rate of reaction is measured over a period short enough for the reaction not to have proceeded significantly, but long enough for it to be unaffected by the time required for mixing at the beginning of the reaction. (What sort of complications do you think might arise if the reaction is monitored for a long period of time?)

The stoichiometric equation (R1) tells us that the rate of consumption of persulfate equals the rate of iodine production. In each experiment, you will measure the time, Δt , taken to consume a known amount of thiosulfate (at which point the solution turns blue).

The same amount of thiosulfate will be used each time, so the total amount of iodine, $\Delta[I_2]$, produced in time Δt will be the same and, provided the amount of thiosulfate added is much less than the initial amount of persulfate, we can make the approximation

$$- \left\{ \frac{d[S_2O_8^{2-}]}{dt} \right\}_{init} = \left\{ \frac{d[I_2]}{dt} \right\}_{init} = \frac{\Delta[I_2]}{\Delta t} \quad (2)$$

Since $\Delta[I_2]$ is the same for each experiment, it follows that the initial rate is inversely proportional to Δt , i.e.

$$-\left\{\frac{d[S_2O_8^{2-}]}{dt}\right\}_{init} = \frac{const}{\Delta t} \quad (3)$$

Taking logs and substituting back into equation 1,

$$\ln \frac{1}{\Delta t} = \ln k + m \ln [S_2O_8^{2-}] + n \ln [I^-] + const \quad (4)$$

Thus a plot of $-\ln \Delta t$ against $\ln[S_2O_8^{2-}]$ at constant $[I^-]$ should yield a straight line of slope m , and a graph of $-\ln \Delta t$ against $\ln [I^-]$ at constant $[S_2O_8^{2-}]$ will give n .

Effect of temperature

The rate coefficients k of many simple reactions are found to vary with temperature T according to the Arrhenius equation

$$k = A \exp^{-E/RT} \quad (5)$$

in which A is the pre-exponential factor and E the activation energy of the reaction. This expression was originally proposed by Arrhenius and Van't Hoff on the basis of the Van't Hoff isochore [3]. We may interpret A as a measure of the collision frequency between reactants in solution and $\exp^{-E/RT}$ as the Boltzmann factor which gives the fraction of the molecules with sufficient energy, E , to react. [4].

Comment: In the gas phase, the value of A is often close to the collision number - the number of collisions suffered by a molecule per second. In solution, however, most collisions which a molecule suffers will not be with anything with which it can react, but instead with solvent molecules or other non-reactive species. The number of collisions with a potential reactant molecule will be much smaller, and accordingly we expect that A will be much less than the actual number of collisions per second. The collision number can readily be calculated using the Kinetic Molecular Theory of Gases.

For reactions such as the present one which show Arrhenius-type behaviour

$$\ln k = \ln A - E/RT \quad (6)$$

provided that E is independent of temperature, which is usually a good approximation over a small temperature range. Thus both A and E may be obtained from a graph of $\ln k$ against $1/T$.

Effect of ionic strength

The rate constant of an ionic reaction depends upon the ionic strength of the solution. This "primary kinetic salt effect" may be understood qualitatively in terms of favourable interactions between the reactants and activated complex and the ionic atmospheres of oppositely charged ions which surround them in solution. Three cases may be identified:

(a) *If the charges on the reactants have the same sign*, the activated complex will be more highly charged than the reactants. Increasing the ionic strength of the solution will therefore have a greater stabilizing effect upon the complex than on the reactants, and will thus increase the rate constant by lowering the effective activation energy.

(b) *If the charges on the reactants have different signs, the charge on the activated complex will be lower than the charges on the reactants, and the rate constant will decrease with ionic strength.*

(c) *If one of the reactants is uncharged, there will be, in a simple picture, no change in the rate constant with ionic strength.*

This qualitative explanation of the primary kinetic salt effect is all that is needed for the present experiment.

Procedure

Prepare the following solutions (a volume of 250 cm³ should be sufficient for solutions (a) and (c), you will need to prepare 500 cm³ of solution (b)):

(a) 0.1M (NH₄)₂S₂O₈

(b) 0.1M (NH₄)₂SO₄

(c) 0.01M Na₂S₂O₃.

Fill burettes with solutions (a) and (b).

Make up a solution (d) by filling a 500 cm³ volumetric flask with 333 cm³ of solution (b), dissolving in it 8.30 g (0.050 moles) of solid KI, and making up to 500 cm³ with deionized water. Verify that the total ionic strength of solution (d) is the same as that of solution (a) and of solution (b); the formula for ionic strength is given in the Appendix.

Rate equation

Place 10 cm³ of solution (a) and one drop of starch solution in a beaker. In a 100 cm³ conical flask place 10 cm³ of 0.1 M KI solution (d) and 5 cm³ solution (c). Mix, start the stopwatch, and record the time to the appearance of the blue colour. Repeat with different volumes of the S₂O₈²⁻ and I⁻ solutions as indicated in the table below, keeping the ionic strength constant in each case by making up the volume with the ammonium sulphate solution.

| S ₂ O ₈ ²⁻ solution (a) | (NH ₄) ₂ SO ₄ solution (b) | S ₂ O ₃ ²⁻ solution (c) | I ⁻ solution (d) |
|---|---|---|--------------------------------|
| 10 | 0 | 5 | 10 |
| 10 | 2 | 5 | 8 |
| 10 | 4 | 5 | 6 |
| 10 | 6 | 5 | 4 |
| 8 | 2 | 5 | 10 |
| 6 | 4 | 5 | 10 |
| 4 | 6 | 5 | 10 |

Effect of temperature

Make up a mixture of 10 cm³ of solution (a) with a few drops of starch solution, and a second solution containing 10 cm³ of (c) and 10 cm³ of (d). Place the persulfate/starch and iodine/thiosulfate solutions in a thermostat bath for 10 minutes, and then record the temperature of the solutions (not the bath! The temperature of the solutions will, especially for the higher temperatures, be appreciably different from that of the bath). Mix and note the time to the appearance of the blue colour. Repeat the procedure at 5 temperatures up to 50°C.

Effect of ionic strength

Compare the initial rates at room temperature for the following two reaction mixtures

10 cm³ S₂O₈²⁻, 5 cm³ S₂O₃²⁻, 10 cm³ I⁻ and 10 cm³ 0.1M (NH₄)₂SO₄ solution.

10 cm³ S₂O₈²⁻, 5 cm³ S₂O₃²⁻, 10 cm³ I⁻ and 10 cm³ demineralised water.

Calculations

For each solution tabulate the composition and the time required for the first appearance of a blue colour.

Calculate *m* and *n*, the order of reaction with respect to persulfate and iodide ions.

Calculate values of the activation energy and pre-exponential factor, showing your working clearly. Find the value of the rate constant at 298 K.

Comment on the effect of the reduction in ionic strength on the rate of reaction and determine whether the reactants which form the activated complex have charges of the same or different sign.

Identify sources of error in the experiment and estimate their magnitude.

References

1. R.J.Field, E.Koros and R.M.Noyes, *J. Am. Chem. Soc.* 94, 8649 (1972).
2. *Physical Chemistry* (Part 3) R.S.Berry, S.A.Rice and J.Ross, John Wiley and Sons.
3. *Chemical Kinetics*, K.J.Laidler, McGraw-Hill, New York.
4. *Physical Chemistry*, P.W.Atkins, Oxford University Press, Oxford and New York.

Chemical properties, hazards and emergency treatment

Avoid skin contact with ammonium persulfate, which is reported to act as a sensitizer in a small number of people if inhaled or in contact with the skin; you may wish to use gloves when handling this material, although the possibility of harm is very low. The chemicals used in this experiment present a negligible risk to health through other routes of exposure.

Appendix

Consider a simple reaction between ions A and B, with charges z_A and z_B , which proceeds through an activated complex $(AB)^*$ with rate constants k_2 and k^* .



The charge on the activated complex is $(z_A + z_B)$, and the rate equation for the second order reaction will be

$$\text{Rate} = k_2 [A] [B] = k^* [(AB)^*] \quad (7)$$

If we assume that the activated complex is in equilibrium with the reactants

$$K^* \frac{a^*}{a_A a_B} = \frac{[(AB)^*] \gamma^*}{[A] [B] \gamma_A \gamma_B} \quad (8)$$

Since the species are ionic, the equilibrium constant K^* must be expressed as a quotient of the activities of the activated complex a^* and the activities of the reactants a_A and a_B . These activities are then expressed as products of concentrations and activity coefficients γ .

Combining equations 7 and 8 and taking logs

$$\log k_2 = \log (k^* K^*) + \log (\gamma_A \gamma_B / \gamma^*) \quad (9)$$

Using the Debye-Huckel limiting law in the form

$$\log \gamma_i = -A z_i^2 I^{\frac{1}{2}}$$

we obtain the Bronsted equation

$$\log k_2 = \text{const} + 2A z_A z_B I^{\frac{1}{2}} \quad (10)$$

The ionic strength is defined by

$$I = \frac{1}{2} \sum_i c_i z_i^2 \quad (11)$$

where c_i is the concentration (strictly molality) of each ionic species, and z_i the charge of each species. The summation must include all ionic species present in the solution, not merely the reactant ions, since the stabilization produced by the ionic atmosphere around each ion does not depend upon the identity of the counterions.