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Reinvestigation of the kinetics of reduction of bromite by hexacyanoferrate(II) in slightly basic solution

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The reaction

$$\mathrm{BrO_2^- + 4\,Fe(CN)_6^{4-} + 2\,H_2O \longrightarrow Br^- + 4\,Fe(CN)_6^{3-} + 4\,OH^-}$$

has been studied by spectrophotometry at 30, 40 and 50 °C and both with equivalent amounts of reactants and with an excess of bromite. It follows the kinetic expression

$$\frac{d\xi}{dt} = k_{\mathrm{obs}}\left[\mathrm{BrO_2^-}\right]\left[\mathrm{Fe(CN)_6^{4-}}\right]^2$$

with $k_{\mathrm{obs}} = 8.2\ \mathrm{M^{-2}\,s^{-1}}$ at 25 °C, $\Delta H^{\neq} = 66\ \mathrm{kJ\,mol^{-1}}$ and $\Delta S^{\neq} = -121.7\ \mathrm{J\,K^{-1}\,mol^{-1}}$. The proposed mechanism is a two-stage process, the first, rate-determining stage being reduction of bromite to hypobromous acid, the second further reduction to bromide. Either stage consists of two bimolecular reactions. The major contribution to the energy barriers comes from electrostatic repulsion between negative ions.

Introduction

Many years ago we studied the reduction of $\mathrm{BrO_2^-}$ by $\mathrm{Fe(CN)_6^{4-}}$:[1]

$$\mathrm{BrO_2^- + 4\,Fe(CN)_6^{4-} + 2\,H_2O \longrightarrow Br^- + 4\,Fe(CN)_6^{3-} + 4\,OH^-}$$

with the aim of finding a reliable method for the separate determination of hypobromite and bromite in solutions of electron- and gamma-irradiated solid bromates.[2] It was demonstrated that the reduction of the former is sufficiently fast to permit its use in a potentiometric titration, whereas the latter reacts so slowly that it will not interfere under normal conditions. Of the reacting species $\mathrm{Fe(CN)_6^{3-}}$ is more strongly coloured than the others, so spectrophotometry is a convenient method for measuring the rate of reaction. It was stated in the paper on the analytical method that the reaction with bromite is first order in either reactant and thus second order overall. However, a recent detailed analysis of the data showed this to be incorrect. The results of the renewed investigation are presented in the present paper.

Whereas the chemical properties of the hexacyanoferrates are well known, not much information on the behaviour of bromite ion in aqueous solution is found in the literature, and statements concerning its stability relative to other oxoanions are often unreliable. Recently, a few studies on the reactivity of bromite have been published by Margerum and coworkers.[3,4] In the former paper they also give a procedure for preparation of barium bromite and a salt mixture containing sodium bromite, but no hypobromite. The latter is removed by reduction with sulfite, which reacts orders of magnitude faster with hypobromite[5] than with bromite.[6] An earlier method is reduction with ammonia,[7,8] but this substance also reacts fairly quickly with bromite, thus reducing the yield.[1]

Experimental

The experimental parameters are given in Table 1. Sodium bromite stock solution was prepared by dissolving crystals of $\mathrm{NaBrO_2{\cdot}3H_2O}$, obtained as a gift from the Société d'Etudes Chimiques pour l'Industrie et l'Agriculture, Paris (SECPIA),[9] in ice-cooled 0.3 M NaOH. A fresh solution was prepared daily, stored at 0 °C and standardized by adding an excess of arsenic(III) oxide solution and titrating the excess with a solution of iodine in potassium iodide. Potassium hexacyanoferrate(II) stock solution, 0.01 M, also contained 0.2 g of sodium carbonate $\mathrm{L^{-1}}$ and was stored in a dark bottle. The solutions for the kinetic experiments were prepared at 0 °C and contained 0.225 mol of $\mathrm{NaHCO_3}$ $\mathrm{L^{-1}}$ as well as a small amount of acetic acid to adjust the pH to 8.9. The total volume of solution for each experiment was 200 mL.

Since at that time, a recording spectrophotometer with thermostatted cell compartment was not available, we had to take samples from the reaction mixture at selected time intervals for absorbance measurements. The flask with solution was placed in the thermostat immediately after mixing, and each sample was cooled in ice to slow down the reaction and then measured as soon as possible.

The measurements were carried out at 423 nm, the absorbance maximum of $\mathrm{Fe(CN)_6^{3-}}$, on a Beckman DU spectrophotometer model G4700. A 1.00 mM solution of $\mathrm{K_4Fe(CN)_6}$ was used as reference, and a standard curve of $\mathrm{Fe(CN)_6^{3-}}$ had previously been recorded, yielding $A_{423} = 1000\ \mathrm{M^{-1}\,cm^{-1}}$.

Results

Experiments with equivalent concentrations of bromite and hexacyanoferrate(II) were carried out at 30, 40 and 50 °C, and one experiment with a 10-fold excess of bromite was carried out at 50 °C. The first sample was taken 10 min after start and subsequent samples at intervals of 10 min up to 1 h, then at intervals of 15 min up to 2 h. The experiment with excess bromite was terminated after 50 min.

As already stated above, the assumption of second-order kinetics turned out to be wrong, because the two experiments at 50 °C do not yield the same rate constant; the discrepancy is significantly larger than expected from experimental uncertainty. Instead, we try the rate expression

$$\frac{d\xi}{dt} = k_{\mathrm{obs}}\left[\mathrm{BrO_2^-}\right]\left[\mathrm{Fe(CN)_6^{4-}}\right]^2 \qquad (1)$$

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Table 1 Experimental parameters and results

T/°C	25	30	40	50	50
$[\mathrm{Fe(CN)_6}^{4-}]_{t=0}$/mM		1.00	1.00	1.00	1.00
$[\mathrm{BrO_2}^{-}]_{t=0}$/mM		0.25	0.25	0.25	2.50
k_{obs}/M^{-2} s^{-1}		13.5 ± 0.4	28.3 ± 0.7	71.1 ± 0.8	71 ± 4
k_{fit}/M^{-2} s^{-1}	8.2 ± 0.6	13.0	30.8	69.5	69.5

The standard deviation of k_{fit} is 7%.

where ξ is the usual degree of advancement. In the case of equivalent concentrations we have

$$-\frac{\mathrm{d}\left[\mathrm{Fe(CN)_6}^{4-}\right]}{\mathrm{d}t}=k_{\mathrm{obs}}\left[\mathrm{Fe(CN)_6}^{4-}\right]^3 \qquad (2)$$

which may be integrated to yield

$$\frac{1}{2\left[\mathrm{Fe(CN)_6}^{4-}\right]^2}-\frac{1}{2a^2}=k_{\mathrm{obs}}t \qquad (3)$$

a being the initial concentration of hexacyanoferrate(II). With nonequivalent concentrations we have $[\mathrm{Fe(CN)_6}^{4-}] = a - 4\xi$ and $[\mathrm{BrO_2}^-] = b - \xi$, and thus

$$\frac{\mathrm{d}\xi}{\mathrm{d}t}=k_{\mathrm{obs}}(b-\xi)(a-4\xi)^2 \qquad (4)$$

On integration this yields

$$\frac{1}{4b-a}\left[\frac{1}{a-4\xi}-\frac{1}{a}+\ln\frac{b(a-4\xi)}{a(b-\xi)}\right]=k_{\mathrm{obs}}t \qquad (5)$$

A plot of the left side of eqns. (3) or (5) *vs.* time should thus yield a straight line with slope k_{obs}. Fig. 1 shows the results.

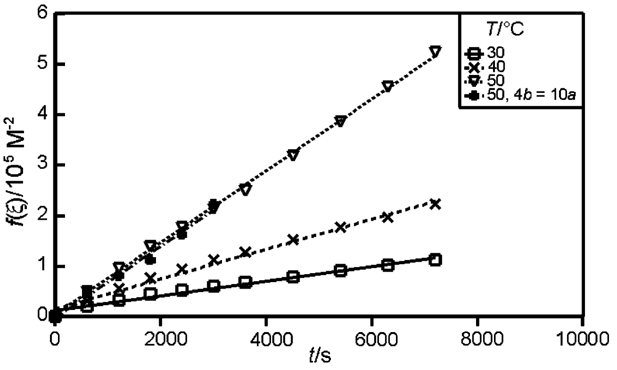

Fig. 1 Plots of third-order kinetics. The ordinate, indicated $f(\xi)$, is .the left-hand side of eqn. (3) in the experiments with equivalent concentrations and the left-hand side of eqn. (5) in the experiment with excess of bromite.

We may conclude that the reduction of bromite by hexacyanoferrate(II) is a third-order reaction, being first order with respect to the former and second order with respect to the latter. The Arrhenius plot yields the activation energy $E_a = 68 \pm 4$ kJ mol^{-1} and the frequency factor $A = 7.8 \times 10^{12}$ M^{-2} s^{-1}, whereas the transition state formalism, plotting $\ln(k_{\mathrm{obs}}/T)$ against $1/T$, yields $\Delta H^{\neq} = 66 \pm 4$ kJ mol^{-1} and $\Delta S^{\neq} = -121.7 \pm 0.6$ J K^{-1} mol^{-1}

Table 1 gives the values of k_{obs} and the fitted values k_{fit} from these plots.

A close inspection of Fig. 1 reveals that the regression lines for the experiments at 30 and 40 °C do not pass precisely through the origin. This is a consequence of the method of sampling and measurement. It took some time to cool the samples, and they were partly reheated when placed in the spectrophotometer, resulting in a small progress of the reaction. The relative error arising from this is more important in the early stage of an experiment, where reactant concentrations are highest, and it increases with decreasing temperature as seen from both Fig. 1 and the standard deviations (on a relative scale) of k_{obs} (Table 1).

Discussion

We propose the following mechanism:

$$\mathrm{Fe(CN)_6}^{4-} + \mathrm{BrO_2}^{-} \longrightarrow [\mathrm{Fe(CN)_6{\cdot}BrO_2}]^{5-} \qquad \text{(I)}$$

$$[\mathrm{Fe(CN)_6{\cdot}BrO_2}]^{5-} + \mathrm{Fe(CN)_6}^{4-} + 2\,\mathrm{H_2O} \longrightarrow 2\,\mathrm{Fe(CN)_6}^{3-} + \mathrm{HBrO} + 3\,\mathrm{OH}^- \qquad \text{(II)}$$

$$\mathrm{Fe(CN)_6}^{4-} + \mathrm{HBrO} \longrightarrow [\mathrm{Fe(CN)_6{\cdot}HBrO}]^{4-} \qquad \text{(III)}$$

$$[\mathrm{Fe(CN)_6{\cdot}HBrO}]^{4-} + \mathrm{Fe(CN)_6}^{4-} \longrightarrow 2\,\mathrm{Fe(CN)_6}^{3-} + \mathrm{Br}^- + \mathrm{OH}^- \qquad \text{(IV)}$$

Both the hexacyanoferrate(II) ion and the bromite ion are very weak bases and are not protonated to any appreciable extent at pH 8.9. On the other hand, hypobromous acid is a very weak acid with pK_a = 8.8 at an ionic strength of 0.5,[5] so a substantial fraction is protonated at pH 8.9 at the present ionic strength of about 0.25, where pK_a is higher. It is therefore reasonable to take the undissociated acid as reactant in reaction (III).

We already know that reactions (III) and (IV) are fast,[1] whence reactions (I) and (II) are likely to be rate-determining. The overall reaction rate is the rate of disappearance of bromite, which equals the rate of formation of hypobromous acid by reaction (II):

$$\frac{\mathrm{d}\xi}{\mathrm{d}t}=k_{\mathrm{II}}[\mathrm{AB}][\mathrm{A}] \qquad (6)$$

where A and B are short-hand notations for hexacyanoferrate(II) and bromite, respectively. We further have for the ion-pair hexacyanoferrate(II)–bromite

$$\frac{\mathrm{d}[\mathrm{AB}]}{\mathrm{d}t}=k_{\mathrm{I}}[\mathrm{A}][\mathrm{B}]-k_{-\mathrm{I}}[\mathrm{AB}]-k_{\mathrm{II}}[\mathrm{AB}][\mathrm{A}] \qquad (7)$$

Using the stationary-state approximation for AB yields

$$[\mathrm{AB}]=\frac{k_{\mathrm{I}}[\mathrm{A}][\mathrm{B}]}{k_{-\mathrm{I}}+k_{\mathrm{II}}[\mathrm{A}]} \qquad (8)$$

which, when inserted in eqn. (6), results in

$$\frac{\mathrm{d}\xi}{\mathrm{d}t}=\frac{k_{\mathrm{I}}k_{\mathrm{II}}[\mathrm{A}]^2[\mathrm{B}]}{k_{-\mathrm{I}}+k_{\mathrm{II}}[\mathrm{A}]} \qquad (9)$$

This is identical with the observed kinetics, provided that $k_{-I} \gg k_{II}[A]$, and we have $k_{obs} = k_I k_{II}/k_{-I}$.

However, a reaction between two negative ions, of which at least one has a high charge, does not seem very probable, whence a theoretical estimate of the kinetic parameters should be attempted. The necessary expressions of rate constants, based on theories of Debye[10] and Fuoss,[11] are found in a classical paper by Eigen.[12] For the rate constant of a diffusion-controlled bimolecular reaction between two ions A and B in solution, represented by k_I and k_{II}, we have

$$k_D = \frac{4\pi N_A Z(r_A + r_B)(D_A + D_B)}{\exp Z - 1} \qquad (10)$$

where

$$Z = \frac{z_A z_B e^2}{4\pi\varepsilon_0 K_r (r_A + r_B) kT} \qquad (11)$$

Each z denotes the charge in units of the electronic charge, each D the diffusion coefficient and each r the radius of the ion, and K_r is the relative dielectric constant of the solution (Eigen uses c.g.s. units, whence his expression of Z is slightly different). Similarly, the rate constant k_{-I} is given by

$$k_{-I} = \frac{3Z(D_A + D_B)}{(r_A + r_B)^2[1 - \exp(-Z)]} \qquad (12)$$

For two positive or two negative ions the exponential in the denominator of eqn. (10) is $\gg 1$, and so the contribution from electrostatic interactions to the activation energy is

$$E_a' = \frac{N_A z_A z_B e^2}{4\pi\varepsilon_0 K_r (r_A + r_B)} \qquad (13)$$

The diffusion coefficients may be obtained from the ionic conductivities, using the Nernst–Einstein equation

$$D_i = \frac{RT\lambda_i}{z_i^2 F^2} \qquad (14)$$

For $Fe(CN)_6^{4-}$ we have[13] $\lambda = 0.0444$ S m^2 mol^{-1}, which yields $D = 0.739 \times 10^{-9}$ m^2 s^{-1}. The value of λ for the bromite ion is unknown, but a reasonable guess on the basis of the values for the oxoions of Cl and for BrO_3^- is $\lambda = 0.0045$ S m^2 mol^{-1}, which gives $D = 1.198 \times 10^{-9}$ m^2 s^{-1}.

For the ionic radii we have several choices, but to avoid the complication of using different values in different expressions, we shall use the hydrodynamic radii calculated from the Stokes–Einstein equation

$$D_i = \frac{kT}{6\pi\eta r_i} \qquad (15)$$

where η, the dynamic viscosity of water at 25 °C, equals 0.8903 mPa s. This yields

$$Fe(CN)_6^{4-}: r = 3.32 \times 10^{-10}\ \text{m}$$
$$BrO_2^-: r = 2.05 \times 10^{-10}\ \text{m}$$

We also need the radius and the diffusion coefficient of the ion pair of hexacyanoferrate(II) and bromite. We assume that the two ions are spherical and then add the volumes calculated from the above radii. If we further assume that the ion pair is also spherical, we find its radius $r = 3.56 \times 10^{-10}$ m. Finally, we calculate its diffusion coefficient from eqn. (15): $D = 0.689 \times 10^{-9}$ m^2 s^{-1}.

When we insert these values in eqns. (10)–(13) together with the relative permittivity of water at 25 °C, $K_r = 78.54$, we find $E_a'(I) = 13.2$ kJ mol^{-1}, $k_I = 2.06 \times 10^8$ M^{-1} s^{-1} and $E_a'(II) = 51.4$ kJ mol^{-1}, $k_{II} = 149.2$ M^{-1} s^{-1}

There is no significant electrostatic contribution to the activation energy related to k_{-I}, because the exponential in the denominator of eqn. (12) is $\ll 1$. We have from eqn. (12)

$$k_{-I} = 1.077 \times 10^{11}\ \text{s}^{-1}$$

The sum of the two activation energies is 64.6 kJ mol^{-1}, to which we should add a contribution from the dependence of diffusion coefficients on temperature. This may be estimated from the temperature dependence of ionic conductivities of $Fe(CN)_6^{4-}$,[13] which yields $E_a^D = 13.8$ kJ mol^{-1}; it enters only once, because two of the factors $D_A + D_B$ cancel as seen from eqns. (10) and (12). We note that the condition $k_{-I} \gg k_{II}[A]$ for third-order kinetics (eqn. (9)) is fulfilled.

The resulting estimated activation energy and rate constant are thus $E_a = 78.4$ kJ mol^{-1} and $k_{calc} = 0.285$ M^{-2} s^{-1}

The former value is significantly higher and the latter significantly lower than the experimental values. However, the theoretical values are highly sensitive to the choice of ionic radii. For instance, by increasing the radii of the hexacyanoferrate(II) ion and the hexacyanoferrate(II)-bromite ion pair by as little as 15%, perfect agreement between theory and experiment is obtained.

A negative activation entropy is typical of second- or higher-order reactions between ions which are not strongly hydrated. The value found in the present study is in line with values for other reactions between negative ions in aqueous solution.[14]

Conclusion

The reduction of bromite by hexacyanoferrate(II) is a third-order reaction in two stages, of which the first, being rate-determining, is the reduction of bromite to hypobromous acid, and the second and much faster, is the further reduction to bromide. The first stage involves two bimolecular reactions, either one between two negative ions, which means that electrostatic repulsion is the main contribution to energy barriers. This also explains the much faster reduction of hypobromite: Due to the low dissociation constant of hypobromous acid, the electrostatic energy barrier is absent in the first elementary process, and in the second it is reduced by 20%. This alone would cause an increase in reaction rate by more than a factor of 10^4 compared to the reduction of bromite, provided that the mechanism proposed above is correct.

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