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Effect of Dissolved Oxygen on the Oxidation of Dithionate Ion. Extremely Unusual Kinetic Traces

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The effect of dissolved oxygen on the acid-dependent disproportionation of dithionate ion ($S_2O_6^{2-}$) and its oxidation with a number of reagents (I_2, Br_2, I_3^-, Br_3^-, IO_3^-, BrO_3^-, IO_4^-, MnO_4^-, Cr(VI), Ce(VI), and H_2O_2) were studied. Dithionate ion is remarkably inert at room temperature, and heating to elevated temperatures (50–90 °C) was necessary to observe detectable reaction rates in all of these processes. It was confirmed that dithionate ion is never oxidized directly; its redox reactions are zeroth-order with respect to the oxidizing agent and proceed through disproportionation and subsequent fast oxidation of the sulfur(IV) formed. The effect of dissolved oxygen is attributable to its reaction with sulfur(IV) produced in the disproportionation. This autoxidation occurs only with a catalyst. Cerium(III) and iodide ions were shown to catalyze the autoxidation, and their effect on the kinetic traces was studied. In a few cases, highly unusual kinetic traces, such as straight lines with sharp break points, inverted parabolas, and a combination of these, were detected and successfully interpreted in terms of simple kinetic and stoichiometric considerations.

Introduction

Dithionate ion ($S_2O_6^{2-}$) is usually formed as a byproduct in various oxidation reactions of sulfur(IV).[1] Its formation was also reported in the iron(III)−sulfite ion redox process.[2−4] Model calculations based on our ongoing studies to clarify mechanistic details of the catalytic role of iron(III) in the autoxidation of sulfur(IV)[5−7] indicated that dithionate ion, if formed, may accumulate in the system. Thus any possible reaction of $S_2O_6^{2-}$ could significantly alter the overall rate of the autoxidation, and kinetic models should include these reaction pathways. As the reactivity of the dithionate ion can be studied independently of the autoxidation of sulfur(IV), we have designed detailed experiments to explore the possible complex formation and redox reactions of $S_2O_6^{2-}$ with special emphasis on the potential role of dissolved oxygen.

As this work unfolded, it became clear that dithionate ion is quite inert in aqueous solution at room temperature but becomes more reactive at elevated temperatures, implying that its reactions are not very significant in the autoxidation of sulfite ion under environmental conditions. However, the mechanistic conclusions drawn from the high-temperature studies can still be quite important in understanding some of the unusual kinetic patterns associated with the decomposition of dithionate ion in the presence of a series of common oxidants such as I_2, Br_2, I_3^-, Br_3^-, IO_3^-, BrO_3^-, IO_4^-, MnO_4^-, Cr(VI), Ce(IV), and H_2O_2. We found several cases in which the shapes of the detected kinetic traces were extremely unusual. These shapes included straight lines with sharp break points, parabolas, and a combination of these and were readily interpreted in terms of very simple kinetics. Apart from the obvious goal of reporting mechanistic details on the reactions of dithionate ion, this paper also aims to give some insight into how very simple kinetics can result in quite surprising absorbance−time traces.

A further point of interest in these studies relates to the Ce(IV)/Ce(III)/$S_2O_6^{2-}$/S(IV) redox system because of the widespread analytical uses of Ce(IV)−sulfur(IV) reaction and the accompanying chemiluminescence.[8−13]

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Experimental Section

Materials. Sodium dithionate dihydrate ($Na_2S_2O_6 \cdot 2H_2O$) was prepared by oxidizing aqueous sulfur dioxide with manganese dioxide as described in the literature.[14] The crystalline product was characterized by thermogravimetry, which indicated two separate endothermic steps. The first step (loss of $2H_2O$) occurred from 90 to 130 °C and was accompanied by a weight loss of 14.92% (calculated: 14.88%). After the second step (loss of SO_2 from 240 to 280 °C) the overall weight loss was 41.23% (calculated: 41.34%). A concentrated aqueous solution of the prepared crystals did not give any detectable precipitation with 0.1 M $Ba(ClO_4)_2$ solution, leading to the conclusion that any possible contamination of sulfite or sulfate ion was present at a very low concentration level. Other chemicals used in this study were of analytical reagent grade and purchased from commercial sources. Doubly deionized and ultrafiltered water from a Millipore Q system was used to prepare the stock solutions and samples. All experiments were carried out at high and constant acid concentration, and additional salt was not used to adjust the ionic strength. Unless otherwise stated, perchloric acid was used in the kinetic experiments.

Instrumentation. UV−vis spectra were recorded on an Hewlett-Packard 8543 diode array and a UNICAM Helios-α scanning spectrophotometer. Kinetic experiments were performed on the diode-array instrument, and a built-in Hewlett-Packard 89090A Peltier thermostat was used to maintain constant temperature. A Metrohm 6.0234.100 combination electrode attached to a Radiometer PHM84 pH meter was used for pH-potentiometric experiments. The electrode was calibrated to yield readings as $-\log [H^+]$.[15]

Results

Acid−Base Properties of Dithionate Ion. The only previous record on the acid−base properties of the dithionate ion known to us dates back to the 1910s.[16] In that work, two successive protonation steps of dithionate ion were reported with $pK_2 = 3.4$ and $pK_1 = 0.2$. However, our experiments did not confirm these results.

pH-potentiometric measurements (Table S1 in Supporting Information) did not indicate any decrease in the free hydrogen ion concentration upon addition of sodium dithionate to an acid sample even with large concentration levels (up to 0.07 M). In another set of experiments, dithionate ion was added to solutions of sulfur(IV) or iron(III). It was not possible to shift the UV−vis spectra of these samples in this way, although they are sensitive to the change in the hydrogen ion concentration under the conditions applied.[6−7,17−21] Kinetic data obtained during the disproportionation of dithionate ion, both published earlier[22−30] and measured in this work, did not indicate a measurable equilibrium between two different protonated forms, which should almost certainly have different reactivities. A quantitative analysis showed that a pK_2 around 0 should have been readily detectable in all of these different sets of experiments; thus the pK_2 (and consequently pK_1) of dithionate ion must be considerably smaller than 0.

In summary, our results show that dithionate ion is predominantly present as a dinegative ion in the acidity range used in this study. This conclusion is supported by three independent methods; therefore we conclude that the earlier data on the protolytic reactions[16] were in error.

Preliminary Kinetic Observations. In agreement with earlier literature data,[22−30] our experiments showed that dithionate ion is rather inert toward complex formation or redox reactions at room temperature. For example, acidic solutions containing dithionate and permanganate ions could be stored for hours at 25 °C without significant loss of permanganate ion, although the redox reaction has a considerable thermodynamic driving force according to relevant standard redox potentials.[31] Spectrophotometric studies under various conditions did not reveal any evidence for complex formation between dithionate ion and iron(III) or cerium(IV). However, when the temperature was increased, a rich group of redox reactions were observed with various oxidizing agents. In agreement with earlier conclusions,[24−29] the disproportionation of dithionate ion was also detected at high temperature. The effect of dissolved oxygen was tested in all processes by comparing kinetic observations in experiments carried out with air-saturated and deoxygenated reactant solutions.

Disproportionation. The disproportionation of dithionate ion was studied earlier,[24−29] and the following stoichiometry and rate equation were found:

$$S_2O_6^{2-} + H_2O + H^+ = HSO_4^- + H_2O \cdot SO_2 \qquad (1)$$

$$v = k[S_2O_6^{2-}][H^+]$$

The stoichiometry indicated in eq 1 was experimentally reconfirmed in this work by analyzing samples from reaction mixtures after small conversions (Table S2 in Supporting Information). The rate equation was verified by a series of kinetic experiments where the buildup of $H_2O \cdot SO_2$, i.e., “sulfurous acid”[32] was followed using its characteristic UV absorption around 275 nm (Figures S1−S3 in Supporting Information). The values of k determined using different

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Table 1. Values of the Rate Constant *k* for the Disproportionation of Dithionate Ion Using Different Acids[a]

acid	k (M^{-1} s^{-1})
$HClO_4$	$(2.5 \pm 0.2) \times 10^{-5}$
HCl	$(2.75 \pm 0.12) \times 10^{-5}$
HBr	$(3.0 \pm 0.2) \times 10^{-5}$
H_2SO_4	$(2.29 \pm 0.13) \times 10^{-5}$

[a] $T = 75$ °C; $\mu = 0.3-1$ M (acid only).

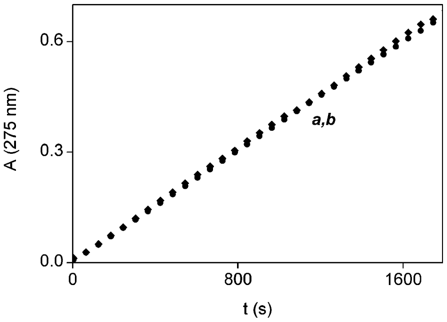

Figure 1. Kinetic traces observed during the disproportionation of dithionate ion in the presence and absence of dissolved oxygen. $[S_2O_6^{2-}] = 0.0646$ M; $[H^+] = 0.624$ M; $[O_2]_0 = 0.2$ mM (a), <0.01 mM (b); $T = 75$ °C; path length 1 cm; $\mu = 0.82$ M ($HClO_4$, $Na_2S_2O_6$).

acids at 75 °C are summarized in Table 1. The differences between different acids are not significant, and anion effects are small. Equation 1 is written in a way that the dominant solution forms of the products sulfite and sulfate ions appear in it. The pK_{a1} and molar absorbance of $H_2O{\cdot}SO_2$ were determined at 75 °C in independent experiments ($pK_{a1} = 2.34 \pm 0.01$, $\epsilon_{275\ nm} = 415 \pm 2\ M^{-1}\ cm^{-1}$) using a method described earlier at different temperatures.[6] The pK_a of hydrogen sulfate ion (or pK_{a2} of sulfuric acid) at 75 °C was estimated to be 1.0 ± 0.2 by a kinetic method used earlier at different temperature.[33] A temperature-dependent study (50−95 °C) of the rate constant *k* (perchloric acid, $\mu = 1.0$ M) gave the activation parameters $\Delta H^{\ddagger} = 120 \pm 1$ kJ mol^{-1} and $\Delta S^{\ddagger} = 11 \pm 1$ J mol^{-1} K^{-1} (Figure S4 in Supporting Information) in good agreement with values obtained by the reevaluation of earlier data found in the literature.[27] Experiments to detect disproportionation were run in neutral solution as well in order to test the possible occurrence of an acid-independent path in reaction 1. However, no detectable amounts of sulfur(IV) were produced over extended time scales. On the basis of these observations, if such a first order, acid-independent path in the disproportionation of dithionate exists, its rate constant cannot be larger than 10^{-7} s^{-1} at 75 °C.

The presence of dissolved oxygen did not affect the kinetic traces during disproportionation (Figure 1), implying that dithionate ion, any potential intermediates of the disproportionation, and sulfur(IV), the monitored product, do not react with dissolved oxygen even at this elevated temperature. The absence of the measurable reaction between oxygen and sulfur(IV) is particularly interesting, as it is clearly allowed thermodynamically:[3]

$$2H_2O{\cdot}SO_2 + O_2 = 2HSO_4^- + 2H^+ \qquad (2)$$

Reaction 2, i.e., the autoxidation of sulfur(IV), is known to be accelerated by a variety of catalysts, especially transition metal complexes.[3,4] In this work, we found that iodide ion also acts as a catalyst of this process. Although oxygen activation by iodide ion is not completely without precedent in organic reactions such as the oxidation of aromatic diamines,[34] the catalytic effect on the autoxidation of sulfur(IV) has been unrecognized thus far.

Kinetic experiments demonstrating this catalytic effect are shown in Figure 2. These traces were recorded in air-equilibrated solutions at 275 nm, where $H_2O{\cdot}SO_2$ is the only absorbing species. In curve a the disproportionation of dithionate ion was initiated in an air-equilibrated solution, which was sealed at room temperature, and a small amount of iodide-containing solution was injected to the reaction mixture mid-course. It is seen that a rapid loss of $H_2O{\cdot}SO_2$ was detected after the injection. When all the dissolved oxygen was consumed, the buildup of $H_2O{\cdot}SO_2$ continued with a rate practically equal to the buildup rate before the addition of iodide ion. The total sulfur(IV) loss could be estimated on the basis of the absorbance difference between the parallel portions of the trace, about 0.18 absorbance unit, indicating a concentration of 0.44 mM for lost $H_2O{\cdot}SO_2$, which is equivalent to 0.22 mM O_2. This concentration is consistent with the fact that an aqueous solution in equilibrium with air contains about 7 mg/L (= 0.2 mM) dissolved oxygen at room temperature. In experiment b, iodide ion was added to the mixture before the disproportionation was initiated. The shape of the curve is clearly different from the one measured without iodide ion in a similar experiment (see Figure 1). The break point on curve b in Figure 2 corresponds to the instant when all oxygen is consumed, but otherwise the trace shows rather unexpected features. One would expect that $H_2O{\cdot}SO_2$ cannot appear in measurable concentration while O_2 is still present because reaction 2, catalyzed by iodide ion, consumes any sulfur(IV) formed by the disproportionation instantly. This is clearly not the case in experiment b; $H_2O{\cdot}SO_2$ and O_2 must coexist for some time in the solution even in the presence of the catalyst. There is a region in this curve where the absorbance at 275 nm and therefore the concentration of sulfur(IV) are practically constant, meaning that sulfur(IV) is formed and oxidized at the same rate. This indicates that iodide ion is probably not a very efficient catalyst for reaction 2, and the mechanism of this catalytic process is quite complex.

Reactions with Oxidizing Agents. In the main part of this work, we studied how the presence of dissolved oxygen influences the redox reactions of $S_2O_6^{2-}$. High-temperature oxidation of dithionate ion was already studied using iodate, bromate, dichromate ions,[23] and iodine[22] as oxidants. The reaction rates were found to be zeroth-order with respect to the oxidizing agents, and first-order with respect to both $S_2O_6^{2-}$ and H^+.[22,23] A convenient way to interpret this rate equation is to assume that disproportionation indicated in

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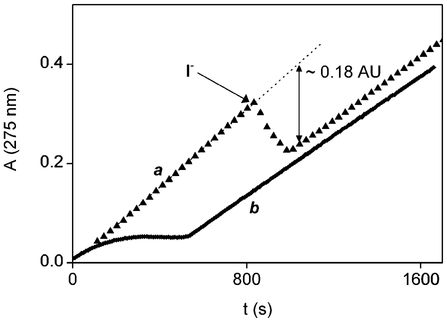

Figure 2. Demonstration of the iodide ion catalyzed autoxidation of sulfur(IV) during the disproportionation of dithionate ion. Curve a: injection of I^- during the course of the reaction. Curve b: I^- initially present in the reaction mixture. $[S_2O_6^{2-}] = 0.0494$ M; $[H^+] = 0.693$ M; $[O_2]_0 = 0.2$ mM; $[I^-] = 0.525$ mM; $T = 75$ °C; path length 1 cm; $\mu = 0.84$ M ($HClO_4$, $Na_2S_2O_6$).

eq 1 occurs in the first and rate-determining step, and the oxidizing agents react only with sulfur(IV) in a subsequent fast reaction.

$$H_2O{\cdot}SO_2 + Ox = HSO_4^- + Prod \qquad (3)$$

In our experiments we used I_2, Br_2, Cl_2, I_3^-, Br_3^-, IO_3^-, BrO_3^-, IO_4^-, MnO_4^-, Cr(VI), Ce(IV), and H_2O_2 as oxidizing agents. In each case, the rate equation of the oxidation reaction and the value of k were the same as shown in eq 1 for the disproportionation, which also means that the rate of oxidation is independent of the identity of the oxidant. These observations are in clear agreement with the scheme outlined in the previous paragraph. Further support for the consistency of this scheme is provided by the fact that all of these oxidizing agents were shown to react with sulfur(IV) quite rapidly (even at room temperature) in independent investigations published earlier.[35−40]

Turning now to the effect of dissolved oxygen on the oxidation reactions, it was observed that the reactions with Br_2, Cl_2, Br_3^-, BrO_3^-, MnO_4^-, Cr(VI), and H_2O_2 were not influenced by the presence or absence of O_2 at any stage (Figures S5−S7 in Supporting Information). It is thus concluded that oxygen, if present, remains unreacted in these systems. Reactions with iodine-containing oxidants (I_2, I_3^-, IO_3^-, IO_4^-) were understandably different in this respect because one of their products, iodide ion, catalyzes reaction 2. These systems feature quite unique kinetic traces, and the course of the oxidation reactions will also be discussed in detail in addition to the effect of oxygen.

The oxidation reaction with I_2 produces iodide ion:

$$I_2 + H_2O{\cdot}SO_2 + H_2O = 2I^- + HSO_4^- + 3H^+ \qquad (4)$$

Figure 3 shows an experiment with iodine as an oxidizing agent in the presence of dissolved oxygen monitored at three different wavelengths. The absorbance trace measured at 465 nm, where only I_2 has absorption, is the expected zeroth-order curve. In contrast, a bell-shaped, symmetrical trace was observed at 360 nm. I_2 does not have absorption at this wavelength, and the clear maximum on the kinetic curve implies the formation of an intermediate. As I_2 (reactant) and I^- (product) are simultaneously present during the course of the reaction, small amounts of triiodide ion are formed in an equilibrium step, and the concentration of triiodide ion can be expressed as

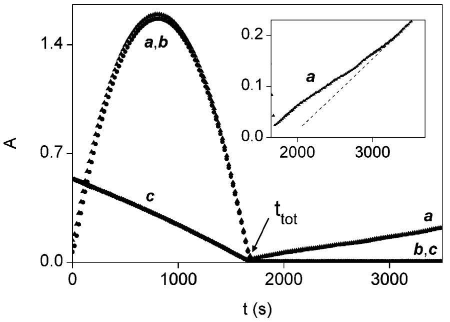

Figure 3. Kinetic traces in the reaction of iodine with dithionate ion. $[S_2O_6^{2-}] = 0.0371$ M; $[H^+] = 0.520$ M; $[I_2] = 0.959$ mM; $[O_2]_0 = 0.2$ mM; $\lambda = 275$ nm (a), 350 nm (b) 465 nm (c); $T = 75$ °C; path length 0.874 cm; $\mu = 0.63$ M ($HClO_4$, $Na_2S_2O_6$). Inset: 275 nm trace on an expanded scale showing the effect of oxygen after 1700 s.

$$[I_3^-] = K[I_2][I^-] \qquad (5)$$

This equilibrium is known to be established very rapidly even at room temperature.[41] The value of K is relatively small, and triiodide ion remains a minor species at any reaction time t:

$$[I_3^-]_t \ll [I_2]_t + [I^-]_t \qquad (6)$$

Thus, one obtains the following equation for any value of time t from mass balance:

$$2[I_2]_0 = 2[I_2]_t + [I^-]_t \qquad (7)$$

The loss of iodine is zeroth-order, and its concentration is a linear function of time t:

$$[I_2]_t = [I_2]_0 - vt \qquad (8)$$

where v is the rate of reaction. For the concentration of triiodide ion one obtains

$$[I_3^-]_t = K[I_2]_t[I^-]_t = K([I_2]_0 - vt)(2vt) \qquad (9)$$

Introducing the new constant $K' = 2Kv^2$, the equation can be rearranged to

$$[I_3^-]_t = K'(t_{tot} - t)t \qquad (10)$$

where $t_{tot} = [I_2]_0/v$ is the reaction time at which the total amount of iodine is consumed. Formula 10 is the equation of an inverted parabola in excellent agreement with the observations shown in Figure 3. Although triiodide ion is

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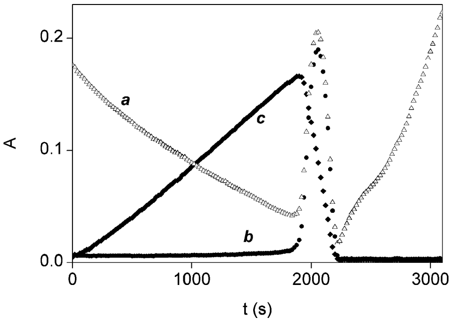

Figure 4. Kinetic traces in the reaction of periodate ion with dithionate ion. $[S_2O_6^{2-}] = 0.0519$ M; $[H^+] = 0.728$ M; $[IO_4^-] = 0.61$ mM; $[O_2]_0 = 0.2$ mM; $\lambda = 275$ nm (a), 350 nm (b) 465 nm (c); $T = 75$ °C; path length 0.874 cm; $\mu = 0.88$ M ($HClO_4$, $Na_2S_2O_6$).

formed in minor concentrations, its molar absorbance is known to be very high (>10000 M^{-1} cm^{-1}) and relatively small concentrations result in large absorbance effects.[37] The curve at 275 nm, where I_3^- and $H_2O{\cdot}SO_2$ absorb, clearly shows that oxygen reacts only after all other oxidizing agents have been consumed. The initial part of this trace runs very close to the one measured at 360 nm, because the molar absorbance of I_3^- is very similar at these two wavelengths. The buildup of $H_2O{\cdot}SO_2$ after the consumption of all iodine is similar to curve b in Figure 2, although the break point (inset of Figure 3) is not as sharp as in the previous case because the initial concentrations are different. This finding also reflects that iodide catalysis in reaction 2 has a complex mechanism.

Experiments with triiodide ion were carried out using small amounts of iodine in the presence of a large excess of iodide ion. These curves gave the expected zeroth-order shape at both 275 and 360 nm, and the effect of dissolved oxygen was detectable at 275 nm very similarly to the case of iodine.

Observations using iodate and periodate ions indicated even more complexity. Kinetic traces recorded in an experiment with periodate ion[42,43] in the presence of oxygen are shown in Figure 4 (see Figure S9 in the Supporting Information for spectral changes). At 465 nm the accumulation of iodine as an intermediate is detected. An increase in the concentration of iodine (phase I) is followed by a decrease (phase II). The decrease is 7 times faster than the increase, in agreement with the stoichiometry (first step, I(VII) → I(0); second step I(0) → I(−1)). Thus, it can be seen that periodate ion is quantitatively transformed to iodine in phase I:

$$2IO_4^- + 7H_2O{\cdot}SO_2 = I_2 + 7HSO_4^- + H_2O + 5H^+ \quad (11)$$

In phase II, iodine is reduced to iodide according to eq 4. In agreement with this interpretation, an inverted parabola similar to the one shown in Figure 3 is detected at 360 nm in phase II because iodine is the stoichiometric oxidizing agent in this phase. At 275 nm IO_4^-, I_3^-, and $H_2O{\cdot}SO_2$ are the absorbing species. Thus the trace measured at 275 nm involves a decrease in phase I and an inverted parabola in phase II; then the effect of oxygen is clearly detectable during the buildup of $H_2O{\cdot}SO_2$ after all IO_4^- and I_2 have been consumed. The observations with iodate ion were very similar. The ratio of the rates measured on the increasing and decreasing parts of the 465 nm curves was 1:5 because of the different stoichiometry, but otherwise the very same conclusions were confirmed.

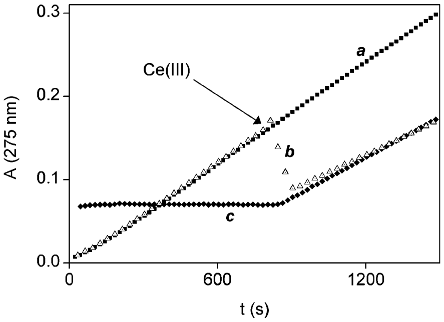

Figure 5. Demonstration of the cerium(III)-catalyzed autoxidation of sulfur(IV) during the disproportionation of dithionate ion. $[S_2O_6^{2-}] = 0.0538$ M, $[H^+] = 0.347$ M, $[Ce(III)] = 1.3$ mM, $[O_2]_0 = 0.2$ mM, $T = 75$ °C, path length 1 cm; $\mu = 0.51$ M ($HClO_4$, $Na_2S_2O_6$). Traces: no cerium(III) (a), mid-course injection of cerium(III) (b), prior addition of cerium(III) (c).

The widespread analytical applications of the Ce(IV)−sulfur(IV) redox reaction[8−13] lend particular significance to the observations in the Ce(IV)/Ce(III) system. Kinetic curves demonstrating the catalytic effect of Ce(III) on reaction 2 are shown in Figure 5. In experiment a, the disproportionation of dithionate ion was initiated in an air-saturated solution without the addition of any catalyst. In experiment b, some Ce(III) solution was added to the same experiment mid-course, whereas Ce(III) was added before initiating the disproportionation in experiment c. At 275 nm both $H_2O{\cdot}SO_2$ and Ce(III) absorb. In experiment c, only the absorption of Ce(III) is detectable until the dissolved O_2 is fully consumed. After the break point, the steady buildup of $H_2O{\cdot}SO_2$ is seen. In experiment b, a sudden drop in the concentration of $H_2O{\cdot}SO_2$ is observed immediately after the addition of Ce(III) and the curve finally runs together with curve c.

When cerium(IV) was used instead of cerium(III), the detected kinetic traces were dependent on the concentration of dissolved oxygen as shown in Figure 6. The kinetic traces showed two distinct kinetic phases at 330 nm, where only Ce(IV) has absorption. An initial slow decay of Ce(IV) was followed by a fast period in which all Ce(IV) disappeared. A linear algebraic analysis of spectra[44,45] showed that only three absorbing species, Ce(IV), Ce(III), and $H_2O{\cdot}SO_2$, were present in the system in the 240−350 nm wavelength range, and intermediates were not detected throughout the process (see Figure S8 in the Supporting Information for spectral changes). The break point on the kinetic curves occurred earlier when the initial concentration of dissolved oxygen was smaller (see curves a and b in Figure 6). This observation

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(42) Periodate ion is mostly present as one of several octahedral $H_xIO_6^{(5-x)-}$ in aqueous solution rather than the tetrahedral IO_4^- analogous to perchlorate ion [see ref 43]. However, we decided to use the simple notation of IO_4^- as only the oxidation state is relevant for this work.

(43) Kerezsi, I.; Lente, G.; Fábián, I. *Dalton Trans.* **2004**, 342.

(44) Peintler, G.; Nagypál, I.; Jancsó, A.; Epstein, I. R.; Kustin, K. *J. Phys Chem. A* **1997**, *101*, 8013.

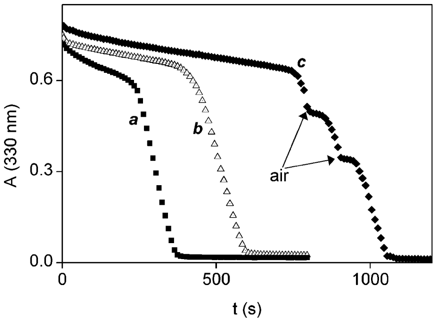

Figure 6. Kinetic traces in the reaction of cerium(IV) with dithionate ion with two mid-course injections of air in trace c. $[S_2O_6^{2-}] = 0.0646$ M (a, b), 0.0861 M (c); $[H^+] = 0.312$ M (a, b), 0.208 M (c); [Ce(IV)] = 0.50 mM (a, b), 0.45 mM (c); $[O_2]_0 = 0.2$ mM (b, c), 0.1 mM (a); $T = 75$ °C; path length 0.874 cm (a, b), 1 cm (c); $\mu = 0.51$ M (a, c) 0.47 M (b) ($HClO_4$, $Na_2S_2O_6$).

suggested that the break point indicates the time when all oxygen has been consumed. The sharp absorbance decay after this point corresponds to the reduction of Ce(IV) in the absence of oxygen. A further experiment supporting this conclusion was curve c in Figure 6. In this experiment, a small amount of air was injected into the reaction mixture when the absorbance decrease reached the steep region. The decay of Ce(IV) became much slower after the addition of air for some time after each injection, and another break point followed.

Discussion

For the interpretation of our disproportionation results, a straightforward mechanism can be envisioned in which dithionate ion is first protonated, and then the sulfur−sulfur bond in hydrogen dithionate ion undergoes heterolytic cleavage to give sulfur(IV) and hydrogen sulfate ions.

$$S_2O_6^{2-} + H^+ \rightleftharpoons HS_2O_6^- \tag{12}$$

$$HS_2O_6^- + H_2O \rightarrow HSO_4^- + H_2O\cdot SO_2 \tag{13}$$

As discussed earlier, we could not detect the protonation of dithionate ion in significant amounts by the usual experimental methods. Consequently, reaction 12 must be very much shifted toward the reactants and only a small amount of hydrogen dithionate is present. However, the decomposition does not occur under neutral conditions and the protonation is likely to be the key step which breaks the symmetry of dithionate ion and yields a species of increased reactivity.

The values of activation parameters deserve particular attention. They imply that the half-life of dithionate ion in a 1.0 M acid solution could be around 400 days at 25 °C and neutral solutions of dithionate ion are indefinitely stable for all practical purposes. Therefore, schemes including dithionate ion as a reactive species at room temperature, not uncommon in the recent literature of analytical chemistry,[12,13,46] are necessarily erroneous. The high enthalpy of activation (120 ± 1 kJ mol^{-1}) for reaction 1 has important implications. The value of the activation energy is close to the range of bond energies. An earlier X-ray study showed that the sulfur−sulfur bond in dithionate ion is quite long (214.2 pm),[47] actually longer than a usual sulfur−sulfur single bond, which implies a low bond energy. Assuming that the standard enthalpy of the protonation of dithionate ion is not extremely high, one can but conclude that the activation of the disproportionation dominantly involves the breaking of the sulfur−sulfur bond of hydrogen dithionate ion.

The absence of the oxygen effect on disproportionation clearly indicates that $SO_3^{-\bullet}$ is not an intermediate of the disproportionation, because $SO_3^{-\bullet}$ is known to react with O_2 very rapidly.[3−5] Thus, homolytic cleavage of the sulfur−sulfur bond of dithionate ion is unlikely. This conclusion is further supported by the fact that no acid-independent pathway for the disproportionation was observed. Such a pathway would almost surely involve the homolytic dissociation of dithionate ion into sulfite ion radicals:

$$S_2O_6^{2-} \rightleftharpoons 2SO_3^{-\bullet} \tag{14}$$

$$v = k_{14}[S_2O_6^{2-}] - k_{-14}[SO_3^{-\bullet}]^2$$

In earlier experiments carried out at room temperature, the equilibrium constant of reaction 14 was obtained as $K_{14} = k_{14}/k_{-14} = 3 \times 10^{-24}$ M,[48] and the rate constant of the self-recombination of sulfite ion radical was estimated as $k_{-14} = 1 \times 10^9$ M^{-1} s^{-1}.[5] These numbers give $k_{14} = 3 \times 10^{-15}$ s^{-1} at room temperature, which does not contradict our experimental findings, i.e., $k_{14} < 1 \times 10^{-7}$ s^{-1} at 75 °C. Homolysis through photochemical decomposition can also be ruled out as dithionate ion does not have absorption above 200 nm.

It is also to be noted that our results showed that the autoxidation of sulfur(IV) was quite slow even at 75 °C. This may lend some support to the earlier proposal that autoxidation of sulfur(IV) always occurs through some kind of catalytic pathway with trace amounts of catalysts present as contamination.[3,49]

Oxidizing agents do not seem to react with dithionate ion directly, only with sulfur(IV) produced by the disproportionation of $S_2O_6^{2-}$. The only possible exception known from earlier studies is silver(II) ion, which was reported to oxidize $S_2O_6^{2-}$ in a process that is first-order with respect to silver(II).[30] In light of these conclusions, it is clear that studying the oxygen dependence of the oxidation of $S_2O_6^{2-}$ may give indirect information on the mechanism of autoxidation of sulfur(IV).

As seen from the results, oxygen consumption in the iodide-related oxidation systems only begins after all other oxidizing agents have been consumed. This indicates that the catalytic reaction between oxygen and sulfur(IV) is definitely slower than reactions with other oxidizing agents. In contrast, the Ce(III)-catalyzed autoxidation of sulfur(IV) is faster than the oxidation by Ce(IV) (see Figure 6). As

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Ce(III) is not present initially in the system, there should be a fast Ce(IV) decay at the very beginning, which produces some Ce(III). This initial reaction may well occur in the dead time of mixing (i.e., the time between the initiation of the reaction and the beginning of the detection), and it should not necessarily involve a substantial loss of Ce(IV). An alternative possibility is that the reaction of Ce(IV) with sulfur(IV), similarly to the iron(III)−sulfur(IV) system,[3−7] initiates a chain reaction which consumes the dissolved oxygen and keeps the rate of Ce(IV) loss relatively low. Both of these are plausible interpretations in agreement with the experimental data, and it is not possible to reject one of them at this point.

Finally, we would like to point out that some kinetic traces observed during the oxidation reactions, although highly unusual, can be very readily interpreted by simple stoichiometric or equilibrium considerations. Under appropriately selected experimental conditions, these reactions may serve as textbook examples of purely inorganic zeroth-order processes.

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Supporting Information Available: Tables of data from pH-potentiometric measurements and a study of the stoichiometry of disproportionation. Plots of data from kinetic studies and absorbance spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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