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Mechanism of Reaction of the Hydrated Electron with Ozone, Perbromate, and Other Strongly Oxidizing Inorganic Oxocompounds

Ulrik K. Kläning* and Jørgen R. Byberg

Chemistry Department, Aarhus University, Langelandsgade 140, DK-8000 Aarhus C, Denmark

Knud Sehested

Chemical Reactivity, bld 313, Risø National Laboratory, DK-4000 Roskilde, Denmark

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A model is proposed for the mechanism of reaction of the hydrated electron with strongly oxidizing inorganic oxocompounds, according to which such reactions comprise three steps: (1) a primary split-off of O^- occurring immediately upon the transfer of the electron to the oxocompound, (2) after which O^- becomes fully solvated, acquiring properties as in the bulk phase, and (3) finally, the solvated O^- either escapes from the cage or forms an electron adduct by reacting back within the cage with its partner. The model is based on studies of the photochemistry of aqueous solution of the oxoanions O_3^- and ClO_3^- (Walhaut, P. K.; Silva, C.; Barbara, P. F. *J. Phys. Chem.* **1996**, *100*, 5188. Kläning, U. K.; Sehested, K. *J. Phys. Chem.* **1991**, *95*, 740.), which suggest that solvation of the photoproduct O^- precedes cage-back reactions. Measurements of the reactions of the hydrated electron with the perbromate ion and the periodate ion and of the reactions of O^- with the bromate and iodate ion support the model by verifying that no electron adduct is formed unless O^- and its partner react in the bulk phase at a diffusion-controlled rate.

Introduction

The encounter distance for the very fast reactions of the hydrated electron, e_{aq}^-, with strongly oxidizing agents, as estimated from the Debye−Smoluchowski theory[1,2] for diffusion-controlled reactions, may be as large as 2−3 times the sum of the effective radius of e_{aq}^- (2.5−3 Å)[3] and the crystal radius of the coreactant.[3,4] These "abnormally" fast reactions are thought to proceed by electron tunneling[3,5] via excited states. Since such states may be repulsive, the fact that the formation of an electron adduct in its ground state rather than immediate bond fission is the predominant reaction suggests that the relaxation to the ground state of the electron adduct is a very efficient process. The reactions of the hydrated electron with ozone[6] and the oxoanions IO_4^-,[7] $H_4TeO_6^{2-}$,[8] and $HXeO_6^{3-}$[9] are particularly remarkable in this context because a split-off of O^- is observed to occur thermally from the ground state of the electron adduct and not directly from the excited initial state.

These observations were all made in pulse radiolysis experiments, which cannot yield direct information on how the initial excited states generated by attachment of e_{aq}^- relax to the ground state of the electron adduct. However, recent photochemical studies of oxoanions with a time resolution of ∼100 fs,[10−12] which have shown that solvent reorganization plays an important role in the relaxation of the excited anion, may help to understand the tunneling-type reactions of e_{aq}^- with oxoanions. The relaxation of the excited state (1^2A_2) of the ozonide ion O_3^- (the electron adduct of ozone) has been studied by pump−probe spectroscopy.[10] It was found that upon excitation at 390 nm to the 1^2A_2 state, O_3^- immediately dissociates into O_2 and O^-. The subsequent recombination of O^- and O_2 to ground-state O_3^- takes place in a delayed process with a time constant of 3.5 ps. The delay is ascribed to the strong interaction of the charged species with the polar solvent. Thus, the high energy of hydration of O^- (5 eV)[13] is taken to suggest that a fast solvation of this species occurs already *during* the initial dissociation. Consequently, the delayed regeneration of O_3^- results from recombination of the fully solvated species O^- and O_2 on the potential energy surface of ground-state O_3^-.

The suggestion that O^- is fully solvated when it recombines with O_2 gains support by a study of the photochemistry of ClO_3^-,[12] which showed that the ratio of the the quantum yield for formation of O_2,

$$ClO_3^- \ (+h\nu) \rightarrow ClO^- + O_2 \qquad (1)$$

to the quantum yield for the return of ClO_3^- to the ground state,

$$ClO_3^- \ (+h\nu) \rightarrow ClO_3^- \text{ (ground state)} \qquad (2)$$

equals the ratio of the rate constants for the thermal reactions,

$$ClO_2 + O^- \rightarrow ClO^- + O_2 \qquad (3)$$

$$ClO_2 + O^- \rightarrow ClO_3^- \qquad (4)$$

This result indicates that the two photochemical channels observed in the steady-state photolysis of ClO_3^- represent competing secondary reactions between O^- and ClO_2 with the same branching ratio as if the reactants were in thermal equilibrium with the solvent.

These photochemical studies suggest that the electron adduct formed in an abnormally fast reaction of an inorganic oxocompound with the hydrated electron may in fact be a secondary product formed by geminate recombination of O^- and the corresponding fragment, both apparently in equilibrium with the solvent.

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In the present paper we test the validity of this mechanism indirectly, making use of an earlier pulse radiolysis study of the reaction of perbromate ion BrO_4^- with e_{aq}^-.[14] This very fast and highly exergonic reaction is exceptional in the sense that, in contrast to the above-mentioned reactions of e_{aq}^-, it appears to proceed without formation of an electron adduct:

$$BrO_4^- + e_{aq}^- \rightarrow BrO_3^- + O^- \qquad \text{ref 14} \qquad (5)$$

$k_5 = 2.4 \times 10^{10}$ M^{-1} s^{-1}, ref 15;

$\Delta G_{15}^\circ = -252$ kJ mol^{-1}, refs 16,17

although the electron adduct BrO_4^{2-} has been observed as a well-defined, stable species in solid matrixes,[18] where it can be formed not only by electron capture on BrO_4^- but also in a thermal reaction between O^- and BrO_3^-.[19]

Reaction 5 and the reaction of BrO_3^- with O^- should provide a test of the suggested mechanism because the structure of BrO_4^{2-} closely resembles that of the electron adduct IO_4,$^{2-}$ [20] which, however, is formed not only in solid matrixes[20] but also in aqueous solution by the reactions

$$IO_4^- + e_{aq}^- \rightarrow IO_4^{2-} \qquad \text{ref 7} \qquad (6)$$

$k_6 = 4.0 \times 10^{10}$ M^{-1} s^{-1}, ref 4;

$\Delta G_6^\circ = -217$ kJ mol^{-1}, refs 16, 17, 21

and

$$IO_3^- + O^- \leftrightarrow IO_4^{2-} \qquad (7,-7)$$

$$k_7 = 3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}; \quad k_{-7} = 3.3 \times 10^3 \text{ s}^{-1}, \text{ ref 21}$$

We set out verifying that the failure to detect BrO_4^{2-} in the pulse radiolysis study of reaction 5 is a nontrivial result that cannot simply be ascribed to an insufficient optical absorbance of BrO_4^{2-} or to a too short lifetime of BrO_4^{2-} in aqueous solution (detection of BrO_4^{2-} in these experiments would require an extinction coefficient in the region 250−700 nm greater than 50 M^{-1} cm^{-1} and a lifetime longer than 3×10^{-7} s). To this end we have measured the optical absorption spectrum of BrO_4^{2-} embedded in solid $KBrO_4$, from which we infer that BrO_4^{2-} has a strong absorption in the wavelength region probed in the pulse radiolysis experiments. Moreover, we have measured the kinetics of the reduction of BrO_4^- by ferrocyanide, a reaction that supposedly proceeds adiabatically by one-electron-transfer rather than through excited dissociative states and, if so, should favor the formation of an intermediate species *before* dissociation occurs. We have hereby found evidence for the formation of a Br(VI) intermediate, which we assume is $HBrO_4^-$. The mechanism that fits the kinetic measurements allows an estimate of the lower limit of the lifetimes of $HBrO_4^-$ and BrO_4^{2-} in aqueous solution. This limit enables us to conclude that BrO_4^{2-}, if formed in reaction 5, would have persisted long enough to be detected in the earlier pulse radiolysis study.[14]

Having established that a Br(VI) species *can* exist in aqueous solution we studied, with pulse radiolysis technique, the reaction of BrO_3^- with O^-, which by analogy with the corresponding reaction 7 of IO_3^- might be expected to yield BrO_4^{2-}.

On the basis of these experiments, we argue that the difference between the mechanisms of reaction 5 and those of reaction 6 reflects the different reactivities of BrO_3^- and IO_3^- toward O^-, in agreement with the proposed secondary nature of electron adducts formed in such reactions.

Experimental Section

Materials. Aqueous solutions were prepared with triply distilled water. $KBrO_4$ and perbromic acid in aqueous solution were supplied by Dr. Evan H. Appelman, Argonne National Laboratory. Single crystals of $KBrO_4$ in the form of plates measuring approximately 1 mm × 2 mm × 3 mm with the large face parallel to (001) were obtained from an aqueous $KBrO_4$ solution by evaporation at room temperature. Acidimetric and iodimetric analysis of the perbromic acid solution showed a content of perbromic acid of (3.11 ± 0.01) M and (2.99 ± 0.11) M, respectively. The content of bromide and bromate in the perbromic acid solution was 1.5×10^{-3} and 1.8×10^{-3} M, respectively. Nitrous oxide (N48) was ALPHAGAZ. Argon, oxygen, and nitrogen (all N40) were supplied by Dansk Ilt og Brint. Potassium ferricyanide and sodium bromate were recrystallized from water. Analysis of the recrystallized sodium bromate showed a content of 4×10^{-3} mol % Br^-. Other materials were reagent grade. Solutions of lithium perbromate were prepared by neutralization of perbromic acid with lithium hydroxide. Stock solutions containing 0.1 M lithium ferrocyanide and 0.6 M lithium perchlorate were prepared from potassium ferrocyanide and lithium perchlorate by metathesis and purged of oxygen by bubbling N_2 through the solution.

Analysis. Bromide was measured potentiometrically using a radiometer bromide Selectrode type F 1022 Br. BrO_3^- in the presence of BrO_4^- was determined as Br_3^- as described.[22] Perbromic acid was determined by titration with a standardized sodium hydroxide solution. The acidimetric analysis was checked by iodometric analysis of the perbromic acid. Aliquots of 0.05 mL of neutral solution containing less than 5×10^{-3} M BrO_4^- were tranferred to stoppered 1 cm optical cells containing 3.5 mL of 0.2 M KI. The cells were heated to 60−70 °C in a water bath for 45 min. After the solution was cooled to room temperature, the optical density was measured at 352 nm. The extinction coefficient of I_3^- formed was taken to be equal to 2.5×10^4 M^{-1} cm^{-1}, a value determined by using $KBrO_4$ solutions of known concentrations.

Measurements. Pulse radiolysis was made at ambient temperature (21 ± 1 °C), with the HCR linac at Risø delivering 10 MeV in single square pulses with a pulse length of 1 μs. The experimental setup for pulse radiolysis at the high pressure used in the present experiments is previously described.[23,24] The dose was measured with the ferrocyanide dosimeter.[25]

ESR spectra were obtained with a Varian E-15 spectrometer operating at 9.3 GHz in conjunction with an AC-2-110 cryotip. Irradiation with 50 kV X-rays and subsequent irradiation with light at 633 nm from a 10 mW SpectraPhysics He−Ne laser were made in the microwave cavity along the *c*-axis on the same face of the sample. Optical spectra of crystals were measured as desribed using a Cary 219 spectrophotometer equipped with a Rehovoth dichroism accessory model CD-LD-HC.[26]

The kinetics of the reaction between ferrocyanide and perbromate was monitored spectrophotometrically at 420 nm at which wavelength the difference between the extinction coefficients of ferricyanide and ferrocyanide is 1020 M^{-1} cm^{-1}. The spectrophotometer was a Cary 219 with thermostated cell compartments and equipped for measurements at intervals up to 90 min. Reaction temperatures were controlled to ±0.1 °C.

Results and Discussion

Optical Spectrum of BrO_4^{2-}. The shape of the spectrum of BrO_4^{2-} embedded in a $KBrO_4$ crystal was determined by

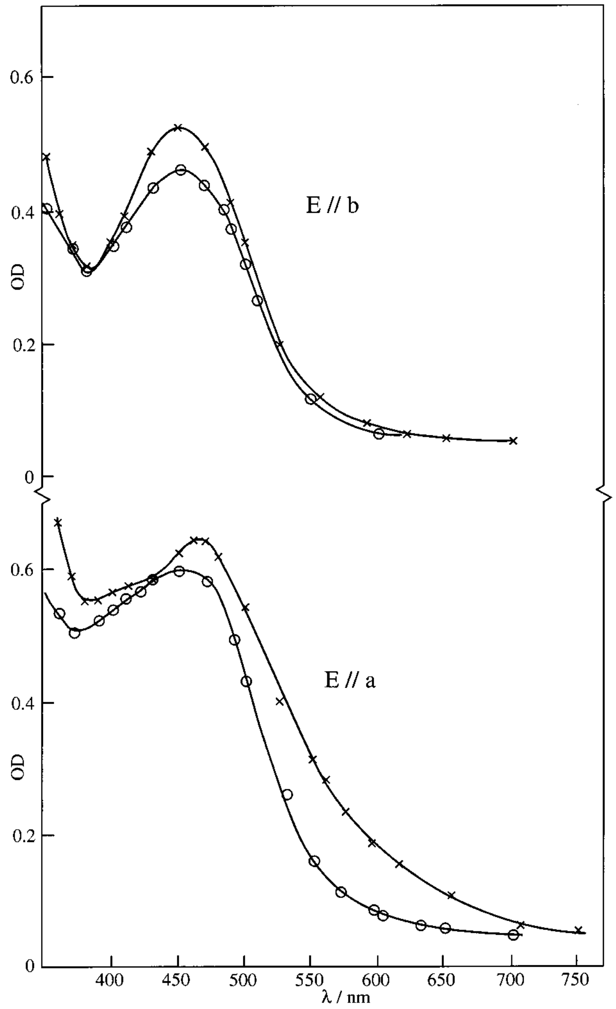

Figure 1. Absorbances of an X-irradiated $KBrO_4$ crystal recorded with light polarized along the crystallographic axis *a* (*E* || *a*) and along the crystallographic axis *b* (*E* || *b*). Crosses (×) and open circles (○) indicate measurements taken before and after bleaching at 20 K and subsequent annealing at 140 K, respectively.

correlating light-induced changes of ESR signal heights with the simultaneous changes of the optical absorbance. ESR measurements showed formation of BrO_4^{2-} [18] and $BrO_2{-}O_2$[27] after X irradiation at 20 K and subsequent annealing at 140 K. $BrO_2{-}O_2$ is a weakly bound complex in which both components retain their integrity. BrO_4^{2-} and $BrO_2{-}O_2$ both conform to the mirror symmetry of the BrO_4^- site in $KBrO_4$, the molecular plane of the BrO_2 being perpendicular to the mirror plane, i.e., parallel to the crystallographic axis *b*. The ESR signals from these species were both found to decrease by irradiation (bleaching) at 20 K with light from the He−Ne laser. After a second annealing at 140 K, the only changes detected in the ESR spectrum were a reduction of the heights of the signals from BrO_4^{2-} and $BrO_2{-}O_2$. With the assumption that the corresponding changes of the optical absorbance were caused solely by the decrease of the amounts of BrO_4^{2-} and $BrO_2{-}O_2$, the shapes of the spectra of BrO_4^{2-} and $BrO_2{-}O_2$ were obtained from the differences between the absorbances measured before and after the bleaching and subsequent annealing at 140 K.

The absorbances measured with light polarized along the crystallographic axis *a* (*E* || *a*) and along the crystallographic axis *b* (*E* || *b*) before and after bleaching and subsequent annealing are shown in Figure 1, and the absorbance changes produced by the bleaching and annealing are shown in Figure 2.

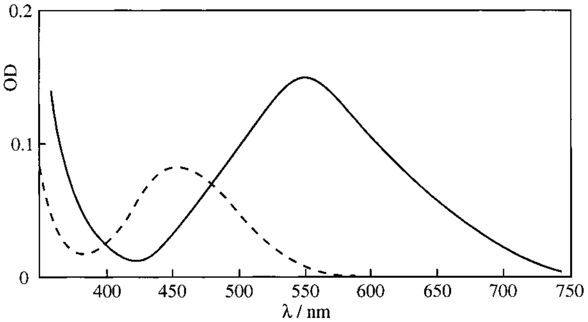

Figure 2. Shape of the absorption bands assigned to $BrO_2{-}O_2$ (dashed curve) and to BrO_4^{2-} (solid curve), calculated as the differences between the absorbances shown in Figure 1 for *E* || *a* and *E* || *b*.

We assign the band centered at 460 nm and polarized along the *b* axis to the parallel transition $^2C(^2A_2) \leftarrow {}^2X(^2B_1)$ of the BrO_2 moiety of $BrO_2{-}O_2$. This transition accounts for the absorption of BrO_2 in the gas phase where a band centered at ~500 nm is observed.[28, 29]

The absorbance measured with *E* || *a* is assigned to BrO_4^{2-}. The steep increase with decreasing wavelength observed below 400 nm indicates that BrO_4^{2-} has a strong band in the near-ultraviolet in addition to the band at 550 nm. Thus, the spectrum of BrO_4^{2-} resembles that of IO_4^{2-} [21] in aqueous solution, which consists of a strong band at 350 nm (extinction coefficient of 3000 M^{-1} cm^{-1}) and a low shoulder at 550 nm (extinction coefficient of 500 M^{-1} cm^{-1}). With the reasonable assumption that the extinction coefficient of BrO_4^{2-} is of the same magnitude as that of IO_4^{2-}, it easily meets the requirement for detection in the pulse radiolysis experiments (50 M^{-1} cm^{-1} at 100% yield of BrO_4^{2-}). Hence, the failure to detect BrO_4^{2-} shows that if this species is formed in a significant yield, its lifetime in aqueous solution has to be shorter than the time resolution of the pulse radiolysis experiments, i.e., shorter than 3×10^{-7} s.

Reaction of Perbromate with Ferrocyanide. Apart from reaction 5 the only one-electron reductions of perbromate studied so far are the reactions of BrO_4^- with Fe(II) complexes of 2,2′-bipyridine and substituted 1,10-phenanthrolines.[30] No evidence of a Br(VI) intermediate was obtained in that study. However, even if a Br(VI) species were present, the complex stoichiometry of the reactions would preclude its detection. In contrast, the reaction of perbromate with ferrocyanide shows a simple stoichiometry, allowing the presence or absence of a Br(VI) intermediate to be established. The stoichiometry was determined in solutions with perbromate in excess. Analysis for bromate after completion of the reaction at 35 and 45 °C at pH 5 in phosphate buffer showed formation of 0.50 ± 0.03 mol bromate per mol ferricyanide formed. The absorption spectrum between 250 and 460 nm of a solution originally containing 8×10^{-3} M potassium perbromate, 1.01×10^{-3} M potassium ferrocyanide, and 2.5×10^{-2} M Borax buffer (pH 8.5) was recorded as a function of time at 45 °C. The absorption curves showed an isosbestic point at 281 nm. After completion of the reaction, the absorbance at $\lambda > 281$ nm was found to be identical to that of a 1.01×10^{-3} M solution of potassium ferricyanide. These results indicate that in Borax and phosphate-buffered solutions perbromate reacts with ferrocyanide solely by

$$BrO_4^- + 2Fe(CN)_6^{4-} + H_2O \rightarrow BrO_3^- + 2Fe(CN)_6^{3-} + 2OH^- \quad (8)$$

The kinetic measurements were made with perbromate in large excess. Thus, the initial concentration of ferrocyanide was less than $^1/_6$ of the concentration of perbromate. Measurements were made in 1 M lithium perchlorate at 25 °C at pH 13 (0.1 M LiOH), 10, 8.5, 8.0, and 7.4 and at 35 and 45 °C at pH 8.5. In the region from 7.4 to 10, the pH was adjusted with 0.05 or 0.01 M Borax, perchloric acid, or lithium hydroxide. The initial concentration of bromate was either zero or 0.01 M. The initial concentration of ferricyanide was varied between zero and 0.02 M. Runs were made with solutions saturated with oxygen at 1 atm and with oxygen-free solutions. No effect of oxygen on the kinetics was detected in these runs.

The rate of reaction 8 was found to be independent of the concentration of buffer and of the initial concentration of bromate and to be proportional to the perbromate concentration and to the acidity. Reaction 8 was found to be inhibited by ferricyanide, which immediately suggests the presence of a Br(VI) intermediate that reacts back with ferricyanide so that ferrocyanide and perbromate are reformed. We take that the Br(VI) species formed is $\mathrm{HBrO_4^-}$, i.e., the acid form of the species $\mathrm{BrO_4^{2-}}$ observed in solids. Moreover, we found that the relative change of rate brought about by a change of acidity is independent of the ferricyanide concentration. The reciprocal of the pseudo-first-order constant for formation of ferricyanide, when ferricyanide is present in large excess over ferrocyanide, appears to increase linearly with the concentration of ferricyanide.

In agreement with these observations, the following mechanism was found to fit the data,

$$\mathrm{BrO_4^- + Fe(CN)_6^{4-} + H^+ \leftrightarrow HBrO_4^- + Fe(CN)_6^{3-}} \qquad (9,-9)$$

followed by

$$\mathrm{HBrO_4^- \rightarrow BrO_3^- + OH} \qquad (10)$$

$\mathrm{HBrO_4^-}$ takes part in protolytic reactions with the solvent water and with the buffer:

$$\mathrm{HBrO_4^- + H_2BO_3^- \leftrightarrow BrO_4^{2-} + H_3BO_3} \qquad (11,-11)$$

Since no reactions between OH and $\mathrm{BrO_4^-}$ [14] and between OH and $\mathrm{Fe(CN)_6^{3-}}$ have been observed, we take that OH disappears solely by

$$\mathrm{Fe(CN)_6^{4-} + OH \rightarrow Fe(CN)_6^{3-} + OH^-}$$
$$k_{12} = 1.05 \times 10^{10}\ \mathrm{M^{-1}\ s^{-1}}, \text{ ref 16} \qquad (12)$$

Assuming stationary concentrations of $\mathrm{HBrO_4^-}$ and OH and noting that perbromate is in large excess, we obtain by integration of the rate equation for formation of ferricyanide the expression

$$t = -(2k_9[\mathrm{BrO_4^-}])^{-1}\left(\left(1 + \frac{k_{-9}}{k_{10}}C_t\right)\ln\left(1 - \frac{\Delta\mathrm{OD}}{\Delta\mathrm{OD}_\infty}\right) + \frac{k_9}{k_{10}\Delta\epsilon l}\Delta\mathrm{OD}\right) \qquad (13)$$

In eq 13 C_t is equal to $[\mathrm{Fe(CN)_6^{3-}}] + [\mathrm{Fe(CN)_6^{4-}}]$, $\Delta\epsilon$ the difference between the extinction coefficients of ferricyanide and ferrocyanide, and l is the length of the optical cell. Moreover, we have substituted the absorbance change at 420 nm, ΔOD for the difference between the concentration of ferricyanide at time t and at $t = 0$, and the absorbance change $\Delta\mathrm{OD}_\infty$ for the difference between the concentrations of ferricyanide at $t = \infty$ and $t = 0$.

TABLE 1: Rate Constants k_9 and the Ratio k_{-9}/k_{10} in the Mechanism for the Oxidation of Ferrocyanide by Perbromate

temp/°C	pH	$k_9/10^{-3}$ M^{-1} s^{-1}	k_{-9}/k_{10}/M^{-1}
25	7.4	1.0 ± 0.3[a]	550 ± 200[a]
25	8.0	0.5 ± 0.2[a]	440 ± 200[a]
25	8.5	0.16 ± 0.03[a]	510 ± 90[a]
25	8.5	0.14 ± 0.016[b]	560 ± 60[b]
25	10	~0.02[c]	
25	13	nil	
35	8.5	0.5 ± 0.12[a]	250 ± 70[a]
35	8.5	0.4 ± 0.13[b]	230 ± 100[b]
45	8.5	1.8 ± 0.3[a]	140 ± 30[a]
45	8.5	1.7 ± 0.5[b]	200 ± 100[b]

[a] Calculated from plots of $y = [\mathrm{BrO_4^-}]/k_{\mathrm{obs}}$ in Figure 3 by use of eq 15. [b] Values obtained by fitting eq 13 to measured values of t and ΔOD by adjusting k_9, k_{-9}/k_{10}, and $\Delta\mathrm{OD}_\infty$. [c] Value estimated from a single run.

By adjustment of the three parameters k_9, k_{-9}/k_{10}, and $\Delta\mathrm{OD}_\infty$, eq 13 was fitted to sets of corresponding values of ΔOD and t measured at 25, 35, and 45 °C under fixed conditions of pH = 8.5 and $[\mathrm{Fe(CN)_6^{4-}}]_0 \gg [\mathrm{Fe(CN)_6^{3-}}]_0$ and at varying C_t . The averages of the values of k_9, k_{-9}/k_{10} obtained by this procedure are shown in Table 1.

For the experiments in which $[\mathrm{Fe(CN)_6^{3-}}]_0 \gg [\mathrm{Fe(CN)_6^{4-}}]_0$ so that the reaction is pseudo-first-order in $[\mathrm{Fe(CN)_6^{4-}}]$, the expression

$$t = -k_{\mathrm{obs}}^{-1} \ln(1 - \Delta\mathrm{OD}/\Delta\mathrm{OD}_\infty) \qquad (14)$$

was similarly fitted to sets of corresponding values of t and ΔOD by adjusting the parameters k_{obs}^{-1} and $\Delta\mathrm{OD}_\infty$. When $[\mathrm{Fe(CN)_6^{3-}}]_0 \gg [\mathrm{Fe(CN)_6^{4-}}]_0$, eq 14 is a valid approximation to eq 13, yielding

$$k_{\mathrm{obs}} = 2k_9[\mathrm{BrO_4^-}](1 + (k_{-9}/k_{10})C_t)^{-1} \qquad (15)$$

k_9 and k_{-9}/k_{10} were determined from plots of $y = [\mathrm{BrO_4^-}]/k_{\mathrm{obs}}$ against C_t (Figure 3). The resulting values are shown in Table 1. We note that the values of k_9 and k_{-9}/k_{10} determined from eq 15 and calculated from eq 13 agree, and we conclude that the above mechanism gives a satisfactory representation of the measured kinetics.

Lifetime of $\mathrm{BrO_4^{2-}}$ in Aqueous Solution. The key issue in the present context is the lifetime of $\mathrm{BrO_4^{2-}}$, or equivalently, the rate constant k_{10a} of the reaction

$$\mathrm{BrO_4^{2-} \rightarrow BrO_3^- + O^-} \qquad (10a)$$

on which the measured kinetics of reaction 8 unfortunately yields no direct information. However, combining the observation that the ratio k_{-9}/k_{10} is independent of $[\mathrm{H^+}]$ (Table 1) with an estimated lower limit for the acidity constant of $\mathrm{HBrO_4^-}$, we deduce that k_{10a} is smaller than k_{10}, for which in turn an upper limit can be determined from the present results.

We first derive a lower limit for the acidity constant of $\mathrm{HBrO_4^-}$. Recalling that $\mathrm{IO_4^{2-}}$ and $\mathrm{BrO_4^{2-}}$ closely resemple each other, we may take the acid strengths of $\mathrm{HIO_4^-}$ and $\mathrm{HBrO_4^-}$ to be similar. A lower limit for the acid strength of $\mathrm{HIO_4^-}$ may be estimated from reactions of $\mathrm{IO_4^{2-}}$ in water. $\mathrm{IO_4^{2-}}$ reacts in neutral unbuffered solution with $\mathrm{IO_4^-}$ with a rate constant equal to 1.3×10^8 M^{-1} s^{-1}.[7] No deviation from a pseudo-first-order decay of $\mathrm{IO_4^{2-}}$ was detected by a reaction of $\mathrm{IO_4^{2-}}$ with 5 ×

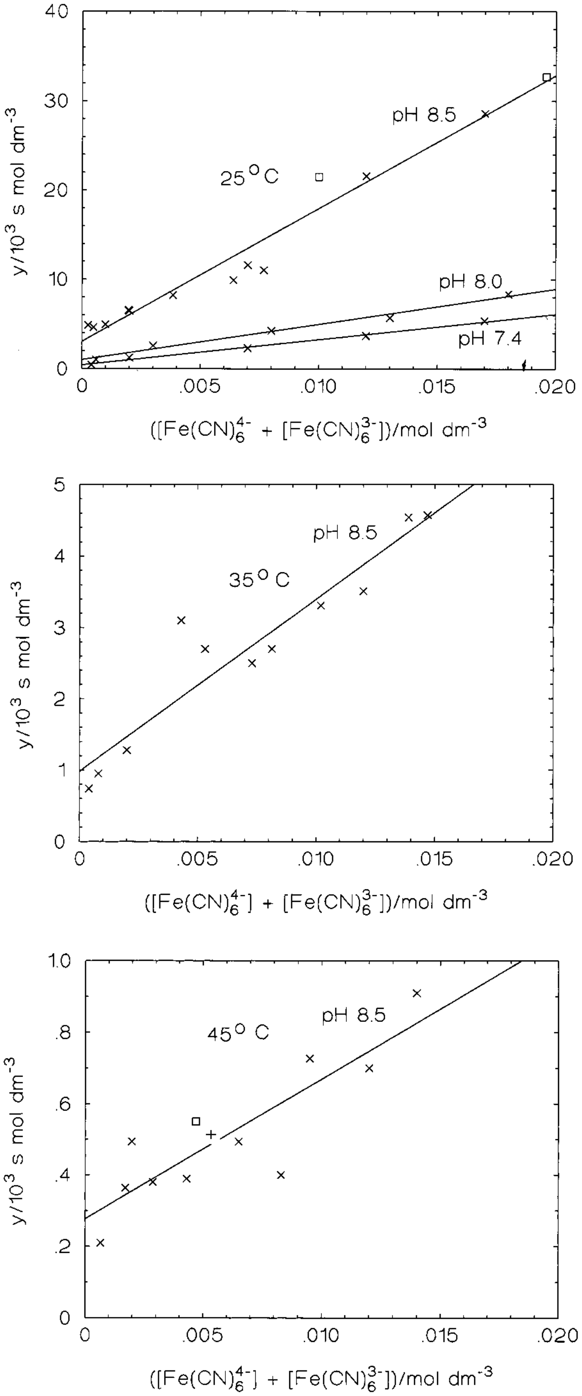

Figure 3. Plots of $y = [BrO_4^-]/k_{obs}$ against $C_t = ([Fe(CN)_6^{4-}] + [Fe(CN)_6^{3-}])$, at 25, 35, and 45 °C, obtained from measurements of the pseudo-first-order rate constant k_{obs} for formation of ferricyanide by reaction 8, in solutions containing ferricyanide in large excess over ferrocyanide. The initial concentrations of BrO_4^- are the following: +, 0.0475 M; ×, 0.085−0.1 M; □, 0.19 M. The straight lines represent least-squares fits to the experimental points.

10^{-4} M IO_4^- followed to 90% convertion of IO_4^{2-}.[7] This indicates that the rate constant for the hydrolysis af IO_4^{2-} is smaller than 10^4 s^{-1}, and since the rate constant for the reverse reaction of HIO_4^- with OH^- is on the order of 10^{10} M^{-1} s^{-1},[32] the base constant of IO_4^{2-} is smaller than 10^{-6}. Consequently, the acidity constant of HIO_4^-, and by assumption, also that of $HBrO_4^-$, is larger than 10^{-8}. Combining this result with rate constants measured for proton transfer from acids to bases,[31] we find that reactions 11 and −11 are fast compared to reactions −9 and 10 at the actual Borax concentration (0.05 M). Hence, $HBrO_4^-$ remains in protolytic equilibrium with the buffer throughout the decay, and we may reasonably include reaction 10a in the mechanism for reaction 8. This formally amounts to replacing in eqs 13 and 15 the ratio k_{-9}/k_{10} by the quantity $q = k_{-9}[H^+]/(k_{10}[H^+] + k_{10a}K)$, where K is the acidity constant of $HBrO_4^-$. For q to be insensitive to changes of $[H^+]$ as observed, the term $k_{10}[H^+]$ in the denominator must be larger that the term $k_{10a}K$, i.e., $k_{10}/k_{10a} > K/[H^+]$, which, with the actual values of $[H^+]$ and the lower limit of K, leads to the inequality $k_{10a} < k_{10}$. An upper limit for k_{10} is finally estimated from the observed ratios k_{-9}/k_{10}. By extrapolation, we find $k_{-9}/k_{10} \approx 700$ M^{-1} at the temperature of the pulse radiolysis experiments (21 °C). The value of k_{-9} cannot exceed that of a diffusion-controlled reaction, which at the actual charge product of +3 for the reactants, can hardly be larger than 10^8 M^{-1} s^{-1}.[32] Thus, we find that k_{10} must be smaller than 2×10^5 s^{-1}, which is a fortiori also an upper limit for k_{10a}. We conclude that the lifetime of BrO_4^{2-} in aqueous solution is at least a few microseconds so that BrO_4^{2-}, if formed, would have been detected by the pulse radiolysis technique used.[14]

Reactions of BrO_3^- with OH and O^-. Having verified that BrO_4^{2-} exists in aqueous solution, we now test our model to see whether the reactions of O^- (and OH) with BrO_3^- are slow compared to the corresponding reaction(s) with IO_3^-. These reactions were studied by electron pulse irradiation of 0.01 and 0.02 M BrO_3^- solutions saturated with N_2O at 4.5 MPa. In solutions with this composition, more than 99% of the hydrated electrons formed in the primary radiolysis react with N_2O, forming O^- or OH.[16]

The reaction of O^- with BrO_3^- was studied in solutions containing 0.1 M NaOH, which were irradiated with 20 Gy in 1 μs pulses. No formation of BrO_4^{2-} was detected. Only small transient increases of the optical absorbance with a maximum at 430 nm was observed, which we ascribe to O_3^-. By taking the concentration of O_2 to be 5×10^{-6} M, the G value for formation of O^- in the electron pulse to be 7.1,[33] the extinction coefficient of O_3^- at 430 nm to be 2000 M^{-1} cm^{-1}, and the pK of OH to be 11.9,[16] we found that the growth of the transient could be simulated by the reactions

$$O^- + O_2 \leftrightarrow O_3^-; \quad k_{16} = 3.6 \times 10^9\ M^{-1} s^{-1}, \text{ref 16;} \quad k_{-16} = 3.3 \times 10^3\ s^{-1}, \text{ref 34} \quad (16,-16)$$

$$O^- + O^- + H_2O \rightarrow HO_2^- + OH^-; \quad k_{17} = 10^9\ M^{-1} s^{-1}, \text{ref 16} \quad (17)$$

$$O^- + OH \rightarrow HO_2^-; \quad k_{18} = 2 \times 10^{10}\ M^{-1} s^{-1}, \text{ref 16} \quad (18)$$

From this result we infer that the rate constant for the reaction between O^- and BrO_3^- must be smaller than 10^6 M^{-1} s^{-1}.

The reaction of OH with BrO_3^- was studied in neutral unbuffered 0.02 M BrO_3^- solutions by irradiation with 20−60 Gy in 1 μs pulses.. A small, dose-independent absorbance was observed at 360 nm. A 5-fold increase of this transient absorbance was observed in solutions, to which 5×10^{-6} M KBr was added. Accordingly, the transient absorbance is ascribed to $BrOH^-$ formed in a reaction of OH with Br^- present in the concentration of 10^{-6} M.[35,36] The fact that the transient absorbance was independent of the dose shows that the rate of reaction of OH with 0.02 M BrO_3^- is small compared to the rate of reaction of OH with 10^{-6} M Br^-. Taking the rate constant for the reaction between OH and Br^- to be 10^{10} M^{-1} s^{-1},[36] we find the rate constant for the reaction of OH with BrO_3^- to be smaller than 5×10^5 M^{-1} s^{-1}. This result, that the reaction between OH and BrO_3^- is immeasurably slow, is in accordance with the mechanism of reaction 8, which does not contain the back reaction −10 of OH with BrO_3^-.

Conclusion

We conclude that in contrast to the diffusion-controlled reaction of O^- with IO_3^-, the reaction between O^- and BrO_3^- is clearly too slow to compete with the separation of these fragments when formed by the reaction of e_{aq}^- with BrO_4^-. Combined with the observation that IO_4^{2-} is formed, but BrO_4^{2-} is not, by the reactions of e_{aq}^- with IO_4^- and BrO_4^-, this result supports our proposal that the electron adduct produced in a highly exergonic reaction of e_{aq}^- with an inorganic oxocompound is formed by geminate recombination of O^- and the corresponding fragment *after* thermal equilibrium with the solvent has been attained.

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