of activation should be negative. This expectation was realized in the case of TNT ($\Delta S^{\dagger} = -16$ eu) but not in RDX and HMX. Calculations using the kinetic parameters shown in Table V indicated that the entropy of activation for RDX was approximately +27 eu and that for HMX it was in range +19 to 22 eu (Table V) depending on the temperature. Such positive entropy of activation values clearly rule out a cyclic transition state. One is forced to consider a chain reaction which is generally associated with large frequency factors. Therefore, while the lack of temperature dependence suggests merely a nonlinear (bent) transition state, the entropy values suggest an additional role of chain reactions in the condensed-phase decomposition of RDX and HMX. However, the unimolecular process in the mass spectrometer source may involve a cyclic transition state in the gas-phase decomposition.

Initial Steps in the Decomposition Mechanisms of RDX and HMX. Any mechanism considered for the condensed-phase decomposition RDX or HMX has to be consistent with a clear primary deuterium kinetic isotope effect. Furthermore, the mechanism has to account for the predominant formation of N-¹⁵N–O in the solid-state decomposition of HMX–($^{15}NO_2$)₄ and $RDX-(^{15}NO_2)_3$, previously reported from this laboratory.¹⁷ The nearly constant value of the DKIE during all stages of the reaction suggests a single predominant rate-controlling reaction. The temperature independence of the DKIE, the autocatalytic nature of the decomposition, high-frequency factors, and large positive entropy of activation suggest an intermolecular chain process involving the C-H bond cleavage in the rate-determining step. An intermolecular hydrogen transfer in a chain reaction is easy to envisage in the condensed phase also since the crystal structures of RDX and δ -HMX consist of several short intermolecular O---H distances.^{11,13} In general, the lattice structures of RDX and all HMX polymorphs are characterized by weak intermolecular hydrogen bonding.12

The debate about the many different mechanisms^{14,15,34} proposed for the decomposition of RDX and HMX often centers around the relative importance of N-N bond vs. C-N bond rupture in the early stages prior to the collapse of the nitramine skeleton

(34) Kimura, J.; Kubota, N. Propellants Explos. 1980, 5, 1-8.

forming the observed products, namely CH₂O, N₂O, N₂, NO, CO₂, CO, HCN and, in the gas-phase decomposition, minor amounts of NO₂ and/or HNO₂ also. A clear primary deuterium kinetic isotope effect determined in this work focuses attention on the C-H cleavage. The C-H bond rupture would require an activation energy in excess of 90 kcal/mol, which is higher than any experimentally found value. This may mean that the overall reaction is complex, perhaps involving several parallel and consecutive steps giving a low activation energy for the global reaction or, more likely, that the C-H cleavage is assisted by the NO₂ group in the transition state operating through the short O---H distances. The radical left behind after an intra- or intermolecular hydrogen transfer can readily collapse to the observed major and minor products.^{17,19,34} While many variations of these steps have been proposed from time to time, the experimental findings of the present work do not shed light on that discussion.

Conclusions

This investigation using the kinetic isotope effect as an experimental probe firstly suggests that the radical left behind after an intermolecular hydrogen transfer to a nitro group in the rate-determining step proceeds to decompose further to the observed products. More significantly, this study suggests that the rate-controlling steps in the slow thermal decomposition and the shock-induced initiation of RDX and HMX are likely to be the same just as in the case of TNT reported previously. Thus, the DKIE served as a probe for the important step in the shock-induced chemistry which is otherwise difficult to investigate experimentally. These findings further suggest that the many past and present investigations of thermal degradation of explosives are indeed pertinent to the detonation or shock chemistry.

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Registry No. RDX, 121-82-4; HMX, 2691-41-0; RDX-*d*₆, 34729-66-3; HMX-*d*₈, 51446-35-6; D₂, 7782-39-0.

Supplementary Material Available: Experimental details of the mass spectrometric study of thermal decomposition products of HMX (ref 20) (4 pages). Ordering information is given on any current masthead page.

Complex Kinetics in the Bromate–Iodide Reaction: A Clock Reaction Mechanism

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A reinvestigation of the kinetics and mechanism of the bromate-iodide reaction in acidic medium has been undertaken. The stoichiometry of the reaction in excess iodide concentrations over bromate is $BrO_3^- + 9I^- + 6H^+ \rightarrow Br^- + 3I_3^- + 3H_2O$ (A), and in excess bromate concentrations the stoichiometry is $BrO_3^- + 6I^- + 6H^+ \rightarrow Br^- + 3I_2 + 3H_2O$ (B). In excess bromate concentrations a second reaction is observed in which the iodine produced by reaction B is consumed rapidly and suddenly in a typical clock reaction fashion according to the reaction $2BrO_3^- + I_2 \rightarrow 2IO_3^- + Br_2$ (C). Reaction C does not commence until reaction B is complete, i.e., when all the iodide ions have been consumed. This is explained via a combination of kinetic factors which favor the production of iodine and the fact that higher oxidation states of iodine are thermodynamically unstable with respect to iodine in the presence of iodide ions in acidic media. At 25 ± 0.1 °C and ionic strength 0.2 M (NaClO₄), the rate law in both high iodide and high bromide environments was found to be $-d[BrO_3^-]/dt = k_0[BrO_3^-][H^+]^2[I^-]$, with $k_0 = 44.3 \pm 1.1 M^{-3} s^{-1}$. The postulated mechanism involves an initial nucleophilic attack on the protonated bromate species by iodide, followed by elimination of HOI.

Introduction

The stoichiometry of the bromate-iodide reaction in acidic medium has been established $as^{1,2}$

 $BrO_3^- + 9I^- + 6H^+ \rightarrow Br^- + 3I_3^- + 3H_2O$ (R1)

A few kinetic studies have been performed on this reaction $^{3\mathchar`-5}$ and the rate law was found to be

$$-d[BrO_3^{-}]/dt = k_0[BrO_3^{-}][H^+]^2[I^{-}]$$
(1)

(3) Clark, R. H. J. Phys. Chem. 1909, 10, 679-683.

Randall, D. L. J. Am. Chem. Soc. 1910, 32, 644-648.
 Britton, H. T. S.; Britton, H. G. J. Chem. Soc. 1952, 3887-3891.

⁽⁴⁾ Barton, A. F. M.; Wright, F. A. J. Chem. Soc. A 1968, 1747-1753.

with a value of k_0 of about 49 M⁻³ s⁻¹.³ The reaction was also found to be catalyzed by a variety of oxy anions like carboxylate, acetate,4 and molybdate.5

However, the product of reaction R1, iodine, is known to displace bromine from aqueous bromate solutions.⁶

$$I_2 + 2BrO_3^- \rightarrow Br_2 + 2IO_3^-$$
 (R2)

This reaction was found to occur in four well-defined stages which included an induction period, an iodine disappearance period, an iodine bromide appearance, and a bromine appearance. The product of reaction R2, iodate, reacts with iodide ions in acidic media to give iodine:^{7,8}

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$$
 (R3)

Reaction R3 is moderately fast,^{9,10} and is used as an analytical tool for the determination of iodide.¹¹

All three reactions, R1, R2, and R3, are viable in acidic mixtures of bromate and iodide ions. Interpretation of the kinetic behavior should be able to accommodate the role each of the reaction plays.

The few kinetics studies that had been performed on this reaction gave no indication of any nonlinearity or complex kinetics.^{4,5} What made us feel this reaction deserved a second look was the recent study that reported sustained oscillations and bistability being observed in this reaction in a continuous stirred tank reactor.¹² In such a reactor, the BrO₃-I⁻ system shows bistability, over a range of nearly 5 orders of magnitude in the iodide input concentration. At sufficiently high input concentrations of iodide and bromate, sustained oscillations in the redox potential and iodide and iodine concentrations have been observed. At intermediate iodide concentrations, the system exhibits a Hopf bifurcation.13

It is not quite certain what conditions are necessary for a chemical oscillator to evolve, but nonlinearity in the reaction system enhances the likelihood of oscillation.^{14,15} Nonlinearity can be brought about by phenomena like autoinhibition, cross-catalysis, and autocatalysis. Bistability coupled to any appropriate feedback loop can also yield oscillations.¹⁶

The simple nature of the reaction as reported in the literature, combined with the observed oscillatory behavior, dictated that the reaction deserved reinvestigating. This reported lack of nonlinearity in the reaction was inconsistent with the subsequent observation of chemical oscillations in a CSTR based on the expected preconditions for establishment of oscillatory behavior.¹⁵

Experimental Section

Materials. The following reagents were used without further purification: potassium iodide (free flowing granular), potassium bromate, sodium perchlorate (Fisher), and perchloric acid (70-72%) (PAL Chemicals). The concentrated perchloric acid was diluted to appropriate strength and standardized by standard sodium carbonate or sodium hydroxide. A 1 M stock sodium perchlorate was prepared and this was used as the inert electrolyte to maintain the ionic strength at 0.2 M. All reagent solutions

- (5) Barton, A. F. M.; Loo, B.-H. J. Chem. Soc. A 1971, 3032-3035.
- (6) King, D. E. C.; Lister, W. M. Can. J. Chem. 1968, 46, 279–286.
 (7) Dushman, S. J. J. Phys. Chem. 1904, 8, 453–482.
- (8) Morgan, K. J.; Peard, M. G.; Cullis, C. F. J. Chem. Soc. 1951, 1865-1867
- (9) Schildcrout, S. M.; Fortunato, F. A. J. Phys. Chem. 1975, 79, 31-34. (10) Liebhafsky, H. A.; Roe, G. M. Int. J. Chem. Kinet. 1979, 11, 693-703
- (11) Vogel, A. I. Quantitative Inorganic Analysis; Longman: London,
- (12) Alamgir, M.; De Kepper, P.; Orban, M.; Epstein, I. R. J. Am. Chem.
 (12) Alamgir, M.; De Kepper, P.; Orban, M.; Epstein, I. R. J. Am. Chem.
 Soc. 1983, 105, 2641–2643.
 (12) Margin L. McCracken M. The Hopf Bifurcation and Its Appli-
- (13) Marsden, J.; McCracken, M. The Hopf Bifurcation and Its Applications; Springer-Verlag: New York, 1976.
 (14) De Kepper, P.; Epstein, I. R.; Kustin, K. J. Am. Chem. Soc. 1981, 103 6121-6127
- 103, 6121-6127.
- (15) De Kepper, P.; Epstein, I. R.; Kustin, K. J. Am. Chem. Soc. 1981, 103, 2133-2134
- (16) Boissonade, J.; De Kepper, P. J. Phys. Chem. 1980, 84, 501-506.

were prepared by using doubly distilled water. The 0.05 M stock solutions of potassium iodide were prepared fresh every day.

Methods. The reaction vessel used was a 150-mL reactor with a thermostatable jacket. The reaction temperature was maintained at 25 ± 0.1 °C. Potentiometric measurements were accomplished by using a platinum reference electrode with a double-junction calomel electrode. Ammonium nitrate, 10% solution, was used as the contact electrolyte. Specific-ion electrodes like Orion's specific-bromide and specific-iodide electrodes were also used. However, the iodide concentration was high enough in the reaction vessel to interfere with the quantitative measurement of the bromide ion concentration, and vice versa for the specific-iodide electrode. The trace from the specific-bromide electrode was, however, qualitatively similar to the redox potential trace. In many experiments then, because of its better response time, the specific-bromide electrode was used instead of the platinum electrode.

Spectrophotometric measurements were done on a Pve Unicam SP1750 UV spectrophotometer and a Varian Techtron Model 635 UV-visible spectrophotometer. Both spectrophotometers are equipped with thermostatable compartments. The Varian Techtron spectrophotometer is equipped with a stirrer. No difference was observed in absorbance and redox potential traces of stirred and unstirred solutions. The iodine concentration was monitored by measuring its absorption at the I_2/I_3^- isobestic point of 460 nm. The molar absorptivity coefficient of iodine was taken as 770 M⁻¹ cm⁻¹ at this wavelength.¹⁷

Stoichiometric determinations were carried out by both spectrophotometric and volumetric techniques. In low bromate concentrations (R1), the concentration of iodine produced was determined by titration against standard thiosulfate solution with starch as the indicator.¹⁸ The iodide left was determined by adding acidified iodate and titrating the liberated iodine against standard thiosulfate. A correction was made for the iodine that had been produced via reaction R1.

The concentration of the I_3^- species was determined by monitoring its absorption at 353 nm.^{6,9} While the consumption of iodine according to reaction R2 is very rapid, the production of bromine is very slow.^{6,19} For this reaction, the cuvettes were tightly sealed to prevent the escape of the rather volatile bromine. The final bromine concentration was determined spectrophotometrically by its absorption at 390 nm.

For initial rate measurements, the absorbance vs. time trace which corresponds to about 2% of the reaction was fed into the university's ICL 2946 mainframe computer where it was analyzed by the initial rate method. In pseudo-first-order kinetics environments a number of absorbance-time traces at the same conditions were first tested for first-order kinetics before being analyzed for the apparent rate constant, k^{app} . A statistical analysis was next performed and any trace that gave a value of k^{app} outside $\pm 2\sigma$ was discarded.

Experiments with acid concentrations greater than 0.1 M were so fast the kinetic measurements were made with a Gibson-type stopped-flow spectrophotometer with stainless steel drive syringe barrels.²⁰ Potassium bromate, perchloric acid, and sodium perchlorate were mixed in one of the solution reservoirs, and potassium iodide and sodium perchlorate were mixed in the other. The trace from the stopped-flow apparatus was captured on a Biomation 610B transient recorder and digitalized. The digitalized trace was then fed into a PDP-11/23 minicomputer where it was analyzed by both the initial rate and the pseudo-first-order kinetics methods

Results

In conditions of excess iodide concentrations the stoichiometry of the reaction was established as

$$BrO_3^- + 9I^- + 6H^+ \rightarrow Br^- + 3I_3^- + 3H_2O$$
 (R1)

- (20) Honig, D. S.; Kustin, K.; Martin, J. E. Inorg. Chem. 1972, 11, 1895-1898.

⁽¹⁷⁾ Autrey, A. D.; Connick, R. E. J. Am. Chem. Soc. 1953, 73, 1842. (18) Reference 11, p 357.
(19) Simoyi, R. H., to be submitted for publication.



Figure 1. Optical density trace at $\lambda = 460$ nm for the production of iodine in conditions of low iodide concentrations. Two traces, at different initial acid concentrations, have been chosen to show the effect of acid. $[BrO_3^{-1}]_0 = 5 \times 10^{-3}$ M, $[I^{-1}]_0 = 5 \times 10^{-4}$ M.



Figure 2. Optical density traces at different initial acid concentrations in high iodide concentrations. The iodine is not consumed at the end of the reaction as in Figure 1. $[BrO_3^{-}]_0 = 2 \times 10^{-4} M$, $[I^{-}]_0 = 5 \times 10^{-2} M$.

In excess bromate concentrations over iodide the stoichiometry is

$$BrO_3^- + 6I^- + 6H^+ \rightarrow Br^- + 3I_2 + 3H_2O$$
 (R4)

The iodine produced in reaction R4 is next consumed according to the reaction

$$2BrO_3^- + I_2 \rightarrow 2IO_3^- + Br_2$$
 (R2)

The UV spectrum of the final products of the reaction in excess bromate concentrations did show the characteristic molecular bromine species absorption peak at $\lambda = 390$ nm. Typical absorbance traces can be seen in Figures 1 and 2. Both reactions R2 and R4 can be observed in Figure 1, but only one reaction, R1, is observed in excess iodide conditions (Figure 2).

We noted that reaction R4 goes to completion before R2 can commence. This could be proved by observing the final iodine absorbance before the commencement of R2. In all cases, the iodide concentration expected from the stoichiometry of R4 was achieved before the reaction "clocked". Our experiments further show that iodide poisons reaction R2. As long as some iodide ions remained in the reaction mixture, no iodine is consumed. Doping the reaction mixture with a few iodide ions, just before the reaction was due to clock, invariably delayed the commencement of R2. Iodide is so efficient in poisoning R2 that from our experiments we estimate that the iodide concentration has to fall below 10^{-6} M before R2 can proceed. This estimate was arrived at by relating the lag time (the time it takes to clock) to the initial iodide concentration in acidic mixtures of bromate and iodine. A plot of the roughly linear relationship between lag time and iodide concentration yields $[I^-] \approx 1.2 \times 10^{-6}$ M for zero lag time.



Figure 3. Redox potential traces at different initial acid concentrations. The sharp increase in redox potential corresponds to the consumption iodine as in Figure 1. $[I^-]_0 = 4 \times 10^{-4} \text{ M}$, $[BrO_3^-] = 2 \times 10^{-2} \text{ M}$.

The absorbance traces are very simple. For both high and low iodide concentrations we worked in pseudo-first-order kinetics environments (Figures 1 and 2). The redox potential and specific-electrode signals in low iodide concentrations show a slow increase in potential until, in a typical clock reaction fashion, the potential suddenly and rapidly increases (Figure 3). The corresponding redox potential traces in stoichiometric excess of iodide did show a simple monotonic increase in potential which finally stabilizes at a particular value, but no clocking is observed. The rapid redox potential increase step corresponds to the consumption of iodine step in the absorbance trace (Figure 1). The lag times were decreased by higher bromate and acid concentrations. The effect of acid was the largest, as can be seen in Figure 3. With acid concentrations less than 1×10^{-2} M, the reaction is so slow it needs up to 8 h to go to completion, while at acid concentrations higher than 0.1 M, the reaction is so fast that we had to employ a stopped-flow ensemble.²⁰

Order of Reaction. Two methods were employed to evaluate the reaction order and kinetic constants: the initial-rate method and the pseudo-first-order kinetics method.

Low Iodide Concentrations. In this environment, the initial iodide concentration was maintained at 4×10^{-4} M. Bromate and acid concentrations were at least 100-fold excess over iodide.

rate =
$$\frac{1}{3}d[I_2]/dt = k^{app}[I^-]$$
 (2)

where

$$k^{\text{app}} = k_0 [\text{BrO}_3^-]^x [\text{H}^+]^y$$
 (3)

A semilogarithmic plot of production of iodine against time was linear for over 95% of the reaction. Acid and bromate dependence series of experiments were next performed. These can be seen in Figure 4a,b. The best straight lines for Figures 4a,b were first plotted with the aid of a linear least-squares computer analysis in which points were equally weighted. This analysis gave k_{app} intercepts which were experimentally indistinguishable from zero. The final value of k_0 was obtained from analysis in which the origin was heavily weighted. Our experimental data showed that x =1 and y = 2. The initial rate method also gave the same values for x and y. The rate equation can be written as

$$\frac{1}{3} d[I_2] / dt = k_0 [BrO_3^{-}] [H^+]^2 [I^-]$$
 (1)

The value of k_0 was next calculated as

$$k_0 = 43.8 \pm 0.3 \text{ M}^{-3} \text{ s}^{-1}$$
 (4)

We tried to explore the possibility of another term in rate-law equation (1). More than one bromate concentration value was used in acid dependence experiments (Figure 4a) and more than one acid concentration value was used in the bromate dependence experiments (Figure 4b). The idea we employed was that if another term existed in the rate equation, then the values of k_0 deduced from, e.g., acid dependence experiments at different



Figure 4. (a) Variation of pseudo-first-order rate constant, k^{app} , in conditions of low iodide concentrations on the initial acid concentrations. All traces gave $k_0 = 43.8 \pm 0.3$. $[I^-]_0 = 4 \times 10^{-4}$ M. (b) Bromate anion dependence of the pseudo-first-order rate constant k^{app} in low iodide concentrations. All traces gave a value of k_0 as in Figure 4a.

bromate concentrations would differ, or show a trend that could lead us to deduce the nature of the other term(s). In these experiments, however, the value of k_0 was quite robust, and the value of 43.8 M^{-3} s⁻¹ was reproducible over wide ranges of reactant concentrations.

High Iodide Concentrations. The initial bromate concentration was fixed at 2×10^{-5} M, while the iodide and acid concentrations were maintained at about 1000-fold excess over bromate. The absorbance-time trace was also exponential

$$\frac{1}{3}d[I_3^{-}]/dt = k^{app}[BrO_3^{-}]$$
 (5)

where now

$$k^{\rm app} = k_1 [{\rm H}^+]^{\nu} [{\rm I}^-]^z \tag{6}$$

Using the same analysis as in low iodide environments we deduced the values of y and z to be 2 and 1, respectively. A number of acid and iodide dependence experiments were also performed without any discernible variation in the rate constant (Figure 5b). In pseudo-first-order kinetics environments, the value of k_1 was deduced to be 44.2 \pm 0.4 M⁻³ s⁻¹.

The initial-rate method gave values of the rate constant which were about 1.5% higher than those given by pseudo-first-order kinetics (Figure 5a). We did not treat this as too significant because the relative error given by the initial-rate method (-2.5%) was much higher than that from the pseudo-first-order method (-1.0%).



Figure 5. (a) Dependence of initial rate on initial bromate concentrations at different acid concentrations. At $[H^+]_0 = 5 \times 10^{-3}$ M, $k_0 = 46.75 \oplus$ $1.5 \text{ M}^{-3} \text{ s}^{-1}$; at $[H^+]_0 = 4 \times 10^{-3}$ M, $k_0 = 47.5 \pm 1.7 \text{ M}^{-3} \text{ s}^{-1}$; and at $[H^+]_0 =$ 3×10^{-3} M, $k_0 = 46.3 \pm 1.45 \text{ M}^{-3} \text{ s}^{-1}$. For all traces, $[I^-]_0 = 1 \times 10^{-3}$ M. (b) Dependence of the pseudo-first-order rate constant, k^{app} (apparent rate constant), in high iodide concentrations on the initial acid concentrations. All three different initial iodide concentrations gave k_0 $= 44.15 \oplus 0.4 \text{ M}^{-3} \text{ s}^{-1}$. $[\text{BrO}_3^{-1}]_0 = 2 \times 10^{-5} \text{ M}$.

The final value of k_0 (44.3 ± 1.1 M⁻³ s⁻¹) was obtained from a statistical average of the values obtained from all the different sets of initial conditions studied.

Discussion

The second stage of the reaction, the consumption of iodine, seems to be extraneous to the first stage. Thus we can postulate a mechanism for this stage without interference from the second stage.

The first step in the oxidation of the bromate seems to involve a reaction that is analogous to the first step of the Field, Koros, and Noyes (FKN) mechanism for the Belousov–Zhabotinskii reaction:²¹

$$BrO_3^- + Br^- + 2H^+ \Longrightarrow HBrO_2 + HOBr$$
 (R5)

In our reaction, reaction R5 is

$$BrO_3^- + I^- + 2H^+ \rightleftharpoons HBrO_2 + HOI$$
 (R6)

For reaction R6 the equilibrium lies more to the right than that for R5, considering the increase in metallic character in going from bromine to iodine. The products of reaction R6 can react

⁽²¹⁾ Field, R. J.; Koros, E.; Noyes, R. M. J. Am. Chem. Soc. 1972, 94, 8649-8664.

with more iodide to give iodine or further intermediates that will give iodine eventually.

$$HOI + I^- + H^+ \rightarrow I_2 + H_2O \qquad (R7)$$

$$HBrO_2 + I^- + H^+ \rightarrow HOBr + HOI$$
 (R8)

$$HOBr + 2I^- + H^+ \rightarrow I_2 + Br^- + H_2O$$
 (R9)

Reaction R7. This reaction has been studied by Eigen and Kustin using temperature-jump spectrophotometry.²² Its equilibrium lies far to the right ($K_{eq} = 1.5 \times 10^{12} \text{ M}^{-2}$), and the attainment of this equilibrium is very rapid ($k_r = 4.4 \times 10^{12} \text{ M}^{-2}$ s^{-1}). We would expect this to be a very important reaction in the mechanism since it would consume instantaneously all the HOI as soon as they are formed by R6 as long as iodide ions still existed in the reaction mixture.

Reaction R8. An analogous reaction with bromide as the nucleophile has been studied by Noszticzius et al.23 in which they deduced a forward rate constant k_f of 2 × 10⁶ M⁻² s⁻¹ with a negligible reverse rate constant. With iodide instead of bromide, we would expect this reaction to be viable and thermodynamically more favorable. In our reaction mixture, any reaction that raises the oxidation state of iodine while lowering that of bromine would be in most cases thermodynamically favorable.^{24,25}

Reaction R9. This is a composite reaction that occurs via a number of steps. The first step is most likely the formation of IBr followed by the hydrolysis of the IBr to yield HOI which is instantly consumed via R7

$$HOBr + I^- + H^+ \rightarrow IBr + H_2O \qquad (R10)$$

$$IBr + H_2O \rightleftharpoons HOI + Br^- + H^+$$
 (R11)

$$HOI + I^- + H^+ \rightarrow I_2 + H_2O \qquad (R7)$$

The hydrolysis equilibrium constant for R11 should lie overwhelmingly to the left.²⁶ The incentive to hydrolyze should be provided by R7 which consumes HOI molecules as soon as they are formed. The reaction of HOBr with bromide has also been studied by Eigen and Kustin.22 They found a forward rate constant of 8×10^9 M⁻¹ s⁻¹ and an equilibrium constant of 7.3×10^7 M⁻². We would expect the rate constant and equilibrium constant for R10 to lie between those for HOBr + Br^- and those for R7.

The stoichiometry of reaction R4 can be satisfied by R6 + 2(R7) + R8 + R9. The stoichiometry of R1 can be obtained by adding the reaction

$$I_2 + I^- \rightarrow I_3^ K_{eq} = 725 \text{ (ref 27)}$$
 (R12)

Mechanism. Using known values of rate constants and those estimated by analogy from the bromate-bromide reactions, we note that reactions, R7, R8, R9, and R12 are very fast, and on the time scales on which we were studying the bromate-iodide reaction, we feel they cannot be rate-determining. This leaves reaction R6 as the rate-determining step. We suggest R6 as a composite of reactions R13, R14, and R15.

The first step is the protonation of the bromate ion

$$\operatorname{BrO}_{3}^{-} + \operatorname{H}^{+} \xrightarrow[]{k_{1}}{k_{-1}} \operatorname{HBrO}_{3} (\operatorname{rapid})$$
 (R13)

The next step is the nucleophilic attack by iodide on the protonated bromate species

$$HOBrO_2 + I^- \xrightarrow{k_2}_{k_{-2}} HOBrO_2 I^-$$
(R14)

This is next followed by elimination of HOI

- (24) Sharma, K. R.; Noyes, R. M. J. Am. Chem. Soc. 1976, 98, 4345-4349.
 - (25) J. Phys. Chem. Ref. Data 1982, 11, Suppl. No. 2.
 - (26) Citri, O.; Epstein, I. R. J. Am. Chem. Soc., submitted for publication. (27) Davies, M.; Gwynne, E. J. Am. Chem. Soc. 1952, 74, 2748-2752.

$$HOBrO_2I^- + H^+ \xrightarrow{\kappa_3} HBrO_2 + HOI$$
 (R15)

Step R15 is rate-determining, and so the rate expression becomes

$$d[HOI]/dt = k_3[HOBrO_2I^-][H^+]$$
(7)

$$=\frac{k_2[\text{HBrO}_3][\text{H}^+]}{k_3[\text{H}^+]+k_{-2}}$$
(8)

Since R15 is rate-determining, $k_{-2} \gg k_3$ [H⁺]. Using the relationship

$$[HBrO_3] = (k_1/k_{-1})[BrO_3^{-1}][H^+]$$
(9)

We can thus write

rate:
$$d[HOI]/dt = k_0[BrO_3^-][H^+]^2[I^-]$$
 (1)

where

$$k_0 = k_1 k_2 / k_{-1} k_{-2}$$

This agrees with our experimentally determined rate law.

Clock Mechanism. The clock mechanism, which allows reaction R4 to proceed to completion before R2 can commence, can be deduced from examining the steps involved in the two reactions starting from the products of reaction R6: HBrO₂ and HOI.

Route to Iodate. We deduce the following route leading to the formation of iodate

$$HBrO_2 + HOI \rightarrow HIO_2 + HOBr \qquad (R16)$$

$$HIO_2 + HOBr \rightarrow IO_3^- + Br^- + 2H^+ \qquad (R17)$$

$$BrO_3^- + HIO_2 \rightarrow IO_3^- + HBrO_2$$
 (R18)

Reaction R16 should be a rapid oxygen transfer. The rate constant for HClO₂ + HOI has been reported to be about $6 \times 10^7 \text{ M}^{-1}$ $s^{-1.28}$ We would expect the rate constant for R16 to be around this value or slightly larger. The rate constant for R16 is thus 4-5 orders of magnitude smaller than that for R7 which will be competing with R16 for HOI molecules. Reaction R17 will also be competing with reaction R10 for HOBr molecules. Citri and Epstein²⁶ have deduced a rate constant of 2.25×10^8 M⁻¹ s⁻¹ for R17, while from thermodynamic considerations we would expect the forward rate constant for reaction R10 to lie between 8×10^9 $M^{-2} s^{-1}$ and $4.4 \times 10^{12} M^{-2} s^{-1}$.²²

Thus as long as iodide ions remain in solution, reaction R7 will dominate since it is by far the fastest in the reaction mixture. This effectively shuts down reactions R16-R18 which can yield higher oxidation states of iodine. As soon as the iodide ions are exhausted, further oxidation of iodine can commence.

Role of Bromide. As the reaction progresses, the bromide concentration is expected to rise according to R1 and R4. We have explored the possible consequences of introducing bromide ions into the reaction mixture and have concluded that the effect would be minimal in this batch environment. Apart from reaction R5, the following are other reactions in which bromide could be involved in

HBrO₂ + Br⁻ + H⁺ → 2HOBr (ref 29) (R19)
$$k_{\rm f} = 2 \times 10^6 \,{\rm M}^{-2} \,{\rm s}^{-1}, \quad k_{\rm r} \sim 0$$

$$HOBr + Br^- + H^+ \rightarrow Br_2 + H_2O \text{ (ref 22)} \quad (R20)$$

$$k_{\rm f} = 8 \times 10^9 \,{\rm M}^{-2} \,{\rm s}^{-1}, \ k_{\rm r} = 1.1 \times 10^2$$

Reactions R5 and R19 will yield HOBr (instead of HOI), which we would expect to yield the product iodine (reaction R9), via IBr (reaction R10). Reaction R20 appears most viable, although it would also be competing with R9. We, however, found no evidence of bromine during the first stage of the reaction. It would appear reasonable that if any bromine is formed via reaction R20, in the presence of iodine (reaction R7), then iodine bromide would be quantitatively formed,³⁰ and the IBr would hydrolyze (reaction

⁽²³⁾ Noszticzius, Z.; Noszticzius, E.; Schelly, Z. A. J. Phys. Chem. 1983, 87, 510-514.

⁽²⁸⁾ Kern, D. M.; Kim, C.-H. J. Am. Chem. Soc. 1965, 87, 5309-5313. (29) Orban, M.; Epstein, I. R. J. Phys. Chem. 1983, 87, 3212-3219.

Computer Simulations. In an independent study, Citri and Epstein,²⁶ using Hindmarsh's version³¹ of the Gear algorithm³² for stiff differential equations, simulated the bromate-iodide reaction in both batch and flow conditions. The same 13 elementary reactions were found sufficient to simulate both conditions satisfactorily. Their model only fails to predict in batch the pH-dependence of the iodine disappearance at the instant of clocking (reaction R2). The major reactions they proposed are the same as ours. They used our value of k_1 for reaction R6. One difference between their mechanism and ours is their inclusion of the reaction

HOBr + I₂
$$\rightleftharpoons$$
 HOI + IBr $k_{\rm f} = 8 \times 10^7$, $k_{\rm r} = 1 \times 10^2$ (R21)

They considered reaction R21 as the starting point for the oxidation of iodine. Closer examination shows that reaction R21 is a composite of reaction R10 and the reverse of R7 (hydrolysis of iodine), both of which are included in our mechanism. Their study showed that the most important reactions in the mechanism are R5, R7, R11, and R21, which concurs with our findings.

Conclusion

Our experiments have shown that, though the bromate-iodide reaction displays simple kinetic behavior in the production of iodine, it, however, possesses a built-in clock mechanism which can separate the production of iodine from the oxidation of iodine to iodate. Our preliminary investigations on the iodine-bromate reaction indicate that the reaction is very complex with at least one autocatalytic step.¹⁹ In a flow reactor, however, we expect the major species, bromate, iodide, bromide, iodine, bromine, and iodate to coexist, the relative quantities of each varying under

bistable conditions from one steady state to the other.²⁶

The biggest shortcoming in our experimental work is our inability to quantitatively assess IBr which is a very important species in our mechanism. Under batch conditions we expect this species to rise during the course of the reaction, but in the later stages of the reaction it should hydrolyze before giving iodine and bromide (R10 + R6). Under flow conditions the IBr will maintain a finite concentration throughout.

The role of R13 was examined and found to be insignificant under batch conditions. Our reasoning is based on the fact that since R3 is faster than R4, the final reaction would be R4 + R3

$$2BrO_{3}^{-} + I_{2} + 10I^{-} + 12H^{+} \rightarrow Br_{2} + 6I_{2} + 6H_{2}O \qquad (R22)$$

which would be autocatalytic in iodine. Such a scenario would yield a distortion of our exponential kinetics in the later stages of the reaction. Our experimental data analysis did not show this. It appears then that the kinetic control is so efficient that reaction R16 which leads to higher oxidation states of iodine (>+1) is insignificant in the presence of iodide ions. In general, any higher oxidation state of iodine is thermodynamically unstable with respect to iodine in the presence of iodide.

There are two points of note from our study. Firstly, there is no global evidence of autocatalysis in the first stage of the reaction. The nonlinearity which is responsible for the oscillatory behavior comes from a combination of the two reactions (R4 + R2). Secondly, the mechanism we propose does not involve any freeradical mechanisms as most bromate reduction mechanism often do.

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Mechanism for the Reaction of CH_2OO with SO_2

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The gas-phase reaction of CH₂OO produced by the reaction of ozone with ethylene was investigated. The pressure dependence of the yield of H_2SO_4 formed in the reaction of CH_2OO with SO_2 was studied in the pressure range of 10-1140 Torr. The H₂SO₄ yield (0.40 at the high-pressure limit) decreased as the total pressure decreased but did not fall to zero even at low pressure, which implies that stabilized ground-state CH2OO species are formed at low pressure as a primary product. Vibrationally excited CH_2OO^{\dagger} as well as another excited CH_2OO^{\ast} , which does not suffer collisional stabilization even at the highest pressure studied, is also produced in the reaction. The formation ratio was obtained as CH₂OO:CH₂OO[‡]:CH₂OO* = 0.20:0.20:0.60. The ratio of the rate constant for collisional deactivation of CH_2OO^{\dagger} with air to that for decomposition for CH₂OO[‡] was determined to be $(1.0 \pm 0.9) \times 10^{-19} \text{ cm}^3/\text{molecule}$. As for the reaction mechanism for the reaction of CH2OO with SO2, the formation of adduct between CH2OO and SO2 was concluded. The adduct is proposed to react with another SO₂ molecule to produce HCHO and SO₃ or to decompose to HCOOH and SO₂ with the rate constant ratio of $(4.9 = 2.0) \times 10^{-15} \text{ cm}^3/\text{molecule}.$

Introduction

It is well recognized that the Criegee intermediates (RR'COO, peroxymethylene-type biradicals) are formed in the reactions of ozone with olefins, although they have not as yet been detected

spectroscopically. Recently, much attention has been given to this intermediate in view of acid rain, since oxidation of SO₂ with Criegee intermediates is indicated to be a potential source of atmosperic H₂SO₄.¹ Calvert and Stockwell² reported on the basis of computer simulation that under highly polluted atmosphere

⁽³⁰⁾ Faull, J. H. Jr. J. Am. Chem. Soc. 1934, 56, 522-526. (31) Hindmarsh, A. C. GEAR: Ordinary Differential Equation Solver; UCID-30001, Rev. 3, Lawrence Livermore Laboratory, 1974. (32) Gear, C. W. Commun. ACM 1971, 14, 176.

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⁽¹⁾ Calvert, J. G., Ed. SO₂, NO, and NO₂ Oxidation Mechanism: Atmospheric Considerations; Butterworths: Boston, MA, 1984. (2) Calvert, J. G.; Stockwell, W. R. Environ. Sci. Technol. 1983, 17, 428A.