methods described in ref 11. The shape groups, shape graphs, and other shape descriptors of charge densities, as functions of nuclear configurations, are associated with various domains of the configuration space.[11d,12a,b] In the general case, the formal reaction path passes through several of these shape domains of the configuration space, and segments of the path can be characterized by the shape domains they belong. The order of occurrence and the relative lengths of these path segments can characterize the shape changes of charge density during the reaction. Nonetheless, van der Waals surfaces approximate surprisingly well some isodensity surfaces, and many of the shape changes found and analyzed here are expected to be found also for isodensity surfaces.

The VDWSs can be characterized by alternative methods. A global descriptor, for example, the change of the molecular volume along a reaction path, may provide helpful information. A continuous change in volume provides a *continuous* characterization. Discrete characterizatons, such as that provided by the graphs $g(G(K))$, are advantageous for automated, computer-assisted shape comparison.

Acknowledgment. The authors thank a referee for useful suggestions. This work was supported by a research grant from the Natural Sciences and Engineering Research Council (NSERC) of Canada.

Registry No. HCN, 74-90-8; O_2, 7782-44-7; N, 7727-37-9.

Uncatalyzed and V(V)-Catalyzed Reaction of Methylene Blue with Potassium Bromate in Aqueous Sulfuric Acid

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The uncatalyzed and V(V)-catalyzed kinetics of reaction between methylene blue (phenothiazinium, 3,7-bis(dimethylamino)-, chloride) and acidic bromate has been studied monitoring the absorbance of methylene blue (MB) at 665 nm. Both the reactions involved competitive and sequential steps, having slow reaction in the initial stages. A rapid reaction followed after an induction time. For the two reactions, the orders with respect to the reactants are the same: second order with H^+, first order each with respect to bromate ion and MB. In addition, the catalyzed raction had first order dependence on catalyst concentration. In both the reactions HOBr is found to be the reaction intermediate. HOBr competed with bromate ion in the depletion of MB to give an intermediate, possibly phenothiazin-5-ium, 3-methylamino-7-dimethylamino-, chloride. The intermediate is further oxidized possibly by HOBr in fast step to final product, phenothiazin-5-ium, 3-amino-7-dimethylamino-, chloride. The stoichiometric ratios of MB to bromate are 2:3. The dual role of bromide ion as an inhibitor at low concentrations and as an autocatalyst at higher concentrations above a certain critical concentration in the reaction mechanism is discussed.

Introduction

The chemistry of reactions involving acidic bromate ion has been extensively studied in the past decade due to its unique capability to generate complex temporal behavior in closed systems during oxidation of certain organic substrates. Elegant schemes and models were proposed for the metal ion catalyzed and uncatalyzed reactions leading to oscillatory phenomena.[1–4] A number of reactions have also been reported in the literature involving studies of various inorganic and organic reagents using acidic bromate as oxidant.[5–7] Indicator reactions with bromate ion in acid medium were also reported for kinetic determination of Mo(VI),[8] Os(VIII),[9] V(V),[10] etc.

Methylene blue (phenothiazin-5-ium, 3,7-bis(dimethylamino)-, chloride) (MB), an intense blue dye, is known as a staining and sensitizing agent in biological reactions.[11] MB is also used as a catalyst, as a polymerization inhibitor, and as a complexing agent in a number of studies.[12] Burger and Field reported an uncatalyzed oscillatory reaction between MB and sulfide.[13] Literature survey shows no other kinetic studies were done using MB and any oxidizing agent.

In pursuit of a selective indicator reaction for analysis of V(IV)/V(V), using acidic bromate as oxidant which is known to be catalyzed by V(V),[14] a number of organic reagents were scanned. During the preliminary investigations, MB was found to satisfy certain criteria as substrate: a sharp absorption peak (λ_{max} 665 nm, ln ϵ 4.95) in the visible region, and a positive response to the presence of V(V). Further, when the kinetics were monitored, MB was found to have two depletion steps in reaction with acidic bromate: an initial slow step followed by a fast one after an induction time, I_t. Again the induction period was sensitive to vanadium(V) concentration. Hence, the kinetics of uncatalyzed and vanadium(V) ion catalyzed reactions between MB and potassium bromate in aqueous sulfuric acid were studied in detail. In this communication, we summarize the results of the

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kinetic studies and propose plausible mechanisms for the reactions investigated.

Experimental Section

Reagents. All the reagents employed were of AnalaR grade or of high purity. All the standard solutions and dilutions were made in deionized distilled water following standard procedures. Standard solution of V(V) 0.1 M was prepared by dissolving the requisite amount of ammonium vanadate in 0.1 M sulfuric acid.

Methods. Kinetic Studies. All the kinetic studies were conducted at 25 ± 0.5 °C by circulating water from a thermostat through a water jacket surrounding the reaction vessel. Reaction mixtures were stirred magnetically. In all the experiments requisite volumes of stock solutions of dilute sulfuric acid and MB were thermostated, together with the other required reagents. The reaction was started by addition of separately thermostated bromate solution. Measurements were done on Cecil C.E-272 Linear Radian UV–visible spectrophotometer. Absorbance (A) was monitored at 665 nm. No interference from the reactants or products was observed at the wavelength. In the concentration range of MB employed Beer's law was obeyed.

Emf Measurements. The overall electrochemical potential of the reaction mixtures was measured (Pye-Unicam pH meter with expanded scale and recorder attachment) dipping a platinum electrode in solution which connected to a reference saturated calomel electrode by a KNO_3 Agar salt bridge. Solutions were maintained at 25 ± 0.5 °C.

Determination of (BrO_3^- + *HOBr*) *Concentration.*[15] Aliquots of the reaction solution at fixed times were pipetted into a mixture containing 0.1 M perchloric acid (10 mL), 10% w/v potassium iodide (10 mL), and 1.0×10^{-5} M ammonium molybdate (2 mL). After incubation for about 40 min the liberated iodine was titrated with 0.002 M sodium thiosulfate solution with starch as indicator. A correction for blank was made (6 M thiosulfate ion = 1 M bromate ion).

Determination of (*HOBr*) *Concentration.*[15] Aliquot of reaction mixture was added to a fixed volume of NaOH solution raising the pH to neutral. This was followed by the addition of a mixture of 0.1 M acetate buffer (10 mL) and 10% w/v KI solution (10 mL). (Reaction between bromate and iodide ions does not occur at the mixture pH 4.5.) After incubation for about 40 min the liberated iodine was titrated iodometrically as above. After the blank correction, the HOBr concentration was calculated by using the equation 2 M thiosulfate = 1 M HOBr.

Actual concentrations of bromate ions were determined by subtracting [HOBr]/3 from the corresponding value of [BrO_3^- + HOBr].

Stoichiometry. For the determination of stoichiometric ratios of the uncatalyzed and catalyzed reactions, reactants were mixed in molar ratios of 2:1, 1:1, and 1:2 with acid in excess. The concentrations of residual reactants in the mixture were determined after reaction durations of 14, 24, and 48 h. MB was found to react with bromate ion in 3:2 ratio in all the reactions. The overall reaction can be represented by the equation

$$3\text{MB} + 2\text{BrO}_3^- = 3\text{P} + 6\text{HCHO} + 2\text{Br}^-$$

Product Analysis. The product analysis of the uncatalyzed and catalyzed reactions was done by mixing 10 M sulfuric acid (100 mL), 0.005 M MB (200 mL), and 10^{-5} M ammonium vanadate (10 mL) in the case of catalyzed reaction and 0.1 M potassium bromate (100 mL). The mixture was let stand for 24 h at room temperature. The organic components were partitioned with diethyl ether. A portion of concentrate when treated with sodium hydroxide gave a reddish brown precipitate which is soluble in diethyl ether, indicating the reaction product is Azure A.[16] The GC mass analysis (VG-12-250 quadrapole GC mass spectrometer) showed the major compound m/z 256 (M^+, 10%) with other significant peaks at 240 (17), 228 (45), 225 (22), and 93 (82) confirming the major product is phenothiazin-5-ium, 3-amino-7-dimethylamino-, chloride (Azure A).

TABLE I: Dependence of Initial Reaction Rate on MB Concentration: (a) Uncatalyzed Reaction;[a] (b) V(V)-Catalyzed Reaction[b,c]

		a		
$[MB]_0/10^{-3}$ M	5.00	7.50	10.00	15.00
$k_0'/10^{-5}$ s^{-1}	4.50	4.43	4.53	4.42
		b		
$[MB]_0/10^{-6}$ M	5.00	7.50	10.0	15.0
$k_1'/10^{-5}$ s^{-1}	6.37	6.52	6.40	6.61

[a] $[H^+]_0$ 0.375 M and $[\text{bromate}]_0$ 4.00×10^{-3} M. [b] $[H^+]_0$ 0.235 M, $[\text{bromate}]_0$ 0.01 M, and V(V) 1.33×10^{-6} M. [c] k_0' is the pseudo-first-order rate coefficient. k_1' is the pseudo-first-order rate coefficient for overall reaction in presence of V(V). All the rate coefficients are averages of duplicate experiments and the values had about 4% deviation.

Analysis of the reaction mixture after about 10 min reaction time by partitioning with diethyl ether and reacting with sodium hydroxide gave a reddish color, suggesting that the intermediate of the reaction is possibly phenothiazin-5-ium, 3-methylamino-7-dimethylamino-, chloride.

Results and Discussion

Preliminary studies employing excess concentrations of sulfuric acid and bromate ion, both for uncatalyzed and V(V) catalyzed reactions, showed that the depletion of MB occurred evidently in two stages: a slow reaction followed by a swift one after an induction time, I_t. This points toward the possible existence of a sequence of competitive and consecutive reactions with an autocatalytic step. Hence, to determine the order with respect to each reactant and the total reaction order, the effect of reactants concentrations on the reaction rate was studied, both in uncatalyzed and catalyzed reactions.

Order with Respect to MB. Kinetic data were collected with fixed initial concentrations of H^+, bromate, and V(V) in case of catalyzed reaction with a threefold variation in $[MB]_0$. Figure 1 a log A versus time plot represents typical curves obtained. The characteristics of all the kinetic curves both for uncatalyzed and catalyzed reactions were identical: an initial slow step followed by a rapid one after an induction time. Catalyzed curves had shorter induction time and, in both cases, I_t decreased with increased $[MB]_0$. Further analysis of the data showed that the tangents for the initial stage (slow reaction) of the log A–time curves for various $[MB]_0$ had the same gradient for all the uncatalyzed sets. Similarly all the catalyzed reaction curves had the same value of gradient.

Table I summarizes the rate constants obtained from the tangents of the log A–time curves for different $[MB]_0$. Fairly constant values were obtained for k_0, the pseudo-first-order rate coefficient for uncatalyzed reaction and for k_1', the pseudo-first-order rate coefficient for V(V)-catalyzed reaction. This suggests that the order with respect to MB is one in the slow step, and the initial stage of the reaction follows pseudo-first-order kinetics in both uncatalyzed and catalyzed reactions. Considering the complex nature of the reaction, analysis of the kinetic data was restricted only to the slow phase of the reaction, but extended to a qualitative treatment of the rapid phase.

Order with Respect to Bromate Ion. The kinetics of both uncatalyzed and catalyzed reactions were monitored with fixed initial concentrations of all the other reactants and varying the bromate ion concentration (Table II). The log–log plots of rate coefficient versus bromate concentration yielded straight lines. The log k_0'–log $[\text{bromate}]_0$ for uncatalyzed reaction gave a line with gradient of 1.062 ± 0.017 (r 0.99) and the log k_1'–log $[\text{bromate}]_0$ plot had a slope of 1.009 ± 0.006 (r 0.99), indicating that the reaction order is unity with respect to bromate ion in both the cases.

Order with Respect to Hydrogen Ion. Hydrogen ion concentration was found have significant influence on the reaction rate of the uncatalyzed and catalyzed reactions. The results obtained with different initial concentrations of H^+ and with fixed con-

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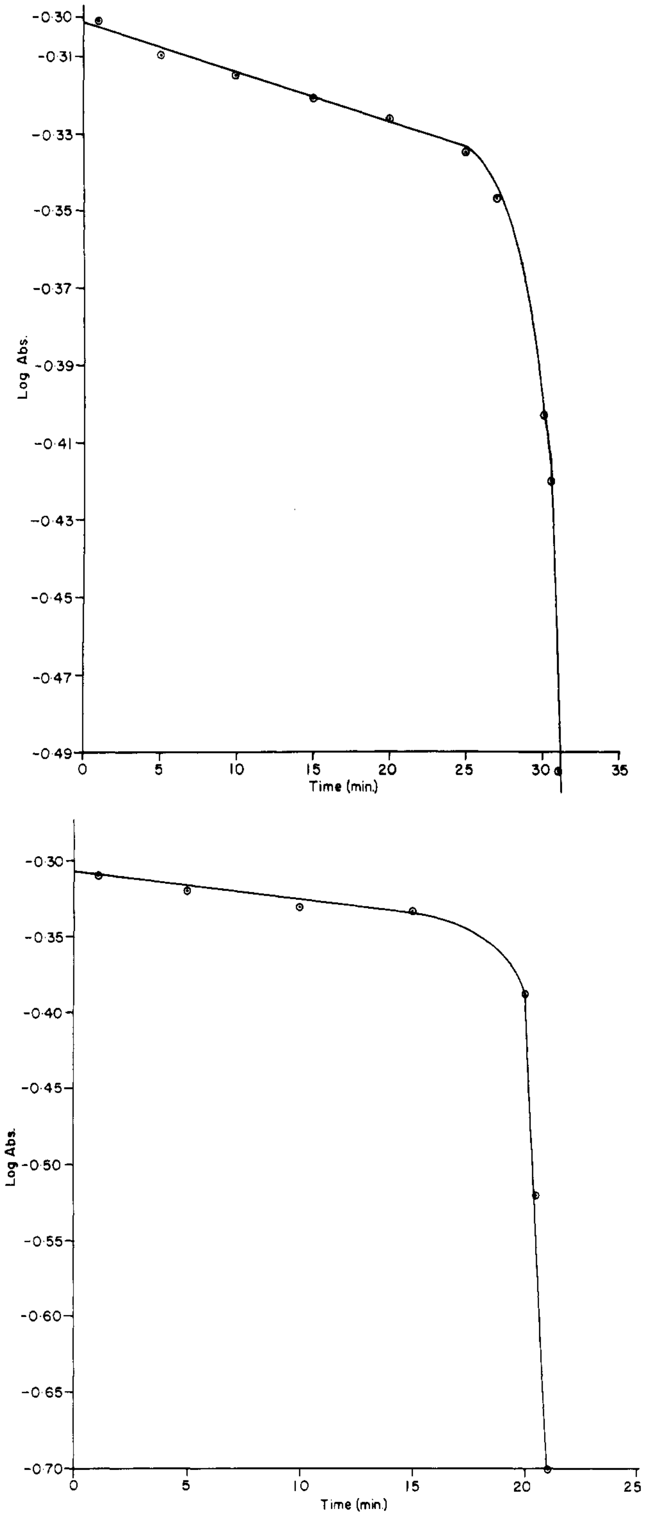

Figure 1. Typical kinetic curves: log A versus time plots. (a, top) Uncatalyzed reaction; $[H^+]_0$ 0.375 M, $[\text{bromate}]_0$ 4.0×10^{-3} M, and $[MB]_0$ 7.5×10^{-6} M. (b, bottom) V(V) catalyzed reaction; $[H^+]_0$ 0.235 M, $[\text{bromate}]_0$ 0.01 M, $[MB]_0$ 7.5×10^{-6} M, and $[V(V)]_0$ 1.33×10^{-6} M.

centrations of the other reactants are shown in Table III. The log–log plot of k_0' and H^+ concentration gave a linear curve with a gradient of 2.026 ± 0.031 (r 0.99) and the log k_1' vs log $[H^+]_0$ graph, a straight line, had a slope of 2.104 ± 0.039 (r 0.99). Hence the reaction order is two with respect to H^+ both for uncatalyzed and V(V)-catalyzed reactions. The k_0 and k_1 values calculated from Tables I and III support the inferences.

TABLE II: Dependence of Reaction Order on the Bromate Ion Concentration: (a) Uncatalyzed Reaction;[a] (b) V(V)-Catalyzed Reaction[b,c]

	a			
$[BrO_3^-]_0/10^{-3}$ M	4.00	6.00	9.00	11.00
$k_0'/10^{-5}$ s^{-1}	4.42	6.68	10.5	12.81
$k_0''/10^{-2}$ M^{-1} s^{-1}	1.11	1.11	1.17	1.16
	b			
$[BrO_3^-]_0/10^{-2}$ M	0.50	1.00	1.50	2.00
$k_1'/10^{-5}$ s^{-1}	5.01	10.10	15.31	20.26
$k_1''/10^{-2}$ M^{-1} s^{-1}	1.00	1.01	1.02	1.01

[a] $[H^+]$ 0.375 M and $[MB]_0$ 1.50×10^{-5} M. $k_0'' = k_0'/[\text{bromate}]_0$. [b] $[H^+]_0$ 1.5×10^{-5} M and V(V) 1.33×10^{-6} M. $k_1'' = k_1'/[\text{bromate}]$. [c] Rate constants were averages of duplicate experiments and the values had about 4% deviation.

TABLE III: Dependence of Reaction Order on Acid Concentration: (a) Uncatalyzed Reaction;[a] (b) V(V)-Catalyzed Reaction[b,c]

		a			
$[H^+]_0/10^{-1}$ M	2.81	3.75	4.69	5.63	7.50
$k_0'/10^{-5}$ s^{-1}	3.82	6.68	11.09	15.67	27.54
$k_0/10^{-2}$ M^{-3} s^{-1}	8.06	7.92	7.87	8.24	8.15
		b			
$[H^+]_0/10^{-1}$ M	1.88	2.35	2.81	3.28	3.75
$k_1'/10^{-5}$ s^{-1}	4.26	6.61	10.10	13.49	18.11
$k_1/10^{-1}$ M^{-3} s^{-1}	1.21	1.20	1.28	1.25	1.29

[a] $[\text{bromate}]_0$ 6.0×10^{-3} M and $[MB]_0$ 1.50×10^{-5} M. Mean $k_0 = 8.04 \times 10^{-2} \pm 2.03 \times 10^{-3}$ M^{-3} s^{-1}, where $k_0 = k_0'/[H^+]_0^2[\text{bromate}]$. [b] [bromate] 0.01 M, $[MB]_0$ 1.50×10^{-5} M, and $[V(V)]$ 1.33×10^{-6} M. Mean $k_1 = 0.125 \pm 0.004$ M^{-3} s^{-1}, where $k_1 = k_1'/[H^+]_0^2[\text{bromate}]_0$ (at fixed $[V(V)]_0 = 1.33 \times 10^{-6}$ M). [c] Rate coefficients were averages of duplicate experiments and the values had about 4% deviation.

TABLE IV: Dependence of k_1' on Vanadium(V) Concentration[a]

V(V)/10^{-6} M	1.00	1.33	1.99	2.32	2.65
$k_1'/10^{-5}$ s^{-1}	5.22	6.61	9.66	11.00	12.56

[a] $[H^+]$ 0.235 M, $[\text{bromate}]_0$ 0.01 M, and $[MB]_0$ 1.50×10^{-5} M. k_1' values were the means of duplicate experiments with a deviation of about 4%.

Effect of Ionic Strength. The ionic strength of the reactions were varied from 0.286 to 0.661 for both reactions by adding different amounts of potassium sulfate. Both k_0' and k_1' were unaffected except for a marginal increase of about 4–5% in the values. The insignificant effect could be possibly due to the high ionic strength of the reaction mixtures even in absence of added neutral salt.[6]

Effect of Bromide Ion Concentration. The role of bromide in the mechanism of the oscillatory chemical reactions involving acidic bromate, as a control intermediate triggering the temporal behavior, is well established.[1,2] Further, the reaction between bromide and bromate in acid medium had also been extensively studied.[17] In the present case to establish the role of bromide ion under both catalyzed and uncatalyzed conditions, experiments were done with fixed concentrations of H^+, bromate ion, and MB (plus V(V) in the case of catalyzed reaction) and by addition of varied amounts of potassium bromide (Figures 2 and 3). In both the figures curve a represents a condition with no initial added bromide. In both the figures curves b, c, and d are with $[Br^-]_0$ 1.0×10^{-6}, 2.0×10^{-5}, and 5.0×10^{-5} M, respectively. A perusal of the curves in Figures 2 and 3 shows that addition of low concentration of Br^- in the range 10^{-6} M increases marginally the rates of depletion in the slow step but lengthens the induction time I_t, whereas the $[Br^-]_0$ in the range 2.0×10^{-5} M and above increases the initial reaction rates and also reduces the induction times. This points toward a dual role played by bromide ion as an inhibitor at low concentrations and then as an autocatalyst after a higher threshold concentration[18,19] in the reaction mechanisms of the uncatalyzed reactions.

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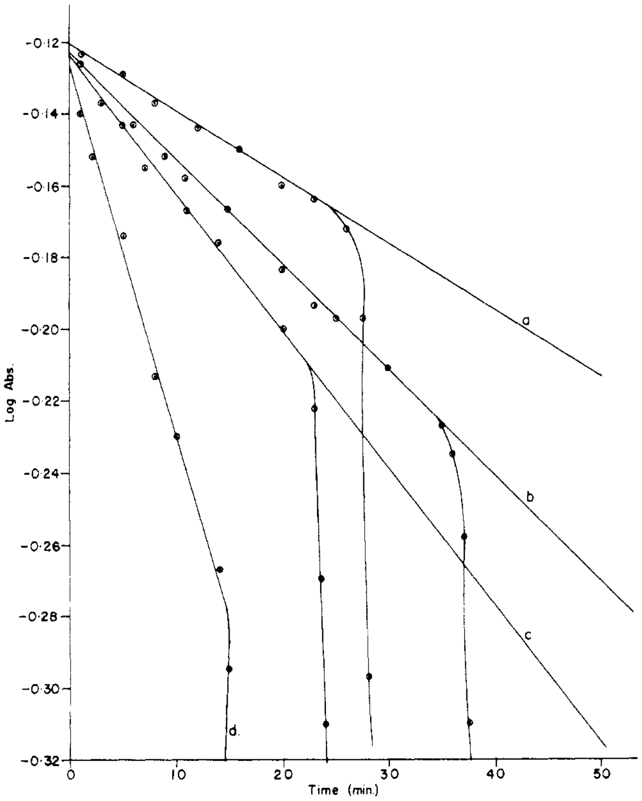

Figure 2. Effect of bromide ion on uncatalyzed reaction. Initial concentrations: H^+ 0.281 M, bromate 0.01 M, MB 1.50×10^{-5} M, and $[Br]_0$ (a) no bromide added; (b) 1.0×10^{-6} M, (c) 2.0×10^{-5}, and (d) 5.0×10^{-5} M.

Order with Respect to Vanadium(V) Ion. The increase in zero time concentration of vanadium ion increased the value of k_1' (Table IV). The plot of k_1', the pseudo-first-order overall rate constant versus the V(V) concentration gave a linear curve. The y intercept value fairly agreed with the k_0' calculated for the uncatalyzed reaction under comparable conditions. The linear relation ship between k_1' and $[V(V)]_0$ indicate the order is one with respect to V(V).

Mechanism

Uncatalyzed Reaction. The chemistry of the bromate ion in acid solution can be represented by the following equations.[6,15]

$$2H^+ + Br^- + BrO_3^- \rightleftharpoons HOBr + HBrO_2 \quad (1)$$

$$H^+ + Br^- + HBrO_2 \rightleftharpoons 2HOBr \quad (2)$$

$$2HBrO_2 \rightleftharpoons H^+ + HOBr + BrO_3^- \quad (3)$$

$$H^+ + Br^- + HOBr \rightleftharpoons Br_2 + H_2O \quad (4)$$

With sufficient bromide ion present, a rapid equilibrium establishes between the concentrations of bromate and HOBr through eq 1 and 2 which can be represented by

$$BrO_3^- + 3H^+ + 2Br^- \rightleftharpoons 3HOBr \quad (5)$$

where the equilibrium constant

$$K_5 = \frac{[HOBr]^3}{[BrO_3^-][H^+]^3[Br^-]^2} \quad (6)$$

Under the present experimental conditions with no initial bromide ion added, equilibrium would not be attained between the species. In the initial slow phase of the reaction, the observed order of dependence of reaction on bromate (first order), MB (first order), and H^+ (second order), similar to reactant orders in eq 1, points toward a direct reaction betweem MB and bromate ion in presence of H^+, analogous to eq 1. The role of bromide in the initial stages is replaced by MB, which in turn undergoes oxidation yielding an intermediate, I.

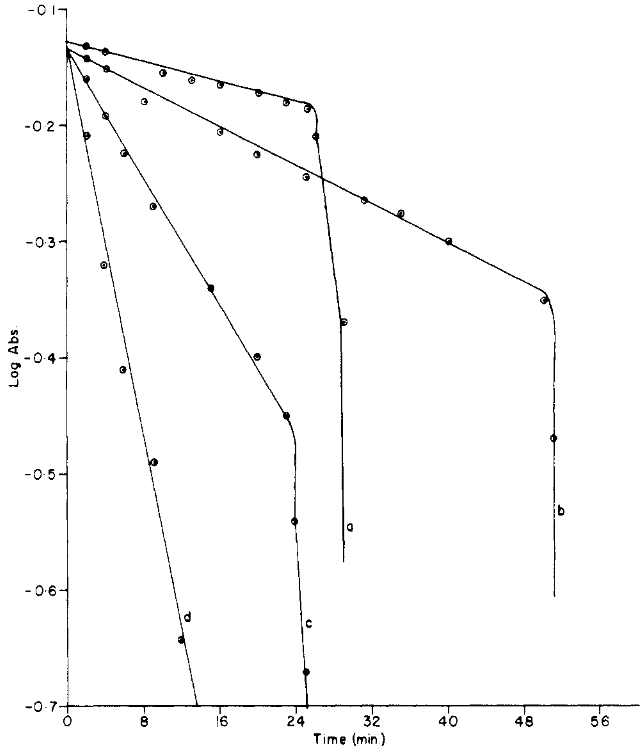

Figure 3. Effect of bromide ion catalyzed reaction. Initial concentrations: H^+ 0.281 M, bromate 0.01 M, MB 1.50×10^{-5} M, V(V) 1.33×10^{-6} M, and $[Br^-]_0$ (a) no bromide added, (b) 1.0×10^{-6} M, (c) 2.0×10^{-5} M, (d) 5.0×10^{-5} M.

$$2H^+ + MB + BrO_3^- \xrightarrow{k_0} I + HBrO_2 + HCHO + H^+ \quad (7)$$

In the absence of bromide ion in the initial stages of the reaction, $HBrO_2$ disproportionates rapidly (eq 3, 4×10^7 M^{-1} s^{-1}) into HOBr which in turn competes with bromate ion for MB.

$$MB + HOBr \xrightarrow{k_8} I + HCHO + H^+ + Br^- \quad (8)$$

It is possible that HOBr further oxidizes the intermediate, I, in a fast reaction step giving the final products phenothiazine, 3-amino-7-dimethylamino-, chloride (P), Br^-, and H^+ ions.

$$I + HOBr \xrightarrow[\text{fast}]{} P + HCHO + H^+ + Br^- \quad (9)$$

The final product of the reaction is identified to be phenothaizin-5-ium, 3-amino-7-dimethylamino-, chloride. From the qualitative test it is found that the intermediate I is phenothiazin-5-ium, 3-methylamino-7-dimethylamino-, chloride.[15]

Equations 7 and 8 are consecutive reactions and both the bromate ion and HOBr react with MB competitively. With increase in HOBr concentration eq 8 predominates. The role of HOBr as a competitive reacting species was verified by studying the reaction with low $[bromate]_0$ conditions. MB–acidic bromate reaction was run under pseudo-second-order conditions taking H^+ in excess (8.26 M), $[MB]_0$ 5.0×10^{-4} M and $[bromate]_0$ 3.0×10^{-4} M. The residual concentrations of MB, bromate ion, and HOBr were simultaneously monitored with time along with the profile of overall electrochemical potential (Figure 4). A perusal of the profiles of the concentration–time curves shows that as anticipated MB and bromate ion deplete with slow rate in the initial stages. The consumption rate of MB increases fast with increase in [HOBr]. Further, the concentration of HOBr, the reaction intermediate, increases reaching a maximum and then decreases. The same trend is observable in the emf curve to some extent the peak synchronizing with the maximum of [HOBr] (redox potential $BrO_3^-/HOBr$ -1.58 V), supporting the assumption that HOBr is the species competing with bromate for MB. The observed increase in depletion of MB with concomitant increase

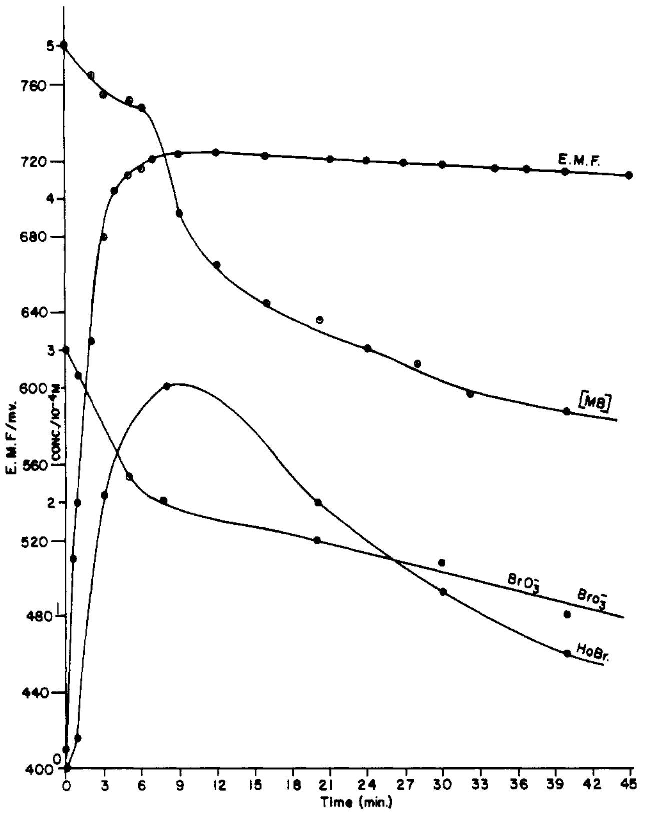

Figure 4. Pseudo-second-order kinetic curve of MB–acidic bromate reaction. Initial conditions H^+ 8.26 M, bromate 3.0×10^{-4} M, and MB 5.0×10^{-4} M.

in HOBr concentration further confirms the role of HOBr as the competitive intermediate.

V(V)-Catalyzed Reaction. The kinetic data obtained show that both the uncatalyzed and catalyzed reactions have similar reaction orders with respect to MB, bromate, and H^+. In addition, the reaction has first-order dependence on V(V) concentration. Hence for the catalyzed reaction a scheme is proposed consistent with the observed experimental results, which involves a fast equilibrium between VO^{2+} (V(IV)) and VO_2^+ (V(V))[14,20] followed by a slow reaction between VO_2^+, BrO_2, and MB in presence of H^+, in the rate-limiting step.

$$VO^{2+} + BrO_3^- \overset{\text{fast}}{\rightleftharpoons} VO_2^+ + BrO_2 \qquad (10)$$

$$VO_2^+ + BrO_2 + MB + 2H^+ \xrightarrow{k_c''} I + HCHO + VO^{2+} + HBrO_2 + H^+ \qquad (11)$$

Possibly VO_2^+ and BrO_2 may form an adduct $[VO_2\text{–}BrO_2]^+$ in a fast reaction. Similar, higher orer reactions are common for oxidations by acidic haltates.[21] Further, as in the uncatalyzed reaction in the initial stages, in the absence of bromide $HBrO_2$ disproportionates (eq 3) giving HOBr, which in turn competes with eq 11 for MB (eq 8). The reaction intermediate I is further oxidized by HOBr in a fast reaction yielding the final product

$$I + HOBr \rightarrow P + HCHO + Br^- + H^+ \qquad (9)$$

The suggested mechanism for catalyzed reaction explains the limited role of the catalyst in oxidizing MB, i.e., no direct step involving the catalyst to increase HOBr concentration which is the reactive intermediate, except through eq 11. This explains the low efficiency of the catalyst noticed during the studies.

Role of Bromide Ion. The dual role played by the bromide ion in both the uncatalyzed and catalyzed reactions can be explained taking into consideration the forward reaction rate constants for eq 1, 2, and 4, respectively, 2.1 $M^{-3}\ s^{-1}$, $2.0 \times 10^9\ M^{-2}\ s^{-1}$, and $8.0 \times 10^9\ M^{-2}\ s^{-1}$.[15] At low bromide ion concentrations below a critical level, a situation such as that of eq 4 prevails causing the depletion of HOBr concentration. Thus, the Br^- acts as inhibitor for transition from the slow reaction step to the fast one thereby increasing I_t, a situation observed with 1.0×10^{-6} M Br^- in the present studies. In contrast, an increase in the concentration of Br^- beyond a critical limit through eq 8 and 9 allows the bromide ion to play the role of an autocatalyst fast increasing HOBr concentration through eq 1 and 2, thus leading to an equilibrium between different oxybromo species. This results in rapid depletion of MB witnessed in the fast step of the reaction which can also be visualized with addition of higher concentrations of bromide ion. A dual role of bromide ion as an inhibitor as well as an autocatalyst was reported by Hasty et al. from their studies on the oxidation of methyl orange by acidic bromate.[18,19] A similar behavior of bromide was also observed during the studies on oxidation of indigo carmine with acidic bromate.[22] A computer simulation using the proposed mechanism for indigo carmine–acidic bromate reaction was done. The NAG version of the Gear algorithm was implemented. Using the literature values for eq 1–4, estimated values for reactions 5, 8, and 9 and evaluated value of reaction 7 simulation results were very similar to the experimental observations.[22] The results of MB–acidic bromate reaction compare to that of indigo carmine–acidic bromate reaction; hence the same model for mechanism fits well for the present reaction.

Rate Laws. Uncatalyzed Reactions. The rate of depletion of MB can be represented by the following equations

$$r_0 = \frac{-d[MB]}{dt} = k_0[H^+]^2[BrO_3^-][MB] + k_8[HOBr][MB] \qquad (12)$$

Under initial reaction conditions [HOBr] = 0; then

$$r_0 = k_0[H^+]^2[BrO_3^-][MB] \qquad (13)$$

when concentrations of acid and bromate ion are in excess eq 13 reduces to

$$r_0 = k_0'[MB] \qquad (14)$$

where $k_0' = k_0[H^+]^2[BrO_3]$, a pseudo-first-order rate constant. For later stages of the reaction, when HOBr is appreciable in concentration, substituting [HOBr] from eq 6 into eq 12, we get

$$r_0 = \{k_0[H^+]^2[BrO_3^-] + k_8''[H^+][BrO_3^-]^{1/3}[Br^-]^{2/3}\}[MB] \qquad (15)$$

where $k_8'' = k_8k^{1/3}$, the rate constant for reaction 8 in terms of bromate and bromide ion concentrations. Under excess H^+ and bromate concentration conditions, eq 15 reduces to

$$r_0 = \{k_0' + k_8'[Br^-]^{2/3}\}[MB] \qquad (16)$$

where $k_8' = k_8''[H^+][BrO_3^-]^{1/3}$. Rate eq 16 explains the observed slow and rapid depletion rates of MB in the initial and later stages of the reaction, respectively. The presence of Br^- ion in the rate equation also explains the role played by bromide ion as autocatalyst.

V(V)-Catalyzed Reaction. In the presence of catalyst the reaction will have both the uncatalyzed and catalyzed path ways.[22] Hence the rate of depletion of MB can be represented by the equation

$$r_1 = \frac{-d[MB]}{dt} = \underbrace{k_0[H^+]^2[BrO_3^-] + k_8[HOBr][MB]}_{\text{uncatalyzed path}} + \underbrace{k_c''[H^+]^2[VO_2^+][BrO_2][MB]}_{\text{catalyzed path}} \qquad (17)$$

For initial concentration conditions when HOBr = 0, eq 17 reduces to

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$$r_1 = \{k_0[H^+]^2[BrO_3^-] + k_c''[H^+]^2[VO_2^+][BrO_2]\}[MB] \qquad (18)$$

But,

$$[VO_2^+][BrO_2] = K_{10}[VO^{2+}][BrO_3^-] \qquad (19)$$

where k_{10} is the equilibrium constant for eq 10. Substituting eq 19 into eq 18, we get

$$r_1 = \{k_0[H^+]^2[BrO_3^-] + k_c[H^+]^2[VO^{2+}][BrO_3^-]\}[MB] \qquad (20)$$

where $k_c = k_c'' = k_c''K_{10}$, the catalytic constant.

In the presence of excess concentrations of H^+ and bromate ions, eq 20 can be written as

$$r_1 = k_0' + k_c'[VO^{2+}][MB] \qquad (21)$$

and

$$r_1 = k_1'[MB] \qquad (22)$$

where $k_c' = k_c[H^+]^2[BrO_3^-]$, the pseudo-first-order rate constant for catalyzed reaction.

$$k_1' = k_0' + k_c'[VO^{2+}],$$
the overall pseudo-first-order rate coefficient (23)

The plot of k_1' versus $[VO^{2+}]$ should yield a straight line with an intercept k_0' and a gradient of value k_c',[22] which is observed to be the case (Table IV). For the later stages of the reaction with significant amount HOBr, the overall rate equation can be represented by eq 24, which explains the slow and fast phases of the reaction and also the role of bromide ion.

$$r_1 = k_0[H^+]^2[BrO_3^-] + k_8[H^+][BrO_3^-]^{1/3}[Br^-]^{2/3} + k_c[H^+]^2[VO^{2+}][BrO_3^-][MB] \qquad (24)$$

Acknowledgment. We thank the Dr. P. G. McDowell International Centre for Insect Physiology and Ecology, Nairobi, for running the mass spectra of the product samples and Deutscher Akademischer Austauschdienst, Federal Republic of Germany, for financial support.

Registry No. MB, 61-73-4; Azure A, 531-53-3; V(V), 22537-31-1.

Kinetics and Product Studies of the Reaction ClO + BrO Using Discharge-Flow Mass Spectrometry

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(Received: August 10, 1988; In Final Form: December 20, 1988)

The kinetics and product branching ratios of the BrO + ClO reaction have been characterized at 1 Torr of total pressure over the temperature range 220–400 K with the technique of discharge-flow mass spectrometry. The measured overall reaction rate coefficient is $k_1 = (4.70 \pm 0.50) \times 10^{-12} \exp[(320 \pm 40)/T]$ cm^3 molecule^{-1} s^{-1}. Three product channels, identified as Br + ClOO (1a), Br + OClO (1b), and BrCl + O_2 (1c) have been quantified: $k_{1a} = (2.9 \pm 1.0) \times 10^{-12} \exp[(217 \pm 50)/T]$ cm^3 molecule^{-1} s^{-1}; $k_{1b} = (1.6 \pm 0.4) \times 10^{-12} \exp[(426 \pm 50)/T]$ cm^3 molecule^{-1} s^{-1}; $k_{1c} = (5.8 \pm 2.0) \times 10^{-13} \exp[(168 \pm 50)/T]$ cm^3 molecule^{-1} s^{-1}. On the basis of these results, it is argued that the reaction mechanism for ClO + BrO, like those of halogen monoxide self-reactions, involves metastable intermediate formation. In addition, emphasis is placed on the significant impact of these results on current models of stratospheric ozone depletion, which neglect channel 1c and the temperature dependence of k_1.

Introduction

The gas-phase self-reactions of halogen monoxide radicals (XO, X = F, Cl, Br, I) exhibit a range of product channels and pressure and temperature dependences.[1-6] The ClO self-reaction, for example, is strongly dependent on pressure and yields a host of chlorine-containing products, i.e., Cl, Cl_2, OClO, and Cl_2O_2. The BrO self-reaction, on the other hand, displays no pressure dependence and apparently produces only Br and Br_2 as the bromine-containing species. The mechanisms for all of these reactions, however, are thought to be the same: formation of a metastable intermediate (X_2O_2*) followed by collisional stabilization or unimolecular decomposition along one of several possible potential energy surfaces.

$$\begin{aligned} XO + XO \rightarrow X_2O_2^* &\rightarrow X + XOO && (a)\\ &\rightarrow X + OXO && (b)\\ &\rightarrow X_2 + O_2 && (c)\\ &\rightarrow X_2O_2 && (d)\end{aligned}$$

According to this mechanism, the relative importance of the possible product channels depends on the rates at which the isomeric forms of X_2O_2 (XOOX, XOXO, etc.) are produced, the stabilization rates and thermodynamic stabilities of the dimers, and the rates for X_2O_2* decomposition. Experimental studies of the halogen oxide self-reactions have begun to provide, only recently, the information required to critically assess the validity of this mechanism as well as to provide it with a rigorous, quantitative foundation.

Cross-reactions of halogen monoxide radicals can provide additional insight into the details of halogen oxide reaction mechanisms and thermochemistry. The data base for these types of reactions, however, is limited to a few, contradictory reports on the reaction between ClO and BrO. Basco and Dogra,[7] in the earliest of these studies, concluded that the reaction proceeds at 298 K with a rate coefficient of $(2.4 \pm 0.5) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} and yields mainly BrCl and O_2. Subsequently, Clyne and Watson[8] measured a room-temperature rate coefficient of $(1.34 \pm 0.3) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} and provided strong evidence for the equal importance of reaction channels yielding Br + ClOO and Br + OClO. Both of these studies were limited, however, by the fact that the ClO + BrO reaction was studied as part of a complex reaction system in which a multitude of reactions were occurring.

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