around the copper(II) ion affects the magnitude of the exchange energy and also the position of the electronic absorption bands. The band in the 700–1000-nm region of the spectrum apparently is characteristic of the dimeric structure of the molecule. The electron distribution may be affected by changing the crystal field strength of the ligand through substitution or changing the symmetry of the crystal field by steric interactions or by intermolecular interactions. While the direct relationship between the singlet–singlet transition in the 700–1000-nm range and the singlet–triplet separation corresponding to infrared frequencies has not been elucidated, it appears to be reasonable qualitatively.

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The Oxidation of Hydrazoic Acid by Bromate Ion in Perchlorate Solution

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Nitrogen and nitrous oxide are the only oxidation products produced when *excess* hydrazoic acid is oxidized by bromate ion in perchloric acid–lithium perchlorate solution. The reduction products of the bromate ion are hypobromous acid and bromine. The rate expression is $-d[BrO_3^-]/dt = k_0[BrO_3^-][HN_3][H^+]$. At 25.0° and 2.0 *M* ionic strength, the value of k_0 is $(6.22 \pm 0.06) \times 10^{-2}\ M^{-2}\ sec^{-1}$, and the associated activation parameters are $\Delta H^{\ddagger} = 13.5 \pm 0.2$ kcal/mol and $\Delta S^{\ddagger} = -18.7 \pm 0.6$ eu. Oxygen-18 tracer studies reveal that most, but not all, of the oxygen in the nitrous oxide product is derived from the solvent.

Introduction

Ce(IV),[1] Co(III),[2] and Mn(III)[3] react with HN_3 to produce the stoichiometric quantity of N_2. While HNO_2 oxidizes HN_3 to produce the stoichiometric amounts of N_2 and N_2O,[4] most multiequivalent oxidizing agents, if they react at all, have been reported to produce in addition higher oxidation states of nitrogen.[5] A previous report[2] has demonstrated that the reaction of HN^{15}–N^{14}–N^{15} with bromate produces N^{15}–N^{14} and N^{15}–N^{15}–O. This communication reports a stoichiometric and kinetic study of this latter reaction. In addition, we have investigated the source of the oxygen in the N_2O product through oxygen-18 tracer studies.

Experimental Section

Reagents.—Reagent grade sodium bromate and allyl alcohol were used without further purification. The preparation and standardization of the perchloric acid and lithium perchlorate solutions have been described in a previous communication.[6] Purified sodium azide was recrystallized twice using previously reported procedures,[7] and solutions of this salt were standardized by the cerate procedure.[1] A mixture of bromine and hypobromous acid was prepared in the dark by vacuum distillation from a mixture of bromine water and mercuric oxide at 0°. These solutions were used the same day. Bromine water was prepared by the dissolution of reagent grade bromine. The water used was doubly distilled in an all-glass apparatus after distillation of deionized water from an alkaline permanganate still.

Oxygen-18-enriched sodium bromate was prepared by allowing a nearly saturated solution of the salt to equilibrate with enriched solvent in 2 *M* perchloric acid for 1 hr at 25°. The solution was then neutralized with solid sodium hydroxide, and the enriched sodium bromate was precipitated with a minimum amount of anhydrous, reagent grade methanol. Blank experiments demonstrated that no sodium perchlorate is precipitated in this procedure. The precipitate was washed with additional methanol, dissolved in the minimum amount of water, and reprecipitated as before. The salt was then carefully dried under vacuum and stored in a desiccator. The oxygen-18 enrichment of the sodium bromate was determined by conversion to carbon dioxide by the Anbar technique,[8] separation by gas chromatography, and mass spectrometric analysis of the $46/(44 + 45)$ mass ratio on a nuclide RMS-16 mass spectrometer. The oxygen-18-enriched water was purchased from Volk Radiochemical Co.

Procedures. Kinetic Studies.—Attempts to monitor the reaction by spectrophotometry proved to be impractical for reasons to be discussed later. Consequently, a titrimetric method for determining the bromate concentration during the reaction was used. Allyl alcohol in *ca.* 50% excess over the initial bromate concentration was present to scavenge the hypobromous acid product (*vide infra*). In a typical run, 400 ml of a solution containing the desired amounts of sodium bromate, lithium perchlorate, and perchloric acid was brought to temperature equilibrium in a constant-temperature bath. The desired amount of allyl alcohol was then added, and the reaction was initiated by addition of a sodium azide solution with vigorous stirring. All reactions were run in the absence of light. Suitable aliquots were withdrawn at appropriate times and added to an excess of acidified sodium iodide solution. The recorded time corresponded to half-delivery of the reaction solution; time

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errors were negligible in all cases owing to the slow rates of reaction under the conditions employed. The iodine liberated was determined by titration with standard sodium thiosulfate solution. Air oxidation of iodide in these acid solutions was eliminated by addition of solid reagent grade sodium carbonate. Blank experiments were made with solutions identical with those used in the kinetic runs except that sodium azide was absent. The results of these experiments showed that: (1) the reaction between allyl alcohol and bromate under the conditions of these experiments is $<0.5\%$ for the times required for the reaction with hydrazoic acid and is even less since bromate and allyl alcohol are continuously being consumed in the kinetic runs; (2) the stoichiometry $6H^+ + BrO_3^- + 6I^- = 3I_2 + Br^- + 3H_2O$ is followed in the titrimetric procedure used even in the presence of allyl alcohol. Allyl alcohol is an effective scavenger for hypobromous acid through rapid addition at the double bond of the alcohol.[9] No bromide ion is released in this reaction, and consequently there is no interference from the bromate–bromide reaction in the rate studies.

Tracer Studies.—The reaction was carried out in a two-tube mixing chamber which could be evacuated to better than 10^{-5} mm. One tube contained the sodium bromate in water, and the other, the sodium azide, perchloric acid, and allyl alcohol. The reactant solutions were frozen at liquid air temperature, and the mixing tube was evacuated. The solutions were thawed, warmed to 25°, and quickly mixed in the dark. Bromate oxygen exchange is extremely slow in water,[10,11] and even if small amounts of hydrazoic acid distilled into the bromate solution during the thawing procedure, the oxygen-exchange rate would be negligible during the time period involved. After the reaction was complete, the N_2 was pumped away from the frozen reaction solution, and the N_2O was collected at liquid air temperature after warming with a Dry Ice–acetone slush. The remaining N_2O was collected in the same manner after warming the reaction mixture to room temperature and again freezing with a Dry Ice–acetone slush. The N_2O was purified by gas chromatography. In particular, CO_2 is quantitatively separated from N_2O by means of the Porapak column employed. The 46/(44 + 45) mass ratio of the purified N_2O was then measured as before. Standard N_2O samples were prepared by the nitrous acid–hydrazoic acid reaction, and solvent enrichments were determined in the same manner after allowing sufficient time for the nitrous acid to equilibrate.[12]

Results

Stoichiometry of the HN_3–BrO_3^- Reaction.—The stoichiometry of the reaction is tenable provided that the ratio (hereafter defined as R_1) is $[HN_3]_0/[BrO_3^-]_0 \geq 2.00$. The reduction products of BrO_3^- under this condition are HOBr and smaller quantities of Br_2. Spectral scans of the reaction solutions revealed the growth of an absorption peak at 3950 Å. A maximum value was attained in time periods quite short compared to the rates of side reactions such as the decomposition of HOBr.[9] This wavelength is identical with an absorption peak of Br_2 solutions (ϵ 175.6 M^{-1} cm[13]). However, the amount of Br_2 produced was considerably less than stoichiometric based on initial BrO_3^- concentrations. Solutions identical with those used in the spectrophotometric experiments were titrated iodometrically at the same time that the maximum absorbance at 3950 Å had been attained. Assuming HOBr to be the other reduction product, its concentration could be determined by the difference in the residual oxidizing power of the solution and the determined Br_2 concentration. The spectral determination of the final Br_2 concentration was complicated by small contributions to the absorbance from the HOBr product and further by an alteration in the Br_2 spectrum in the presence of HN_3. This latter effect was not studied in detail, but although the iodometric titer of Br_2 solutions is unaffected by HN_3, the extinction coefficient for Br_2 is lowered at the 3950-Å maximum. The results of the stoichiometric experiments for $R_1 \geq 2.00$ are summarized in Table I. $R_2 \equiv \Delta$(milliequivalents of oxidizing power)/(milliequivalents of BrO_3^- initially) values are listed in column 2. It is seen that the values of R_2 are constant (0.702 ± 0.004) for the first five entries. The value of R_2 would be 0.667 if all the BrO_3^- were reduced to HOBr and 0.833 if Br_2 were the sole reduction product. The observed R_2 value can be used to calculate the relative amounts of Br_2 and HOBr produced; these values are in close agreement with those observed ($\pm 3\%$). The reason for both Br_2 and HOBr as reduction products will be discussed later, but blank experiments indicated that oxidation of HN_3 by Br_2 or HOBr is insignificant during the times required for the BrO_3^- oxidation. R_2 values drop below 0.667 when $R_1 = 2.00$ because some BrO_3^- is left at the end of the reaction. The results in Table I strongly suggest that the oxidation products of HN_3 conform to the half-reaction: $H_2O + 2HN_3 = 2N_2 + N_2O + 4H^+ + 4e$. This is most easily seen by the value of 1.98 ± 0.01 for the ratio Δ(milliequivalents of oxidizing power)/Δ(millimoles of HN_3) for the last four entries where Δ(millimoles of HN_3) corresponds to complete consumption of the HN_3 present. The gaseous products were not quantitatively determined, but during the course of the tracer studies (*vide infra*) it was found that the only gaseous products of the reaction were N_2 and N_2O.

TABLE I

STOICHIOMETRY OF THE HN_3–BrO_3^- REACTION[a]

R_1[b]	R_2[c]	Δ(mequiv of oxidizing power)/Δ(mmol of HN_3)
18.0	0.705	
10.8	0.696	
7.20	0.699	
4.99	0.706	
3.08	0.705	
2.00	0.647	1.95
2.00	0.662	1.99
2.00	0.663	1.99[d]
2.00	0.656	1.97[e]

[a] $[BrO_3^-]_0 = 4.18 \times 10^{-3}$ to 9.59×10^{-3} M; $[HN_3]_0 = 9.78 \times 10^{-3}$ to 7.50×10^{-2} M; $[HClO_4]_0 = 2.0$ M unless otherwise noted. [b] $R_1 = [HN_3]_0/[BrO_3^-]_0$. [c] $R_2 \equiv [\Delta$(milliequivalents of oxidizing power)/(milliequivalents of initial BrO_3^-)]. [d] $[HClO_4]_0 = 0.10$ M. [e] $[HClO_4]_0 = 0.05$ M.

A large number of experiments were performed to determine the stoichiometry under the conditions of $(HN_3)_0/(BrO_3^-)_0 < 2.00$. Very complicated results were obtained which can best be summarized by stating

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(11) M. Anbar and S. Guttmann, *ibid.*, **83**, 4741 (1966).

(12) C. A. Bunton and G. Stedman, *J. Chem. Soc.*, 3466 (1959).

(13) Our value of ϵ_{Br_2} is in good agreement with the value *ca.* 178 M^{-1} cm^{-1} given in ref 9. HN_3 is essentially transparent at 3950 Å, while ϵ_{HOBr} is *ca.* 4.4 M^{-1} cm^{-1}.

that, in addition to N_2 and N_2O, higher oxidation states of nitrogen are produced. Only a detailed study of the stoichiometry and kinetics of at least the NO, HNO_2, and NO_2 reductions of Br_2, HOBr, and BrO_3^- will allow a detailed interpretation of the experimental results. A few examples, however, will verify the notion that nitrogen species of oxidation state greater than +1 are produced and illustrate the complexity of the reactions. For R_1 values less than 2, the ratio Δ(milliequivalents of oxidizing power)/(millimoles of initial HN_3) continues to increase for very long time periods. For example, with $[BrO_3^-]_0 = 5.00 \times 10^{-3}\ M$ and $[HN_3]_0 = 9.00 \times 10^{-4}\ M$ in 2 *M* $HClO_4$ at 25°, ratio values of 3.37, 3.72, 4.05, and 4.46 were determined at 1300, 2800, 5600, and 8900 min, respectively. Under the same conditions but with $[HN_3]_0 = 4.05 \times 10^{-3}\ M$, values of 2.44, 2.62, 2.88, and 3.16 were obtained at the same times. It was also found that somewhat lower values resulted in the absence of the usual amount of dissolved oxygen; this effect was not observed in experiments with $R_1 \geq 2.00$.

Kinetic Results.—All of the kinetic runs were made with $[HN_3]_0/[BrO_3^-]_0 > 2.00$ to ensure that only N_2 and N_2O would be produced in the oxidation of HN_3. The reaction was monitored titrimetrically to avoid the problems incurred in the spectrophotometric measurements. The runs were performed in the presence of allyl alcohol in order to scavenge the HOBr product. Any Br_2 formed under these conditions would interfere since Br^- is formed in the allyl alcohol–bromine reaction and reacts rapidly with BrO_3^-. However, Br_2 is not formed in these reactions *if* the HOBr product is scavenged (*vide infra*). The kinetic results substantiate this conclusion. The titrimetric data yield the bromate concentration at any time *t* ($[BrO_3^-]_t$), and the hydrazoic acid concentration at the same time ($[HN_3]_t$) can be calculated from the stoichiometric relationship $[HN_3]_t = [HN_3]_0 - 2([BrO_3^-]_0 - [BrO_3^-]_t)$. At constant $[HClO_4]$, the rate law $-d[BrO_3^-]/dt = k'[HN_3]\cdot[BrO_3^-]$ was obeyed in all of the kinetic runs for at least 95% of the reaction. Values of k' were determined from a least-squares analysis of the integrated form of this expression. From 10 to 14 kinetic points were determined for each run, and the standard deviation in k' was $\leq 0.6\%$. Values of k' are listed in Table II. Entries 7 and 8 suggest that k' is not affected by the presence of allyl alcohol. This point was further checked by substituting phenol for allyl alcohol as a scavenger.[14] The phenol addition product that resulted was not miscible with the reaction solution, and less precise data were collected. However, the values of k' obtained in these experiments agreed to within 4% of those obtained in the presence of allyl alcohol. Entries 1, 7, and 9 indicate a small decrease in k' as the ionic strength is increased.

The empirical dependence of k' with variation in hydrogen ion concentration at $I = 2.0$ is

$$\log k' = \log k_0 - n \log (H^+)$$

TABLE II

KINETIC RESULTS[a]

Expt	$[H^+]$, *M*	*I*, M^b	Temp, °C	k', $M^{-1}\ sec^{-1}$
1	0.172	2.05	24.7	0.0105
2	0.381	2.05	24.7	0.0236
3	0.697	2.05	24.7	0.0448
4	0.942	2.05	24.7	0.0582
5	1.39	2.05	24.7	0.0856
6	2.04	2.05	24.7	0.127
7	0.160	0.165	24.7	0.0133
8	0.158	0.163	24.7	0.0136^c
9	0.159	0.978	24.7	0.0110
10	0.694	2.05	32.0	0.0777
11	0.694	2.05	17.0	0.0231
12	2.07	2.07	10.0	0.0379

[a] $[BrO_3^-]_0 = 2.45 \times 10^{-3}$ to $4.90 \times 10^{-3}\ M$; $[HN_3]_0 = 7.45 \times 10^{-3}$ to $1.47 \times 10^{-2}\ M$; $[CH_2{=}CHCH_2OH]_0 = 1.47[BrO_3^-]_0$. In all runs, $[HN_3]_0/[BrO_3^-]_0 > 3.0$. [b] Maintained with $LiClO_4$. [c] $[CH_2{=}CHCH_2OH]_0 = 7.35[BrO_3^-]_0$.

At 25°, the least-squares-computed values were $n = 1.00 \pm 0.01$ and $k_0 = 0.0622 \pm 0.0006\ M^{-2}\ sec^{-1}$.

The activation energy calculated from k_0 values over the temperature range employed is 14.1 ± 0.2 kcal/mol. Values of $\Delta H^{\ddagger} = 13.5 \pm 0.2$ kcal/mol and $\Delta S^{\ddagger} = -18.7 \pm 0.6$ eu were calculated in the usual manner by means of absolute reaction rate theory.

Oxygen-18 Tracer Results.—The results of experiments designed to determine whether the oxygen in the N_2O product is derived from the solvent water or an oxybromine species are listed in Table III. The data are listed in terms of enrichments, where enrichment ≡ 46/(44 + 45) mass ratio of the species in question relative to the same ratio for the species at normal isotopic composition.

TABLE III

OXYGEN-18 TRACER RESULTS[a] AT 25°

Expt	$N_{BrO_3^-}$	$N_{solvent}$	N_{N_2O}	$(N_{N_2O} - N_{solvent})/N_{BrO_3^-} - N_{solvent})$
1	1.000	2.700 ± 0.008^b	2.507	0.114
2	1.000	2.700 ± 0.008	2.564	0.0800
3	1.000	2.700 ± 0.008	2.564	0.0800
4	1.000	2.700 ± 0.008	2.568	0.0776
5	4.147 ± 0.011^b	1.000	1.389	0.124
6	4.147 ± 0.011	1.000	1.353	0.112
7	4.147 ± 0.011	1.000	1.343	0.109
8	4.147 ± 0.011	1.000	1.351	0.112
9[c]	4.147 ± 0.011	1.000	1.215	0.0683
10[c]	4.147 ± 0.011	1.000	1.234	0.0744

[a] $[HN_3]_0 = 0.050\ M$; $[BrO_3^-]_0 = 0.010\ M$; $[CH_2{=}CHCH_2OH]_0 = 0.014\ M$; $[HClO_4]_0 = 0.094\ M$ unless otherwise noted. [b] Uncertainties are average deviations. [c] $[HClO_4]_0 = 0.360\ M$.

Discussion

The stoichiometric, kinetic, and nitrogen-15 tracer data can be rationalized by the reaction scheme

$$BrO_3^- + HN^*NN^* + H^+ = HBrO_2 + N^*N + N^*OH \quad (1)$$

$$HBrO_2 + HN^*NN^* = HOBr + N^*N + N^*OH \quad (2)$$

$$2N^*OH = N^*N^*O + H_2O \quad (3)$$

where step 1 is rate determining. The nitrogen-15 tracer notation is used to illustrate the observed isotopic composition of the N_2 and N_2O products. This scheme requires that BrO_3^- and $HBrO_2$ react only with

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(14) P. B. D. De La Mare, A. D. Ketley, and C. A. Vernon, *J. Chem. Soc.*, 1290 (1954).

HN_3. The presence of excess HN_3 apparently prevents any oxidation of NOH prior to dimerization reaction 3. In addition, the HOBr product must be scavengered, since it is proposed that if the HOBr product is allowed to accumulate, the reaction

$$HBrO_2 + 2HOBr = BrO_3^- + Br_2 + H_3O^+ \qquad (4)$$

will occur. This point would appear to elude a direct demonstration since $HBrO_2$ solutions cannot be prepared. In fact, a system such as the present one in which neither Br_2 nor HOBr reacts with the reducing agent and $HBrO_2$ is continually produced as an intermediate may be the only type that will allow a demonstration of reaction 4. In the analogous chlorine system, a rapid reaction between $HClO_2$ and HOCl to produce ClO_3^- (and ClO_2) has been reported.[15] The Br_2 product in the present system cannot arise from a HOBr–HN_3 reaction, since under the conditions of all the experiments reported here, the HOBr (and Br_2) oxidation of HN_3 is quite slow relative to the BrO_3^- oxidation.

The formation of higher oxidation states of nitrogen in the presence of excess BrO_3^- presumably arises through the oxidation of NOH by BrO_3^- or $HBrO_2$ prior to reaction 3. Any oxidation of HN_3 by multiequivalent oxidants, in fact, will produce solely N_2 and N_2O only if reaction 3 competes favorably with the oxidation of NOH by either the oxidant or intermediates derived from it. For example, there is no report in which conditions have been found in the MnO_4^- oxidation of HN_3 that do not yield higher oxidation states of nitrogen. We have tentatively confirmed these results over a fairly large range of $[HN_3]_0/[MnO_4^-]_0$.

The conditions for the oxygen-18 tracer studies were selected in an effort to minimize BrO_3^- oxygen exchange with solvent[10,11] during the reaction. The half-time for the BrO_3^-–HN_3 reaction for the first eight experiments in Table III is 0.15 times that for the BrO_3^- oxygen exchange.[16] If the latter reaction is neglected, the fraction of oxygen not derived from solvent in the N_2O product can be calculated in the usual manner. These calculations are summarized in the last column of Table III. This fraction is 0.101 ± 0.017 for the experiments in 0.094 *M* $HClO_4$. The decrease in the BrO_3^- oxygen transfer to N_2O in 0.36 *M* $HClO_4$ is consistent with the greater increase in the BrO_3^- oxygen-exchange rate compared to the rate of reduction by HN_3.

Thus, BrO_3^- and/or the proposed $HBrO_2$ intermediate are in close proximity of the HN_3 in at least one path of the reaction. Numerous possibilities exist for rationalizing the large defect from complete BrO_3^- oxygen transfer to the N_2O product, such as both "inner-sphere" and "outer-sphere" paths, rapid $HBrO_2$ oxygen exchange, and rapid NOH oxygen exchange. One plausible possibility invokes the refinement of reaction 1 into

$$BrO_3^- + HN_3 + H^+ = NNNBrO_2 + H_2O \qquad (5)$$

$$H_2O + NNNBrO_2 = N_2 + NOH + HBrO_2 \qquad (6)$$

where reaction 5 is rate determining and only part of the BrO_3^- oxygen is transferred in reaction 6. Some support for this scheme is obtained from the HN_3–HNO_2 reaction in which strong evidence for the formation of an N–N–N–NO complex has been reported.[17]

The proposed reaction sequence is by no means the only one that is consistent with the results reported in this communication. However, some possibilities have been rendered unlikely. For example, N_3 radicals are probably not formed in this system, since earlier work suggests that they combine rapidly to form exclusively N_2.[2] Also, the production of N_3^+ is difficult to reconcile with the oxygen-18 tracer data.

Several negative results obtained in preliminary experiments are of interest. Chromium(VI) and iodate react orders of magnitude more slowly with HN_3 than BrO_3^- under the conditions employed in the present study. Periodic acid reacts at a measurable rate with HN_3, however, and conditions in which N_2 and N_2O are the only oxidation products can probably be found. Attempts to study the oxidation of the azide ion coordinated to substitution-inert metal ions rather than hydrogen ions have been unsuccessful to date. For example, the oxidation of $(H_2O)_5CrN_3^{2+}$ by BrO_3^- appears to be nearly as slow as the aquation rate of the complex unless enormous excesses of BrO_3^- are employed.

Acknowledgment.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

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[15] F. Emmenegger and G. Gordon, *Inorg. Chem.*, **6**, 633 (1967).

[16] The rate law reported in ref 11 was used to calculate the half-time for the redox reaction, and the expression rate = $(4.44\ M^{-2}\ sec^{-1})[BrO_3^-][H^+]^2$ (ref 10) was used for the BrO_3^- oxygen-exchange calculation.

[17] (a) K. Clausius and E. Effenberger, *Helv. Chim. Acta*, **38**, 1834 (1955); (b) C. A. Bunton and G. Stedman, *J. Chem. Soc.*, 1702 (1960), and preceding papers.