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CHEMICAL KINETICS _____ AND CATALYSIS _____

Interaction between Gaseous Ozone and Crystalline Potassium Bromide

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Abstract—The formation of nonvolatile products of the oxidation of a bromide ion during the interaction between gaseous ozone and powdered crystalline KBr is studied. It is found that potassium bromate KBrO₃ is the main product of the reaction. The influence of major experimental factors (the duration of ozonation, the concentration of ozone, the humidity of the initial gas, and the temperature) on the rate of formation of bromate is studied. The effective constants of the formation of bromate during the interaction between O₃ and Br⁻ in a heterogeneous gas—solid body system and in a homogeneous aqueous solution are compared.

Keywords: ozone, bromide, bromate, kinetics, topochemical reactions **DOI:** 10.1134/S0036024416070189

INTRODUCTION

Halogens are crucial to the atmospheric chemistry [1, 2]. Bromine in various forms has a substantial effect on the concentration of atmospheric ozone [3, 4]. Atomic bromine in particular initiates a sequence of chemical reactions leading to a very strong reduction in the concentration of ozone in the arctic troposphere as the sun appears [5-10]. A humid or dry aerosol of sea salt is a powerful source of halogens in the marine atmospheric boundary layer.

Despite a great many studies, the mechanism behind the evolution of active forms of halogens from a marine aerosol has not been conclusively established [1, 11, 12]. It is believed that the heterogeneous oxidation of halogenides is an important route of their activation. The chemical reaction between ozone and bromide ions in an aqueous solution [13-19] or on the surface of a liquid aerosol [20-24] has been studied in multiple works. The evolution of bromine from a humid aerosol containing bromide ions into the gas phase has been studied in some detail [21, 23-28]. It appears that the rate of formation of $Br_2(gas)$ is much higher than the one predicted using a mechanism developed on the basis of known chemical reactions in an aqueous solution and in the gas phase. In order to explain this phenomenon, a hypothesis regarding the substantial increase in the reactivity of bromide ions on the surface of the liquid aerosol (when compared to bromide ions in a volume) was proposed and confirmed by calculations and a series of experimental data [24].

At the same time, very few works have been devoted to the interaction between ozone and crystalline bromides. In [29], the interaction between ozone and sodium chloride, bromide, and iodide was studied in a fluid bed reactor. The concentration of ozone is reduced slightly when it is passed through powdered NaBr. In [26], the heterogeneous reaction between ozone and sodium bromide was conducted by passing an ozone-containing gas through a plate made of porous glass, on which a sample of NaBr had been placed. No interaction between the ozone and the dry NaBr was detected. Molecular bromine has been detected in gaseous reaction products after adding water vapor to an initial gas mixture. Here, the concentration of water vapors was close to deliquescence of sodium bromide. The heterogeneous decomposition of ozone over crystals of alkali metal bromides and samples of sea salt was studied in [30]. The decomposition of ozone over samples of pure alkali metal bromides has never been detected. Ozone decomposes quite rapidly over sea salt, and a certain amount of Br₂ molecular bromine evolves into the gas phase. All of the cited works contain only qualitative data on the interaction between ozone and crystalline alkali metal bromides, and only the gaseous products of interaction have been determined. It has been firmly established that under certain conditions, Br_2 molecular bromine can evolve into the gas phase during interaction between ozone and bromides. Products that could have formed in the solid phase (the main products of interaction) have yet to be studied.

The aim of this work was to study the interaction between gaseous ozone and dry polycrystalline potassium bromide to determine the qualitative composition of the products formed in the solid phase and the kinetics of their accumulation. No such studies have ever been performed. The $O_3(gas) + KBr(cryst)$ system was chosen because it simulates the natural process of interaction between ozone and dry marine aerosol. Dry sea salt is itself not suited for laboratory studies because it is a complex multicomponent system in which the content of bromide ions is not high.

EXPERIMENTAL

Powdered potassium bromide was treated with ozone in a glass thermostatted reactor. The working section of the reactor was a vertically positioned glass cylinder, in the lower part of which a disk made of porous glass was sealed. During the experiments, powdered potassium bromide was placed onto this disk, and the gases entered the reactor through the disk as well. The amount of potassium bromide in the reactor was either 10 or 25 g. In order to ensure effective contact between the surfaces of small crystals of potassium bromide and the gases, the reactor was shaken vertically during the experiments. The amplitude of movements was ~10 cm, and the frequency of shaking (7 s⁻¹) was specially selected.

Ozone was obtained by passing extra pure oxygen through a barrier discharge in an ozone generator. The concentration of ozone was measured using a Medozon photometric ozone measuring device and verified with an Agilent 8453 spectrophotometer. The maximum concentration of ozone was 3.5–4 vol %. The flow rate of the initial oxygen was 21.75 L/h (STP) in all experiments. The gas pipelines were made of polytetrafluoroethylene or polyvinylchloride tubing resistant to ozone.

The humidity of the initial oxygen was estimated from the increase in the weight of a trap placed into a cooling bath with temperatures of -65 to -70° C, through which the gas was passed at a constant rate over a certain time. Since the increase in the weight was due only to the condensation of water, we found that the content of water vapor (the absolute humidity of the oxygen) was 0.15 vol %.

To add known concentrations of water vapor into the gas mixture, the gases were passed through a thermostatted bubble flask filled with distilled water upstream of the inlet to the reactor. The humidity of the gases was determined by the temperature of the bubble flask. In order to avoid the condensation of water vapor in the gas pipelines, the temperature of the bubble flask did not exceed room temperature in our experiments.

Chemically pure grade potassium bromide (GOST (State Standard) 4160-74) with an assay of 99.97% was used in the experiments. The weight loss upon heating

to 320° C was 0.01%. The specimen of potassium bromide was not specially purified or dried; when preparing an experiment, all operations with it were performed in an ordinary laboratory atmosphere at 20- 25° C. Prior to treatment with ozone, the specimen of potassium bromide was kept in the reactor in a flow of oxygen at the specified temperature and humidity for 20 min.

The specific surface area of crystalline potassium bromide was estimated by measuring the dimensions of its crystals with a microscope. As is well known, potassium bromide forms crystals with a face-centered cubic lattice of the NaCl type. Using a microscope, it is easy to measure the length of diagonal *d* of the square face of a small crystal. This parameter varied within the range of 525–675 µm for seven samples, and the average value was 581 µm. Assuming that the crystals were regular cubes, the specific surface area was calculated using the formula $S/m = 3 \times 2^{3/2}/(\rho d)$, where $\rho = 2.75$ g/cm³ is the density of crystalline KBr. We found that S/m = 46-59 cm²/g, and the average value was 53 cm²/g.

In [31], the specific surface area of powdered crystalline KBr was determined via the Brunauer– Emmett–Teller (BET) method and was 440 (by water) and 600 cm²/g (by krypton) for the 125–200- μ m fraction. If we extrapolate this data to the sizes of our small crystals of KBr under the assumption that the specific surface area is inversely proportionate to the length of the diagonal of the square face, we obtain values of 100 (water) and 137 cm²/g (Kr).

A qualitative analysis of our sample of powdered potassium bromide after the treatment with ozone was performed by means of IR spectroscopy. The sample was pressed into a pellet that was placed into a cell holder of an EQUINOX 55/S IR spectrometer (Bruker), and the IR absorption spectrum was registered in the range of $360-4000 \text{ cm}^{-1}$.

Quantitative determination of the bromate in our ozonated powdered KBr was performed based on the concentration of tribromide ions formed upon dissolving the sample in an acid, using an indirect spectrophotometric method. It is known that the following reaction occurs during the acidification of an aqueous solution containing bromate and bromide ions:

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_3^- + 3H_2O$$
,

as a result of which one bromate ion forms three tribromide ions [32]. A tribromide ion has strong UV absorbance (λ_{max} is 266 nm and ϵ is 40 900 M⁻¹ cm⁻¹) [33].

For the quantitative determination of bromate, 5 g of the sample of potassium bromide was dissolved in 50 mL of 2.5 M H_2SO_4 , the solution was placed into an optical cell with a path length of 1 cm, and the absorption spectrum was registered relative to air. An Agilent 8453 spectrophotometer was used. The concentration



Fig. 1. Infrared absorption spectra of (1) ozone-treated powdered crystalline KBr, (2) KBrO₃ in a KBr pellet, and (3) pure KBr. The initial gases contained 3.3 vol % O₃, 0.15 vol % H₂O, and the remainder was O₂; the temperature was 60°C; and the duration was 50 min.

of bromate was determined from the value of the absorbance density at 266 nm (low concentrations of bromate), 380 nm (medium concentrations), or 445 nm (high concentrations) using preliminarily constructed calibration dependences. The detection limit was $\sim 1 \times 10^{-6}$ M bromate in the solution, which corresponded to $\sim 0.25 \mu$ mol of bromate in 25 g of potassium bromide. The relative error of the procedure did not exceed 5%.

RESULTS AND DISCUSSION

New strong absorption bands with maxima at 432 and 793 cm⁻¹ emerged in the IR spectrum of ozonetreated powdered KBr (Fig. 1, spectrum *I*). A comparison to the experimental spectrum of potassium bromate (diluted 50-fold by weight, in a KBr pellet) (Fig. 1, spectrum 2) and to the literature data [34–41] shows that these bands belong to a bromate ion BrO_3^- . There were no other new bands in the spectrum of the sample of KBr. It was therefore found for the first time in this work that potassium bromate KBrO₃ was the only nonvolatile product of the interaction between solid KBr and gaseous ozone. It is interesting that similar salts formed during the interaction between ozone and crystalline chlorides and iodides; sodium chlorate NaClO₃ is thus a product of the reaction between O_3 (gas) and NaCl(cryst) [42], and potassium iodate KIO₃ is the product of the reaction between O_3 (gas) and KI(cryst) [43–45].

The rest of this work is devoted to studying the quantitative kinetics of the formation of bromate. The number of moles of KBrO₃ formed during the experiment was directly proportional to the size of the sample of the initial potassium bromide. It is worth to note that the amount of bromate is also proportional to the duration of ozonation, allowing for the error (Fig. 2). In other words, the rate of formation of bromate is roughly constant during the experiment. Generally speaking, the process of interaction of gaseous ozone with solid potassium bromide is a topochemical reaction. Specific kinetics, particularly the S-shaped appearance of the integral kinetic curve, the presence of an induction period, and the transiting of the reaction rate through the maximum and its subsequent substantial drop to zero or some time-independent value are characteristic of such reactions [46]. Our understanding is that under the conditions of our experiments, the constancy of the rate of formation of the product is determined by the emergence of a steady-state concentration of the nucleation centers of a new phase of KBrO₃. Due to the shaking of the reaction substrate, the nucleation centers, once they form, are constantly reproduced rather than blocked by a layer of the product, as happens in the normal mode of



Fig. 2. Dependences of the amount of bromate formed in treating powdered KBr with ozone on the duration of treatment. The initial gases contained 3.3 vol % O_3 , 0.15 vol % H_2O , and the remainder was O_2 ; the temperature was $60^{\circ}C$. The dashed lines show the margins of the error interval of the linear regression at a confidence level of 95%.

performing topochemical reactions. The probable mechanism of formation of the new phase of potassium bromate can be described as follows: At the initial stage, as in all topochemical reactions, nucleation centers form. Crystallites of KBrO₃ grow quite rapidly over these nucleation centers. With the gain in the size of the crystallites, they detach from the surface of the crystals of the substrate because of the mutual collisions during shaking. At the same time, a small amount of the new phase stays at the place of detachment. This residue is an already formed nucleation center over which the crystallite grows once again, and so on.

These perceptions are confirmed by the characteristic value of the rate of formation of bromate in our experiments being 0.1 µmol g⁻¹ min⁻¹ = 6 × 10¹⁴ particles cm⁻² min⁻¹ (assuming that the reaction proceeds over the surface of a crystal of potassium bromide, while the value of the specific surface area s =100 cm²/g). The number of superficial bromide ions can be estimated using the formula $n_{\rm Br-} =$ $(\rho_{\rm KBr}N_{\rm A}/M_{\rm KBr})^{2/3}$, where $\rho_{\rm KBr} = 2.75$ g/cm³ is the density of crystalline KBr [47], $N_{\rm A} = 6.02 \times 10^{23}$ mol⁻¹ is the Avogadro constant, and $M_{\rm KBr} = 199.00$ g/mol is the molecular weight of KBr. It is 5.8×10^{14} particles/cm², i.e., nearly equal to the number of bromate ions formed on the surface over 1 min. If the reactive



Fig. 3. Typical dependences of the specific rate of formation of bromate on the content of ozone in the initial gas mixture. The temperature is 60° C and the content of water vapor is (**●**) 0.15 and (**▲**) 2.4 vol %.

surface was not renewed but was blocked by a layer of the product, a substantial drop in the rate of formation of bromate would have been observed in our experiments (duration, 20–60 min). However, this does not actually occur.

Since the amount of bromate is directly proportional to the weight of KBr and the duration of treatment, the kinetics of its formation can be character-

ized using the specific rate $n(BrO_3)/(\Delta tm(KBr))$,

μmol min⁻¹ g⁻¹, which is equal to the ratio of the number of moles of bromate $n(BrO_3^-)$, μmol, to the duration of ozonation Δ*t*, min, and weight of initial potassium bromide, m(KBr), g. The typical dependences of the specific rate of formation of potassium bromate on the concentration of ozone in the gas phase at the inlet of the reactor are presented in Fig. 3. In all our experiments, the specific rate was directly proportional to the concentration of O₃. It was therefore logical to determine the effective rate constant of the formation of bromate, which is equal to the ratio of the specific rate, μmol min⁻¹ g⁻¹, to the concentration of ozone in the gas phase $C(O_3)$, μmol/L:

$$k(\text{BrO}_{3}^{-}) = \frac{n(\text{BrO}_{3}^{-})}{C(\text{O}_{3})\Delta tm(\text{KBr})}, \text{ Lg}^{-1} \text{ min}^{-1}.$$

Humidity and temperature are the key factors affecting the formation of bromate. The rate constant of the formation of bromate $k(BrO_3^-)$ grows substantially with a rise in the humidity of the initial gases (Fig. 4).



Fig. 4. Dependence of the effective rate constant of the formation of bromate on the content of water vapor in the initial gases. The initial gases contained 1.6 vol % O₃ and the remainder was O₂ and H₂O; the temperature was 60°C.

Note that when dried oxygen (passed through a trap cooled to -70° C) is used, the rate of formation of bromate is almost the same as when the content of water vapor is 0.15 vol % in the initial gas. This is probably due to the water absorbed from the atmosphere, with which the substrate comes into contact prior to the experiment, remaining on the surface of the potassium bromide.

The dependence of the logarithm of the rate con-

stant of formation of bromate $k(BrO_3^-)$ on the reciprocal temperature is shown in Fig. 5. The Arrhenius law is obeyed in the temperature range of 24–70°C and at the water vapor content of 0.15 vol % in the initial gas; the expression for the temperature dependence of the constant is written as

$$k(BrO_3) = 2.48 \times 10^5 exp(-6390/T), L g^{-1} min^{-1}$$

The deviations at high temperatures are most likely due to the drop in the actual concentration of ozone near the surface of the crystals as a result of the thermal decomposition of ozone or the transition to the diffusion mode.

At a 2 vol % content of moisture, the dependence

of $\ln k(\text{BrO}_3^-)$ on T^{-1} has a more complex character. At a temperature of 30°C, the constant is lower when compared to the dry gas. At higher temperatures, the constant becomes higher in the humid gas, compared to the dry gas. Our understanding is that this character of the dependence is due to an increase in the mobility of superficial bromide ions under the action of two



Fig. 5. Dependences of the effective rate constant of formation of bromate on temperature. The concentration of water vapor in the initial gases is (\bullet) 0.15 and (\bigstar) 2 vol %.

factors such as the temperature and amount of adsorbed water. At low temperatures, when the mobility of ions is relatively low, it would seem adsorbed water can partially block the reactive surface. At an elevated temperature, under the conditions of a substantial increase in the mobility of ions, adsorbed water, on the contrary, promotes higher freedom of movement of bromide ions and thus facilitates their contact with ozone.

It is known that the formation of a bromate ion in the reaction between bromide and an ozone molecule in an aqueous solution occurs according to the mechanism [16]

$$Br^- + O_3 \to BrO^- + O_2, \tag{1}$$

$$BrO^- + O_3 \rightarrow Br^- + 2O_2, \qquad (2)$$

$$BrO^- + O_3 \rightarrow BrO_2^- + O_2, \qquad (3)$$

$$\operatorname{BrO}_2^- + \operatorname{O}_3 \to \dots \to \operatorname{BrO}_3^- + \operatorname{O}_2.$$

The formation of hypobromite is the limiting stage. The hypobromite ion interacts quite readily with the second ozone molecule and can either transform back into bromide or oxidize into bromite. The bromite ion readily interacts with ozone to form bromate [48]. During the interaction between ozone and crystalline potassium bromide, bromate probably also forms as a result of the successive oxidation of the bromide ion according to the scheme

$$Br^- \rightarrow BrO^- \rightarrow BrO_2^- \rightarrow BrO_3^-$$

It was of interest to compare our kinetic data on the interaction between gaseous ozone and a bromide ion in the composition of crystalline KBr with the kinetics of the reaction between O_3 and Br^- in an aqueous solution. We perform this comparison for 60°C because most of the results of this work are related to this particular temperature. In the solution, the effective constant of formation of bromate is determined by

the formula $k_{aq}(BrO_3^-) = k_1/(1 + k_2/k_3)$, where k_1, k_2 , and k_3 are the rate constants of stages (1)–(3). At 60°C, the constant k_1 adopts values of 1.5 × $10^3 L mol^{-1} s^{-1} = 2.5 \times 10^{-18} cm^3 particle^{-1} s^{-1}$ [14], $1.0 \times 10^3 L mol^{-1} s^{-1} = 1.7 \times 10^{-18} cm^3 particle^{-1} s^{-1}$ [16], and $1.3 \times 10^3 L mol^{-1} s^{-1} = 2.2 \times 10^{-18} cm^3 par$ $ticle^{-1} s^{-1}$ [17]. The value of the ratio k_2/k_3 is only known at 25°C and is 3.3 [16]. We assume that $k_2/k_3 \approx$ 3.3 at 60°C as well, and we find that the effective con $stant of formation of bromate <math>k_{aq}(BrO_3^-) = (5.0-7.5) \times$ $10^{-19} cm^3 particle^{-1} s^{-1}$ at this temperature. By definition, parameter $k_{aq}(BrO_3^-)$ is equal to the fraction of

those bromide ions in 1 cm^3 of the solution that undergo oxidation with ozone with the formation of bromate over a time of 1 s at a concentration of ozone in the solution of 1 molecule/cm³.

The effective rate constant of the formation of bromate during the interaction between O₃(gas) and KBr(cryst) is presented in Fig. 4, depending on the humidity of the initial gas at 60°C. It is obvious that the reaction proceeds over the surface of the crystal, and we express the constant in units such as cm³ parti $cle^{-1} s^{-1}$, allowing us to compare it to the similar parameter in the solution using the ratio $k_{\text{het}}(\text{BrO}_3)$ = $(1000/60) \times k(BrO_{3}^{-})/(sn_{Br-})$. In this formula, $k_{\text{het}}(\text{BrO}_3)$ and $k(\text{BrO}_3)$ is the constant in such units as cm^3 particle⁻¹ s⁻¹ and L g⁻¹ min⁻¹, respectively; s, cm^2/g , is the specific surface area of the crystals of KBr; $n_{\rm Br-} = 5.8 \times 10^{14}$ particles/cm² is the number of bromide ions on the surface of the crystal (see the estimate above). Based on the data presented above, we assume $s \sim 100 \text{ cm}^2/\text{g}$. Constant $k_{\text{het}}(\text{BrO}_3)$, cm³ particle⁻¹ s⁻¹, is the fraction of bromide ions per 1 cm² of the crystal surfaces that undergo oxidation with ozone with the formation of bromate over 1 s at a concentration of ozone in the gas phase near the surface of 1 molecule/cm³. At different humidities of the initial gas, we obtain the following values of the constant $k_{\text{het}}(\text{BrO}_3^-)$, cm³ particle⁻¹ s⁻¹, and the ratios of constants $k_{\text{het}}(\text{BrO}_3^-)/k_{\text{aq}}(\text{BrO}_3^-)$ at 60°C:

Concentration of H_2O	0.15	2.4	3.1
	20	20	10
$k_{\rm het}({\rm BrO}_3)$	3.2×10^{-20}	7.2×10^{-20}	1.0×10^{-19}
$k_{\text{het}}(\text{BrO}_3)/k_{\text{aq}}(\text{BrO}_3)$	0.04-0.06	0.10-0.14	0.13-0.20

The above data show that bromide ion reacts with ozone faster in an aqueous solution than on the surface of a crystal of KBr. The humidity (and thus the amount of superficially adsorbed water) has a strong influence on the reactivity of a superficial Br⁻ bromide ion toward ozone. With an increase in humidity, the rate of interaction increases substantially; in our experiments, the rate constant of the heterogeneous reaction reached ~20% of the value of the constant in our aqueous solution.

CONCLUSIONS

It was found for the first time that potassium bromate KBrO3 is the main product of the reaction between gaseous ozone and powdered crystalline potassium bromide. The influence of significant experimental factors (the duration of ozonation, concentration of ozone, humidity of the initial gas, and temperature) on the rate of formation of bromate was studied. In our experiments, this rate did not depend on time and grew along with the concentration of ozone and temperature. In most experiments, the effective rate constant of formation of bromate during the heterogeneous reaction was one to two orders of magnitude lower than that of the $O_3(sol) + Br^{-}(sol)$ process in an aqueous solution. At temperatures above 45°C, an increase in the humidity leads to a substantial rise in the constant of formation of bromate.

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