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Interaction of ozone and carbon dioxide with polycrystalline potassium bromide and its atmospheric implication

Alexander V. Levanov [a, *], Oksana Ya. Isaikina [a, b], Ivan B. Maksimov [a], Valerii V. Lunin [a, b]

[a] *Department of Chemistry, M.V. Lomonosov Moscow State University, Leninskiye Gory 1, Building 3, 119991 Moscow, Russia*
[b] *A.V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Leninsky Prospect 29, 119991 Moscow, Russia*

HIGHLIGHTS

- Br_2 is produced from the reaction of KBr crystals with gaseous O_3, CO_2, and H_2O.
- The equation is $2KBr(cr) + O_3(g) + 2CO_2(g) + H_2O(g) \rightarrow 2KHCO_3(cr) + Br_2(g) + O_2(g)$.
- The primary process in the kinetic scheme is BrO^- formation on Br^- oxidation with O_3.
- Br2 is formed via proposed reaction $BrO^- + 2CO_2 + H_2O + Br^- \rightarrow Br_2 + 2HCO_3^-$.

GRAPHICAL ABSTRACT
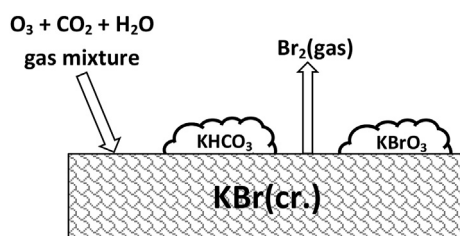
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ABSTRACT

It has been discovered for the first time that gaseous ozone in the presence of carbon dioxide and water vapor interacts with crystalline potassium bromide giving gaseous Br_2 and solid salts $KHCO_3$ and $KBrO_3$. Molecular bromine and hydrocarbonate ion are the products of one and the same reaction described by the stoichiometric equation $2KBr(cr.) + O_3(gas) + 2CO_2(gas) + H_2O(gas) \rightarrow 2KHCO_3(cr.) + Br_2(gas) + O_2(gas)$. The dependencies of Br_2, $KHCO_3$ and $KBrO_3$ formation rates on the concentrations of O_3 and CO_2, humidity of initial gas mixture, and temperature have been investigated. A kinetic scheme has been proposed that explains the experimental regularities found in this work on the quantitative level. According to the scheme, the formation of molecular bromine and hydrocarbonate is due to the reaction between hypobromite BrO^-, the primary product of bromide oxidation by ozone, with carbon dioxide and water; bromate results from consecutive oxidation of bromide ion by ozone $Br^- \xrightarrow{+O_3, -O_2} BrO^- \xrightarrow{+O_3, -O_2} BrO_2^- \xrightarrow{+O_3, -O_2} BrO_3^-$.

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1. Introduction

The composition and chemistry of the troposphere exert a major influence on life on Earth. Reactive halogens are of significance in tropospheric chemistry, and reactive bromine species such as Br_2, HOBr, BrO, play a dominant role in the destruction of ozone. The

detailed information on the subject and the references to the original literature can be found in the comprehensive reviews (Abbatt et al., 2012; Saiz-Lopez and von Glasow, 2012; Simpson et al., 2007; von Glasow and Crutzen, 2014). Despite the great importance of active bromine (see e.g (von Glasow et al., 2004).), its primary sources and the mechanism of the release to the troposphere are not well understood (Hunt et al., 2004; von Glasow and Crutzen, 2014).

A significant primary contributor of active bromine can result

* Corresponding author.
  E-mail address: levanov@kge.msu.ru (A.V. Levanov).

from the complex interaction between ozone and dry or deliquescent marine aerosol containing bromide ions. The reaction of ozone with bromide ion in the bulk of aqueous solution (Disselkamp et al., 1999; Garland et al., 1980; Haag and Hoigné, 1983; Haruta and Takeyama, 1981; Liu et al., 2001; Taube, 1942) and in liquid aqueous aerosol particles (Anastasio and Mozurkewich, 2002; Clifford and Donaldson, 2007; Hunt et al., 2004; Nissenson et al., 2009, 2014; Oldridge and Abbatt, 2011; Oum et al., 1998) has been comprehensively investigated. In our work (Levanov et al., 2016) the interaction of ozone with crystalline KBr has been studied, which models the reaction of O_3 with Br^- incorporated into dry marine aerosol. Its only product detected was bromate ion BrO_3^- remaining in the solid phase. At the same time, one would expect that carbon dioxide, an important atmospheric constituent, can exert an appreciable influence on the direction and rate of the complex reaction of ozone with bromide ion. However, this problem has not been investigated until the present time.

The subject of this work is the research on the interaction of gaseous ozone and carbon dioxide with powdered crystalline potassium bromide, namely, the determination of the composition of the products formed in the solid phase and released into the gas phase, a quantitative study of the kinetics of their formation, and the elucidation of a plausible chemical mechanism of the process. The system $KBr(cr.) + O_3(gas) + CO_2(gas)$ is a convenient laboratory model of the natural process of interaction of dry marine aerosol with the mentioned components of the troposphere.

2. Experimental methods

The scheme of the experimental setup is shown in Fig. 1. The interaction between crystalline KBr powder and gaseous mixture $O_3-CO_2 - O_2$ took place in a glass reactor provided with a thermostatically controlled jacket. The accuracy of temperature maintenance was within ± 0.5 °C. In single experiments, NaBr was used instead of KBr. The working part of the reactor constituted a glass cylinder with a porous glass filter plate at its bottom, through which the initial gases were fed in. 10 or 25 g of bromide powder were placed in the reactor, and resided above the filter. To ensure an effective contact of the surface of bromide crystals with the gases, during the experiments the reactor was shaken in vertical direction with the frequency ~7 s^{-1} and amplitude of motion ~10 cm. It should be noted that the experiments of this work and of our study (Levanov et al., 2016) were carried out on the same setup, and the experimental procedures were by and large similar.

Ozone was synthesized from molecular oxygen of very high purity grade in a self-made barrier discharge ozonizer. Its concentration was measured by UV photometric ozonometers "Medozon" verified by means of Agilent 8453 spectrophotometer. The maximum attainable ozone concentration was 4 vol.% at oxygen flow rate 22 L/h (STP). A flow of carbon dioxide (GOST 8050–85 first-rate grade) was added through a tee to the flow of ozonized oxygen before entering the reactor. In all the experiments the sum of flow rates of initial gases O_2 and CO_2 was 22 L/h (STP). The gas communications were made of polytetrafluorethylene or medical polyvinylchloride tubes resistant to the action of ozone.

The moisture content of oxygen and carbon dioxide gases was estimated in the same way as in the work (Levanov et al., 2016), by measuring the weight increase of a trap cooled to −65 to −70 °C, through which the gas was passed at a constant rate for a definite time. The absolute humidity (the content of water vapor in vol.%) of oxygen proved to be 0.15 vol.% and of carbon dioxide 1.06 vol.%. To attain the required humidity of the initial gases in the course of the experiments, before entering the reactor they were passed through the bubbler filled with distilled water and maintained at a constant temperature. The humidity was determined by the bubbler

temperature, which did not exceed room temperature.

Potassium bromide reagent (GOST 4160–74, chemically pure grade, 0.01% weight loss on heating to 320 °C) was used in the experiments. Single experimental runs were performed with sodium bromide reagent (GOST 4169–76, pure grade). Its weight loss on heating was 3.8% at 100 °C and 4.4% at 320 °C, which is due to the hygroscopicity of NaBr and the possibility of $NaBr \cdot 2H_2O$ crystalline hydrate formation. Bromide specimens were not additionally purified or dried; their handling was carried out in usual laboratory atmosphere at temperature 20–25 °C. Before treatment with $O_3-CO_2 - O_2$ gas mixture, powdered bromide salts were held in the reactor in the flow of CO_2 and O_2 at required temperature and humidity for 20 min. The characterization of potassium bromide specific surface area has been given in work (Levanov et al., 2016).

Qualitative analysis of potassium bromide powder after the treatment with $O_3-CO_2 - O_2$ gas mixture was carried out by infrared spectroscopy. From the powder a pellet was pressed off, and its IR spectra were taken by means of Equinox 55/S IR spectrometer (Bruker) in the range 360–4000 cm^{-1}.

Qualitative analysis of gaseous products formed on the treatment of bromide powder with the gas mixture was performed by UV−visible spectrophotometry. 25 g of bromide were placed in the reactor, the initial gases were passed through the sample without shaking, and exit gases were promptly directed into the optical cell of Agilent 8453 spectrophotometer, where the UV−vis spectra were recorded.

Quantitative determination of bromate BrO_3^- in the treated potassium bromide powder was carried out in the same way as in work (Levanov et al., 2016), by an indirect spectrophotometric method, measuring the concentration of tribromide ion Br_3^- formed on dissolution of 5 g of the sample in 50 ml of 2.5 M H_2SO_4.

Quantitative determination of hydrocarbonate in the treated KBr samples was conducted by acid-base titration. 10 g of the sample were dissolved in sufficient amount of distilled water. Then a drop of methyl orange indicator was poured, and the solution
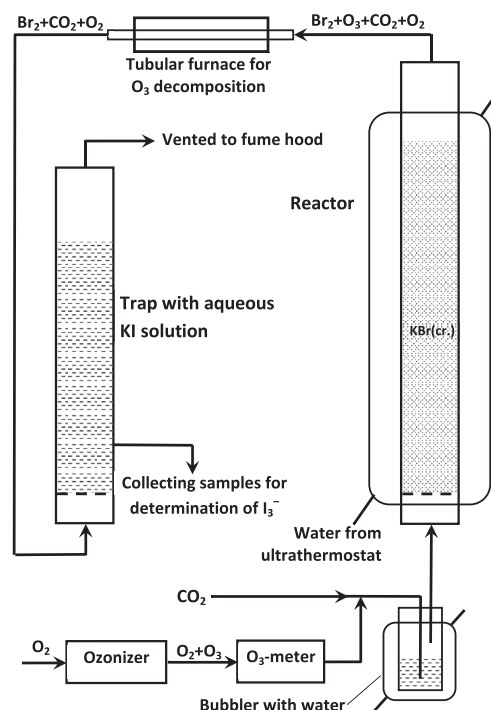

Fig. 1. Scheme of the experimental setup.