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Concentration-dependence of the explosion characteristics of chlorine dioxide gas

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ABSTRACT

The explosion characteristics of chlorine dioxide gas have been studied for the first time in a cylindrical exploder with a shell capacity of 20 L. The experimental results have indicated that the lower concentration limit for the explosive decomposition of chlorine dioxide gas is 9.5% ([ClO_2]/[air]), whereas there is no corresponding upper concentration limit. Under the experimental conditions, and within the explosion limits, the pressure of explosion increases with increasing concentration of chlorine dioxide gas; the maximum pressure of explosion relative to the initial pressure was measured as 0.024 MPa at 10% ClO_2 and 0.641 MPa at 90% ClO_2. The induction time (the time from the moment of sparking to explosion) has also been found to depend on the concentration of chlorine dioxide gas; thus, at 10% ClO_2 the induction time was 2195 ms, but at 90% ClO_2 the induction time was just 8 ms. The explosion reaction mechanism of ClO_2 is of a degenerate chain-branching type involving the formation of a stable intermediate (Cl_2O_3), from which the chain-branching occurs. Chain initiation takes place at the point of ignition and termination takes place at the inner walls of the exploder.

1. Introduction

In recent years, chlorine dioxide has attracted significant commercial attention as a novel neutral oxy-chlorine species acting as a powerful oxidant and disinfectant, not only from an environmental viewpoint, but also due to its wide application in the fields of bleaching, oxidation, and disinfection [1–10].

Chlorine dioxide gas is normally mixed with air and appears yellowish–green in color. In its pure state, chlorine dioxide is unstable and can decompose into chlorine and oxygen upon heating or irradiation. Dilute solutions in water, however, can be handled safely. ClO_2 cannot be compressed or stored commercially because it decomposes with time and is highly explosive at high concentrations (>10% in air). Therefore, ClO_2 is generated on-site. The permissible exposure limit or time-weighted average of ClO_2 gas in air is 0.1 ppm, as specified by the Occupational Safety and Health Administration [11].

Chlorine dioxide is produced from acidic solutions of either sodium chlorite [12–14] or sodium chlorate [15–18]. Most of the small- and medium-scale generators use sodium chlorite as the precursor material. For other applications, in which large quantities of chlorine dioxide are needed, sodium chlorate is utilized. Though the conditions for the production of ClO_2 from sodium chlorite can be more easily controlled than those for its production from sodium chlorate, the chlorite is a more expensive and unstable chemical. Thus, from the industrial point of view, sodium chlorate is the most suitable raw material for ClO_2 generation.

The explosive decomposition of chlorine dioxide has been studied over the pressure and temperature ranges 26.7–5332 Pa and 54–134 °C [19]. According to this report, the explosive decomposition reaction is characterized by long induction periods, which were measured as a function of temperature, pressure, vessel size, added gases, and the presence of other chlorine oxides. The explosion was found to be of the degenerate chain-branching type, and the intermediate responsible for the delayed reaction was identified as Cl_2O_3. The experimental results together with reliable enthalpy data from other studies on chlorine oxides have allowed the delineation of a mechanism.

The explosion limit and pressure of explosion of chlorine dioxide gas have not reported during the past few decades. The research reported herein concerns the explosion characteristics of chlorine dioxide, including the explosion limit, the induction time prior to explosion, and the maximum pressure of explosion relative to the initial pressure. These parameters have been measured by igniting chlorine dioxide gas with an ignition electrode, and the data obtained should prove useful in the design of chlorine dioxide gas generators and for further studies on fundamental aspects of generator safety, which are key to exploiting the rather bulky generators for the generation of this useful gas.

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2. Experimental

2.1. Chlorine dioxide generation unit

Chlorine dioxide was synthesized as needed by mixing $NaClO_2$ with 20% (w/w) hydrochloric acid at about 50 °C.

$$5NaClO_2 + 4HCl \xrightarrow{\Delta} 5NaCl + 4ClO_2 + 2H_2O \quad (1)$$

The reaction was carried out at atmospheric pressure. The ClO_2 was passed through Drierite, which removed most of the H_2O, and then it was transferred to the exploder, which was connected to a vacuum system. The purity of the gas was checked by measuring its vapor pressure and infrared spectrum. No impurities were ever found and the purity was estimated to be at least within a few tenths of 100%. Preparations and handling operations were all carried out in darkness.

2.2. Apparatus for chlorine dioxide gas explosion

An apparatus for studying chlorine dioxide gas explosions was constructed entirely from stainless steel alloy, and its applicability for this type of study was verified. It consisted of a 20 L cylinder explosion tank that was connected by 12 mm tubing and a 12 mm bore straight-through stopcock to a vacuum system. The temperature was controlled at 25 ± 2 °C by means of a bimetal thermoregulator, and this controlled relay in turn activated an electric heater. The physical dimensions of the exploder are indicated in Fig. 1 and a photograph of the set-up is shown in Fig. 2.

The vacuum system consisted of storage bulbs, traps, and a digimatic manograph. An absolute pressure of <5 kPa could be attained by means of a mechanical pump.

The characteristic parameters measured in this study were the explosion limit, the induction time prior to explosion, and the maximum pressure of explosion relative to the initial atmospheric pressure at the ambient temperature before ignition. These characteristic parameters could be measured by means of a pressure transducer. The preset parameters for control tests were as follows: test specification of pressure 0–5 MPa, sensitivity shift 11.37 mV/10^5 Pa, sampling frequency 10.00 kHz, sampling length 50 k, sampling time delay −5 k, triggering level 0.0156 V, filter frequency of the electric amplifier 0.3–100 kHz, and ignition voltage output 8 kV. When the concentration of chlorine dioxide gas was below 50% ([ClO_2]/[air]), the voltage range selected was ± 1 V; when the concentration of chlorine dioxide gas was greater than 60%, the voltage range selected was ±2 V.

The procedure involved admitting ClO_2 from a reservoir bulb (covered with a black cloth bag) into the explosion tank by turning the straight-through stopcock after evacuation of the tank; the percent by volume of chlorine dioxide gas admitted into the tank was controlled through the partial pressure. The delay time from admission into the tank was 500 ms prior to autoignition.

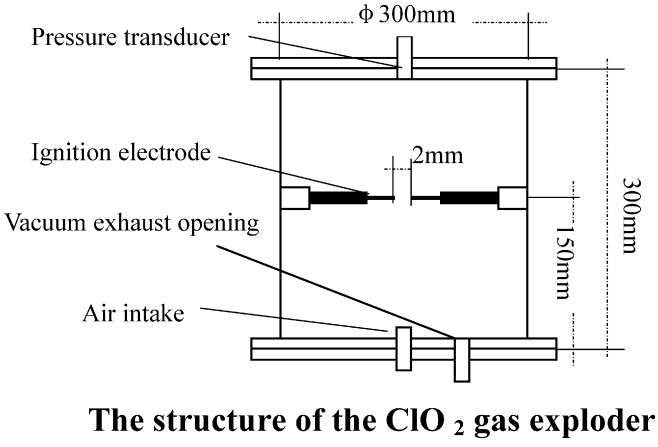

Fig. 1. The structure of the ClO_2 gas exploder.

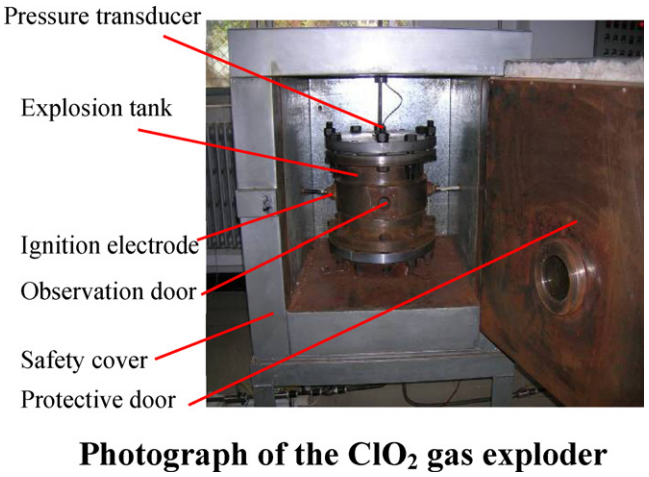

Fig. 2. Photograph of the ClO_2 gas exploder.

2.3. IR spectra

Infrared spectrum analysis of the explosive products ignited $C1O_2$ determined that the intermediate were Cl_2O_3 and Cl_2O_6, and the IR spectra of gaseous and matrix-isolated Cl_2O_6 and Cl_2O_3 were recorded in the range 1500–300 cm^{-1} by using the FTIR spectrometer: FTS 3000 by digilab of America, with the infra-red spectrogram shown in Figs. 3 and 4, respectively.

3. Results and discussion

3.1. General remarks on the explosive reaction

Explosions of chlorine dioxide gas were obtained at normal temperatures and atmospheric pressure. When the concentration of chlorine dioxide gas was 10%, in a series of five experiments, a signal intensity indicative of explosion was obtained only once after ignition (as shown in Fig. 5), with a signal strength of 24.414 mV, but in the other cases no detonator signal was obtained.

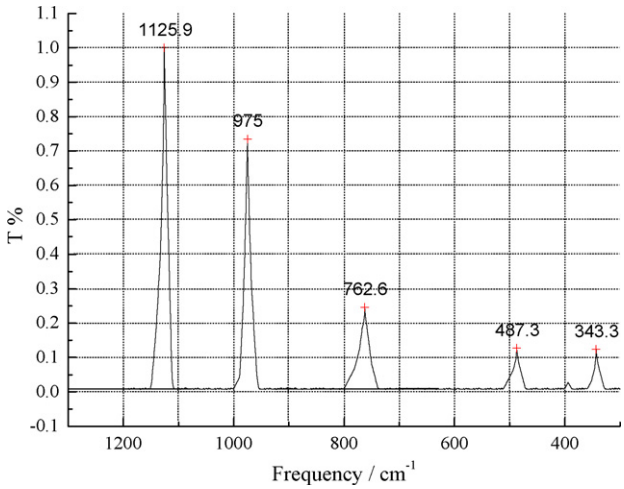

Fig. 3. Infrared spectrum analysis of the explosive products ignited $C1O_2$ determined that the intermediate were Cl_2O_3.