



## 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% ( $[\text{ClO}_2]/[\text{air}]$ ), 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%  $\text{ClO}_2$  and 0.641 MPa at 90%  $\text{ClO}_2$ . 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%  $\text{ClO}_2$  the induction time was 2195 ms, but at 90%  $\text{ClO}_2$  the induction time was just 8 ms. The explosion reaction mechanism of  $\text{ClO}_2$  is of a degenerate chain-branching type involving the formation of a stable intermediate ( $\text{Cl}_2\text{O}_3$ ), 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.

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### 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.  $\text{ClO}_2$  cannot be compressed or stored commercially because it decomposes with time and is highly explosive at high concentrations (>10% in air). Therefore,  $\text{ClO}_2$  is generated on-site. The permissible exposure limit or time-weighted average of  $\text{ClO}_2$  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  $\text{ClO}_2$  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  $\text{ClO}_2$  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  $\text{Cl}_2\text{O}_3$ . The experimental results together with reliable enthalpy data from other studies on chlorine oxides have allowed the delineation of a mechanism.

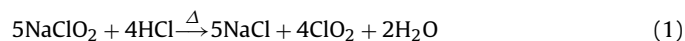
The explosion limit and pressure of explosion of chlorine dioxide gas have not reported during the past few decades. The research reported herein concerns the explosion characteristics of chlorine dioxide, including the explosion limit, the induction time prior to explosion, and the maximum pressure 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  $\text{NaClO}_2$  with 20% (w/w) hydrochloric acid at about  $50^\circ\text{C}$ .



The reaction was carried out at atmospheric pressure. The  $\text{ClO}_2$  was passed through Drierite, which removed most of the  $\text{H}_2\text{O}$ , 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.

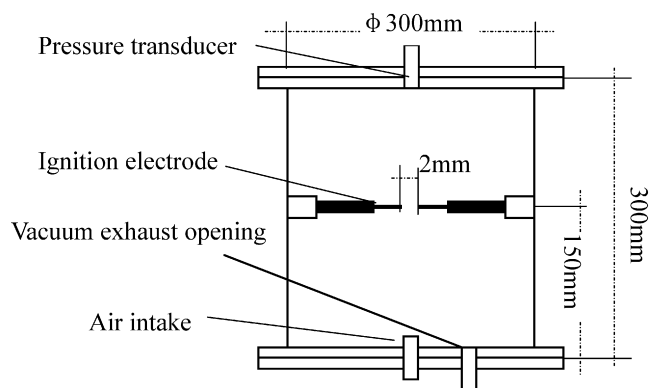
### 2.2. Apparatus for chlorine dioxide gas explosion

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 20L 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  $25 \pm 2^\circ\text{C}$  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  $<5\text{ kPa}$  could be attained by means of a mechanical pump.

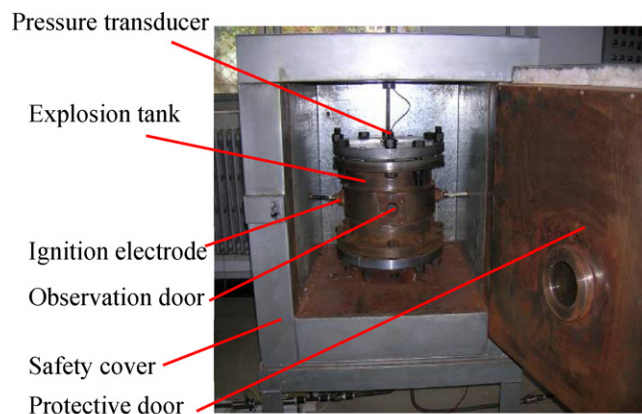
The characteristic parameters measured in this study were the explosion limit, the induction time prior to explosion, and the maximum pressure of explosion relative to the initial atmospheric pressure at the ambient temperature before ignition. These characteristic parameters could be measured by means of a pressure transducer. The preset parameters for control tests were as follows: test specification of pressure 0–5 MPa, sensitivity shift  $11.37\text{ mV}/10^5\text{ Pa}$ , sampling frequency 10.00 kHz, sampling length 50 k, sampling time delay  $-5\text{ k}$ , 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% ( $[\text{ClO}_2]/[\text{air}]$ ), the voltage range selected was  $\pm 1\text{ V}$ ; when the concentration of chlorine dioxide gas was greater than 60%, the voltage range selected was  $\pm 2\text{ V}$ .

The procedure involved admitting  $\text{ClO}_2$  from a reservoir bulb (covered with a black cloth bag) into the explosion tank by turn-



**The structure of the  $\text{ClO}_2$  gas exploder**

Fig. 1. The structure of the  $\text{ClO}_2$  gas exploder.



**Photograph of the  $\text{ClO}_2$  gas exploder**

Fig. 2. Photograph of the  $\text{ClO}_2$  gas exploder.

ing 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.

### 2.3. IR spectra

Infrared spectrum analysis of the explosive products ignited  $\text{ClO}_2$  determined that the intermediate were  $\text{Cl}_2\text{O}_3$  and  $\text{Cl}_2\text{O}_6$ , and the IR spectra of gaseous and matrix-isolated  $\text{Cl}_2\text{O}_6$  and  $\text{Cl}_2\text{O}_3$  were recorded in the range  $1500\text{--}300\text{ cm}^{-1}$  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.

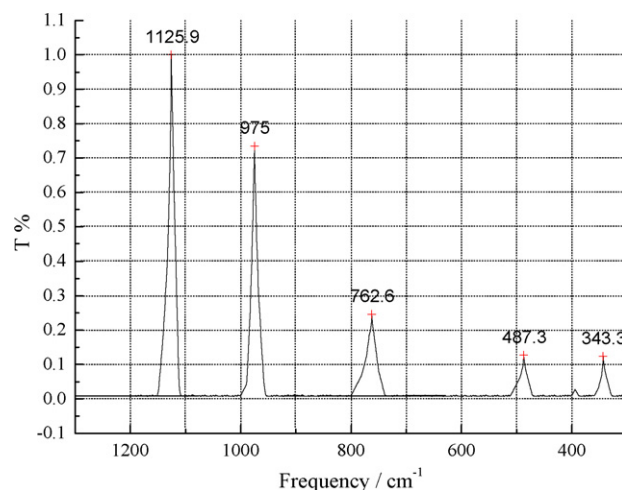
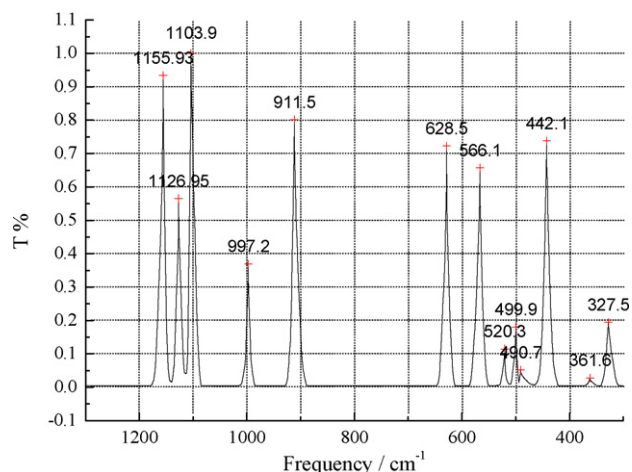


Fig. 3. Infrared spectrum analysis of the explosive products ignited  $\text{ClO}_2$  determined that the intermediate were  $\text{Cl}_2\text{O}_3$ .



**Fig. 4.** Infrared spectrum analysis of the explosive products ignited  $\text{ClO}_2$  determined that the intermediate were  $\text{Cl}_2\text{O}_6$ .

**Table 1**

The results of explosion tests on  $\text{ClO}_2$  gas.

Serial number	$\text{ClO}_2$ concentration (vol.% in air)	Order number of experiment				
		First	Second	Third	Fourth	Fifth
1	9.5	×	×	×	×	×
2	10	×	✓	×	×	×
3	20	✓	✓	✓	✓	✓
4	30	✓	✓	✓	✓	✓
5	40	✓☆	✓☆	✓☆	✓☆	✓☆
6	50	✓☆	✓☆	✓☆	✓☆	✓☆
7	60	✓☆	✓☆	✓☆	✓☆	✓☆
8	70	✓☆	✓☆	✓☆	✓☆	✓☆
9	80	✓☆	✓☆	✓☆	✓☆	✓☆
10	90	✓☆	✓☆	✓☆	✓☆	✓☆

Explanation of symbols: ×: combustion or explosion did not occur. ✓: combustion or low-level explosion occurred, ✓☆: explosive reaction occurred.

When the concentration of chlorine dioxide gas was 9.5%, no signal waves indicative of an explosion were obtained after ignition in any of a series of five batch experiments.

Typical experimental results are shown in Table 1.

When the concentration of chlorine dioxide gas was greater than 20%, the signal intensities obtained were clearly indicative of

explosions. The higher the concentration of chlorine dioxide gas, the greater the explosive intensity was. Typical curves showing the pressure of explosion of chlorine dioxide at different concentrations are presented in Figs. 6 and 7.

In Figs. 5–7, irrespective of the concentration of chlorine dioxide, using the same preset parameters as for the control tests and the same ignition voltage output, similar types of pressure wave curves were obtained, except when the concentration of chlorine dioxide was 10%. These trend curves of the respective explosion waves all featured a peak of maximum explosion; the pressure of explosion attained a maximum value, and then decreased thereafter. On extending the monitoring time of the explosive reaction, the trend curve of each explosion wave gradually decreased to a negative pressure, and then a relatively flat explosion wave curve with a less oscillatory wave was seen between the positive and negative pressures.

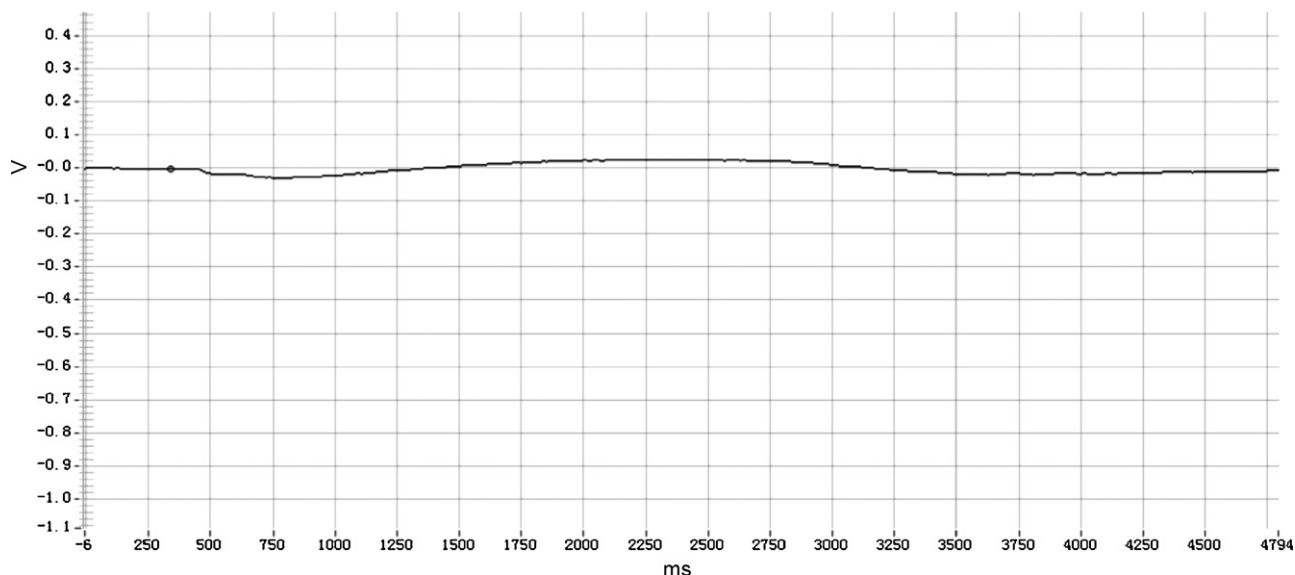
To sum up the reaction process of explosive decomposition, when chlorine dioxide gas was ignited by the electrode, an explosion occurred, which then translated into conflagration in an extremely short time; finally, a slow decomposition reaction occurred over a period of about 5 min.

### 3.2. Results and discussion of the explosive reaction

From Table 1, it is apparent that there is no upper concentration limit for the explosion of chlorine dioxide gas, but that the lower concentration limit for explosion is 9.5% ( $[\text{ClO}_2]/[\text{air}]$ ). That is to say, when the concentration of chlorine dioxide gas in air is below 9.5%, it does not present an explosion hazard. The dependences of the induction time and the maximum pressure of explosion relative to the initial pressure on the concentration of chlorine dioxide are shown in Figs. 5–7. The higher the concentration of chlorine dioxide, the greater the pressure of explosion was by the shorter the induction time.

Data from experiments performed with various concentrations of chlorine dioxide gas, namely the maximum pressure of explosion relative to the initial pressure and the induction time, are shown in Table 2.

As noted above, the higher the concentration of chlorine dioxide gas, the shorter the induction time. When the concentration of  $\text{ClO}_2$  was increased from 10% to 80%, the induction time was reduced from 2195 ms to 8 ms, but it did not decrease further on increasing the concentration of  $\text{ClO}_2$  to 90%.



**Fig. 5.** The maximum pressure of explosion curve for  $\text{ClO}_2$  gas (10% concentration) relative to the initial atmospheric pressure.

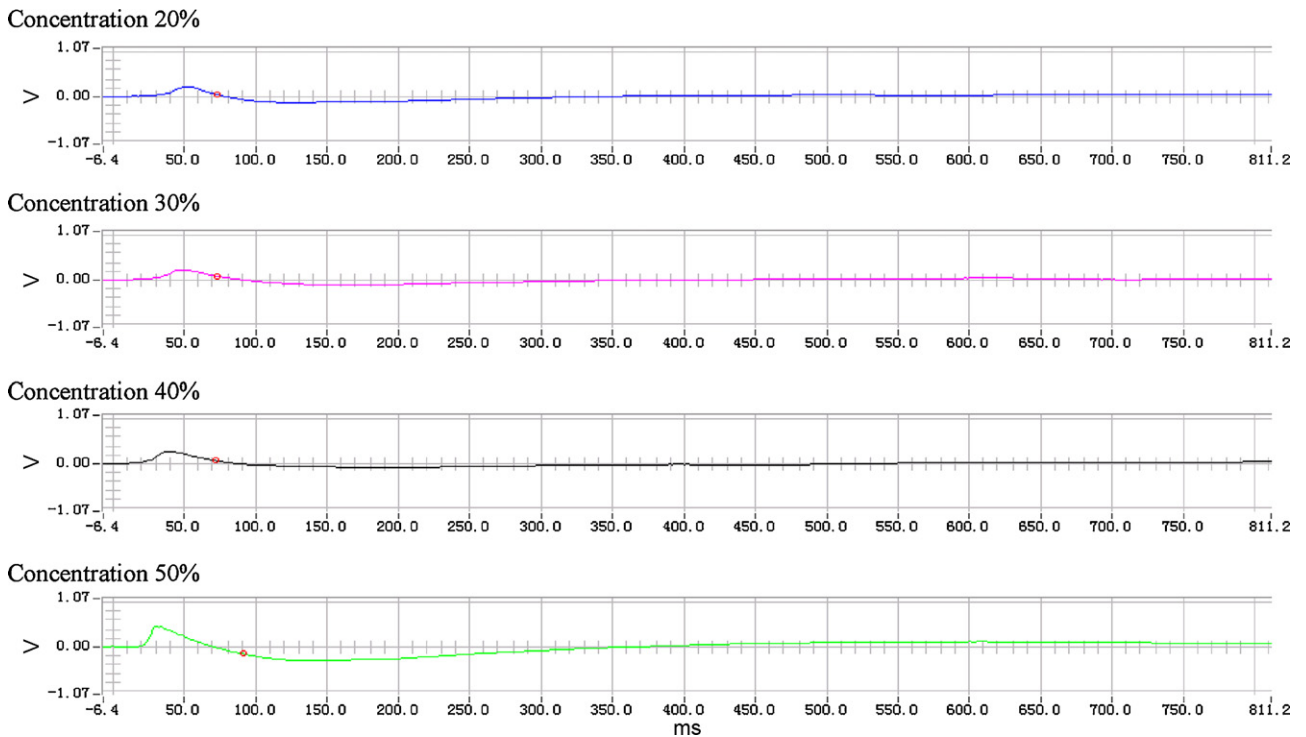


Fig. 6. Maximum pressure of explosion curves for  $\text{ClO}_2$  gas (at concentration of 20,30,40,and 50%) relative to the initial atmospheric pressure.

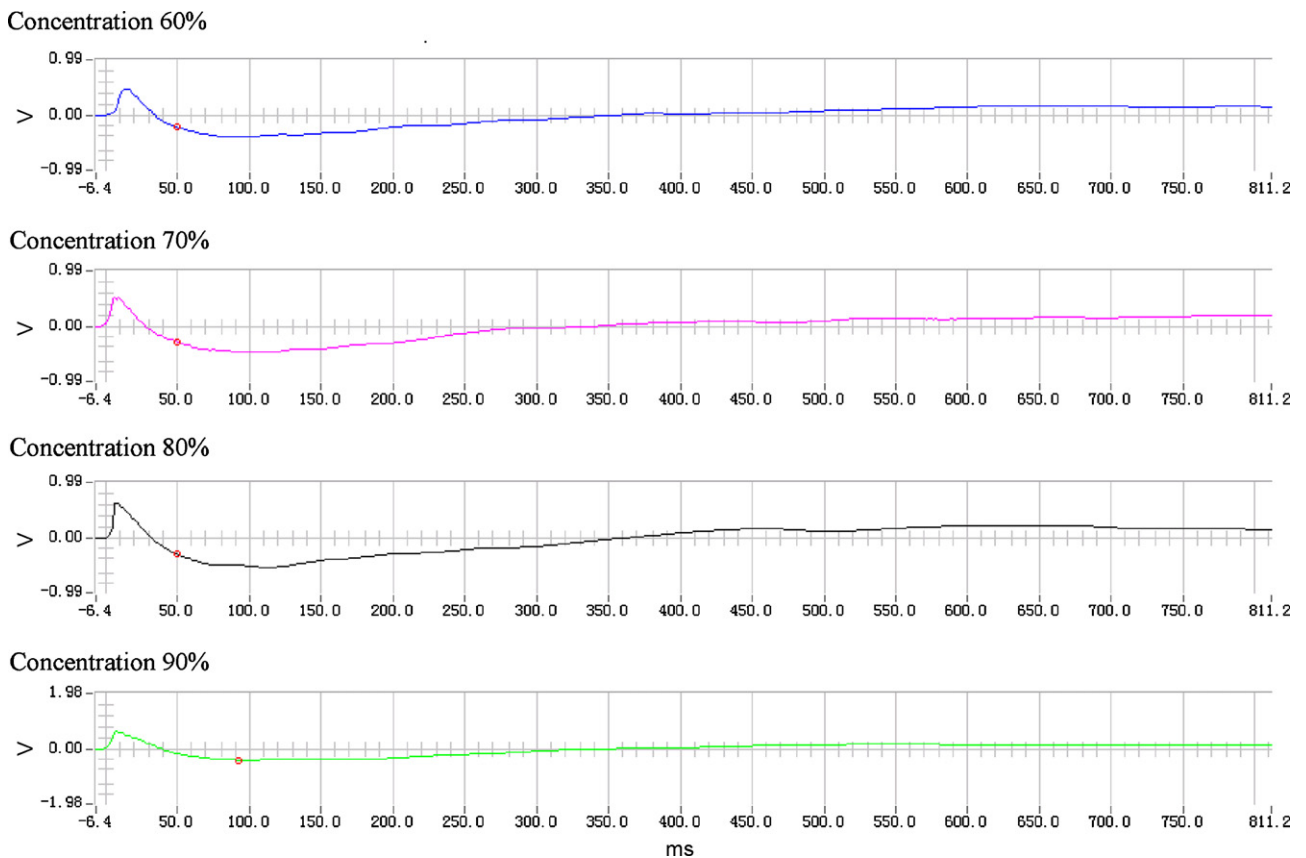


Fig. 7. Maximum pressure of explosion curves for  $\text{ClO}_2$  gas (at concentration of 60%,70%, 80%, and 90%) relative to the initial atmospheric pressure.

**Table 2**  
Dependences of the maximum pressure of explosion relative to the initial pressure and induction time prior to explosion on the concentration of ClO<sub>2</sub> gas.

	ClO <sub>2</sub> concentration (vol.% in air)								
	10	20	30	40	50	60	70	80	90
Maximum pressure of explosion relative to the initial pressure (MPa)	0.024	0.203	0.213	0.257	0.451	0.473	0.514	0.621	0.641
Induction time (ms)	2195	52.80	49.60	40.00	33.60	14.40	9.60	8.00	8.00

The higher the concentration of chlorine dioxide gas, the greater the maximum pressure of explosion relative to the initial pressure. When the concentration of ClO<sub>2</sub> was increased from 10% to 90%, the maximum pressure of explosion relative to the initial pressure increased from 0.024 MPa to 0.641 MPa.

### 3.3. Infrared spectrum analysis

In order to confirm the explosive products ignited ClO<sub>2</sub>, we gave the infrared spectrum analysis of products. It can be seen from Fig. 3, the three bands are observed in the region of the asymmetric stretching modes of the ClO<sub>2</sub> and ClO<sub>3</sub> groups (1200–1100 cm<sup>-1</sup>), respectively, and the other two bands are also found in the region of the symmetric stretching modes of the ClO<sub>2</sub> and ClO<sub>3</sub> groups (1000–900 cm<sup>-1</sup>), respectively. Furthermore, the bands at 628 cm<sup>-1</sup> and 566 cm<sup>-1</sup> should correspond to the stretching modes of asymmetry in the two groups, as is agreement with the spectra of Cl<sub>2</sub>O<sub>6</sub> observed by Jansen et al. [20]. So the Cl<sub>2</sub>O<sub>6</sub> was determined in the explosive products. On the other hand, The most important three vibrational frequencies of Cl<sub>2</sub>O<sub>3</sub>, from Fig. 4, the 1126.0 cm<sup>-1</sup> and 975.0 cm<sup>-1</sup> can be approximately described as the antisymmetric and symmetric stretching of Cl–O of ClO<sub>2</sub> group, respectively, the 487.3 cm<sup>-1</sup> as the stretching mode of Cl–O of ClO<sub>2</sub> group, as was almost accordance with the spectra of Cl<sub>2</sub>O<sub>3</sub> observed by Muller and Willner and Burkholder et al. [21,22], in which the corresponding values were 1203.1 cm<sup>-1</sup>, 1060 cm<sup>-1</sup> and 506 cm<sup>-1</sup>, respectively. Thus, the Cl<sub>2</sub>O<sub>3</sub> was also confirmed in the explosive products.

### 3.4. Discussion of the explosion reaction mechanism

The explosion of ClO<sub>2</sub> is of a degenerate chain-branching type involving the formation of a stable intermediate [19]. When different concentrations of chlorine dioxide gas were ignited by an electrode, explosive decomposition reactions were observed as opposed to a slow spontaneous process. In an explosion, the rate of decomposition of chlorine dioxide was greatly accelerated, and the pressure of explosion increased rapidly at first and then reached a maximum. It could be concluded that ignition by an electric spark gave rise to a branched-chain reaction. This explosive decomposition cannot be thermal in nature or of the ordinary chain-branching type. Rather, it belongs to a special case in which the reactant forms a stable intermediate, in the present case a mixture of dark-brown solid forms of Cl<sub>2</sub>O<sub>6</sub> and Cl<sub>2</sub>O<sub>3</sub>, and this intermediate subsequently gives rise to chain-branching. The Cl<sub>2</sub>O<sub>3</sub> volatilizes readily, while the Cl<sub>2</sub>O<sub>6</sub> remains involatile; this permits a facile separation, so that the Cl<sub>2</sub>O<sub>6</sub> is accumulated on the internal walls of the exploder, while Cl<sub>2</sub>O<sub>3</sub> vaporizes into the ClO<sub>2</sub> gaseous phase. This type of reaction system must follow a general scheme, which must essentially resemble the following [19]:



Here, *R* is the reactant; *x* and *y* are highly reactive species (radicals); *I* is the stable intermediate; and *n* and *m* are branching coefficients  $\geq 2$ .

A mechanism applicable to the ClO<sub>2</sub> explosion would have to be of the general form of that shown above. So, after ignited the initiation reaction is believed to be:



This reaction accounts for the formation of the ClO<sub>3</sub> that is found in the explosive reaction, and has the virtue of a low enthalpy and low activation energy. The intermediate is undoubtedly formed through the association reaction:



As the concentration of the intermediate built up, its reaction with the chain carrier ClO became increasingly important. The most reasonable way for this reaction to occur would be as follows:



This would readily lead to branching and explosion through Cl–OO–Cl, which is a free-radical-type species similar to Cl–OO. It seems likely that Cl–OO–Cl will behave in approximately the same way.

Thus, the dissociation reactions believed to occur are as follows:



Once Cl atoms are produced, the branching reaction:



is expected to occur.

The dominant termination reactions under the conditions of this study were determined by observation of the kinetics. The reactions:



would seem to adequately describe the system.

In fact, Gray and IP [23,24] have already investigated the spontaneously explosive decomposition of gaseous chlorine dioxide with helium, hydrogen, methane, ethane, propane, ethyl and butadiene as diluents, and they found that it was branched-chain rather than thermal in character, which is supported indirectly by the pressure–time histories and by the induction periods observed the explosion of mixtures of chlorine dioxide. Moreover, Green et al. [25] observed that the photolysis of ClO<sub>2</sub> could lead to the formation of Cl<sub>2</sub>O<sub>3</sub> as a result of the addition of the ClO at low temperatures in 2004. Furthermore, Croce et al. [26] reported that the products Cl<sub>2</sub>O<sub>4</sub>, Cl<sub>2</sub>O<sub>6</sub>, Cl<sub>2</sub> and O<sub>2</sub> were formed under the photochemical decomposition of 5–80 Torr gaseous ClO<sub>2</sub> at 293 and 303 K in 2008. In particular, Davis and Lee [27] used photo fragment translational energy spectroscopy to study the dissociation dynamics of a range of electronically excited OClO vibrational states, and they observed that for all levels studied, the dominant product (>96%) was ClO + O, accompanied by the production of Cl + O<sub>2</sub> with a quantum yield of up to 3.9 ± 0.8%. Compared with the results mentioned above, it

can be seen that our explosion reaction mechanism in this paper is reliable.

#### 4. Conclusions

Experiments aimed at delineating the conditions for the explosive decomposition of chlorine dioxide gas at different concentrations in air have been performed in a 20 L cylinder explosion tank constructed from stainless steel alloy. The explosion characteristics of chlorine dioxide gas may be summarized as follows:

- There is no upper concentration limit for the explosion of chlorine dioxide gas, but the low concentration limit for explosion has been found to be 9.5% ( $[\text{ClO}_2]/[\text{air}]$ ). Thus, when the concentration of chlorine dioxide gas in air is below 9.5% it does not present an explosion hazard.
- The induction time and the maximum pressure of explosion relative to the initial pressure are dependent on the concentration of chlorine dioxide gas. The higher the concentration of chlorine dioxide gas, the greater the pressure of explosion, and the shorter the induction times. When the concentration of chlorine dioxide is 10%, the induction time is 2195 ms and the maximum pressure of explosion relative to the initial pressure is 0.024 MPa; when the concentration is 90%, however, the induction time is 8 ms and the maximum pressure of explosion relative to the initial pressure is 0.641 MPa.
- The explosive decomposition of  $\text{ClO}_2$  is of a degenerate chain-branching type involving the formation of a stable intermediate ( $\text{Cl}_2\text{O}_3$ ), from which chain-branching occurs. Chain initiation takes place at the point of ignition, and termination takes place on the inner walls of the exploder.

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