

# The study of reaction of 1,2-dichlorobenzene with ozone

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## ABSTRACT

The reaction of 1,2-dichlorobenzene with ozone have been conducted. FTIR and GC/MS were applied to analyze the sample solution at various reaction time. New vibrational absorptions were observed in IR spectrum contained C=O and O-H functional groups after ozone passes through 1,2-dichlorobenzene. At the end of the reaction, a brown precipitate was produced. The IR spectrum detected new peaks of the stretching vibration of =C-H, C=C, C=O and O-H. Precipitate was dissolved in different solvents and measured by GCMS, many high molecular weight products were detected. It shows that there may be a polymerization reaction after the reaction between 1,2-dichlorobenzene and ozone.

**KEYWORDS:** VOC, 1,2-dichlorobenzene, ozone

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## I. INTRODUCTION

Semiconductors and optoelectronics are the main production technologies in high-tech industries. The convenience brought by these industries also causes great environmental pollution. The main reason is that organic solvents are used in the production process, and the volatile organic compounds (VOCs) derived from them cause serious damage to the environment.

The current methods for treating VOCs mainly include condensation, absorption, adsorption, combustion, biodegradation, and advanced oxidation processes (AOP), etc. The condensation method has limits on the concentration of VOCs; the absorption method requires the use of solvents, which will increase pollution. The adsorption method often uses activated carbon as the adsorbent, but activated carbon that loses its effect after use will cause increased costs and secondary pollution to the environment. The combustion method can degrade organic matter, but burning produces carbon dioxide, which will make the greenhouse effect more severe. The biodegradation method often leads to the death of bacteria in many organic substances and requires a lot of time to cultivate, so it is not cost-effective in industry. The advanced oxidation method is widely used in wastewater treatment, the high oxidation activity can effectively destroy and decompose organic matter.

1,2-Dichlorobenzene is the main raw material for the production of herbicides which will remain in soil or sediment. The dichlorobenzene in the soil is hard to be decomposed by organic matter in the soil, in turn, it will be then absorbed by plants or fish. Inhaling or ingesting related dichlorobenzene compounds can cause damage to the liver and can also affect the kidneys and blood.

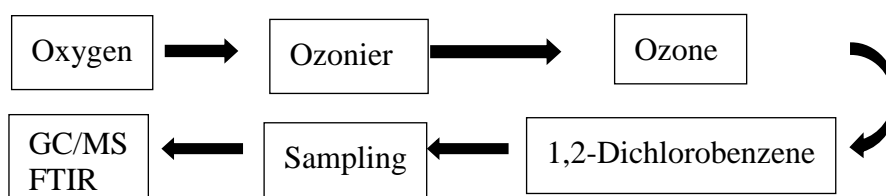
Ozone is strong oxidant and plays an important role in reaction of atmospheric chemistry. During past twenty years, the research of reaction of ozone has attracted interest<sup>[1]</sup>. There have been many studies on the reaction of benzene and dimethylbenzene with ozone<sup>[2-5]</sup>. Methyl group is an electron-donating group which is conducive to the electrophilic reaction of ozone while chlorine is an electron withdrawing group. Therefore, this study will explore the reaction between benzene ring containing electron withdrawing groups, such as 1,2-dichlorobenzene, with ozone. The analysis of the products generated after the reaction between 1,2-dichlorobenzene and ozone will help to understand the possible reaction mechanism.

## II. EXPERIMENTAL

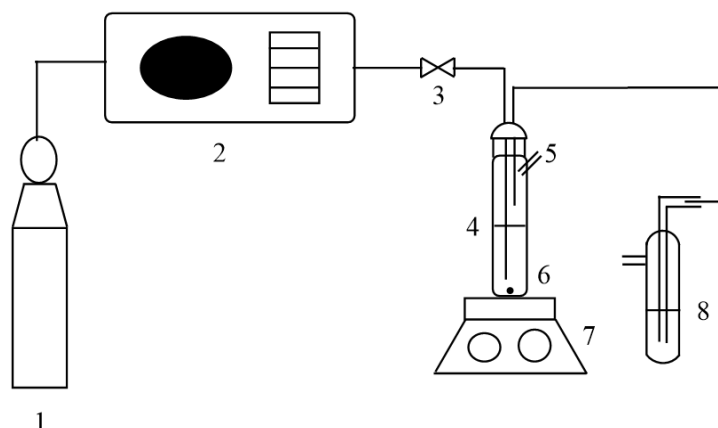
1,2-Dichlorobenzene (Aldrich, 99%) and O<sub>2</sub> (99.999%, Liu Yi Gas Co.) were used as received. Ozone were generated by silent discharge ozone generator (model AS-100, Three Oxygen Enterprise, Co., Ltd.) Infrared spectra were recorded on a Perkin Elmer Frontier L128002 FTIR spectrometer with DTGS detector and

single reflection diamond Attenuated total reflection (ATR, PIKE Miracle) sample compartment at a resolution of  $4\text{ cm}^{-1}$  with 32 scans average. GC/MS were recorded on the Agilent 6890N/Agilent 5975 SERIES MS with Agilent DB-5 column ( $0.25\text{ mm} \times 30\text{ m} \times 0.25\text{ }\mu\text{m}$ ) coupled to a quadrupole mass spectrometer (MS Detector).

The ozone was directly pass through 1,2-dichlorobenzene sample tube with a rate  $\sim 2\text{ L/min}$ , and the reacted solution were sampling 1 mL every hour. The sampling solution were then analyzed with FTIR and GC/MS. Experimental flow chart and set up are similar to previous study<sup>[6-8]</sup>, and show in Figure 1 and Figure 2, respectively.



**Figure 1** Experimental flow chart of ozone passing through 1,2-dichlorobenzene.



- |                                    |                  |
|------------------------------------|------------------|
| 1. Oxygen gas                      | 5. Sampling port |
| 2. Ozone generator                 | 6. Magnetic stir |
| 3. Control valve                   | 7. Hot plate     |
| 4. 1,2-Dichlorobenzene sample tube | 8. Oil tube      |

**Figure 2** Experimental setup of reaction of 1,2-dichlorobenzene with ozone.

### III. RESULTS

#### Analysis of IR spectra

Ozone was directly passed through the 1,2-dichlorobenzene liquid and the color of the reaction solution was changed with time, as shown in Figure 3. When the reaction time exceeds over 13 hours, oil droplets were observed. The reaction solution stand for 4 to 5 days, brown precipitate was appeared. Infrared spectra of 1,2-dichlorobenzene after ozone passing through at various time were summarized as Figure 4. The peak shape was observed a slightly change near the peak at  $1747\text{ cm}^{-1}$  and  $3400\text{ cm}^{-1}$  which is in the range of C=O and O-H stretching vibrational absorption, respectively, suggested the product may contain C=O and -OH functional group. The intensity of these two peaks were increased with reaction time, indicating the amount of product was increased.

The IR spectrum of brown precipitate was compared with 1,2-dichlorobenzene, as Figure 5, Parent bands of 1,2-dichlorobenzene were disappeared and several distinct new peaks were observed at  $893\text{ cm}^{-1}$ ,  $1636\text{ cm}^{-1}$ ,  $1727\text{ cm}^{-1}$ ,  $3212\text{ cm}^{-1}$ , and a broad band of  $1350\text{ cm}^{-1}$  to  $1000\text{ cm}^{-1}$ . Peak of  $893\text{ cm}^{-1}$  is in the range of bending vibration mode of C=C-H,  $1636\text{ cm}^{-1}$  is in the range of stretching vibration mode of C=C,  $1727\text{ cm}^{-1}$  is in the range of C=O stretching vibration mode, and  $3212\text{ cm}^{-1}$  is in the range of -OH stretching mode. Table 1 summarized the new absorption peak after reaction and brown precipitation.

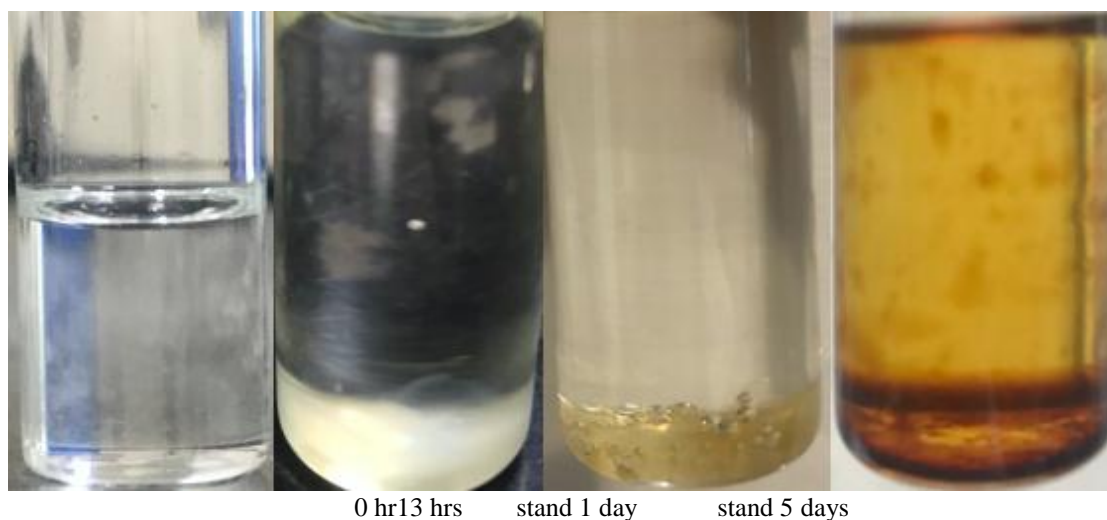


Figure 3 The color change of 1,2-dichlorobenzene/O<sub>3</sub> solution at varied time.

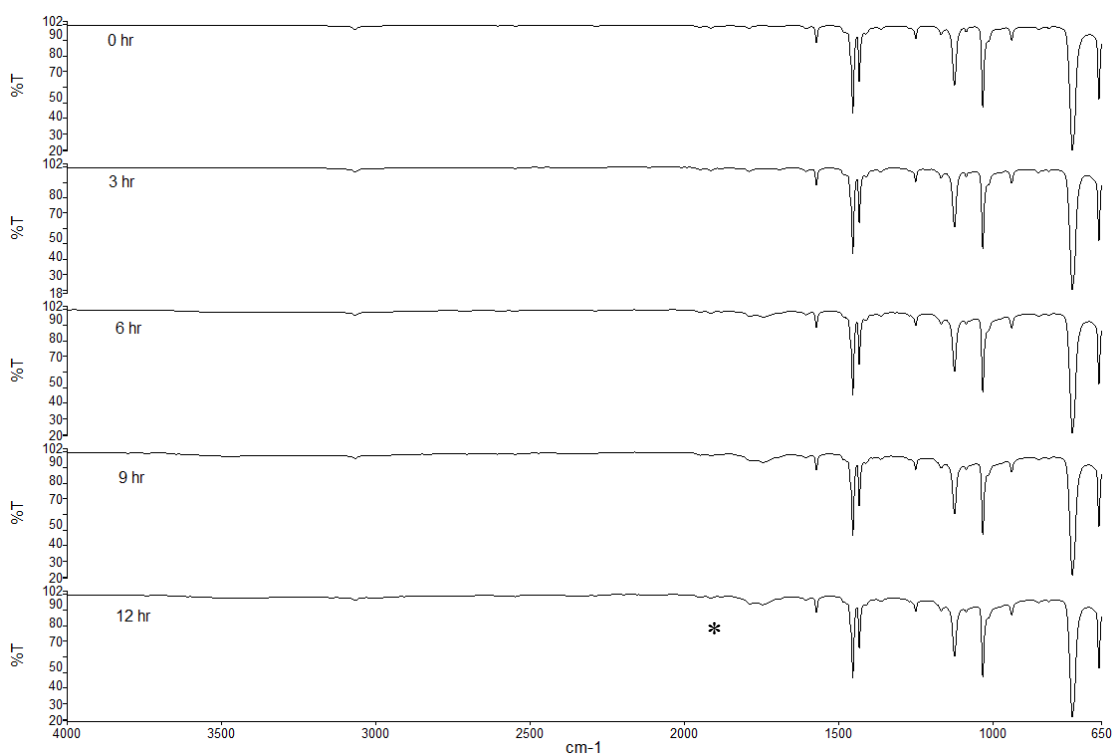


Figure 4. Infrared spectra of reaction solution after ozone passing through 1,2-dichlorobenzene at various time. \* represents a new peak

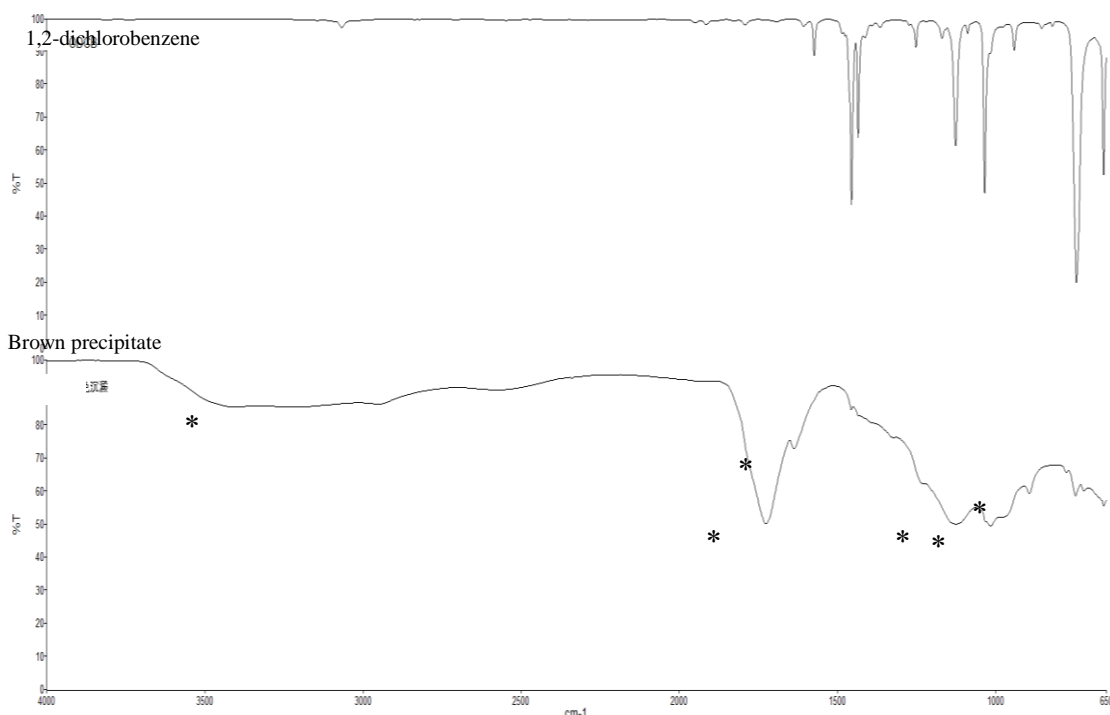


Figure 5. The comparison of infrared spectrum of brown precipitate with 1,2-dichlorobenzene. \* represents a new peak

Table 1. The position ( $\text{cm}^{-1}$ ) of new peak in IR after ozone passing through 1,2-dichlorobenzene and brown precipitate.

Reaction > 13 hrs	brown precipitate	assignment
	893	=C-H out-of-plane bending ( $900-690 \text{ cm}^{-1}$ )
	1636	C=C stretching ( $1660-1600 \text{ cm}^{-1}$ )
1747	1727	C=O stretching ( $1650-1750 \text{ cm}^{-1}$ )
3400	3212	O-H stretching ( $3200-3500 \text{ cm}^{-1}$ )

### The GC/MS analysis at various reaction time

The GC spectra at various reaction time were summarized as Figure 6. After ozone passed through 1,2-dichlorobenzene for 1 hour, a new peak was observed at retention time 1.151 min with corresponding  $m/z$  is 44 as shown in Figure 7. Analyzed the MS spectrum, suggested the product might be  $\text{CO}_2$ . The peak area variation of this new peak was summarized as Figure 8, its intensity was increased with reaction time and indicated a stable product was formed. In the meantime, the brown precipitate was dissolved in acetone and ethanol and use GC/MS spectrum to identify the molecular structure of the precipitated compounds. Figure 9 and Figure 10 were GC spectra and corresponding MS spectra of the precipitate dissolved in acetone solvent, respectively. The GC and MS spectra of the brown precipitate dissolved in ethanol solvent was shown in Figure 11 and Figure 12, respectively. For the GC spectra of acetone solution, there are five new peaks were observed at retention time 2.222 min, 2.917 min, 3.403 min, 3.593 min, and 6.360 min with corresponding  $m/z$  value of 98, 98, 184, 193, and 152, respectively. For the ethanol solution, five new peaks were detected at retention time 2.462 min, 2.948 min, 3.311 min, 3.925 min, and 6.385 min with corresponding  $m/z$  value of 57, 103, 177, 74, and 168, respectively. Table 2 summarized the retention time and corresponding  $m/z$  value of new peaks of GC/MS spectra of brown precipitate dissolved in acetone and ethanol.

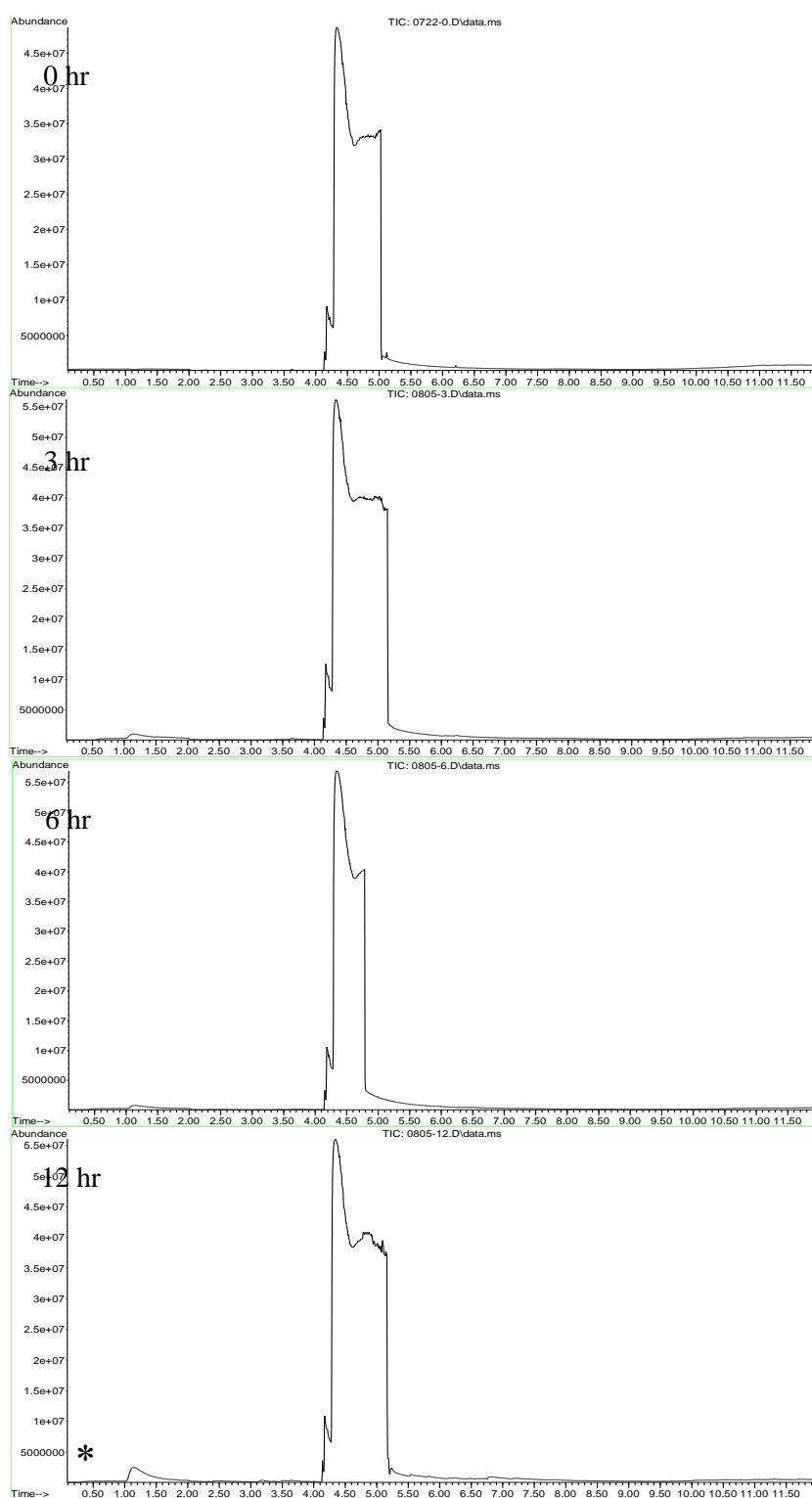


Figure 6. The GC spectra of 1,2-dichlorobenzene before and after O<sub>3</sub> passing through at various time.

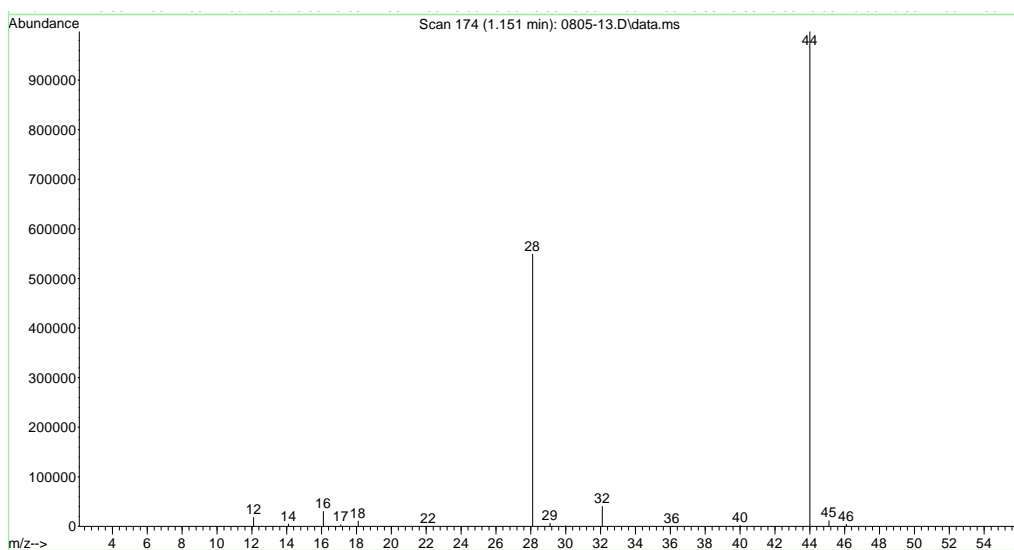


Figure 7. The MS spectrum of new peak at retention time 1.51min after ozone passing through 1,2-dichlorobenzene over 13 hrs.

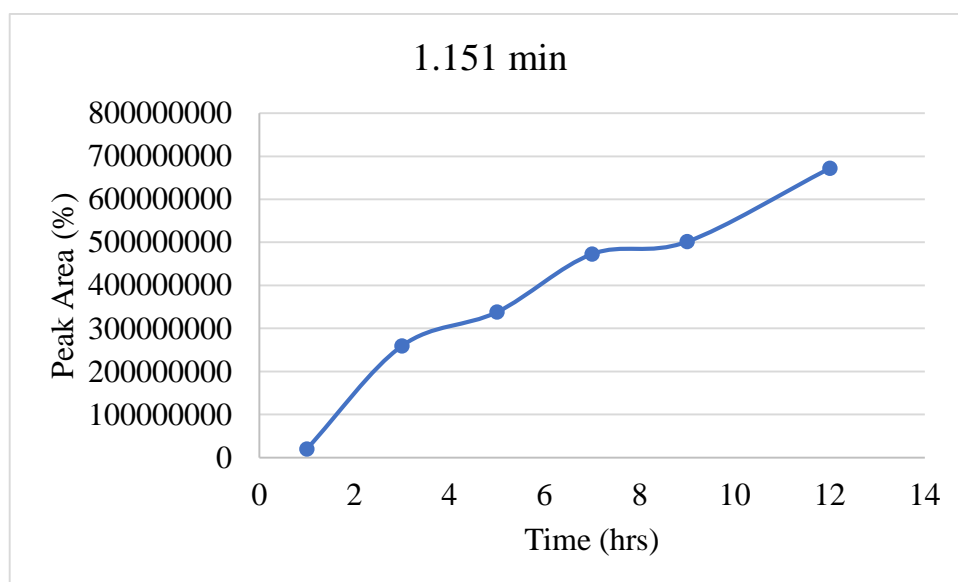


Figure 8. The peak area of retention time 1.151 min varied with reaction time of 1,2-dichlorobenzene/O<sub>3</sub> reaction.

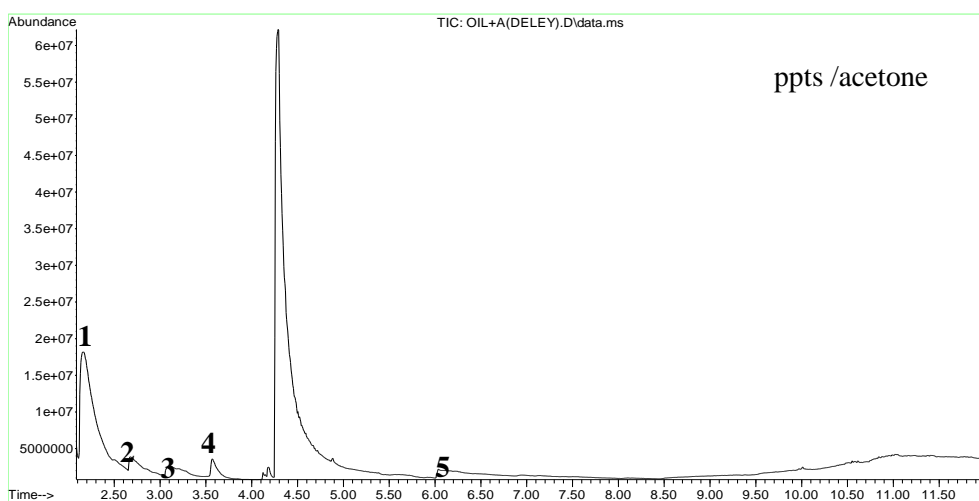
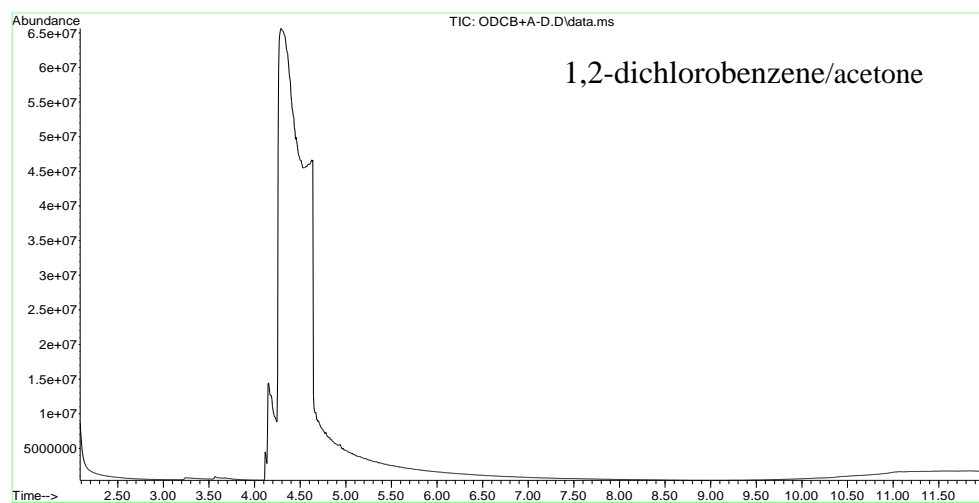


Figure 9. The GC spectra of 1,2-dichlorobenzene and brown precipitate dissolved in acetone.

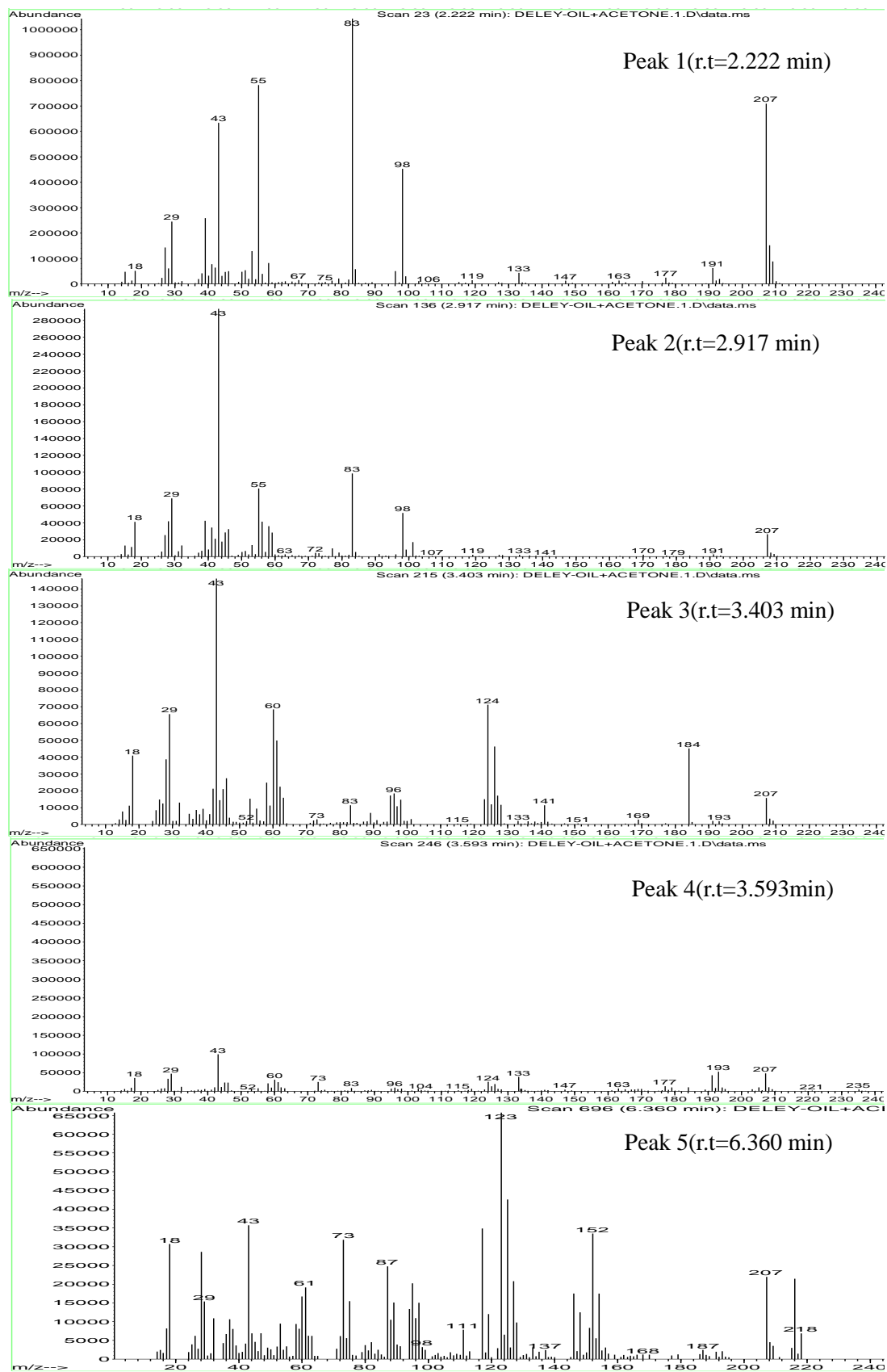


Figure 10. The MS spectra corresponded to GC spectra of brown precipitate dissolved in acetone.



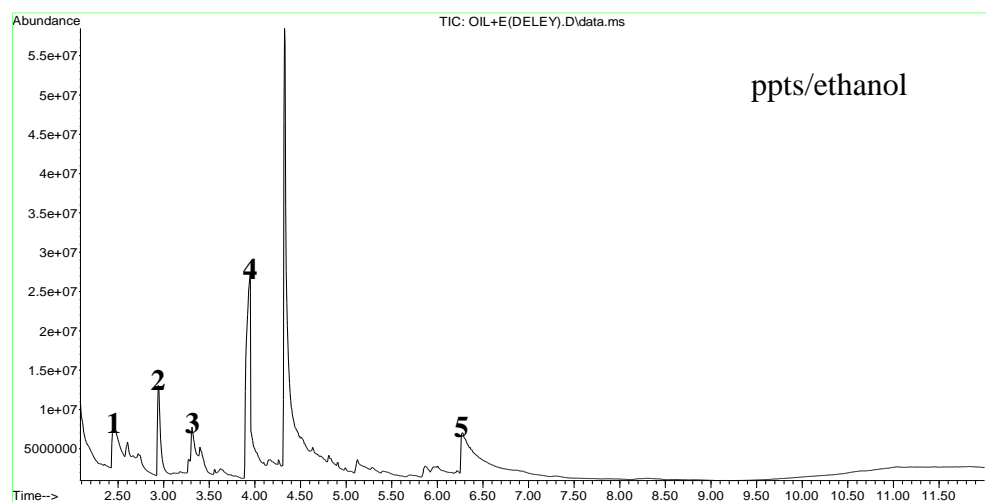
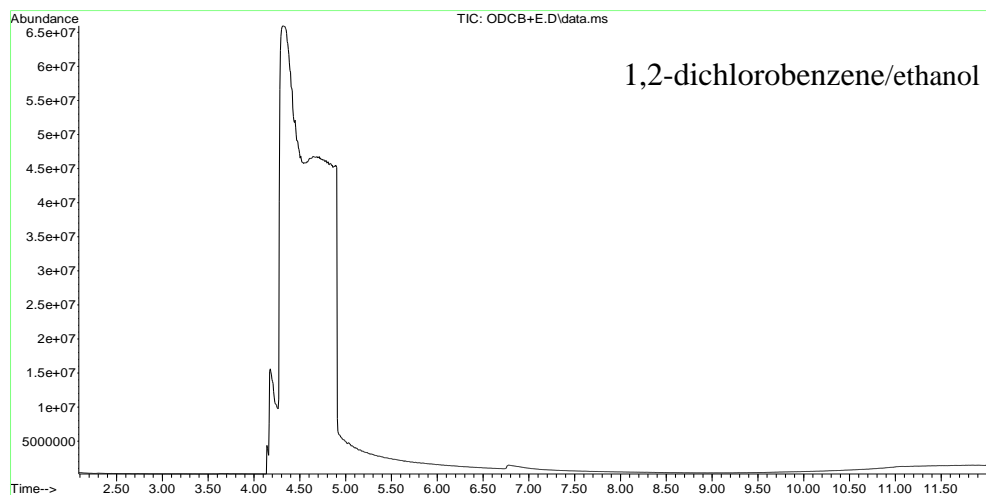


Figure 11. The GC spectra of 1,2-dichlorobenzene and brown precipitate dissolved in ethanol.

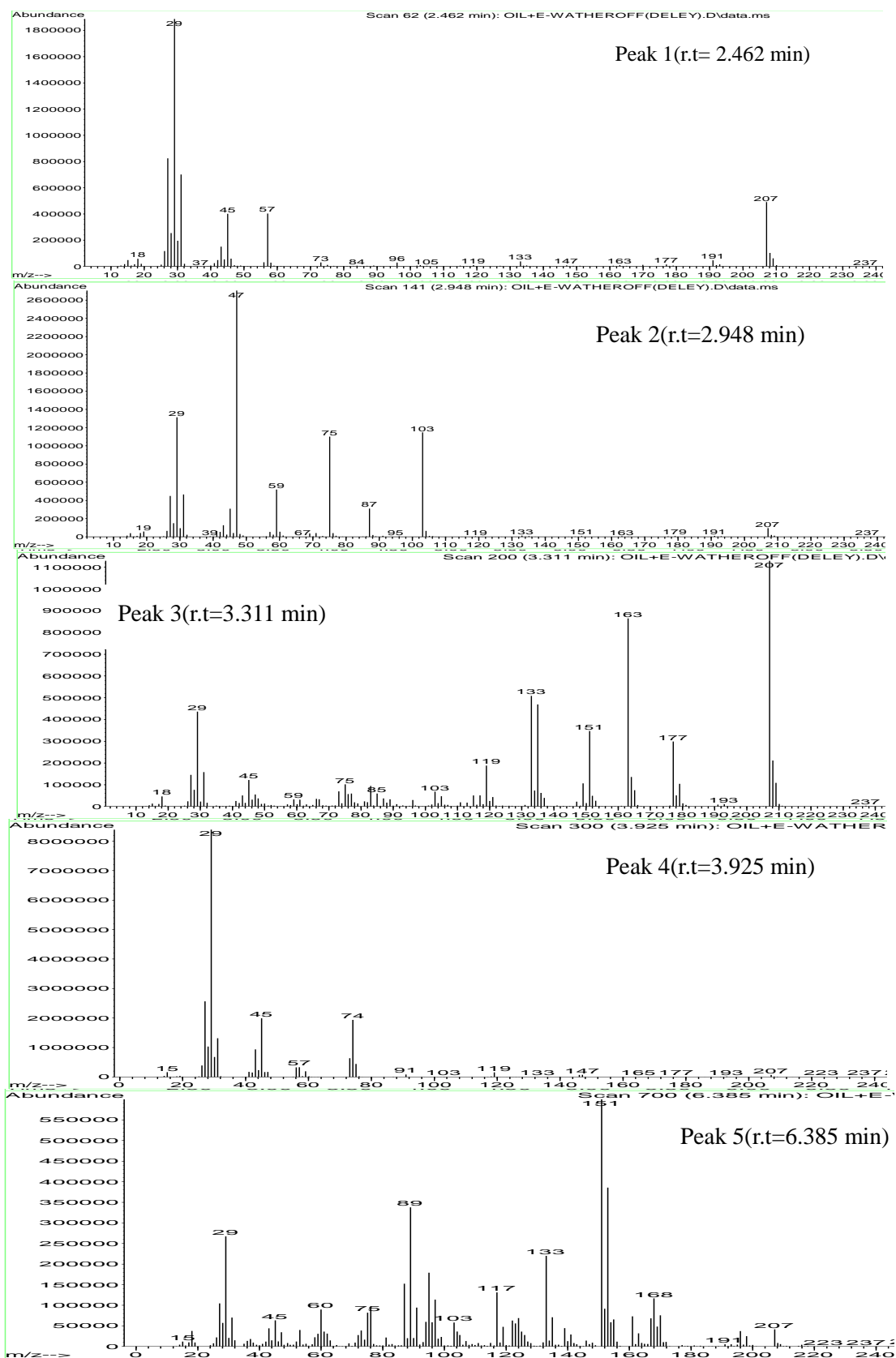


Figure 12. The MS spectra corresponded to GC spectra of brown precipitate dissolved in ethanol.

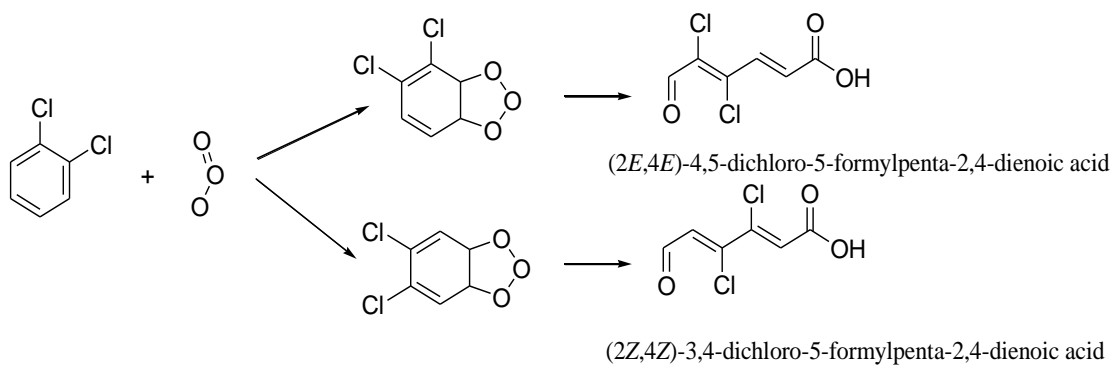
Table 2 The retention time and corresponding m/z value of new peaks of GC/MS spectra of brown precipitate dissolved in acetone and ethanol.

ppts/acetone		ppts/ethanol	
r.t. (min)	m/z	r. t. (min)	m/z
2.222	98	2.462	57
2.917	98	2.948	103
3.403	184	3.311	177
3.593	193	3.925	74
6.360	152	6.385	168

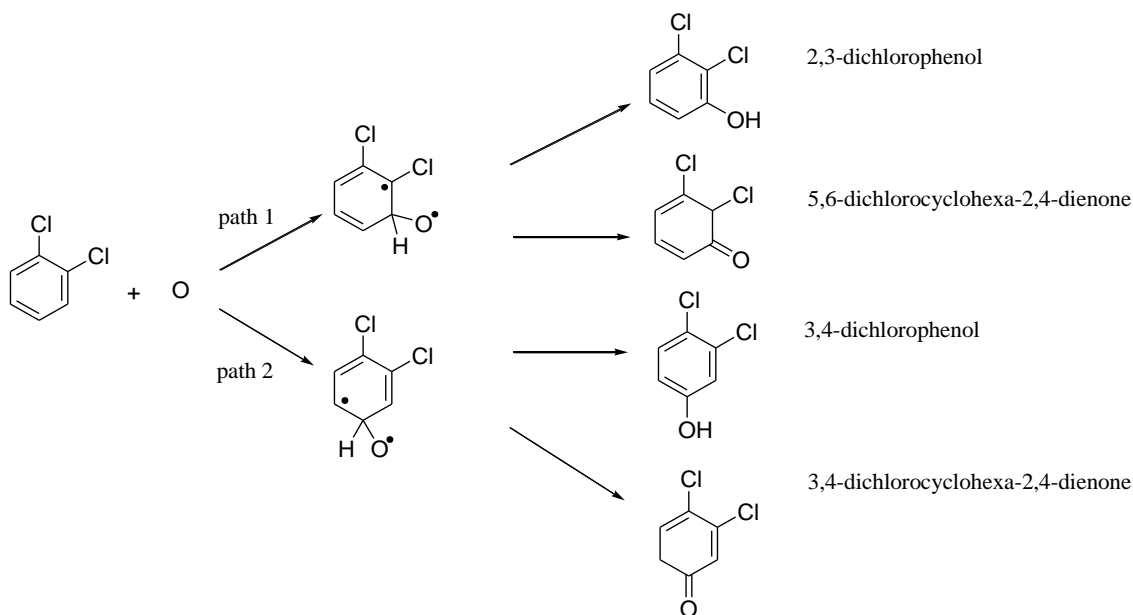
ppts : precipitates, r.t. : retention time

#### IV. Discussions

The reaction of ozone with organic compound has two possible reaction paths. One is the direct addition of  $O_3$  to the double bond to form a cyclization reaction, and then under electron transfer and bond breaking to form the final product. The other path is ozone to decompose into  $O_2$  molecule and  $O$  atom, and the oxygen atom then react with compounds. Refer to the reaction of ozone with o-xylene<sup>[3,5,9]</sup>, the reaction mechanism of 1,2-dichlorobenzene with ozone may be proposed as Scheme I and Scheme II.



Scheme I The reaction mechanism of 1,2-dichlorobenzene with ozone.



Scheme II The reaction of oxygen atoms with 1,2-dichlorobenzene.

If ozone is directly added to the benzene ring (Scheme I), the possible products are 4,5-dichloro-5-formylpenta-2,4-dienoic acid and 3,4-dichloro-5-formylpenta-2,4-dienoic acid. Both compounds have the molecular weight 194 which was not found in the GC/MS spectra. The reaction of oxygen atom with 1,2-dichlorobenzene (Scheme II) may produce 2,3-dichlorophenol, 5,6-dichloro-2,4-cyclohexadienone, 3,4-dichlorophenol and 3,4-dichloro-2,4-cyclohexadienone, etc., all the products with molecular weight of 162 which were not found in the GC/MS spectra. It is suggested that the reaction mechanism may be different from the reaction of o-xylene with ozone. The GCMS diagram of the reaction solution at different reaction times only detected the signal at 1.51 min with m/z 44 and increased the intensity with reaction time. Analyzed the MS spectrum, suggested the product might be CO<sub>2</sub>, while the IR spectrum did not detect the characteristic absorption peak of CO<sub>2</sub>. This may be due to the concentration of the product is too low resulted in the IR absorption peak is not obvious. Therefore, the identify of this peak need further information. At the end of the reaction, a brown precipitate will be produced. The precipitate was dissolved in different solvents, many high molecular weight products are detected by GCMS, indicating that there may be a polymerization reaction after the reaction of 1,2-dichlorobenzene and ozone. The current data cannot confirm the possible reaction path and further purification and analysis is necessary to determine its reaction mechanism.

## V. Conclusion

This research was applied IR and GC/MS to explore the reaction between ozone and 1,2-dichlorobenzene. New peaks of C=O and O-H stretching vibration absorption were found in the IR spectrum. The GC/MS spectrum detected that the molecular weight of the new peak did not agree with the expected molecular weight of product. A brown precipitate was produced at the end of the reaction. Precipitate was dissolved in different solvents and measured GCMS spectrum. Many high molecular weight products were detected in GCMS, showing that there may be a polymerization reaction after the reaction between 1,2-dichlorobenzene and ozone. The current data cannot confirm the possible reaction path. Further purification and analysis should need for determining the reaction mechanism.

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