

The study of reaction of isoprene with ozone

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ABSTRACT

The reaction of isoprene with ozone have been conducted. The reaction samples were analyzed by FTIR and GC/MS at various time. After reaction, new observed absorptions in IR spectrum included -OH, C=O, and C-O vibrational modes combined with the fragment analysis of new observed peaks of GC/MS spectrum, indicated the isolated products are formaldehyde, methacrolein, methyl vinyl ketone, 3-methylfuran, 3,4-epoxy-3-methyl-1-butene, 3,4-epoxy-2-methyl-1-butene, methacrylic acid, and methyl-1,2,3,4-diepoxybutane. These products were resulted in three possible reaction paths, reaction of isoprene with O₃ (as Scheme I), isoprene with O atom (as Scheme III), and isoprene with OH and O₂ (as Scheme IV).

KEYWORDS: VOC, IR, isoprene, ozone

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I. INTRODUCTION

The production of volatile organic compounds (VOCs) can be artificial and natural source. Artificial mainly come from fuel combustion and transportation, such as industrial waste gas, automobile exhaust, photochemical pollution, etc. However, the VOCs emitted by plants are much higher than those emitted by human, indicated that biologically volatile organic compounds (BVOCs) have a certain degree of contribution to the generation of secondary organic aerosols. BVOCs included the VOCs emitted by plants, animals, and microorganism. Most BVOCs are produced by plants^[1] and the main compound is isoprene. Compared with other VOCs, the emission of isoprene is higher with year production of 594 (±34) tons, ~ 62.2 % relatively contribution^[2].

Isoprene is the largest VOC released by biological arrangement, and is one of the important raw materials in the rubber industry. Its main source of production is through C₅ fraction of the by-product in the process of high temperature cracking of petroleum hydrocarbons to ethylene. In recent years, isoprene has been used in the synthesis of linalool, squalene, etc., which are intermediates for the further synthesis of spice, medicines, pesticides, etc. Although the amount of this aspect is relatively small, it has been paid attention.

Both liquid and vapor isoprene can cause irritation to the eyes, nose, and throat. Short-term exposure may cause central nervous system effects, leading to respiratory depression and decreased consciousness. Long-term exposure may cause effects on the lungs. Isoprene may be carcinogenic to humans and cause genetic damage to human germ cell. 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^[3]. Many reactions such as the decomposition of organic compounds, oxidation of sulfur oxide, and conversion of NO_x are related with ozone.

Therefore, this research will apply FTIR and GCMS to study the reaction of isoprene with ozone. The isolation of products will be helpful for understanding the reaction mechanism.

II. EXPERIMENTAL

The sample of isoprene (99%, Alfa) and O₂ (99.999%, Liu Yi) were used as received. Ozone was 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 ATR sample component at a resolution of 4 cm⁻¹ with 8 scans average. GC/MS were recorded on a Shimadzu GC-2030 (FID) Gas Chromatograph/Shimadzu GCMS-QP2020 NX with SH-Rxi-5Sil MS column (0.25 mm x 30 m x 0.25 μm).

The ozone was directly pass through isoprene sample tube with a rate ~ 1 L/min, and the reacted solution were sampling 1 mL every 5 minutes. The sampling solution were then analyzed with FTIR and GC/MS. Experimental set up and flow chart are similar to previous study^[4], and show in figure 1 and 2, respectively.

1. Oxygen gas
2. Ozone generator
3. Isoprene sample tube
4. Sampling port
5. Magnetic stir
6. Hot plate
7. Oil tube

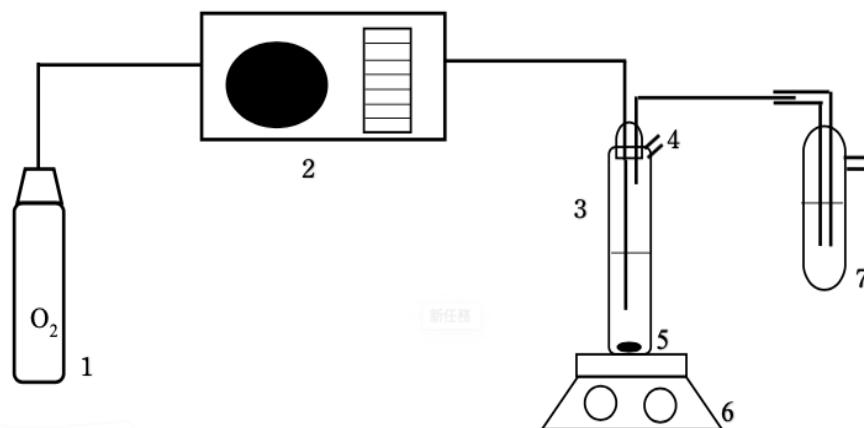


Figure 1 Experimental setup of reaction of ozone with isoprene.

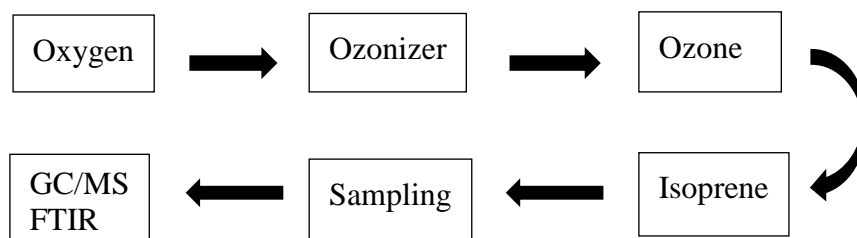


Figure 2 Experimental flow chart of ozone passing through isoprene liquid.

III. RESULTS

The absorption positions of isoprene blank IR spectrum was consistent with literature spectra^[5] and summarized in table 1. After ozone passing through isoprene sample tube and sampling every 5 minutes, many new peaks were observed, the change in IR spectra and absorption position of new bands at various time were summarized in figure 3 and table 2, respectively. New observed bands included 3415 cm^{-1} , 2974 cm^{-1} , 1764 cm^{-1} , 1731 cm^{-1} , 1710 cm^{-1} , 1678 cm^{-1} , 1448 cm^{-1} , 1413 cm^{-1} , 1372 cm^{-1} , 1351 cm^{-1} , 1321 cm^{-1} , 1198 cm^{-1} , 1167 cm^{-1} , 1139 cm^{-1} , 1111 cm^{-1} , 1046 cm^{-1} , 992 cm^{-1} , 927 cm^{-1} , 891 cm^{-1} , 759 cm^{-1} , and 682 cm^{-1} . The intensities of these new bands are increased with reaction time. The peaks of parent band at 2963 cm^{-1} , 2857 cm^{-1} , 2838 cm^{-1} , 1454 cm^{-1} , 1439 cm^{-1} , 1377 cm^{-1} , 1148 cm^{-1} , 990 cm^{-1} , and 889 cm^{-1} were disappeared as increase in reaction time. The peak of 3415 cm^{-1} is belong to the range of -OH stretching vibrational mode. Band of 2974 cm^{-1} can be easily assigned as the C-H stretching mode. The peak of 1764 cm^{-1} , 1731 cm^{-1} , and 1710 cm^{-1} are belong to the range of C=O stretching vibrational mode, therefore these bands can be assigned as C=O stretching mode. The range of C=C stretching mode is in the range of 1600 cm^{-1} to 1680 cm^{-1} , therefore, the peak of 1678 cm^{-1} can be assigned as the vibrational of C=C stretching mode. The frequency of C-O stretching is in the range of 1050 cm^{-1} to 1250 cm^{-1} , therefore, the new bands of 1198 cm^{-1} , 1167 cm^{-1} , 1139 cm^{-1} , 1111 cm^{-1} , and 1046 cm^{-1} can be easily assigned as C-O stretching mode. The other bands at 927 cm^{-1} , 759 cm^{-1} , and 682 cm^{-1} can be assigned as C-H bending vibrational frequencies.

When ozone passed isoprene for 7.5 minutes, eight new peaks were observed in GC spectrum as Figure 4. The retention time of new peak and corresponding MS spectrum were summarized as Figure 5. When ozone passing through isoprene for 2.5 minutes, 6 new peaks were observed at retention time 1.537 min, 1.775 min, 1.827 min, 1.902 min, 1.956 min, and 3.556 min with corresponding $m/z = 30, 70, 70, 82, 84, \text{ and } 100$, respectively. After 5 minutes, further two new peaks were detected at retention time 2.147 min and 2.748 min with corresponding m/z is 84 and 86, respectively. As reaction last 7.5 min, no further new peak was

detected.

Analysis the fragment of MS spectrum of new peaks, suggested these new peaks might be product offormaldehyde, methacrolein (MAC),methyl vinyl ketone (MVK), 3-methylfuran, 3, 4-epoxy-3-methyl-1-butene, methacrylic acid and 2-methyl-1,2,3,4-diepoxybutane as listed in Table 3. Figure 6 indicated the intensities of these new peaks were increased with reaction time, represent the products are stable.

Table1The position of infrared absorptions (cm^{-1})of isoprene.

This work*	Literature ^a	Calculated ^b	Assignment
—	3101	3104	asy =CH ₂ str
3086 (m)	3091	3093	asy =CH ₂ str
—	—	3018	asy CH ₃ str
—	—	3012	sy =CH ₂ str
—	3017	3001	CH str
—	—	2996	sy =CH ₂ str
2963 (s)	2985	2988	asy CH ₃ str
2923 (vs)	—	2913	sy CH ₃ str
2880 (sh)	—	—	—
2857 (m)	—	—	—
2838 (vw)	—	—	—
1784 (vw)	—	—	—
1645 (s)	—	1646	C=C str
1598 (m)	1604	1600	asy C=C str
—	1467	1478	CH ₃ def
1454 (s)	1444	1454	asy CH ₃ def
1439 (s)	1428	1435	=CH ₂ sci
—	1417	1407	=CH ₂ sci
1377 (s)	1384	1371	sy =CH ₂ def
—	1303	1312	C-C str
—	—	1288	C-C def
1261 (w)	—	—	—
1148 (w)	—	—	—
—	1071	1075	sy CH ₃ rock
—	1069	1066	asy CH ₃ rock
—	1003	1003	=CH ₂ rock
990 (m)	992	984	CH wag
—	—	954	=CH ₂ rock
906 (m)	906	902	CH ₂ wag
889 (vs)	894	898	CH ₂ wag
824 (w)	—	—	—
802 (w)	—	—	—
783 (w)	—	777	—
—	—	764	=C-CH ₂ twist
—	—	625	=C-CH ₂ twist

*: sh: shoulder; vw: very weak; w: weak; m:medium; s: strong; vs:verystrong

^a:Gas-phase values, refer to ref. [6, 7]

^b:Refer to ref.[8]

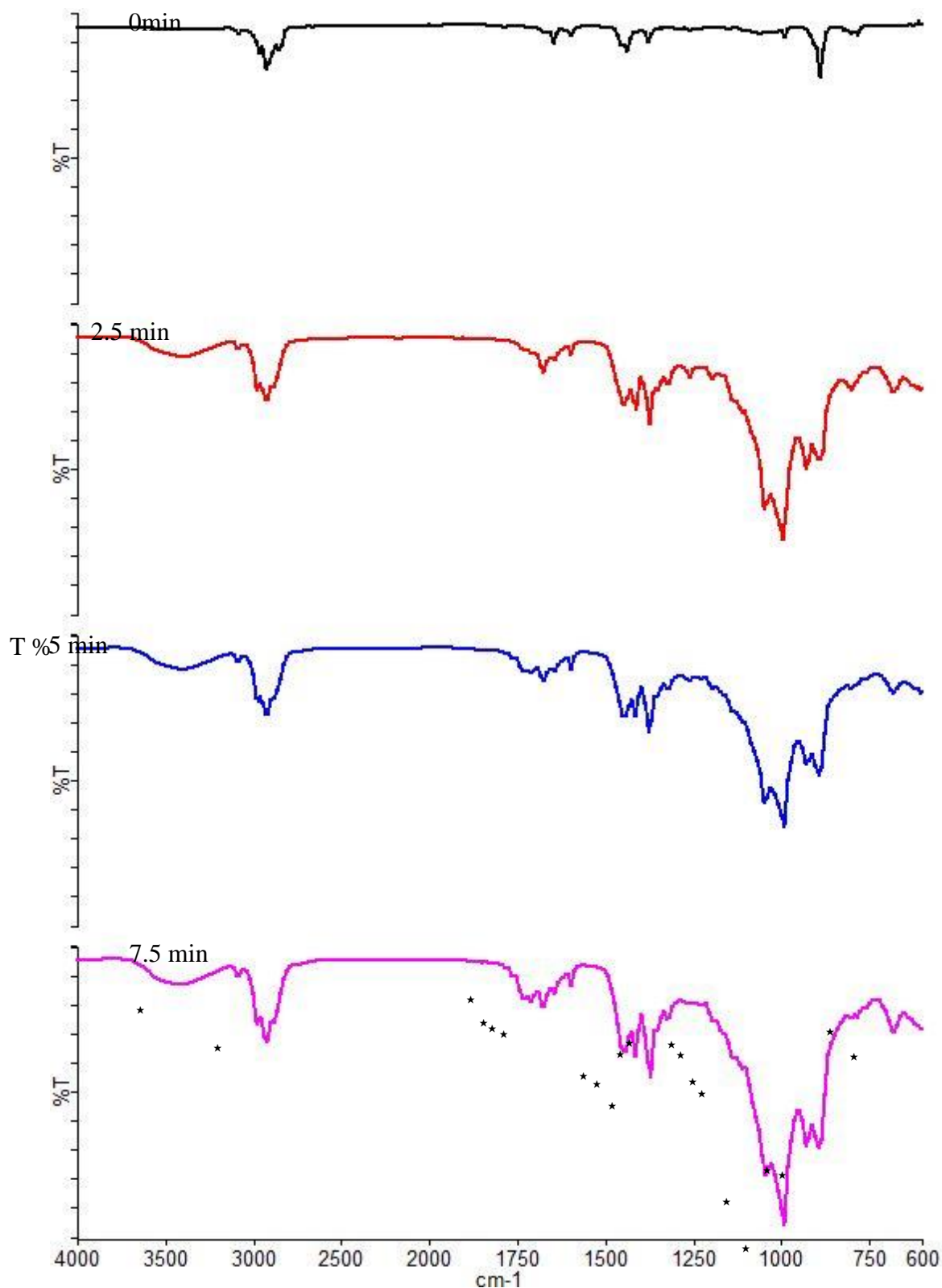


Figure 3. Infrared spectra after ozone passing through isoprene at various time.
*observed new peak

Table 2. The position of newpeak (cm⁻¹) in IR after ozone passing through isoprene at various time.

Frequency(cm ⁻¹)	assignment
3415	-OH
2974	C-H ₃
1764	C=O
1731	C=O
1710	C=O
1678	C=C
1448	=CH ₂
1413	=CH ₂
1372	C-H ₃
1351	C-H ₃
1321	C-H ₃
1198	C-O
1167	C-O
1139	C-O
1111	C-O
1046	C-O
992	=CH ₂
927	=CH ₂
891	=CH ₂
759	C-H ₃
682	C-H ₃

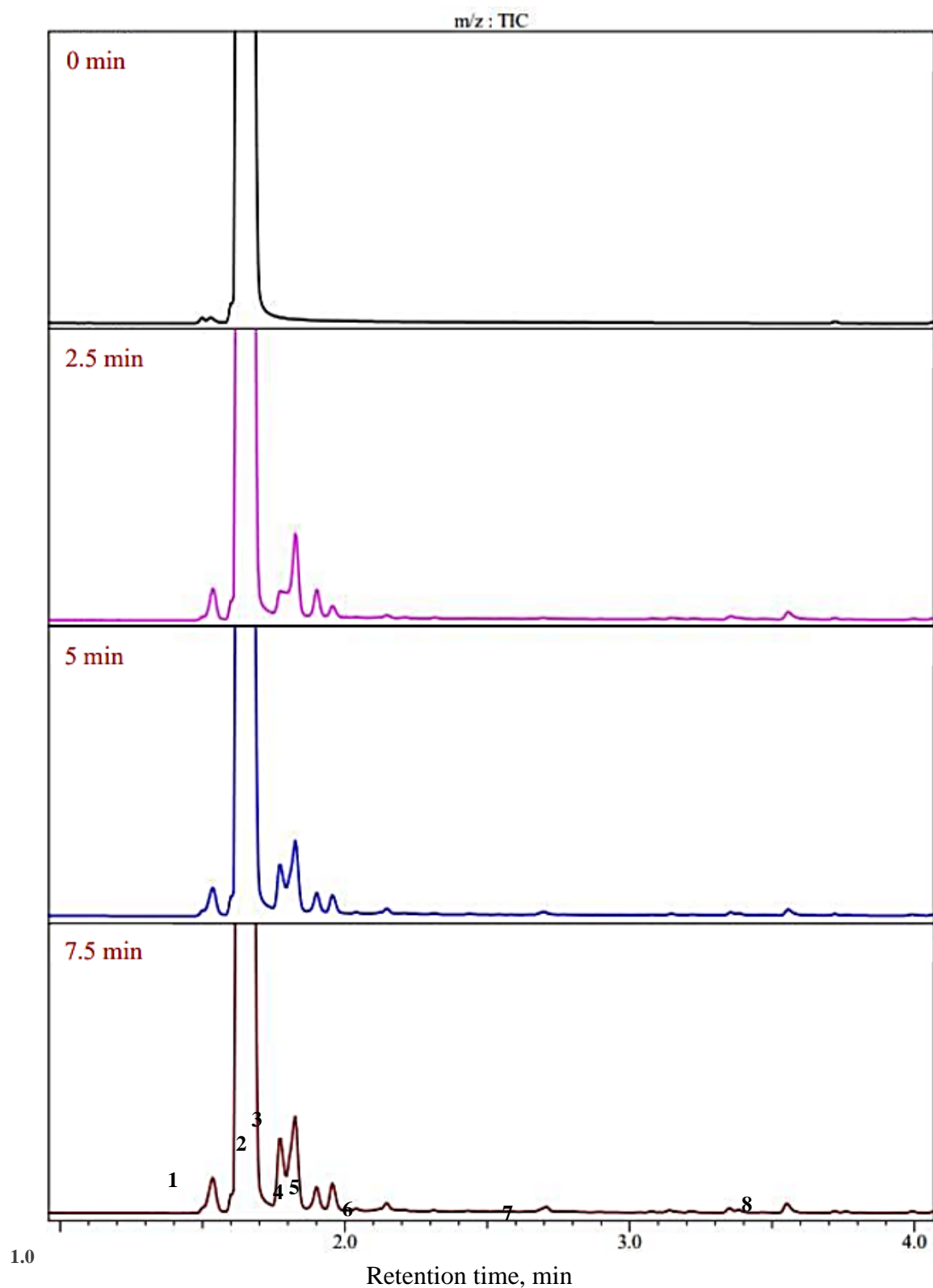


Figure 4. The GC spectra of ozone passing through isoprene at various time.

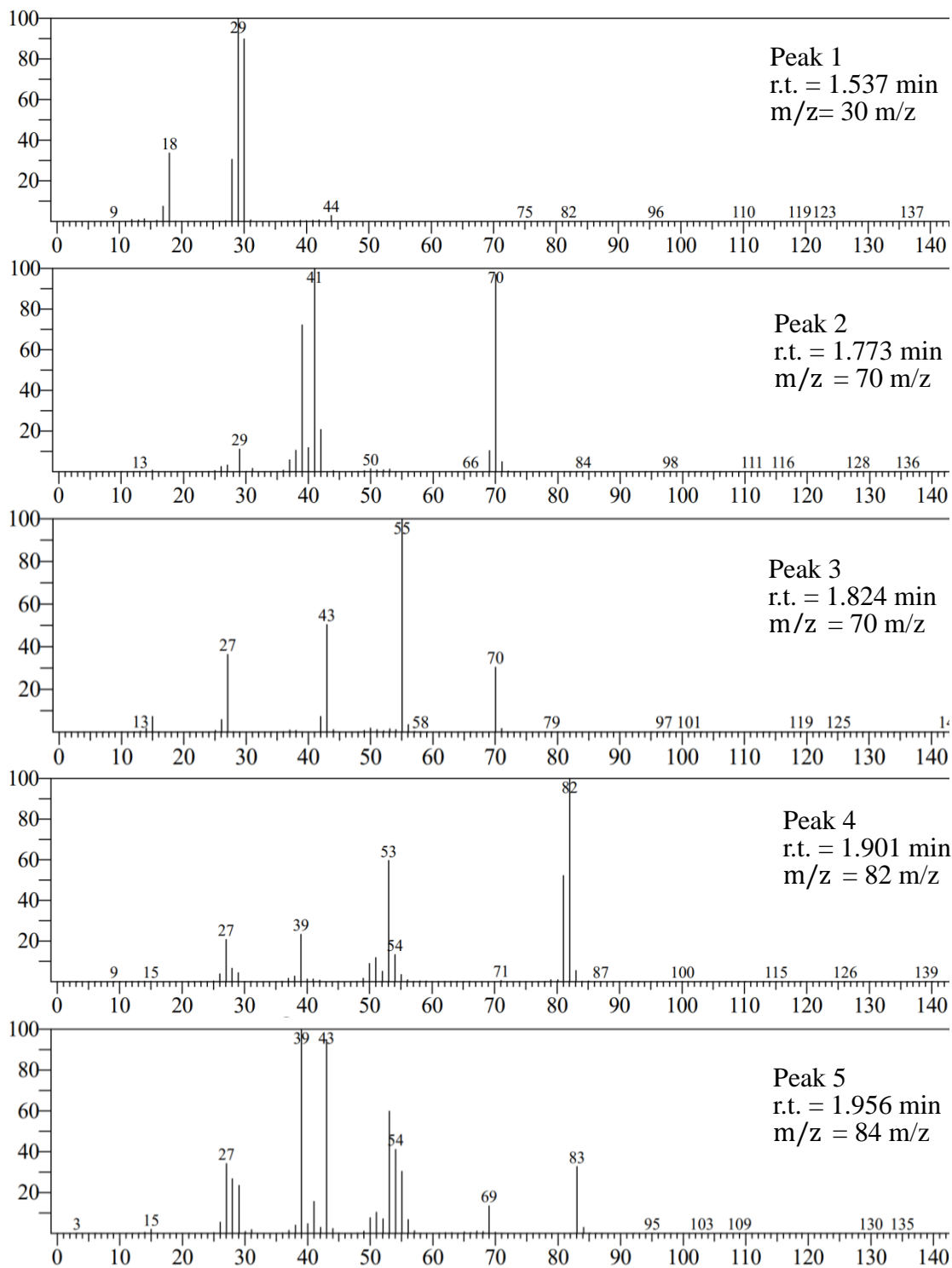


Figure 5. The mass spectra of ozone passing through isoprene after 7.5 minutes, peak number is referred to figure 4.

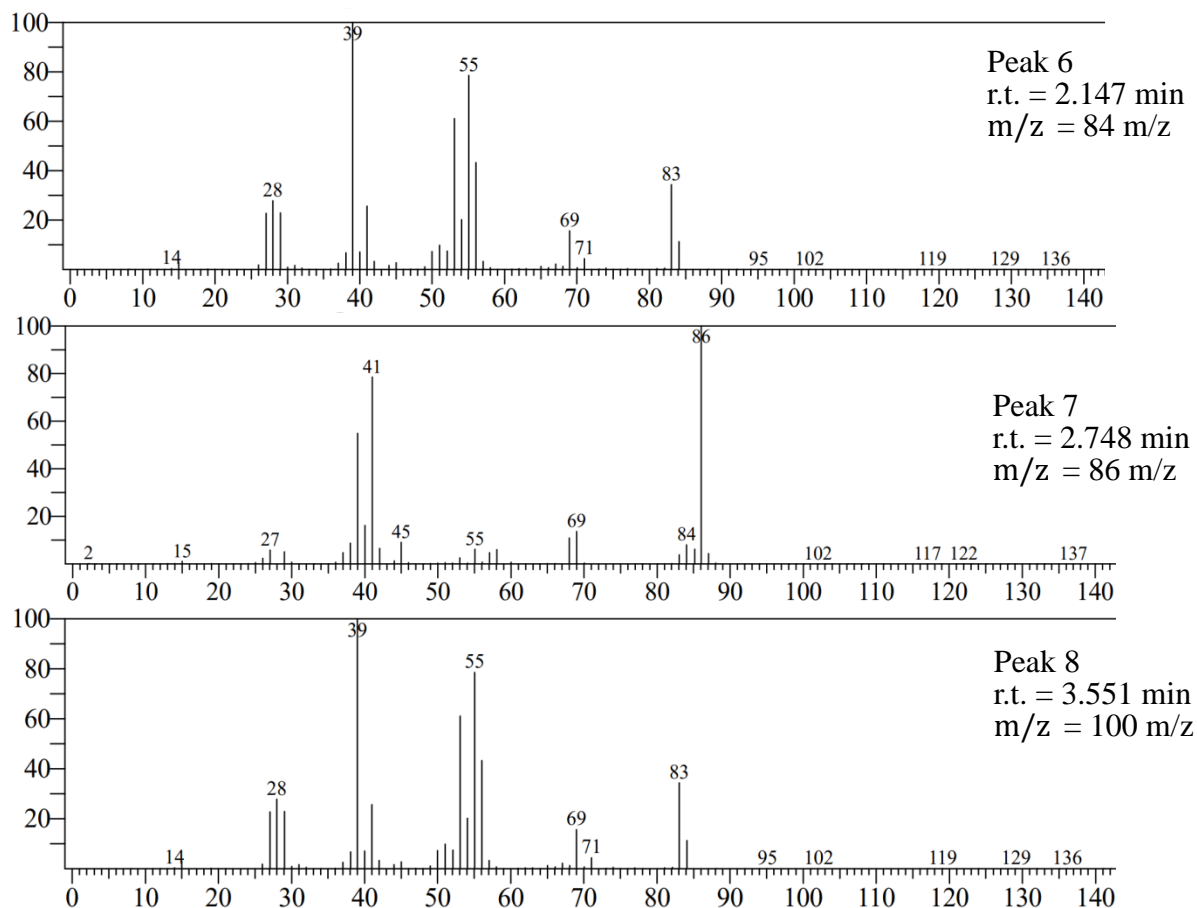


Figure 5(cont'd). The mass spectra of ozone passing through isoprene after 7.5 minutes, peak number is referred to figure 4.

Table 3. The retention time and corresponding m/z value of new peak in GC/MS spectrum after isoprene reacted with ozone at various time.

	反應時間			m/z	compound
	2.5min	5min	7.5min		
Retention time (min)	1.537	1.536	1.537	44	Formaldehyde
	1.775	1.773	1.773	70	Methacrolein
	1.827	1.826	1.824	70	Methyl vinyl ketone
	1.902	1.901	1.901	82	3-Methylfuran
	1.956	1.956	1.956	84	3,4-Epoxy-3-methyl-1-butene
		2.147	2.147	84	3,4-Epoxy-2-methyl-1-butene
		2.748	2.748	86	Methacrylic acid
	3.556	3.556	3.551	100	2-Methyl-1,2,3,4-diepoxybutane

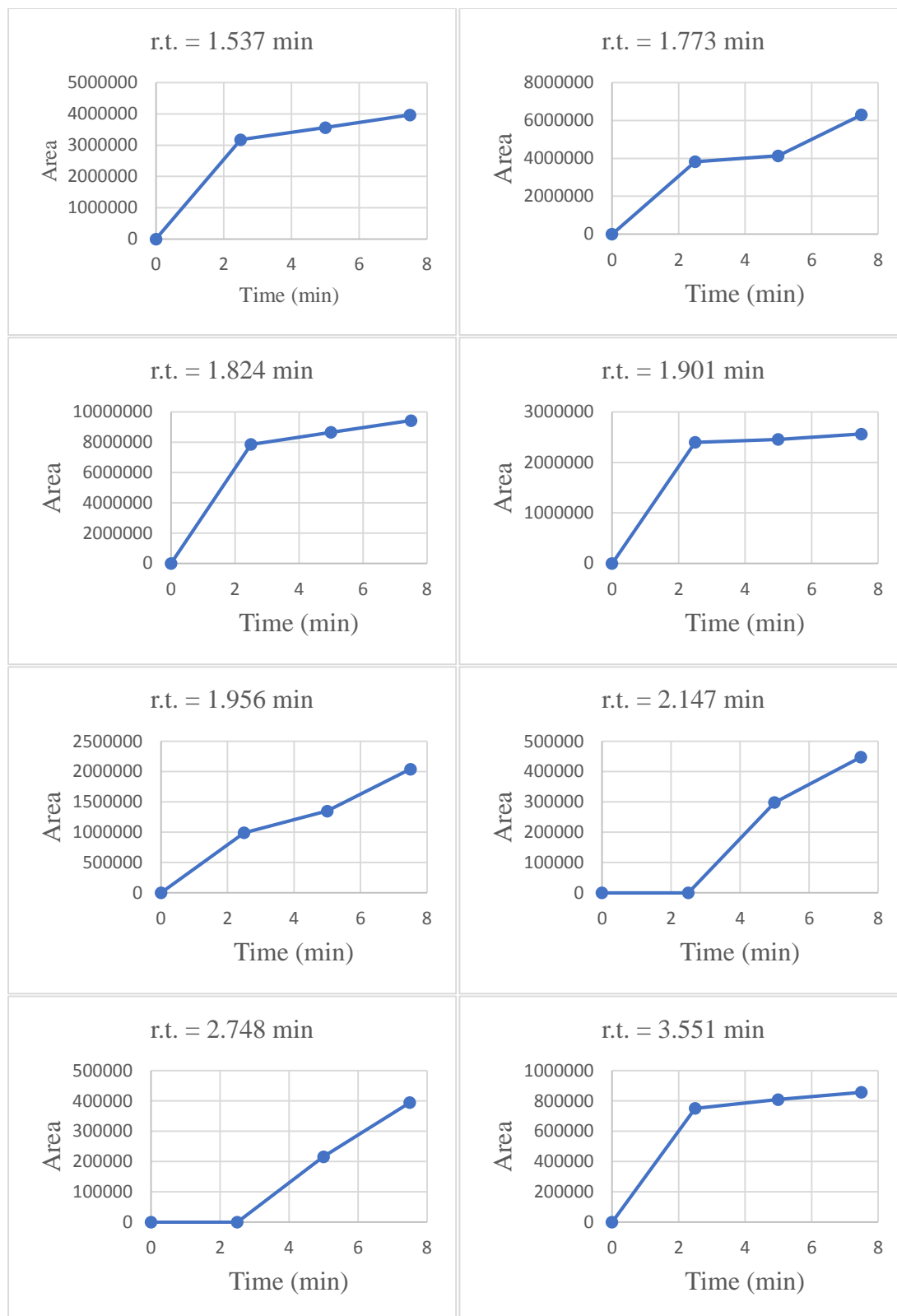


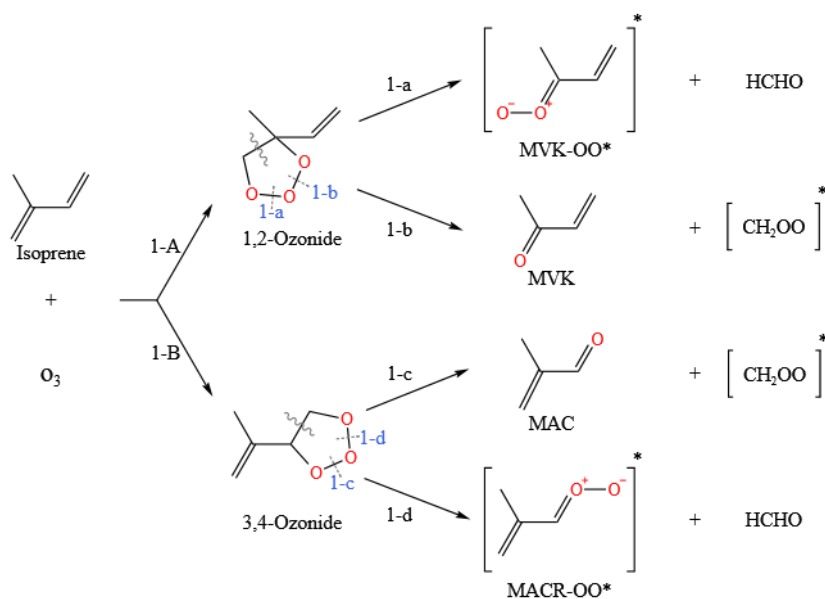
Figure 6 The curve of intensity change of new peakof GC at different retention time.

IV. Discussions

Refer to the study of Saueret al.^[9] and Wennberg et al.^[10], the reaction of mechanism of isoprene with ozone was proposed as Scheme I. The addition of ozone to isoprene has two positions, path 1-A and path 1-B. The addition through path 1-A will form 1,2-ozonide, then break via path 1-a or 1-b, path 1-a will produce

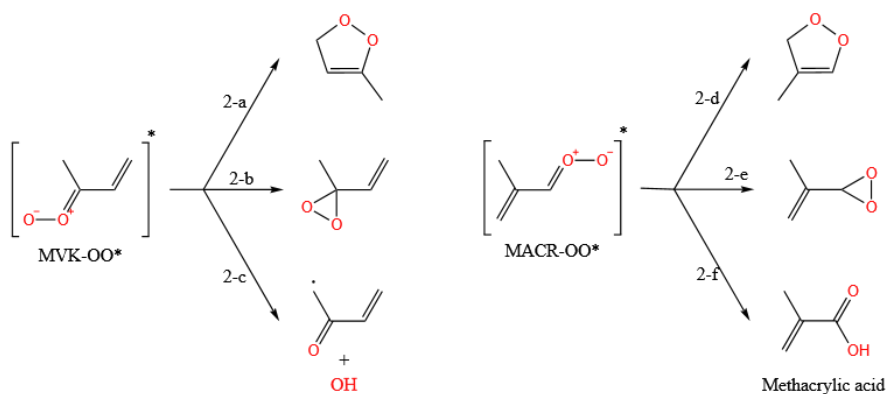
formaldehyde and MVK-OO*, path 1-b will form methyl vinyl ketone(MVK) and CH₂OO*. The addition of ozone via path 1-B will produce 3,4-ozonide and then break via path 1-c and 1-d, path 1-c lead to the formation of methacrolein (MAC) and CH₂OO*; path 1-d will form formaldehyde and MACR-OO*. Based on the results of IR and GC/MS, formaldehyde was not observed, therefore, path 1-a and 1-d may be excluded. Path 1-b and path 1-c will form MVK and MAC, respectively, which were detected on both IR spectrum and GC/MS spectrum, indicated the reaction is go through path b and c. The final products also include many higher molecular weight species, suggested the polymerized reaction might be occurred.

From the information of IR spectrum, different C=O vibrational absorption were detected at 1764 cm⁻¹, 1737 cm⁻¹, and 1707 cm⁻¹, which was coincided with the vibrational modes of formaldehyde(1764 cm⁻¹), MAC (1737 cm⁻¹), and MVK (1707 cm⁻¹), respectively. GC/MS also detected the corresponding new peak of formaldehyde, MAC, and MVK. Therefore, the reaction path of isoprene with ozone was the formation of ozonide first and then break to the possible product as proposed Scheme I.



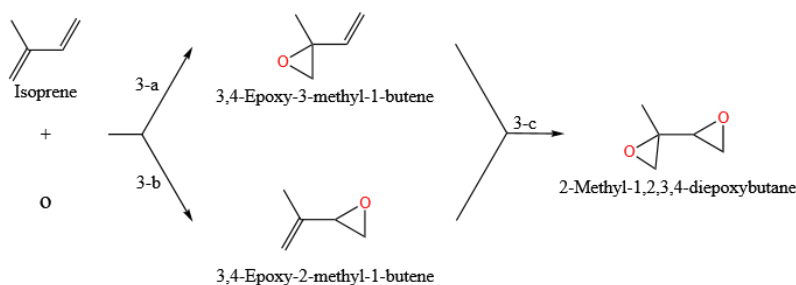
Scheme I. The reaction path of isoprene reacted with ozone.

MVK-OO* and MACR-OO* each will undergo 1,2-shift to form three compounds with different structure, as pathway 2a-2c and 2d-2f in Scheme II. A new peak of methacrylic acid ($m/z = 86$) was detected on GC/MS spectrum and an correspond O-H band was also observed on IR spectrum, indicated that methacrylic acid may be formed via MACR-OO* rearrangement as path 2-f in Scheme II.



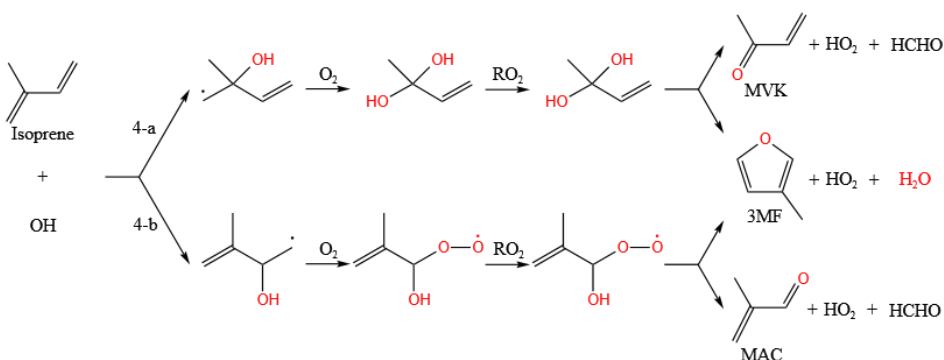
Scheme II. The path of forming stable product from MVK-OO* and MACR-OO*.

Ozone may decompose to O_2 molecule and O atom, O atom will react with unsaturated double bond to form oxirane^[11]. Two possible positions of O atom added to isoprene, as path 3-a and 3-b in Scheme III. Path 3-a will form 3,4-epoxy-3-methyl-1-butene and path 3-b produce 3,4-epoxy-2-methyl-1-butene, both were further reaction with O atom to form product 2-methyl-1,2,3,4-diepoxybutane. Corresponding 3,4-epoxy-3-methyl-1-butene ($m/z = 84$), 3,4-epoxy-2-methyl-1-butene ($m/z = 84$), and 2-methyl-1,2,3,4-diepoxybutane ($m/z = 100$) were detected on GC/MS spectrum. Therefore, the reaction path of O atom with isoprene was proposed as Scheme III.



Scheme III. The reaction mechanism of isoprene with O atom.

Oxygen atom may abstract hydrogen plus O_2 will form OH radical which may react with isoprene. Lee et al. has monitored the OH radical initial oxidation with isoprene and observed the products including 3-methylfuran, MVK, MAC, formaldehyde, HO_2 , and H_2O . MVK, MAC and formaldehyde three products were overlapped with the products in Scheme I. Two new absorptions were observed at 1198 cm^{-1} and 1167 cm^{-1} which were coincided with the vibrational frequencies 1195 cm^{-1} and 1165 cm^{-1} of 3-methylfuran. The GC/MS also detected the corresponding peak with $m/z = 82$. Based on the above information, suggested the reaction mechanism of $IPM+OH+O_2$ was as Scheme IV.



Scheme IV. The reaction mechanism of isoprene with OH and O_2 .

V. Conclusion

The reaction of isoprene with ozone have been studied. The reaction samples after ozone passing through isoprene at various times were analyzed by FTIR and GC/MS. After reaction, the new absorption bands of IR spectra including $-OH$, $C=O$, $C-O$ vibrational modes which were compared with literature and theoretical calculation frequencies. Combined with the fragment analysis of new observed peaks of GC/MS spectrum, indicated the products were formaldehyde, methacrolein (MAC), Methyl vinyl ketone (MVK), 3-methylfuran, 3,4-epoxy-3-methyl-1-butene, 3,4-epoxy-2-methyl-1-butene, methacrylic acid, and 2-methyl-1,2,3,4-diepoxybutane. These products were resulted in three possible reaction paths, including the reaction of isoprene with ozone as described in Scheme I; isoprene reacted with O atom as shown in Scheme III; the reaction of isoprene with OH and O_2 molecule as Scheme IV.

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