

## The study of reaction of isoprenol with ozone

Jyh-Ferng Yang, Yu-Ting Ai, Mei-Lee Hwang\*

Department of Chemical Engineering, I-Shou University, Ta-Hsu, Kaohsiung, 84008, Taiwan

\*corresponding author: mlhwang@isu.edu.tw

### ABSTRACT

The reaction of isoprenol with ozone have been studied. FTIR and GC/MS were applied to analyze the reaction solution at various time. After ozone passes through isoprenol, new observed vibrational absorptions in IR spectrum contained C=O, and C-O functional groups. GC/MS revealed 5 new peaks, with corresponding m/z were 58, 70, 88, 68, and 68. Combined with the fragment analysis of new observed peaks of GC/MS spectrum, confirmed products included acetone, butenone, 4-hydroxy-2-butanone. The reaction mechanism between ozone and isoprenol is that O<sub>3</sub> attacks the C=C double bond of isoprenol and form primary ozonide, which was then break to form smaller Criegee Intermediate and 4-hydroxy-2-butanone. The product of acetone may due to the small amount impurity of prenol with ozone. Another observed product of butenone which was not derived from the proposed mechanism, therefore different reaction mechanism may be involved.

**KEYWORDS:** VOC, isoprenol, ozone

Date of Submission: 18-10-2023

Date of acceptance: 02-11-2023

### I. INTRODUCTION

The production of volatile organic compounds (VOCs) can be artificial and natural source. Artificial VOCs 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<sup>[1]</sup> and the main compound is 3-methyl-3-buten-1-ol (isoprenol). Compared with other VOCs, the emission of isoprenol is higher with year production of 594 (±34) tons, ~ 62.2 % relatively contribution<sup>[2]</sup>.

Isoprenol 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, isoprenol 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 isoprenol 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. Isoprenol 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 substituted enols with ozone has attracted interest<sup>[3-10]</sup>. Many reactions such as the decomposition of organic compounds, oxidation of sulfur oxide, and conversion of NO<sub>x</sub> are related with ozone. Carrasco et al.<sup>[3]</sup> explored the oxidation reaction of ozone with 2-methyl-3-buten-2-ol in dry air conditions and humid air conditions. There were three products of 2-hydroxy-2-methylpropanal (HMP), acetone, and formaldehyde were found in dry air conditions and only two products of formaldehyde and HMP were detected under humid air conditions. Mansour H. Almatarneh<sup>[5]</sup> has studied the reaction mechanism of 2-methyl-3-buten-2-ol with ozone and suggested two possible paths, a primary ozonide (POZ) will form first and the POZ further reacted to form 2-hydroxy-2-methylpropanol and formadehyde-oxide or to form formaldehyde and Criegee intermediate which will form stable epoxide and oxygen molecule. LePerson et al.<sup>[10]</sup> has studied the reaction of isoprenol with OH radical and ozone at 231 K -373 K, the main products included formaldehyde, glycolaldehyde, minor products included methanol, carbon monoxide and carbon dioxide.

Less study was involved for the reaction of isoprenol with ozone, therefore, this research will apply FTIR and GC/MS to study the reaction of isoprenol with ozone. The isolation of products will help for understanding the reaction mechanism.

## II. EXPERIMENTAL

The sample of isoprenol (3-methyl-3-buten-1-ol) (98 %, Tokyo chemical industry) 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 ATR sample component at a resolution of 4 cm<sup>-1</sup> with 16 scans average. GC/MS were recorded on the Shimadzu GCMS-QP2020 NX which has SH-Rxi-5Sil MS gas chromatograph column (30 m x 0.25 mm $\phi$  x 0.25  $\mu$ m) coupled to a quadrupole mass spectrometer (MS Detector).

The ozone was directly pass through isoprenol sample tube with a rate ~2 L/min, and the reacted solution were sampling 1 mL every 30 minutes. The sampling solution were then analyzed with FTIR and GC/MS. Experimental set up and flow chart are similar to previous study<sup>[11-12]</sup>, and show in Figure 1 and Figure 2, respectively.

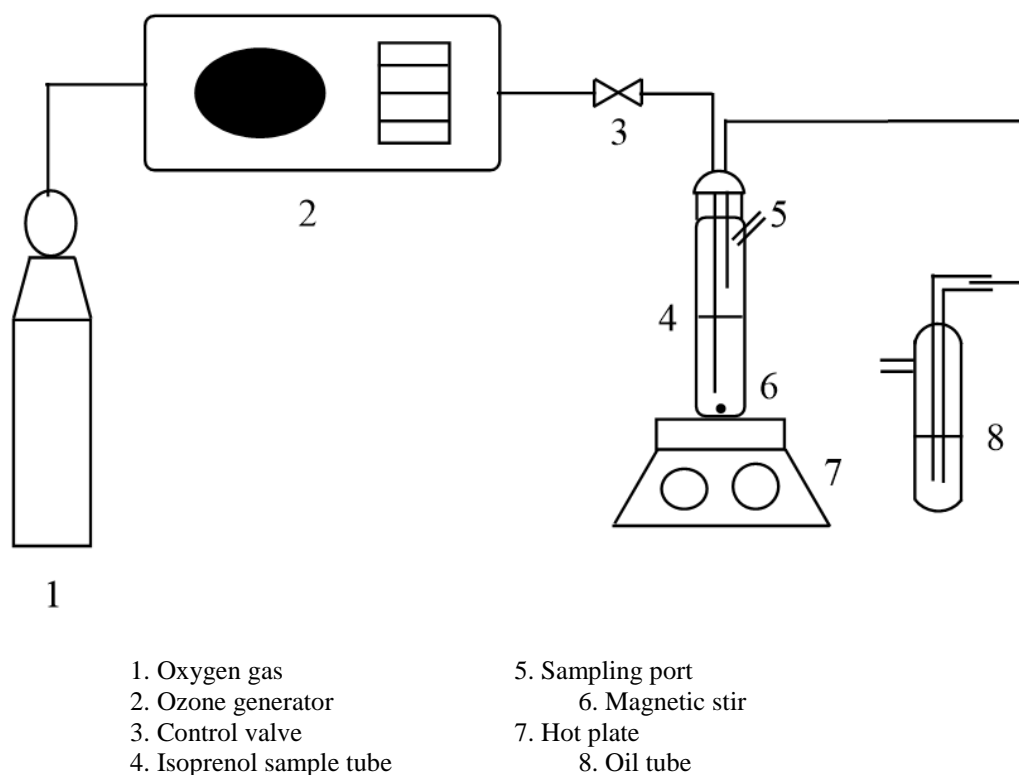


Figure 1 Experimental setup of reaction of isoprenol with ozone.

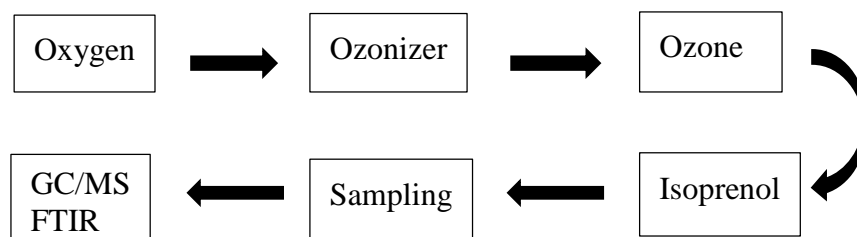


Figure 2 Experimental flow chart of ozone passing through isoprenol liquid.

### III. RESULTS

The absorption positions of isoprenol blank IR spectrum was consistent with literature spectrum<sup>[13]</sup> and summarized in Figure 3 and Table 1. After ozone passing through isoprenol sample tube 60 minutes, three new peaks were observed at  $1710.3\text{ cm}^{-1}$ ,  $1225.4\text{ cm}^{-1}$ , and  $1114.7\text{ cm}^{-1}$ , their intensities were increased with reaction time. The vibrational frequencies of C=O stretching mode is in the range of  $1690\text{ cm}^{-1} \sim 1760\text{ cm}^{-1}$ , therefore, the peak of  $1710.3\text{ cm}^{-1}$  can be easily assigned as C=O stretching vibrational mode. The frequencies of C-O stretching mode are during the range of  $1300\text{ cm}^{-1} \sim 1000\text{ cm}^{-1}$ , the new peaks of  $1225.4\text{ cm}^{-1}$ , and  $1114.7\text{ cm}^{-1}$  can be assigned as C-O stretching vibrational modes. The intensity of parent peak of isoprenol at  $1649.5\text{ cm}^{-1}$  was decreased as reaction time increased and the peak at  $1375.9\text{ cm}^{-1}$  was enhanced as reaction time increased. The peak of  $1649.5\text{ cm}^{-1}$  is belong to the C=C stretching vibrational mode, suggested that isoprenol might react with ozone and resulted in the decrease of intensity of parent band. The parent band of  $1375.9\text{ cm}^{-1}$  is belong to the bending mode of  $-\text{CH}_3$  group, the increase in intensity of this peak might due to the overlap of  $-\text{CH}_3$  bending mode of new product.

As the reaction time reach to 120 min, additional new peaks were observed at  $1256.2\text{ cm}^{-1}$  and  $825.2\text{ cm}^{-1}$ , which were increased in intensity as the reaction time increased. The new band of  $1256.2\text{ cm}^{-1}$  can be easily assigned as C-O stretching mode and  $825.2\text{ cm}^{-1}$  is C-H bending vibrations out of plane. The parent bands at  $1010.3\text{ cm}^{-1}$  and  $982.4\text{ cm}^{-1}$  were weakened as reaction time increased. After 180 min, another additional new band was detected at  $1158.2\text{ cm}^{-1}$  which can be assigned as C-O stretching vibrational mode.

Several new peaks in GC spectrum after ozone passed through isoprenol at various time were observed, the retention time and corresponding value of  $m/z$  were summarized as Figure 4 and Table 3. The corresponding MS spectrum of new peaks at various retention time were summarized as Figure 5 and Figure 6.

When ozone was passing through isoprenol for 30 minutes, 3 new peaks were observed at retention time 1.825 min, 2.783 min, and 3.540 min with corresponding  $m/z = 70, 88,$  and  $68$ , respectively. After 60 minutes, another new peak was detected at retention time 1.657 min with  $m/z = 58$ . At 90 minutes, further new 2.855 min with corresponding  $m/z$  is  $68$ . The intensities of these new peaks were increased as the reaction time increased.

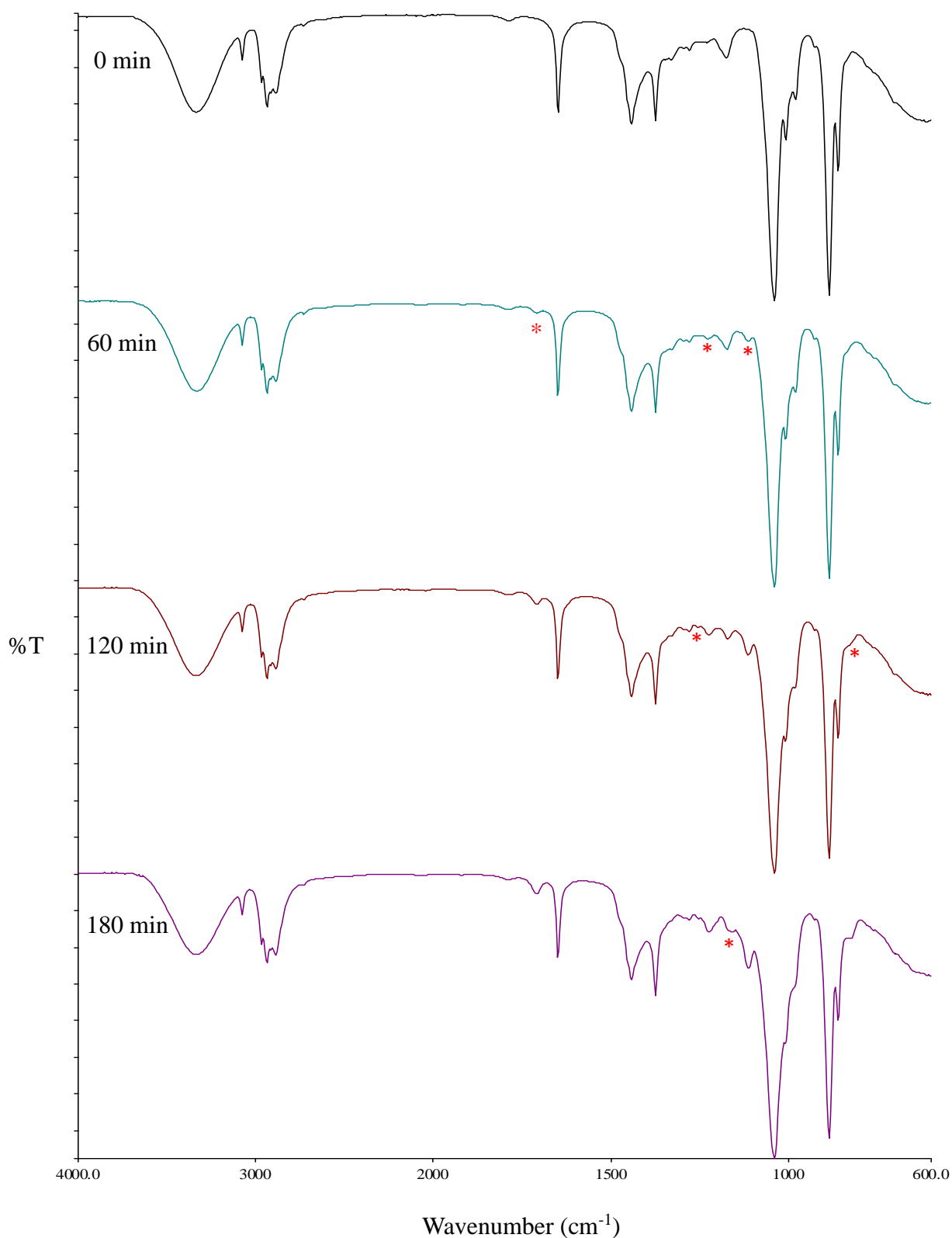


Figure 3. Infrared spectra of isoprenol after ozone passing through at various time.  
\*observed new peak

Table 1 The peak positions of infrared spectrum of isoprenol.

This work (cm <sup>-1</sup> )	Literature (cm <sup>-1</sup> ) <sup>a</sup>	Assignment
	3343	
3338.5 m, b	3333	O-H stretching
3077.7 m	3078	C-H stretching (alkene)
2969.8 m	2970	C-H stretching (alkane)
2938.5 m	2940	C-H stretching (alkane)
2917.2 w	2919	C-H stretching (alkane)
2886.6 w	2906	C-H stretching (alkane)
2730.1 w	2730	
	1793	
1788.6 w	1785	
	1780	
1649.5 m	1651	C=C stretching
1479.0 sh		
1455.3 sh		
1443.5 m	1445	-CH <sub>3</sub> bending (alkane)
1375.9 m	1376	-CH <sub>3</sub> bending (alkane)
1330.3 w		
1297.4 w	1298	
1280.5 w	1281	
1175.8 m	1179	
1041.5 s	1049	C-O stretching
1010.3 m	1011	
982.4 w	983	C-H bending (alkene)
930.1 w		
887.8 s	890	C-H bending (alkene)
862.5 m	854	C-H bending (alkene)

s: strong; m: medium; w: weak; sh: shoulder; b: broad

<sup>a</sup>: Spectral Database for Organic Compounds, SDBS#10050

[https://sdb.db.aist.go.jp/sdbs/cgi-bin/direct\\_frame\\_top.cgi](https://sdb.db.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi)

Table 2. The position of new peak in IR after ozone passing through isoprenol at various time.

	Time (min)			
	60	120	180	Assignment
Peak position (cm <sup>-1</sup> )	1710.3	1710.3	1710.3	C=O stretching
	1225.4	1225.4	1225.4	C-O stretching
	1114.7	1114.7	1114.7	C-O stretching
		1256.2	1256.2	C-O stretching
		825.2	825.2	C-H bending
			1158.2	C-O stretching

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

Peak Time (min)	Retention time (m/z)				
	1	2	3	4	5
30		1.825 (70)	2.783 (88)		3.540 (68)
60	1.657 (58)	1.826 (70)	2.782 (88)		3.541 (68)
90	1.657 (58)	1.825 (70)	2.776 (88)	2.855 (68)	3.539 (68)
120	1.657 (58)	1.826 (70)	2.775 (88)	2.855 (68)	3.539 (68)

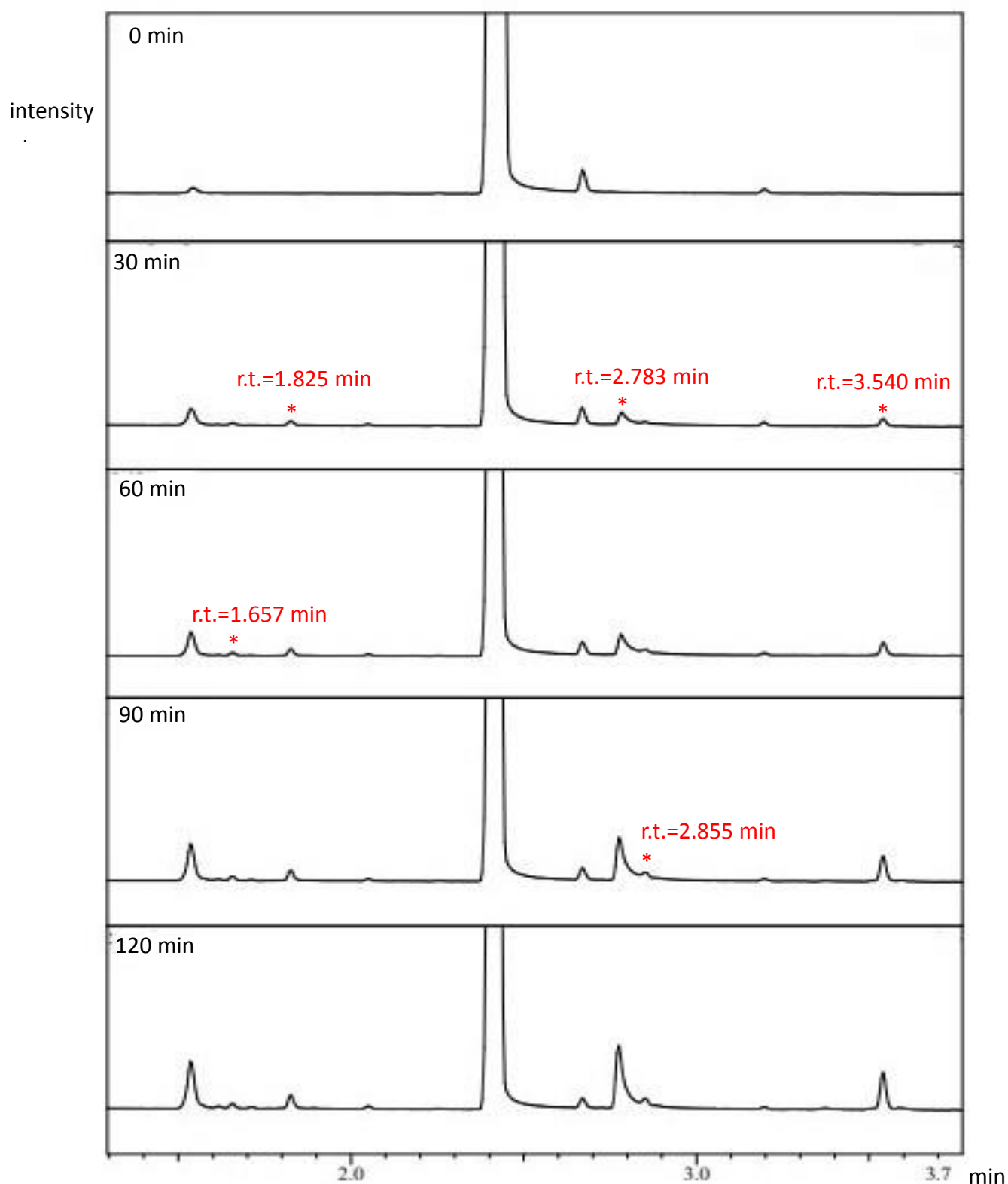


Figure 4. The GC spectra of ozone passing through isoprenol at various time.  
\* represents a new peak, r.t.= retention time.

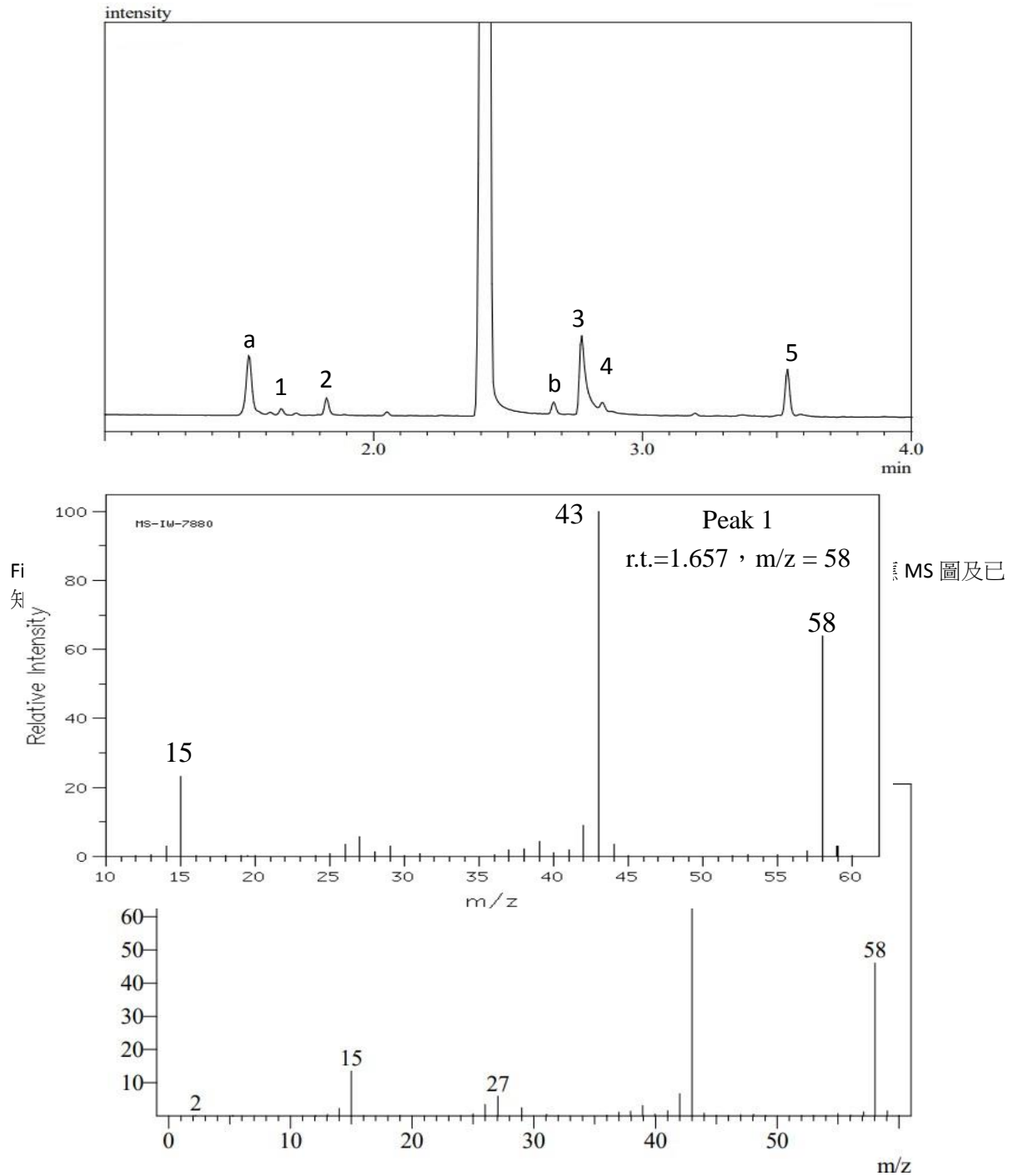


Figure 5. The corresponding mass spectra of new peaks at r.t=1.657 min of GC spectrum after ozone passing through isoprenol for 120 minutes and comparison with standard MS spectrum of acetone.



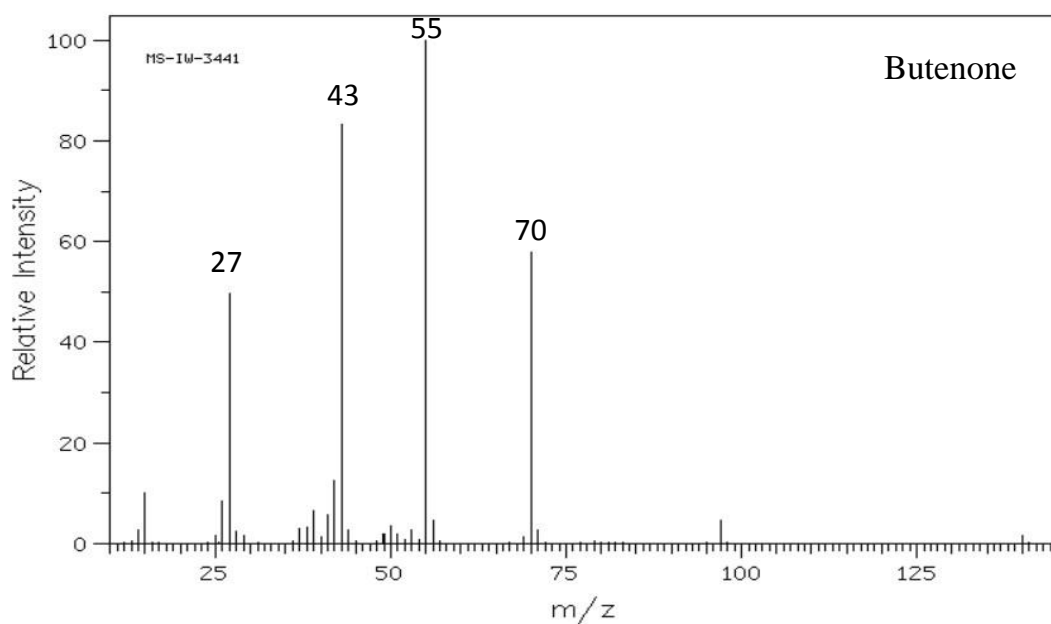
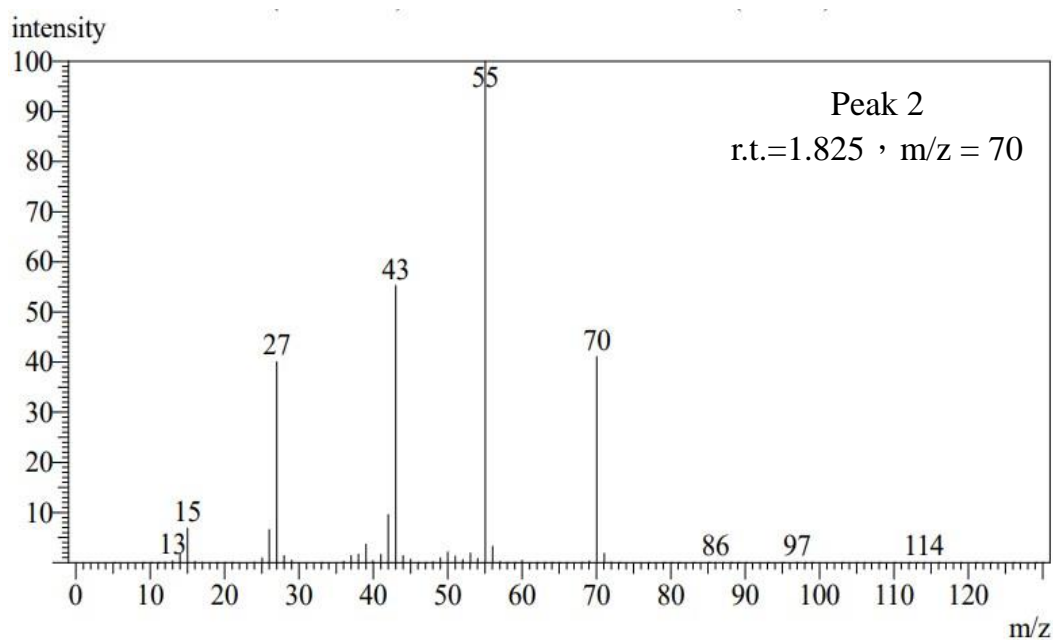


Figure 5 (cont'd). The corresponding mass spectra of new peaks at r.t.=1.826 min of GC spectrum after ozone passing through isoprenol for 120 minutes and comparison with standard MS spectrum of butenone.

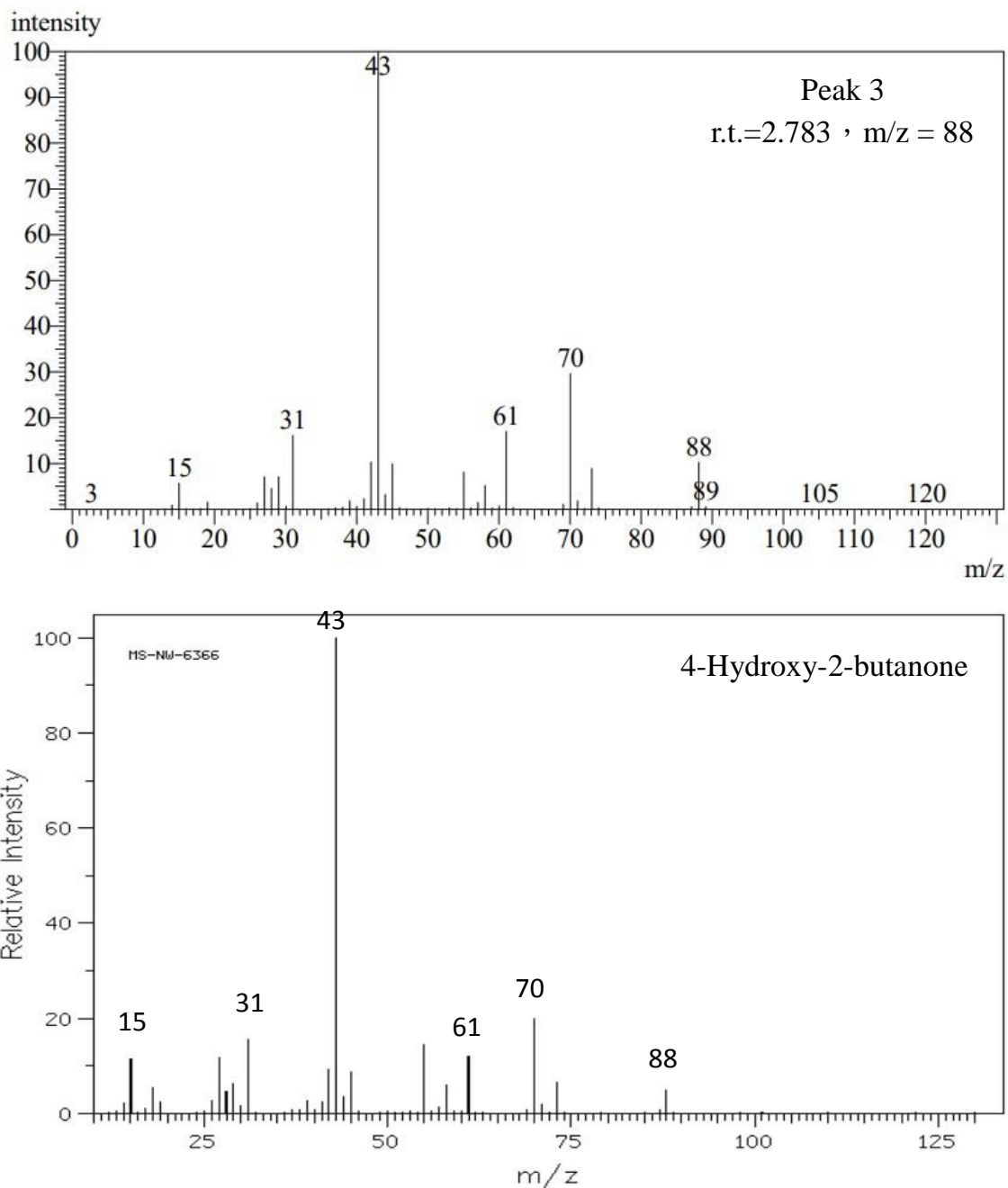


Figure 5 (cont'd). The corresponding mass spectra of new peak at  $r.t.=2.775$  min of GC spectrum after ozone passing through isoprenol for 120 minutes and comparison with standard MS spectrum of 4-hydroxy-2-butanone.

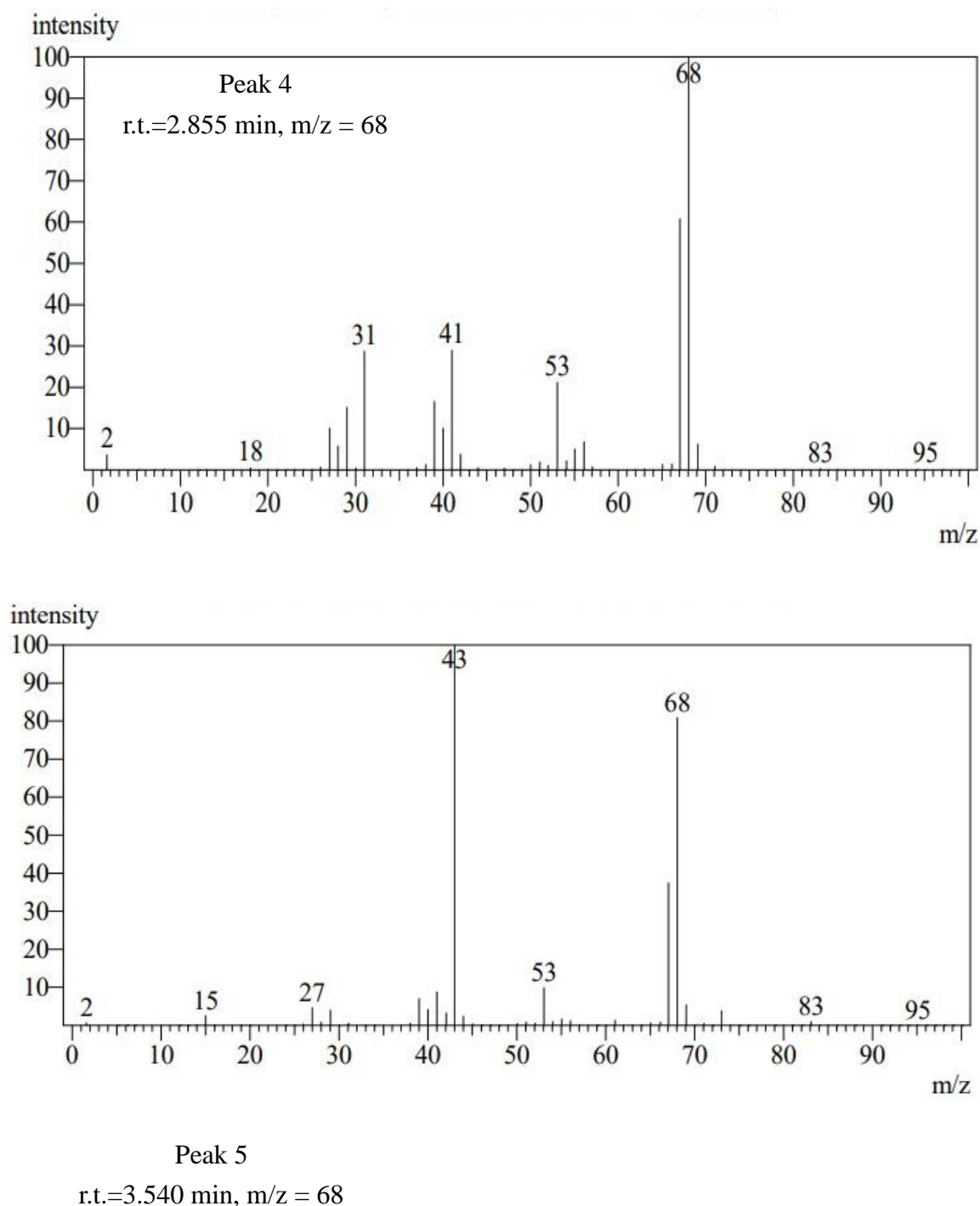


Figure 6. The corresponding mass spectra of new peaks at r.t =2.855 min and 3.539 min of GC spectrum after ozone passing through isoprenol for 120 minutes.

The two parent peaks at retention time 1.543 min (peak a, m/z = 30) and 2.671 min (peak b, m/z = 86) were presented and show the variation in intensity before and after reaction, as show in Figure 7 and Figure 8. The intensity of peak a of 1.543 min was weak in the beginning and enhanced as reaction time increased, the MS spectrum of this peak was different before and after reaction. The intensity of peak b of 2.671 min was decreased as reaction increased and the MS spectrum was same before and after reaction. Comparison with NIST 17 data bank and standard MS spectrum, indicated this peak was prenol which is an isomer of isoprenol. Prenol may also react with ozone which led to the decrease in intensity. Analysis of the fragment of MS spectrum for new peaks, indicated the products including acetone, butenone, 4-hydroxy-2-butanone and the other two unknown

compounds. Figure 9 indicated the intensities of these new peaks were increased with reaction time, represent the products are stable.

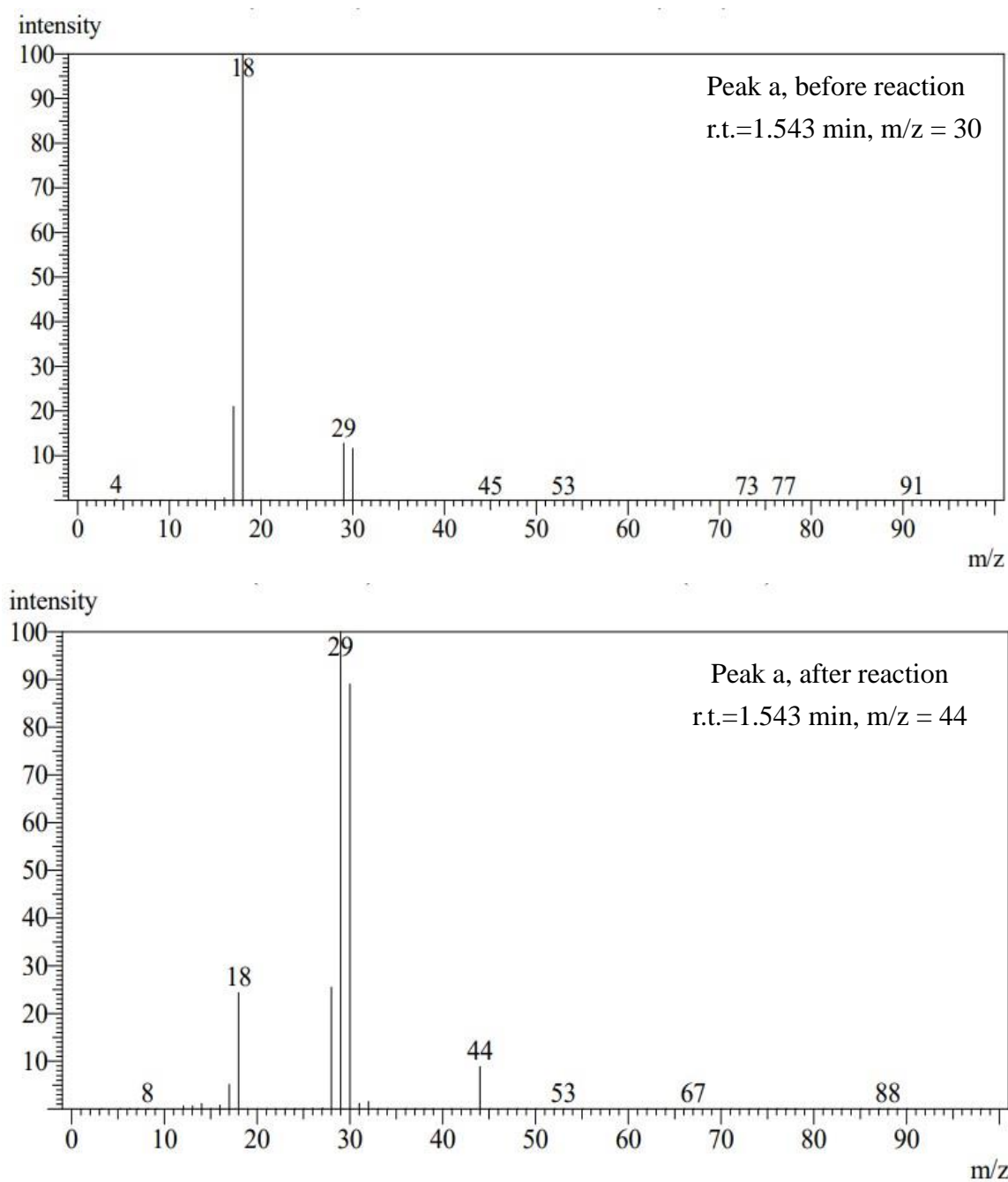


Figure 7. The variation of intensity in MS spectrum for peak at retention time 1.543 min before and after reaction.

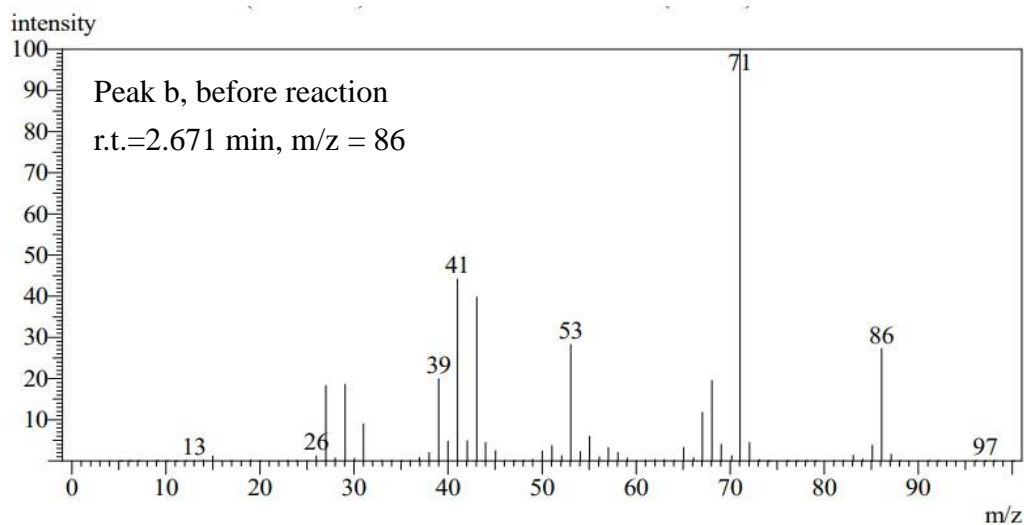
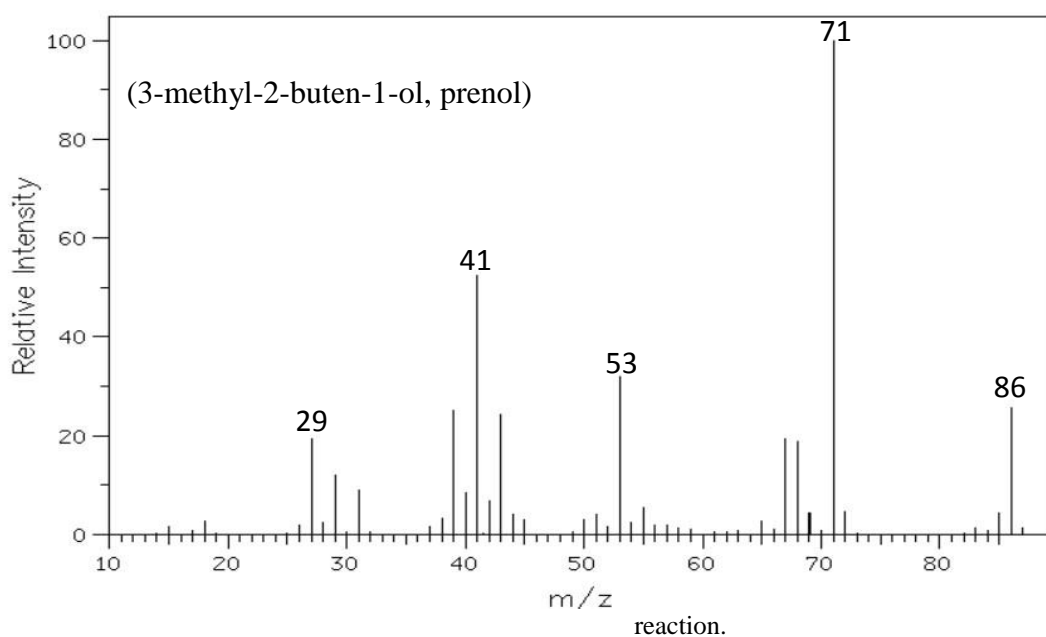
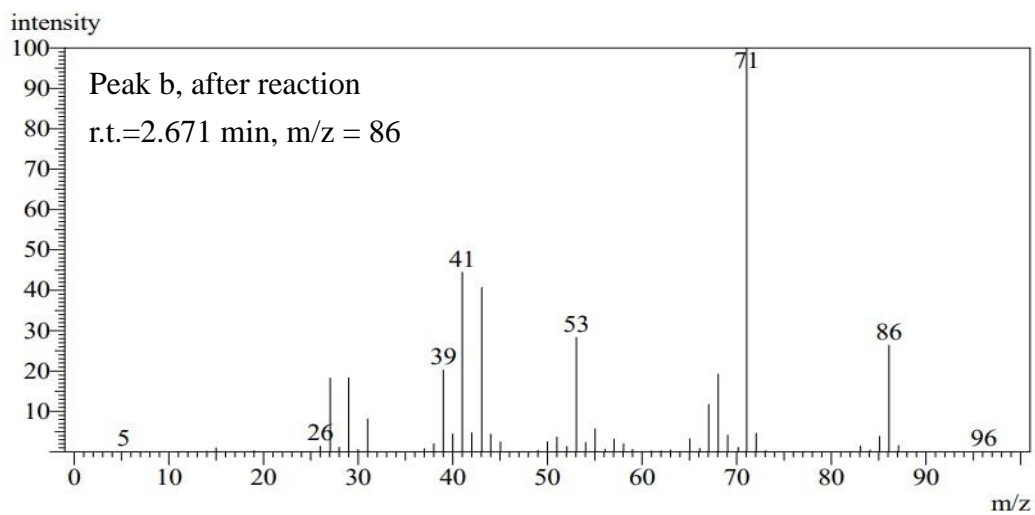


Figure 8. The variation of intensity in MS spectrum for peak at retention time 2.671 min before and after



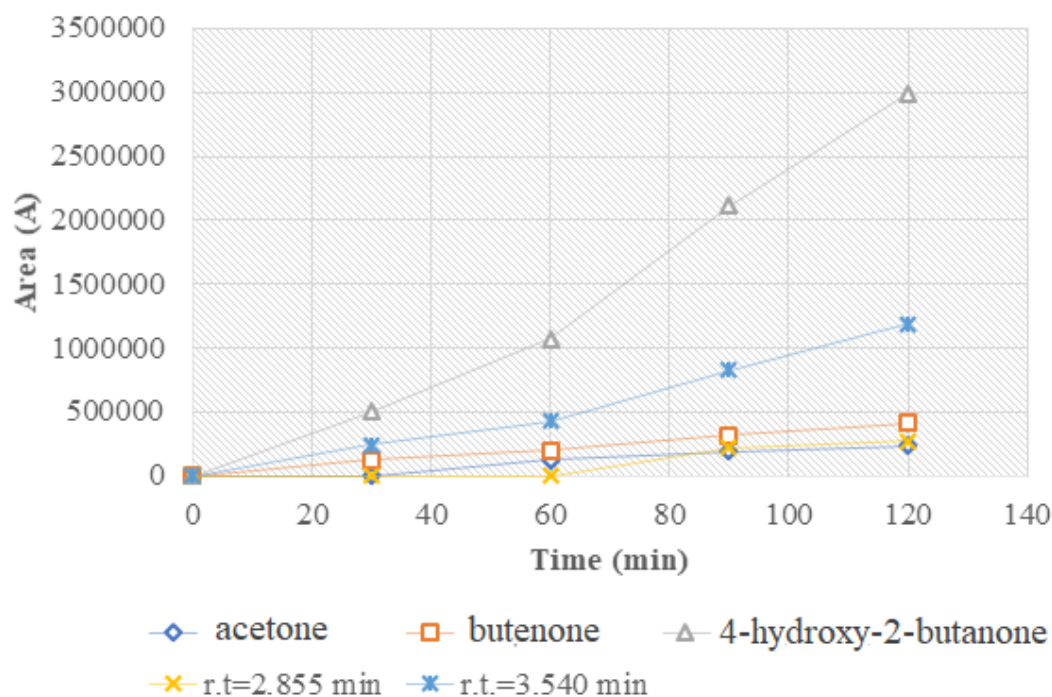
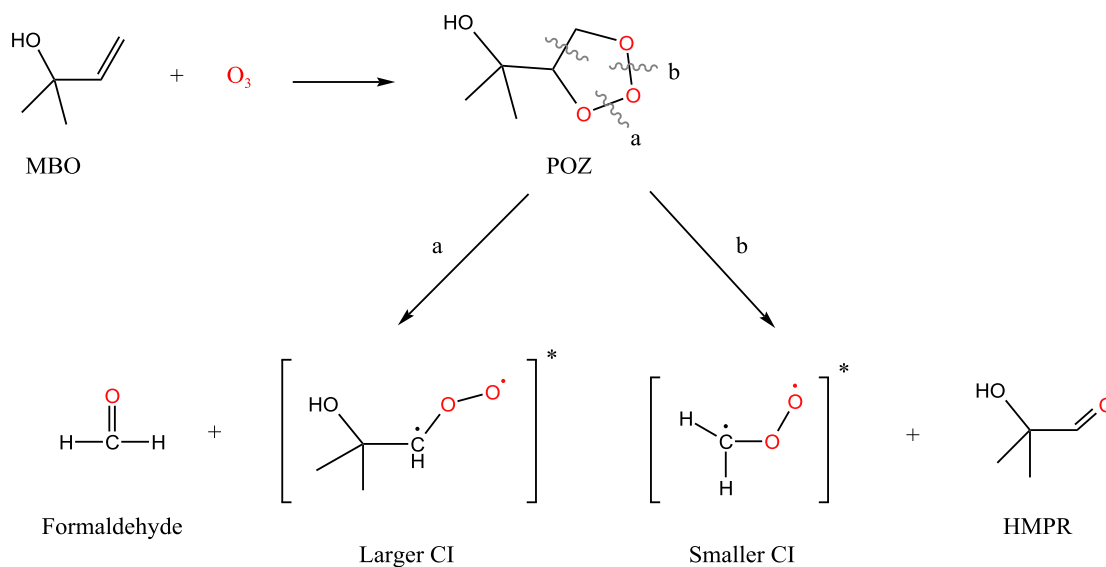


Figure 9. The peak area variation of new peaks of GC spectra for reaction of isoprenol

#### IV. Discussions

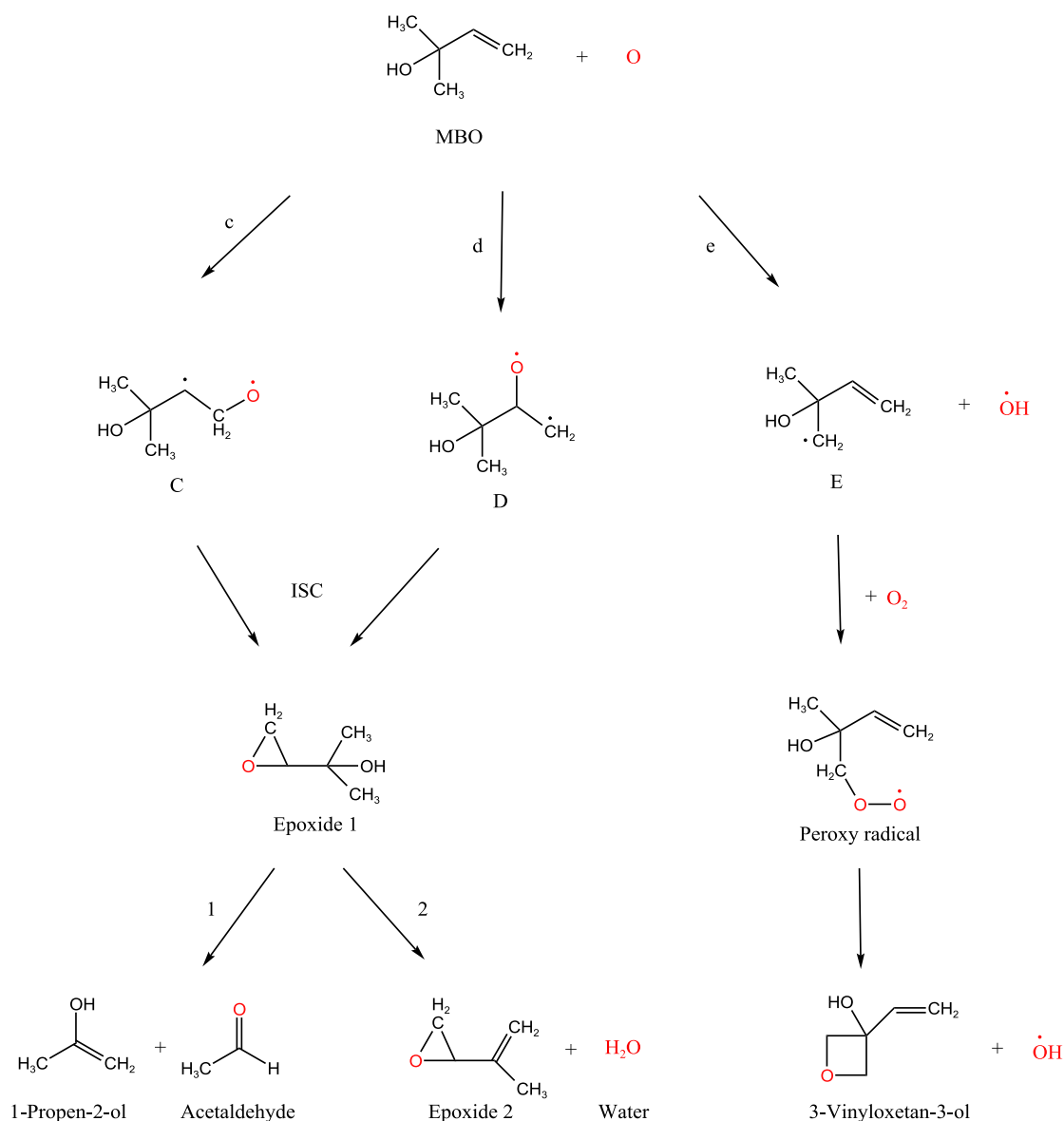
Based on the position of new absorptions in IR spectrum, indicated the new products included C=O and C-O functional group. At the range of C-O stretching vibrational mode, the observation of different peaks ( $1225.4\text{ cm}^{-1}$ ,  $1114.7\text{ cm}^{-1}$ ,  $1256.2\text{ cm}^{-1}$ , and  $1158.2\text{ cm}^{-1}$ ) suggested more than one product which contains C-O functional group. The intensity of parent band  $1375.9\text{ cm}^{-1}$  was increased with reaction time might due to the overlap of the new product band with parent peak. From the  $m/z$  value of MS spectrum, the molecular weights of product were 58, 70, 68, 68, and 88. Compared the IR functional group and fragment of MS spectrum, indicated  $m/z = 58$ , 70, and 88 represent the product of acetone, butenone, and 4-hydroxy-2-butanone, respectively. The two peaks of  $m/z = 68$  need further information to confirm.

Carrasco et al.<sup>[3]</sup> studied the reaction of 2-methyl-3buten-2-ol with ozone and proposed the mechanism as Scheme I. Ozone attack the C=C double bond of 2-methyl-3buten-2-ol to form primary ozonide (POZ) and then undergo path (a) or (b) to get different intermediate and product. Path (a) was the breakage of C-C and O-O bond and get formaldehyde and larger Criegee intermediate (CI); path (b) was the fracture of C-C and O-O bond to form 2-hydroxy-2-methylpropanal (HMPP) and smaller CI.



Scheme I. The reaction path of 2-methyl-3-buten-2-ol reacted with ozone.<sup>[3]</sup>

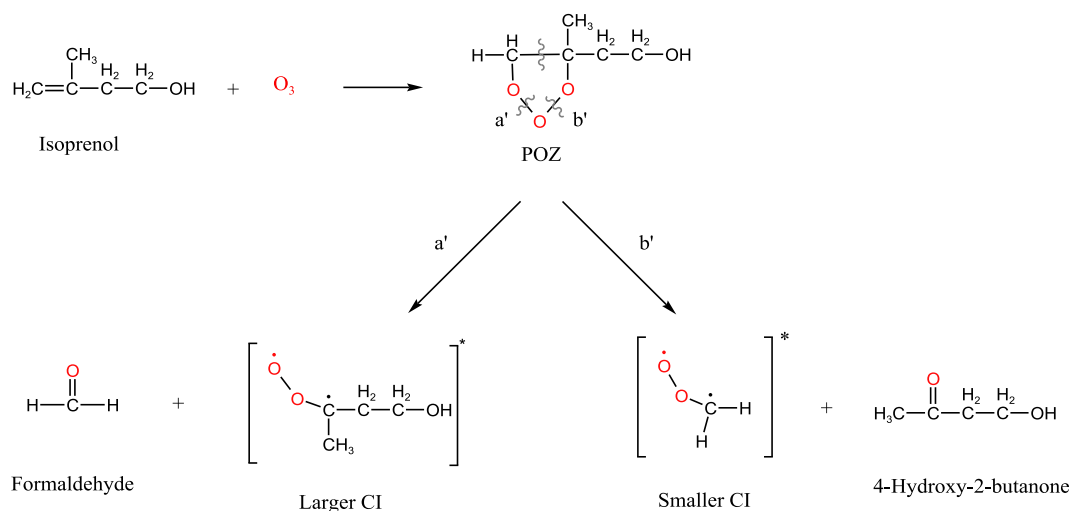
Ozone may decompose to O atom and O<sub>2</sub> molecule, therefore, the isoprenol may reaction with O atom or O<sub>2</sub> molecule. Fathi et al.<sup>[4]</sup> studied the reaction of 2-methyl-3-buten-2-ol with O atom and proposed the mechanism as Scheme II. Two possible ways of O atom reacted with 2-methyl-3-buten-2-ol, an addition of O atom to C=C double bond as path (c) and (d) and abstraction of hydrogen of O atom as path (e). Path (c) and (d) will form radical C or D which was then undergo intersystem crossing (ISC) to form epoxide 1. The epoxide 1 was taken path (1) and (2) to get different products. Path (1) gave the product of acetaldehyde and 1-propen-2-ol, path (2) led to the product of epoxide 2 and water. Path (e) was led to the formation of peroxy radical which formed the product of 3-vinyltetrahydro-2H-pyran-2-ol and OH radical.

Scheme II The reaction mechanism of 2-methyl-3-buten-2-ol with O atom.<sup>[4]</sup>

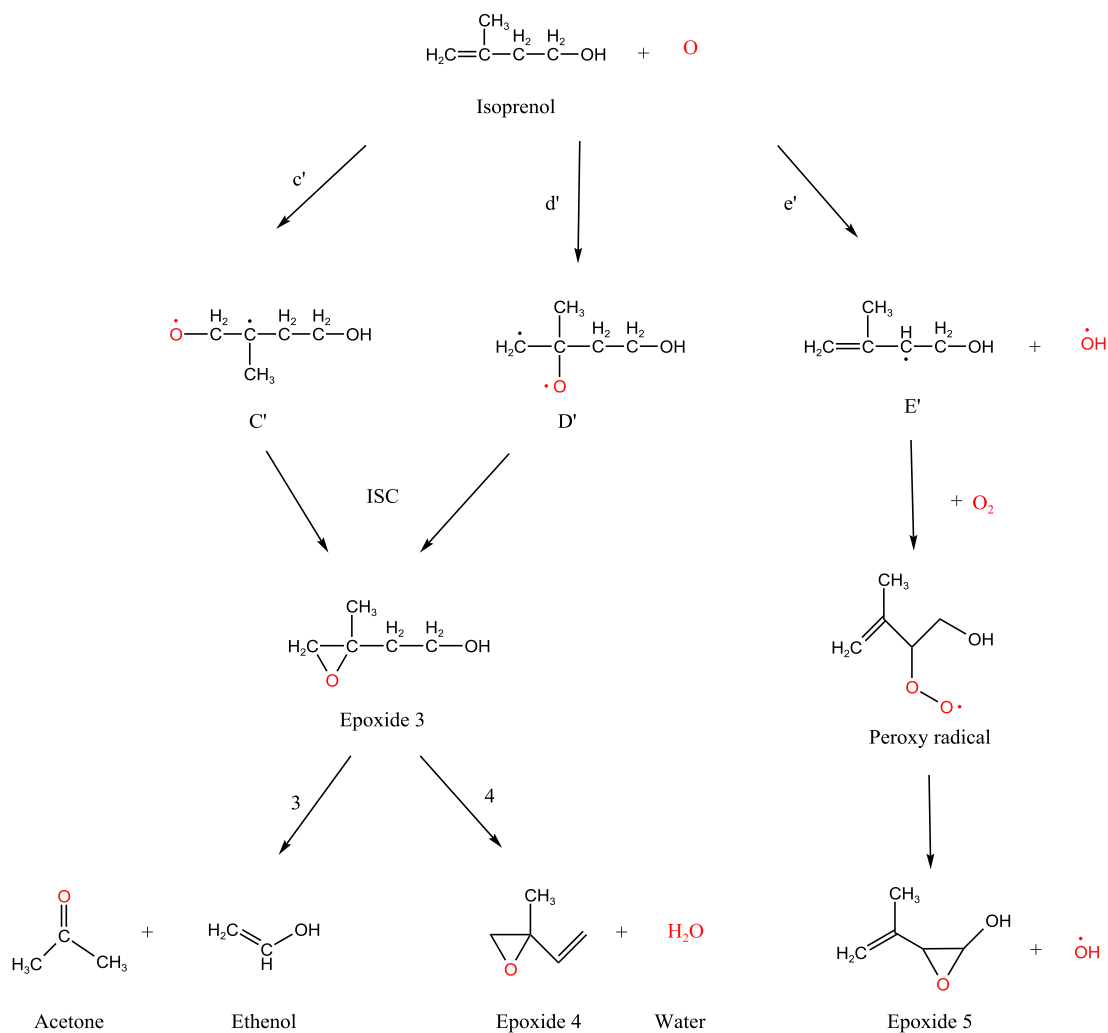
Applied the reaction mechanism of 2-methyl-3-buten-2-ol with ozone proposed by Carrasco et al. and Fathi et al. to the reaction system of isoprenol with ozone. The reaction mechanism of isoprenol with ozone might be similar and proposed as Scheme III and IV. Ozone attack on the C=C double bond of isoprenol forms a POZ epoxide structure which will form formaldehyde and larger CI via path (a') or form 4-hydroxy-2-butanone and smaller CI via path (b').

When isoprenol reacts with ozone via the form of oxygen atom which may undergo addition reaction or abstract reaction. In the addition reaction, oxygen atom added to the carbon of C=C double bond (path c' and d') and formed free radicals C' and D' which undergo ISC to form epoxide 3. The further reaction of epoxide 3 might take path 3, a hydrogen transfer and the broken of C-C bond of  $\gamma$  and  $\beta$ , led to the product of acetone and vinyl alcohol (ethanol) or take path 4 via hydrogen atom transfer to -OH functional group reorganization to form product of another epoxide 4 and water. The reaction path e' is oxygen atom abstract hydrogen of  $\gamma$ -C and form E' radical and OH radical. Free radical E' was then reacted with oxygen molecule to form epoxide 5 and OH radical.

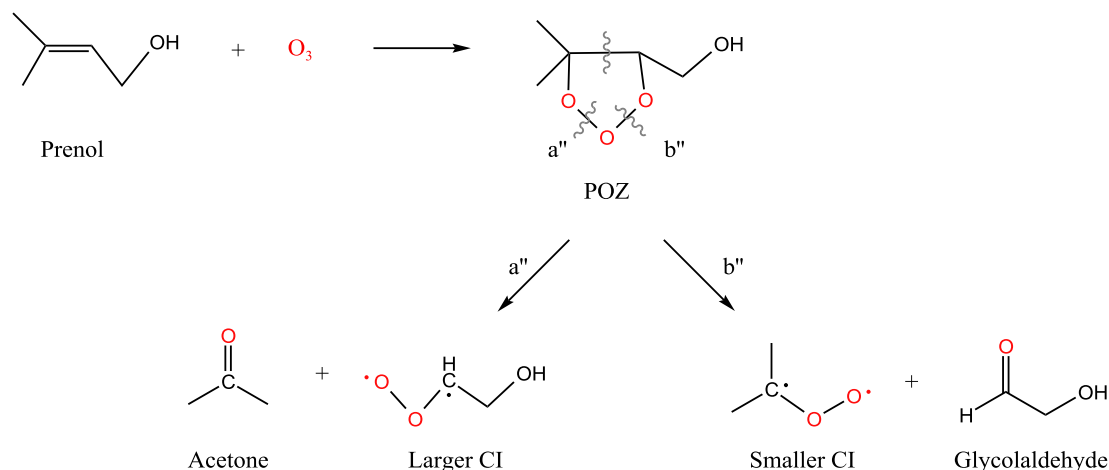




Scheme III The reaction mechanism of isoprenol with Ozone.



Scheme IV The reaction mechanism of isoprenol with O atom.



Scheme V The reaction mechanism of prenol with ozone.

Based on the variation of intensity of GC peak with reaction time, indicated there is isomer prenol present. Assume the mechanism of prenol with ozone is similar to the path proposed by N. Carrasco, the possible reaction path would show as Scheme V. The ozone attacked the C=C bond of prenol and formed a primary ozonide, and then POZ undergo path a'' to form acetone with larger CI or path b'' led to product glycolaldehyde with smaller CI.

GC/MS has detected the new peaks with  $m/z$  58, 68, 68, 70, 88. Comparison the fragment of MS,  $m/z$  88 is consisted with 4-hydroxy-2-butanone which is a product of path b' in Scheme III. Path a' should form product of formaldehyde ( $m/z=30$ ) which was not observed in GC/MS, therefore, path a' may be excluded. The POZ and smaller CI in Scheme I was not detected in GC which might due to their instability.

The value of  $m/z$  58 is agree with acetone shown in Scheme V. However, the other products in Scheme IV, included epoxide 3 (M.W.=102), ethenol (M.W.= 44), epoxide 4 (M.W.= 84), water (M.W.=18), and epoxide 5 (M.W.=100), were not observed in GC/MS. Although there is a peak at retention time 1.543 min with  $m/z$  is 44, the MS spectrum is not consistent with ethenol. Therefore, the possibility of reaction mechanism as Scheme II can be neglected.

## V. Conclusion

This study explores the reaction between isoprenol and O<sub>3</sub>. FTIR and GC/MS were applied to analyze the sample solution before and after introduced ozone into the isoprenol sample for different times to confirm the possible products and reaction mechanism. Analyzing the new peak position of the IR spectrum and the  $m/z$  value of the MS spectrum of the isoprenol/O<sub>3</sub> reaction, the IR spectrum detected new vibrational absorption peaks of C=O, C-O, and C-H; the GC/MS detected the  $m/z$  of the new peak as 58, 68, 68, 70, and 88. The products after the reaction should be acetone (M.W.=58), butenone (M.W.=70), 4-hydroxy-2-butanone (M.W.= 88), and the other two peaks of  $m/z = 68$  could not be confirmed and need to be further study. The reaction path between isoprenol and O<sub>3</sub> should be that O<sub>3</sub> attacks the C=C double bond position of isoprenol to form a POZ epoxy structure, and then breaks the bond to form smaller CI and 4-hydroxy-2-butanone. The isoprenol sample contains a small amount of prenol, which will also be decomposed by ozone to form acetone and a larger CI. Butenone was not found in the reaction mechanism, and its reaction mechanism needs to be further discussed.

## REFERENCES

- [1] Kopppmann, R.; Williams, J., "Volatile Organic Compounds in the Atmosphere: An Overview." Blakwell Publishing Ltd, **2007**, 1-32.
- [2] Sindelarova, K.; Granier, C.; Bouarar, I.; Guenther, A.; Tilmes, S.; Stavrakou, T.; Müller, J. F.; Kuhn, U.; Stefani, P.; Knorr, W., "Global data set of biogenic VOC emissions calculated by the MEGAN model over the last 30 years." *Atmospheric Chemistry and Physics*, **2014**, 14(17), 9317-9341.
- [3] Carrasco, N.; Doussin, J. F.; O'Connor, M.; Wenger, J. C.; Picquet-Varrault, B.; Durand-Jolibois, R.; Carlier, P., "Simulation Chamber Studies of the Atmospheric Oxidation of 2-Methyl-3-Buten-2-ol: Reaction with Hydroxyl Radicals and Ozone Under a Variety of Conditions." *Journal of Atmospheric Chemistry*, **2007**, 56 (1), 33-55.
- [4] Fathi, Y.; Price, C.; Meloni, G., "Low-Temperature Synchrotron Photoionization Study of 2-Methyl-3-buten-2-ol (MBO) Oxidation Initiated by O(3P) Atoms in the 298–650 K Range." *The Journal of Physical Chemistry A*, **2017**, 121 (15), 2936-2950.
- [5] Almatameh, M. H.; Elayan, I. A.; Abu-Saleh, A. A.-A. A.; Altarawneh, M.; Ariya, P. A., "The gas-phase ozonolysis reaction of methylbutenol: A mechanistic study." *International Journal of Quantum Chemistry*, **2019**, 119 (10), e25888.

- [6] Noda, J.; Nyman, G.; Langer, S., "Kinetics of the Gas-Phase Reaction of Some Unsaturated Alcohols with the Nitrate Radical." *The Journal of Physical Chemistry A*, **2002**, 106 (6), 945-951.
- [7] Imamura, T.; Iida, Y.; Obi, K.; Nagatani, I.; Nakagawa, K.; Patroescu-Klotz, I.; Hatakeyama, S., "Rate coefficients for the gas-phase reactions of OH radicals with methylbutenols at 298 K." *International Journal of Chemical Kinetics*, **2004**, 36 (7), 379-385.
- [8] Rudich, Y.; Talukdar, R.; Burkholder, J. B.; Ravishankara, A. R., "Reaction of Methylbutenol with the OH Radical: Mechanism and Atmospheric Implications." *The Journal of Physical Chemistry*, **1995**, 99 (32), 12188-12194.
- [9] Kalalian, C.; Roth, E.; El Dib, G.; Singh, H. J.; Rao, P. K.; Chakir, A., "Product investigation of the gas phase ozonolysis of 1-penten-3-ol, cis-2-penten-1-ol and trans-3-hexen-1-ol." *Atmospheric Environment*, **2020**, 238, 117732.
- [10] Le Person, A.; Solignac, G.; Oussar, F.; Daële, V.; Mellouki, A.; Winterhalter, R.; Moortgat, G. K., "Gas phase reaction of allyl alcohol (2-propen-1-ol) with OH radicals and ozone." *Physical Chemistry Chemical Physics*, **2009**, 11 (35), 7619-7628.
- [11] Lin, I.-T. "The Study of Reaction of Methyl Ethyl Ketone and 3-Methyl-2-Butanone with Ozone" I-Shou University, MS Thesis, **2019**.
- [12] Jeng, R.-L., Yang, J.-F., Hsu, C.-C., Hwang, M.-L., *The International Journal of Engineering and Science*, 2023, 12(4), 22-23.
- [13] <https://webbook.nist.gov/cgi/cbook.cgi?ID=C763326&Mask=80#IR-Spec>