Matrix isolation study of photolysis reactions of allyl halides with ozone

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---**ABSTRACT**---
IR/matrix isolation technique has applied to study the photolysis reactions of allyl chloride and allyl bromide with ozone in Ar matrix.   The isolated intermediate and products were identified by comparison of new IR frequencies of experimental results with theoretical calculation.   The reaction mechanism was first 1,3 dipolar cycloaddition of ozone to double bond of allyl halide to form 4-(halomethyl)-1,2,3-trioxolane (POZ), POZ was then decomposed to carbonyl component and HC(O)CH₂X which were retro-cycloaddition to carbonyl component to form 3-(halomethyl)-1,2,4-trioxolane (SOZ), and finally the SOZ was decomposed to a stable formic haloacetic anhydride.
KEYWORDS: matrix isolation, IR, allyl halide, ozone

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I.   INTRODUCTION

Allyl halide has both halide atom and C=C double bond, which can undergo alkyl halide reaction and unsaturated alkene reaction.   These characteristics let allyl halides became important chemical intermediates.   Therefore, the relative reaction of ozone with alkenes gave a lot interesting in atmosphere chemistry. [1-6]

Ozone is strong oxidant and plays an important role in reaction of atmospheric chemistry.   During the past twenty years, the research of reaction of ozone has attracted much interests.[7]   Many reactions such as the decomposition of organic compounds, oxidation of sulfur oxide, and conversion of NO_x are related with ozone.

In 1975, Criegee[1] have studied the reaction of olefins with ozone and proposed a mechanism as Scheme I.   Kohlmiller[2] have studied the reaction of ethylene with ozone in Xe matrix at 1985, no product was observed at 50 K, primary ozonide (POZ) and secondary ozonide (SOZ) were detected as temperature anneal to 80-100 K and confirmed by experiment with isotopes of ^{18}O and D.

In 2002, Clark et al[3] have studied the photolysis reaction of 1,2-dibromoethene and 1,2-dichloroethene with ozone in Ar matrix with various wavelength, intermediate and product of POZ, SOZ, HC(O)X, and OC…HX were also observed and lack of conclusive evidence confirming the presence of a SOZ.

The reactions of ethylene with ozone in Ar matrix (15-26 K) and CO_2 matrix (12-20 K) were also studied by Samuni et al[4] in 1996.   There is no reaction occurred, while POZ and SOZ were observed in amorphous CO_2 matrix at temperature less than 25 K.   In crystalline CO_2 matrix, POZ and SOZ was not detected at 65 K and observed at temperature larger than 77 K.

Most of the studies of olefins with ozone were various alkyl substituent on C=C double bond, alkyl group is an electron-donating group, therefore, the C=C bond would has higher electron density which would favor the cycloaddition of ozone.   Was the distribution will be changed when the substituent was electron-withdrawing group?

Matrix isolation technique[8-10] was developed in mid-1950's and applied to the study of unstable molecules and free radicals.[11]   Therefore, this research will apply matrix isolation/infrared spectrum to study the reaction of allyl halide with ozone.   Halides were chosen as substituent in this research to study whether the product distribution will be affected by the electron-withdrawing alkyl halide group.   The isolation and identification of intermediates and products in matrix will helpful for proposing reaction mechanism.

Scheme I [1]
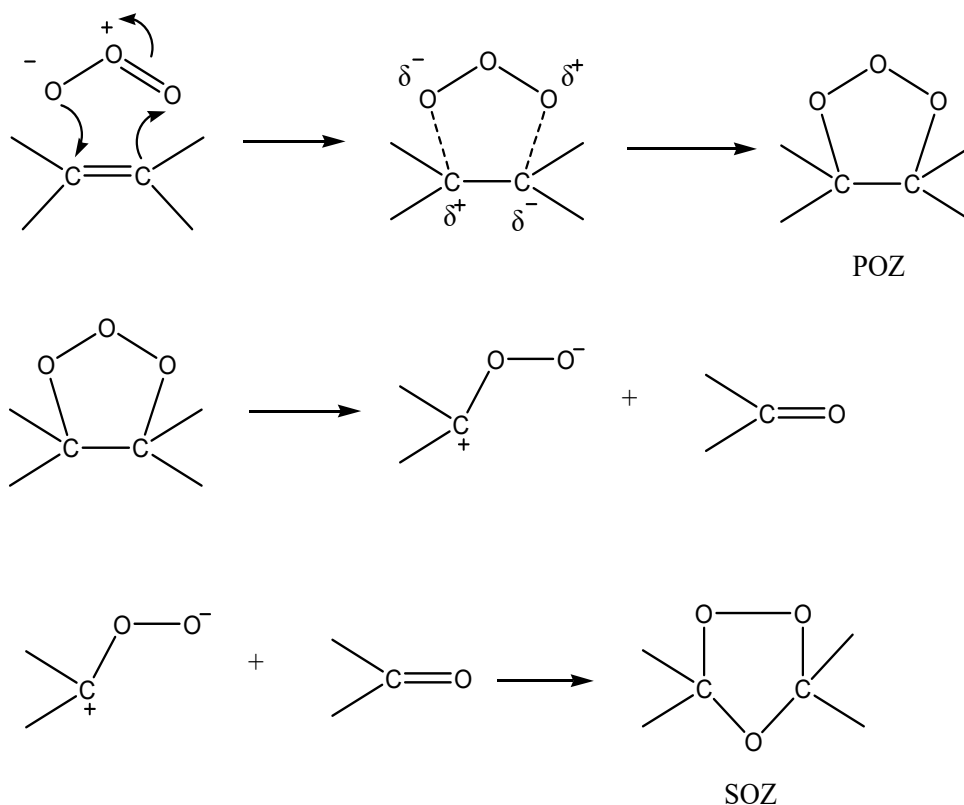
II.   EXPERIMENTAL

All of the experimental in the present study were carried out on conventional matrix isolation setup as previous.[12]   The experimental system consisted of four basic parts, the vacuum system, the cryogenic system, the cold cell vacuum vessel, and Fourier transform infrared spectrometer.   The vacuum manifold was stainless steel (Cajon fitting) with Nupro valves.   The vacuum vessel was equipped with CsI windows and quartz windows and sat in tile sample beam of the infrared spectrometer.

Cryogenics were supplied by a CTI M-22 cold head unit and a CTI 8200 helium closed cycle refrigerator, which maintained a temperature below 12 K.   The temperature at the cryogenic CsI surface was monitored by a silicon diode thermal sensor (Lake Shore Model 321 auto temperature controller).   The window temperature was regulated by supplying a constant voltage to a 25 W cartridge heater mounted on the cold copper block to anneal tile matrix or warm the matrix at the end of experiment.

The concentration of matrix/reactant (M/R) ratio was in the range of 200/1 to 2000/1.   Sample was deposited via single jet mode with rate of ~ 2 mmol/h for about 1.5 hours before spectra were recorded.   Infrared spectra were recorded on a Perkin Elmer Model 2000 FTIR spectrometer with MCT detector at a resolution of 2 cm^{-1} with 64 scans average.   The photolysis was applied with a 200 W Hg lamp by in-situ photolysis or photolysis during deposition.

The samples of Ar (99.9995%, Lienhwa) and O_2 (99.995%, San Fu or Matheson) were used as received. Allyl bromide (99%, Aldrich) and allyl chloride (98%, ACROS) were purified by trap-to-trap distillation before use.   Ozone were generated by silent discharge ozone generator (model AS-10, Three Oxygen Enterprise, Co., Ltd.) and trapped with liquid nitrogen and then carried out by argon and mixed with sample in sample tank.

III.   RESULTS

Blank experiments of deposition and IR spectrum measurement of each parent reagent were run.   In each case, the blank spectra were in good agreement with literature spectra.[13]

Ar/Allyl Chloride (Ar/C₃H₅Cl)   The spectrum of Ar/C_3H_5Cl at varied concentration (2000/1~200/1) were conducted.   The position of absorptions in spectrum were summarized in Table 1.   After the photolysis with Hg lamp, there is no new peak was observed even the concentration increased to 200/1.

Table 1 The frequency positions (cm^{-1}) of IR spectrum of Ar/allyl chloride (2000/1)

Ar matrix	Literature(gas)[*,13]	Assignment
3101	3105.9, 3099.2, 3094	ν_1, vinyl CH stretching
3077	3078	$\nu_6 + \nu_7$
3023	3034.1, 3025.2	ν_2, vinyl CH stretching
2999	3010.6, 3002.8, 2996	ν_3, vinyl CH stretching ν_4, methylene asymmetric CH$_2$ stretching
2963	2973, 2962.4	ν_5, methylene symmetric CH$_2$ stretching
2877	2894.9, 2881.4	$2\nu_7$
2854	2850	$\nu_7 + \nu_8$
	2719.3, 2711.6, 2705	$\nu_7 + \nu_{10}$
	2520, 2509	$2\nu_{10}$
	2400 broad	$\nu_8 + \nu_{18}$
	1965.8	$2\nu_{13}$
1855	1868.1,1859.1	$2\nu_{15}$
1654	1657.2	ν_6, a', cis isomer
1645	1651, 1644.8	ν_6, C=C stretching
1447	1457.7, 1452.6, 1443	ν_7, methylene CH$_2$ bending
1432	1429.2	ν_8, a', cis isomer
1415, 1406	1425.1, 141.7, 1410.6	ν_8, vinyl CH$_2$ bending
	1330	$\nu_{17} + \nu_{18}$
1295, 1288	1299.1, 1294.3, 1288	ν_9, vinyl hydrogen in-plane bending ν_{10}, cis isomer
1262, 1257	1267.7, 1259.6, 1254	ν_{10}, methylene CH$_2$ wagging
1205, 1216	1220.8, 1210.3	ν_{11}, vinyl hydrogen in-plane bending
1178	1180.5	ν_{12}, a', cis isomer
1091, 1025	1180, 1101, 1095.6	ν_{12}, methylene CH$_2$ twisting
995	995.5, 989.7	ν_{13}, vinyl hydrogen out-of-plane bending
980	982.6	ν_{13}, a', cis isomer
	950	ν_{14}, C-C stretching
939	941	
917	936.6, 929.9, 921.7	ν_{15}, vinyl hydrogen out-of-plane bending
898	898.1	ν_{16}, methylene CH$_2$ rocking
751, 745	758.6, 751.8, 745	ν_{17}, C-Cl stretching
	690	$\nu_{19} + \nu_{20}$
	602.5	ν_{18}, vinyl hydrogen out-of-plane deformation

[*]: The low frequency below 600 cm^{-1} were not list here.

Ar/C₃H₅Cl/O₃   The codeposition of O₃ and Ar/C₃H₅Cl (2000/1) did not show new peak.   After the photolysis of 10 minutes, the intensities of parent absorption of O₃ and C₃H₅Cl were weaken and many new peaks were observed at 1340 cm⁻¹, 987 cm⁻¹, 971 cm⁻¹, 856 cm⁻¹, 846 cm⁻¹, 799 cm⁻¹, 733 cm⁻¹, 705 cm⁻¹ and 639 cm⁻¹.   As the time of photolysis last 30 minutes, the intensity of peak at 1340 cm⁻¹, 987 cm⁻¹, and 733 cm⁻¹ were decreased, while additional peaks at 2835 cm⁻¹ and 1737 cm⁻¹ were detected and the peak at 760 cm⁻¹ became broader.   As the photolysis were lasting to 1 hour, the peak of 1737 cm⁻¹ weaken and new absorption group were observed at 1327 cm⁻¹, 1123 cm⁻¹, 1054 cm⁻¹, and 823 cm⁻¹. The band of 760 cm⁻¹ was getting broader.   Continue the photolysis, the intensities of 1327 cm⁻¹ and 1054 cm⁻¹ were weaken while further new peaks at 1765 cm⁻¹ and 1390 cm⁻¹ were observed.   The intensity of 1123 cm⁻¹ and 760 cm⁻¹ bands were increased as the time of photolysis increased.   The infrared spectra change before and after photolysis and the position of new bands are summarized in Figure 1 and Table 2.
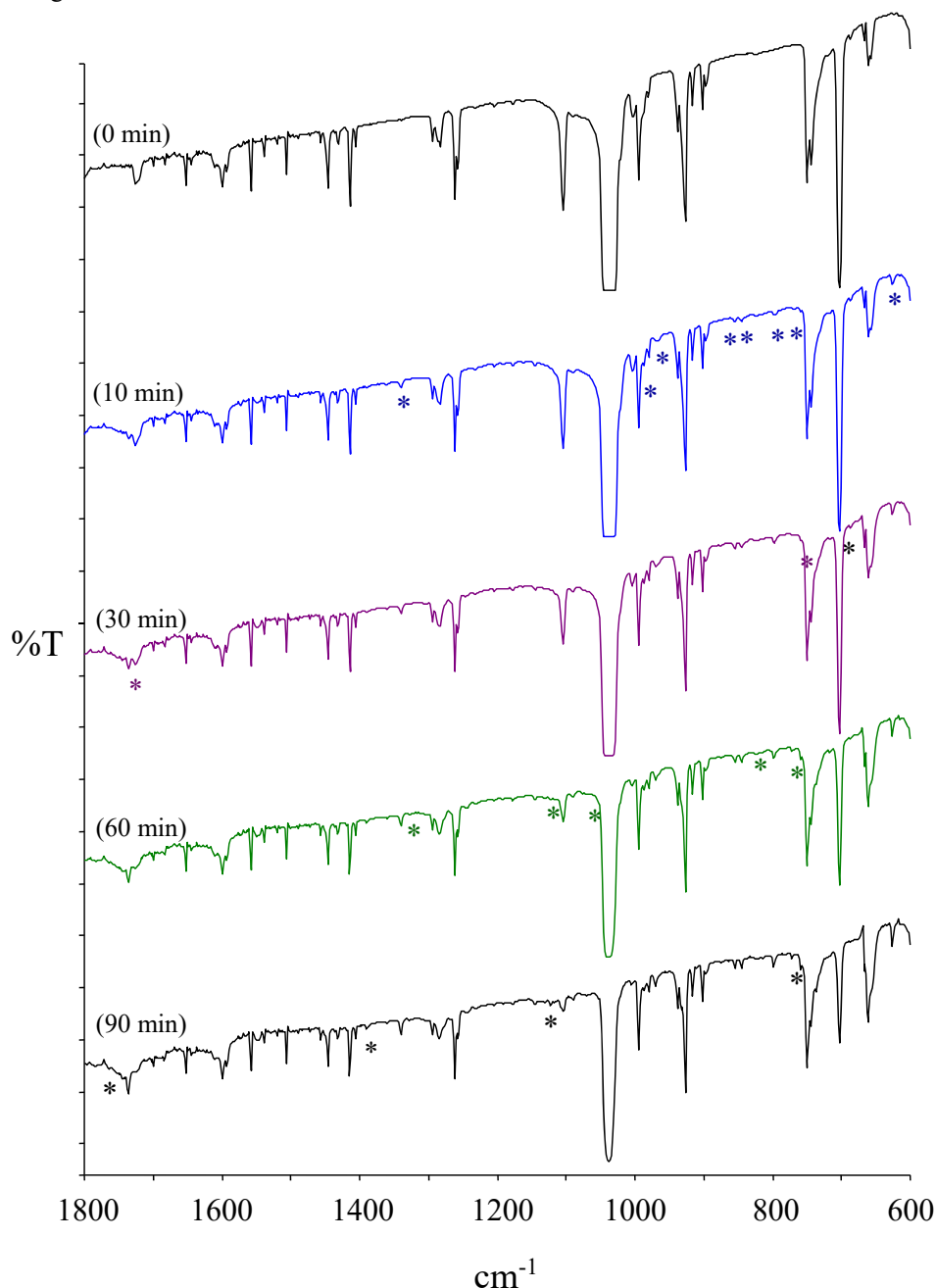

Fig. 1 Infrared spectra (1800-600 cm⁻¹) of Ar/C₃H₅Cl/O₃ before and after photolysis at

various time.

Table 2. The peak position of new absorptions (cm^{-1}) of Ar/C$_3$H$_5$Cl/O$_3$ matrix after photolysis at various time.

Time of photolysis	Frequency (cm^{-1})*	Literature[14]	Calculation[15]	Assignments
10 min	1340		1333	C-H bending
	987		991	C-O st.
	971	974	974	C-O st.
	856, 846		861	O-O-O symm. st.
	799			?
	773			?
	705		705	C-Cl st.
	639	640	647	O-O-O asymm. st.
30 min	2835		2811	C-H st.
	1737		1737	C=O st.
	760		762	C-Cl st.
60 min	1327	1328	1334	CH$_2$ bending
	1123	1122	1099	C-O-C asymm. st.
	1054	1052	1067	C-O-O asymm. st.
	823	829	812	O-O st.
	760, I↑		743	C-Cl st.
90 min	1765		1772	C=O asymm. st
	1390		1386	-CH$_2$ bend
	1123, I↑		1152	C-O-O asymm. st.
	760, I↑		761	C-Cl st.

*: Only additional new bands were listed here after 10 min.

Ar/Allyl Bromide (Ar/C$_3$H$_5$Br)   The spectrum was taken after the deposition of Ar/C$_3$H$_5$Br (2000/1) and coincided with the spectrum of literature in gas phase.   The spectrum was shown in Figure 2 and positions of absorption peaks were listed on Table 3.   After photolysis, two new peaks were detected at 849 cm^{-1} and 843 cm^{-1} which were increased in intensities as the photolysis time increased.   As the concentration of Ar/C$_3$H$_5$Br was increased to 500/1 or 200/1, no additional new peak was observed, while the very weak band at 1248 cm^{-1} and 975 cm^{-1} turn to apparent band as the photolysis time last longer.
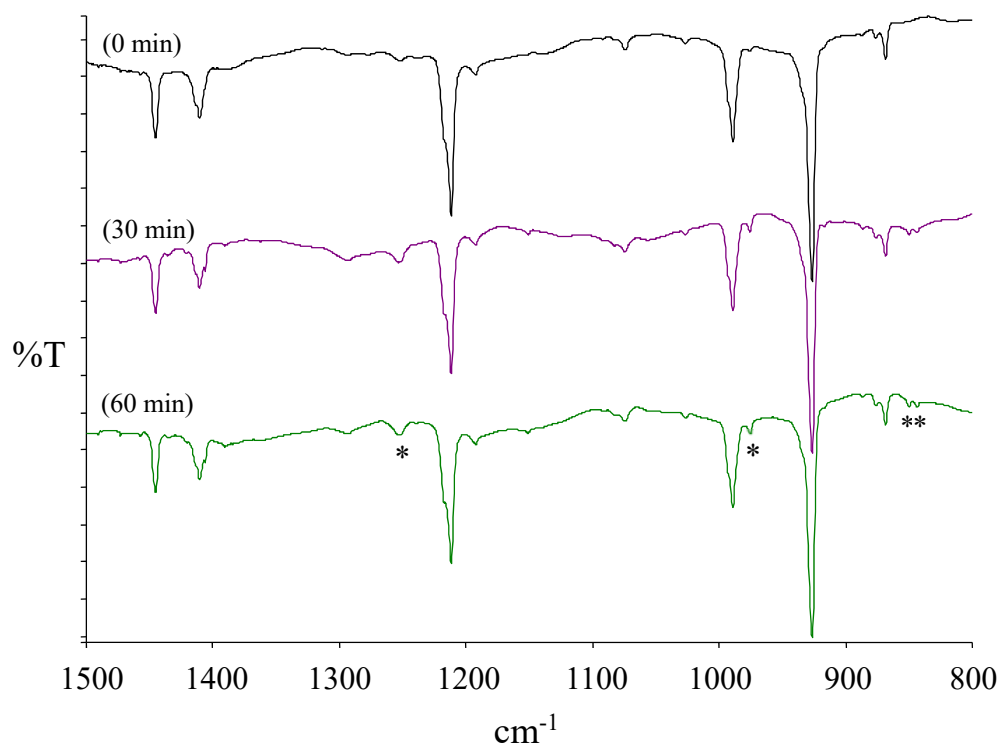
Fig. 2 Infrared spectra of Ar/allyl bromide (2000/1) before and after photolysis.

Table 3 The frequency positions (cm^{-1}) of IR spectrum of Ar/allyl bromide (2000/1)

Ar matrix	Literature(gas)[*, 13]	Assignment
3109, 3103	3106.8, 3101.9, 3090	ν_1, vinyl CH stretching
3076	3070	$\nu_6+\nu_7$
3019	3025.7, 3019.1	ν_2, vinyl CH stretching
2999	2998, 2992	ν_3, vinyl CH stretching ν_4, methylene asymmetric CH$_2$ stretching
2970, 2965	2986.1, 2972.9	ν_5, methylene symmetric CH$_2$ stretching
2877	2881.5, 2870	$2\nu_7$
2345, 2340	2670, 2660	$\nu_7+\nu_{10}$
	2420, 2409	$2\nu_{10}$
	1955 broad	$2\nu_{13}$
1853	1859.9, 1850.9	$2\nu_{15}$
1652, 1646	1651.1, 1646.5, 1638	ν_6, C=C stretching
	1530	$\nu_{13}+\nu_{18}$
1445	1455.7, 1449.9, 1444	ν_7, methylene CH$_2$ bending
1410	1421.6, 1416.4, 1410	ν_8, vinyl CH$_2$ bending
	1300	ν_9, vinyl hydrogen in-plane bending
1251	1259, 1252.5, 1240	ν_{10}, cis isomer

1217, 1211	1222.1, 1210.5	ν_{10}, methylene CH$_2$ wagging
1191	1190$^\#$	ν_{11}, vinyl hydrogen in-plane bending
1151(vw)	1154	ν_{12}, cis isomer
1074	1079.5, 1069.1	ν_{12}, methylene CH$_2$ twisting
989, 975	993.2, 987.5, 983.4	ν_{13}, vinyl hydrogen out-of-plane bending
934	935$^\#$	ν_{14}, C-C stretching
926	933, 924.2	ν_{15}, vinyl hydrogen out-of-plane bending
868	876, 868.8, 864.5	ν_{16}, methylene CH$_2$ rocking $\nu_{17}+\nu_{19}$
763	778	$2\nu_{19}$
695, 691	704.1, 693.3	ν_{17}, C-Br stretching
	651.5	$\nu_{19}+\nu_{20}$

*: The low frequency below 600 cm^{-1} were not list here.
$^\#$: solution phase

Ar/(C$_3$H$_5$Br)/O$_3$ There is no apparent change in infrared spectrum after the codeposition of Ar/C$_3$H$_5$Br/O$_3$. After the photolysis of 10 min, the peak intensities of parent bands of allyl bromide and ozone were decreased. Several new peaks were detected at 1389 cm^{-1}, 1361 cm^{-1}, 1333 cm^{-1}, 1266 cm^{-1}, 952 cm^{-1}, 901 cm^{-1}, 837 cm^{-1}, 785 cm^{-1}, 761 cm^{-1}, and 620 cm^{-1}.   As the photolysis lasting 30 min, the peak at 1389 cm^{-1}, 1361 cm^{-1}, 1333 cm^{-1}, and 1266 cm^{-1} were weaken, the shape of 620 cm^{-1} peak was broader, and a new band at 1731 cm^{-1} was observed.   Further photolysis led to the decrease in intensity of 970 cm^{-1} and 867 cm^{-1} parent bands, while additional new bands at 1744 cm^{-1} and 992 cm-1 were detected.   The intensity of 655 cm^{-1} band was increased as the time of photolysis increased.   The infrared spectra change after photolysis and the position of new bands are summarized in Figure 3 and Table 4.   Some of these new peaks stated above were not apparent at low concentration of Ar/C$_3$H$_5$Br (2000/1 or 500/1).   Increased the distance of co-deposition (mixed time) or the time of photolysis did not observe new absorption.
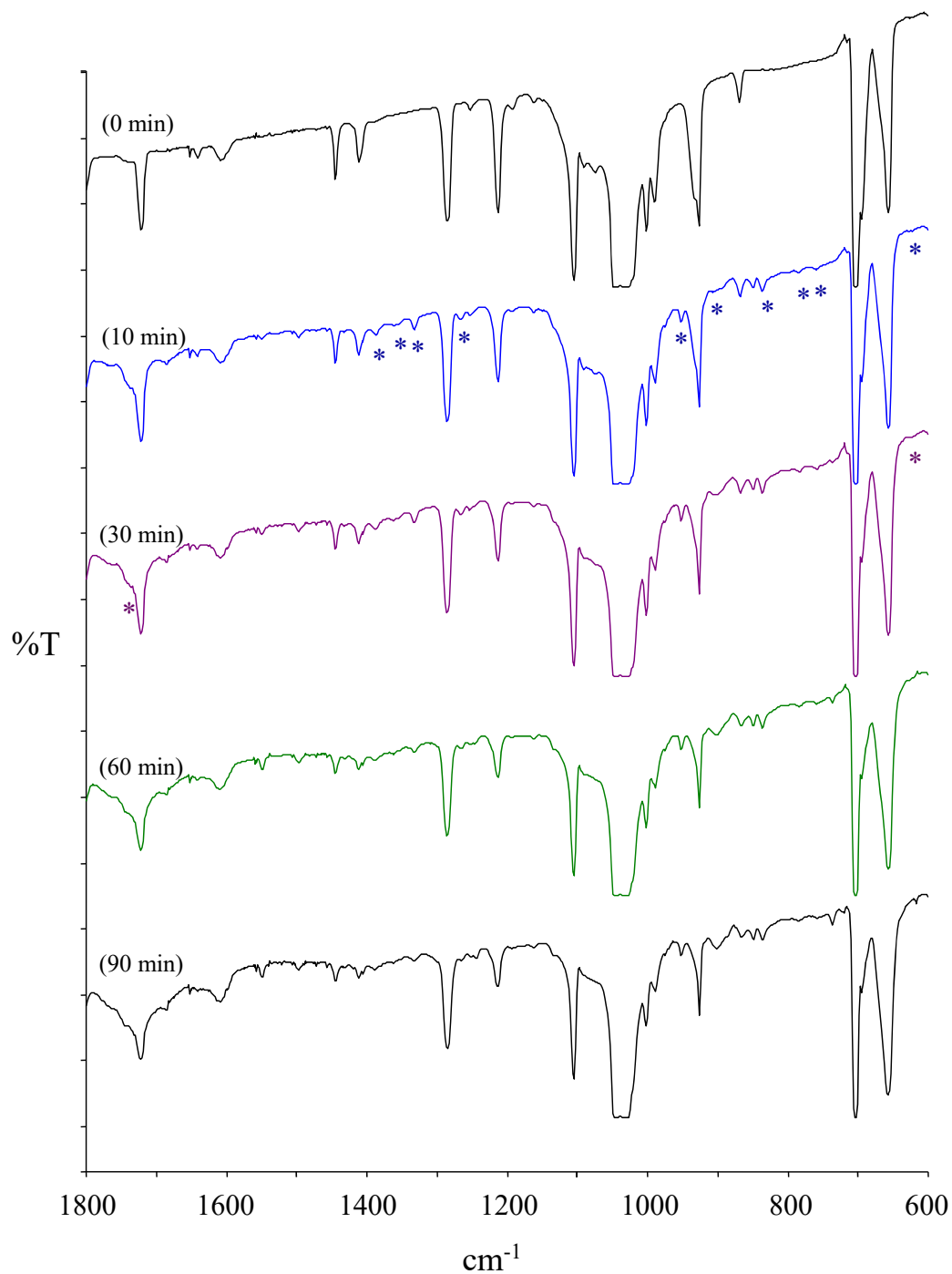
Fig. 3 Infrared spectra (1800-600 cm^{-1}) of Ar/C$_3$H$_5$Br/O$_3$ after photolysis at various time. (a)

0 min； (b) 10 min； (c) 30 min；(d) 60 min；(e) 90 min

Table 4. The peak position of new absorptions (cm^{-1}) of Ar/C$_3$H$_5$Br/O$_3$ matrix after photolysis at various time.

Time of photolysis	Frequency (cm^{-1})*	Literature[14]	Calculation[15]	Assignments
10 min	1389		1402	CH$_2$ bend
	1361			?

	1333		1328	CH$_2$ bend
	1266			?
	952		941	C-O st.
	901		874	C-O st.
	837	846 (POZ)	856	O-O-O symm. st.
	785			?
	761			?
	620		622	C-Br st.
30 min	1731		1730	C=O st.
	620 I↑		598	C-Br st.
60 min	970	967 (SOZ)	979	C-O-C symm. st.
	867	847 (SOZ)	839	C-O-O symm. st.
	720		718	Ring skeletal bend
	655 I↑		634	C-Br st.
90 min	1744		1770	C=O asymm. st
	992		996	C-O-C asymm. st.
	655 I↑		657	C-Br st.

*: Only additional new bands were listed here after 10 min.

Band Assignments

Ar/C$_3$H$_5$Cl/O$_3$ The new peaks at 987 cm^{-1} and 971 cm^{-1} were detected after 10 minutes photolysis of matrix of Ar/C$_3$H$_5$Cl/O$_3$.   Usually, the range of 970 cm^{-1} ~ 1260 cm^{-1} is the absorption of C-O stretching vibrational mode.   Andrew et al[14] have studied the reaction of propene with ozone and indicated that the product of primary ozonide (POZ), 4-methyl-1,2,3-trioxolane, which has a C-O stretching vibration at 974 cm^{-1}.   If the reaction of allyl chloride/ozone was similar to propene/ozone, the POZ product should be 4-(chloromethyl)-1,2,3-trioxolane **(A)**, therefore, the band assignment would compare the value of experimental results with theoretical calculation of vibrational frequencies of 4-(chloromethyl)-1,2,3-trioxolane.

From the list on Table 3, the calculated frequencies of two C–O stretching mode of –OCHCH$_2$Cl and –CH$_2$O group of product **(A)** are 991 cm^{-1} and 974 cm^{-1}, respectively.   Therefore, the experimental value of 987 cm^{-1} and 971 cm^{-1} can be assigned as the two C–O stretching vibrational frequencies of compound **(A)**.   The observed new peak at 856 cm^{-1} was agreed with the calculated frequency of 861 cm^{-1} which is the symmetry stretching vibrational mode of O–O–O of product **(A)**.   The new absorption at 639 cm^{-1} can be assigned as the asymmetry stretching vibrational mode of O–O–O of compound **(A)**, which was agreed with 640 cm^{-1} for 4-methyl-1,2,3-trioxolane and calculated 647 cm^{-1} for molecule **(A)**.   Another new band at 705 cm^{-1} can be assigned as C–Cl stretching vibrational mode of product **(A)**.   All the above suggested observed new peaks at 987 cm^{-1}, 971 cm^{-1}, 856 cm^{-1}, 639 cm^{-1}, 705 cm^{-1} are belong to the vibrational of product of POZ, 4-(chloromethyl)-1,2,3-trioxolane.   Another two peaks at 799 cm^{-1} and 733 cm^{-1} were not assigned due to no enough literature and calculated data.

Additional group of new absorptions were detected after the photolysis of 30 minutes, including an apparent band at 1737 cm^{-1} which is in the range of C=O stretching mode.   The stretching vibrational mode of C=O of aldehyde is in the range of 1645 cm^{-1}~1745 cm^{-1}.   Calculation of the C=O stretching mode of possible intermediate HC(O)CH$_2$Cl **(B)** is 1737 cm^{-1}, therefore, 1737 cm^{-1} can assign as the C=O stretching vibrational of **(B)**.   The observed new peak at 2835 cm^{-1} is C–H stretching of HC(O)- group compared to the calculated value 2811 cm^{-1} of **(B)** molecule.   Another new band at 760 cm^{-1} can be assigned as C-Cl stretching mode of **(B)** which was 762 cm^{-1} by calculation.   Therefore, new absorption bands after further photolysis were belong to the vibrational frequencies of intermediate HC(O)CH$_2$Cl.

When the photolysis continuous to 1 hour, new observed band at 823 cm^{-1} which is belong to the range of stretching vibrational frequency of O–O group, 800 cm^{-1} ~ 1000 cm^{-1}.   Comparison with the stretching vibrational mode of O–O group was 829 cm^{-1} for the secondary ozonide product (SOZ), 3-methyl-1,2,4-trioxolane, of propene/ozone system and calculated value of 812 cm^{-1} for 3-(chloromethyl)-1,2,4-trioxolane **(C)**.   Thus, 823 cm^{-1} should belong to the vibrational mode of O–O group.   Another new band at 1054 cm^{-1} is in the range of C–O–O asymmetry stretching (1000 cm^{-1}~1200 cm^{-1}), comparing with the literature frequency of 1052 cm^{-1} for correspond frequency of 3-(methyl)-1,2,4-trioxolane and calculated frequency 1067 cm^{-1} for product **(C)**.   Therefore, the peak of 1054 cm^{-1} can easily assigned to be asymmetry stretching mode of C–O–O group of molecule **(C)**.   Additional new peaks of 1123 cm^{-1}, similarly comparison with frequency (1122 cm^{-1}) of 3-methyl-1,2,4-trioxolane and the calculated value (1099 cm^{-1}) for compound **(C)**, can be assigned as the asymmetry

stretching vibrational mode of C–O–C.   Similarly, the peak of 1327 cm^{-1} can assigned to be the bending vibrational frequency of –CH$_2$ group which is 1328 cm^{-1} for 3-methyl-1,2,4-trioxolane and 1334 cm^{-1} for compound **(C)**.   The intensities of parent bands at 2928 cm^{-1} and 760 cm^{-1} were increased as the time of photolysis increased.   The calculated value of C-Cl stretching mode is 762 cm^{-1} for **(B)** and 743 cm^{-1} for **(C)**, therefore, the increase in intensity of 760 cm^{-1} might due to these two products.   All the above suggested these new absorptions should belong to the vibrational modes of 3-(chloromethyl)-1,2,4-trioxolane.

Further photolysis resulted in an apparent new band at 1765 cm^{-1} which is in the range of vibrational mode of C=O functional group.   The stretching vibrational mode of C=O of acid anhydrous is about 1725 cm^{-1}~1870 cm^{-1} and the calculation value of C=O asymmetry stretching mode of possible product formic chloroacetic anhydride **(D)** was 1772 cm^{-1}, therefore, 1765 cm^{-1} may assigned as the C=O asymmetry stretching mode. Another new band at 1390 cm^{-1} which matched the calculation frequency (1386 cm^{-1}) of C–H bending vibrational mode of CH$_2$Cl group for molecule **(D)**.   The intensity of 1123 cm^{-1} was increased as the time of photolysis increased.   The calculated frequency of asymmetry stretching mode of C–O–C of compound **(D)** is 1152 cm^{-1}, the enhanced in intensity of 1123 cm^{-1} might arise from the asymmetry stretching mode of C–O–C of product **(D)**. The calculation frequency of stretching vibrational mode of C–Cl of compound **(D)** is 761 cm^{-1}, which might explain the enhancement of 760 cm^{-1}.   Based on the characteristics of above, suggested that a stable product as formic chloroacetic anhydride was formed.

Ar/C$_3$H$_5$Br/O$_3$ Similar to the assignment of allyl chloride/O$_3$ in argon matrix, the frequencies of observed new bands were compared to related frequency of product of propene/ozone, 3-methyl-1,2,4-trioxolane, and the calculated frequencies of possible products, 4-(bromomethyl)-1,2,3-trioxolane **(E)**, HC(O)CH$_2$Br **(F)**, formic bromoacetic anhydride **(G)**, and 3-(bromomethyl)-1,2,4-trioxolane **(H)**.

After the first photolysis of Ar/C$_3$H$_5$Br/O$_3$ matrix, the new bands at 1389 cm^{-1} and 1333 cm^{-1} can be assigned as CH$_2$ bending mode which is 1402 cm^{-1} and 1328 cm^{-1} for compound **(E)**, respectively.   The new peaks of 952 cm^{-1} and 901 cm^{-1} were belong to C-O stretching mode which was 941 cm^{-1} and 874 cm^{-1} of C–O of –OCHCH$_2$Br and –CH$_2$O group of molecules **(E)**, respectively.   The absorption at 837 cm^{-1} was stretching mode of O–O–O which was 846 cm^{-1} for 1,2,3-trioxolane and 856 cm^{-1} for compound **(E)**.   Another new band observed at 620 cm^{-1} was agreed with the calculated frequency of C–Br stretching mode (622 cm^{-1}) for **(E)**, therefore, 620 cm^{-1} should be assigned as the stretching vibrational frequency of C–Br.   All the above suggested the new groups observed at this stage were belong to the frequencies of possible product 4-(bromomethyl)-1,2,3-trioxolane.

After the photolysis of 30 minutes, a shoulder at 1731 cm^{-1} was appeared.   The stretching vibrational frequency of C=O is in the range 1645 cm^{-1}~1765 cm^{-1}, the calculated frequency for this mode of HCOCH$_2$Br **(F)** is 1730 cm^{-1}, therefor, 1731 cm^{-1} should be assigned as C=O stretching mode.   The intensity of above new band 620 cm^{-1} was increased, the calculated value of C–Br stretching mode of molecule **(F)** is 598 cm^{-1}, the enhancement in 620 cm^{-1} might due to the contribution of C–Br group of HCOCH$_2$Br and therefore increased as the increase in photolysis time.

New band at 720 cm^{-1} was detected after 1 hr photolysis, which is agreed with the calculated frequency of ring skeletal bending mode (718 cm^{-1}) of 3-(bromomethyl)-1,2,4-trioxolane **(G)**.   Another new band of 867 cm^{-1} was assigned as C–O–O stretching mode which is 847 cm^{-1} for 3-methyl-1,2,4-trioxolane, SOZ product of propene/O$_2$ reaction and 839 cm^{-1} for calculated value for molecule **(G)**.   Compared to the frequency of C–O–C stretching mode (967 cm^{-1}) of compound **(G)** and calculated value (979 cm^{-1}) of molecule **(G)**, the new peak at 970 cm^{-1} can be assigned as C–O–C stretching mode.   Around the band 655 cm^{-1}, the intensity of new band was increased, which might due to the absorption of C–Br stretching mode of compound **(G)** with a calculated value 634 cm^{-1}.   All the above indicated additional new bands observed after the photolysis of 1 hour were arise from the product of 3-(bromomethyl)-1,2,4-trioxolane.

Further photolysis, a new band was observed at 1744 cm^{-1} which was in the range of C=O stretching of acid anhydride (1725 cm^{-1}~1870 cm^{-1}).   The calculated value of this mode for formic bromoacetic anhydride **(H)** was 1770 cm^{-1}.   Therefore, 1744 cm^{-1} was assigned as the asymmetry stretching vibration of C=O bond. Another new band at 992 cm^{-1} can be assigned to the stretching mode of C–O–C, which was 1050 cm^{-1}~900 cm^{-1} for acid anhydride and 996 cm^{-1} for calculated value for molecule **(H)**.   Finally, the position of 655 cm^{-1} is nearly match with the calculated value (657 cm^{-1}) of C–Br of compound **(H)** and therefore led to the increase in intensity of 655 cm^{-1}.   From the character of these new peaks, suggesting a final stable product of formic bromoacetic anhydride was formed.
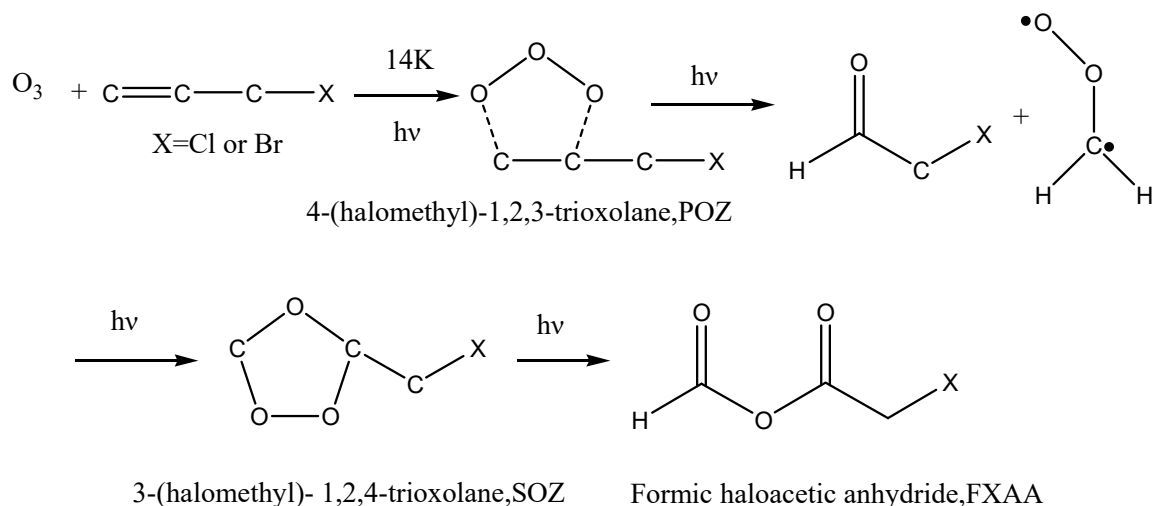
IV.   DISCUSSIONS
Based on the assignment of new absorptions by comparison with literature and calculated value of possible molecules, indicated that allyl halide reacted with ozone will produce 4-(halomethyl)-1,2,3-trioxolane

(POZ), $HCOCH_2Br$, 3-(halomethyl)-1,2,4-trioxolane (SOZ), and formic haloacetic anhydride (FXAA) were formed at different stage of photolysis. These intermediates and product were very similar to the products of reaction of propene/ozone. The photolysis of ozone may decompose to O_2 and O atom, which might give additional new product when they reacted with allyl halide, however, we did not find additional band in IR spectrum.

From the intensity change of new bands, we found that POZ was first formed, the intensities of these bands will decrease as the photolysis continuously and then the formation of $HC(O)CH_2X$ was detected. Keep further photolysis, the bands due to $HC(O)CH_2X$ was weaken and peaks of SOZ was appeared and finally the formation of FXAA was observed. The reaction of allyl halide with ozone might similar to the reaction of propene with ozone. The possible mechanism was summarized on Scheme II.

Scheme II

4-(halomethyl)-1,2,3-trioxolane,POZ

3-(halomethyl)- 1,2,4-trioxolane,SOZ   Formic haloacetic anhydride,FXAA

For the reaction of propene/O_3, the breakage of ozone ring of POZ might produce two possible intermediates (1) or (2), both can form SOZ[1]. Criegee suggested the path of forming SOZ from intermediate (1) is more possible.
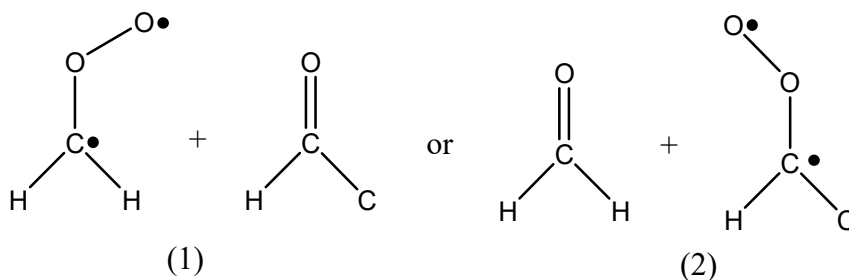
Similarly, the cyclic addition of ozone to allyl halide would led to the formation of POZ, and then ozone ring break to intermediate (3)/(4) or (5)/(6) which would form SOZ. Finally, the breakage of O–O bond to form a stable product formic haloacetic anhydride.
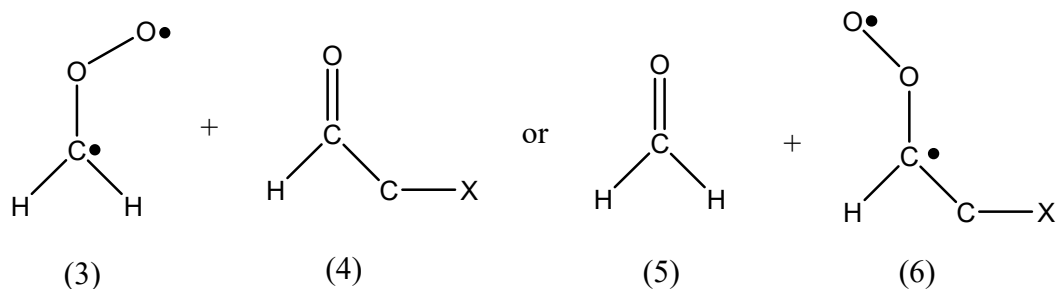
The vibrational frequencies[16] of intermediate (5) were 2863 cm^{-1}, 1743 cm^{-1}, and 1498 cm^{-1}. These peaks were not observed in our experiment, however, we found the new bands of intermediate (4), HC(O)CH$_2$X, for both reactions of allyl chloride and allyl bromide with ozone. On the other hand, both intermediates (3) and (6) are two unpaired electron radicals which were more electrophilic, –CH$_2$X group is electron-withdrawing group which would less favor the formation of intermediate (6) compared to the formation of (3). Therefore, the breakage of ozone ring should occur at the O–O side which connected to –CH$_2$X group to form the intermediate (4). Based on the above evidences, the breakage of POZ would produce intermediate (3)/(4). Furthermore, previously discussion of reaction mechanism of propene/ozone was only to the formation of SOZ. We found that more stable products of formic haloacetic anhydride were formed after the photolysis of SOZ.

V. CONCLUSION

The photolysis reactions of allyl chloride and allyl bromide with ozone in Ar matrix have been conducted. After photolysis, the new absorption bands of IR spectra were compared with frequencies of literature and theoretical calculation, indicated the isolated products are 4-(halomethyl)-1,2,3-trioxolane (POZ), HCOCH$_2$X, 3-(halomethyl)-1,2,4-trioxolane (SOZ), and formic haloacetic anhydride. The reaction mechanism was first 1,3 dipolar cycloaddition of ozone to double bond of allyl halide to form POZ, POZ was then decomposed to carbonyl component and HC(O)CH$_2$X, HC(O)CH$_2$X were retro-cycloaddition to carbonyl component to form SOZ, and finally the SOZ was decomposed to a stable formic haloacetic anhydride.

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