

Matrix isolation study of reactions of propargyl halides with ozone

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ABSTRACT

The photolysis reactions of propargyl halide with ozone in Ar matrix have been conducted. After photolysis, the new absorption bands of IR spectra were compared with literature and theoretical calculation frequencies of possible products, indicated the isolated products are 4-(halomethyl)-1,2,3-trioxolene (POZ), 1-(halomethyl)-2,3,5-trioxo-bicyclo[2.1.0]pentane (SOZ), and formic haloacetic anhydride. The reaction mechanism was first 1,3 dipolar cycloaddition of ozone to triple bond of propargyl halide to form POZ and then decomposed to ionic component and rearranged to form SOZ, and finally the SOZ decomposed to stable formic haloacetic anhydride.

KEYWORDS: IR, matrix isolation, propargyl halides, ozone

Date of Submission: 03-03-2022

Date of Acceptance: 17-03-2022

I. INTRODUCTION

Propargyl halide has both halide atom and unsaturated bond which can undergo alkyl halide reaction and unsaturated bond reaction. These characteristics let propargyl halides become important chemical intermediates. Although the addition reaction of propargyl halide is not easy as allyl halide, alkyne has two π -electrons led to more type of reactions. Therefore, the relative reaction of ozone with alkynes gave a lot interesting in atmosphere chemistry.^[1-6]

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.^[7] Many reactions such as the decomposition of organic compounds, oxidation of sulfur oxide, and conversion of NO_x are related with ozone.

Most reaction of alkynes with ozone molecule are based on theoretical calculation to study its reaction mechanism.^[5-10] There are relative less research data of reactions of ozone molecule with alkynes. Previous study^[9] of chloroacetylene has an electron withdrawing -Cl group connected to $\text{C}\equiv\text{C}$ triple bond, while propargyl halide has methyl halide ($-\text{CH}_2\text{X}$) group connected to triple bond, whether the $-\text{CH}_2\text{X}$ substituted group will affect the reaction mechanism. Matrix isolation technique^[11-13] was developed in mid-1950's and applied to the study of unstable molecules and free radicals.^[14] Therefore, this research will apply matrix isolation/infrared spectrum to study the reaction of propargyl halide with ozone and oxygen molecule.

II. EXPERIMENTAL

All of the experiments were carried out on conventional matrix isolation setup as previous.^[15-18] The experimental system consisted of four basic parts, the cryogenic system, the cold cell vacuum vessel, the vacuum system, and Fourier transform 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 vacuum vessel was equipped with CsI windows and quartz windows and sat in tile sample beam of the infrared spectrometer. The vacuum manifold was stainless steel (Cajon fitting) with Nupro valves.

The samples of Ar (99.9995%, Lien Hwa) and O_2 (99.995%, San Fu or Matheson) were used as received. Propargyl bromide $\text{C}_3\text{H}_3\text{Br}$ (99%, Aldrich) and propargyl chloride $\text{C}_3\text{H}_3\text{Cl}$ (98%, ACROS) were purified by trap-to-trap distillation before use. 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.

III. RESULTS

Ar/Propargyl Chloride ($\text{C}_3\text{H}_3\text{Cl}$) The deposition of Ar/ $\text{C}_3\text{H}_3\text{Cl}$ at varied concentration (2000/1~200/1) were conducted and IR spectrum was measured before and after photolysis. The absorption positions of blank spectrum was consistent with previous study^[17] and literature spectra.^[19] After photolysis, a new peak was observed at 867 cm^{-1} which is increased in intensity as concentration of $\text{C}_3\text{H}_3\text{Cl}$ increased. The infrared spectra before and after photolysis and the positions of absorption have been summarized in previous study.^[17]

Ar/ $\text{C}_3\text{H}_3\text{Cl}/\text{O}_3$ The codeposition of O_3 and Ar/ $\text{C}_3\text{H}_3\text{Cl}$ (2000/1) resulted in no new peak. After the photolysis of 10 minutes, the parent absorption of O_3 and $\text{C}_3\text{H}_3\text{Cl}$ were weakened and several new peaks were observed at 1670 cm^{-1} , 1150 cm^{-1} , 1132 cm^{-1} , 1021 cm^{-1} , 991 cm^{-1} , 928 cm^{-1} , 752 cm^{-1} , and 727 cm^{-1} . As the time of photolysis last 30 minutes, the intensity of peak at 1021 cm^{-1} , 928 cm^{-1} , and 727 cm^{-1} were decreased, while additional peak at 1060 cm^{-1} , 985 cm^{-1} , 975 cm^{-1} , and 908 cm^{-1} were detected and the intensity of 752 cm^{-1} was enhanced. As the photolysis were continued to 1 hour, the peak of 985 cm^{-1} and 975 cm^{-1} were decreased in intensity and two new absorptions were observed at 1744 cm^{-1} and 953 cm^{-1} . While the intensity of 752 cm^{-1} peak became stronger. The infrared spectra change and the position of new bands before and after photolysis were summarized in Figure 1 and Table 1. As the concentration of Ar/ $\text{C}_3\text{H}_3\text{Cl}$ increased to 500/1 and 200/1, the intensities of new peaks were increased and no further new peak was detected. No new additional absorption peak was observed in the photolysis during deposition or change the distance of deposition.

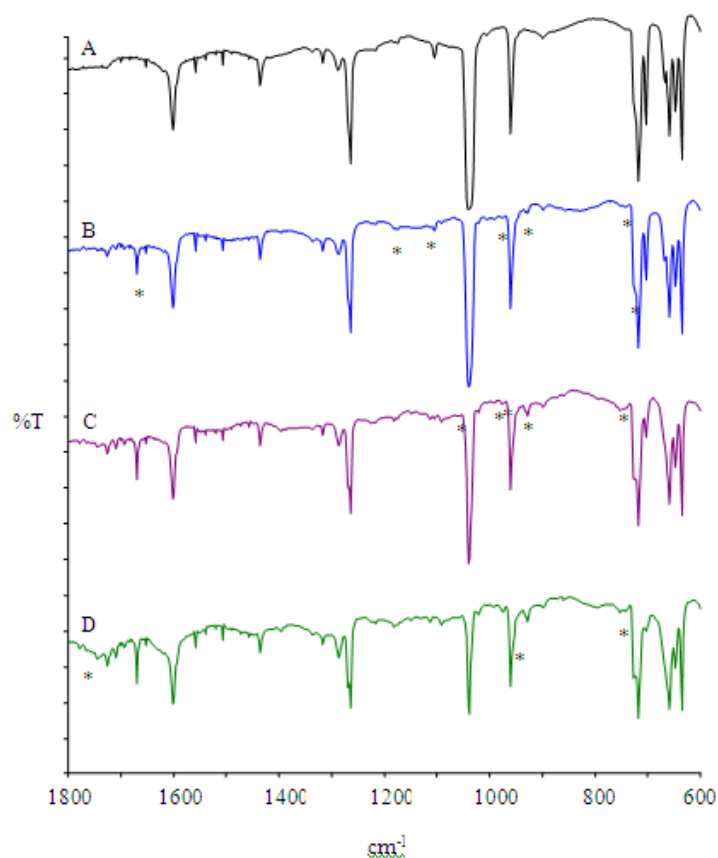


Fig. 1 Infrared spectra of Ar/ $\text{C}_3\text{H}_3\text{Cl}$ (2000/1) before and after photolysis in the range at $1800\text{--}600\text{ cm}^{-1}$. (A) 0 min; (B) 10 min; (C) 30 min; (D) 60 min; (E) 90 min

Table 1. The positions of new peaks (cm^{-1}) of $\text{Ar}/\text{C}_3\text{H}_3\text{Cl}/\text{O}_3$ after photolysis at various time.

Photolysis time (min)	Experiment frequency (cm^{-1})	Calculation frequency (cm^{-1})*	Assignment
10	1670	1692	C=C st.
	1150	1152	-CH bend
	1132	1125	C-H bend
	991	995	C-O st.
	928	919	C-O st.
	752	751	C-Cl st.
	727	720	ring skeletal bend
30	1060	1068	asym C-O-O st.
	985	993	sym C-O st.
	975	991	C-O st.
	908	909	C-O st.
	752 \uparrow	732	C-Cl st.
60	1744	1751	asym C=O st.
	953	981	asym C-O-C st.
	752 \uparrow	761	C-Cl st.

* : Calculation frequencies of 4-(chloromethyl)-1,2,3-trioxolene, 1-(chloromethyl)-2,3,5-trioxa-bicyclo[2.1.0]pentane, formic chloroacetic anhydride, unpublished results^[20].

Ar/Propargyl Bromide ($\text{C}_3\text{H}_3\text{Br}$) The spectrum of the deposition of $\text{Ar}/\text{C}_3\text{H}_3\text{Br}$ (2000/1) is in good agreement with literature gas phase spectrum^[19] and previous study. The spectra and the positions of $\text{Ar}/\text{C}_3\text{H}_3\text{Br}$ before and after photolysis have described in previous study.^[17] After the photolysis, several new peaks were detected at 3068cm^{-1} , 1965cm^{-1} , 1425cm^{-1} , 1212cm^{-1} , 1199cm^{-1} , 1082cm^{-1} , 996cm^{-1} , 865cm^{-1} , 804cm^{-1} , and 675cm^{-1} which were similar to the vibrational modes of bromopropadiene^[15] and have assigned bromopropadiene as the product of photolysis of $\text{C}_3\text{H}_3\text{Br}$.^[17] The intensities of these new peak were increased as the concentration of $\text{Ar}/\text{C}_3\text{H}_3\text{Br}$ was increased to 500/1 and 200/1.

Ar/ $\text{C}_3\text{H}_3\text{Br}/\text{O}_3$ There is no apparent change in infrared spectrum after the codeposition of ozone with $\text{Ar}/\text{C}_3\text{H}_3\text{Br}$ (2000/1). After the photolysis of 10 min, the peak intensities parent absorptions of propargyl bromide and ozone were decreased. Several new peaks were detected at 1670cm^{-1} , 984cm^{-1} , 922cm^{-1} , 715cm^{-1} , and 620cm^{-1} . As the photolysis lasting 30 min, the peak at 984cm^{-1} , 922cm^{-1} , 715cm^{-1} and 620cm^{-1} were weaken while the parent peak at 656cm^{-1} was stronger. Two additional new bands at 1055cm^{-1} and 996cm^{-1} were also observed. Further photolysis up to 60 min led to the decrease in intensity of 1055cm^{-1} and 996cm^{-1} bands and increase of 656cm^{-1} , while another additional new bands at 1771cm^{-1} and 1118cm^{-1} were detected. The infrared spectra change and the position of new bands after photolysis are summarized in Figure 2 and Table 2. Increased the concentration of $\text{Ar}/\text{C}_3\text{H}_3\text{Br}$ (500/1 or 200/1) enhanced the intensity of these new peaks stated above while no additional new band was observed. Increased the distance of codeposition (mixed time) or photolysis during deposition did not result in new absorption.

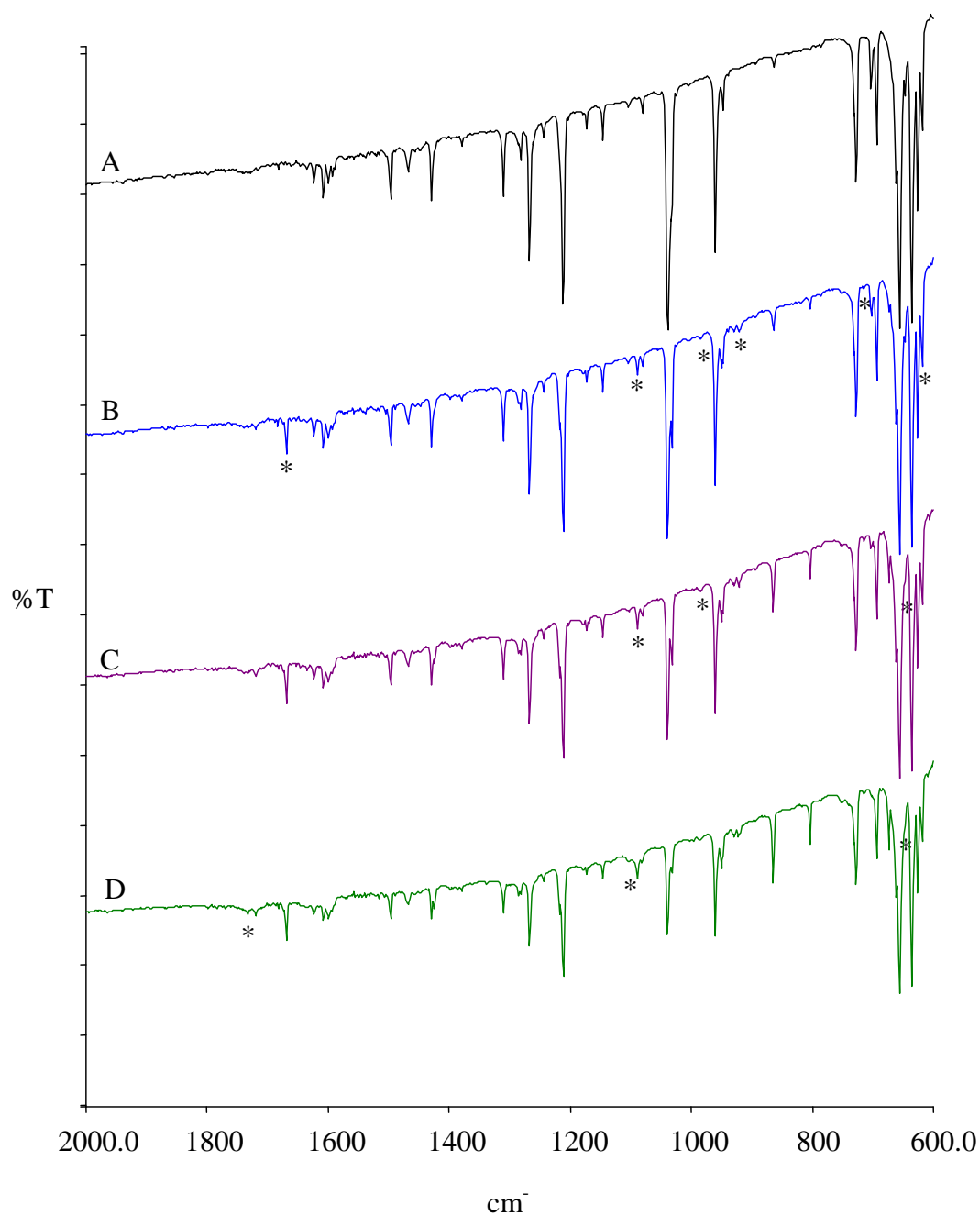


Fig. 2 Infrared spectra (2000-600 cm^{-1}) of $\text{Ar}/\text{C}_3\text{H}_3\text{Br}/\text{O}_3$ after photolysis at various time. (a) 0 min; (b) 10 min; (c) 30 min; (d) 60 min

Table 2. The positions of new peaks (cm^{-1}) of $\text{Ar}/\text{C}_3\text{H}_3\text{Br}/\text{O}_3$ after photolysis at various time.

Time	Frequency (cm^{-1})	Calculation (cm^{-1}) ^a	Assignments
10 min	1670	1691	C=C st.
	1021		?
	984	995	C-O st.
	922	912	C-O st.
	715	713	ring skeletal bend
30 min	620	654	C-Br st.
	1055	1059	asym C-O-O st.

	996	998	sym C-O st.
	655 ↑	648	C-Br st.
60 min	1771	1770	asym C=O st.
	1118	1127	asym C-O-C st.
	655 ↑	657	C-Br st.

*: Calculation frequencies of 4-(bromomethyl)-1,2,3-trioxolene, 1-(bromomethyl)-2,3,5-trioxa-bicyclo[2.1.0]pentane, and formic bromoacetic anhydride, unpublished results^[20]

Band Assignments

Referred to the theoretical study^[6] of reaction of acetylene/O₃, Cremer et al. proposed the product was first formed 1,2,3-trioxolene and transfer to final products include formic anhydride, glyoxal, formaldehyde, formic acid, and glyoxylic acid. Parker et al.^[8] have applied matrix isolation and theoretical calculation to study the reaction of ozone with dimethylacetylene indicated the stable products included dimethylketene, (E)(Z)methyl vinyl ketone, butane-2,3-dione, and acetic anhydride. If the reaction of propargyl halide with O₃ is similar to the reaction of acetylene/O₃ and dimethylacetylene/O₃, the possible stable products will be 4-(halomethyl)-1,2,3-trioxolene, 1-(halomethyl)-2,3,5-trioxa-bicyclo[2.1.0]pentane, and formic haloacetic anhydride. Therefore, the band assignment were accomplished by comparison of observed vibrational bands to the literature value and theoretical calculated frequency of 4-(halomethyl)-1,2,3-trioxolene, 1-(halomethyl)-2,3,5-trioxa-bicyclo[2.1.0]pentane, and formic haloacetic anhydride.

Ar/C₃H₃Cl/O₃ After the photolysis in 10 min, the position new peaks are 1670 cm⁻¹, 1150 cm⁻¹, 1132 cm⁻¹, 1021 cm⁻¹, 991 cm⁻¹, 928 cm⁻¹, 752 cm⁻¹, and 727 cm⁻¹ which are closed to the theoretical calculation frequencies of 4-(chloromethyl)-1,2,3-trioxolene molecule. The peak at 1670 cm⁻¹, 991 cm⁻¹, 928 cm⁻¹, and 727 cm⁻¹ can be assigned as the C=C stretching (1692 cm⁻¹), C-O stretching (995 cm⁻¹ and 919 cm⁻¹), and ring skeletal bending mode (720 cm⁻¹) of 4-(chloromethyl)-1,2,3-trioxolene compound, respectively. The new bands of 1150 cm⁻¹ and 1132 cm⁻¹ are assigned as -CH₂ bending mode (1152 cm⁻¹) of and -CH bending mode (1125 cm⁻¹) of -CH₂Cl group, respectively. The bands of 860 cm⁻¹ is closed to the calculated value of O-O-O stretching (862 cm⁻¹), therefore, this band can be assigned as the O-O-O stretching of 4-(chloromethyl)-1,2,3-trioxolene. The band at 752 cm⁻¹ is closed to the C-Cl stretching mode (751 cm⁻¹) of 4-(chloromethyl)-1,2,3-trioxolene. Usually, the range of 970 cm⁻¹ ~ 1260 cm⁻¹ is the absorption of C-O stretching vibrational mode. All the above indicated these new observed bands are belonged to the vibrational modes of 4-(chloromethyl)-1,2,3-trioxolene molecule.

Further photolysis to 30 minutes, the second group of new absorptions are 1060 cm⁻¹, 985 cm⁻¹, 975 cm⁻¹, and 908 cm⁻¹. Compared to the calculated frequencies of 1-(halomethyl)-2,3,5-trioxa-bicyclo[2.1.0]pentane, the peak at 1060 cm⁻¹ and 985 cm⁻¹ can be assigned as C-O-O asymmetry stretching (1068 cm⁻¹) and C-O stretching mode (993 cm⁻¹). The weak bands of 991 cm⁻¹ and 908 cm⁻¹ were two C-O stretching mode (991 cm⁻¹ and 909 cm⁻¹) of 1-(halomethyl)-2,3,5-trioxa-bicyclo[2.1.0]pentane. The broaden of 752 cm⁻¹ might due to the C-Cl stretching vibration mode (751 cm⁻¹) of 1-(halomethyl)-2,3,5-trioxa-bicyclo[2.1.0]pentane. Based on the above comparison, the new observed bands of second group are belonged to the vibrational modes of 1-(halomethyl)-2,3,5-trioxa-bicyclo[2.1.0]pentane compound.

Continued the photolysis resulted in third group of new peaks are 1744 cm⁻¹, 953 cm⁻¹, and 761 cm⁻¹. These peaks are closed to the C=O stretching vibrational mode (1751 cm⁻¹), C-O-C asymmetry stretching mode (981 cm⁻¹), and C-Cl stretching mode (761 cm⁻¹) of formic chloroacetic anhydride (FCAA), respectively. Therefore, this new group suggested a stable product of formic chloroacetic anhydride (FCAA) was formed.

Ar/C₃H₃Br/O₃ Similar to the assignment of propargyl chloride/O₃ in argon matrix, the frequencies of observed new bands were compared to related calculated frequency of possible products. After the photolysis of Ar/C₃H₃Br/O₃ matrix in 10 minutes, the new bands at 1670 cm⁻¹, 984 cm⁻¹, 922 cm⁻¹, 715 cm⁻¹, and 620 cm⁻¹. Compared with the calculated vibrational frequency of 4-(bromomethyl)-1,2,3-trioxolene, peak of 1670 cm⁻¹ can be assigned as C=C stretching mode (1691 cm⁻¹). The two weak bands at 984 cm⁻¹ and 922 cm⁻¹ are in the range of C-O stretching mode (970 cm⁻¹ ~ 1260 cm⁻¹) and therefore can be assigned as C-O stretching modes (995 cm⁻¹ and 912 cm⁻¹) of 4-(bromomethyl)-1,2,3-trioxolene. Peak at 715 cm⁻¹ are closed to the ring skeletal bending mode (713 cm⁻¹) and 655 cm⁻¹ are consisted with the C-Br stretching mode (654 cm⁻¹) of 4-(bromomethyl)-1,2,3-trioxolene. From the character of these new peaks suggested the new groups observed were belong to the frequencies of possible product 4-(bromomethyl)-1,2,3-trioxolene.

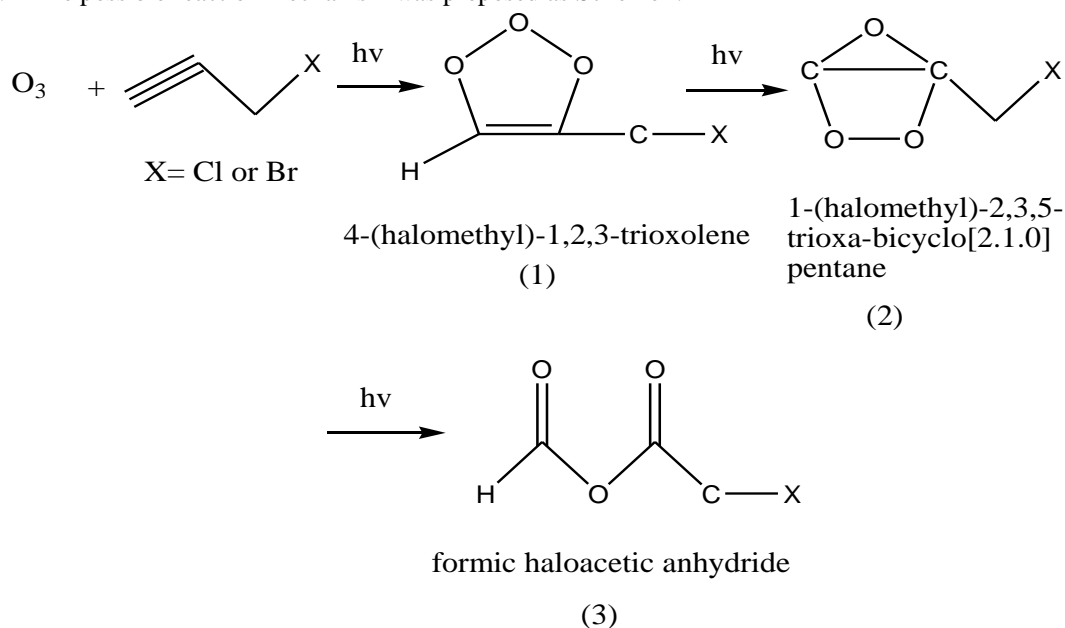
When the photolysis lasted in 30 minutes, new absorption group were 1055 cm⁻¹ and 996

cm^{-1} accompanied with the apparent growth in intensity of 655 cm^{-1} . The peak of 1055 cm^{-1} and 996 cm^{-1} are assigned to the asymmetry stretching mode of C-O-O (1095 cm^{-1}) and C-O stretching mode (998 cm^{-1}) of 1-(bromomethyl)-2,3,5-trioxa-bicyclo[2.1.0]pentane, respectively. The enhancement of 755 cm^{-1} might be due to the C-Br stretching mode which is 648 cm^{-1} . All the above indicated the formation of 1-(bromomethyl)-2,3,5-trioxa-bicyclo[2.1.0]pentane.

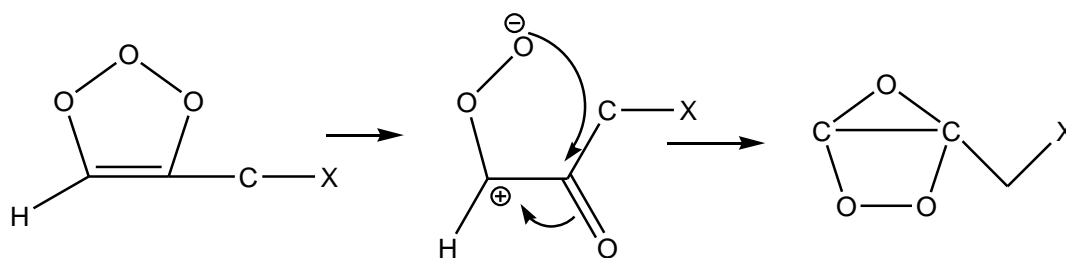
Further photolysis led to the new absorptions at 1771 cm^{-1} , 1118 cm^{-1} and increased in intensity of 655 cm^{-1} . The frequency of 1771 cm^{-1} is in the range of C=O stretching mode ($1725\sim 1870 \text{ cm}^{-1}$) and can be assigned as C=O stretching mode (1770 cm^{-1}) of formic bromoacetic anhydride (FBAA). The peak of 1118 cm^{-1} is close to the C-O-C stretching mode (1127 cm^{-1}). The calculated frequency of C-Br stretching mode (657 cm^{-1}) which can explain the intensity growth in 655 cm^{-1} peak. These characters confirmed the formation of formic bromoacetic anhydride.

IV. Discussions

Most studies of reaction of alkynes with ozone were based on theoretical calculation and lack of experimental evidences. From the comparison of position of observed new peaks with calculated frequencies of possible molecules, 4-(halomethyl)-1,2,3-trioxolene (1), 1-(halomethyl)-2,3,5-trioxa-bicyclo[2.1.0]pentane (2), and formic haloacetic anhydride (3) were detected at different stages of photolysis. The change in intensity of new absorption was first showed up of product (1) which was weakened and peak of second product (2) were detected. Further photolysis led to the decrease of C-O stretching mode of product (2) and new bands of product (3) were observed. The photolysis of propargyl bromide would lead to the formation of allyl bromide which might also react with ozone. Also, the photolysis of ozone would produce oxygen molecule and oxygen atom which might also react with propargyl halides and formed another new product. However, based on the spectral change, there is no additional new band was observed indicated both possible reaction paths were not found. The possible reaction mechanism was proposed as Scheme I.



The reaction of ozone with propargyl halide is cycloaddition of ozone to $\text{C}\equiv\text{C}$ triple bond and form 4-(halomethyl)-1,2,3-trioxolene (1) which was then rearranged to 1-(halomethyl)-2,3,5-trioxa-bicyclo[2.1.0]pentane (2), and finally form stable product of formic haloacetic anhydride (3). The formation of compound (2) is due to directly break of O-O bonding of compound (1). Ando et al.^[21] have confirmed the existence of trioxabicyclo[2,1,0]pentane from the study of oxidation of 2-diazo-3-butanone, therefore compound (2) might be a stable intermediate. The possible path of forming compound (2) from compound (1) was shown as following.



In previous study of allyl halide/O₃ reaction, the reaction mechanism was first 1,3 dipolar cycloaddition of ozone to double bond of allyl halide to form POZ, POZ was then undergo breakage of O-O and C-C bond and decomposed to carbonyl component and HC(O)CH₂X, HC(O)CH₂X were retro-cycloaddition to carbonyl component to form SOZ, and finally the SOZ was decomposed to a stable formic haloacetic anhydride. In this study, the POZ product of propargyl halide/O₃ has C=C double bond which is not easy to break, therefore, only the breakage of O-O bond of POZ and formed ionic intermediate and then rearranged to form 1-(halomethyl)-2,3,5-trioxa-bicyclo[2.1.0]pentane (2), and finally to stable product formic haloacetic anhydride.

V. Conclusion

The photolysis reactions of propargyl chloride and propargyl 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-trioxolene (POZ) which was then rearranged to 1-(halomethyl)-2,3,5-trioxa-bicyclo[2.1.0]pentane (SOZ), and finally form stable product of formic haloacetic anhydride. The reaction mechanism was first 1,3 dipolar cycloaddition of ozone to triple bond of propargyl halide to form POZ and then decomposed to ionic component and rearranged to form SOZ, and finally the SOZ decomposed to stable formic haloacetic anhydride.

ACKNOWLEDGEMENT

This research is part of contents of MS thesis of Meng-Shu Wu.

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Rong-Luh Jeng, et. al. "Matrix isolation study of reactions of propargyl halides with ozone." *The International Journal of Engineering and Science (IJES)*, 11(3), (2022): pp. 07-13.