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FTIR/Matrix isolation study of photolysis reactions of allyl halides with oxygen

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--ABSTRACT--

The photolysis of allyl chloride and allyl bromide with oxygen in Ar matrix resulted in several new bands in IR spectrum. Comparison of the observed frequencies with theoretical calculation indicated the isolated products were 3-(halomethyl)-1,2-dioxetane. The reaction mechanism was oxygen molecule added to the double bond of allyl halide and formed a stable product 3-(halomethyl)-1,2-dioxetane.

KEYWORDS*: matrix isolation, IR, ally halides, oxygen*

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I. INTRODUCTION

Allyl halides are important chemical intermediates for they have both halide atom and C=C double bond, which can undergo alkyl halide reaction and unsaturated alkene reaction. The reaction of atomic oxygen with small, unsaturated hydrocarbons belongs to an important class of reactions due to its occurrence in combustion processes, atmospheric reactions, and biological systems [1-3].

Most of researches were focused on reaction of oxygen molecule with alkynes [4-6], including theoretical calculation, to study its reaction mechanism. Lastin et al [5] have studied the mechanism of oxidation of acetylene with oxygen in shock tube. Hwang et al [6] have studied the reaction of chloroacetylene with O_2 in Ar matrix. There are relative less researchof reactions of oxygen molecule with alkenes [7].

The literature data of olefins reacted with oxygen were only propene/O_2. Alkyl group was an electron-donating group connected to the C=C double bond. The product distribution might be changed when the substituent was electron-withdrawing group. Halides were electron-withdrawing group and choose as substituent in this research to study whether the product distribution will be effect by the electron-withdrawing alkyl halide group. Matrix isolation technique [8-10] was developed in mid-1950's and applied to study the unstable molecules and free radicals [11]. Therefore, this research would apply infrared spectrum/matrix isolation technique to study the reaction of allyl halides with oxygen molecule. The isolation and identification of intermediates and products in matrix would useful for understanding reaction mechanism.

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 cold cell vacuum vessel, the cryogenic system, 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 samples of Ar (99.9995%, Lienhwa) and O_2 (99.995%, San Fu or Matheson) were used as received. Allyl bromide C_3H_5Br (99%, Aldrich) and allyl chloride C_3H_5Cl (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

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

Ar/C_3H_5Cl/O_2The spectra of Ar/O_2 and Ar/C_3H_5Cl (2000/1~100/1)didnot change after deposition during photolysis. After in-situ photolysis of matrix at low concentration, there is no apparent new band was observed. As the concentration of Ar/C_3H_5Cl increased to 100/1 and photolysis 90 minutes, the intensities of parent bands of C_3H_5Clwere weaken and several weak new absorptions were appeared at 1192 cm^{-1}, 1102 cm^{-1}, 1005 cm^{-1}, and 718 cm^{-1}. The spectral changed are shown in Figure 1 and the positions of new bands are summarized in Table 1.

Ar/C_3H_5Br/O_2 There was no apparent new band was detected after the deposition during photolysis of O_2 with Ar/C_3H_5Br at concentration between 2000/1~200/1. When the concentration of Ar/C_3H_5Br raised up to 100/1, after 90 minutes in-situ photolysis, several new weak bands were observed at 1095 cm^{-1}, 1032 cm^{-1}, 886 cm^{-1}, 744 cm^{-1}, and 615 cm^{-1}, accompanied the decrease in intensity of parent bands. The positions of new bands are summarized in Table 2and the spectral changed are shown in Figure 2.

Band Assignments

Based on the proposed reaction mechanism of propene/O_2 by Sanhueza et al [14], if oxygen was added to the double bond of allyl halide would form 3-(halomethyl)-1,2-dioxetane. Therefore, the band assignment was made by comparing the observed new peak position with calculated vibrational frequencies of 3-(halomethyl)-1,2-dioxetane.

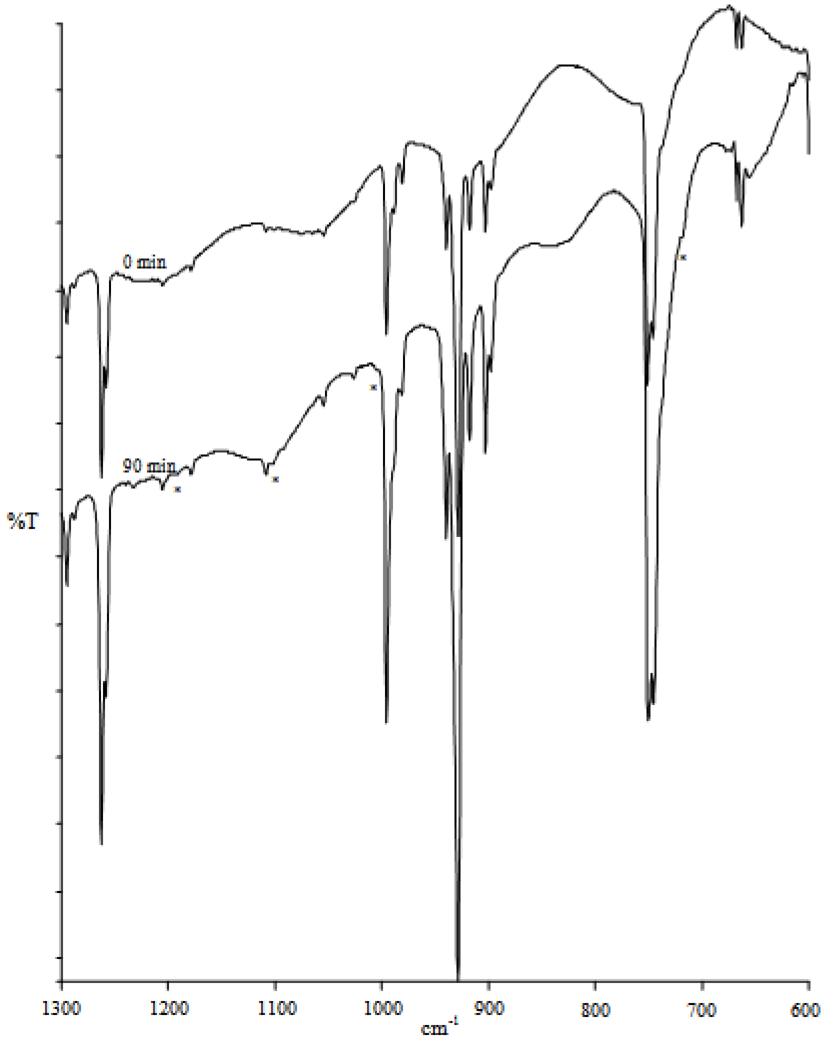


Fig. 1 The infrared spectra of Ar/C3H5Cl/O2 matrix before and after photolysis.

Table 1The positions of new absorptions in IR spectrum of Ar/C_3H_5Cl/O_2 matrix after photolysis 90 minutes.

Frequency (cm^{-1})	Calculation*	Assignments
1192	1176	CH_2 bend.
1102	1095	CH_2 bend.
1005	998	sym C-O st.
718	702	C-Cl st.

*: M. L. Hwang, C. L. Pan, calculated frequency of 3-(chloromethyl)-1,2-dioxetane with Gaussion 03 software, unpublished results.

Table 2The positions of new absorptions in IR spectrum of Ar/C_3H_5Br/O_2 matrix after photolysis 90 minutes.

Frequency (cm^{-1})	Calculation*	Assignments
1095	1101	-CH_2 bend
1032	1060	asym C-O st.
886	885	O-O st.
744	757	C-C st.
615	616	C-Br st.

*: M. L. Hwang, C. L. Pan, calculated frequency of 3-(bromomethyl)-1,2-dioxetane with Gaussion 03 software, unpublished results.

Ar/C_3H_5Cl/O_2After 90 min photolysis of allyl chloride/O_2 matrix, the new band at 1192 cm^{-1} could be assigned as bending vibrational mode of -CH_2 compared with calculated value 1176 cm^{-1} for -CH_2Cl group. The new band detected at 1102 cm^{-1} was assigned as the bending vibrational mode of -CH_2 which was 1095 cm^{-1} by calculation for –C(O)H_2 group. Another weak band was 1005 cm^{-1} should belong to symmetry stretching mode of C-O bond which was closed to calculated frequency 998 cm^{-1}. Near the parent band of C-Cl vibrational mode (751 cm^{-1} and 745 cm^{-1}), a shoulder at 718 cm^{-1} was observed which was closed to calculated value of 702 cm^{-1}, therefore 718 cm^{-1} would be assigned as the C-Cl stretching vibrational mode. All the above evidences suggested these new absorptions were due to product 3-(chloromethyl)-1,2-dioxetane.

Ar/C_3H_5Br/O_2The new band at 1095 cm^{-1} was –CH_2 bending mode which is 1101 cm^{-1} by calculation for –CH_2Br group of 3-(bromomethyl)-1,2-dioxetane. The peak at 1032 cm^{-1} could be assigned as C-O stretching mode by comparison with calculated value 1060 cm^{-1}. Another new band at 886 cm^{-1} was O-O stretching mode which was 885 cm^{-1} for calculation. The band of 744 cm^{-1} was belong to C-C stretching vibrational mode comparing to calculated value 757 cm^{-1}. Finally, the peak at 615 cm^{-1} could be easily assigned as stretching mode of C-Br which was 616 cm^{-1} by calculation. Based on the assignment of new bands, indicated 3-(bromomethyl)-1,2-dioxetane was formed during photolysis of Ar/O_2/C_3H_5Br matrix.

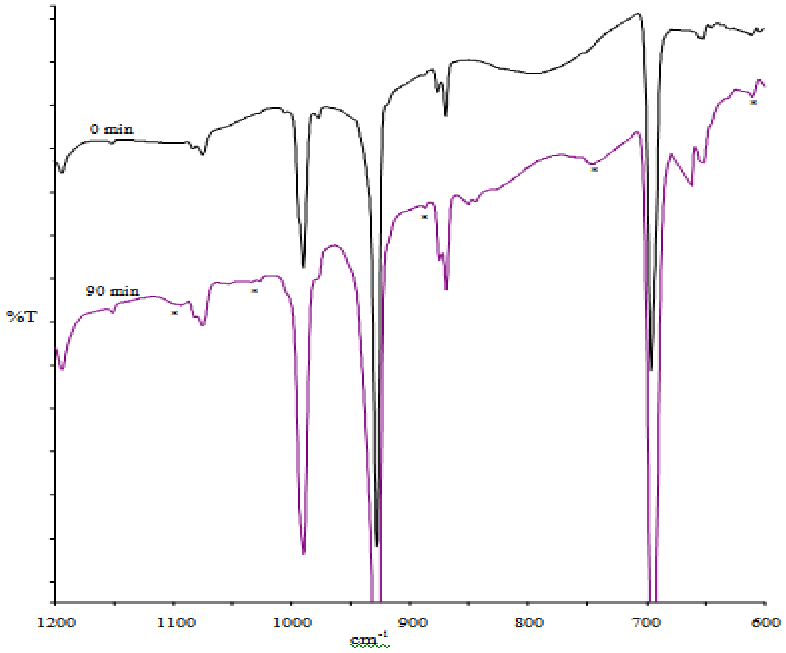
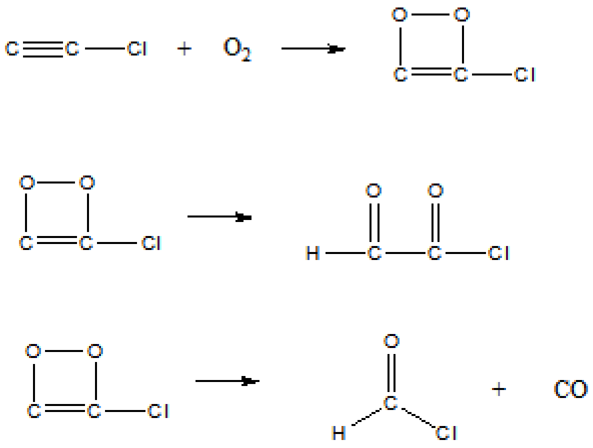


Fig. 2 The infrared spectra of Ar/C_3H_5Br/O_2 matrix after 90 minutes photolysis during deposition.

IV. DISCUSSIONS

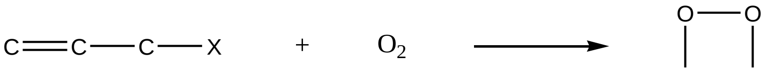
Previous study [6] for the reaction of O_2/HC≡CCl observed intermediate HC(OO)CCl and final product HC(O)C(O)Cl, HCOCl, and CO, suggested the possible reaction mechanism as Scheme I. Oxygen was first added to the triple bond and formed an intermediate peroxide which was then decomposed to final products.

Scheme I



Based on the assignment of new absorptions by comparison with literature and calculated value, indicated that only 3-(halomethyl)-1,2-dioxetane were formed for both allyl chloride and allyl bromide reacted with oxygen. The photolysis of oxygen might produce ozone which might further reacted with allyl halide and form new species. However, we did not observe additional new product. Therefore, the reaction mechanism was suggested as Scheme II, oxygen molecule added to the double bond of allyl halide and formed 3-(halomethyl)-1,2-dioxetane.

Scheme II



X= Cl or Br

The breakage of O-O bond of molecule 3-(halomethyl)-1,2-dioxetane should produce $HC(O)CH_2X$ and CO which were not observed in this research, indicated the peroxide product, 3-(halomethyl)-1,2-dioxetane was stable.

V. CONCLUSION

The photolysis reactions of allyl chloride and allyl bromide with oxygen 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 was3-(halomethyl)-1,2-dioxetane. The reaction mechanism wasoxygen molecule added to the double bond of allyl halide and formed a stable product 3-(halomethyl)-1,2-dioxetane.

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