# A FT IR Study of a Transitory Product in the Gas-Phase Ozone-Ethylene Reaction

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Further kinetic and spectroscopic characterization was made with the FT IR method for the transitory species (compound X) detected originally by Heath et al. and more recently by Su et al. in the gas-phase reaction between  $O_3$  and  $C_2H_4$ . The results obtained support the earlier suggestion of Su et al. that compound X is HOCH<sub>2</sub>OCHO formed by the secondary reaction of the thermally stabilized  $CH_2OO$  entity with  $CH_2O$ .

# Introduction

In numerous previous studies of the gas-phase ozoneethylene reaction,<sup>1-3</sup> a substantial fraction of the ensuing products escaped detection. Recently, Su et al. reported a FT IR spectroscopic observation of an unidentified major product (compound X) with reactant concentrations in the ppm range in 700 torr O<sub>2</sub>-N<sub>2</sub> mixtures.<sup>4</sup> This compound exhibited a strong absorption in the frequency region characteristic of the carbonyl stretching vibration (1700–1800 cm<sup>-1</sup>) and several bands in the region common to -C-O- stretching motions (900–1200 cm<sup>-1</sup>). It decayed to formic anhydride, (CHO)<sub>2</sub>O, with a lifetime  $\tau \approx 10$  min. These observations have been made also in this laboratory,<sup>5</sup> and appear to substantiate an earlier brief report by Heath et al. who detected a transient absorption band ( $\tau$ = 5–10 min) at about 1160  $cm^{-1}$  with reactant pressures in the torr range.<sup>6</sup> This peak matches well the most intense, unobstructed band belonging to the compound X.5

On the basis of their findings on the effects of added  $CH_2O$ ,  $CH_3CHO$ , CO, and  $SO_2$  on the product distribution, Su et al. tentatively identified compound X as HOCH<sub>2</sub>O-CHO, formed by the secondary reaction of CH<sub>2</sub>O with the thermally stabilized entity of the Criegee intermediate CH<sub>2</sub>OO, as represented by the following simplified reaction scheme:4

$$O_3 + C_2 H_4 \rightarrow C H_2 OO^* + C H_2 O \tag{1}$$

$$CH_2OO^* \rightarrow products (62\%)$$
 (2)

 $CH_2OO^*$  (+M)  $\rightarrow$   $CH_2OO$  (+M) (38%) (3)

$$CH_2OO + CH_2O \rightarrow HOCH_2OCHO$$
 (4)

$$HOCH_2OCHO \rightarrow (CHO)_2O + H_2 \tag{5}$$

where the asterisks indicate chemically activated species.

The present study was undertaken to obtain further kinetic and spectroscopic characterization of the compound X with the FT IR method. In particular, attempts were made to establish whether compound X has an OH group as in HOCH<sub>2</sub>OCHO, and also to verify whether the transitory species detected by Heath et al. at high reactant concentrations is indeed compound X. For this purpose, the  $O_3$ - $C_2H_4$  reaction was examined over a wide range of the reactant pressures (5 mtorr-5 torr) in 700 torr of air with an improved detection sensitivity over the frequency region of 600-4000 cm<sup>-1</sup>.

#### **Experimental Section**

Two IR cells (1 and 180 m path) were used to handle reactants at pressures over the mtorr to torr range. The IR absorption measurements were carried out with a FT IR system consisting of an IDAC Model 1000 interferometer, a PDP 11/60 on-line computer, and in-house developed software.<sup>4</sup> The interferometer was equipped with either a KBr beam splitter–Ge:Cu detector or a  $CaF_2$  beam splitter-InSb detector combination to monitor IR signals in the 450–8000-cm<sup>-1</sup> range with high-detection sensitivity. Spectra were derived from interferograms, ratioed against background, and converted to absorbance. Typical data shown in this paper were recorded in  $1.5-3 \min(16 \text{ scans})$ at a theoretical resolution of  $1/16 \text{ cm}^{-1}$ .

To obtain appropriate standard reference spectra, we monitored partial pressures of sample gases directly in the 1-m path cell (50 cm long, double pass, 1-L Pyrex cylinder, KBr window). For this purpose, all the compounds of interest were handled in pure form. For instance, pure  $O_3$ samples were generated by subjecting small amounts of O<sub>2</sub> to silent discharge and condensing in a liquid-N<sub>2</sub>-cooled trap. Also formic anhydride and ethylene ozonide were prepared according to procedures described by Gillies and Kuczkowski<sup>8</sup> and by Muramatsu et al.,<sup>9</sup> respectively.

Because of the small diameter-to-length ratio of the 180-m path cell (3 m long, 15 cm diameter, Pyrex cylinder), poor mixing of the reactant gases was initially encountered as evidenced by anomalous decay behavior of the reactants. This problem was minimized by introducing prediluted samples through an unevenly multiperforated Pyrex tube extending the full length of the IR cell. The resultant well-behaved decays of the reactants are illustrated in Figure 1. Namely, in two runs containing either  $O_3$  or  $C_2H_4$  as the minor reactant, the bimolecular rate constant derived from their pseudo-first-order decays agreed well with the literature value.<sup>10</sup>

### **Results and Discussion**

Typical time-resolved spectra in the frequency region of 600–3200 cm<sup>-1</sup> obtained from the  $O_3-C_2H_4$  mixtures at ppm levels in 700 torr of air are shown in Figure 2A-C. In addition to the sharp, well-defined bands belonging to

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<sup>(9)</sup> I. Muramatsu, M. Itori, M. Tsuji, and A. Hagitani, Bull. Chem. Soc. Jpn., 37, 756 (1964).

<sup>(10)</sup> R. F. Hampson and D. Garvin, Natl. Bur. Stand. U.S., Spec. Publ., No. 513 (1977).



Figure 1. Pseudo-first-order decay of  $O_3$  and  $C_2H_4$ . Filled points are calculated values corrected for the slight decay of the excess component.



**Figure 2.** Absorbance spectra in the frequency region of 600-3200 cm<sup>-1</sup> from a mixture containing O<sub>3</sub> and C<sub>2</sub>H<sub>4</sub> at approximately 10 ppm each in 700 torr of air. Values in parentheses are concentrations in ppm.

the known products, broad bands indicated by A and B are discernible in Figure 2, B and C. The intensity of A is seen to increase between 15 and 40 min reaction time, whereas that of B remains virtually unchanged. These temporal behaviors are displayed more clearly by the scale-expanded difference spectrum, Figure 3A, which was derived by subtracting Figure 2B from Figure 2C. The residual spectrum, Figure 3B, obtained from this difference spectrum by removing contributions from major known species corresponds to that of compound A and agrees well with that of formic anhydride, shown in Figure 3C. The formic anhydride was first identified as a minor product

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(A) Difference Spectrum [(C) - (B)](x4)





Figure 3. Analysis of the spectra of Figure 2: (A) difference spectrum of Figure 1, B and C; (B) residual spectrum obtained from (A); and (C) reference spectrum of formic anhydride. Values with and without parentheses indicated frequencies and concentrations in ppm, respectively.



Figure 4. Analysis of the spectrum in Figure 2: (A) residual spectrum of Figure 2B; (B) and (C) reference spectra of ethylene ozonide and glycol aldehyde.

in this reaction by Kühne et al. using matrix-IR and microwave spectroscopy.<sup>3</sup> Notably, the Ar-matrix IR spectrum of this compound reported by Kühne et al. is downshifted by as much as  $10 \text{ cm}^{-1}$  from the gas-phase spectrum shown here.<sup>11</sup>

Figure 4A shows the residual spectrum in the frequency region of 600–2000 cm<sup>-1</sup> obtained from Figure 2B by removing the spectra of the reactants and all the known products including formic anhydride. It exhibits several

<sup>(11)</sup> H. Kühne, T.-K. Ha, R. Meyer, and Hs. H. Günthard, J. Mol. Spectrosc., 77, 251 (1979).



**Figure 5.** Difference spectrum in the frequency region of 2800–3700 cm<sup>-1</sup> from a mixture containing  $O_3$  and  $C_2H_4$  at 20 ppm each in 700 torr of air: (A) approxmately 10 min reaction time; (B) residual spectrum of (A) (see text).

broad bands, and the presence of several other potential products,<sup>3</sup> e.g., ethylene ozonide and glycolaldehyde, Figure 4, B and C. The overall features of this spectrum agree well with those of compound X reported by Su et al.<sup>4</sup> Note that the spectrum exhibits two overlapping bands at 1737 and 1760 cm<sup>-1</sup> in the C=O stretching region. This apparent splitting in the carbonyl band will be discussed later. On the basis of carbon balance, the initial yield of compound X was deduced to be  $35(\pm 5)\%$  of the C<sub>2</sub>H<sub>4</sub> reacted, in excellent agreement with the 38% yield determined by Su et al.<sup>4</sup> However, in the present study, the decay rate of compound X to formic anhydride was not reproducible, due presumably to the heterogeneous nature of the process.

To verify an earlier suggestion of Su et al.<sup>4</sup> that compound X is HOCH<sub>2</sub>OCHO formed by reaction 4, evidence for the possible presence of an O-H stretching band was sought by examining the 3000-4000-cm<sup>-1</sup> spectral region. Shown in Figure 5, A and B, are the spectral data obtained from a mixture containing  $C_2H_4$  and  $O_3$  at 20 ppm each in 700 torr of air. Figure 5A is a difference spectrum for the first 10 min of the reaction, and the two broad bands indicated by arrows in this spectrum are seen more clearly in the scale-expanded residual spectrum, Figure 5B. This residual spectrum exhibits two major bands centered at approximately 3405 and 3583 cm<sup>-1</sup> as well as a broad, composite band in the C-H stretching region (~3000 cm<sup>-1</sup>). The band at 3583 cm<sup>-1</sup> can be readily assigned to an O-H stretching vibration, whereas the band at 3405 cm<sup>-1</sup> lies at too low a frequency for the normal alcohol-type O-H stretching mode. Judging from the spectrum of compound X in the low-frequency region, Figure 4A, the latter band does not appear to be an overtone or combination band. It is highly plausible that this band arises from an internally H-bonded O-H group. Well-established cases for strong intramolecular H bonding are peroxyformic acid and peroxyacetic acid which absorb at 3340.7



**Figure 6.** Absorbance in the frequency region of 600–2000 cm<sup>-1</sup> from a mixture initially containing  $O_3$  (~1 torr) and  $C_2H_4$  (~0.5 torr) in 700 torr of air: (A) about 5 min reaction time; (B) residual spectrum of (A).

and 3300.0 cm<sup>-1</sup>, respectively.<sup>12</sup> These results can be explained by the occurrence of an equilibrium between the cis and trans form of the HOCH<sub>2</sub>OCHO as depicted schematically by the following:



Namely, the cis form may be responsible for the downshifted O-H (3405 cm<sup>-1</sup>) and C=O (1737 cm<sup>-1</sup>) bands, and the various trans-type forms for the normal O-H (3583 cm<sup>-1</sup>) and C=O (1760 cm<sup>-1</sup>) bands.

The kinetic and spectroscopic characteristics of compound X were examined also at reactant concentrations in the torr region. Figures 6-8 illustrate typical results. A broad band centered at approximately 1165 cm<sup>-1</sup> is conspicuous in Figure 6A, which confirms the earlier observation of Heath et al.<sup>6</sup> The residual spectrum. Figure 6B, matches reasonably well that of compound X obtained at lower reactant concentrations, except for a slightly different intensity distribution among the various bands. In particular, the two bands at 1047 and 1737  $cm^{-1}$  are seen to be relatively more intense as compared with the corresponding bands shown in Figure 4B. Aged samples showed enhanced intensity variation accompanied by line broadening, as seen in Figure 7. Also, in the high-frequency region, Figure 8B, an extremely broad band extending from 3000 to 3500 cm<sup>-1</sup> underlies the spectrum of compound X recorded at low concentrations. These new spectroscopic features are characteristic of an OH-containing compound in the condensed phase, and strongly suggest that compound X undergoes gas-to-aerosol

<sup>(12)</sup> P. D. Maker, H. Niki, C. M. Savage, and L. P. Breitenbach, Anal. Chem., 49, 1346 (1977).



**Figure 7.** Effect of sample aging on the residual spectra in the frequency region of 600–2000 cm<sup>-1</sup> from a mixture initially containing  $O_3$  (1 torr) and  $C_2H_4$  (0.5 torr) in 700 torr of air: (A) recorded about 2 min after mixing the reactants; (B) and (C) 10 and 20 min aged samples.

transformation at high concentrations rather than decaying heterogeneously to formic anhydride as observed at low concentrations. Formation of aerosols and liquid products in the  $O_3$ -olefin reactions in the torr region is well documented.<sup>13</sup> In fact, light scattering by aerosols could be readily observed with a He–Ne laser under these conditions. An FT IR observation of aerosols generated in situ by gas-phase chemical reactions has been reported pre-

(13) P. A. Leighton, "Photochemistry of Air Pollution", Academic Press, New York, 1961.



**Figure 8.** Absorbance spectra in the frequency region of 2700–3700 cm<sup>-1</sup> from a mixture initially containing  $O_3$  (2 torr) and  $C_2H_4$  (1 torr) in 700 torr of air: (A) about 3 min reaction time; (B) residual spectrum of (A). Values in parentheses are pressures in torr.

viously.<sup>14</sup> Thus, it appears that compound X is a major aerosol precursor at least in the  $O_3-C_2H_4$  reaction at high reactant concentrations. It is also conceivable that because of the gas-to-aerosol conversion this species escaped detection in the matrix-IR and mass spectrometric studies reported earlier.<sup>2,3</sup>

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# ESR Study of DNA Base Cation Radicals Produced by Attack of Oxidizing Radicals

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ESR investigations of  $\gamma$ -irradiated aqueous glasses (8 M NaClO<sub>4</sub>, 12 M LiCl) containing DNA bases and analogues show that oxidizing species produced in the glasses (hydroxyl radicals and Cl<sub>2</sub><sup>-</sup>) at 77 K attack a number of the bases and their analogues after warming to produce  $\pi$ -cation radicals. Compounds which produce  $\pi$  cations include thymine, uracil, 3-methyluracil, 6-methyluracil, orotic acid, isoorotic acid, guanine, and adenine. Compounds which are not found to produce  $\pi$  cations are 1-methylthymine, thymidine, and 1-methyluracil. The overall reaction for formation of the  $\pi$  cations is as follows: base + OH· (Cl<sub>2</sub><sup>-</sup>)  $\rightarrow$  OH<sup>-</sup> (2Cl<sup>-</sup>) + base cation. A pH and substituent dependence is also noted for the pyrimidines. At pHs where the nitrogen at position 1 is protonated,  $\pi$ -cation radicals are not formed. In addition, when there are substituents at position 1,  $\pi$ cations are not found. Analysis of the ESR spectra of the DNA base  $\pi$  cations for hyperfine splittings and g values were performed by aid of computer simulations. The analyses are in agreement with values found for several DNA base cations produce by photolysis and by direct  $\gamma$  irradiation.

#### Introduction

There have been a number of reports that oxidizing radicals such as  $SO_4^-$ , OH, and  $Cl_2^-$  may produce  $\pi$  cations of DNA bases and analogues.<sup>1-3</sup> The production of py-

rimidine  $\pi$  cations<sup>4</sup> by Cl<sub>2</sub><sup>-</sup> reaction was first suggested by Ward and Kuo.<sup>1</sup> In later work,<sup>2</sup> to explain the results of product analysis of irradiated chloride containing solution

<sup>(1)</sup> J. F. Ward and I. Kuo, Int. J. Radiat. Biol. Relat. Stud. Phys., Chem. Med., 15, 293 (1969).

<sup>(2)</sup> G. A. Infante, P. Jirathans, J. H. Fendler, and E. J. Fendler, J. Chem. Soc., Faraday Trans 1, 70, 1162 (1974); 70, 1586 (1974).

<sup>(3)</sup> M. Bansal and W. Fessenden, *Radiat. Res.*, 75, 497 (1978). (4) The term " $\pi$  cation" is used here to mean a radical produced by loss of an electron from the  $\pi$ -electron system and does not refer to the total charge on the molecule.