J. Phys. Chem. 1994, 98, 5065-5067 5065

FTIR Study of the Cl + C_2H_2 Reaction: Formation of *cis*- and *trans*-CHCl=CH Radicals

T. Zhu,[†] **G. Yarwood,**[‡] **J. Chen, and H. Niki***

Centre for Atmospheric Chemistry and Department of Chemistry, York University,
4700 Keele Street, North York, Ontario, Canada M3J 1P3

Received: November 22, 1993; In Final Form: February 18, 1994[®]

FTIR spectroscopic studies of the photolysis ($\lambda \geq 300$ nm) of mixtures containing Cl_2 and C_2H_2, *cis*-CHCl=CHCl, or *trans*-CHCl=CHCl were carried out in 700 Torr of N_2 at 295 ± 2 K. On the basis of the kinetic analysis of *cis*- and *trans*-CHCl=CHCl formed from C_2H_2, the branching ratio k_{1a}/k_{1b} has been determined to be 0.19 ± 0.05. $Cl + C_2H_2 (+M) \rightarrow$ *cis*-ClCH=CH (+M); $Cl + C_2H_2 (+M) \rightarrow$ *trans*-ClCH=CH (+M). Implications of these results for our previously postulated mechanism of Cl atom initiated oxidation of C_2H_2 are discussed.

Introduction

The reactions of halogen atoms (Cl and Br) with C_2H_2 may be of atmospheric significance as a removal process for C_2H_2 in the marine and polar troposphere[1,2] and also as a sink for halogen atoms in the lower stratosphere.[3,4] In our recent FTIR study of the Cl atom initiated oxidation of C_2H_2 in air, it was pointed out that the observed products may depend on the subsequent reactions of the geometric isomers of the chlorovinyl (*cis*- and *trans*-CHCl=CH) radicals formed in the primary step:[5]

$$\mathrm{Cl + C_2H_2\ (+M) \leftrightarrow (\alpha)\mathit{cis}\text{-}ClCH{=}CH\ (+M)} \qquad (1a)$$

$$\mathrm{\leftrightarrow (1-\alpha)\mathit{trans}\text{-}ClCH{=}CH\ (+M)} \qquad (1b)$$

Namely, the *cis*- and *trans*-CHCl=CH radicals react with O_2 to yield the corresponding isomeric (chlorovinyl)peroxy radicals (*cis*- and *trans*-CHCl=CHOO) which lead to the formation of the observed products via unimolecular isomerization/decomposition and bimolecular O_2 reaction. Possible steric effects for the isomerization/decomposition step may be more favorable for the *trans*-CHCl=CHOO radicals,

$$\mathrm{\mathit{trans}\text{-}CHCl{=}CHOO \rightarrow HCO + HC(O)Cl} \qquad (2a)$$

$$\mathrm{\rightarrow HCOCHO + Cl} \qquad (2b)$$

$$\mathrm{\rightarrow HCO + CO + HCl} \qquad (2c)$$

whereas the *cis*-CHCl=CHOO radicals may not readily undergo the isomerization/decomposition and partly react with O_2 to produce O_3 and CHCl=CH—O or CHCl—CH=O radical via reaction 3.

$$\mathrm{\mathit{cis}\text{-}CHCl{=}CHOO + O_2 \rightarrow O_3 + (CHCl{=}CH{-}O\ or\ CHCl{-}CH{=}O)} \qquad (3)$$

The O_3 yield was found to be dependent on O_2 pressure, consistent with the occurrence of reactions 2 and 3. However, there appears to be no previous experimental determination of the branching ratio $k_{1a}/k_{1b} = \alpha/(1-\alpha)$ for the formation of *cis*- and *trans*-CHCl=CH radicals in reactions 1a and 1b, respectively. Recent theoretical calculations by Zhu *et al.*[6] indicate that the trans isomer is slightly (ca. 1 kcal/mol) more stable than the cis isomer. Therefore, on thermochemical grounds, both isomers are likely to be produced with comparable yields, although the exact value of the branching ratio $\alpha/(1-\alpha)$ would no doubt depend on kinetic factors as well.

In the present study, the photoinitiated chlorination of C_2H_2 in N_2 was employed to determine the branching ratio $\alpha/(1-\alpha)$ for reactions 1a and 1b from the yields of *cis*- and *trans*-1,2-dichloroethenes (DCE), (i.e., $Cl_2 + h\nu \rightarrow 2Cl$, $Cl + C_2H_2 \rightarrow$ *cis*- and *trans*-CHCl=CH, and *cis*- and *trans*-CHCl=CH + $Cl_2 \rightarrow$ *cis*- and *trans*-CHCl=CHCl + Cl). The isomeric DCE thus formed can undergo further chlorination reactions to yield not only 1,1,2,2-tetrachloroethane (TCE) but also the isomeric counterparts of the reacting DCE via the following elementary steps:[7]

$$\mathrm{Cl + \mathit{cis}\text{-}CHCl{=}CHCl\ (\mathit{cis}\text{-}DCE) \rightarrow [CHCl_2{-}CHCl]^*} \qquad (4)$$

$$\mathrm{Cl + \mathit{trans}\text{-}CHCl{=}CHCl\ (\mathit{trans}\text{-}DCE) \rightarrow [CHCl_2{-}CHCl]^*} \qquad (5)$$

$$\mathrm{[CHCl_2{-}CHCl]^* \rightarrow (\beta)\mathit{cis}\text{-}CHCl{=}CHCl\ (\mathit{cis}\text{-}DCE) + Cl} \qquad (6a)$$

$$\mathrm{\rightarrow (1-\beta)\mathit{trans}\text{-}CHCl{=}CHCl\ (\mathit{trans}\text{-}DCE) + Cl} \qquad (6b)$$

$$\mathrm{[CHCl_2{-}CHCl]^*\ (+M) \rightarrow CHCl_2{-}CHCl\ (+M)} \qquad (7)$$

$$\mathrm{CHCl_2{-}CHCl + Cl_2 \rightarrow CHCl_2{-}CHCl_2\ (TCE) + Cl} \qquad (8)$$

where the asterisks indicate chemically activated adducts. The branching ratio $\beta/(1-\beta)$ for reactions 6a and 6b can be derived from the yields of *cis*- and *trans*-DCE in the photochlorination of *trans*- and *cis*-DCE (overall reactions 9 and 10), respectively.

$$\mathrm{\mathit{trans}\text{-}CHCl{=}CHCl + Cl \rightarrow (\gamma)\mathit{cis}\text{-}CHCl{=}CHCl + (1-\gamma)CHCl_2CHCl_2} \qquad (9)$$

$$\mathrm{\mathit{cis}\text{-}CHCl{=}CHCl + Cl \rightarrow (\delta)\mathit{trans}\text{-}CHCl{=}CHCl + (1-\delta)CHCl_2CHCl_2} \qquad (10)$$

Thus, in order to take into account the secondary reactions of *cis*- and *trans*-CHCl=CHCl in the derivation of the branching ratio $\alpha/(1-\alpha)$ from the observed yields of *cis*- and *trans*-CHCl=CHCl in the photochlorination of C_2H_2, values of β, γ, and δ were also determined in the present study under identical experimental conditions, i.e., 298 K and 700 Torr of N_2.

Experimental Section

FTIR spectroscopy was used to quantify the reactants and products. The details of the experimental facility have been

---

[*] Author to whom correspondence should be addressed.

[†] Present address: Centre for Land and Biological Resource Research, Agriculture Canada, Ottawa, Ontario.

[‡] Present address: Systems Applications International, 101 Lucas Valley Rd., San Rafael, CA 94903.

[®] Abstract published in *Advance ACS Abstracts*, April 1, 1994.

0022-3654/94/2098-5065$04.50/0

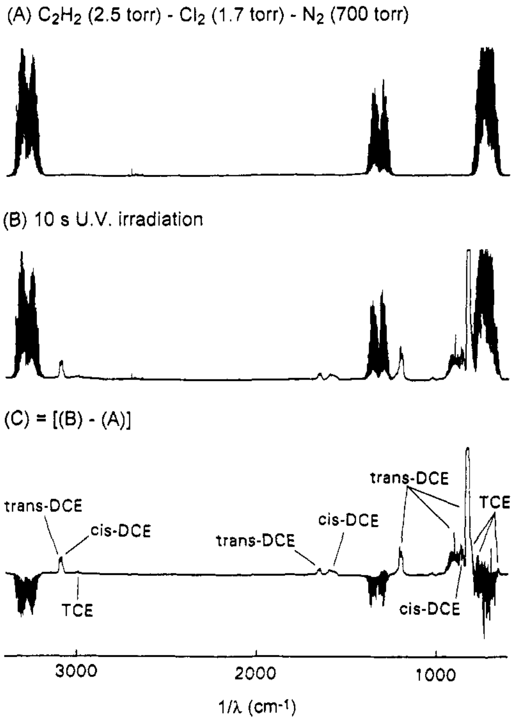

Figure 1. IR absorbance spectra recorded in the UV irradiation of Cl_2 (1.7 Torr) and C_2H_2 (2.5 Torr) in 700 Torr of N_2: (A) before irradiation, (B) after 10 s irradiation, and (C) difference spectrum (B – A). DCE denotes CHCl=CHCl and TCE denotes $CHCl_2$—$CHCl_2$.

described previously.[11] Absorbance spectra in the 500–3700-cm^{-1} range were recorded typically at 1/16 cm^{-1} resolution in 90 s (16 scans) by using a Ge-coated KBr beam splitter and a liquid He-cooled Cu–Ge detector. Cl atoms were generated by the UV (300 nm $< \lambda <$ 400 nm) photolysis of Cl_2. Mixtures of Cl_2 and C_2H_2, *cis*-CHCl=CHCl, or *trans*-CHCl=CHCl in 700 Torr of N_2 diluent were irradiated at 295 ± 2 K in an IR absorption cell (4.4 cm i.d., 50 cm long, double passed) surrounded by 6 fluorescent lamps (GE F40BLB).

Cl_2 (Matheson) and N_2 (Canadian Liquid Air, zero grade, total hydrocarbons < 1 ppm) were used as received. C_2H_2, *cis*-CHCl=CHCl, *trans*-CHCl=CHCl, and $CHCl_2$—$CHCl_2$ (Aldrich) were purified by trap-to-trap distillation over liquid N_2 before use. Their reference spectra were recorded at known pressures in the neighborhood of 1 Torr in the presence of 700 Torr of N_2. C_2H_2 was analyzed using its spectral features in the frequency range 1250–1400 cm^{-1}. The following IR peaks were used for product analysis: *cis*-CHCl=CHCl (858.2 cm^{-1}, ϵ = 0.71 $Torr^{-1}$ m^{-1}), *trans*-CHCl=CHCl (828.6 cm^{-1}, ϵ = 1.41 $Torr^{-1}$ m^{-1}), and $CHCl_2$—$CHCl_2$ (809.7 cm^{-1}, ϵ = 0.81 $Torr^{-1}$ m^{-1}), where ϵ is absorptivity given in log base 10.

Results and Discussion

Photochlorination of C_2H_2. An initial series of runs was made by irradiating mixtures containing ca. 2 Torr each of Cl_2 and C_2H_2 in 700 Torr of N_2 for 6–10 s. Spectra recorded before and after a 10-s irradiation of a mixture containing Cl_2 (1.7 Torr) and C_2H_2 (2.5 Torr) in 700 Torr of N_2 are shown in Figure 1, parts A and B, respectively. Figure 1C shows the difference spectrum (B – A). The consumption of 0.54 Torr of C_2H_2 in a 10-s irradiation led to the formation of *cis*-CHCl=CHCl (0.09 Torr), *trans*-CHCl=CHCl (0.33 Torr), and $CHCl_2$—$CHCl_2$ (0.13 Torr). After subtracting the spectral contributions of C_2H_2, *cis*-CHCl=CHCl, *trans*-CHCl=CHCl, and $CHCl_2$—$CHCl_2$ from Figure 1C, there were no discernible IR peaks remaining, and in four replicate runs the carbon balance was 100 ± 5%. In these runs, the formation of $CHCl_2$—$CHCl_2$ as the stable end product is consistent with the secondary chlorination of *cis*- and *trans*-CHCl=CHCl via reactions 4, 5, 7, and 8.

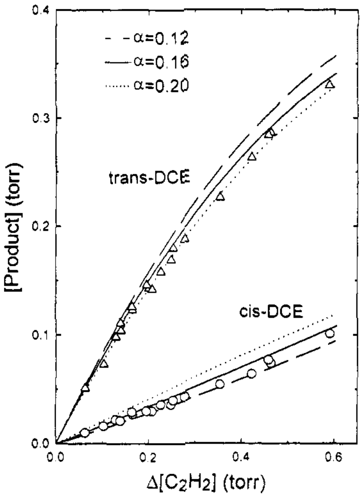

Figure 2. Yields of *cis*- and *trans*-DCE as a function of C_2H_2 reacted in the UV irradiation (6–10 s) of mixtures initially containing Cl_2 (2 Torr) and C_2H_2 (2 Torr) in 700 Torr of N_2. The data points were obtained from four replicate runs. The lines were calculated for α = 0.16 (solid lines), 0.20 (dashed lines), and 0.12 (dotted lines) with γ = 0.12 and δ = 0.34.

The observed yields of *cis*- and *trans*-CHCl=CHCl against the conversion of C_2H_2 from four such series of runs using multiple irradiation are plotted in Figure 2. The negative curvature seen for the *trans*-CHCl=CHCl yield is indicative of its partial consumption by secondary reaction with Cl atoms. In contrast, the *cis*-CHCl=CHCl yield exhibits a slight positive curvature. Since the rate constants for the Cl atom reactions of *cis*- and *trans*-CHCl=CHCl are known to be nearly identical,[7] the product *cis*-CHCl=CHCl must also have undergone secondary reaction under these conditions. Therefore, the positive curvature of the *cis*-DCE yield suggests that its formation via reaction 6a outweighed its removal by reaction 4. At any rate, it is evident that in order to derive the branching ratio $\alpha/(1-\alpha)$ for reactions 1a and 1b from the data shown in Figure 2, the extent of secondary reactions consuming the products *cis*- and *trans*-CHCl=CHCl must be taken into account. The calculated curves shown in Figure 2 will be described later.

Photochlorination of *cis*- and *trans*-CHCl=CHCl. The product yields in the Cl atom initiated reactions of isomeric CHCl=CHCl were determined in a series of photochemical runs (3–16 s irradiation) with mixtures initially containing Cl_2 (1–2 Torr)/*cis*-CHCl=CHCl (0.8–2.3 Torr), or Cl_2 (2 Torr)/*trans*-CHCl=CHCl (1.8–2.3 Torr) in 700 Torr of N_2. The observed products were $CHCl_2$—$CHCl_2$ and the isometric counterpart of the reagent *cis*- or *trans*-CHCl=CHCl. The experimental data plotted in Figures 3 and 4 were obtained from four and six runs, respectively. The calculated curves in Figures 3 and 4 were obtained by numerical integration of reactions 9 and 10, using the literature values of the rate constants k(Cl + *cis*-CHCl=CHCl) = 9.65×10^{-11} cm^3 $molecule^{-1}$ s^{-1} and k(Cl + *trans*-CHCl=CHCl) = 9.58×10^{-11} cm-3 $molecule^{-1}$ s^{-1} at 298 ± 2 K in 735 Torr of air.[7] The values of γ and δ were adjusted to best fit the experimental data. The solid curves shown in Figures 3 and 4 are for the best fit values of γ = 0.34 and δ = 0.12, and the dashed and dotted curves for γ and δ values changed by 0.04 from these best-fit values to indicate the range which encompasses most of the experimental data points.

Atkinson and Aschmann reported γ = 0.199 ± 0.011 and δ = 0.087 ± 0.003 in 735 Torr of air,[7] which are 41% and 28% lower than the corresponding values determined here in 700 Torr of N_2 (i.e., γ = 0.34 and δ = 0.12). The values of γ and δ, which reflect the competition between unimolecular dissociation vs collisional deactivation for the chemically activated adduct $[CHCl_2$—$CHCl]^*$

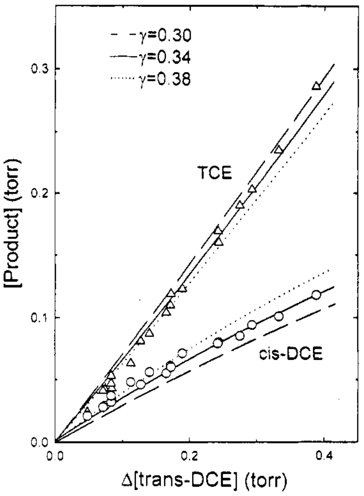

Figure 3. Yields of *cis*-DCE and TCE as a function of *trans*-DCE reacted in the UV irradiation (3–16 s) of mixtures initially containing Cl_2 (2 Torr) and *trans*-DCE (2 Torr) in 700 Torr of N_2. The data points were obtained from four replicate runs. The lines were calculated for $\gamma = 0.34$ (solid lines), 0.30 (dashed lines), and 0.38 (dotted lines) with $\delta = 0.12$.

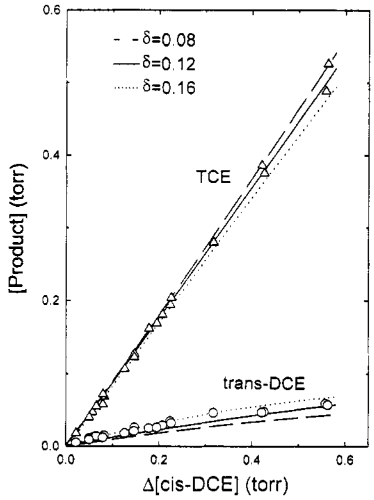

Figure 4. Yields of *trans*-DCE and TCE as a function of the amount of *cis*-DCE reacted in the UV irradiation (3–16 s) of mixtures containing Cl_2 (2 Torr) and *cis*-DCE (2 Torr) in 700 Torr of N_2. The data points were obtained from six replicate runs. The lines were calculated for $\delta = 0.12$ (solid lines), 0.16 (dashed lines), and 0.08 (dotted lines) with $\gamma = 0.34$.

formed in reactions 9 and 10, will depend upon the identity and pressure of the diluent gas M. Furthermore, in the case of air used as diluent, O_2 will undergo not only collisional deactivation but also chemical reaction with the chemically activated adduct. Thus, the comparison of our values of γ and δ with those of Atkinson and Aschmann implies that air is as much as 40% and 30% more efficient than N_2 in collisionally removing $[CHCl_2—XHCl]^*$ formed in reactions 9 and 10, or in other words, O_2 is about 10 times more efficient than N_2. If confirmed, a difference of this magnitude suggests that quenching of $[CHCl_2—CHCl]^*$ by O_2 has a chemical reaction component. However, further work is required to quantify the diluent effect on γ and δ values.

The value β for the fraction of *cis*-CHCl═CHCl formed by unimolecular decomposition of the chemically activated $[CHCl_2—CHCl]^*$ radical (i.e., reaction 6a) can be expressed analytically by eq I.

$$\beta = \gamma(1 - \delta)/(\gamma + \delta - 2\gamma\delta) \qquad \text{(I)}$$

A value of $\beta = 0.79 \pm 0.06$ has been derived from this equation using the values of $\gamma = 0.34 \pm 0.04$ and $\delta = 0.12 \pm 0.04$. This value of β is in reasonable agreement with the literature values of 0.70 ± 0.05,[7] 0.78,[9] and 0.64.[10]

Determination of k_{1a}/k_{1b}. The values for γ and δ derived above were used in the numerical analysis of the data shown in Figure 2 for the photochlorination of C_2H_2. With $\gamma = 0.34$ and $\delta = 0.12$, the best fit (solid curve) to the experimental data points was obtained with $\alpha = 0.16$. Numerical results with values of α varied by ±25% from 0.16 are also plotted in Figure 2 (dashed and dotted curves), from which the fraction of *cis*-CHCl═CH formed in the Cl + C_2H_2 reaction has been determined as 0.16 ± 0.04, or $k_{1a}/k_{1b} = \alpha/(1 - \alpha) = 0.19 \pm 0.05$.

Conclusions

The observation of *cis*- and *trans*-CHCl═CHCl as products of the photochlorination of C_2H_2 confirms the formation of both *cis*- and *trans*-CHCl═CH radicals in the Cl + C_2H_2 reaction. From the yields of *cis*-CHCl═CHCl (16%) and *trans*-CHCl═CHCl (84%), a branching ratio $\alpha/(1 - \alpha)$ for the formation of *cis*- and *trans*-CHCl═CH radicals in reactions 1a and 1b has been determined as 0.19 ± 0.05 at 295 ± 2 K and in 700 Torr of N_2. A major motivation for this study was to compare this branching ratio to the O_3 yields observed in the Cl atom initiated oxidation of C_2H_2.[5] As mentioned in the Introduction, O_3 formation was attributed to a reaction between *cis*-CHCl═CHOO radicals and O_2 (reaction 3).[5] The yield of *cis*-CHCl═CH radicals from reaction 1a determined here (16 ± 4%) is the same, within experimental error, as the O_3 yield (14 ± 1%) in the Cl atom initiated oxidation of C_2H_2 in 700 Torr of O_2.[5] If O_3 was indeed formed by reaction 3, then at 700 Torr of O_2, bimolecular reaction with O_2 dominated over unimolecular decomposition as the fate of *cis*-CHCl═CHOO radicals. At lower pressures of O_2, the O_3 yields were reduced (10 ± 1% at 140 Torr and 6 ± 1% at 10 Torr), consistent with competition between bimolecular O_2 reaction (reaction 3) and unimolecular decomposition (reaction 2a).

Acknowledgment. We thank NSERC and British Gas/Consumers Gas for financial support. H. Niki is the holder of the British Gas/Consumers Gas/NSERC/AES Industrial Research Chair in Atmospheric Chemistry.

References and Notes

(1) Singh, H. B.; Kasting, J. F. *J. Atmos. Chem.* **1988**, *7*, 261.

(2) McConnell, J. C.; Henderson, G. S. In *The Tropospheric Chemistry of Ozone in the Polar Regions*; Niki, H., Becker, K. H., Eds.; p. 89, NATO ASI Series I: Global Environmental Change; Springer-Verlag: Berlin Heidelberg, 1993; Vol. 7.

(3) Lee, F. S. C.; Rowland, F. S. *J. Phys. Chem.* **1977**, *81*, 684.

(4) Payne, W. A.; Nava, D. F.; Brunning, J.; Stieff, L. J. *J. Geophys. Res.* **1986**, *91*, 4097.

(5) Yarwood, G.; Peng, N.; Niki, H. *J. Phys. Chem.* **1991**, *95*, 7330.

(6) Zhu, Z.; Chen, W.; Hase, W. L.; Kaiser, E. W. *J. Phys. Chem.* **1993**, *97*, 311.

(7) Atkinson, R.; Aschmann, S. M. *Int. J. Chem. Kinet.* **1987**, *19*, 1097.

(8) Wallington, T. J.; Andino, J. M.; Lorkovic, I. M.; Kaiser, E. W.; Marson, G. *J. Phys. Chem.* **1990**, *94*, 3644.

(9) Knox, J. H.; Riddick, J. *Trans. Faraday Soc.* **1966**, *62*, 1190.

(10) Ayscough, P. B.; Dainton, F. S.; Fleischfresser, B. E. *Trans. Faraday Soc.* **1966**, *62*, 1846.

(11) Maker, P. D.; Niki, H.; Savage, C. M.; Breitenbach, L. P. *ACS Symp. Ser.* **1979**, *94*, 161.