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A Gas-Phase Reactivity Study of OH Radicals with 1,1-Dichloroethene and *cis*- and *trans*-1,2-Dichloroethene over the Temperature Range 240–400 K

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Rate constants have been measured for the reactions of hydroxyl radicals with the three dichloroethenes over the temperature range 240–400 K by using the flash photolysis–resonance fluorescence technique. The Arrhenius equations derived from the data obtained predominantly at 35-Torr total pressure (in Ar) are (in units of cm^3 $molecule^{-1}$ s^{-1}) k(*trans*-1,2-dichloroethene) = $(9.37 \pm 1.47) \times 10^{-13} \exp[(283 \pm 85)/T]$, k(*cis*-1,2-dichloroethene) = $(2.21 \pm 0.34) \times 10^{-12} \exp[(65 \pm 89)/T]$, and k(1,1-dichloroethene) = $(2.30 \pm 0.44) \times 10^{-12} \exp[(472 \pm 105)/T]$. There was no apparent effect of pressure on the rate constant for the reaction of OH with *trans*-1,2-dichloroethene over the range 5–50 Torr (with Ar).

Introduction

Although there have been numerous investigations of the reactions of the hydroxyl radical (OH) with alkenes and other unsaturated organic compounds, the data base for halogenated alkenes is less comprehensive[1] For example, there exists only a room-temperature relative rate study for the three isomeric dihalogenated ethenes,[2,3] and with the exception of a very recent report on 1,1-dichloroethene,[4] no studies have been conducted as a function of temperature. The investigation of the reactivity of the various dihalogenated ethenes provides an opportunity to examine halogen substituent effects as a function of positioning about the double bond. In addition, these results are useful in calculating the atmospheric lifetimes of such compounds, some of which may be used in refrigerants mixtures. Thus, as part of a systematic study of OH radical reactivity, we report here rate constants for the reactions of OH with the three isomeric dichloroethenes.

Experimental Section

Rate measurements were carried out using the flash photolysis–resonance fluorescence technique[5] over the temperature range 240–400 K. Reaction mixtures containing the alkene, Ar, and H_2O were prepared manometrically in glass storage bulbs and flowed through the double-walled Pyrex reaction cell at a typical total pressure of 35 Torr (1 Torr = 133.33 Pa = $9.6582 \times 10^{18}/T$ (K) molecule cm^{-3}). This procedure minimized the buildup of possible reactive products during the course of an experiment. The argon diluent gas had a manufacturer's stated purity of ≥99.998% and was used without further purification. The 1,1-dichloroethene was obtained from Aldrich with a stated purity of 99% and was vacuum-distilled to remove the 200 ppm hydroquinone monomethyl ether inhibitor. It was then refrigerated and stored in the dark to prevent polymer formation. The *cis*-1,2-dichloroethene was obtained as a 97% purity sample from Aldrich, while the *trans*-1,2-dichloroethene was provided by the E. I. du Pont de Nemoures Co. under the alternate fluorocarbon environmental acceptability study (AFEAS) with a purity level of better than 99%. Both were vacuum-distilled before use.

The OH radicals were produced by the flash photolysis ($\lambda >$ 165 nm) of ≈0.1 Torr of H_2O and monitored in real time following the flash by their resonance fluorescence at 308 nm (excited by

TABLE I: Rate Constants Measured in the Present Work for the Reactions of OH with Dichloroethenes[a]

	$k \times 10^{12}$, cm^3 $molecule^{-1}$ s^{-1}		
T, K	CCl_2CH_2	*cis*-CHClCHCl	*trans*-CHClCHCl
240	17.2 ± 0.9	3.09 ± 0.22	2.87 ± 0.11
258	15.1 ± 1.1		
263			2.80 ± 0.12
270	12.3 ± 0.5	2.67 ± 0.14	
283	12.6 ± 0.7		
298	11.2 ± 0.6	2.71 ± 0.28	2.50 ± 0.30
330	9.60 ± 0.92	2.75 ± 0.18	2.11 ± 0.24
350			2.09 ± 0.28
360	9.19 ± 0.87	2.68 ± 0.31	
400	7.60 ± 1.43	2.69 ± 0.36	1.79 ± 0.48

[a] The error limits are two standard deviations from the least-squares analysis and do not include the 5–10% uncertainty estimated for possible systematic errors.

a microwave discharge resonance lamp). In all cases, the concentration of the stable reactant was in great excess over that of the OH so that first-order kinetic decay of the OH radical was observed. The fluorescence decay was recorded on a microprocessor based multichannel scaler, and the results from at least 100 flashes were summed. The raw data were reduced by weighted linear least-squares analysis to derive the first-order OH decay rate (Figure 1). For each set of experimental conditions, several determinations were made. Decay rates were determined at several reactant partial pressures (Figure 2), and second-order rate constants were derived from weighted linear least-squares fits of plots of first-order decay rates vs reactant concentration.

Results

Since the reaction of OH with an alkene can involve the reversible addition of the radical to the double bond, the observed rate constant may depend on the total pressure. To investigate this possibility under our experimental conditions, we examined the effect of total pressure (from 5 to 50 Torr) on the observed room-temperature second-order rate constant for the reaction of OH with *trans*-1,2-dichloroethene. The rate constants obtained at 5, 15, 35, and 50 Torr were 2.8×10^{-12}, 2.9×10^{-12}, 2.5×10^{-12}, and 2.6×10^{-12} cm^3 $molecule^{-1}$ s^{-1}, respectively (clearly independent of pressure over this range). All other measurements were carried out at 35-Torr total pressure. We also verified the lack of any dependence of the rate constant on the amount of water vapor in the reaction mixture. For example, the rate constant for the reaction with *cis*-1,2-dichloroethene at 400 K and 35-Torr total pressure was measured to be (in units of 10^{-12} cm^3 $molecule^{-1}$ s^{-1}) 2.7 at 110 mTorr of H_2O and 2.6 at 270 mTorr of H_2O.

Given the absence of any apparent pressure dependence of the rate constants, measurements were carried out over the temperature range 240–400 K at 35-Torr total pressure. The results are

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(2) Tuazon, E. C.; Atkinson, R.; Aschmann, S. M.; Goodman, M. A.; Winer, A. M. *Int. J. Chem. Kinet.* **1988**, *20*, 241.
(3) Edney, E. O.; Kliendienst, T. E.; Corse, E. W. *Int. J. Chem. Kinet.* **1986**, *18*, 1355.
(4) Kirchner, K.; Helf, D.; Ott, P.; Vogt, S. *Ber. Bunsen-Ges. Phys. Chem.* **1990**, *94*, 77.
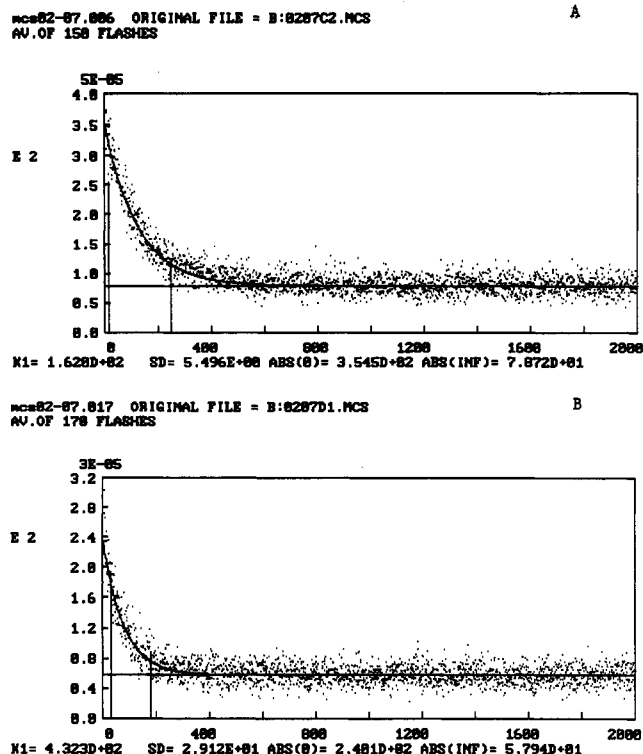(5) Wallington, T. J.; Neuman, D. M.; Kurylo, M. J. *Int. J. Chem. Kinet.* **1987**, *19*, 725.

mcs82-87.886 ORIGINAL FILE = B:8287C2.MCS
AV.OF 158 FLASHES

A

X1= 1.628D+82   SD= 5.496E+08 ABS(0)= 3.545D+82 ABS(INF)= 7.872D+01

mcs82-87.817 ORIGINAL FILE = B:8287D1.MCS
AV.OF 178 FLASHES

B

X1= 4.323D+82   SD= 2.912E+01 ABS(0)= 2.481D+82 ABS(INF)= 5.794D+01

Figure 1. Decay of the OH resonance fluorescence at 298 K after the flash photolysis of 100 mTorr of water at a total pressure of 35 Torr of Ar in the presence of (A) 0.15 mTorr of 1,1-dichloroethene and (B) 0.65 mTorr of 1,1-dichloroethene. The x axis is the channel number, and the y axis is the number of counts. The dwell time per channel is 50 μs in (A) and 30 μs in (B).
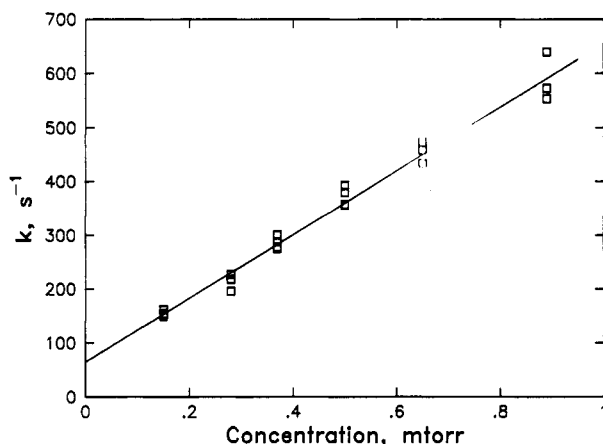

Figure 2. Plot of the first-order rate constant for the decay of the OH resonance fluorescence vs 1,1-dichloroethene concentration at 258 K.

summarized in Table I and plotted in Arrhenius form in Figure 3. The lines drawn in the figure correspond to the following expressions (*trans*-1,2-dichloroethene, k_1; *cis*-1,2-dichloroethene, k_2; and 1,1-dichloroethene, k_3)

$$k_1 = (9.37 \pm 1.47) \times 10^{-13} \exp[(283 \pm 85)/T] \quad cm^3 molecule^{-1} s^{-1}$$

$$k_2 = (2.21 \pm 0.34) \times 10^{-12} \exp[(65 \pm 89)/T] \quad cm^3 molecule^{-1} s^{-1}$$

$$k_3 = (2.30 \pm 0.44) \times 10^{-12} \exp[(472 \pm 105)/T] \quad cm^3 molecule^{-1} s^{-1}$$

where the error limits are two standard deviations from the linear least-squares fit and do not include the 5–10% uncertainty estimated for possible systematic errors.
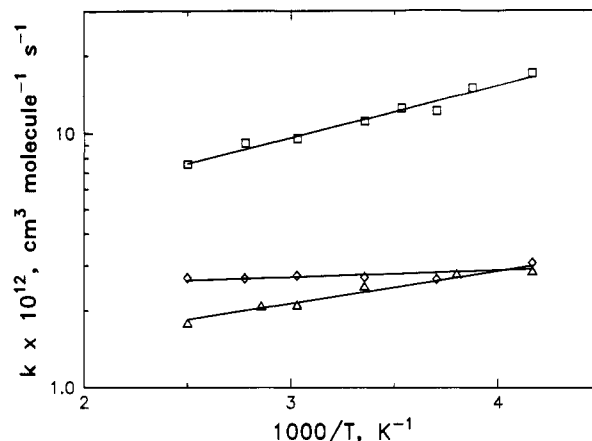

Figure 3. Arrhenius plot for the reactions of OH with 1,1-dichloroethene (□), *cis*-1,2-dichloroethene (◇), and *trans*-1,2-dichloroethene (△).

TABLE II: Arrhenius Parameters and Calculated Room-Temperature Rate Constants (in cm^3 $molecule^{-1}$ s^{-1}) for the Reactions of OH with Various Ethenes

reactant	$k \times 10^{12}$	$A \times 10^{12}$	E/R, K	ref
C_2H_4	8.06	2.03	−411	1
C_2H_3Cl	6.66	1.14	−526	7
CH_2CCl_2	10.4	0.226	−1140	4
	14.9			3
	8.11			2
	11.2	2.30	−472	this work
cis-CHClCHCl	2.38			2
	2.75	2.21	−65	this work
trans-CHClCHCl	1.80			2
	2.42	0.937	−283	this work
C_2HCl_3	1.75	0.780	−240	4
	2.37	0.532	−445	8
C_2Cl_4	0.172	5.53	1034	4
	0.170	9.44	1197	8

Discussion

In Table II the results from the present work are compared with rate constants obtained by previous investigators for the three dichloroethenes as well as for the other chloroethenes and ethene itself. In the cases of ethene and chloroethene (for which the OH rate constant has an observed pressure dependence), the results cited are for the high-pressure bimolecular limit. Despite some differences in the Arrhenius parameters (which we will address later), a number of general observations can be made about the room-temperature rate constants that have a bearing on the mechanistic interpretation. First, the addition of a single chlorine to ethene leads to a small reduction in the OH rate constant; the addition of a second chlorine on the same carbon leads to a rate constant increase above that for ethene. If the two chlorine atoms are situated on different carbons, however, there is a considerable decrease in the rate constant. Addition of a third chlorine leads to a further small decrease in the rate constant. Finally, for tetrachloroethene, with four chlorine atoms, the rate constant for reaction with OH is about 0.02 times that for ethene.

The rate constants for the reactions of OH with several halo-ethenes have been determined by Howard[6] in a discharge-flow system over the pressure range 0.7–7 Torr of He. Ethene and chloroethene were found to be markedly pressure dependent over this range while the rate constant measured for trichloroethene was found to level off at a few Torr. (No rate constants for dichloroethenes were reported.) Interestingly enough, at *low* pressure the rate constant for the C_2H_3Cl reaction approaches a limit of about 1×10^{-12} cm^3 $molecule^{-1}$ s^{-1}, nearly a factor of 7 lower than the high-pressure limiting rate constant.[1] This nonzero low-pressure limit has been interpreted[1] as due to a purely bimolecular channel involving the addition of OH to the chlorine-substituted carbon followed by the rapid subsequent elimi-

(6) Howard, C. J. *J. Chem. Phys.* **1976**, *65*, 4771.

nation of the chlorine atom. The pressure-dependent rate constant, then, corresponds to the addition of OH to the unsubstituted carbon. In the present work, we found that the room-temperature rate constants for the 1,2-dichloroethenes are each about twice the low-pressure limit for chloroethene. We thus interpret the reaction of these ethenes to occur by the addition of OH to either of the two carbons followed by elimination of Cl to yield 1-hydroxy-2-chloroethene. Comparison of the rate constants for the two chloroethene reaction channels with that for ethene implies that a chlorine atom deactivates the carbon on which it is attached toward OH attack while activating the carbon on the other side of the double bond. The higher rate constant for 1,1-dichloro-ethene suggests that the second chlorine further activates the carbon on the other side of the double bond in a roughly additive manner.

The rate constant for the reaction of OH with trichloroethene is only slightly lower than the rate constant for the 1,2-dichloroethenes, while the rate constant for tetrachloroethene is about 10 times lower. These results further support the idea that addition is more rapid at the less substituted carbon and that substitution of chlorine on one side of the double bond activates the other side.
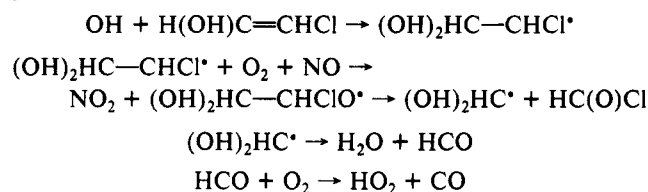
Another interesting observation relates to the temperature dependencies determined here of the rate constants for *cis*-1,2-dichloroethene (little temperature dependence) and *trans*-1,2-dichloroethene (a more negative temperature dependence similar to that found for 1,1-dichloroethene in this work and to that for chloroethene[7] and for trichlorethene).[8] These differences, while not exceptionally large, might result from changes in the electron density due to the positioning of the chlorine atoms about the double bond.

There have been two relative rate measurements on the reaction of OH with 1,1-dichloroethene, one yielding a room-temperature rate constant 25% greater than ours[3] and the other a value 38% lower.[2] In this latter study, rate constants were also reported for *cis*- and *trans*-1,2-dichloroethene, which are 16% and 34%, respectively, below our values. Thus, there appears to be a slight systematic difference between the absolute rate constants determined here and the rate constants derived from the relative rate measurements of Tuazon et al.[2] It should be noted that the relative rate studies were complicated by reactions involving product Cl and a chlorine atom scavenger was required to obtain consistent

results. In the present experiments, any product Cl atoms would react with the excess alkene and should not affect the kinetic results. Nevertheless, the agreement with the relative rate studies is within the combined uncertainties of both investigations.

There has been a very recent study of the OH reactions with 1,1-di-, tri-, and tetrachloroethene over the temperature range 298–459 K using a discharge-flow mass spectrometric technique.[4] At room temperature, the results for 1,1-dichloroethene agree well with ours. At our highest temperature (400 K), their result is about half of ours and the temperature dependence much more negative than found here with an Arrhenius preexponential factor 10 times smaller. Such a marked temperature dependence is at odds with the consistency of all previous results and the mechanistic interpretations offered. Although these investigators indicated that there was no pressure effect on this reaction at room temperature, this discrepancy in the temperature dependence suggests that at higher temperatures the reaction may have been in the falloff region under their low-pressure experimental conditions.

Our suggestion that the reaction of OH with the 1,2-dichloroethenes leads to the elimination of a Cl atom and the formation of 1-hydroxy-2-chloroethene appears to be consistent with the product studies of Tuazon et al.[2] In their experimental system, the subsequent reaction of this product with OH would lead primarily to the dihydroxy-2-chloroethyl radical which, after reaction with O_2 and NO, would cleave to give the observed product, $HC(O)Cl$:

$$OH + H(OH)C{=}CHCl \rightarrow (OH)_2HC{-}CHCl^\bullet$$

$$(OH)_2HC{-}CHCl^\bullet + O_2 + NO \rightarrow$$
$$NO_2 + (OH)_2HC{-}CHClO^\bullet \rightarrow (OH)_2HC^\bullet + HC(O)Cl$$

$$(OH)_2HC^\bullet \rightarrow H_2O + HCO$$

$$HCO + O_2 \rightarrow HO_2 + CO$$

The chlorine atom produced in the initial reaction would also produce $HC(O)Cl$, but this path would be suppressed by chlorine atom scavengers, as observed in their experiments.

Registry No. $Cl_2C{=}CH_2$, 75-35-4; (*Z*)-ClCH=CHCl, 156-59-2; (*E*)-ClCH=CHCl, 156-60-5; OH•, 3352-57-6.

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(8) Chang, J. S.; Kaufmann, F. *J. Chem. Phys.* **1977**, *66*, 4989.