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Laser Photolysis/Laser-Induced Fluorescence Studies of the Reaction of OH with 1,1,1-Trichloroethane over an Extended Temperature Range

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Absolute rate coefficients are determined for the gas-phase reaction of OH radicals with 1,1,1-trichloroethane over an extended temperature range. Employing a laser photolysis/laser-induced fluorescence technique, experiments were conducted with a flow system at a total pressure of 740 ± 10 Torr using He as diluent and carrier gas. The rate coefficients, obtained over the temperature range 298-761 K, exhibited pronounced non-Arrhenius behavior and were best described by the modified Arrhenius equation $k(T) = (3.95 \pm 0.78) \times 10^{-13} (T/300)^{2.08} \exp\{(-1068 \pm 108)/T\} \text{ cm}^3$ molecule⁻¹ s⁻¹. Comparison of the data with numerous lower temperature measurements is presented. The temperature dependence of the data is compared with empirical and transition-state model calculations. The reactivity of this compound with OH compared to other chlorinated ethanes at both lower and higher reaction temperatures is presented and discussed.

Introduction

The use of 1,1,1-trichloroethane (CH₃CCl₃) as a degreasing and cleaning agent in industry has focused considerable attention on its potential involvement in the ClO_x catalytic cycle for stratospheric ozone depletion.¹ Its estimated lifetime of ~ 10 years is considerably less than for fully halogenated compounds, e.g., CF_2Cl_2 and $CFCl_3$, because of the tropospheric sink due to OH radical attack:

$$CH_3CCl_3 + OH \rightarrow CH_2CCl_3 + H_2O$$
 k_1

However, this reaction is nonetheless relatively slow, and as a result considerable effort has been expended to make an accurate determination of its atmospheric temperature rate constant.²

Comparison of the room temperature reactivity of CH₃CCl₃ with other chlorinated ethanes is shown in Table I. The data indicate CH₃CCl₃ is much less reactive with OH. Previous in-

TABLE I: Room Temperature Rate Coefficients for Chlorinated Ethanes at 298 K

compound	k_{298} (cm ³ molecule ⁻¹ s ⁻¹)	ref		
CH ₁ CCl ₁	1.08×10^{-14}	this work		
CH ₃ CH ₃ Cl	4.28×10^{-13}	3		
CH ₄ CHCl ₂	2.90×10^{-13}	4		
CH ¹ CICH ¹ CI	2.54×10^{-13}	5		
CH,CICHCI,	2.02×10^{-13}	6		

vestigators have suggested the difference in reactivity may be due to inductive effects arising from the full chlorine substitution adjacent (β) to the reactive site.^{1,4,5}

Controlled high-temperature incineration is a viable technology for the complete and permanent destruction of this environmentally significant compound. Arrhenius parameters for k_1 at temperatures approaching incineration conditions have not been previously reported. This study is thus motivated by the need to determine the reactivity of OH with CH₃CCl₃ compared to other chlorinated ethanes at high temperatures.

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Figure 1. Fitted raw data showing typical OH decay profile versus probe laser time delay.

In this paper, we report atmospheric pressure $(740 \pm 10 \text{ Torr})$ absolute rate coefficient measurements for k_1 over the temperature range 298–771 K. The data are compared with previous measurements at lower temperatures (222–457 K). The temperature dependence of k_1 is compared with transition-state⁸ and empirical^{7,9} model predictions over the temperature range 295–1000 K. The reactivity of chlorinated ethanes with OH over this temperature range is presented and discussed.

Experimental Techniques and Data Reduction

All experiments were performed using a refined laser photolysis/laser-induced fluorescence (LP/LIF) technique. A detailed description of this technique and its application of OH kinetic studies has been reported previously;^{3,4,10} hence, we only briefly summarize the experiment.

All experiments were carried out under "slow flow" conditions, i.e., the buildup of reaction products was minimized. Individually controlled gas flows of CH₃CCl₃/N₂O/H₂O/He were thoroughly mixed before entering the reactor. The composite flow conditioned the reactor for 45–90 s prior to the onset of data collection, thereby minimizing any effects due to reactant adsorption on the reactor walls. All experiments were conducted at a total pressure of 740 \pm 10 Torr. The gas temperature in the reaction zone was measured with two chromel/alumel thermocouples and was observed to be constant within \pm 2 K over both the dimensions of the probed volume and the duration of the experiment.

Hydroxyl radicals were produced by 193.3-nm photodissociation of CH₃CCl₃/N₂O/H₂O/He gas mixtures with a ArF excimer gas laser (Questek Model 2320). Initial OH concentrations, estimated using published values of the N₂O absorption coefficient,¹¹ ranged from 2×10^{10} to 8×10^{10} molecules cm⁻³ and were linearly dependent on the photolysis laser intensity (1–4 mJ cm⁻²). Following reaction initiation, time-resolved OH profiles were measured as functions of CH₃CCl₃ concentration using laser-induced fluorescence with a pulsed Nd:YAG pumped dye laser (Quanta Ray Model DCR-2/PDL-2). As illustrated in Figure 1, OH decays were obtained over 2–3 decay lifetimes. Over the entire temperature range, reactive and diffusive OH decay profiles exhibited exponential behavior and were fit by the following nonlinear expression:

$$[OH] = [OH]_0 \exp(-k't) + \gamma \tag{1}$$

where $\gamma = \text{background}$ (constant) signal level. Because [CH₃C-Cl₃] > 1000[OH] in all reactive experiments, exponential "reaction only" OH dependences, of pseudo-first-order decay constant $k' = k_1$ [CH₃CCl₃] + k_d were observed. (k_d is the first-order rate coefficient for OH disappearance because of diffusion from the reaction volume and reaction with background impurities.) Bimolecular rate coefficients, k_1 , were obtained from the slope of the least-squares straight line through the (CH₃CCl₃, k') data points (cf. Figure 2). Values of k' ranged from about 80 to 750 s⁻¹, depending on the reactant concentration and the temperature. The first-order OH decay rate constants in the absence of reactant, k_d , ranged from 70 to 140 s⁻¹ and increased with increasing reactor temperature.



Figure 2. Pseudo-first-order rate constant, k', as a function of $[CH_3CCl_3]$ at various reaction temperatures.

TABLE II: Absolute Rate Coefficient Values for k_1

T (K)	$10^{13}k \text{ (cm}^{3} \text{ molecule}^{-1} \text{ s}^{-1})$	T (K)	$10^{13}k \text{ (cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$
298	0.11 ± 0.01	535	2.02 ± 0.10
350	0.29 ± 0.06	560	2.18 ± 0.28
400	0.50 ± 0.10	601	2.35 ± 0.38
457	0.94 ± 0.06	642	3.31 ± 0.81
460	1.09 ± 0.29	671	3.68 ± 0.36
495	1.22 ± 0.12	720	5.45 ± 0.20
513	1.27 ± 0.09	761	7.26 ± 0.39
527	1.85 ± 0.13		

TABLE III: Arrhenius Rate Expressions (in cm³ molecule⁻¹ s⁻¹) for k_2-k_4

constant	rate expression
k,	$1.7 \times 10^{-11 a}$
k_{3}	$3.2 \times 10^{13} \exp(-17100/RT)^{b}$
k₄	$2.3 \times 10^{-12} \exp(938/RT)^{\circ}$
$k_{4'}$	$2.5 \times 10^{-11} \exp(-6020/RT)^d$

^{*a*}A factor estimated by analogy with other chlorocarbon radical recombination reactions.¹³ ^{*b*}A factor calculated from transition-state theory.¹⁴ Activation energy calculated from following expression: $E_a = \Delta H_r + 2$ kcal mol⁻¹. ^{*c*} Reference 15. ^{*d*}Rate expression estimated by analogy with other chloroolefin H atom transfer reactions.¹⁶

The chemicals used in this study had the following stated minimum purities: He, 99.999+%; N₂O, 99.9%; H₂O, HPLC organic-free reagent grade. 1,1,1-Trichloroethane (Aldrich) had an initial purity of ~99.9%. Extensive purification procedures as described by Jeong and Kaufman¹² increased the purity to 99.99% (GC/MS analysis). No detectable olefinic impurities, specifically CH₂==CCl₂, were observed.

Results and Discussion

Absolute rate coefficient values for k_1 from 298 to 761 K are listed in Table II. Random error limits (2σ) , derived from a propagation of error analysis, ranged from $\pm 6\%$ to $\pm 27\%$. This analysis indicated that substrate concentration, probe laser intensity (pulse to pulse), and reaction temperature were the major sources of uncertainty in the error analysis. The possibility that OH decay could be due to reaction with photolytically generated but unreacted O atoms was investigated by varying the H₂O concentration. Bimolecular rate determinations were unaffected by a factor of 5 change in H_2O concentration, indicating that unreacted O atoms had no effect on the observed measurements. In the absence of reactant impurities, sources of systematic error are then limited to thermally and photolytically induced secondary reactions. No photolytic effects were evident, as measured rate constants were independent of photolysis laser intensity at the low intensities employed $(1-4 \text{ mJ cm}^{-2})$.

The importance of thermally induced secondary reactions was first evaluated by numerical integration of additional OH decay routes. These decay routes were postulated to result from collisional stabilization or decomposition of the primary trichloroethyl



Figure 3. Arrhenius plot of kinetic data for k_1 . Also shown are the results from previous investigations (see legend).

radical produced from the H abstraction process yielding 1,1dichloroethylene:

> k_2 $CH_2CCl_3 + OH \rightarrow CH_2OHCCl_3$

$$CH_2CCl_3 \rightarrow CH_2:CCl_2 + Cl$$
 k_3

 $CH_2 = CCl_2 + OH \rightarrow CH_2OHCCl_2$ (298-600 K) k₄

 $CH_2 = CCl_2 + OH \rightarrow CHCCl_2 + H_2O$ (600-800 K) $k_{4'}$

Arrhenius parameters used in this analysis are given in Table III. Although the ratio of the relative rates of OH attack for $k_4:k_1$ is ~ 1000 at room temperature.¹⁵ the numerical results indicated no pronounced effect on the observed OH decays. This is attributed to the substantial activation energy for β -Cl bond scission of the primary radical (cf. Table III), resulting in low CH₂==CCl₂ concentrations and the relatively large CH₃CCl₃:OH ratios for these experiments.

An Arrhenius plot of the data indicated significant curvature as illustrated in Figure 3. A nonlinear, least-squares fit of the rate data (weighted as $\omega_k = 1/\sigma_k^2$) to the modified Arrhenius equation $k(T) = A(T/300)^b \exp(-E/RT)$ produced the following expression, depicted as a solid line in Figure 3:

$$k_1 = (3.95 \pm 0.78) \times 10^{-13} (T/300)^{2.08} \exp\{(-1068 \pm 108)/T\} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

Error limits are 2σ values. Due to the significant curvature in the Arrhenius plot at elevated temperatures, the possibility of high-temperature thermal artifacts was investigated experimentally by varying the total gas flow rate. k_1 was found to be independent of residence time in the high-temperature region, implying the lack of secondary reaction chemistry associated with the thermal decomposition of the substrate.

Numerous measurements of k_1 have been reported, with the majority of these at lower temperatures. As illustrated in Figure 3, our results overlap well with the most recent of these measurements.^{1,12,17} Extrapolation of our measurements from room temperature to 200 K are also in good agreement with the results of Kurylo et al.,¹⁷ with the exception of their measurement at 222 K. The other studies shown in Figure 3 have been reported to be influenced by the presence of the reactive impurity, CH_2 = CCl₂.¹⁸⁻²² For example, room-temperature (298 K) measurements with CH2=CCl2-contaminated samples yielded a fairly scattered set of larger ((1.5-3.5) \times 10⁻¹⁴ cm³ molecule⁻¹ s⁻¹) rate coefficients that now appear to be inconsistent with the recent, more reproducible, smaller room-temperature coefficients ((1.1-1.3) \times 10⁻¹⁴ cm³ molecule⁻¹ s⁻¹) obtained with extensively purified samples.

Comparison of our measurements of k_1 versus the predictions of Atkinson's SAR model,7 TST calculations of Cohen and Benson,8 and the empirical model of Cohen and Benson9 are shown in Figure 4. It is evident that both the TST and SAR models are excellent predictors of the temperature-dependent rate behavior of k_1 , being within $\pm 10\%$ of the experimental measurements over the entire temperature range. The empirical model underpredicts the magnitude of the rate constants by $\sim 45-70\%$.



Figure 4. Arrhenius plot of the three parameter fit for k_1 . Also shown are the predictions of three semiempirical models (see legend).

TABLE IV: Rate Coefficients for Chlorinated Ethanes at 800 K

compound	k_{800} (cm ³ molecule ⁻¹ s ⁻¹)	ref	
	8.00×10^{-13}	this work	
CH ₃ CH ₂ Cl	4.33×10^{-12}	3	
CH ₄ CHCl ₂	1.82×10^{-12}	4	
CH ₂ ClCH ₂ Cl	3.88×10^{-12}	. 5	
CH ₂ ClCHCl ₂	2.37×10^{-12}	6	

The low room-temperature reactivity of CH₃CCl₃ compared to other chlorinated ethanes (cf. Table I) has prompted us^{4,5} and other investigators¹ to consider the influence of inductive effects within the activated complex that arise from β -Cl substitution of the substrate. Table IV presents rate coefficients at 800 K for a series of chlorinated ethanes calculated from best-fit Arrhenius and modified Arrhenius expressions derived from our extended temperature studies.³⁻⁶ The results show a spread of reactivity very similar to that observed at room temperature, i.e., a decreasing order of reactivity as follows: $CH_3CH_2Cl > CH_2ClCH_2Cl >$ $CH_2ClCHCl_2 \sim CH_3CHCl_3 \gg CH_3CCl_3$. These results suggest that the same factors that are controlling the room temperature reactivity are also controlling the higher temperature reactivity, viz., β -Cl-induced partial polarization of the activated complex.

It is interesting to note that there does not appear to be a narrowing of the range of reactivity of these compounds at elevated temperatures, as observed for the chlorinated methanes.^{10,23} This "leveling" of reactivity for chlorinated methanes has been attributed to reductions in activation energy caused by the nearly 6 kcal mol⁻¹ decrease in the C-H bond dissociation energy with increasing chlorine substitution. Perhaps its absence for the chlorinated ethanes is not that surprising due the relative small spread in R-H bond dissociation energies $(\pm 2-3 \text{ kcal mol}^{-1})$.

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Registry No. OH radical, 3352-57-6; CH₃CCl₃, 71-55-6.

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Laser Photolysis/Laser-Induced Fluorescence Studies of the Reaction of OH with 1,1-Dichloroethane over an Extended Temperature Range

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Absolute rate coefficients are determined for the gas-phase reaction of OH radicals with 1,1-dichloroethane over an extended temperature range using a laser photolysis/laser-induced fluorescence technique. Experiments were performed in a flow system at a total pressure of 740 \pm 10 Torr using He as diluent and carrier gas. The rate coefficients, obtained over the temperature range 294-800 K, exhibited pronounced non-Arrhenius behavior and were best described by the modified Arrhenius equation $k(T) = (8.29 \pm 0.36) \times 10^{-14} (T/300)^{2.67} \exp\{(378 \pm 18)/T\} \text{ cm}^3$ molecule⁻¹ s⁻¹. Comparison of the data with one previous room-temperature measurement is presented. The temperature dependence of the data is compared with empirical and transition-state model calculations. The influence of C-H bond energy and Cl substitution is discussed.

Introduction

We have initiated a systematic study of the gas-phase reactivity of hydroxyl radicals (OH) with the chlorinated ethanes. The motive for this work is a more accurate assessment of the chemical processes involved in the thermal destruction of hazardous wastes. In this vein, accurate rate constant measurements have been reported for these reactions over extended temperature ranges, typically from 295 to 850 K.¹⁻³ The best-fit Arrhenius expressions, which often depict significant curvature in the Arrhenius plots, are then compared with empirical and transition state models.⁴⁻⁶ Since all possible reactants cannot be studied, the accuracy of these models is important and must be verified by comparison with high-temperature experimental data.

A second, more fundamental objective of these studies is to gain insight into the molecular parameters that most strongly influence the reactivity of these compounds. Previous studies have focused particular attention on the relative strengths of the carbon-hydrogen bonds being broken during the abstraction process.^{1-3,7} We have also considered how differences in the partial polarization of the activated complexes may be related to differences in reactivity.²

In this paper, we report absolute rate coefficient measurements for the reaction of OH with 1,1-dichloroethane:

$$CH_3CHCl_2 + OH \rightarrow CH_3CCl_2 (+CH_2CHCl_2) + H_2O k_1$$

over the temperature range 295–850 K. The room-temperature reactivity of these compounds is discussed based on comparisons with previous measurements for chloroethane¹ and 1,2-dichloroethane² and recommended values for ethane.⁷ Comparisons of the temperature dependence of the data with empirical^{4,5} and transition-state models⁸ are also presented.

Experimental Technique and Data Reduction

All experiments were performed using a refined laser photolysis/laser-induced fluorescence (LP/LIF) technique. A detailed description of this technique and its application to OH kinetic studies has been previously reported.^{1,9} Thus, we focus on recent refinements of the experimental approach.

All experiments were carried out under "slow flow" conditions, i.e., the buildup of reaction products was minimized. Individually

controlled gas flows of CH₃CHCl₂/N₂O/H₂O/H₂O/He were thoroughly mixed before entering the reactor. The composite flow conditioned the reactor for 45-90 s prior to the onset of data collection, thereby minimizing any effects due to reactant adsorption on the reactor walls. All experiments were conducted at a total pressure of 740 ± 10 Torr. The gas temperature in the reaction zone was measured with two chromel/alumel thermocouples and was observed to be constant within ± 2 K over both the dimensions of the probed volume and the duration of the experiment.

Hydroxyl radicals were produced by 193.3-nm photodissociation of $CH_3CHCl_2/N_2O/H_2O/He$ gas mixtures. Initial OH concentrations, estimated using published values of the N₂O absorption coefficient,¹⁰ ranged from 2×10^{10} to 4×10^{10} molecules cm⁻³ and were linearly dependent on the photolysis intensity (1–2 mJ cm⁻²). Following reaction initiation, time-resolved OH profiles were measured as functions of CH₃ClCHCl₂ concentration using laser-induced fluorescence. As illustrated in Figure 1a, OH decays were obtained over 2–3 decay lifetimes. Over the entire temperature range, reactive and diffusive OH decay profiles exhibited exponential behavior and were fitted by the following nonlinear expression:

$$[OH] = [OH]_0 \exp(-k't) + \gamma \tag{1}$$

where $\gamma = \text{background}$ (constant) signal level. Because [CH₃C-HCl₂] > 1000[OH] in all reactive experiments, exponential "reaction only" OH dependences, of pseudo-first-order decay constant $k' = k_1$ [CH₃CHCl₂] + k_d were observed. (k_d is the first-order rate coefficient for OH disappearance because of diffusion from the reaction volume and reaction with background impurities.) Bimolecular rate coefficients, k_1 , were obtained from the slope of the least-squares straight line through the (CH₃CHCl₂, k') data points (cf. Figure 2). Values of k' ranged from about 150 to 1800 s⁻¹, depending on the reactant concentration. The first-order OH decay rate constants in the absence of reactant, k_d , ranged from 70 to 140 s⁻¹ and increased with increasing reactor temperature.

For improved data acquisition and averaging, a gated integrator and boxcar averager (SRS Model SR250) have replaced the custom-built electronics. Our custom-built electronics limited the initial time delay between the two lasers to the built in RC time constant (\sim 500 µs). This combined with the timing jitter in our

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