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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<sup>-1</sup> s<sup>-1</sup>. 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.<sup>1-3</sup> The best-fit Arrhenius expressions, which often depict significant curvature in the Arrhenius plots, are then compared with empirical and transition state models.<sup>4-6</sup> 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.<sup>1-3,7</sup> We have also considered how differences in the partial polarization of the activated complexes may be related to differences in reactivity.<sup>2</sup>

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 chloroethane<sup>1</sup> and 1,2-dichloroethane<sup>2</sup> and recommended values for ethane.<sup>7</sup> Comparisons of the temperature dependence of the data with empirical<sup>4,5</sup> and transition-state models<sup>8</sup> 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.<sup>1,9</sup> 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 CH<sub>3</sub>CHCl<sub>2</sub>/N<sub>2</sub>O/H<sub>2</sub>O/H<sub>2</sub>O/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  $CH_3CHCl_2/N_2O/H_2O/He$  gas mixtures. Initial OH concentrations, estimated using published values of the N<sub>2</sub>O absorption coefficient,<sup>10</sup> ranged from  $2 \times 10^{10}$  to  $4 \times 10^{10}$  molecules cm<sup>-3</sup> and were linearly dependent on the photolysis intensity (1–2 mJ cm<sup>-2</sup>). Following reaction initiation, time-resolved OH profiles were measured as functions of CH<sub>3</sub>ClCHCl<sub>2</sub> 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 [CH<sub>3</sub>C-HCl<sub>2</sub>] > 1000[OH] in all reactive experiments, exponential "reaction only" OH dependences, of pseudo-first-order decay constant  $k' = k_1$ [CH<sub>3</sub>CHCl<sub>2</sub>] +  $k_d$  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 (CH<sub>3</sub>CHCl<sub>2</sub>, k') data points (cf. Figure 2). Values of k' ranged from about 150 to 1800 s<sup>-1</sup>, 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<sup>-1</sup> 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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Figure 1. (a, top) Fitted raw data showing typical OH decay profile versus probe laser time delay. (b, bottom) Fitted raw data showing OH decay profile versus probe laser time delay. Note change in scale of ordinate as compared to (a).



**Figure 2.** Pseudo-first-order rate constant, k', as a function of [CH<sub>3</sub>C-HCl<sub>2</sub>] at various reaction temperatures.

previous excimer laser prevented data acquisition prior to delay times of 1000  $\mu$ s. This problem has been solved with the combined interface of a new excimer laser (Questek Model 2320) and the gated integrator and boxcar averager. Initial time delays in our system can now be as short as 10  $\mu$ s. For rapid OH decays, it is imperative that data be obtained in the submillisecond time window for an accurate fit to the exponential decay curve (cf. Figure 1b). This refinement will allow rate measurements of the type discussed in this work to be obtained at even higher temperatures.

The chemicals used in this study had the following stated minimum purities: He, 99.999+%; N<sub>2</sub>O, 99.9%; H<sub>2</sub>O, HPLC organic-free reagent grade. 1,1-Dichloroethane was used without additional purification. GC/MS analysis indicated a purity of >99% with no detectable olefinic impurities.

### **Results and Discussion**

Absolute rate coefficients for  $k_1$  are listed in Table I. Random error limits  $(2\sigma)$ , derived from a propagation of error analysis, were nearly always less than  $\pm 10\%$ . The possibility that OH decay could be due to reaction with photolytically generated but un-

TABLE I: Absolute Rate Coefficients (in  $10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) for  $k_1$ 

T (K)	<i>k</i> <sub>1</sub>	T (K)	<b>k</b> <sub>1</sub>	
294	$2.82 \pm 0.14^{a}$	560	8.91 ± 0.38	
321	$3.09 \pm 0.20$	602	$9.78 \pm 0.27$	
338	$3.58 \pm 0.19$	640	$11.4 \pm 0.44$	
362	$3.92 \pm 0.06$	680	$12.2 \pm 0.94$	
401	$4.65 \pm 0.19$	719	$13.4 \pm 1.21$	
441	$5.42 \pm 0.12$	760	$16.2 \pm 1.80$	
482	$6.45 \pm 0.21$	800	$18.8 \pm 0.76$	
521	7.58 ± 0.22			

<sup>a</sup>Uncertainties represent  $\pm 2\sigma$  estimates of the random experimental error from the least-squares analysis.

TABLE II: Arrhenius Rate Expressions (in cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) for  $k_2-k_7$ 

constant	rate expression	
k2*	$1.7 \times 10^{-11 a}$	
$k_{3}$	$3.2 \times 10^{13} \exp(-45700/RT)^{b}$	
k,	$2.3 \times 10^{-12} \exp(938/RT)^{c}$	
$k_{4'}$	$2.5 \times 10^{-11} \exp(-6020/RT)^d$	
k5	$1.7 \times 10^{-11 a}$	
k <sub>6</sub>	$3.2 \times 10^{13} \exp(-26100/RT)^{b}$	
$k_{\gamma}$	$2.1 \times 10^{-12} \exp(700/RT)^{\epsilon}$	
k7'	$3.0 \times 10^{-11} \exp(-4020/RT)^{\epsilon}$	

<sup>a</sup>A factor estimated by analogy with other chlorocarbon radical recombination reactions.<sup>11</sup> <sup>b</sup>A factor calculated from transition-state theory.<sup>12</sup> Activation energy calculated from following expression:  $E_a = \Delta H_r + 2$  kcal mol<sup>-1</sup>. <sup>c</sup>Reference 13. <sup>d</sup>Rate expression estimated by analogy with other chloroolefin H atom transfer reactions.<sup>14</sup> <sup>c</sup>Reference 14.

reacted O atoms was investigated by varying the  $H_2O$  concentration. Bimolecular rate determinations were unaffected by factor of 5 changes in  $H_2O$ , 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 intensity at the low intensities employed (1-2 mJ cm<sup>-2</sup>).

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 primary dichloroethyl radicals produced from the abstraction process yielding 1,1-dichloroethylene or vinyl chloride:

 $\alpha$ -H abstraction

$$CH_3CCl_2 + OH \rightarrow CH_3OHCCl_2$$
  $k_2$ 

$$CH_3CCl_2 \rightarrow CH_2:CCl_2 + H$$
  $k_3$ 

$$CH_2:CCl_2 + OH \rightarrow CH_2OHCCl_2$$
 (298–600 K)  $k_4$ 

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

 $\beta$ -H abstraction

$$CH_2CHCl_2 + OH \rightarrow CH_2OHCHCl_2 \qquad k_5$$

$$CH_2CHCl_2 \rightarrow CH_2:CHCl + Cl \qquad k_6$$

$$CH_2:CHCl + OH \rightarrow CH_2OHCHCl$$
 (298–600 K)  $k_7$ 

$$CH_2:CHCl + OH \rightarrow CH_2CCl + H_2O$$
 (600-800 K)  $k_{\gamma}$ 

Arrhenius parameters used in this analysis are given in Table II. The results indicated no pronounced effect on the observed OH decays. This finding was primarily due to the negligibly low olefinic concentrations produced by  $\beta$ -H (and Cl) bond scission of the primary radical at the relatively modest temperatures of these rate determinations. The possibility of additional thermal artifacts were further investigated experimentally by varying the total gas flow rate.  $k_1$  was found to be independent of residence



Figure 3. Arrhenius plot of kinetic data for  $k_1$ . Also shown are the results of Howard and Evenson<sup>15</sup> and the predictions of three semiempirical models.4.5.8

time in the high-temperature region implying lack of thermal reaction of the substrate.

An Arrhenius plot of the data indicated pronounced 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:

$$k_1 = (8.29 \pm 0.36) \times 10^{-14} (T/300)^{2.67} \exp\{(378 \pm 18)/T\} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

Error limits are  $2\sigma$  values.

Only one previous measurement of  $k_1$  has been reported. Howard and Evenson,<sup>15</sup> employing a discharge flow/laser magnetic resonance technique, reported  $k_1$  at 293 K. As illustrated in Figure 3, the two measurements of  $k_1$ , with different techniques, are in excellent agreement.

Comparisons of our measurements of  $k_1$  versus the predictions of Atkinson's SAR model,<sup>4</sup> TST calculations of Cohen and Westberg,<sup>8</sup> and the empirical model of Cohen and Benson<sup>5</sup> are also depicted in Figure 3. Two SAR representations are shown, one based on the initial estimate of  $F_{CHCl_2}$  of Atkinson,<sup>4</sup> and a second revised curve based on our previous calculation of  $F_{CHCl}$ .<sup>3</sup> It is evident that the TST calculation provides the best description of  $k_1$ , being within  $\pm 10-20\%$  of the experimental measurements. The revised SAR curve matches well the temperature dependence and curvature of  $k_1$  yet overpredicts the magnitude of the rate constants by  $\sim 45-70\%$ .

The TST calculation is based purely on the  $\alpha$ -H abstraction channel. The 10% decrease in predicted versus observed roomtemperature rate predictions is due to fitting the slightly lower room-temperature data of Howard and Evenson.<sup>15</sup> The slightly larger deviation at higher temperatures ( $\sim 20\%$ ) may be attributed to an increasing contribution from the higher energy  $\beta$ -H abstraction channel.

Figure 4 illustrates the effect of R-H bond energy on the room-temperature reactivity of numerous chlorinated ethanes with OH. The quoted reactivity is based on the recommendations of Atkinson,<sup>7</sup> our previously published measurements,<sup>1-3</sup> and recently obtained (unpublished) values from our laboratory. In the two sets of data, we have isolated the effects of  $\alpha$ - and  $\beta$ -chlorine substitution. For  $\alpha$ -chlorine substitution, the expected correlation is apparent, i.e., increased reactivity with decreasing R-H bond energy. For the case of  $\beta$ -chlorine substitution, however, it is evident that chlorinated ethane reactivity does not increase with decreasing R-H bond energy. It has been suggested in other investigations of substituted alkanes<sup>22,23</sup> that an inductive effect



Figure 4. Room-temperature rate coefficient (normalized to the number of abstractable  $\alpha$ -H atoms) for select chlorinated ethanes versus  $D^{\circ}(R-$ H). Heats of formation used to calculate D<sup>6</sup>(R-H) were obtained from the following sources: CH<sub>3</sub>CH<sub>3</sub>,<sup>16</sup> CH<sub>3</sub>CH<sub>2</sub>,<sup>16</sup> CH<sub>3</sub>CH<sub>2</sub>Cl,<sup>17</sup> CH<sub>3</sub>CH-Cl,<sup>17</sup> CH<sub>3</sub>CHCl<sub>2</sub>,<sup>18</sup> CH<sub>3</sub>CCl<sub>2</sub>,<sup>19</sup> CH<sub>2</sub>ClCHCl<sub>2</sub>,<sup>20</sup> CH<sub>2</sub>ClCCl<sub>2</sub>,<sup>19</sup> CHCl<sub>2</sub>-CHCl<sub>2</sub>,<sup>21</sup> CHCl<sub>2</sub>CCl<sub>2</sub>,<sup>21</sup> CCl<sub>3</sub>CHCl<sub>2</sub>,<sup>21</sup> and CCl<sub>3</sub>CCl<sub>2</sub>.<sup>21</sup> The uncertainty in the heats of formation are  $\pm 2$  kcal mol<sup>-1</sup> (except CH<sub>3</sub>CH<sub>3</sub> which is ±1 kcal mol<sup>-1</sup>.  $\Box$  denotes a homologous series of identical  $\beta$ -Cl substitution and varying  $\alpha$ -Cl substitution.  $\times$  denotes a homologous series of identical  $\alpha$ -Cl substitution but varying  $\beta$ -Cl substitution.

in the transition state involving polar repulsion between the electrophilic OH radical and the abstracted H atom may influence (decrease) reactivity. The observed trend of decreasing reactivity with increasing  $\beta$ -chlorine substitution (cf. Figure 4) is consistent with such an effect. Additional measurements for other chlorinated ethanes are continuing to further explore this hypothesis and will be more fully discussed in future papers.

Acknowledgment. The partial support of this work by the Environmental Protection Agency (Grant R-815871-01-0) is gratefully acknowledged.

Registry No. Cl<sub>2</sub>CHCH<sub>3</sub>, 75-34-3; OH radical, 3352-57-6.

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