REACTION OF HYDROXYL RADICALS WITH TRICHLOROETHYLENE: EVIDENCE FOR CHLORINE ELIMINATION CHANNELS AT ELEVATED TEMPERATURES

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Rate coefficients are reported for the gas-phase reaction of the hydroxyl radical (OH) with C₂HCl₃ (*k*₁) over an extended temperature range at 740 ± 10 torr in a He bath gas. Rate measurements exhibited complex behavior with a slight negative temperature dependence at temperatures below 650 K and positive temperature dependence at higher temperatures (650–750 K). The three-parameter modified Arrhenius equation adequately describes all of the data and is given by (in units of cm³ molecule⁻¹ s⁻¹)

$$k_1(291\text{--}750\text{ K}) = (3.76 \pm 0.36) \times 10^{-21} T^{2.76 \pm 0.18} \exp(1266.3 \pm 41.2)/T$$

Error limits are 2σ values. The activation energy derived from an Arrhenius fit to the data below 650 K is in good agreement with previous studies (<0.6 kcal/mol deviation).

Quantum Rice-Ramsperger-Kassel (QRRK) modeling results are in reasonable agreement with experimental results and indicate the reaction is chemically activated. Although adduct stabilization and chlorine elimination channels are pressure dependent, the overall reaction is pressure independent above 0.1 atm. At temperatures characteristic of postcombustion conditions (i.e., ~1000 K), Cl elimination is the dominant reaction. H abstraction was found to be significant only at very high temperatures. The lack of a measurable kinetic isotope effect for *k*₁ is consistent with the modeling results. Based on the new measurements reported here and with the assumption that Cl elimination accounts for the entire measured rate at ~750 K, the extrapolated product-specific rate constant is given by (in units of cm³ molecule⁻¹ s⁻¹)

$$k_{\text{Cl}}(298\text{--}1500\text{ K}) = (6.87 \pm 0.30) \times 10^{-10} T^{-0.50 \pm 0.04} \exp(-1530.5 \pm 42.4)/T$$

Error limits are 2σ values. This Cl elimination rate constant at 1000–1500 K is a factor of 5–8 times larger than extrapolation of previous low-temperature measurements. At 2000 K, H abstraction is a factor of 2–3 times faster than Cl elimination.

Introduction

Trichloroethylene (C₂HCl₃) is a widely used chlorinated solvent with an annual global emission rate of 200,000 metric tons [1,2]. High-temperature incineration remains the best available technology for the complete and permanent disposal of this toxic compound. An important process contributing to the initial destruction of halogenated hydrocarbons is reaction with OH radicals [3,4]

Previous measurements of the reaction of OH with C₂HCl₃ are limited to low temperatures (220 to 459 K) [5–8]. The reaction mechanism is presumed to be addition to the π electrons associated

with the C = C double bond. Kirchner et al. [8] measured the kinetics and reaction products from OH reactions with C₂HCl₃ at low temperatures (300–459 K) and pressures (~1 torr) using electron impact mass spectrometry. The observed product distributions were complex, with the dominant mass spectra signals interpreted in terms of a reaction mechanism involving OH addition and subsequent Cl elimination. Chang and Kaufman [7] measured OH decay rates at low temperatures (234–420 K) and pressures (1.1 and 6.2 torr) for *k*₁, using the discharge-resonance fluorescence technique. They reported that the rate coefficients were independent of pressure, thus inferring that the addition complex is rapidly

thermalized by collisions with He buffer gas at pressures of ~ 1 torr or greater or that a decomposition pathway is available.

Given the lack of available data above 450 K, knowledge of the reaction rate constants and reaction mechanisms over an extended temperature range is essential to accurately predict the flame and postflame combustion behavior of these compounds. Of specific interest is the relative importance of adduct stabilization, Cl elimination, and H abstraction. We present absolute rate coefficients for the reaction of OH with C_2HCl_3 (and C_2DCl_3) (k_1) at atmospheric pressure over an extended temperature range:

Arrhenius parameters are derived from the data. A comparison of these measurements with prior measurements at lower temperatures and pressures is discussed. *Ab initio* calculations were performed to estimate thermodynamic properties, enthalpies of formation, entropies, and heat capacities. Quantum Rice Ramsperger Kassel (QRRK) calculations were performed to calculate energy-dependent rate constants, $k(E)$, using the above thermodynamic properties.

Experimental Approach and Data Reduction

The experimental procedures were similar to those used in previous studies of the reaction of OH radicals with halogenated hydrocarbons [9,10]. Experimental aspects unique to this study are described briefly in the following paragraphs.

To minimize substrate photolysis at wavelengths < 300 nm, HONO was used as a hydroxyl radical source [11]. Parts per million concentrations of pure HONO ($> 99\%$) were generated as described by Febo et al. [12] and Brust et al. [13] HONO dissociates primarily into NO and OH when exposed to near-UV radiation of 351 nm. A competing dissociation channel, production of NO_2 and H atoms, has been observed to be negligible under similar experimental conditions [14]. A XeF excimer laser (Lamba Physik Compex Model 102) was used as the photodissociation source. Initial $[\text{OH}]_0$ ranged from $\sim 3\text{--}9 \times 10^{10}$ molecules cm^{-3} and was determined based on the measured excimer fluence (9–18 mJ cm^{-2}), the most recent published value of the absorption cross-section for HONO (1.54×10^{-19} $\text{cm}^2/\text{molecule}$ at 351 nm [13], a quantum yield of unity [15], and measured values of $[\text{NO}_2]$ taken to represent [HONO] determined using ion chromatography ($\sim 1\text{--}3 \times 10^{13}$ molecules cm^{-3}).

Initial substrate concentrations in the reactor, based on measured flow rates, ranged from $\sim 3 \times 10^{13}$ to $\sim 1 \times 10^{15}$ molecules cm^{-3} . The absence of adsorption on the injector probe (coated with boric

acid) and reactor walls was verified using gas chromatography–mass spectrometry (GC-MS) analysis. All experiments were conducted at a total pressure of 740 ± 10 torr. Samples of C_2HCl_3 (99.9% pure) were obtained from Aldrich. GC-MS analyses indicated that this purity was met or exceeded.

The rate of disappearance of the OH may be presented as

$$-d[\text{OH}]/dt = k[\text{A}_0][\text{OH}] + k_d[\text{OH}]$$

where k is the bimolecular rate constant, A_0 is the substrate concentration, and k_d is the first-order rate for the reaction of OH with HONO and also includes diffusion out of the reaction volume. This relationship holds in the absence of any secondary reactions that may form or deplete OH. Solution of this equation yields $[\text{OH}] = [\text{OH}]_0 \exp -(k't)$, where $k' = k + k_d$. For all experiments, reactive and diffusive OH radical decay profiles exhibited exponential behavior and were fitted by the nonlinear expression

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

where γ is the constant background signal level and t is the time delay between the laser pulses. Because the organic concentration was much greater than the $[\text{OH}]$, pseudo-first-order exponential OH decays were observed, and the individual temperature-dependent rate constants were determined by $k' = k[\text{substrate}] + k_d$, where the bimolecular rate constant, k , is the slope of the least squares fit of k' versus the [organic]. Numerical modeling indicated that the dominant source of OH decay in the absence of C_2HCl_3 was reaction with HONO ($k_{298} = 4.5 \times 10^{-12}$ $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) [14]. Typical values of k_d decreased from $\sim 250 \text{ s}^{-1}$ at low temperatures to $\sim 100 \text{ s}^{-1}$ at elevated temperatures and were indicative of reduced HONO concentrations in the reactor at elevated temperatures. With the addition of C_2HCl_3 , values of k' varied from ~ 275 to $\sim 1550 \text{ s}^{-1}$.

Results

Rate data were obtained from ambient temperatures to ~ 750 K, under atmospheric pressure conditions. OH signals were obtained at higher temperatures using the HONO source; however, a rapid OH consumption channel occurring on the time-scale of 1 ms prevented further measurements. This competing OH consumption pathway was observed only above 750 K with the addition of C_2HCl_3 . Gas-phase thermal decomposition of C_2HCl_3 has been shown to be negligible at these temperatures (gas-phase residence times $\ll 1$ s) [16]. A surface-mediated decomposition process resulting in the production of chlorinated radicals is a plausible explanation for the rapid OH consumption observed.

FIG. 1. Arrhenius plot of kinetic data for k_1 . Error bars denote $\pm 2\sigma$ random error limits. Also shown are the results of previous studies at lower temperatures and pressures and a three-parameter modified Arrhenius fit to the data ($p = 740 \pm 10$ torr).

All known absolute rate measurements for k_1 are summarized in Fig. 1 [1]. (Note: Our previous measurements for trichloroethylene [17] using 193 nm radiation to generate OH radicals are believed to be in error due to substrate photolysis and are not included in Fig. 1.) This work extends experimental measurement beyond the limit of ~ 450 K reported previously. A variety of techniques were used in collecting these data. Examination of Fig. 1 shows agreement at room temperature, within combined experimental uncertainties, between our work and that reported previously [5–8].

Rate measurements for k_1 exhibited complex behavior with a slight negative temperature dependence at temperatures below 650 K and positive temperature dependence at higher temperatures. The three-parameter modified Arrhenius equation, calculated using a weighted, nonlinear least squares Levenberg-Marquardt algorithm, adequately describes all of the data and is given by (in units of $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)

$$k_1(291\text{--}750 \text{ K}) = (3.76 \pm 0.36) \times 10^{-21} T^{2.76 \pm 0.18} \exp(1266.3 \pm 41.2)/T$$

Error limits are 2σ values. The activation energy derived from an Arrhenius fit to the data below 650 K is also in good agreement with previous studies (<0.6 kcal/mol deviation). The agreement between our rate measurements at 740 torr and prior measurements obtained between ~ 1 and 200 torr provides further verification that the reaction is in the high-pressure limit at temperatures below 1000 K.

Rate coefficient measurements were also obtained with deuterated C_2HCl_3 to provide further insight

into the reaction mechanism. Rate coefficient measurements with C_2DCl_3 at 292 and 699 K indicate the absence of a measurable isotope effect. This result indicates that C-H bond breaking is not rate determining and infers that an OH addition mechanism dominates the measured OH decay rates throughout the temperature range of investigation.

Theoretical Approach

The composite *ab initio* calculation method, G3(MP2) [18], and density functional theory (DFT) B3LYP/6-311 + G(3df,2p)//B3LYP/6-31G(d) were used to calculate thermodynamic properties of reactants, intermediate radicals, transition states (TSs), and products with the Gaussian94 [19] and Gaussian98 [20] computer codes. G3(MP2) uses HF/6-31G(d) level of theory to calculate frequencies and zero point energies (ZPEs), followed by MP2(full)/6-31G(d) level of theory to determine the final geometries. G3(MP2), then, uses QCISD(T)/6-31G(d) and MP2(fc)/G3MP2large for the higher-energy correction [18]. The enthalpies of formation of the reactants were obtained from the literature [21,22]. The enthalpies of formation at 298 K for intermediates and products were determined by the energy differences from the reactants, calculated by G3(MP2) [18]. ZPE and thermal correction to 298 K were incorporated to estimate enthalpies of formation [23]. The activation energies, except for the addition entrance channel ($\text{C}\cdot\text{Cl}_2\text{CHCl}\text{---OH}$ and $\text{C}\cdot\text{HClCCl}_2\text{---OH}$), were determined by the relative energy differences between each respective intermediate and TS whose energies were calculated by B3LYP/6-311 + G(3df,2p)//B3LYP/6-31G(d) level of theory. QCISD(T)/6-31G(d) calculation, which is one of G3(MP2) calculation steps, was not successful for several TSs, and necessitated the use of DFT. Entropy and heat capacity were calculated based on calculated moments of inertia and frequencies using statistical mechanics.

For the reactions where thermodynamic properties of transition states were calculated by *ab initio* methods, k values were fitted by three parameters, B , n , and C , over a temperature range of 200 to 2000 K, as expressed by

$$k = B(T)^n \exp(-C/RT)$$

High-pressure limit A factors of unimolecular reactions were calculated using transition-state theory (TST) [24] along with *ab initio* data for the determination of the structure, and vibrational and rotational contributions to the entropies of the TSs. Loss (or gain) of internal rotors and change of optical isomer and symmetry numbers were also incorporated into the calculation of entropy for each TS. Entropies of reactants and TSs were then used to determine the pre-exponential factor, A , via classical TST for a unimolecular reaction

FIG. 2. Classical energies (no ZPE) relative to OH + C₂HCl₃ for addition of OH at the CHCl end (α , squares) and the CCl₂ end (β , circles), calculated at the PMP4/6-311 + G(d,p)/HF6-31(d,p) level of theory.

$$A = (k_b T/h) \exp(\Delta S^\ddagger/R)$$

where h is Planck's constant, k_b is the Boltzmann constant, and $\Delta S^\ddagger$ is equal to $S_{298,TS}^\circ - S_{298,reactant}^\circ$. A QRRK analysis [25–28] for $k(E)$, combined with the modified β collision analysis of Gilbert et al. [29] or fall-off, was used to predict pressure-dependent rate constants.

Variational transition-state theory (VTST) calculations were performed to estimate the rate of OH addition to C₂HCl₃. The calculations were carried out as follows. First, the reaction coordinates for addition of OH to each end of the C=C bond were defined as intrinsic reaction coordinates (IRCs) at the HF/6-31G(d,p) level. For each IRC, the geometry of the system was optimized at various fixed C-O separations, and frequencies were obtained normal to the IRC, also at the HF/6-31G(d,p) level of theory. The results were scaled by a factor of 0.90.

Then, energies were computed at the spin-projected PMP4/6-311 + G(d,p) level, relative to reactants [19]. These energies, geometries, and frequencies were used to derive canonical TST rate constants as a function of position along the IRC. At each temperature, the VTST result was obtained by interpolation to find the minimum rate constant.

These VTST results correspond to the high-pressure limit for OH addition, where the initially formed excited adduct is always stabilized by collisions. At finite pressures, some fraction of the excited adducts can dissociate back to OH + C₂HCl₃ before collisional stabilization or fragmentation, and thus the observed rate constant is likely to be smaller than the calculated one. At a given pressure, this effect will become more pronounced at elevated temperatures, because the reaction moves further from the high-pressure limit.

The variationally located transition states lie at C-O separations approximately 0.05 Å smaller than the local maxima along the IRCs. As seen in Fig. 2, the barrier for α addition lies approximately 1 kcal/mol below the reactants' energy, whereas β addition requires overcoming a positive barrier of around +1 kcal/mol. The β addition channel is also found to be somewhat less favorable in an entropy context as well (the pre-exponential factor is approximately 8 times smaller, see Tables 1 and 2). The derived VTST rate constants are plotted in Fig. 3. The β channel has a simple positive temperature dependence. The α channel is more important at all temperatures and has a more complex behavior. The negative relative transition state energy implies a negative temperature dependence for the rate constant, an effect which dominates at low temperatures, however, increases in temperature more rapidly increase the partition function of the loose TS as compared to

TABLE 1
Input QRRK parameters, high-pressure limit rate constants for α addition of OH to C₂Cl₃H

Reaction	B (s ⁻¹ or cm ³ /(molecule s))	n	C (kcal/mol)
1 C ₂ Cl ₃ H + OH $\Rightarrow$ C·Cl ₂ CClHOH	1.98E - 19	2.40	-1.49
-1 C·Cl ₂ CClHOH $\Rightarrow$ C ₂ Cl ₃ H + OH	6.20E + 06	2.40	36.14
2 C·Cl ₂ CClHOH $\Rightarrow$ C ₂ Cl ₃ OH + H	4.28E + 07	2.21	47.12
3 C·Cl ₂ CClHOH $\Rightarrow$ CCl ₂ CHOH + Cl	1.69E + 13	0.00	24.74
4 C·Cl ₂ CClHOH $\Rightarrow$ CCl ₂ HCClHO·	7.10E + 08	0.72	41.18
-4 CCl ₂ HCClHO· $\Rightarrow$ C·Cl ₂ CClHOH	3.63E + 09	0.41	26.77
5 C·Cl ₂ CClHOH $\Rightarrow$ CCl ₃ C·HOH	1.23E + 10	1.10	12.41
-5 CCl ₃ C·HOH $\Rightarrow$ C·Cl ₂ CClHOH	9.63E + 10	0.76	2.98
6 CCl ₃ C·HOH $\Rightarrow$ CCl ₂ CHOH + Cl	1.69E + 13	0.00	15.86
7 C ₂ Cl ₃ H + OH $\Rightarrow$ C·ClCCl ₂ + H ₂ O	2.67E - 16	1.30	7.45

Note: Grouped geometric mean frequencies of the adduct with effective degeneracies: 100.0 cm⁻¹ (5.304), 757.5 cm⁻¹ (8.050), 1980.8 cm⁻¹ (3.646). Lennard-Jones parameters: C₂Cl₃HOH adduct: σ = 5.327 Å, ϵ/k_B = 469.4 K; He bath gas: σ = 2.576 Å, ϵ/k_B = 470.0 K.

TABLE 2
Input QRRK parameters, high-pressure limit rate constants for β addition of OH to C_2Cl_3H

Reaction	B (s^{-1} or $cm^3/(molecule \cdot s)$)	n	C (kcal/mol)
1 $C_2Cl_3H + OH \Rightarrow C \cdot ClHCCl_2OH$	$4.32E - 20$	2.43	1.43
–1 $C \cdot ClHCCl_2OH \Rightarrow C_2Cl_3H + OH$	$1.90E + 05$	2.43	38.33
2 $C \cdot ClHCCl_2OH \Rightarrow CClHCClOH + Cl$	$1.69E + 13$	0.00	27.41
3 $C \cdot ClHCCl_2OH \Rightarrow CClH_2CCl_2O \cdot$	$2.42E + 09$	0.52	37.37
–3 $CClH_2CCl_2O \cdot \Rightarrow C \cdot ClHCCl_2OH$	$1.18E + 10$	0.39	25.13
4 $C \cdot ClHCCl_2OH \Rightarrow CHCl_2C \cdot ClOH$	$3.73E + 13$	–0.86	6.45
–4 $CHCl_2C \cdot ClOH \Rightarrow C \cdot ClHCCl_2OH$	$1.04E + 13$	–0.55	7.53
5 $CHCl_2C \cdot ClOH \Rightarrow CClHCClOH + Cl$	$1.69E + 13$	0.00	28.58
6 $CHCl_2C \cdot ClOH \Rightarrow C_2Cl_3OH + H$	$1.31E + 09$	1.62	46.55

Note: Grouped geometric mean frequencies of the adduct with effective degeneracies: 623.0 cm^{-1} (8.425), 596.8 cm^{-1} (6.341), 2225.0 cm^{-1} (2.734). Lennard-Jones parameters: C_2Cl_3HOH adduct: $\sigma = 5.327\text{ \AA}$, $\epsilon/k_B = 469.4\text{ K}$; He bath gas: $\sigma = 2.576\text{ \AA}$, $\epsilon/k_B = 470.0\text{ K}$.

FIG. 3. Variational transition state theory rate constants for OH addition to C_2HCl_3 . Addition of OH to both carbon sites is shown. The OH rotation was treated as a hindered rotor with a barrier of 2.4 kcal/mol.

the reactants, leading to a positive activation energy at higher temperatures.

Modeling Results

Tables 1 and 2 present the high-pressure-limit Arrhenius parameters for the various pathways for α and β OH addition reactions, respectively. Figs. 4 and 5 present a comparison of the modified Arrhenius fit of the experimental data (extrapolated to 2000 K) with the QRRK-predicted expression. The fit between the two expressions is within 10% at the extremes of the temperature range (285 and 2000 K) and within a factor of ~ 2 at intermediate temperatures. Overall, given the lack of adjusted parameters, the agreement is quite remarkable, though

FIG. 4. Arrhenius plot of the QRRK model results ($p = 1\text{ atm}$). Shown are the predicted forward rate for the α and β sites. Also shown are the stabilization (α site only) and chlorine elimination channel and the H-atom abstraction channel. The experimental data and a best fit extrapolated to 2000 K have also been included.

QRRK modeling consistently predicts larger values throughout the temperature range, with slightly positive temperature dependence. This contrasts with the slight negative temperature dependence of the experimental data below 600 K. (The stabilized adduct ($C \cdot Cl_2CClHOH$) is the only path that shows a negative temperature dependence, and though it is a substantial dependence, it has a markedly smaller relative rate.)

Figure 4 also shows the QRRK-estimated temperature-dependent reaction rate constants for the various path products. The predicted dominant product is 1,1-dichloroethenol, formed by OH addition to the α site, followed by Cl elimination from

FIG. 5. QRRK-determined forward rate constants as a function of pressure and temperature. Included are the forward rate constant and the selected, individual rate constants at pressures of 0.001, 0.1, and 10.0 atm (α site only).

FIG. 6. Potential energy diagrams for the OH addition to C_2HCl_3 (α site). Energies are ΔH°_{f298} in kcal/mol. Thick lines represent energetically favorable pathways.

the stabilized adduct ($C\cdot Cl_2COHClH$, see Fig. 6). The second dominant product is 1,2-dichloroethanol, which is formed by OH addition to the β site, followed by isomerization and Cl elimination (intermediate radicals are $C\cdot HClCOHCl_2$ and $CHCl_2C\cdot OHCl$, see Fig. 7). The temperature dependence of these two separate paths is shown in Fig. 4. At temperatures characteristic of flame conditions (2000 K), H-atom abstraction is two times faster than Cl elimination. The formation of C_2Cl_3OH by H displacement is insignificant, even under flame conditions.

These results compare favorably with those previously reported by Kirchner et al. [8], who found by mass spectrometry that the dominant products were likely formed by Cl elimination processes.

FIG. 7. Potential energy diagrams for the OH addition to C_2HCl_3 (β site). Energies are ΔH°_{f298} in kcal/mol. Thick lines represent energetically favorable pathways.

Chang and Kaufman [7] reported that the reaction was not pressure dependent under their experimental conditions (1.1–6.2 torr, 234–420 K). This is consistent with the modeling results. As seen in Fig. 5, the overall forward reaction is not a function of pressure above 0.1 atm. Cl elimination and the formation of the initial stabilized adduct does show the expected pressure dependence. Under the conditions of the previous experiments (~ 0.001 atm), Cl elimination is the only reaction channel that is important, that is, all adducts eliminate Cl atoms. The formation of 1,1-dichloroethanol has recently been observed as a significant product in flame studies of C_2HCl_3 combustion under low Cl/H ratio conditions [30]. A mechanism involving OH addition to C_2HCl_3 followed by Cl elimination was proposed to account for the formation of 1,1-dichloroethanol. This study supports the proposed pathway.

Summary

New, atmospheric pressure, absolute rate measurements are presented for the reaction of OH radicals with C_2HCl_3 . In contrast to previous studies at lower temperatures, where a slight negative temperature dependence was observed, the new measurements at higher temperatures and pressures indicated more complex behavior with a slight negative temperature dependence at temperatures below 650 K and a positive temperature dependence at higher temperatures (650–750 K).

Theoretical calculations indicate that this reaction involves a chemically activated system. The lack of any observed pressure dependence in previous low-temperature studies is consistent with this analysis. At room temperature, the dominant reaction channel is adduct stabilization. Our calculations indicate that adduct stabilization accounts for $\sim 85\%$ of the

overall reaction at 1 atm and 298 K. At higher temperatures encompassing postcombustion conditions (1000 K), Cl elimination yielding 1,1-dichloroethanol is the dominant reaction. The lack of a measurable kinetic isotope effect under these conditions is consistent with this analysis. At even higher temperatures that encompass flame conditions (2000 K), H abstraction is the dominant pathway, and *ab initio* calculations suggest a rate factor of 2 greater than Cl elimination. Based on the new measurements reported here and with the assumption that Cl elimination accounts for the entire measured rate at ~ 750 K, the extrapolated product-specific rate constant is given by (in units of $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)

$$k_{\text{Cl}}(298\text{--}1500) = (6.87 \pm 0.30) \times 10^{-10} T^{-0.50 \pm 0.04} \exp(-1530.5 \pm 42.4)/T$$

Error limits are 2σ values. This Cl elimination rate coefficient at 1000–1500 K is a factor of 5–8 times larger than extrapolation of previous low-temperature measurements [5–8].

In previously completed studies of $\text{OH} + \text{C}_2\text{Cl}_4$, the room temperature rate constant and the observed positive temperature dependence of the rate measurements was consistent with the location of a transition state for OH addition to the π electron system that lies higher in energy than that of the reactants [11]. This is in contrast to OH addition to C_2HCl_3 where the energy of the transition state (for OH addition to the α site, the dominant reaction channel) is below the energy of the reactants. The order of magnitude increase in room temperature rate constant for C_2HCl_3 versus C_2Cl_4 is due, in part, to the relative energies of the initial transition state. Future efforts will attempt to verify the predicted products and measure the branching ratios to confirm these mechanisms.

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