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Kinetics and Thermochemistry of the Reaction of 2-Chloroallyl Radicals with Molecular Oxygen

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The kinetics of the $CH_2CClCH_2 + O_2 \rightleftarrows CH_2CClCH_2O_2$ (3,−3) reaction has been studied using laser photolysis/photoionization mass spectrometry. Room-temperature decay constants of the CH_2CClCH_2 radical were determined in time-resolved experiments as a function of bath gas density ($[He] = (3-24) \times 10^{16}$ molecule cm^{-3}). The rate constants are in the falloff region under the conditions of the experiments. Relaxation to equilibrium in the addition step of the reaction was monitored within the temperature range 340−410 K. Equilibrium constants were determined as a function of temperature and used to obtain the enthalpy of the addition step of reaction 3. At high temperature (730 K), no reaction of CH_2CClCH_2 with molecular oxygen could be observed and an upper limit to the rate constants was determined (3×10^{-16} cm^3 $molecule^{-1}$ s^{-1}). Molecular structures and vibrational frequencies of CH_2CClCH_2 and $CH_2CClCH_2O_2$ were obtained in quantum chemical calculations and used to compute the reaction entropy. The experimentally determined equilibrium constants combined with the calculated reaction entropy resulted in an $R-O_2$ bond energy $-\Delta H^\circ_{298}(3,-3) = 76.5 \pm 2.8$ kJ mol^{-1}, which coincides with the $R-O_2$ bond energy for the allyl radical. The results demonstrate the absence of any effects of chlorine substitution in the β position on the $R-O_2$ bond energy.

I. Introduction

Oxidation of hydrocarbon free radicals (R) by molecular oxygen represents the key elementary steps in combustion processes.[1] Reactions of chlorinated hydrocarbon radicals with O_2 play similar roles in the oxidation of chlorinated hydrocarbons. For many radical types (including alkyl, substituted alkyl, and delocalized alkenyl radicals), at low temperatures the main channel of the $R + O_2$ reaction is the reversible formation of a peroxy radical:

$$R + O_2 \rightleftarrows RO_2 \tag{1}$$

At higher temperatures the equilibrium is shifted to the left and the overall reaction is dominated by further rearrangement and decomposition of the excited RO_2 adduct:

$$R + O_2 \rightleftarrows RO_2 \rightarrow \text{products} \tag{2}$$

Knowledge of the thermodynamic parameters of the RO_2 adduct and, in particular, the enthalpy of the $R-O_2$ bond formation ($\Delta H^\circ_{298}(R+O_2 \rightleftarrows RO_2)$) is central to understanding and predicting the change of the mechanism of the $R + O_2$ reactions with temperature from reversible addition to rearrangement and decomposition of the adduct. The values of $\Delta H^\circ_{298}(R+O_2 \rightleftarrows RO_2)$ depend on the chemical composition of the R radical, including the nature, number, and location of chemical substituent groups.

A number of experimental studies of relaxation to equilibrium in the $R + O_2$ reactions have demonstrated significant effects of Cl substitution in the α position relative to the radical site on the enthalpy of the $R-O_2$ bond.[2−5] These studies were reanalyzed and summarized in ref 6. The results demonstrated that each consecutive Cl substitution reduces the strength of the $R-O_2$ bond by ∼16 kJ mol^{-1}. At the same time, potential effects of Cl substitution in the β position relative to the radical site are unknown. In the case of alkyl radicals, such effects are difficult to study experimentally because of the low thermal stability of β-chlorinated alkyl radicals: they decompose forming an olefin and a chlorine atom at temperatures above ∼400 K even at low pressures.[7] However, delocalized alkenyl radicals present an opportunity for an experimental study of such β-substitution effects. These radicals are more thermally stable than their alkyl counterparts; for example, at pressures of 2−10 Torr, 2-chloroallyl radical decomposes only at temperatures above 700 K.[8]

Reactions of chlorinated allyl radicals with O_2 are also interesting from the standpoint of their fate in the combustion of chlorinated hydrocarbons. Resonantly stabilized (due to electron delocalization) hydrocarbon radicals are known to play an important role in the chemical mechanisms of hydrocarbon oxidation and pyrolysis. The stability and low reactivity of these radicals results in their accumulation in large concentrations during the processes of oxidation and pyrolysis of hydrocarbons. High concentrations of stabilized polyatomic radicals result in appreciable rates of their recombination, ultimately leading to molecular growth, which has been linked to the formation of polycyclic aromatics and soot. In the oxidation and pyrolysis of chlorinated hydrocarbons, chlorinated delocalized radicals can be expected to play a role similar to their role in hydrocarbon combustion. Molecular weight growth due to the buildup and recombination of delocalized chlorinated hydrocarbon radicals is likely to produce aromatic and chlorinated aromatic species characterized by high toxicity and carcinogenicity (e.g., refs 9 and 10). The principal issue pertaining to the ability of such radicals to accumulate in combustion systems is their stability. In particular, the rates of the two most important processes of

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radical removal, reactions with O_2 and unimolecular decomposition, are the most critical parameters that determine the stability of radicals in flames. No information is currently available in the literature on kinetics of these reactions of delocalized chlorinated hydrocarbon radicals at elevated temperatures.

Here we report the results of an experimental investigation of the reaction

$$CH_2CClCH_2 + O_2 \rightleftarrows \text{products} \tag{3}$$

over wide intervals of temperatures and pressures. The distinctly different behavior of reaction 3 at low, intermediate, and high temperatures was quantitatively characterized. Equilibrium constants of the addition step in reaction 3 were determined as a function of temperature. Properties of CH_2CClCH_2 and $CH_2CClCH_2O_2$ were determined in a quantum chemical study and used to calculate the entropies of these radicals. These calculated entropy values, together with the experimental equilibrium constants, were used to obtain the $R-O_2$ bond energy.

II. Experimental Section

CH_2CClCH_2 radicals were produced at elevated temperatures by pulsed laser photolysis (LP), and their decay was subsequently monitored in time-resolved experiments using photoionization mass spectrometry (PIMS). Details of the experimental apparatus[11] used have been described before and so are only briefly reviewed here.

Pulsed unfocused 248-nm radiation (4 Hz) from a Lambda Physik EMG 201MSC excimer laser was directed along the axis of a heatable quartz reactor (1.05-cm i.d., coated with boron oxide[12]). Gas flowing through the tube at ≈ 4 m s^{-1} contained the radical precursors ($<2\%$), molecular oxygen in varying concentrations, and an inert carrier gas (He) in large excess. The flowing gas was completely replaced between laser pulses. Gas was sampled through a hole (0.04-cm diameter) in the side of the reactor and formed into a beam by a conical skimmer before the gas entered the vacuum chamber containing the photoionization mass spectrometer. As the gas beam traversed the ion source, a portion was photoionized and mass selected. CH_2CClCH_2 radicals were ionized using the light from a chlorine resonance lamp (8.9−9.1 eV) with a CaF_2 window. Temporal ion signal profiles were recorded on a multichannel scaler from a short time before each laser pulse and up to 25 ms following the pulse. Data from 1000 to 40 000 repetitions of the experiment were accumulated before the data were analyzed.

At temperatures of 410 K and below, CH_2CClCH_2 radicals were produced by the pulsed, 248-nm laser photolysis of oxalyl chloride[13−16]

$$(CClO)_2 \xrightarrow{h\nu} 2Cl + 2CO \tag{4a}$$

$$\rightarrow Cl + CO + CClO \rightarrow 2Cl + 2CO \tag{4b}$$

followed by the fast reaction of Cl atoms with allene[17−19]

$$Cl + CH_2CCH_2 \rightarrow CH_2CClCH_2 \tag{5a}$$

$$\rightarrow HCl + C_3H_3 \tag{5b}$$

Experimental studies[17,18] of reaction 5 demonstrated that addition (reaction 5a) is the major channel of reaction 5 at low temperatures; the abstraction channel (reaction 5b) becomes dominant at temperatures above ~650 K. A theoretical investigation[19] of the potential energy surface of reaction 5a led to the conclusion that formation of the 2-chloroallyl radical is the only addition channel; initial addition of Cl to the terminal carbon atom of allene results in formation of an unstable CH_2CCH_2Cl intermediate that undergoes a rapid isomerization to CH_2ClCH_2 or decomposes back to $Cl + CH_2CCH_2$.

In high-temperature experiments (730 K), the combination of reactions 4 and 5a could not be used because of the dominance of the abstraction channel (reaction 5b) in reaction 5 and the contribution of the thermal decomposition of CH_2CClCH_2 (reverse of reaction 5a). Instead, laser photolysis of 2,3-dichloropropene was used as a source of 2-chloroallyl radicals:

$$CH_2CClCH_2Cl \xrightarrow{h\nu} Cl + CH_2CClCH_2 \tag{6a}$$

$$\rightarrow Cl + CH_2CHCHCl \tag{6b}$$

$$\rightarrow \text{other products} \tag{6c}$$

Reaction 6 forms 2-chloroallyl and 1-chloroallyl radicals in an approximate ratio of 10:1, as was demonstrated in our recent LP/PIMS experimental study of the thermal decomposition of 2-chloroallyl radical.[8] In that study, the ion signal at $m/z = 75$ (C_3H_4Cl) consisted of two components, the major one of which decayed with time in a manner consistent with the thermal decomposition of a radical (decay rate increased with temperature and pressure); this component was attributed to the 2-chloroallyl radical. The minor component of the ion signal displayed a slow decay consistent with heterogeneous wall loss of a radical. The rate constant of this decay did not increase with temperature in the 600−1000 K interval and coincided with that obtained in separate experiments for the $CH_2CHCHCl$ radical produced in the photolysis of the $CHClCHCH_2Si(CH_3)_3$ precursor. This minor component was thus attributed to 1-chloroallyl radical.

Initial conditions (precursor concentration and laser intensity) were selected to provide low radical concentrations ($\leq 2 \times 10^{11}$ molecule cm^{-3}) such that reactions between radical products had negligible rates compared to those of the reaction of CH_2CClCH_2 with molecular oxygen.

The gases used were obtained from Aldrich (oxalyl chloride, ≥99%; allene, 97%; 2,3-dichloropropene, 98%; (3-chloroallyl)-trimethylsilane, 97%), MG Industries (helium, 99.999%), and Matheson (O_2, >99.6%). Radical precursors and oxygen were purified by vacuum distillation prior to use. Helium was used as provided.

III. Results

In the absence of molecular oxygen, the kinetics of the CH_2CClCH_2 radicals was that of an exponential decay with a first-order constant in the range 9−24 s^{-1}. This was attributed to the heterogeneous wall reaction:

$$CH_2CClCH_2 \rightarrow \text{heterogeneous loss} \tag{7}$$

The reaction with O_2 displayed distinctly different behavior at low (room temperature), intermediate, and high (730 K) temperatures. While it was possible to experimentally determine bimolecular rate constants of the reaction of CH_2CClCH_2 radicals with O_2 at room temperature, the reaction exhibited nonexponential radical decay in an excess of molecular oxygen at intermediate temperatures. The observed decay curves could be fitted to a double-exponential function. This behavior is

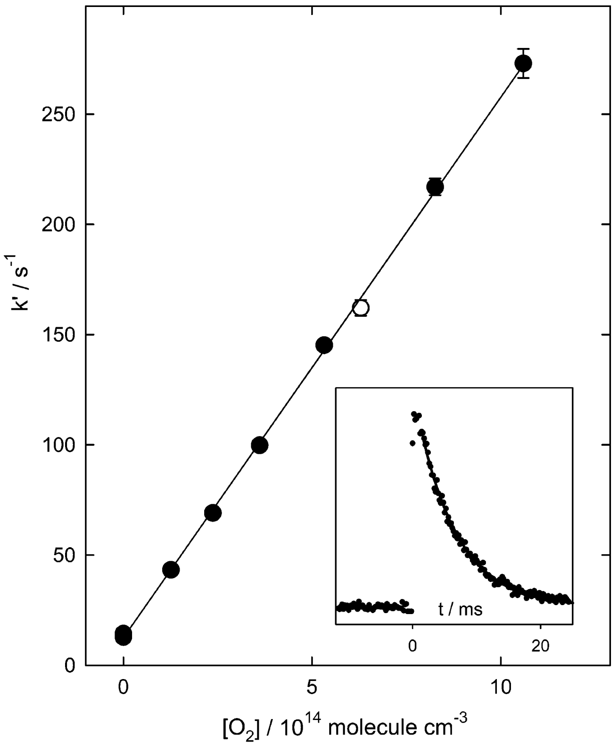

Figure 1. First-order CH_2CClCH_2 decay rate k' vs $[O_2]$. The intercept at $[O_2] = 0$ corresponds to the rate of heterogeneous decay of CH_2CClCH_2 radicals. $T = 304$ K, $[He] = 12 \times 10^{16}$ molecules cm^{-3}, $[(COCl)_2] = 2.35 \times 10^{13}$ molecules cm^{-3}, $[C_3H_4] = 1.48 \times 10^{14}$ molecules cm^{-3}. The inset shows the recorded CH_2CClCH_2 decay profile for the conditions of the open plotted point: $[O_2] = 6.29 \times 10^{14}$ molecules cm^{-3}, $k' = 162.1 \pm 3.6$ s^{-1}.

indicative of relaxation to an equilibrium of the type $R + O_2 \rightleftarrows RO_2$:

$$CH_2CClCH_2 + O_2 \rightleftarrows CH_2CClCH_2O_2 \qquad (3,-3)$$

At high temperature (730 K), no reaction with O_2 could be observed. An upper limit to the rate constant was obtained.

III.1. Reaction 3 at Room Temperature and in the High-Temperature Region. At room temperature, the decay of CH_2CClCH_2 radicals in an excess of O_2 was exponential. The experiments were conducted under pseudo-first-order conditions with $[O_2]$ in the range $(1.3-10.6) \times 10^{14}$ molecules cm^{-3}. The radical signal profiles were fit to an exponential function ($[R]_t = [R]_0 \exp(-k't)$) by using a nonlinear least-squares procedure. The pseudo-first-order radical decay constants, k', were obtained as a function of the concentration of molecular oxygen. The values of the second-order rate constant, k_3, were determined from the slopes of linear plots of k' vs $[O_2]$ ($k' = k_3[O_2] + k_7$, Figure 1). The room-temperature rate constants of reaction 3 were determined at $[He] = (3-24) \times 10^{16}$ molecules cm^{-3}. These bimolecular rate constants of the reactions of CH_2CClCH_2 radicals with molecular oxygen (interpreted as an addition reaction) exhibit a pronounced falloff behavior. The values of k_3 increase with pressure within the experimental pressure range (Figure 2). The conditions and results of these experiments are presented in Table 1.

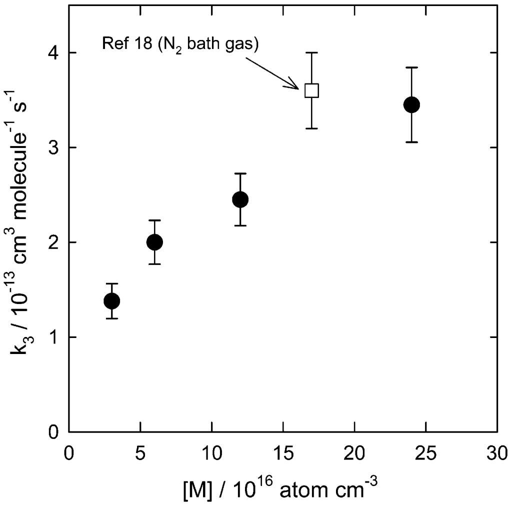

Figure 2. Room-temperature dependence of k_3 on the bath gas density (M). Filled circles, current work (helium bath gas); open square, ref 18 (nitrogen bath gas).

TABLE 1: Conditions and Results of Experiments to Measure $k_3(T,[M])$[a]

T/K	[M]/ 10^{16} [b]	[precursors]/ 10^{13} [c]	L[d]	$[R]_0$/ 10^{10} [e]	$[O_2]/10^{14}$	k_7/ s^{-1}	k_3[f]/10^{-13} cm^3 molecule^{-1} s^{-1}
304	3.0	1.44/9.3	33	4.4	1.9−7.0	28.1	1.38 ± 0.18
304	6.0	1.30/14.0	36	4.4	2.3−10.3	15.2	2.00 ± 0.23
304	12.0	2.35/14.8	43	9.4	1.3−10.6	12.5	2.45 ± 0.27
305	24.0	2.11/13.3	46	9.1	1.2−7.5	10.9	3.45 ± 0.39
730	12.0	2.1[g]	44	18	83−171	85.7	$\leq 3 \times 10^{-3}$

[a] Concentrations are in molecules cm^{-3}. [b] Total concentration of the bath gas (helium) and reactants. [c] Concentrations of radical precursors: $[(COCl)_2]/[C_3H_4]$ or $[CH_2CClCH_2Cl]$. [d] Photolyzing laser intensity (mJ cm^{-2} pulse^{-1}). [e] Initial radical concentrations. [f] Error limits represent a sum of 2σ statistical uncertainty and estimated systematic uncertainty. [g] CH_2CClCH_2Cl was used as a radical precursor (a combination of oxalyl chloride and allene was used in all other experiments).

At the temperature of 730 K, no reaction of CH_2CClCH_2 radicals with molecular oxygen could be observed. An upper limit value of $k_3 \leq 3 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} was obtained by adding up to 1.7×10^{16} molecules cm^{-3} of O_2. (The concentration of He was reduced accordingly so that the total concentration of bath gas remains constant, Table 1.) In these experiments, the CH_2CClCH_2 decay rates displayed no change upon addition of O_2. The k_3 upper limit value was estimated from the experimental uncertainties of the decay rates and the concentrations of O_2 added. The 730 K upper temperature limit of the experiments was determined by the onset of thermal decomposition of the CH_2CClCH_2 radicals.[8] Addition of O_2 modified the composition of the bath gas and hence could influence the decomposition rate, thus mimicking the expected effect of the reaction with O_2. However, any effect of such bath gas modification (7−14% of O_2 in He as opposed to pure He) is expected to be minor. In fact, if any such effect was present, its influence was less than the uncertainties in the radical decay rates.

III.2. Intermediate Temperature Range. Determination of Equilibrium Constants. In the intermediate temperature range (340−410 K), the decay of CH_2CClCH_2 radicals in the presence of O_2 displays a nonexponential behavior, which can be fitted with a double-exponential function. The kinetics of CH_2CClCH_2 decay was analyzed under the assumption that the following processes are important under these conditions: (1) heterogeneous loss of CH_2CClCH_2, reaction 7; (2) reversible addition of O_2, reaction (3,−3); and (3) decay of the adduct, $CH_2CClCH_2O_2$, due to heterogeneous loss, which is described by a first-order rate constant k_d. The kinetics of the CH_2CClCH_2 radical signal, $I(t)$, in such a system can be described by the following double-exponential expression:[6,20]

$$I(t) = I_1 \exp(-\lambda_1 t) + I_2 \exp(-\lambda_2 t) \qquad \text{(I)}$$

TABLE 2: Conditions and Results of Experiments to Measure the Equilibrium Constants of Reaction (3,−3)[a]

T/K	[He]/10^{16}	[precursors]/10^{13} [b]	L [c]	$[R]_0/10^{10}$ [d]	$[O_2]/10^{15}$	k_7/s^{-1}	$k_3[O_2]/s^{-1}$	k_{-3}/s^{-1}	k_d/s^{-1}	$\ln(K_P)$ [e]	f [f]
340	12.0	2.38/20.4	36	8.1	0.904	10.8	206.2	43.2	6.1	11.63 ± 0.20	0.19
340	12.0	2.38/20.4	36	8.1	0.495	11.8	95.7	34.0	2.5	11.70 ± 0.52	0.19
350	12.0	2.73/22.4	31	8.0	1.950	13.9	349.6	57.2	4.0	11.08 ± 0.17	0.23
350	12.0	2.73/22.4	31	8.0	1.130	12.7	204.3	60.5	2.6	11.03 ± 0.16	0.23
355	6.0	2.26/15.0	38	8.0	0.545	12.7	62.1	60.4	2.2	10.56 ± 0.64	0.25
355	6.0	2.26/15.0	38	8.0	1.070	13.3	116.0	44.0	1.6	10.83 ± 0.54	0.25
360	12.0	1.30/181	43	5.2	1.380	17.3	235.4	96.5	4.8	10.48 ± 0.17	0.27
370	12.0	1.43/216	35	4.6	1.370	19.1	181.0	161.4	4.1	9.68 ± 0.24	0.31
370	12.0	2.65/52.4	35	8.6	2.150	18.2	227.6	128.3	4.8	9.69 ± 0.32	0.31
370	12.0	2.65/52.4	35	8.6	2.410	17.2	336.4	190.6	6.4	9.57 ± 0.30	0.31
375	12.0	3.51/17.9	15	4.8	2.310	18.3	322.0	212.7	2.8	9.45 ± 0.27	0.33
375	12.0	3.51/17.9	33	10.8	2.310	18.0	280.6	191.3	2.1	9.41 ± 0.17	0.33
380	12.0	1.72/39.2	43	6.9	1.130	17.8	118.1	187.5	1.6	9.27 ± 0.15	0.35
380	12.0	1.72/39.2	43	6.9	2.370	19.5	289.5	225.4	2.1	9.24 ± 0.20	0.35
385	12.0	1.94/15.9	14	2.5	2.640	9.0	362.1	326.2	2.6	8.98 ± 0.37	0.37
385	12.0	1.94/15.9	31	5.7	2.110	13.6	236.3	296.1	1.8	8.87 ± 0.22	0.37
390	12.0	1.94/30.3	36	6.6	2.210	18.6	214.0	310.2	1.5	8.67 ± 0.26	0.38
390	12.0	4.00/30.3	36	13.5	2.210	23.5	198.0	317.9	1.6	8.56 ± 0.24	0.38
395	6.0	2.18/18.3	49	10.1	0.819	13.7	49.4	336.6	1.5	8.10 ± 0.28	0.40
395	6.0	2.18/18.3	49	10.1	1.480	16.6	83.3	317.6	1.5	8.09 ± 0.25	0.40
400	12.0	2.97/25.8	35	9.6	1.680	20.5	96.3	337.5	1.2	8.03 ± 0.24	0.42
400	12.0	2.97/25.8	35	9.6	0.849	21.2	24.4	158.8	0.9	8.10 ± 0.28	0.42
400	12.0	2.97/25.8	35	9.6	4.260	19.8	349.7	436.7	1.4	8.13 ± 0.38	0.42
410	12.0	2.94/22.2	41	11.3	2.200	21.7	87.7	456.8	1.1	7.34 ± 0.39	0.46
410	12.0	2.94/22.2	41	11.3	3.190	21.5	142.7	487.6	1.2	7.39 ± 0.38	0.46

[a] Concentrations are in molecules cm^{-3}. [b] Concentrations of radical precursors: $[(COCl)_2]/[C_3H_4]$. [c] Photolyzing laser intensity (mJ cm^{-2} $pulse^{-1}$). [d] Initial radical concentrations. [e] Error limits represent a sum of 2σ statistical uncertainty and estimated systematic uncertainty. [f] Values of the correction function (see text).

where

$$I_1 = I_0 \frac{k_3[O_2] + k_7 - \lambda_2}{\lambda_1 - \lambda_2}$$

$$I_2 = I_0 - I_1$$

$$\lambda_{1,2} = (1/2)(A \pm [A^2 - 4(k_{-3}k_7 + k_3[O_2]k_d + k_7k_d)]^{1/2})$$

$$A = k_3[O_2] + k_{-3} + k_7 + k_d$$

The values of k_7 were measured directly in the absence of O_2. The temporal profile of the CH_2CClCH_2 signal was fitted to formula I using k_3, K_3, I_0, and k_d as adjustable parameters (here $K_3 = k_3/k_{-3}$ is the equilibrium constant of the reaction (3,−3), and I_0 is the signal value at $t = 0$). After the values of the above parameters were found, the fitting procedure was repeated several times with K_3 fixed at selected values in the vicinity of the best value and the other three parameters floated. As a result, the sum of squares of deviation was determined as a function of K_3 (with the three other parameters optimized) in the vicinity of its minimum and fitted with a parabolic function. From that information, the experimental relative uncertainty ϵ of the fitted values of K_3 was determined using standard procedures[21] (also, see ref 5). The equilibrium constants of reaction (3,−3) were determined as a function of temperature from 340 to 410 K. The conditions and results of these experiments are presented in Table 2. Equilibrium constants are plotted in Figure 3 as a function of temperature. The inset in Figure 3 presents an example of a double-exponential radical decay profile for reaction 3. Experiments were performed to establish that the K_3 values obtained did not depend on the concentrations of the radical precursors ($(COCl)_2$ and C_3H_4), the initial radical concentration, or the photolyzing laser intensity.

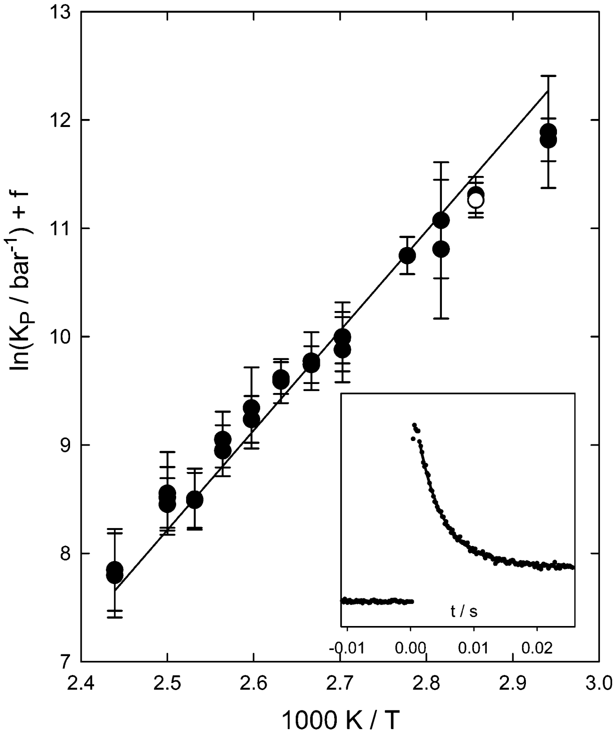

Figure 3. Modified van't Hoff plot of ($\ln(K_P) + f(T)$) vs 1000 K/T for reaction (3,−3). The line represents the result of the third-law fit (see text). The inset shows the recorded CH_2CClCH_2 decay profile for the conditions of the open plotted point: $T = 350$ K, $[O_2] = 1.13 \times 10^{15}$ molecules cm^{-3}.

The conditions of the experiments were selected to optimize only the determination of the equilibrium constants. This results in expected high uncertainties of the $k_3[O_2]$, k_{-3}, and k_d kinetic parameters listed in Table 2, uncertainties that, moreover, are not easily estimated. The values of k_3 and k_{-3} are expected to be in the falloff region which will complicate any potential use of these data. Their temperature dependences exhibit the anticipated qualitative behavior: k_{-3} values, on average, increase with temperature (as expected for the rate constant of a decomposition reaction) and the values of k_3 (corresponding to the second-order addition rate constant) slightly decrease with temperature (as expected for a barrierless addition in the falloff region). The rate constant of the decay of the adduct, k_d, as mentioned above, is interpreted as the rate constant of RO_2 heterogeneous loss. The fitted values of k_d for reaction 3 lie within the range 0.9−6.4 s^{-1}.

IV. Thermochemistry of Reaction (3,−3)

The enthalpy of reaction (3,−3) at room temperature was obtained from the values of $K_3(T)$ using a third-law analysis. The procedures used have been described before.[4−6,20] These calculations require knowledge of the temperature dependences of the thermodynamic functions (entropy and enthalpy) of the reactants and products of reaction (3,−3), which were obtained using the results of quantum chemical calculations. Four method/basis set combinations were used to determine the molecular structures, vibrational frequencies, and torsional potential energy surfaces of CH_2CClCH_2 and $CH_2CClCH_2O_2$: B3LYP/aug-cc-pvdz, BH&HLYP/6-311G(d,p), BH&HLYP/aug-cc-pvdz, and MP2/cc-pvdz (see refs 22−29 for the details of these methods and basis sets). A version of the BH&HLYP functional implemented in the Gaussian 98 program[26] was used (Gaussian 98 was used in all calculations) which, as described in the program manual, is different from that of ref 24. Detailed results of these calculations are presented in the Supporting Information.

The most uncertain aspect of the properties of the peroxy $CH_2CClCH_2O_2$ radicals pertinent to the calculation of their entropy is the treatment of the hindered internal rotations. All computational methods used yielded similar potential energy surfaces (PESs) for the CC−CO and CC−OO torsions. The PES of the CC−CO internal rotation has three unequal maxima ranging from 7 to 22 kJ mol^{-1} and three minima (equal at the DFT levels but differing by up to 5 kJ mol^{-1} at the MP2 level of calculations). The largest barrier corresponds to the conformation with the CO and the C−Cl bonds eclipsed. The PES of the CC−OO torsion has two unequal maxima (3.6 and 13.8 kJ mol^{-1}) at the B3LYP/aug-cc-pvdz level of calculations. The entropy values corresponding to these two torsional degrees of freedom were calculated using individual energy levels evaluated via a numerical solution of the Schrödinger equation. The FGH1D program[30] of Johnson was used in the energy level and entropy calculations. Reduced moments of inertia for internal rotations were calculated from the structural data by the method of Pitzer and Gwinn.[31,32] The standard entropy values of CH_2CClCH_2 and $CH_2CClCH_2O_2$ resulting from the four quantum chemical methods/basis set combinations used ranged from 286.8 to 288.6 and from 365.6 to 370.7 J mol^{-1} K^{-1}, respectively. The B3LYP/aug-cc-pvdz based values $S^\circ_{298}(CH_2CClCH_2O_2) = 370.7$ J mol^{-1} K^{-1} and $S^\circ_{298}(CH_2CClCH_2) = 288.6$ J mol^{-1} K^{-1} were selected for further use. The value of ΔS°_{298} of reaction (3,−3) was calculated using the above entropies of the radicals and the entropy of O_2 from ref 33:

$$\Delta S^\circ_{298,t}(3,-3) = -123.0 \pm 6.7 \text{ J mol}^{-1} \text{ K}^{-1} \qquad \text{(II)}$$

Here, the uncertainty in ΔS°_{298} was estimated as twice the largest difference between the values of ΔS°_{298} resulting from quantum chemical calculations performed with different method/basis set combinations.

The room-temperature enthalpy of reaction (3,−3) was obtained from the data on $K_3(T)$ using a third-law analysis. First, the values of ΔG°_T of reaction (3,−3) were obtained directly from the values of the observed equilibrium constant

$$\ln(K_P/\text{bar}^{-1}) = -\Delta G^\circ_T/RT \qquad \text{(III)}$$

where K_P is the equilibrium constant in bar^{-1}. The addition of a small "correction" (Table 2)

$$f(T) = \frac{\Delta H^\circ_T - \Delta H^\circ_{298}}{RT} - \frac{\Delta S^\circ_T - \Delta S^\circ_{298}}{R} \qquad \text{(IV)}$$

converts the right-hand-side of eq III to a linear function of $1/T$ with the intercept at $1/T = 0$ equal to $\Delta S^\circ_{298}/R$ and the slope of the function equal to $-\Delta H^\circ_{298}/R$:

$$\ln(K_P) + f(T) = \frac{\Delta S^\circ_{298}}{R} - \frac{\Delta H^\circ_{298}}{RT} \qquad \text{(V)}$$

The values of the correction function, $f(T)$, were calculated using the models of CH_2CClCH_2 and $CH_2CClCH_2O_2$ radicals described above. The value of ΔH°_{298} was obtained from the slope of the line drawn through the experimental values of $(\ln(K_P) + f(T))$ and the calculated intercept $\Delta S^\circ_{298}/R$ (Figure 3):

$$\Delta H^\circ_{298}(3,-3) = -76.5 \pm 2.8 \text{ kJ mol}^{-1} \qquad \text{(VI)}$$

Error limits include additive contributions resulting from the uncertainty in the reaction entropy (eq II, the resultant uncertainty in $\Delta H^\circ_{298}(3,-3)$ is 2.5 kJ mol^{-1}) and from 2σ of the fit of the experimental data to eq V (0.3 kJ mol^{-1}).

A second-law analysis can be used to obtain both ΔH°_{298} and ΔS°_{298} for reaction (3,−3) from the $(\ln(K_P) + f(T))$ vs $1/T$ dependence:

$$\Delta H^\circ_{298}(\text{2nd law}) = -66.0 \pm 2.5 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(\text{2nd law}) = -95.0 \pm 6.7 \text{ J mol}^{-1} \text{ K}^{-1}$$

(here, error limits are 2σ from statistical deviations of fit only). However, considering the narrow temperature intervals of the experiments to determine $K_3(T)$ and the scatter of data due to experimental uncertainties, we prefer to use the third-law analysis based on the entropy values calculated using quantum chemical methods.

V. Discussion

This study provides the first experimental investigation of the thermochemistry of the reaction of 2-chloroallyl radical with molecular oxygen. The value of the $R-O_2$ bond energy (negative of $R + O_2 \rightleftarrows RO_2$ reaction enthalpy) obtained for $R = CH_2CClCH_2$, 76.5 ± 2.8 kJ mol^{-1}, virtually coincides with that of the allyl radical, 77.0 ± 2.7 kJ mol^{-1} (obtained in ref 20 in a third-law analysis of the equilibrium constant data of refs 34, 35, and those resulting from reanalysis of the kinetics of relaxation to equilibrium in the allyl + O_2 reaction reported in ref 36). This result demonstrates the absence of any effect of the Cl substitution in the β position to the radical site of R on the $R-O_2$ bond energy.

The only experimental information on the kinetics of CH_2CClCH_2 existing in the literature is the room-temperature rate constants of reaction 3 and that of recombination of 2-chloroallyl radicals reported by Atkinson and Hudgens.[18] These authors generated 2-chloroallyl radicals in the reaction of Cl with allene and studied their kinetics using cavity ring-down spectroscopy. The rate constant of reaction 3 obtained at 298 K and 5.3 Torr of nitrogen buffer gas ($[N_2] = 17 \times 10^{16}$ molecules cm^{-3}), $k_3 = (3.6 \pm 0.4) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}, is consistent with the values obtained in the current study using helium bath gas (Table 2 and Figure 2), which increase with pressure from $(1.38 \pm 0.18) \times 10^{-13}$ at $[He] = 3 \times 10^{16}$ molecules cm^{-3} to $(3.45 \pm 0.39) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at $[He] = 24 \times 10^{16}$ molecules cm^{-3}. The results of the current study and those of ref 18 are not sufficient to allow a reliable extrapolation of the rate constant to the high-pressure limit. However, it seems plausible that the high-pressure limit rate constant of reaction 3 at room temperature can be similar to that of the allyl + O_2 reaction, $(6 \pm 2) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}, obtained in the experiments of Jenkin et al.[37] at the pressure of 760 Torr of synthetic air.

The high-temperature reaction of 2-chloroallyl radical with O_2 is slow ($k_3 \le 3 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 730 K). This result is consistent with the low high-temperature rate constants for the prototype reaction, that of allyl radical with O_2 (a rate constant of $\sim 2 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} was reported by Stothard and Walker[38] at comparable temperatures).

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Supporting Information Available: Detailed results of the quantum chemical study of the molecular structures, vibrational frequencies, and torsional potential energy surfaces of the CH_2CClCH_2 and the $CH_2CClCH_2O_2$ radicals. This material is available free of charge via the Internet at http://pubs.acs.org.

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