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A Kinetic and Mechanistic Study of the Reaction of Cl Atoms with Acrolein: Temperature Dependence for Abstraction Channel

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Rate coefficients for the reaction $CH_2CHCHO + Cl \rightarrow P$ (1) at different temperatures (260−333 K) have been determined using a discharge flow-mass spectrometric technique (DF-MS) at low total pressure. $k(1)$ was found to be pressure-independent at $T = 298$ K in the pressure range 0.5−3 Torr. The temperature dependence of the reaction rate constant has been determined under pseudo-first-order kinetic conditions in excess of acrolein over Cl atoms, with no significant changes in the rate constant. At room temperature and 1 Torr, products of both abstraction (1a) and addition (1b) channels have been detected. The branching ratio for abstraction channel at 298 K and 1 Torr was determined as 0.83 ± 0.13 and led to HCl and CH_2CHCO^* radical. The temperature dependence of this abstraction channel has also been studied, giving the Arrhenius expression $k(1a) = (5.4 \pm 2.0) \times 10^{-10} \exp\{(-748 \pm 110)/T\}$ cm^3 molecule^{-1} s^{-1} in the temperature range 260−333 K. The results obtained are related to previous studies, and the mechanism of reaction is discussed.

Introduction

The fate of many atmospheric trace species, including pollutants such as nitrogen oxides and some volatile organic compounds (VOCs), is controlled by oxidation reactions which are initiated by OH radicals during the day, by NO_3 radicals at night, and by O_3 during both day and night.[1] In addition, it has been recently pointed out that Cl radicals also may play an important role in the chemical transformation of organic compounds in marine environments where the maximum predicted Cl atom levels occur shortly after sunrise, peaking at 1.3×10^5 atoms cm^{-3}.[2] The main source of tropospheric Cl atoms is the photolysis of photolabile chlorine-containing molecules generated by heterogeneous reactions of sea salt aerosols. For example, the reaction of N_2O_5 on a salt surface forms gaseous $ClNO_2$, which photolyzes to NO_2 and Cl atoms.[3,4] Furthermore, molecular chlorine is generated from the photolysis of ozone in the presence of sea-salt particles above their deliquescence point.[5] Another relevant tropospheric source of Cl atoms is the reaction of OH radicals with gaseous HCl,[3] which can be released by acidification of NaCl aerosols by sulfuric or nitric acid. An anthropogenic source of precursors of tropospheric Cl atoms results from the heating of ceramic raw materials. Due to atmospheric emissions by brick factories, local concentrations of HCl and chlorides as high as 40−200 ppm have been reported.[6] Since Cl is generally more reactive than OH, $k_{Cl}/k_{OH} \geq 10$, it may also play a role in VOC−NO_x chemistry, in much the same manner as OH, and then it is important to obtain knowledge of these reaction rates.

The present paper describes the study of reaction of Cl atoms with acrolein

$$CH_2CHCHO + Cl \rightarrow \text{products} \qquad (1)$$

Acrolein (CH_2CHCHO) is released into the environment from natural and anthropogenic sources. It has been identified as a volatile component of essential oils extracted from the wood of oak trees.[7] It is also emitted by forest fires as a product of the incomplete combustion of organic matter[8] and produced by photochemical oxidations of hydrocarbons in the atmosphere.[9] The principal anthropogenic source of emissions is estimated to be activities involving the combustion of organic matter: incinerators, diesel motor, etc.[10] In Canada, for example, the mean concentration of acrolein in 24 h samples in urban areas was 0.18 μg m^{-3}.[11]

Several reactions of acrolein with different oxidants have been studied. The study of reaction with OH radical has been carried out by several authors by means of different techniques.[12−16] The mean value obtained for the rate constant at room temperature was 1.9×10^{-11} cm^{-3} molecule^{-1} s^{-1}. Atkinson et al.,[17] Canosa-Mas et al.,[18] and Cabañas et al.[19] studied the reaction of acrolein with NO_3 using either a relative or absolute method. With regard to reaction of CH_2CHCHO with Cl, recently, it has been the subject of different studies.[20−23] These authors reported the results for the rate constant at room temperature and 760 Torr of pressure and using a relative method (however in the study of Canosa-Mas et al.,[22] some experiments were carried out at 1 Torr with an absolute technique). The obtained results for $k(1)$ in these conditions ranged from $(1.8-2.2) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. Only in the work of Canosa-Mas et al.[22] has a study of the products of reaction 1 been made. Up to now no study of the temperature dependence of reaction 1 has been carried out and no study of the branching ratio at 1 Torr of pressure for the products channel has been made. These facts make further investigations necessary. In this work we report now a wider kinetic and mechanistic study by means of an absolute technique, including the study of temperature (260−333 K) and pressure (0.5−3 Torr) dependence, together with the quantitative determination of the

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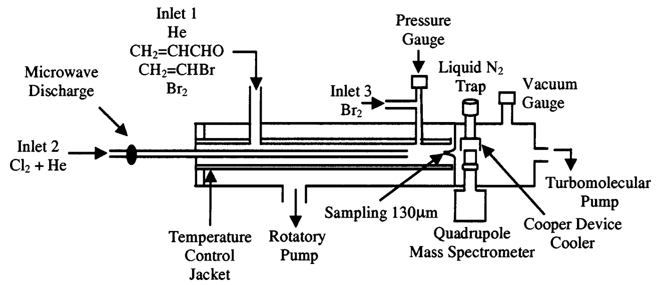

Figure 1. Experimental setup.

products of reaction. Furthermore, the temperature dependence of the abstraction channel is reported here for the first time.

Experimental Section

All the kinetic and mechanistic experiments in this work were conducted using the absolute technique of discharge flow-mass spectrometry (DF-MS). The flow tube and the rest of apparatus have been described previously[24,25] and are shown schematically in Figure 1. The flows of the helium carrier gas in the reactor and the injector were regulated and measured with mass flow controllers. All the reactants were diluted in helium and stored in balloons of known volume. Concentrations of reactants in the reactor were calculated from the pressure decrease rate inside the storage flasks. The reaction between the Cl radical and the organic molecule was followed downstream of the end of the axial injector.

Cl atoms were produced by microwave discharge in Cl_2 (checked by mass spectrometry at $m/e = 70, 72$), diluted by helium, and then flowed into the main reactor through the injector (inlet 2 in Figure 1). The absolute concentration of Cl atoms was measured by a titration reaction with $BrCHCH_2$ in excess

$$Cl + BrCHCH_2 \rightarrow ClCHCH_2 + Br \tag{2}$$

$k(2) = 1.4 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1},[26] following the consumption of $BrCHCH_2$ and the rising signal of $ClCHCH_2$ at their parent peaks, $m/e = 106$ and 62, respectively. Reference signals of these two species were obtained from known flows from their respective volume-calibrated storage balloons. A good agreement was found between these two measurements for the concentration of Cl atoms. Typical concentrations for Cl_2 and Cl were $(2-5) \times 10^{11}$ and $(1-5) \times 10^{11}$ molecules cm^{-3}, respectively. The detection limit for [Cl] was 5×10^9 molecules cm^{-3}.

As described elsewhere,[27] Cl atoms were detected as BrCl at $m/e = 116$ during a kinetic run, after scavenging with Br_2 at the end of the reactor through inlet 3 by the fast reaction

$$Cl + Br_2 \rightarrow BrCl + Br \tag{3}$$

$k(3) = (2.3 \pm 0.4) \times 10^{-10} \exp[-(135 \pm 60)/T]$ cm^3 molecule^{-1} s^{-1}.[28]

To ensure the complete consumption of Cl atoms by Br_2, molecular bromine was added in excess over acrolein in experiments. For Br_2, typical concentrations were $(1-7) \times 10^{13}$ molecules cm^{-3} with a detection limit of 4×10^{10} molecules cm^{-3}.

The reactions were studied under pseudo-first-order conditions with acrolein, in excess over Cl atoms, being added to the main reactor through a sidearm tube (inlet 1). The range of concentrations for acrolein was $(0.2-2.5) \times 10^{13}$ molecules cm^{-3}, and it was measured at its parent peak, $m/e = 56$. The detection limit for acrolein was 4×10^{10} molecules cm^{-3}.

All the reactants were purified by trap-to-trap distillation before use. Helium was passed through a N_2 trap before flowing into the reactor. The source and purity of the gases used were as follows: He (Praxair, 99.999%), Cl_2 (Praxair, >99.8%), CH_2CHCHO (Supelco, neat EPA), Br_2 (Fluka, ≥99.5%), $BrCHCH_2$ (Aldrich, 98%), $ClCHCH_2$ (Fluka, ≥99.5%), HCl (Aldrich, >99%).

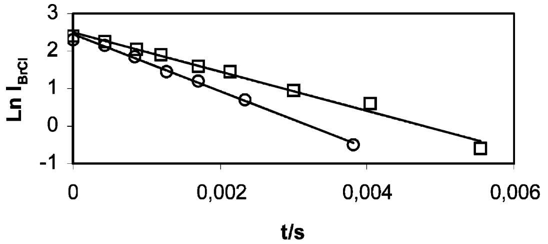

Figure 2. Typical first-order plots for the reaction of Cl atoms with acrolein at 1 Torr and 298 K. $[CH_2CHCHO] = 7.13 \times 10^{12}$ (□); 1.05×10^{13} (○) molecules cm^{-3}.

Results and Discussion

The temperature range to study reaction 1 was 260−333 K for the experiments carried out at 1 Torr of pressure. We have also checked the possible changes with pressure between 0.5 and 3 Torr at room temperature. For this reaction the range of flow velocities was 1800−2600 cm s^{-1} (800 cm s^{-1} for reaction at 3 Torr) giving reaction times of up to 7 ms.

Preliminary experiments were carried out in order to check the possible reactions between Cl_2 (precursor of Cl), Br_2 (used to capture Cl atoms), and CH_2CHCHO, and no reaction was observed within the contact time used in the experiments. Since acrolein can polymerize under light exposure, it was stored inside a dark storage flask and we verified its stability inside the flask with time. For the low radical concentrations used, Cl self-reactions (homogeneous losses) do not contribute to the observed decaying temporal profiles. On the other hand, the heterogeneous wall losses of Cl on the reactor, k_w, were checked separately before the kinetic runs but in the same conditions, monitoring the formation of BrCl and in the absence of acrolein (with Cl atoms entering the main tube from the injector and Br_2 from inlet 3). The mean value obtained for these constants was $k_w = 20 \pm 10$ s^{-1}.

For a bimolecular reaction between Cl and acrolein, the integrated rate constant that applies to our experimental conditions with the organic compound in excess over Cl atoms is

$$\ln[Cl]_t = \ln[Cl]_0 - k't \tag{I}$$

where $k' = k[CH_2CHCHO] + k_w$.

Typical pseudo-first-order plots for the reaction of acrolein with Cl are shown in Figure 2. The obtained values of k' were corrected to take into account the axial and radial diffusion of Cl atoms by means of the equation[29]

$$k' = k' \exp(1 + k'_{exp}D_{Cl/He}/v^2 + k'_{exp}r^2/48D_{Cl/He}) \tag{II}$$

where v is the linear velocity of the gas mixture in the reactor (cm s^{-1}), r is the tube radius (cm), and $D_{Cl/He}$ is the diffusion coefficient (cm^2 s^{-1}). The diffusion coefficient of Cl in He was calculated from the volumes of atomic diffusion.[30] The values obtained for the temperature range used (260−333 K) were $D_{Cl/He} = 280-580$ cm^2 s^{-1}, leading to corrections up to 25% on the kinetic coefficients obtained from eq I.

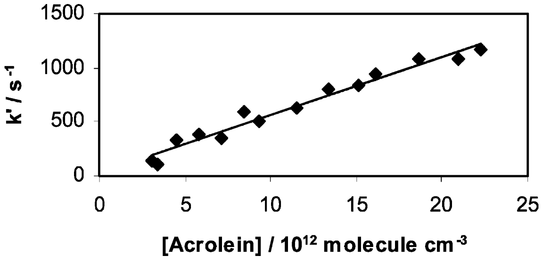

Figure 3. Second-order plot obtained for the reaction of Cl atoms with acrolein at 315 K and 1 Torr.

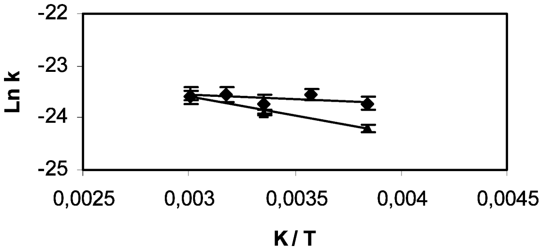

Figure 4. Arrhenius plots for the global reaction of Cl + acrolein (◆) and for the H-atom abstraction channel (▲). Errors are $2\sigma + 10\%$.

TABLE 1: Summary of Second-Order Rate Constants for Cl + Acrolein Reaction at the Different Temperatures and Pressures Studied[a]

temp. (K)	pressure (Torr)	$k(1)$ (cm^3 molecule^{-1} s^{-1})
260	1	$(5.0 \pm 0.6) \times 10^{-11}$
280	1	$(5.9 \pm 0.6) \times 10^{-11}$
	0.5	$(5.0 \pm 0.3) \times 10^{-11}$
298	1	$(5.0 \pm 0.9) \times 10^{-11}$
	3	$(4.8 \pm 0.7) \times 10^{-11}$
315	1	$(5.9 \pm 0.8) \times 10^{-11}$
333	1	$(5.8 \pm 0.9) \times 10^{-11}$

[a] Errors are $2\sigma + 10\%$.

The corrected first-order k' values for reaction 1 at a given temperature were plotted against the reactant concentration, and the second-order rate constants were obtained as the slope of least-squares fits of these data. Figure 3 shows, as an example, the results obtained from the experiments at 315 K. The mean intercept in these plots, 23 ± 12 s^{-1}, is in fair agreement with the Cl wall loss rate, 20 ± 10 s^{-1}, measured in the absence of acrolein. This indicates that the heterogeneous losses of Cl observed for the contact time in this work were negligible in the kinetic experiments.

A summary of the absolute second-order rate coefficients obtained for the reaction of Cl with acrolein at different temperatures and pressures is given in Table 1. The data are shown in Figure 4 in the form of Arrhenius plots, where ln $k(1)$ has been plotted vs $1/T$. In the range of temperatures studied (260−333 K), no significant changes were observed in the rate constants within the experimental error. The reaction rate is found to increase very slightly with increasing temperature, giving the following Arrhenius expression

$$k(1) = (9.3 \pm 9.7) \times 10^{-11} \times \exp\{(-149 \pm 297)/T\}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

$T = 260-333$ K, where the quoted uncertainties represent 2σ and 10% to cover systematic errors.

The pressure range studied, from 0.5 to 3 Torr, was very small due to the limitations of the experimental technique. The obtained values at room temperature and the experimental error bars indicate that the reaction Cl + acrolein is not sensitive to pressure changes within this limited range.

We attempted the study of products, identification and quantification, for reaction 1 at 1 Torr and 298 K using the same technique of kinetic study, DF-MS. The reaction can proceed through two different pathways: an abstraction channel (eq 1a) and the formation of the corresponding adduct (combination of $ClCH_2C^*HCHO$ and $^*CH_2CHClCHO$) (eq 1b).

$$CH_2CHCHO + Cl \rightarrow CH_2CHCO^* + HCl \qquad (1a)$$

$$CH_2CHCHO + Cl \rightarrow [CH_2CHCHOCl]^* \qquad (1b)$$

These experiments have been carried out at higher concentrations of Cl atoms. [Acrolein] ranged from 1×10^{13} to 4×10^{13} molecules cm^{-3} and [Cl] from 1×10^{12} to 7×10^{12} molecules cm^{-3}. One of the main observations that should be noted is the production of HCl ($m/e = 36, 38$) as a function of time, which would suggest an abstraction channel (eq 1a). On the other hand, the following peaks increasing with time have also been observed by mass spectrometry, $m/e = 90, 91, 92, 93$, and 110. If we consider an abstraction channel, the signals at $m/e = 90$, 92 which seemed to require an induction time typical of the consecutive chain reaction can be attributed to a subsequent reaction of CH_2CHCO^* with Cl_2 molecules (present in the reactor), giving the chlorinated species $CH_2CHCOCl$ considering the two different isotopic Cl. This reaction is expected to occur in the experiments designed to monitor products, where Cl_2 concentrations were enhanced to enable the detection of products, but not in the kinetic experiments. Under these conditions, CH_2CHCO^* radicals may also undergo self-recombination giving $(CH_2CHCO)_2$, justifying the peak observed at $m/e = 110$.

Two additional peaks with intensities increasing with time were also observed at $m/e = 91, 93$. These signals may be tentatively assigned to the formation of the corresponding adduct ($ClCH_2C^*HCHO$ and $^*CH_2CHClCHO$) (eq 1b), but it may be also attributed to the M + 1 peak of $CH_2CHCOCl$ coming from the secondary reaction of $CH_2CHCO^* + Cl_2$. To clarify this point, similar experiments have been carried out introducing additional Cl_2 (up to 5×10^{13} molecules cm^{-3}) together with acrolein from inlet 1 at different reaction times. Signals at $m/e = 90, 92$ were affected by this additional Cl_2, increasing in intensity compared to the signal observed without additional Cl_2 for a given reaction time. With regard to the signals at $m/e = 91, 93$, no change has been observed in the intensity of these peaks with the additional Cl_2, and thus, these peaks could be assigned to the adduct of reaction. This fact shows that reaction 1 proceeds simultaneously through the two possible channels, abstraction and addition, as will be confirmed later from a measurement of the branching ratio for the abstraction channel. As expected, the intensity of the $(CH_2CHCO)_2$ signal ($m/e = 110$) decreased when Cl_2 was added due to the preference of the CH_2CHCO^* radical for the reaction with Cl_2, when present in a great excess.

To determine the branching ratio of the acrolein + Cl reaction, quantitative measurements of the concentration were made for HCl. These experiments were carried out at $p = 1$ Torr in the temperature range 260−333 K. Concentrations of acrolein, Br_2, and Cl atoms were $(0.7-3) \times 10^{13}$, $(2-8) \times 10^{13}$, and $(1-7) \times 10^{12}$ molecules cm^{-3}, respectively. To avoid the problems with the relatively high levels of background signals coming from the reactants at $m/e = 36, 38$, the following procedure was carried out: Cl atoms were introduced into the reactor through inlet 2 as in the kinetics studies. First, with Br_2 added into the reactor through inlet 3 and acrolein through inlet 1, HCl formed in reaction 1 was measured at $m/e = 36$. The

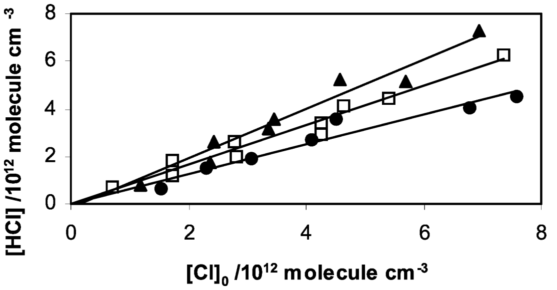

Figure 5. Experimental plots for HCl concentration formed in reaction Cl + acrolein (1) versus initial Cl atoms concentration at different temperatures: 260 (●), 298 (□), and 333 K (▲).

reaction time was chosen via the measurement of HCl produced at different reaction times to achieve the maximum in the production of HCl from initial Cl atoms at a given time, and it was fixed at ca. 8 × 10^{-3} s. Then, without changing the chemical composition in the reactor, Br_2 was introduced through inlet 1 together with acrolein. $[Br_2]$ was high enough to capture all Cl atoms, preventing the reaction of these atoms with acrolein (Br_2 in excess over acrolein). In these conditions, there was no formation of any products of reaction 1 and the residual signal at $m/e = 36$ was measured. The obtained signal for HCl was calibrated from freshly prepared HCl in a storage balloon with a known concentration. To calculate the branching fraction for the abstraction reaction, $k(1a)/k(1) = [HCl]/[Cl]_0$, $[Cl]_0$ must be known. This concentration could be obtained from the calibration reaction with $BrCHCH_2$ as described in the Experimental Section.

The possible impact of the secondary reactions on the obtained results was negligible. Secondary reactions of Cl atoms with the products of reaction 1 can be considered of minor importance because of the very rapid titration of Cl atoms in the reaction with acrolein, with the formation of HCl. Furthermore, the absence of visible changes in the concentration of the rapidly formed HCl for larger reaction times indicated that there was no impact on the reaction of CH_2CHCO^* with Cl_2 (which would reproduce Cl atoms), and thus, this secondary reaction must be much slower than reaction 1. From the relative intensity of signals, assuming the same sensitivity for detection of CH_2CHCHO and $CH_2CHCOCl$ by MS, the formation of this secondary product constitutes a minor product of reaction 1, less than 4% in the final time of reaction.

Results obtained at three temperatures are shown in Figure 5. The ratio $k(1a)/k(1)$ was derived from the slopes of the straight lines in Figure 5. The obtained results for 260, 298, and 333 K were (0.62 ± 0.15), (0.83 ± 0.13), and (1.01 ± 0.19), respectively. The branching ratio obtained at 298 K confirms, as mentioned above, that reaction 1 proceeds through the two possible channels, abstraction and addition. Errors are 2σ + 10% to cover systematic errors. From these data, the value for $k(1a)$ at each temperature was calculated, giving (3.1 ± 1.1), (4.1 ± 1.4), and (5.8 ± 2.0) × 10^{-11} cm^3 $molecule^{-1}$ s^{-1} for 260, 298, and 333 K, respectively. The temperature dependence of the rate-constant ratio derived from these data is shown in Figure 4 in Arrhenius form. All data could be fitted by the following expression:

$$k(1a) = (5.4 \pm 2.0) \times 10^{-10} \times \exp\{(-748 \pm 110)/T\}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

$T = 260-333$ K, with $k(1a)_{298K} = (4.4 \pm 3.2) \times 10^{-11}$.

From these results, in the temperature (260−333K) and low pressure (0.5−3 Torr) ranges studied, the major reaction channel is abstraction. For temperatures higher than 333 K and low pressure, the contribution of addition to the global rate constant may be considered as negligible.

The rate constant obtained in this work at 298 K, $k(1) = (5.0 \pm 0.9) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}, is in disagreement with the values obtained in the previous studies of this reaction, with a range for $k(1) = (1.8-2.2) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}. The reason for the discrepancy may be due to the different experimental conditions used. As shown above, CH_2CHCHO has two potential reaction sites: the double bond where the chlorine atom may undergo addition and the aldehydic hydrogen, which can be abstracted. The rate constant can be considered as the sum of the contribution for each reaction site. Here, we show the results of reaction 1 at 1 Torr of pressure and using an absolute technique while the rest of authors[20−23] obtained the rate constant using a relative method at 760 Torr, conditions where the addition channel is enhanced driving to a higher value of the global kinetic rate constant. Then, the discrepancy between the obtained values for $k(1)$ seems to be based in the different channel of reaction 1 studied. At 298 K and 760 Torr, the acrolein + Cl reaction proceeds predominantly via the pressure-dependent channel forming the adduct (1b), and at 1 Torr, reaction 1 proceeds predominantly via the pressure-independent channel forming HCl (1a).

Our results also disagree with the value reported by Canosa-Mas et al.,[22] (1.1 ± 0.2) × 10^{-10} cm^3 $molecule^{-1}$ s^{-1}, using an absolute technique and 1.6 Torr of pressure. Nevertheless, the discrepancies are close outside of the combined quoted error limits. The results reported in this work are supported by a previous estimate[23] of the rate constant for abstraction $k(1a) = 4.8 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}, obtained from the known rate constant for the reaction of Cl with CH_3CHO[31] and structure−reactivity relationships. Furthermore, Canosa-Mas et al.[22] obtained a yield of HCl of 0.22 ± 0.13 at $T = 298$ K and 760 Torr. Considering the yield data and their results for the global rate constant, we estimate a rate constant of (4.8 ± 3.5) × 10^{-11} cm^3 $molecule^{-1}$ s^{-1} for the abstraction channel giving HCl, in good agreement with our measurement.

Concerning the influence of pressure, although Canosa-Mas et al. reported a pressure dependence in a slightly wider range 1.6−4.5 Torr, the error bars are relatively high $k(1) = (1.1 \pm 0.2) \times 10^{-10}$ to $(1.4 \pm 0.4) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}. Under our experimental conditions, 1 Torr and 298 K, the measured branching ratio for abstraction was 0.83. Since pressure would affect only the minor process, its influence on the overall kinetic rate constant (0.5−3 Torr) may be slight and rest within the experimental errors.

In relation to the atmospheric implications, taking into account the global rate constant at atmospheric pressure, $k(1) = (1.8-2.2) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}, and the measure of the rate constant for the abstraction mechanism, $k(1a) = 4.4 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}, significant amounts of the radical CH_2CHCO^* may be formed, which is expected to react predominantly with oxygen under atmospheric conditions, and undergo subsequent reactions with NO, NO_2, HO_2, and CH_3O_2. These reactions may be particularly relevant in the tropospheric chemistry of the marine boundary layer and in coastal regions, where concentrations of Cl atoms peaks much earlier than OH at dawn.[2] Also, in urban contaminated areas, as in southern Europe where Galán et al.[6] demonstrated the high levels of Cl precursors emitted by the brick ceramic industries, the reaction studied here may be an important sink of acrolein.

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