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Pulsed Laser Photolysis Vacuum UV Laser-Induced Fluorescence Kinetic Study of the Gas-Phase Reactions of Cl($^2P_{3/2}$) Atoms with C_3−C_6 Ketones

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The gas-phase reactions of Cl atoms with acetone, butanone, 2-pentanone, 3-pentanone, 2-hexanone, 3-hexanone, and cyclopentanone at 295 ± 2 K were studied using pulsed laser photolysis vacuum UV laser-induced fluorescence (PLP-LIF) techniques. Cl($^2P_{3/2}$) atoms were produced by photolysis of Cl_2 at 351 nm and monitored by LIF spectroscopy at 134.72 nm ($3p^5\ ^2P_{3/2}$–$3p^4 4s\ ^2P_{3/2}$ transition). Rate coefficients for reactions of Cl atoms with acetone, butanone, 2-pentanone, 3-pentanone, 2-hexanone, 3-hexanone, and cyclopentanone are $(2.30 \pm 0.12) \times 10^{-12}$, $(4.08 \pm 0.21) \times 10^{-11}$, $(1.23 \pm 0.13) \times 10^{-10}$, $(8.87 \pm 0.92) \times 10^{-11}$, $(2.08 \pm 0.32) \times 10^{-10}$, $(1.43 \pm 0.19) \times 10^{-10}$ and $(1.16 \pm 0.12) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, respectively. The results for acetone and butanone are consistent with previous studies. The results for 2-pentanone, 3-pentanone, 2-hexanone, and 3-hexanone are approximately a factor of 2−3 higher than those from previous absolute rate studies. Likely explanations for these discrepancies are discussed. Tropospheric lifetimes of ketones with respect to reaction with Cl atoms are estimated and discussed.

1. Introduction

Ketones are an important class of volatile organic compounds (VOC) used widely as industrial solvents. During use, a fraction of these solvents escape into the atmosphere. Ketones are also formed as intermediate products in the tropospheric degradation of VOCs such as alkanes and alkenes. Significant concentrations of ketones and other oxygenated compounds are present in the global and local atmospheres.[1,2,3] The atmospheric degradation of organic molecules is initiated by their photodissociation and chemical reactions with oxidants such as OH radicals, Cl atoms, and O_3 molecules.[4] Enhancement of urban O_3 formation by Cl-atom-initiated oxidation of VOCs has been reported, and it has been recommended that reduction of chlorine emissions should be considered in urban ozone management strategies.[5] Accurate kinetic data for reactions of Cl atoms with ketones are needed as inputs for global atmospheric chemistry models.

To improve our understanding of the kinetics of the reactions of Cl atoms with organic compounds, we report determinations of rate coefficients for reactions of Cl atoms with acetone (CAS registry # 67-64-1), butanone (78-93-3), 2-pentanone (107-87-9), 3-pentanone (96-22-0), 2-hexanone (591-78-6), 3-hexanone (589-38-8), and cyclopentanone (120-92-3) at 295 ± 2 K.

$$\mathrm{Cl} + \mathrm{CH_3C(O)CH_3} \rightarrow \text{products} \quad k_1 \tag{1}$$

$$\mathrm{Cl} + \mathrm{CH_3C(O)C_2H_5} \rightarrow \text{products} \quad k_2 \tag{2}$$

$$\mathrm{Cl} + \mathrm{CH_3C(O)C_3H_7} \rightarrow \text{products} \quad k_3 \tag{3}$$

$$\mathrm{Cl} + \mathrm{C_2H_5C(O)C_2H_5} \rightarrow \text{products} \quad k_4 \tag{4}$$

$$\mathrm{Cl} + \mathrm{CH_3C(O)C_4H_9} \rightarrow \text{products} \quad k_5 \tag{5}$$

$$\mathrm{Cl} + \mathrm{C_2H_5C(O)C_3H_7} \rightarrow \text{products} \quad k_6 \tag{6}$$

$$\mathrm{Cl} + \textit{cyclo}\text{-}\mathrm{C_5H_8O} \rightarrow \text{products} \quad k_7 \tag{7}$$

Reaction 1 has been the subject of relative rate,[6−11] pulsed laser photolysis resonance fluorescence (PLP-RF),[12,13] and discharge flow system mass spectrometric (DF-MS)[14] studies. The results from most of these studies of reaction 1 are in good agreement. Reaction 2 has been studied using relative rate and PLP-RF techniques. Interestingly, the values of k_2 reported in the PLP-RF studies[12,13,15] are approximately 20% lower than those found in the relative rate studies.[6,16] Reactions 3−6 have been studied by PLP-RF,[13,15] DF-MS,[17] and relative rate techniques.[16] The results from the recent relative rate study of reactions 3−6[16] are substantially (approximately a factor of 2−3) larger than those from the absolute rate studies.[13,15,17] We have argued that Cl regeneration was a severe complication in the

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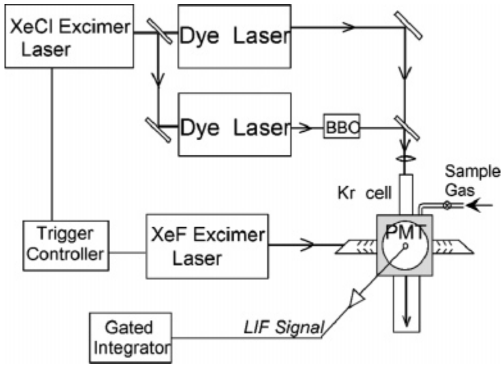

Figure 1. Schematic diagram of the experimental setup.

previous absolute rate studies leading to a substantial underestimation of the reactivity of these ketones toward Cl atoms. Reaction 7 has been the subject of two relative rate studies. Unfortunately, there is a disagreement of approximately a factor of 2 between the results from the studies of Olsson et al.[7,18] and Wallington and co-workers.[19] The uncertainties in modern experimental studies of Cl atom kinetics are typically approximately 10−15%. It is perplexing that there are such large discrepancies in the literature data for reactions of Cl atoms with ketones.

In this work, the kinetics of reactions 1−7 were studied using pulsed laser photolysis−vacuum ultraviolet laser-induced fluorescence (PLP-LIF) techniques. Chlorine atoms were monitored via LIF at 134.72 nm ($3p^5$ $^2P_{3/2}$−$3p^44s$ $^2P_{3/2}$ transition). The decay of chlorine atoms in the presence of known concentrations of ketones was used to derive kinetic data. Previous work has established the reliability of the PLP-LIF technique in studies of reactions of Cl atoms with organic compounds.[20−24] The goal of the present work is to use the PLP-LIF technique to improve our understanding of the kinetics of the reactions of Cl atoms with ketones. Atmospheric implications of our present results are discussed briefly.

2. Experimental

Figure 1 shows a schematic diagram of the experimental setup. All experiments were performed at 295 ± 2 K. Gas mixtures of Cl_2 and ketone diluted in Ar were slowly introduced into a reaction chamber which was evacuated continuously by a rotary pump (Edwards, RV-12) through a liquid N_2 trap. Reaction mixtures consisted of 0.2−0.7 mTorr of Cl_2 and 1.6−277.3 mTorr of the ketone of interest in 6.5 Torr of Ar diluent. An excimer laser (Lambda Physik, COMPex102) was operated in a XeF mode to generate 351-nm light to photolyze Cl_2. On the basis of the Cl_2 absorption cross section at 351 nm[25] and the photolysis laser fluence, the initial concentration of Cl(^2P_j) atoms in the reaction chamber was estimated to be about 3×10^{10} to 1×10^{11} atoms cm^{-3}. Loss of Cl atoms by their self-reaction ($Cl + Cl + Ar \rightarrow Cl_2 + Ar$) proceeds slowly with a rate coefficient of the order of 10^{-33} cm^6 molecule^{-2} s^{-1} [26] and is not significant under the present experimental conditions. All the experiments were carried out under pseudo-first-order conditions with [ketone] >> $[Cl]_0$.

Cl($^2P_{3/2}$) atoms were detected by VUV-LIF at 134.72 nm ($3p^5$ $^2P_{3/2}$−$4p^44s$ $^2P_{3/2}$ transition). Tunable VUV radiation was generated by four-wave difference frequency mixing ($2\omega_1 - \omega_2$) in 35 Torr of Kr, using two dye lasers pumped by a single XeCl excimer laser (Lambda Physik, COMPex 201, FL3002, and Scanmate 2E). The fundamental output of the ω_1 laser at 425.12 nm was frequency-doubled in a BBO crystal to generate 212.56-nm light which is two-photon resonant with the $5p1/2_0$ level of Kr. The wavelength of the ω_2 laser was ∼500 nm. Typical pulse energies of the ω_1 and ω_2 lasers were 0.3 and 4 mJ, respectively. The laser beams were overlapped collinearly and focused by a fused silica lens ($f = 200$) into a cell containing Kr. The Kr cell and the reaction chamber were separated by a thin MgF_2 window. The VUV laser line width was estimated to be 0.64 cm^{-1} full width at half-maximum (fwhm) with a Gaussian shape.

The VUV-LIF signal was detected by a solar-blind photomultiplier tube (EMR, 541J-08-17) with a KBr photocathode sensitive at 106−150 nm. The PMT tube was mounted at right angles to the propagation direction of the VUV probe beam and the 351-nm photolysis beam. The 351-nm laser light and the vacuum UV laser light crossed perpendicularly in the reaction cell. The pump and probe lasers were operated at a repetition rate of 10 Hz. The time delay between the dissociation and probe laser pulses was controlled by a pulse generator (Stanford Research, DG535), the jitter of the delay time was less than 20 ns. When the 351-nm laser light was turned off, no discernible LIF signal was observed, indicating that neither the probe, ω_1, nor ω_2 lasers photolyze Cl_2 to any appreciable extent.

Previous kinetic studies of Cl atom reactions using the PLP-LIF technique[20−24] have employed photolysis of HCl at 193 nm to generate Cl atoms. However, preliminary experiments showed that the 193-nm irradiation of HCl/ketone/Ar mixtures led to the formation of rovibrationally excited CO molecules which interfered with the LIF detection of Cl atoms. Ketone molecules absorb strongly at 193 nm,[27] and the subsequent formation of rovibrationally excited CO molecules has been reported by several groups.[28−30] The (7, 0) and (11, 2) bands of electronic $A^1\Pi$−$X^1\Sigma^+$ transition of CO overlap the Cl($3p^5$ $^2P_{3/2}$−$3p^44s$ $^2P_{1/2}$) and Cl($3p^5$ $^2P_{3/2}$−$3p^44s$ $^2P_{3/2}$) transitions, respectively.[31,32] To avoid problems associated with the formation of CO, the 351-nm laser photolysis of Cl_2 was used as a source of Cl atoms in the present study. There was no discernible CO LIF signal following the 351-nm photolysis of Cl_2/ketones/Ar mixtures.

Laser light with wavelengths of 212.6, 500, and 135 nm is used in the present experiments. Ketones have absorption cross sections at 212.6 nm which are of the order of 10^{-22} cm^2 molecule^{-1}.[4] The 212.6-nm laser fluence used in the present work was approximately 1×10^{16} photon cm^{-2}. Taking an upper limit of unity for the photodissociation quantum, we estimate that <0.01% of the ketone will be photolyzed. Even if the radical photolysis products were to react with Cl atoms at the gas kinetic limiting rate, photolysis of ketones at 212.6 nm would not complicate our kinetic analysis. Ketones do not absorb at 500 nm. Absorption cross sections for ketones at 135 nm are not available. Assuming the absorption cross sections at 135 nm are $<10^{-17}$ cm^2 molecule^{-1} and considering the 9×10^{13} photon cm^{-2} fluence of the probe laser, we conclude that <0.09% of ketone sample would be photolyzed by the probe laser and that photolysis of ketones by the probe laser is not a significant complication in the present work.

Reagents diluted with Ar were stored in 10-L glass bulbs which were blackened to avoid any dark chemistry. The reagents were introduced into the reaction cell through mass flow controllers (Horiba STEC, SEC-400MARK3). The total pressure in the reaction cell was monitored using a capacitance manometer (MKS Baratron, model 622A). The gases used in the experiments had the following stated purities: Cl_2, >99% (Sumitomo Seika Co.); acetone, >99% (Wako Pure Chemical Industries); butanone, >95% (Wako); 2-pentanone, >95%

(Wako) and >99% (TCI Lancaster); 3-pentanone, >98% (Wako); 2-hexanone, >95% (Wako); 3-hexanone, >99% (Wako); cyclopentanone, >99% (Wako); and Ar, >99.999% (Nihon Sanso). Three sets of control experiments were performed to check for interferences caused by impurities in the reactant samples. First, samples of 2-pentanone were purchased from two different chemical suppliers, namely, Wako Pure Chemical and TCI Lancaster. Second, samples of the ketones were used both before and after freeze−pump−thaw cycling. Third, reaction mixtures were prepared in blackened glass bulbs and used either immediately or after standing for 5 days. There was no discernible effect of (i) choosing different chemical suppliers, (ii) freeze−pump−thaw cycling, or (iii) leaving reaction mixtures to stand in the dark for 5 days.

3. Results

In the present study, Cl_2/ketone/Ar gas mixtures were subjected to 351-nm pulsed laser irradiation to initiate reactions 1−7. Cl_2 has a broad absorption between 280 and 500 nm,[34] and Cl(^2P_j) atoms are produced following the photoabsorption. Matsumi et al.[34] measured the branching ratios between the spin−orbit states of Cl(^2P_j) produced from Cl_2 photodissociation between 266 and 500 nm by means of resonance-enhanced multiphoton ionization spectroscopy. The reported value of [Cl*-($^2P_{1/2}$)]/[Cl($^2P_{3/2}$)] = 0.016 ± 0.001 at 355 nm is expected to be close to that at 351 nm. Actually, in our present study, the LIF intensity of Cl*($^2P_{1/2}$) at 135.17 nm corresponding to the Cl($3p^5\ ^2P_{1/2}$−$3p^44s\ ^2P_{1/2}$) transition was found to be negligibly small compared with that of Cl($^2P_{3/2}$) at 134.72 nm. We conclude that physical quenching and/or chemical reaction of Cl*($^2P_{1/2}$) does not interfere with our kinetic measurements.

The Cl atoms produced from photodissociation of Cl_2 at 351 nm have a nascent kinetic energy of 12.1 kcal mol^{-1} in laboratory frame. To thermalize the translationally hot Cl atoms, ~6.5 Torr of Ar diluent was added to the reaction mixtures. Doppler profiles of the Cl atoms as a function of delay time were recorded by scanning the VUV laser wavelength to ensure that the entire thermalization of the translational energy of Cl atoms was achieved before their reaction with ketones. The Doppler shifts reflect the velocity components of the Cl fragments along the propagation direction of the probe laser beam.[35] We observed that the translational energy distribution of Cl atoms was thermalized by collisions with Ar within 1 μs. Kinetic data were acquired by fitting the Cl atom decay traces at times > 1 μs.

Figure 2 shows a typical trace of the Cl($^2P_{3/2}$) LIF signal at 134.72 nm obtained in an experiment using a mixture of 0.2 mTorr of Cl_2 and 38 mTorr of butanone in 6.57 Torr of Ar diluent. The probe laser wavelength was fixed at the center of resonance line Cl($3p^5\ ^2P_{3/2}$−$3p^44s\ ^2P_{3/2}$) at 134.72 nm. The LIF signal exhibits an initial jump at $t = 0$ reflecting the instantaneous production of Cl atoms by the 351-nm pulsed laser photolysis of Cl_2. After the initial jump, there is a slow decay of the LIF signal which we attribute to chemical loss of Cl atoms.

To check for interference caused by fluorescence from species other than Cl($^2P_{3/2}$) atoms, the VUV laser wavelength was scanned around the Cl atom resonance line using the same experimental conditions as for the time profile shown in Figure 2. Only the sharp peak of the Cl($^2P_{3/2}$) LIF signal was observed at 134.72 nm; there was no discernible signal at wavelengths around the Cl atom resonance line. This result suggests that the present work is free from complications caused by fluorescence from species such as CO molecules other than Cl($^2P_{3/2}$) atoms.

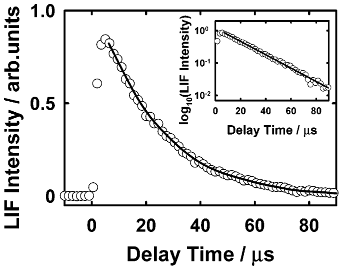

Figure 2. Typical Cl($^2P_{3/2}$) (= denoted Cl) decay profile observed in an experiment using a mixture of 0.2 mTorr Cl_2 and 38 mTorr butanone in 6.57 Torr of Ar diluent. The Cl atoms were detected directly by the VUV-LIF spectroscopy technique at 134.72 nm. At each time delay, the LIF signal was averaged over 10 laser shots. The $[Cl]_0$ value was 6.8×10^{10} cm^{-3}. The initial jump in the profile reflects the photolytic formation of Cl atoms from Cl_2 at 351 nm The insert shows a semilogarithmic plot of the temporal decay of the VUV-LIF signal of Cl. The delay times between the pump and probe laser pulses were controlled by a digital delay generator.

The decay of the Cl($^2P_{3/2}$) LIF signal shown in Figure 2 contains information on the kinetics of the reaction of Cl atoms with butanone. The curve through the data in Figure 2 is a least-squares fit of a first-order decay to the data at delay times >1 μs. As seen from Figure 2, the first-order fit provides a good description of the observed decay of Cl atoms in the system. The temporal losses of Cl($^2P_{3/2}$) followed pseudo first-order kinetics at delay times >1 μs in all experiments. Pseudo first-order rate constants obtained from fits such as that shown in Figure 2 are plotted versus the reactants concentration in Figure 3. As seen from the data in Figure 3, there was no discernible effect of subjecting the ketone samples to freeze−pump−thaw cycling before use or, in the case of 2-pentanone, choosing different chemical suppliers. The straight lines through the data in Figure 3 are linear least-squares fits which have slopes equal to the bimolecular rate coefficients for reactions 1−7. The results are listed in Table 1. Quoted uncertainties include two standard deviations from the least-squares fit analysis and systematic uncertainties such as precision of concentration determinations.

4. Discussion

The results from the present work are compared to the literature data in Table 1. Reaction of Cl atoms with ketones is believed to proceed predominantly via a hydrogen atom abstraction mechanism. In the case of the Cl + acetone reaction, evidence for a small (approximately 1%) contribution of an elimination pathway giving $CH_3C(O)Cl$ and CH_3 radicals has been reported.[36] Larger ketones (butanone, pentanone, etc.) have more C−H bonds, hydrogen abstraction will be even more dominant than with acetone, and the contribution of the elimination channel is expected to be <1%. Given the expectation that the reactions listed in Table 1 proceed via hydrogen abstraction mechanisms, no effect of total pressure on the reaction kinetics is expected. Consistent with this expectation, in all cases in which the reactions have been studied over a range of pressure, no effect of total pressure on the kinetics has been observed.[12,13] The differences in total pressure used in the various studies listed in Table 1 does not explain the differences between the rate coefficients derived in some of the studies. The individual reactions are discussed in turn below.

4.1. Acetone. As shown in Table 1, the rate coefficient for the reaction of Cl atoms with acetone has been the subject of numerous investigations using a variety of absolute and relative rate techniques. The result from the present work is in very

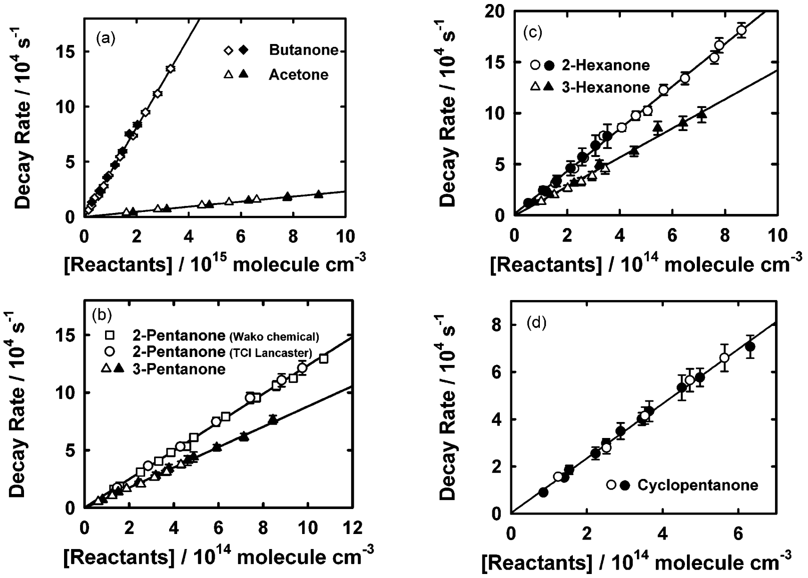

Figure 3. Pseudo-first-order plots for (a) acetone and butanone, (b) 2-pentanone and 3-pentanone, (c) 2-hexanone and 3-hexanone, and (d) cyclopentanone. The ketone samples were used before (open symbols) and after (filled symbols) freeze−pump−thaw cycling. Samples of 2-pentanone were purchased from two different suppliers (Wako Pure Chemical Industries Ltd. and Lancaster Co.). The lines through the data are linear least-squares fits.

TABLE 1: Rate Coefficients for Reactions of Cl Atoms with Selected Ketones at Room Temperature

compound	rate coefficient[a]	total pressure[b]	buffer gas	experimental technique[c]	refs
acetone	$(2.37 \pm 0.12) \times 10^{-12}$	700	N_2	relative	6
	$(1.69 \pm 0.32) \times 10^{-12}$	760	N_2	relative	7
	$(3.06 \pm 0.38) \times 10^{-12}$	15−60	He	PLP-RF	12
	$(2.0 \pm 0.3) \times 10^{-12}$	760	air	relative	8
	$(2.2 \pm 0.4) \times 10^{-12}$	700	O_2/N_2	relative	9
	$(2.93 \pm 0.20) \times 10^{-12}$	20−200	He	PLP-RF	13
	$(2.00 \pm 0.09) \times 10^{-12}$	760	air	relative	10
	$(2.2 \pm 0.4) \times 10^{-12}$	760	N_2, air	relative	11
	$(2.20 \pm 0.14) \times 10^{-12}$	1	He	DF-MS	14
	$(2.30 \pm 0.12) \times 10^{-12}$	6.6	Ar	PLP-LIF	this work
butanone	$(4.13 \pm 0.57) \times 10^{-11}$	700	N_2	relative	6
	$(3.24 \pm 0.38) \times 10^{-11}$	15−60	He	PLP-RF	12
	$(3.30 \pm 0.20) \times 10^{-11}$	20−200	He	PLP-RF	13
	$(3.27 \pm 0.55) \times 10^{-11}$	60−80	He	PLP-RF	15
	$(4.04 \pm 0.33) \times 10^{-11}$	700	N_2, air	Relative	16
	$(4.08 \pm 0.21) \times 10^{-11}$	6.6	Ar	PLP-LIF	this work
2-pentanone	$(4.57 \pm 0.28) \times 10^{-11}$	20-200	He	PLP-RF	13
	$(4.17 \pm 1.21) \times 10^{-11}$	60-80	He	PLP-RF	15
	$(1.11 \pm 0.13) \times 10^{-10}$	700	N_2,air	Relative	16
	$(1.23 \pm 0.13) \times 10^{-10}$	6.6	Ar	PLP-LIF	this work
3-pentanone	$(4.50 \pm 0.32) \times 10^{-11}$	20-200	He	PLP-RF	13
	$(5.9 \pm 0.5) \times 10^{-11}$	1	He	DF-MS	17
	$(8.11 \pm 0.98) \times 10^{-11}$	700	N_2,air	Relative	16
	$(8.87 \pm 0.92) \times 10^{-11}$	6.6	Ar	PLP-LIF	this work
cyclopentanone	$(4.76 \pm 0.33) \times 10^{-11}$	760	N_2	Relative	7
	$(1.11 \pm 0.10) \times 10^{-10}$	700	N_2	Relative	19
	$(1.16 \pm 0.12) \times 10^{-10}$	6.6	Ar	PLP-LIF	this work
2-hexanone	$(6.54 \pm 0.58) \times 10^{-11}$	20-200	He	PLP-RF	13
	$(6.56 \pm 0.98) \times 10^{-11}$	60-80	He	PLP-RF	15
	$(1.88 \pm 0.22) \times 10^{-10}$	700	N_2, air	Relative	16
	$(2.08 \pm 0.32) \times 10^{-10}$	6.6	Ar	PLP-LIF	this work
3-hexanone	$(6.69 \pm 0.62) \times 10^{-11}$	20-200	He	PLP-RF	13
	$(8.3 \pm 1.7) \times 10^{-11}$	1	He	DF-MS	17
	$(1.40 \pm 0.24) \times 10^{-10}$	700	N_2, air	relative	16
	$(1.43 \pm 0.19) \times 10^{-10}$	6.6	Ar	PLP-LIF	this work

[a] Units of cm^3 $molecule^{-1}$ s^{-1}, uncertainties are 2σ statistical errors. [b] Units of Torr. [c] Experimental techniques: RR, relative rate; PLP-LIF, pulsed laser photolysis coupled with vacuum ultraviolet laser-induced fluorescence spectroscopy; PLP-RF, pulsed laser photolysis coupled with resonance fluorescence detection; DF-MS, discharge flow mass spectrometric technique.

good agreement with 6 of the 9 previous studies. The value of k_1 reported by Olsson et al.[7] lies approximately 25% below that measured in the present work. Olsson et al.[7] derived their kinetic data by irradiating $Cl_2/ClONO_2$/acetone/air mixtures and measuring the concentration of NO_3 radicals formed from the $Cl + ClONO_2$ reaction. Acetone competes with $ClONO_2$ for the available Cl atoms and suppresses the concentration of NO_3 radicals. Kinetic data were acquired by studying the competition between acetone and $ClONO_2$ for the available Cl atoms. Acetone was introduced into the system by bubbling a fraction of the diluent gas through liquid acetone at 294 K. The concentration of acetone was calculated from its vapor pressure and the appropriate flow rates. As discussed elsewhere,[19] this method requires accurate knowledge of the diluent flow rates, temperature of the acetone liquid, and the acetone vapor pressure. It seems likely that error in one or more of these quantities explains the erroneously low value of k_1 reported by Olsson et al.[7]

As seen from Table 1, Notario et al.[12] and Albaladejo et al.[13] reported values for k_1 which are approximately 30% higher than those measured in the present work. At first glance, given the similarity of the experimental techniques (pulsed laser photolysis of Cl_2 to generate Cl atoms, VUV fluorescence to detect the Cl atoms) the discrepancy seems rather surprising. However, on inspection of the experimental conditions, it seems likely that additional loss of Cl atoms via reaction with $CH_3C(O)CH_2$ radicals seems a likely explanation for the overestimation of k_1 in the previous PLP-RF studies. The reactions of Cl atoms with alkyl radicals proceed rapidly. It is reasonable to suppose that the reactivity of Cl atoms toward $CH_3C(O)CH_2$ radicals is 2 orders of magnitude greater than toward acetone. In the experiments of Notario et al.[12] and Albaladejo et al.,[13] the $[\text{acetone}]/[\text{Cl}]_0$ ratio was 60−1100. Loss of Cl atoms via reaction with $CH_3C(O)CH_2$ radicals was probably a complicating factor leading to an overestimation of k_1 in the previous PLP-RF experiments. In our present work, the $[\text{acetone}]/[\text{Cl}]_0$ ratio was 2.1×10^4 to 1.1×10^5 and loss of Cl atoms via reaction with $CH_3C(O)CH_2$ radicals will not be significant.

It is worth noting that problems associated with additional loss of Cl atoms via reaction with products will be exacerbated when low-reactivity reactants are studied. This factor probably explains the fact that Notario et al.[12] report $k(\text{Cl} + CH_3C(O)CHCl_2) = 4.16 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}, which is 2.4 times that from relative rate studies $k(\text{Cl} + CH_3C(O)CHCl_2) = 1.7 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} [11]. Also, we note that Notario et al.[12] report a value for $k(\text{Cl} + CH_3C(O)CH_2Cl) = 3.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, which is 1.8 times larger than found in relative rate studies $k(\text{Cl} + CH_3C(O)CH_2Cl) = 2.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} [11].

Averaging the results from Wallington et al.,[6] Orlando et al.,[8] Christensen et al., [9] Sellevag et al.,[10] Carr et al.,[11] Martinez et al.,[14] and the present work gives $k_1 = (2.18 \pm 0.13) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 296 ± 2 K.

4.2. Butanone, 2- and 3-Pentanone, and 2- and 3-Hexanone. As seen from Table 1, the results from the present PLP-LIF study of the reactions of Cl atoms with butanone, 2-pentanone, 3-pentanone, 2-hexanone, and 3-hexanone are in good agreement with previous relative rate studies[6,16] but are in disagreement with the previous absolute rate determinations.[12,13,15,17] The magnitude of the disagreement is quite striking and increases with the reactivity of the ketone. While it is somewhat difficult to provide a definitive explanation for these discrepancies, it is worth noting that the concentration of Cl_2 used in the previous absolute rate work (10^{14} molecule cm^{-3} [12,13,15,17]) was approximately a factor of 7−15 higher, and the average concentrations of ketones were approximately 10 times lower than used in the present work. The presence of Cl_2 can be problematic in absolute rate experiments because alkyl radicals formed in the system will react with Cl_2 to regenerate Cl atoms. Reactions of alkyl radicals with Cl_2 proceed with rate constants which are typically of the order of 10^{-11} cm^3 molecule^{-1} s^{-1}. In the presence of 10^{14} molecule cm^{-3} of Cl_2, the regeneration of Cl atoms will proceed on a time scale comparable to that of the previous experimental observations. The regeneration of Cl atoms will lead to a decrease in the measured rate of Cl atom decay and an underestimation of the rate constants. This problem was recognized by the previous workers,[12,13,15,17] and in some control experiments, oxygen was added to scavenge the alkyl radicals with no impact on the measured kinetics. However, the addition of O_2 quenches the fluorescence signal, and relatively small amounts (1×10^{16} molecule cm^{-3}) of O_2 were added. The sensitivity of these control experiments is unclear. A likely explanation for the underestimation of the reactivities of butanone, 2-pentanone, 3-pentanone, 2-hexanone, and 3-hexanone in the previous absolute rate experiments is the regeneration of Cl atoms via reaction of radicals products with Cl_2. This problem was avoided in the present work by using lower $[Cl_2]$ and higher [ketone] as compared with the previous studies, hence decoupling the time scale for Cl atom regeneration from that of the experimental observations. Finally, we note that, in the present experiments, the concentration ratio $[\text{ketone}]/[\text{Cl}]_0$ was sufficiently high (10^3−10^5) that we can neglect the loss of Cl atoms by reaction with products of the reaction of chlorine atoms with ketones.

TABLE 2: Rate Coefficients for Cl and OH Reactions and Estimated Atmospheric Lifetimes

compound	k^{OH} [a]	k^{Cl} [b]	τ_{OH}/day[c]	τ_{Cl}/day[d]
acetone	1.8×10^{-13} [e]	2.3×10^{-12}	64.3	50−500
2-butanone	1.2×10^{-12} [e]	4.08×10^{-11}	9.6	3−30
2-pentanone	4.56×10^{-12} [f]	1.23×10^{-10}	2.5	0.9−9.0
3-pentanone	2.9×10^{-12} [g]	8.87×10^{-11}	5.6	1.3−13
cyclopentanone	2.94×10^{-12} [h]	1.19×10^{-10}	4.0	1−10
2-hexanone	6.64×10^{-12} [g]	2.11×10^{-10}	1.7	0.5−5.0
3-hexanone	6.96×10^{-12} [i]	1.36×10^{-10}	1.7	0.9−9.0

[a] In units of cm^3 molecule^{-1} s^{-1}. [b] Determined in this work; in units of cm^3 molecule^{-1} s^{-1}. [c] Lifetime with respect to reaction with OH radicals assuming $[\text{OH}] = 10^6$ cm^{-3}. [d] Lifetime with respect to reaction with Cl atoms assuming $[\text{Cl}] = 10^4$−10^5 cm^{-3}. [e] Reference 41. [f] Reference 42. [g] Reference 43. [h] Reference 44. [i] Reference 45.

4.3. Cyclopentanone. The reactivity of Cl atoms toward cyclopentanone measured in the present work is in good agreement with a previous study by Wallington et al.[19] but it is approximately twice that reported by Olsson et al.[7] For reasons discussed in section 4.1, we believe the data from Olsson et al.[7] to be in error. Given the agreement between the present PLP-LIF measurements and the previous relative rate studies, we believe the kinetics of the reaction of Cl atoms with cyclopentanone are now reasonably well established. We recommend the average of the results from the relative rate and present studies (with errors which encompass the extremes of the two determinations); $k_7 = (1.14 \pm 0.14) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 296 ± 2 K.

4.4. Structure Reactivity Relationship to Estimate *k*(Cl + ketones). The present results support and strengthen our previous findings that while the carbonyl functionality has a strong deactivating influence on C−H bonds α to the >C═O group, there is no evidence that this effect extends to C−H bonds β or γ to the >C═O group.[19] Assuming that the reactivity of the alkyl groups in ketones are independent, we derived the following group rate constants which can be used to describe the reactivities of ketones toward Cl atoms: $k(-CH_3) = 1.05 \times 10^{-12}$, $k(-C_2H_5) = 4.05 \times 10^{-11}$, $k(-C_3H_7) = 1.03 \times 10^{-10}$, and $k(-C_4H_9) = 1.86 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}.[16] The results from the present work increase our confidence in the group rate constants derived previously.[16]

4.5. Atmospheric Implications. The kinetic data in Table 1 can be used to estimate the atmospheric lifetime of ketones with respect to reaction with Cl atoms. Cl atoms are present in concentrations of the order of 10^4-10^5 cm^{-3} in the marine boundary layer (lowest approximately 1 km of atmosphere above the oceans).[37,38] Using [Cl] $= 10^4-10^5$ cm^{-3} and assuming [OH] $= 10^6$ cm^{-3} gives the lifetimes with respect to reaction with Cl and OH listed in Table 2. Calvert et al.[39] estimated photolytic loss rates of butanone, 2-pentanone, and 2-hexanone to be approximately 3×10^{-6}, $(1.0 \pm 0.3) \times 10^{-6}$, and $(3 \pm 2) \times 10^{-6}$ s^{-1}, respectively, for a solar zenith angle of 40°. Photolysis, reaction with OH, and reaction with Cl all probably play a role in the removal of ketones from the marine boundary layer. In the free troposphere (altitudes greater than approximately 1 km) and in the terrestrial boundary layer, the concentrations of Cl atoms are lower than 10^4 cm^{-3} and reaction with Cl will not be of any significance. Heterogeneous uptake onto droplets[40] could also be a competing loss mechanism for ketones in the troposphere.

5. Conclusions

This work presents the first application of PLP-LIF techniques to study the kinetics of the gas-phase reactions of Cl atoms with C_3-C_6 ketones. The goal of this work was to resolve the large discrepancies in the literature data base for these reactions. The results from the PLP-LIF study in 6 Torr of Ar diluent are in very good agreement with those from a recent relative rate study in 700 Torr of N_2, or air, diluent. The excellent consistency between these two sets of data, combined with the likelihood that (i) secondary loss of Cl atoms via reaction with products and (ii) regeneration of Cl atoms via reaction of radical products with Cl_2 were significant complications in previous absolute rate studies, serves to resolve the discrepancies in the literature data base.

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