

Atmospheric Chemistry of Cyclohexanone: UV Spectrum and Kinetics of Reaction with Chlorine Atoms

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ABSTRACT: Absolute and relative rate techniques were used to study the reactivity of Cl atoms with cyclohexanone in 6 Torr of argon or 800–950 Torr of N₂ at 295 ± 2 K. The absolute rate experiments gave $k(\text{Cl} + \text{cyclohexanone}) = (1.88 \pm 0.38) \times 10^{-10}$, whereas the relative rate experiments gave $k(\text{Cl} + \text{cyclohexanone}) = (1.66 \pm 0.26) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Cyclohexanone has a broad UV absorption band with a maximum cross section of $(4.0 \pm 0.3) \times 10^{-20} \text{ cm}^2 \text{ molecule}^{-1}$ near 285 nm. The results are discussed with respect to the literature data. © 2008 Wiley Periodicals, Inc. *Int J Chem Kinet* 40: 223–229, 2008

INTRODUCTION

Ketones are an important class of oxygenated volatile organic compounds used as solvents and formed during the atmospheric oxidation of most organic compounds [1,2]. Accurate UV spectra and kinetic data for reactions of chlorine atoms with organic compounds are needed in atmospheric chemistry studies for two reasons. First, they are inputs into global atmospheric models to assess the loss of organics via photolysis and

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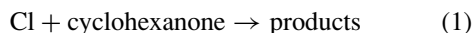
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reaction with Cl atoms. Second, they are used to analyze data from smog chamber experiments in which chlorine atoms are used to initiate the oxidation of organic compounds.

There is significant uncertainty in the rate constant for the reaction of Cl atoms with cyclohexanone.



Literature data for k_1 span a range of approximately a factor of 3 [3–6]. There has been just one study of the UV spectrum of cyclohexanone [7]. The peak absorption cross section reported for cyclohexanone is approximately 40% lower than those of similar cycloketones (cyclopropanone [8], cyclobutanone [9], and cyclopentanone [10]).

To reduce the uncertainties associated with our understanding of the atmospheric chemistry of cyclohexanone, we conducted four sets of experiments (all at 296 ± 1 K). First, pulsed laser photolysis-vacuum ultraviolet laser-induced fluorescence (PLP-LIF) spectroscopic techniques were used at Nagoya University to provide an absolute measurement of k_1 in 6 Torr of argon. Second, relative rate techniques (with gas chromatography used to monitor the loss of cyclohexanone relative to a reference compound) were employed at the University of Michigan–Dearborn to measure k_1 in 800–950 Torr of N_2 . Third, a custom built UV–visible spectrophotometer apparatus was used at National Center for Atmospheric Research (NCAR) to record the UV spectrum. Finally, a commercial UV–visible spectrophotometer apparatus was used at Ford to record the UV spectrum. Results are reported and discussed with respect to the literature data.

EXPERIMENTAL

PLP-LIF Measurement of k_1 at Nagoya

Absolute rate measurements of k_1 were carried out using PLP-LIF spectroscopy at Nagoya University. The experimental setup is described in detail elsewhere [11] and is discussed briefly here. Gas mixtures of 0.3 mTorr of Cl_2 and 1.1–11.6 mTorr of cyclohexanone in argon diluent were flowed slowly through a reaction chamber, which was evacuated continuously by a rotary pump (Edwards, RV-12). The total gas pressure in the reaction cell was monitored using a capacitance manometer (MKS Baratron, model 626IITAE) and kept at 6 Torr. The gas mixtures were irradiated with the pulsed excimer laser at 351 nm to produce $\text{Cl}(^2\text{P}_j)$ atoms from Cl_2 photolysis. $\text{Cl}(^2\text{P}_{3/2})$ atoms were directly detected by the PLP-LIF technique at 134.72 nm that corre-

sponds to the $3p^5\ ^2\text{P}_{3/2}-3p^44s\ ^2\text{P}_{3/2}$ transition. On the basis of the Cl_2 absorption cross section at 351 nm [12] and the photolysis laser fluence (4.8×10^{15} photons cm^{-2}), the initial concentration of $\text{Cl}(^2\text{P}_j)$ atoms in the reaction chamber was estimated to be about 4.5×10^{10} cm^{-3} . The reported value of $[\text{Cl}^*(^2\text{P}_{1/2})]/[\text{Cl}(^2\text{P}_{3/2})] = 0.016 \pm 0.001$ at 355 nm [13] is expected to be close to that at 351 nm. Actually in our present study, the LIF intensity of $\text{Cl}^*(^2\text{P}_{1/2})$ at 135.17 nm corresponding to the $\text{Cl}(3p^5\ ^2\text{P}_{1/2}-3p^44s\ ^2\text{P}_{1/2})$ transition was found to be negligibly small compared with that of $\text{Cl}(^2\text{P}_{3/2})$ at 134.72 nm. We conclude that physical quenching and/or chemical reaction of $\text{Cl}^*(^2\text{P}_{1/2})$ does not interfere with our kinetic measurements. All experiments were carried out under conditions with $[\text{cyclohexanone}] \gg [\text{Cl}]_0$.

Tunable VUV radiation around 135 nm was generated by four-wave difference frequency mixing ($\omega_{\text{vuv}} = 2\omega_1 - \omega_2$) in 35 Torr of Kr, using two dye lasers pumped by a single XeCl excimer laser (Lambda Physik, COM-Pex 201, FL3002 and Scanmate 2E). 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.

The Cl atoms produced from photodissociation of Cl_2 at 351 nm have a nascent kinetic energy of 12.1 kcal mol^{-1} . To thermalize the translationally hot Cl atoms, ~ 6.0 Torr of Ar 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 complete thermalization of the translational energy of Cl atoms was achieved before their reaction with the ketone. The Doppler shifts reflect the velocity components of the Cl fragments along the propagation direction of the probe laser beam [14]. We observed that the translational energy distribution of Cl atoms was thermalized by collisions with Ar within 10 μs . Kinetic data were acquired by fitting the Cl atom decay traces at times $> 10 \mu\text{s}$.

The reagents were introduced into the reaction cell through mass flow controllers (Horiba STEC, SEC-400MARK3). Reagents diluted with Ar were stored in 10-L glass-bulbs, which were blackened to avoid any dark chemistry. The gases used in the experiments had the following stated purities: $\text{Cl}_2 > 99\%$ (Sumitomo

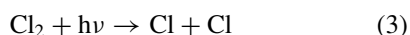
Seika Co.); cyclohexanone >99% (Wako Pure Chemical Industrie); and Ar >99.999% (Nihon Sanso) and were used without further purification.

Relative Rate Measurement of k_1 at Michigan

Relative rate experiments were carried out in a spherical, Pyrex (500 cm³) reactor interfaced to a gas chromatograph (HP 5890 GC/FID with a 30-m, 320 μ DB-1 capillary column with 5 μ coating) at the University of Michigan–Dearborn. Experiments were performed using Cl₂/cyclohexanone/C₃H₈/CH₄ mixtures in N₂ (UHP) diluent (Cl₂ and cyclohexanone purities >99.8%; freeze thaw cycles were performed on the cyclohexanone, and Cl₂ reactants). Methane (research grade, 99.997%) and C₃H₈ (research grade, 99.97%) were used as supplied. Methane was used for internal calibration of the GC analysis since it is essentially unreactive toward Cl ($k = 1 \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹) relative to the other hydrocarbons in the mixture. Propane was used as the reference compound in the GC relative rate experiments because it is convenient to measure using the GC technique and because k_2 is well established and independent of pressure.



Each reactant sample was mixed in the reactor prior to irradiation. Chlorine atoms were generated by irradiation with UV light using a single Sylvania F6T5 BLB fluorescent lamp.



After a chosen irradiation time, a portion of the contents of the reactor was removed (either from the flask through a gas-handling system into the GC sample loop, or indirectly using a 1-cm³ gas-tight syringe to transfer the sample directly into the GC injector port) and analyzed by gas chromatography. The mixture was then irradiated for additional times, and additional analyses were performed. The relative rate method is a well-established technique for measuring the reactivity of Cl atoms with organic compounds [15]. Kinetic data are derived by monitoring the loss of cyclohexanone and the reference compound (C₃H₈ in the present study). The decays of cyclohexanone and C₃H₈ are then plotted using the expression

$$\text{Ln} \left(\frac{[\text{cyclohexanone}]_{t_0}}{[\text{cyclohexanone}]_t} \right) = \frac{k_1}{k_2} \text{Ln} \left(\frac{[\text{C}_3\text{H}_8]_{t_0}}{[\text{C}_3\text{H}_8]_t} \right)$$

where [cyclohexanone]_{t₀}, [cyclohexanone]_t, [C₃H₈]_{t₀},

and [C₃H₈]_t are the concentrations of cyclohexanone and C₃H₈ at times t_0 and t , k_1 and k_2 are the rate constants for reactions of Cl atoms with the cyclohexanone and C₃H₈. Plots of Ln([cyclohexanone]_{t₀}/[cyclohexanone]_t) versus Ln([C₃H₈]_{t₀}/[C₃H₈]_t) should be linear, pass through the origin and have a slope of k_1/k_2 .

Initial reagent concentrations were 13–70 mTorr of cyclohexanone, 27–148 mTorr of C₃H₈, 107–580 mTorr CH₄, and 150–300 mTorr of Cl₂ in N₂ diluent. Total pressure was 800–950 Torr during the experiments, and irradiation times were 2–30 s. In relative rate experiments, it is important to check for unwanted loss of reactants and references via photolysis, dark chemistry, and heterogeneous reactions. Control experiments were performed in which (i) mixtures of reactants (except Cl₂) were subjected to UV irradiation for 3 min and (ii) product mixtures obtained after the UV irradiation of reactant mixtures were allowed to stand in the dark in the reactor for 20–30 min. There was no observable loss of the reactant or reference, suggesting that photolysis, dark chemistry, and heterogeneous reactions are not significant complications in the present work. Unless stated otherwise, quoted uncertainties are two standard deviations from least-squares regressions.

UV-Visible Spectrum Measurements at NCAR

UV absorption measurements at NCAR were made using a diode array spectrometer system (EG&G 1420 spectrometer /1461 detector interface), described previously [16]. Measurements were made in a 90-cm-long Pyrex cell equipped with quartz windows at 296 K. The collimated output from a deuterium lamp was directed through the absorption cell, and focused onto the entrance slit of a 0.3-m Czerny–Turner spectrograph equipped with a 300-groove mm⁻¹ grating. The system provides coverage between about 195 and 450 nm and was calibrated in wavelength using the output from a low-pressure Hg “penray” lamp. The spectral resolution is estimated to be 0.6 nm. Absorption spectra were obtained from a series of measurements made with the cell either empty (I_0) or filled with cyclohexanone sample (I), $A(\lambda) = \ln [I_0(\lambda)/I(\lambda)]$. The cyclohexanone pressure was varied between 0.4 and 2.6 Torr (no diluent gas was added). Absorption spectra were first corrected for any baseline drift and then smoothed, using a ± 0.5 -nm running average. Absorption values were then interpolated to 0.5 nm intervals. Final absorption cross section data (cm² molecule⁻¹) were obtained at each 0.5 nm interval from linear least-squares fits of absorbance versus [cyclohexanone] data:

$A(\lambda) = \sigma(\lambda)lc$, where $\sigma(\lambda)$ is the absorption cross section in $\text{cm}^2 \text{molecule}^{-1}$, l is the pathlength in cm, and c the [cyclohexanone] in molecule cm^{-3} . Uncertainties in the cross-section data are $\pm 5\%$ (the estimated uncertainty in the pathlength and concentration), plus an additional $\pm 1.5 \times 10^{-22} \text{ cm}^2 \text{molecule}^{-1}$ (to account for uncertainty in the absorbance measurements). Cyclohexanone (>99%) was obtained from Sigma-Aldrich, and subjected to several freeze-pump-thaw cycles prior to use.

UV-Visible Spectrum Measurements at Ford

UV absorption spectra of cyclohexanone were measured in the 200–500 nm wavelength range using a commercial dual beam UV spectrometer (Lambda 18, Perkin Elmer) operated at a spectral resolution of 1.0 nm. Gaseous samples of cyclohexanone were introduced using a Pyrex gas-handling system with greaseless valves into a 5.8-cm-long Pyrex cell equipped with BaF_2 windows. Six separate samples of 3.4 Torr cyclohexanone were placed into the cell (no diluent gas was added). All measurements were performed at 296 K. The purity of cyclohexanone was checked using FTIR spectroscopy before and after the UV measurements; no impurities were evident in the IR spectra.

RESULTS

PLP-LIF Measurement of k_1 at Nagoya

Figure 1 shows a typical temporal profile of LIF intensity of $\text{Cl}(^2\text{P}_{3/2})$ following the 351-nm pulsed laser irradiation of a gas mixture of 0.3 mTorr Cl_2 and 5.4 mTorr cyclohexanone in 6.0 Torr of Ar diluent. The LIF signal exhibits an increase jump at $t = 0$, reflecting the 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 is attributed predominantly to chemical loss of Cl atoms (loss via diffusion from the viewing zone makes a minor contribution). As seen from Fig. 1, the semilogarithmic plots of the Cl concentration indicate that the Cl atoms are consumed by a pseudo-first-order decay process at delay times $> 10 \mu\text{s}$.

The pseudo-first-order rate constants, k' , obtained from the decay profiles such as Fig. 1 are plotted versus the reactant concentration in Fig. 2. The line through the data in Fig. 2 is a linear least-squares fit. The slope of the straight line gives the rate coefficient $k(\text{Cl} + \text{cyclohexanone}) = (1.88 \pm 0.38) \times 10^{-10} \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ at $295 \pm 2 \text{ K}$. Quoted uncertainties

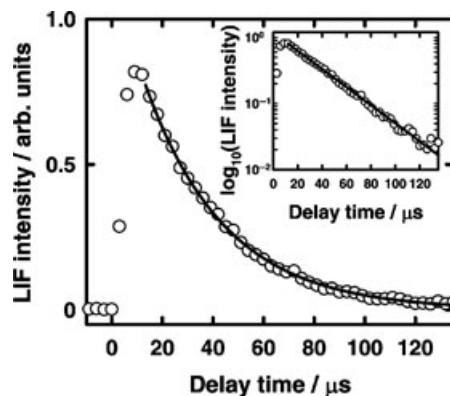


Figure 1 A typical $\text{Cl}(^2\text{P}_{3/2})$ decay profile observed in an experiment using a mixture of 0.3 mTorr Cl_2 and 5.4 mTorr cyclohexanone in 6.0 Torr of Ar diluent at $295 \pm 2 \text{ K}$. The insert shows a semilogarithmic plot of the temporal decay of the VUV-LIF signal of Cl atoms in the profile. The initial jump in the profile reflects the photolytic formation of Cl atoms from Cl_2 at 351 nm. The lines through the data are least-squares fits assuming first-order kinetics.

are two standard deviations from the least-squares fit analysis and also include our estimate of systematic uncertainties such as the accuracy of the concentration measurements. The result obtained in the present PLP-LIF study is listed in Table I together with the values reported previously. This work is the first application of the PLP-LIF technique to determine the rate coefficient for the reaction of Cl with cyclohexanone.

Relative Rate Measurement of k_1 at Michigan

The rate of reaction (1) was measured relative to reaction (2).

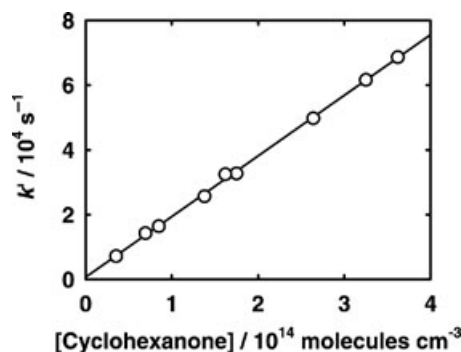


Figure 2 Pseudo-first-order loss of $\text{Cl}(^2\text{P}_{3/2})$ atoms versus cyclohexanone concentrations. The line through the data is a linear least-squares fit to the data. All experiments were performed at $295 \pm 2 \text{ K}$.

Table I Literature Values of $k(\text{Cl} + \text{Cyclohexanone})$

Rate Coefficient ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	Temperature (K)	Total Pressure (Torr)	Diluent	Experimental Technique ^a	Reference
$(7.00 \pm 1.15) \times 10^{-11}$	294	760	Air	RR	Olsson et al. [3]
$(1.81 \pm 0.31) \times 10^{-10}$	295	700	N ₂ , air	RR	Wallington et al. [4]
$(6.75 \pm 0.52) \times 10^{-11}$	298	20–200	He	PLP-RF	Albaladejo et al. [5]
$(1.7 \pm 0.3) \times 10^{-10}$	298	760	Air	RR	Martinez et al. [6]
$(9.6 \pm 1.8) \times 10^{-11}$	273	1	He	DF-MS	Martinez et al. [6]
$(1.0 \pm 0.2) \times 10^{-10}$	283	1			
$(1.3 \pm 0.2) \times 10^{-10}$	298	1			
$(1.4 \pm 0.1) \times 10^{-10}$	315	1			
$(1.4 \pm 0.2) \times 10^{-10}$	333	1			
$(1.88 \pm 0.38) \times 10^{-10}$	295	6	Ar	PLP-LIF	This work
$(1.66 \pm 0.26) \times 10^{-10}$	295	800–950	N ₂	RR	This work

^a RR, relative rate; PLP-RF, pulsed laser photolysis resonance fluorescence; DF-MS, discharge flow mass spectrometry; PLP-LIF, pulsed laser photolysis vacuum ultraviolet laser-induced fluorescence spectroscopy.

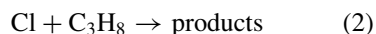
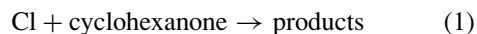


Figure 3 shows the loss of cyclohexanone versus loss of C₃H₈ following the UV irradiation of cyclohexanone/C₃H₈/CH₄/Cl₂ mixtures in 800–950 Torr N₂ diluent. As a check of the experimental reproducibility, three reaction mixtures were used. As seen from Fig. 3, the results obtained using the different reaction mixtures were indistinguishable as were the results from the two sampling techniques. Consistent with expectations (see experimental section “Relative Rate Measurements of k_1 at Michigan”), the plot of $\text{Ln}([\text{cyclohexanone}]_{t0}/[\text{cyclohexanone}]_t)$ versus $\text{Ln}([\text{C}_3\text{H}_8]_{t0}/[\text{C}_3\text{H}_8]_t)$ was linear and extrapolates to the origin.

The line through the data in Fig. 3 is a linear-least squares fit that gives $k_1/k_2 = 1.185 \pm 0.045$. Using $k_2 = (1.4 \pm 0.2) \times 10^{-10}$ [17], we derive $k_1 = (1.66 \pm 0.26) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This result is indistinguishable, within the experimental uncertainties, from that derived in the absolute rate study described in the previous section.

UV-Visible Spectrum Measurements at NCAR

The UV absorption spectrum obtained at NCAR (240–350 nm) is shown in Fig. 4, and data are tabulated at 5 nm intervals in Table II. The curve in Fig. 4 is a cubic spline fit to the spectral data (triangles) that were recorded every 0.5 nm. The peak absorption cross section (near 285 nm) was found to be $(4.0 \pm 0.2) \times 10^{-20} \text{ cm}^2 \text{ molecule}^{-1}$. Some vibrational structure is apparent in the spectrum with five local maxima evident between 265 and 305 nm.

UV-Visible Spectrum Measurements at Ford

The circles in Fig. 4 show the average of six spectra recorded at Ford. As seen from Fig. 4, the data measured at Ford are in good agreement with, but are more scattered than, those measured at NCAR. The scatter in the Ford spectrum reflects the rather short pathlength available with the spectrometer/cell setup and consequently the small absorbances observed with the partial pressures of cyclohexanone that could be admitted into the cell. On the basis of the experimental reproducibility (10%) and our estimate of potential systematic errors associated with sample concentration

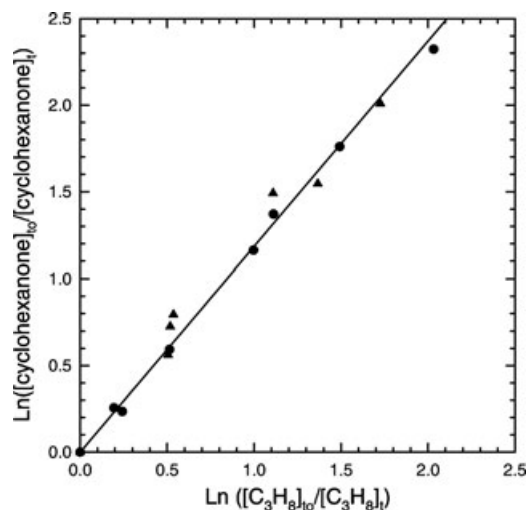


Figure 3 Loss of cyclohexanone versus C₃H₈ with analyses performed with injection into the GC either via a syringe (●) or directly from the reaction flask (▲).

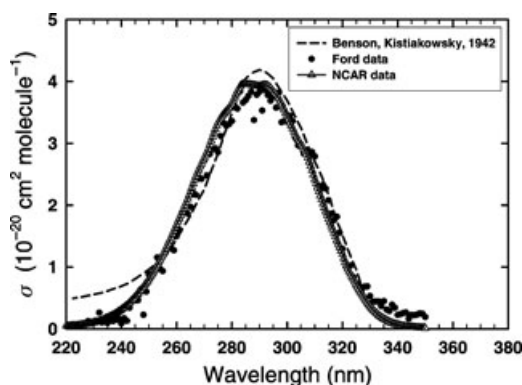


Figure 4 The gas phase UV spectrum of cyclohexanone measured at Ford (●) and NCAR (▲ and □) at 296 K; data of Benson and Kistiakowsky [7], determined in cyclohexane solution are shown as the --- line.

(2%), sample purity (0.1%), and path length (2%), we estimate that the uncertainty associated with the peak absorption cross section measured at Ford is $\pm 15\%$. As seen from Fig. 4, the absorption spectra measured at Ford and NCAR are, within the experimental uncertainties, in agreement. The NCAR spectrum is preferred because of its better signal to noise ratio.

DISCUSSION

$k(\text{Cl} + \text{Cyclohexanone})$

As seen from Table I and Fig. 5, the results obtained in the present study are in excellent agreement with

Table II Cyclohexanone Absorption Cross Sections ($\text{cm}^2 \text{ molecule}^{-1}$) Obtained at NCAR at 296 K, Shown at 5 nm Intervals

Wavelength (nm)	Cross Section	Wavelength (nm)	Cross Section
240	3.12×10^{-21}	300	3.43×10^{-20}
245	5.24×10^{-21}	305	2.98×10^{-20}
250	8.11×10^{-21}	310	2.42×10^{-20}
255	1.20×10^{-20}	315	1.77×10^{-20}
260	1.68×10^{-20}	320	1.21×10^{-20}
265	2.22×10^{-20}	325	7.13×10^{-21}
270	2.76×10^{-20}	330	3.65×10^{-21}
275	3.33×10^{-20}	335	1.63×10^{-21}
280	3.64×10^{-20}	340	6.43×10^{-22}
285	3.96×10^{-20}	345	2.89×10^{-22}
290	3.93×10^{-20}	350	1.18×10^{-22}
295	3.83×10^{-20}		

Uncertainties are estimated at $\pm 5\%$, plus an additional $\pm 1.5 \times 10^{-22} \text{ cm}^2 \text{ molecule}^{-1}$.

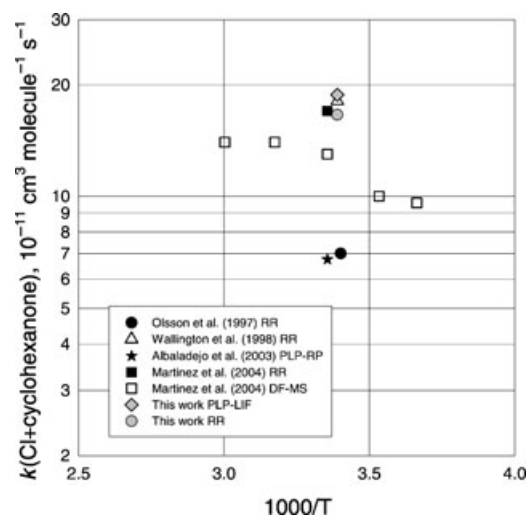


Figure 5 Literature data for $k(\text{Cl} + \text{cyclohexanone})$.

the previous relative studies by Wallington et al. [4] and Martinez et al. [6]. In contrast, the values of k_1 measured in the present work are approximately a factor of 2.5 times greater than those reported by Olsson et al. [3] and Albaladejo et al. [5], and 30%–40% greater than determined in the absolute rate study by Martinez et al. [6].

Olsson et al. [3] derived their kinetic data by irradiating $\text{Cl}_2/\text{ClONO}_2/\text{cyclohexanone}/\text{air}$ mixtures and measuring the concentration of NO_3 radicals formed from the $\text{Cl} + \text{ClONO}_2$ reaction. Cyclohexanone 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 cyclohexanone and ClONO_2 for the available Cl atoms. Cyclohexanone was introduced into the system by bubbling a fraction of the diluent gas through liquid cyclohexanone at 294 K. The concentration of cyclohexanone was calculated from its vapor pressure and the appropriate flow rates. As discussed elsewhere [4], this method requires accurate knowledge of the diluent flow rates, temperature of the cyclohexanone liquid, and the cyclohexanone 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. [3].

Martinez et al. [6] conducted several experimental tests to resolve the discrepancy with their previous [5] pulsed laser photolysis resonance fluorescence (PLP-RF) experiments. Martinez et al. [6] concluded that there were “some problems of regeneration of Cl,” which account for the low value of k_1 in the study by Albaladejo et al. [5]. While Martinez et al. [6] do not specify the mechanism of Cl atom regeneration in their

previous work, it seems likely that regeneration occurs via reaction of radical products of reaction (1) with Cl_2 . Reactions of alkyl radicals with Cl_2 proceed with rate constants that are typically of the order of $10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [17]. In the PLP-RF experiments of Albaladejo et al. [5], the molecular chlorine concentrations were approximately $10^{14} \text{ molecule cm}^{-3}$ and regeneration of Cl atoms would likely occur on a millisecond time scale which is comparable that of the experimental observations. Regeneration of Cl atoms should not be a complication in the discharge flow mass spectrometry (DF-MS) study of Martinez et al. [6], where much lower molecular chlorine concentrations of $(2-6) \times 10^{11} \text{ molecule cm}^{-3}$ were used. The origin of the 30%–40% difference between the DF-MS results of Martinez et al. [6] and the relative rate studies from Martinez et al. [6], Wallington et al. [4], and the present work, and the absolute rate study from the present work is unclear. By analogy to other rapid reactions of Cl atoms with hydrocarbon species [17], little or no temperature dependence is expected for this reaction rate constant. Further work is needed to confirm this expectation.

UV Spectrum and Photolysis in the Atmosphere

The ultraviolet absorption spectrum of cyclohexanone reflects the $n \rightarrow \pi^*$ transition common to all carbonyl compounds; see Fig. 4. However, we note that the maximum in the cross section reported from measurements in hexane solution by Benson and Kistiakowsky [7], $\sigma_{\text{max}} = 4.2 \times 10^{-20}$ (290 nm), is significantly less than σ_{max} observed for the analogous cyclic ketones: cyclopropanone, 6.5×10^{-20} (313 nm) measured in the gas phase by Thomas and Rodriguez [8]; cyclobutanone, 6.9×10^{-20} (291 nm) measured in cyclohexane solution by Carless and Lee [9]; cyclopentanone, 6.9×10^{-20} (299 nm) measured in cyclohexane solution by Nakashima et al. [10]. We see no obvious reason why the transition in cyclohexanone should be less allowed than that of the smaller cyclic ketones. Thus, we have redetermined this spectrum in the gas phase in this study and the results are summarized in Fig. 4. The solution phase data of Benson and Kistiakowsky [7] that they presented graphically as $\log_{10}(\epsilon, \text{L mol}^{-1} \text{ cm}^{-1})$ versus λ in their original report were digitized and transformed to σ versus λ data given in Fig. 4, and they probably do not reflect the accuracy of the original data. However, it can be seen that the measurements of Benson and Kistiakowsky for cyclohexanone in cyclohexane solutions are in reasonable agreement with our current gas phase measurements, and the relatively low values for σ are confirmed. We recommend the use of

the NCAR values reported in Table II for use in subsequent atmospheric modeling. However, a significant improvement in the knowledge of the nature and efficiencies of the primary photodecomposition processes is required before realistic estimates of the atmospheric photolysis rate coefficients for cyclohexanone can be made.

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BIBLIOGRAPHY

1. Brasseur, G. P.; Orlando, J. J.; Tyndall, G. S. *Atmospheric Chemistry and Global Change*; Oxford University Press: Oxford, UK, 1999.
2. Finlayson-Pitts, B. J.; Pitts, J. N., Jr. *Chemistry of the Upper and Lower Atmosphere: Theory, Experiments, and Applications*; Academic Press: New York, 2000.
3. Olsson, B. E. R.; Hallquist, M.; Ljungström, E.; Davidsson, I. *Int J Chem Kinet* 1997, 29, 195.
4. Wallington, T. J.; Guschin, A.; Hurley, M. D. *Int J Chem Kinet* 1998, 30, 309.
5. Albaladejo, J.; Notario, A.; Cuevas, C. A.; Jimenez, E.; Cabañas, B.; Martinez, E. *Atmos Environ* 2003, 37, 455.
6. Martinez, E.; Aranda, A.; Diaz de Mera, Y.; Rodriguez, A.; Rodriguez, D.; Notario, A. *J Atmos Chem* 2004, 48, 283.
7. Benson, S. W.; Kistiakowsky, G. B. *J Am Chem Soc* 1942, 64, 80.
8. Thomas, T. F.; Rodriguez, H. J. *J Am Chem Soc* 1971, 93, 5918.
9. Carless, H. A. J.; Lee, E. K. C. *J Am Chem Soc* 1972, 94, 1.
10. Nakashima, K.; Uchida-Kai, M.; Koyanagi, M.; Kanda, Y. *Bull Chem Soc Japan* 1982, 55, 415.
11. Takahashi, T.; Iwasaki, E.; Matsumi, Y.; Wallington, T. J. *J Phys Chem A* 2007, 111, 1271.
12. Sander, S. P.; Friedl, R. R.; Golden, D. M.; Kurylo, M. J.; Moortgat, G. K.; Keller-Rudek, H.; Wine, P. H.; Ravishankara, A. R.; Kolb, C. E.; Molina, M. J.; Finlayson-Pitts, B. J.; Huie, R. E.; Orkin, V. L. *Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation No. 15*, JPL Publication 06-2, 2006.
13. Matsumi, Y.; Tonokura, K.; Kawasaki, M. *J Chem Phys* 1992, 97, 1065.
14. Zare, R. N.; Herschbach, D. R. *Proc IEEE* 1963, 51, 173.
15. Atkinson, R. *J Phys Chem Ref Data* 1989, Monograph 1.
16. Staffelbach, T. A.; Orlando, J. J.; Tyndall, G. S.; Calvert, J. G. *J Geophys Res* 1995, 100, 14189.
17. Atkinson, R.; Baulch, D. L.; Cox, R. A.; Crowley, J. N.; Hampson, R. F.; Hynes, R. G.; Jenkin, M. E.; Rossi, M. J.; Troe, J. *Atmos Chem Phys Discuss* 2005, 5, 6295.