Relative Rate Studies of the Reactions of Atomic Chlorine with Acetone and Cyclic Ketones

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ABSTRACT: Rate coefficients have been measured for Cl atom reactions under ambient conditions with acetone and four cyclic ketones. Cl was generated by UV photolysis of Cl₂, and other species were monitored by FT-IR spectroscopy. The measurements yield $k(\text{Cl} + \text{acetone}) = (2.0 \pm 0.7) \times 10^{-12}$, $k(\text{Cl} + \text{cyclobutanone}) = (10.1 \pm 0.8) \times 10^{-11}$, $k(\text{Cl} + \text{cycloheptanone}) = (24.0 \pm 2.3) \times 10^{-11}$, $k(\text{Cl} + 2\text{-methyl cyclopentanone}) = (15.2 \pm 1.2) \times 10^{-11}$, and $k(\text{Cl} + 2\text{-methyl cyclohexanone}) = (11.2 \pm 1.0) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, where the uncertainties represent 95% confidence limits. These results are discussed in the context of structure-activity relationships. We also present a prediction for Cl + cyclopropanone based on ab initio properties of the transition state. © 2017 Wiley Periodicals, Inc. *Int J Chem Kinet* 50: 41–46, 2018

INTRODUCTION

Carbonyl compounds are important intermediates in the chain of transformations involved in the atmospheric oxidation of organic species [1]. They are also emitted directly into the atmosphere, for example, via their uses as solvents and fuel additives, and from biogenic sources such as plants and biomass burning [2]. The subsequent fate of ketones is typically initiated via attack of hydroxyl radicals or atomic chlorine, or photochemically, and these steps form part of an autocatalytic sequence for oxidation of hydrocarbons [1]. Carbonyl chemistry may lead to the formation of ozone,

organic acids, and/or secondary aerosols [3]. Degradation of volatile organic compounds (VOCs) is typically by photochemistry or by reaction with hydroxyl, but in some parts of the atmosphere such as the Marine Boundary Layer [4] and polar regions [5] the concentration of chlorine atoms is high enough for its chemistry to be competitive.

Here we focus on the initial hydrogen-atom abstraction step by atomic Cl from the following ketones:

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Table I Initial Concentration of the Reactants, Integrated Wavenumber Regions, and Rate Coefficient Ratios (k_R/k_{ref}), for the Reactions of Cl Atoms with Ketones at (293 ± 2) K

Reactant	[Reactant] ₀ (10 ¹⁶ molecule cm ⁻³)	Integrated Range (cm ⁻¹)	Reference	Integrated Range (cm ⁻¹)	[Reference] ₀ (10 ¹⁶ molecule cm ⁻³)	$k_R/k_{\text{ref}} \pm 2\sigma$
Acetone	3.43	1700–1800	1,2-Dichloroethane	710–745	2.82	1.581 ± 0.094
Cyclobutanone	4.33	1760–1840	Dichloromethane	730–780	3.45	5.512 ± 0.380
	3.24		Isobutane	1476–1483	3.51	0.697 ± 0.008
	2.72		Isobutane		2.41	0.747 ± 0.026
	3.92		Ethene ^a	925–975	2.83	1.267 ± 0.030
Cycloheptanone	3.16		Ethene ^b		1.95	1.166 ± 0.052
	9.24		<i>trans</i> -Dichloroethene	1185–1220	9.61	2.804 ± 0.246
	6.73		<i>trans</i> -Dichloroethene		7.00	2.260 ± 0.354
	2.50		Ethene ^b	925–975	5.01	2.765 ± 0.132
2-Methyl cyclopentanone	1.79	1700–1800	Ethene ^b		3.58	2.842 ± 0.086
	3.45		Isobutane	1476–1483	2.77	1.221 ± 0.036
	2.78		Isobutane		2.23	1.096 ± 0.042
	5.19		Ethene ^a	925–975	8.22	1.686 ± 0.168
2-Methyl cyclohexanone	5.59		Ethene ^b		8.17	1.415 ± 0.180
	4.33		Ethene ^a	925–975	5.04	1.429 ± 0.134
	4.64		Ethene ^b		3.61	1.539 ± 0.092
	3.66		Isobutane	1476–1483	2.74	0.728 ± 0.010
	2.84		Isobutane		1.81	0.943 ± 0.142

^aWith 933 mbar Ar.^bWith 667 mbar Ar.

There have been prior studies of such abstraction reactions with cyclic ketones. Wallington et al. [6] and Takahashi et al. [7] measured Cl plus cyclopentanone and cyclohexanone. The work of Aschmann and Atkinson [8] on Cl plus cycloalkanes and cycloketones included analysis in terms of structure–activity relationships (SAR). These were modified by Farrugia et al. [9], who also highlighted some discrepancies in the prior literature. One goal of this work is to explore the extrapolation of the SAR to new compounds. Because cyclopropanone is unstable at room temperature, we use computational methods to make a prediction for

METHODOLOGY

Commercial samples were purified by repeated freeze–pump–thaw cycles with liquid nitrogen. The general principles of relative rate measurements are well established [10], and we have described our apparatus and procedures in detail elsewhere [11]. Briefly, molecular chlorine is photolyzed by steady UV illumination from a mercury pen lamp in the presence of the reactant ketone and a reference compound in a 100-cm³ Pyrex multipass IR cell, with a path length of 2.4 m. The Pyrex walls are expected to block lamp emission at 184 and 254 nm but not at 365 nm. The cell is mounted within a Nicolet iS50 FT-IR spectrometer. The reference compound is a species whose absolute rate constant for reaction with atomic Cl has been already been characterized at room temperature. The absorbance of the reactant and reference is monitored by infrared (IR) spectroscopy over typically ca. 10 min with a resolution of 2 cm⁻¹.

With the central assumption that the dominant loss path for both the reactant and the reference is reaction with Cl atoms, with second-order rate constants of k_R

Figure 1 Example plots of concentration of reactant versus reference compound for acetone and cyclobutanone while consumed by atomic Cl. The (0,0) points from different runs overlap. [Color figure can be viewed at wileyonlinelibrary.com]

and k_{ref} , respectively, we may write [10] (where the subscript 0 refers to the initial value and t to a later time)

$$\ln \left\{ \frac{[\text{reactant}]_0}{[\text{reactant}]_t} \right\} = \frac{k_R}{k_{ref}} \ln \left\{ \frac{[\text{reference}]_0}{[\text{reference}]_t} \right\} \quad (7)$$

The ratios of concentration were obtained from ratios of the integrated absorbance over selected regions of the IR spectra, given in Table I, along with the initial conditions. Typically, we employed around 1–3 mbar reference compound, around 1–3 mbar reactant, around 4–12 mbar Cl_2 , and ca. 900 mbar of Ar. For each reactant, we verified that over a 10-min period photolysis in the absence of Cl_2 , and storage in the dark with Cl_2 , did not cause major reaction. Changes

in peak area for the ketones under these two conditions were 3–5% and 3–6%, respectively.

The reference compounds employed were isobutane, *trans*-1,2-dichloroethene, ethene, 1,2-dichloroethane, and dichloromethane. Rate constants and error limits were taken from the most recent measurements, which yielded k_{ref} values of $(1.40 \pm 0.08) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for isobutane [12], $(9.8 \pm 0.4) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for *trans*-1,2-dichloroethene [13], $(1.47 \pm 0.21) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for 1,2-dichloroethane [14], and $(3.5 \pm 0.2) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for dichloromethane [15]. We used ethene at two pressures, 667 and 933 mbar, and took rate constants at these pressures from the Troe fit to the measurements by Glowacki et al. [16] to obtain 8.6 and $9.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively. Prior data nearly all lie within 15% of the Troe fit, and so this was taken to be the confidence limit. These results are for N_2 or air as the bath gas but our experiments were made with Ar. At the high-pressure limit, the rate constant is of course independent of the nature of the bath gas, but our context is in the falloff region so some dependence is expected. A preliminary analysis of laser-photolysis resonance fluorescence experiments with Ar and N_2 bath gases suggests that in our pressure regime N_2 data are a factor of ca. 1.07 higher than Ar results [17]. We therefore divide the N_2 results by a factor of 1.07. We combine a 10% uncertainty arising from this scale factor in quadrature with the 15% above to propose $k(\text{Cl} + \text{C}_2\text{H}_4) = (8.0 \pm 1.4)$ and $(9.3 \pm 1.7) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at room temperature and 667 and 933 mbar Ar, respectively.

RESULTS AND DISCUSSION

Figure 1 shows example plots of $\ln\{[\text{reactant}]_0/[\text{reactant}]_t\}$ versus $\ln\{[\text{reference}]_0/[\text{reference}]_t\}$, whose slope is k_R/k_{ref} , for acetone and cyclobutanone reactions with Cl. Further plots are included in the Supporting Information. Table I lists the slopes of plots like those in Fig. 1 together with their 2σ statistical uncertainties. Pairs of k_R/k_{ref} values with each of two references were obtained for the cyclic species. We note that some pairs agree to within the combined 2σ but in other cases do not, which reveals that factors other than the statistical uncertainty in slopes of plots like Fig. 1 influence the reproducibility and can cause differences of around 10%. For each reactant, k_R/k_{ref} is multiplied by the literature value of k_{ref} . We estimate an uncertainty in k_R via 2σ in the k_R/k_{ref} ratio combined in quadrature with a 10% allowance for reproducibility

Table II Summary of the Rate Constants of Ketones with Cl Atoms Obtained with Different Reference Compounds

Reactant	Reference	$k_R \pm 2\sigma$ ($10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)
Acetone	Dichloromethane	0.232 ± 0.043
	1,2-Dichloroethane	0.193 ± 0.026
Cyclobutanone	Isobutane	9.76 ± 1.13
		10.5 ± 1.3
	Ethene	11.8 ± 2.5
		9.33 ± 1.93
Cycloheptanone	<i>trans</i> -1,2-Dichloroethene	27.5 ± 3.8
		22.1 ± 4.2
	Ethene	22.1 ± 4.6
		22.7 ± 4.6
2-Methylcyclopentanone	Isobutane	17.1 ± 2.0
		15.3 ± 1.9
	Ethene	15.7 ± 3.6
		11.3 ± 2.7
2-Methylcyclohexanone	Ethene	13.3 ± 3.0
		12.3 ± 2.6
	Isobutane	10.2 ± 1.2
		13.2 ± 2.5

Table III Comparison of Present Rate Constants for Cl Atoms Plus Ketones with Literature Data and Values from a Structure-Activity Relation

Reactant	k ($10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)		
	This Work	SAR ^a	Literature
Acetone	0.20 ± 0.07	–	0.21 ± 0.03^b
Cyclobutanone	10.1 ± 0.8	6.1	–
Cycloheptanone	24.0 ± 2.3	22.6	24.6 ± 0.7^c
2-Methylcyclopentanone	15.2 ± 1.2	12.2	–
2-Methylcyclohexanone	11.2 ± 1.0	17.7	–

^aParameterization from 9.^bFrom 19.^cFrom 8.

and with the literature uncertainty for the reference compound. These results are summarized in Table II. The weighted mean of k_R was evaluated as outlined by Bevington [18] to yield the final results in Table III. The 1σ uncertainty of the weighted mean multiplied by Student's t value of 3.18 (based on 3 degrees of freedom) was combined in quadrature with a 3% estimate of possible systematic errors in pressure and concentration measurements to obtain 95% confidence limits.

It may be seen that where comparison is possible our measurements agree with the literature, that is, for reactions of atomic Cl with acetone [19] and cycloheptanone [8]. Figure 2 shows a comparison between

Figure 2 Comparison of measured rate constants for Cl + cycloketones with values obtained from SAR parameterization. Solid circles, present work; solid square, Takahashi et al. [7]; open circles, [8]; solid line, SAR from Farrugia et al. [9].

measured rate constants for Cl plus cycloketones and SAR values by Farrugia et al. [9] as a function of ring size. The overall agreement is good, although our data for cyclobutanone lie a factor of 1.7 above the prediction. This could reflect ring strain. To explore this idea further, we considered cyclopropanone. Experimental study of reaction (6) at room temperature is not feasible so we have computed the structures,

Figure 3 Structure of transition state for Cl + cyclopropanone computed with B3LYP/6-31G(2df,p) theory. Bond lengths are shown in 10^{-10} m (see the Appendix for complete geometry). [Color figure can be viewed at wiley-onlinelibrary.com]

vibrational frequencies, and energies of the reactants and transition state (TS) using the G4 method [20], implemented in the Gaussian 16 program [21]. The structure of the TS is shown in Fig. 3, and ab initio data are given in the Appendix; the key result is that the energy of the TS including zero-point vibrational energy is within 0.5 kJ mol^{-1} of the reactants so that the predicted activation energy is effectively zero. Given a preexponential factor for Cl + cyclopropane of $1.8 \times 10^{-10} \text{ cm}^3 \text{ molecule s}^{-1}$ [22], we expect that k_6 for cyclopropanone, which has only two methylene groups rather than three, is about $1.2 \times 10^{-10} \text{ cm}^3 \text{ molecule s}^{-1}$. This is marginally larger than k_2 , about a factor of 20 greater than an SAR extrapolation, and about a factor of 60 greater than k_1 . The C–H bonds adjacent to the carbonyl group in cyclopropanone are clearly much more reactive than the C–H bonds next to the carbonyl group in acetone. Following the reaction coordinate reveals an interesting feature of reaction (6). Abstraction from C–H is concerted with ring opening, so that the initial products of reaction (6) are HCl + 3-oxo 2-propenyl and not oxo-cyclopropyl radicals.

While there is reasonable performance of the SAR for the two methylcycloketones listed in Table III, with agreement with experiment to within a factor of 1.6, we note that the order of reactivity is reversed compared to the predictions. Possibly some further parameterizations are needed to reproduce the experimentally observed behavior.

Finally, we comment that for the cyclic compounds here the rate constants with Cl are on the order of 40 times larger than those for the reactions with OH radicals. This means that in atmospheric regions with high [Cl], such as the Marine Boundary Layer where $[\text{Cl}] \sim (1/4)[\text{OH}]$, we can expect Cl atom chemistry to dominate for these species.

CONCLUSIONS

Relative rate results for Cl + cycloketones show good agreement with a prior structure–activity relation, but results for small rings, especially ab initio analysis of cyclopropanone, show deviations which we attribute to the influence of ring strain. Results for two methyl-substituted cycloketones indicate some deviation from the SAR.

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APPENDIX: COMPUTATIONAL ANALYSIS OF CL + CYCLOPROPANONE WITH G4 THEORY

Cyclopropanone geometry (in 10^{-10} m)

C	−0.000000000	0.785525000	−0.858941000
C	−0.000000000	−0.785525000	−0.858941000
C	0.000000000	−0.000000000	0.385640000
O	0.000000000	−0.000000000	1.580526000
H	−0.913453000	−1.289154000	−1.162689000
H	0.913453000	−1.289154000	−1.162689000
H	−0.913453000	1.289154000	−1.162689000
H	0.913453000	1.289154000	−1.162689000

Unscaled vibrational frequencies (in cm^{-1})

327, 512, 629, 701, 730, 947, 1022, 1057, 1067, 1107, 1166, 1417, 1431, 1957, 3117, 3118, 3197, 3211

TS geometry (in 10^{-10} m)

C	−0.409479000	0.435306000	0.630434000
C	−1.209868000	1.250668000	−0.339451000
C	−1.506232000	−0.256531000	0.072169000
O	−2.238806000	−1.158524000	−0.140921000
H	−1.809734000	2.096240000	−0.013790000
H	−0.903482000	1.261055000	−1.384617000
H	−0.392366000	0.688058000	1.688491000
H	0.854942000	0.027578000	0.229606000
Cl	2.289092000	−0.198906000	−0.092426000

Unscaled vibrational frequencies (in cm^{-1})

847i, 80, 109, 337, 372, 478, 493, 769, 803, 864, 934, 977, 1020, 1066, 1166, 1186, 1449, 1974, 3101, 3159, 3201

G4 energies at 0 K (including zero-point energy, in Hartrees)

Cl	−460.013636
Cyclopropanone	−191.773945
TS	−651.787772

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