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Mechanism of the gas phase reaction of chlorine atoms with butanone

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Abstract

Smog chamber/FTIR techniques were used to study the Cl atom initiated oxidation of CH₃C(O)CH₂CH₃ in 700–760 Torr of N₂ at 296 K. The reaction of Cl atoms with CH₃C(O)CH₂CH₃ proceeds via hydrogen abstraction with $73 \pm 9\%$ of reaction occurring at the – CH₂– group. Relative rate techniques were used to measure $k(Cl + CH_3C(O)CHClCH_3) = (5.62 \pm 0.81) \times 10^{-12} \text{ cm}^3$ molecule⁻¹ s⁻¹. It was deduced that the CH₃C(O)CHCH₃ radical reacts with Cl₂ with a rate constant of the order of 10^{-14} to 10^{-13} cm³ molecule⁻¹ s⁻¹. (© 2007 Elsevier B.V. All rights reserved.

1. Introduction

Ketones are an important class of oxygenated volatile organic compounds (VOCs) used as solvents and formed during the atmospheric oxidation of organic compounds [1,2]. Accurate kinetic data for reactions of chlorine atoms with organic compounds are needed in atmospheric chemistry for two reasons. First, they are inputs into global atmospheric models to assess the loss of organics via reaction with Cl atoms in the marine boundary layer. Second, they are used to analyze data from smog chamber experiments in which chlorine atoms are used to initiate the oxidation of organic compounds.

Mechanistic data concerning the reactions of chlorine atoms with ketones are sparse. The reaction of Cl atoms with acetone has been shown to proceed predominately (>97%) via a hydrogen abstraction mechanism to give CH₃C(O)CH₂ radicals and HCl [3]. The reaction of Cl atoms with butadione (CH₃C(O)C(O)CH₃, biacetyl) proceeds via both CH₃CO displacement and hydrogen abstraction channels. The displacement channel gives CH₃CO radicals and CH₃C(O)Cl in molar yields of $23 \pm 2\%$. The hydrogen abstraction channel accounts for the balance of the reaction and gives CH₃C(O)C(O)CH₂ radicals [4].

There are no available data concerning the mechanism of the reaction of Cl atoms with butanone. To improve our understanding of the reaction of chlorine atoms with ketones a study of the reaction of chlorine atoms with butanone was conducted. The reaction proceeds via three channels:

$Cl+CH_3C(O)CH_2CH_3 \rightarrow HCl+CH_2C(O)CH_2CH_3$	(1a)
$Cl + CH_3C(O)CH_2CH_3 \rightarrow HCl + CH_3C(O)CHCH_3$	(1b)
$Cl + CH_3C(O)CH_2CH_3 \rightarrow HCl + CH_3C(O)CH_2CH_2$	(1c)

By measuring the yield of CH₃C(O)CHClCH₃ following the UV irradiation of butanone/Cl₂ mixtures in 700– 760 Torr of N₂ diluent it was determined that $k_{1b}/(k_{1a}+k_{1b}+k_{1c})=0.73\pm0.09$.

2. Experimental

All experiments were performed using the smog chamber system at Ford Motor Company, consisting of a 140 L Pyrex reactor interfaced to a Mattson Sirus 100 spectrometer [5]. The reactor was surrounded by 22 fluorescent blacklamps (GE F15T8-BL). Relative rate techniques were

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used to measure the reactivity of Cl atoms towards $CH_3C(O)CHClCH_3$. The relative rate method is a well established technique for measuring the reactivity of Cl atoms with organic compounds [6]. Chlorine atoms were generated by photolysis of molecular chlorine in 700 Torr of N₂ diluent at 296 ± 2 K.

$$Cl_2 + hv \rightarrow Cl + Cl$$
 (2)

Kinetic data were derived by monitoring the loss of $CH_3C(O)CHClCH_3$ relative to two reference compounds (C_2H_5Cl or CH_3OCHO). The decays of $CH_3C(O)CHClCH_3$ and reference were then plotted using the expression:

$$\operatorname{Ln}\left(\frac{\left[\operatorname{CH}_{3}\operatorname{C}(\operatorname{O})\operatorname{CHClCH}_{3}\right]_{to}}{\left[\operatorname{CH}_{3}\operatorname{C}(\operatorname{O})\operatorname{CHClCH}_{3}\right]_{t}}\right)$$
$$=\frac{k_{\operatorname{CH3C}(\operatorname{O})\operatorname{CHClCH}_{3}}}{k_{\operatorname{reference}}}\operatorname{Ln}\left(\frac{\left[\operatorname{reference}\right]_{to}}{\left[\operatorname{reference}\right]_{t}}\right)$$

where $[CH_3C(O)CHClCH_3]_{to}$, $[CH_3C(O)CHClCH_3]_t$, $[reference]_{to}$ and $[reference]_t$ are the concentrations of $CH_3C(O)CHClCH_3$ and reference at times 'to' and 't', $k_{CH3C(O)CHClCH_3}$ and $k_{reference}$ are the rate constants for reactions of Cl atoms with $CH_3C(O)CHClCH_3$ and reference. Plots of $Ln([CH_3C(O)CHClCH_3]_{to}/[CH_3C(O)CHClCH_3]_t)$ versus $Ln([reference]_{to}/[reference]_t)$ should be linear, pass through the origin and have a slope of $k_{CH3C(O)CHClCH_3}/k_{reference}$.

The loss of the reactant and reference compounds was monitored by FTIR spectroscopy using an infrared optical path length of 27 m and a resolution of 0.25 cm^{-1} . Infrared spectra were derived from 32 co-added interferograms. Analysis of the IR spectra was achieved through spectral stripping, in which small fractions of the reference spectrum were subtracted incrementally from the sample spectrum. Reagents were obtained from commercial sources at >99% purity and were subjected to repeated freeze/pump/ thaw cycling before use. Ultra-high-purity nitrogen was used as the diluent gas.

In smog chamber experiments it is important to check for unwanted loss of reactants and products via photolysis, dark chemistry and heterogeneous reactions. Control experiments were performed in which (i) mixtures of reactants (except Cl_2) were subjected to UV irradiation for 10– 20 min and (ii) product mixtures obtained after the UV irradiation of reactant mixtures were allowed to stand in the dark in the chamber for 20 min. There was no observable loss of reactants or products, 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.

3. Results

3.1. Relative rate study of $k(Cl + CH_3C(O)CHClCH_3)$

The rate of reaction (3) was measured relative to reactions (4) and (5):

$$Cl + CH_3C(O)CHClCH_3 \rightarrow products$$
 (3)

$$Cl + C_2H_5Cl \rightarrow products$$

$$Cl + CH_3OCHO \rightarrow products$$
 (5)

Reaction mixtures consisted of 22.4–28.1 mTorr of CH₃C(O)CHClCH₃, 5.74–15.0 mTorr of reference, and 100 mTorr of Cl₂ in 700 Torr total pressure of N₂ diluent. Fig. 1 shows plots of Ln([CH₃C(O)CHClCH₃]_{to}/[CH₃C(O)CHClCH₃]_t) vs. Ln([reference]_{to}/[reference]_t) in the presence of Cl atoms. All plots are linear with intercepts which were indistinguishable from the origin, suggesting the absence of complications due to secondary chemistry. Rate constant ratios, obtained from unweighted linear least squares analysis of the data shown in Fig. 1 were $k_3/k_4 = 0.712 \pm 0.062$ and $k_3/k_5 = 3.94 \pm 0.51$. The quoted uncertainties include two standard deviations from the linear regression analyses and our estimate of uncertainties in the spectral analysis.

Using $k_4 = 8.04 \times 10^{-12}$ [7] and $k_5 = 1.4 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ [8] to place our relative rate measurements on an absolute basis gives $k_3 = (5.72 \pm 0.50) \times 10^{-12}$ and $(5.52 \pm 0.71) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹. Indistinguishable values of k_3 were obtained using the two different references. We choose to cite a final value which is the average together with error limits which encompass the extremes of the individual determinations; $k_3 = (5.62 \pm 0.81) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹. Comparing this result to $k(\text{Cl} + \text{CH}_3\text{C}(\text{O})\text{CH}_2\text{CH}_3) = (4.08 \pm 0.37) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ (average from [9–11]) we conclude that substitution of a chlorine atom on the third-position in butanone reduces the reactivity of the molecule by a factor of approximately 7 at 296 K.



Fig. 1. Loss of $CH_3C(O)CHClCH_3$ versus C_2H_5Cl (circles) and CH_3O-CHO (triangles) following exposure to Cl atoms in 700 Torr of N_2 at 296 K.

(4)

3.2. Mechanism of the reaction of Cl with $CH_3C(O)CH_2CH_3$

To investigate the reaction of Cl with CH₃C(O)CH₂CH₃ experiments were performed using UV irradiation of mixtures of 42.5–45.1 mTorr of CH₃C(O)CH₂CH₃ and 2010– 3951 mTorr of Cl₂ in 700 Torr of N₂ diluent. Reaction mixtures were subjected to 5–8 successive irradiations each having a duration of 5–10 s. The CH₃C(O)CHCH₃ radical formed in reaction (1b) reacts with molecular chlorine to give 3-chloro-butanone, CH₃C(O)CHClCH₃. The 3chloro-butanone yield provides a measure of the branching ratio $k_{1b}/(k_{1a} + k_{1b} + k_{1c})$.

$$CH_{3}C(O)CHCH_{3} + Cl_{2} \rightarrow CH_{3}C(O)CHClCH_{3} + HCl$$
(6)

To facilitate measurement of the butanone loss a small amount (4–8 mTorr) of C_2H_4 was added to the reaction mixtures. C_2H_4 has highly structured IR features which can be quantified (to a precision of ±1% of the original concentration) by FTIR spectroscopy more conveniently than those of butanone. The relative reactivity of chlorine atoms towards C_2H_4 and butanone has been established recently; butanone loss was calculated from the observed C_2H_4 loss using $k_1/k_7 = 0.44$ [10].

$$Cl + C_2H_4 \rightarrow products$$
 (7)

Typical spectra obtained before (a) and after (b) a 4 second irradiation of a mixture containing 45.1 mTorr CH₃C(O)CH₂CH₃, 3951 mTorr Cl₂, and 7.8 mTorr of C₂H₄ in 700 Torr of N₂ are shown in Fig. 2. From the observed 40% consumption of C₂H₄ it was calculated that the butanone consumption was 20%. Panel c shows the result of subtracting the IR features attributable to butanone from panel b. Comparison of panel c with reference spectra of CH₃C(O)Cl and CH₃C(O)CHClCH₃ in panels d and e shows the formation of these two products. CH₃CHO was also observed as a product by virtue of its characteristic IR features at 1353, 1395, 1436, and 1746 cm^{-1} . Following the subtraction of features attributable to CH₃C(O)Cl, CH₃C(O)CHClCH₃, and CH₃CHO small unidentified features were observed at 740, 1159, 1366, and 1740 cm^{-1} .

As discussed above, we expect the formation of 1-, 3-, and 4-chlorobutanone. The formation of $CH_3C(O)Cl$ was unexpected and is quite striking (see Fig. 2). There are two possible sources of $CH_3C(O)Cl$. First, as a primary product in the reaction of Cl atoms with butanone via channel (1d).

$$Cl+CH_3C(O)CH_2CH_3\rightarrow CH_3C(O)Cl+C_2H_5 \eqno(1d)$$

Second, as a secondary product following reaction of $CH_3C(O)CHCH_3$ radicals with O_2 impurity in the N_2 diluent in the chamber (reaction of alkoxy and peroxy radicals with Cl_2 is endothermic and not considered in the mechanism below):



Fig. 2. IR spectra before (a) and after (b) UV irradiation of a mixture of 45.1 mTorr $CH_3C(O)CH_2CH_3$, 3951 mTorr Cl_2 , and 7.8 mTorr of C_2H_4 in 700 Torr of N₂ at 296 K. Panel (c) shows the results of subtracting IR features attributable to $CH_3C(O)CH_2CH_3$ from (b). Panels (d) and (e) are reference spectra of $CH_3C(O)Cl$ and $CH_3C(O)CHClCH_3$.

$$\label{eq:Cl} \begin{split} Cl+CH_3C(O)CH_2CH_3 &\to HCl \\ &+CH_3C(O)CHCH_3 \end{split} \tag{1b}$$

 $CH_{3}C(O)CHCH_{3} + Cl_{2} \rightarrow CH_{3}C(O)CHClCH_{3} + Cl \qquad (6)$ $CH_{3}C(O)CHCH_{3} + O_{2} + M \rightarrow CH_{3}C(O)CH(OO)CH_{3} + M \qquad (8)$

$$2CH_3C(O)CH(OO)CH_3 \rightarrow 2CH_3C(O)CH(O^{\boldsymbol{\cdot}})CH_3 + O_2$$

 $CH_3C(O)CH(O^{\boldsymbol{\cdot}})CH_3 + M \rightarrow CH_3C(O) + CH_3CHO \quad (10)$

$$CH_3C(O) + Cl_2 \rightarrow CH_3C(O)Cl + Cl$$
(11)

$$CH_3C(O) + O_2 + M \rightarrow CH_3C(O)O_2 + M$$
(12)

To check for CH₃C(O)Cl formation via reaction (1d) an experiment was performed in 700 Torr of air. Using $k_{11}/k_{12} = 7.91$ [12] it can be calculated that reaction (12) will account for 99% of the CH₃C(O) radical loss in 700 Torr of air. If reaction (11) is a source of CH₃C(O)Cl in the nominally pure N₂ experiments then there should be a large change in the observed CH₃C(O)Cl yield on switching from N₂ to air diluent. If reaction (1d) is important then the yield of CH₃C(O)Cl is not expected to be significantly different in N₂ and air diluent. There was no observable CH₃C(O)Cl formation (<1% yield) following the UV irradiation of

 $CH_3C(O)CH_2CH_3/Cl_2/air$ mixtures. We conclude that reaction (1d) is not a significant contribution to the $CH_3C(O)Cl$ formation observed in the N₂ experiments.

Fig. 3 shows a plot of the observed formation of $CH_3C(O)CHClCH_3$, $CH_3C(O)Cl$, and CH_3CHO versus the fractional loss of butanone. As seen from Fig. 3, the concentration of $CH_3C(O)CHClCH_3$ increased linearly with the loss of butanone. This behavior suggests that $CH_3C(O)CHClCH_3$ is formed as a primary product and that there are no significant losses of $CH_3C(O)CHClCH_3$ in the system. The low reactivity of $CH_3C(O)CHClCH_3$ towards Cl atoms reported in Section 3.1 is consistent with the linearity of the $CH_3C(O)CHClCH_3$ yield plot in Fig. 3. The line through the $CH_3C(O)CHClCH_3$ data is a linear least squares fit which gives a molar yield of 0.54 ± 0.03 .

In stark contrast to the behavior of $CH_3C(O)CHClCH_3$, the yield plots for $CH_3C(O)Cl$ and CH_3CHO in Fig. 3 display pronounced curvature. The $CH_3C(O)Cl$ yield *increases* while the CH_3CHO yield *decreases* with butanone consumption. The simplest chemical mechanism which explains the observed product trends consists of reactions (1b), (6), (8)–(13).

$$Cl + CH_3CHO \rightarrow HCl + CH_3C(O)$$
 (13)

CH₃C(O)Cl is formed by reaction of CH₃C(O) radicals with molecular chlorine. The decomposition of CH₃C(O)-CH(O)CH₃ radicals is both a direct, reaction (10), and indirect, reaction (10) followed by reaction (13), source of CH₃C(O) radicals. The mechanism proposed above is somewhat unusual in two respects. First, we need to invoke the presence of a small O₂ impurity in the chamber. Sec-



Fig. 3. Formation of $CH_3C(O)CHClCH_3$ (stars), $CH_3C(O)Cl$ (circles), and CH_3CHO (triangles) versus $CH_3C(O)CH_2CH_3$ loss following UV irradiation of a mixture of 42.5 mTorr of $CH_3C(O)CH_2CH_3$, 2140 mTorr Cl_2 , and 4.4 mTorr C_2H_4 in 700 Torr of N_2 at 296 K. The lines are least squares fits to the data, see text for details.

ond, the mechanism relies on *inefficient* scavenging of $CH_3C(O)CHCH_3$ radicals by reaction with Cl_2 but *efficient* scavenging of $CH_3C(O)$ radicals.

In attempts to eliminate the O_2 impurity the chamber was flushed with N₂ repeatedly before conducting the experiments, different cylinders of ultra high purity N₂ were employed, and an experiment was performed using argon diluent gas. However, in all experiments significant amounts of CH₃C(O)Cl product were observed indicating the presence of O_2 . We attribute the presence of O_2 to a leak in which air entered the chamber while it was filled. In an experiment conducted using a mixture with low [Cl₂] (100 mTorr Cl₂ and 44.6 mTorr butanone in 700 Torr N_2) the yield of 3-chloro-butanone fell to 9%. In the mechanism proposed above there is a competition between reactions (6) and (8) for the available $CH_3C(O)CHCH_3$ radicals. With low [Cl₂] reaction (6) becomes a less important fate for CH₃C(O)CHCH₃ radicals and the yield of 3chloro-butanone is expected to decrease. The observed decrease in 3-chloro-butanone is consistent with expectations based upon the reactions mechanism proposed above and the presence of O_2 impurity in the system.

To estimate the likely magnitude of the O₂ impurity an experiment was conducted in which 20 mTorr of O2 was added to a mixture of 2004 mTorr Cl₂ and 44.7 mTorr butanone in 700 Torr N₂. In this experiment the yield of 3-chloro-butanone (29%) was approximately a factor of 2 lower than that observed in comparable experiments in the absence of added O_2 (e.g., Fig. 3). We conclude that with regard to the competition between reactions (6) and (8), 20 mTorr of O_2 is approximately as effective as 2004 mTorr of Cl₂ and hence k_6/k_8 is approximately 0.01 and that the O_2 impurity is of the order of 20 mTorr. The rate constants for reactions of alkyl radicals with O₂ are relatively insensitive to the identity of the alkyl radical and are typically of the order of 10^{-12} to 10^{-11} cm³ molecule⁻¹ s⁻¹. For example, Kaiser reported high-pressure limiting rate constants of $k_{\infty}(CH_3 + O_2 + M) = 1.32 \times$ 10^{-12} [13] and $k_{\infty}(C_2H_5 + O_2 + M) = (9.2 \pm 0.9) \times$ 10^{-12} cm³ molecule⁻¹ s⁻¹[14]. In contrast, the rate constants for reactions of alkyl radicals with Cl₂ are sensitive to the identity of the alkyl radical and span the range 10^{-15} (e.g., CH₂ClCCl₂ [15]) to 10^{-11} cm³ molecule⁻¹ s⁻¹ (e.g., CH₃C(O) [12]). The value of $k_6 = 10^{-14}$ to 10^{-13} cm³ molecule⁻¹ s⁻¹ implied by our estimate of $k_6/$ $k_8 = 0.01$ does not appear unreasonable. In contrast to the behavior of CH₃C(O)CHCH₃ radicals, CH₃C(O) radicals react more rapidly with Cl_2 than with O_2 (k_{11} / $k_{12} = 7.91 \pm 0.49$ in 700 Torr of N₂ [12]). CH₃C(O) radicals are approximately 800 times less sensitive to the presence of O₂ impurity than CH₃C(O)CHCH₃ radicals. For experiments conducted with 2010-3951 mTorr of Cl₂ the fate of $CH_3C(O)$ radicals is reaction with Cl_2 to give $CH_3C(O)Cl.$

As discussed above, we believe there are both primary and secondary sources of $CH_3C(O)Cl$ in the system. We attribute curvature of the $CH_3C(O)Cl$ product yield plot Table 1

Experiment	Diluent ^a	[butanone] _o ^b	$[Cl_2]_o^b$	CH ₃ C(O)CHClCH ₃	CH ₃ C(O)Cl ^c	Sum ^d
#1	760 N ₂	45.1	3951	0.56	0.22	0.78
#2	$700 N_2$	42.5	2140	0.54	0.18	0.71
#3	760 N ₂	45.0	2010	0.48	0.16	0.64
#4	760 Ar	44.1	1006	0.54	0.24	0.78
#5	760 N ₂	44.6	100	0.09	0.47	0.56
#6	760 N ₂ /0.02 O ₂	44.7	2004	0.29	0.31	0.60

Measured molar product yields for CH₃C(O)CHClCH₃ and CH₃C(O)Cl

^a Units of Torr.

^b Units of mTorr.

^c Primary component (see text for details).

^d Sum of CH₃C(O)CHClCH₃ and CH₃C(O)Cl.

in Fig. 3 to the secondary source following reaction of Cl atoms with CH₃CHO. This secondary source increases in importance with increasing butanone consumption. Using the analytical solution to the set of differential equations which describe the formation of such a secondary product [16] we can fit expression (I) to the CH₃C(O)Cl data to separate the primary and secondary components

$$Y(CH_{3}C(O)Cl) = (\alpha * x) + \left\{ (\alpha * x) - \left(\frac{\alpha}{1 - \frac{k_{13}}{k_{1}}} (1 - x) \left[(1 - x)^{\left\{ \frac{k_{13}}{k_{1}} - 1 \right\}} - 1 \right] \right) \right\}$$
(I)

where $Y(CH_3C(O)Cl)$ is the ratio of $CH_3C(O)Cl$ concentration to the initial concentration of butanone, α is the yield of $CH_3C(O)CH(O)CH_3$ radicals in the system, x is the fractional conversion of butanone, and k_{13}/k_1 is the ratio of rate constants for reactions (13) and (1). Literature data for $k_{13} = 7.9 \times 10^{-11}$ [17] and $k_1 = 4.08 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ [9–11] were used to fix $k_{13}/k_1 = 1.94$. The solid curve line in Fig. 3 shows a fit of expression (I) to the $CH_3C(O)Cl$ data with α varied to provide a best fit value of 0.18 ± 0.01 . As seen from Fig. 3, expression (I) provides a good description of the trend of the CH₃C(O)Cl data. The dotted line in Fig. 3 is $\alpha * x$ and is the primary component of the CH₃C(O)Cl yield. The dashed line shows the predicted behavior of CH₃CHO in the system from expression (I) and the chemical mechanism described above which provides a reasonable description of the observed CH₃CHO concentrations in the system. The weak IR features, low yield, and reactive nature of CH₃CHO explain the relatively large uncertainties on the CH₃CHO data points in Fig. 3. For reasons which are unclear, the majority of the CH₃CHO data points in Fig. 3 lie below the values expected (dashed line) from the fit to the CH₃C(O)Cl (solid curved line).

The combined yield of 3-chloro-butanone and the primary component of the CH₃C(O)Cl yield provide a measurement of the fraction of Cl atoms which react with butanone at the $-CH_2$ - group. From the experimental data shown in Fig. 3 we derive $k_{1b}/(k_{1a} + k_{1b} + k_{1c}) =$ $(0.54 \pm 0.03) + (0.18 \pm 0.01) = 0.72 \pm 0.04$. An alternative approach is to sum the 3-chloro-butanone yield and 50%

of the combined yields of CH₃C(O)Cl and CH₃CHO. This yields $k_{1b}/(k_{1a}+k_{1b}+k_{1c}) =$ alternative approach 0.71 ± 0.04 . The results from the six sets of experiments conducted in the present work are summarized in Table 1. As discussed above, experiments #5 and 6 were conducted to test the experimental mechanism. These experiments were not designed to give quantitative information concerning $k_{1b}/(k_{1a}+k_{1b}+k_{1c})$ and are shown in Table 1 for completeness. The results from experiments #1-4 provide a consistent picture of the importance of reaction channel k_{1b} . Taking an average of these determinations with an uncertainty which encompasses the extremes of the individual determinations gives $k_{1b}/$ $(k_{1a} + k_{1b} + k_{1c}) = 0.73 \pm 0.09.$

4. Discussion

We present a body of experimental data showing that the reaction of Cl atoms with butanone proceeds predominately via reaction at the $-CH_2$ - site. Combining k_{1b} / $(k_{1a} + k_{1b} + k_{1c}) = 0.73 \pm 0.09$ with $k_1 = (4.08 \pm 0.37) \times 10^{-11}$ gives $k_{1b} = (2.98 \pm 0.46) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹. Based upon recent work in our laboratories [10,11] it seems reasonable to assign $k_{1a} = 0.5 \times k(\text{Cl}+\text{acetone}) = (1.05 \pm$ $(0.10) \times 10^{-12}$ [18], hence we conclude that $k_{1c} = (9.95 \pm 4.70) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹. These values give k_{1a} / $(k_{1a} + k_{1b} + k_{1c}) = 0.026 \pm 0.003, \quad k_{1b}/(k_{1a} + k_{1b} + k_{1c}) =$ 0.73 ± 0.09 , and $k_{1c}/(k_{1a} + k_{1b} + k_{1c}) = 0.24 \pm 0.09$. The reactivity of Cl atoms towards the CH₃- and -CH₂- groups in *n*-butane is 3.0×10^{-11} and 7.3×10^{-11} cm³ molecule⁻¹ s⁻¹, respectively [18]. Compared to *n*-butane, the CH₃- groups α and β to the C=O group in butanone are deactivated towards attack by Cl atoms by factors of approximately 30 and 3, respectively. The -CH₂- group in butanone is approximately a factor of 2.5 less reactive than those in *n*-butane.

It is of interest to compare the behavior of Cl atoms with OH radicals. The reaction of OH radicals with butanone proceeds with a rate constant of 1.2×10^{-12} cm³ molecule⁻¹ s⁻¹ at 298 K [18] with $62 \pm 2\%$ of reaction at the $-CH_2$ - site [19]. Hence, reaction at the $-CH_2$ - site has a rate constant of 7.44×10^{-13} cm³ molecule⁻¹ s⁻¹. The reaction of OH with *n*-butane has a rate constant of $2.3 \times$

 10^{-12} cm³ molecule⁻¹ s⁻¹ [18] with 87% of reaction occurring at the -CH₂- group [20]. Hence, reaction at each -CH₂- site has a rate constant of 1.00×10^{-12} cm³ molecule⁻¹ s⁻¹. The reactivity of OH radicals towards the -CH₂- group in butanone is approximately 25% less than that in *n*-butane. The reactivity of OH radicals towards each of the CH₃- groups in acetone (9.0 × 10⁻¹⁴ [18]) is approximately 40% less than in propane (1.54 × 10⁻¹³ cm³ molecule⁻¹ s⁻¹ [18,21]).

As with the Cl atom reactions, the presence of the >C=O group deactivates adjacent CH₃- and $-CH_{2}$ groups towards attack by OH radicals. However, the magnitude of the deactivation is much smaller for the OH radical reactions.

Thermochemistry offers the simplest explanation of the different magnitudes of the deactivating effect of the C=O group on the Cl atom and OH radical reactions. The strength of the H–OH bond (492 kJ mol⁻¹ [22]) is substantially greater than those of C-H bonds in alkanes (e.g., primary C–H in propane = 423 kJ mol^{-1} , secondary C-H in propane = 416 kJ mol⁻¹ [23]). In contrast, the strength of the H–Cl bond (432 kJ mol⁻¹) is close to those of the C-H bonds in alkanes (e.g., primary C-H in butane = 420 kJ mol^{-1} , secondary C–H in butane = 415 kJ mol⁻¹ [23]). Relatively small changes in the C-H bond strengths resulting from the introduction of the C=O group in the molecule may have significant impacts on the activation energy barriers and hence kinetics of the Cl atom reactions, particularly for attack on the CH₃group. However, it is worth noting that data from the IUPAC compilation [17] indicate that C-H bonds in $-CH_3$ groups α to the carbonyl group in acetaldehyde and acetone are actually weaker than C-H bonds in ethane and propane. Thermochemical arguments are not able to explain the differences in reactivities of -CH₃ groups in acetone, acetaldehyde, ethane, and propane. Theoretical studies of the thermochemistry and dynamics of the reactions of Cl atoms with ketones are needed to provide further insight into the factors affecting the reactions of Cl atoms with ketones.

Finally, we believe that the present work provides the first compelling evidence for a deactivating effect of the >C=O group on C–H bonds beyond the α position. Previous reports of a large and long range deactivating effect [24] were not confirmed in subsequent work [25,26]. We report here that the CH₃– group β to the >C=O group in butanone is approximately 3 times less reactive towards Cl atoms than CH₃– groups in alkanes. However, the magnitude of the deactivation observed at the β position is approximately 10 times less than observed at the α position. We conclude that for the reactions of Cl atoms with ketones, the deactivating effect of the >C=O group is large for α C–H bonds, modest for β C–H bonds, and probably

negligible for γ C–H bonds. Further experiments are required to confirm or refute this conclusion.

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