J. Phys. Chem. A **2004,** *108,* 7027−7031

Kinetic Study of the Gas-Phase Reactions of Cl Radicals with 3-Pentanone and 3-Hexanone

Alfonso Aranda,* Yolanda Díaz de Mera, Ana Rodríguez, Lorena Morales, and Ernesto Martínez

Facultad de Ciencias Químicas, Universidad de Castilla-La Mancha, Avda. Camilo José Cela, No. 10, 13071, Ciudad Real, Spain

Received: April 8, 2004; In Final Form: June 7, 2004

The discharge flow mass spectrometric technique has been used to determine the absolute rate coefficients of the gas-phase reactions of Cl atoms with 3-pentanone (1) and 3-hexanone (2) in the temperature range 260−333 K and at a total pressure of 1 Torr. The rate constant data (*k*(1) and *k*(2) at different temperatures) were used to derive the Arrhenius expressions, $k(1) = (1.5 \pm 0.7) \times 10^{-10} \exp[(-281 \pm 138)/T]$ cm^3 molecule^{-1} s^{-1} and $k(2) = (1.6 \pm 0.4) \times 10^{-9} \exp[(-884 \pm 69)/T]$ cm^3 molecule^{-1} s^{-1}. At 298 K and 1 Torr, the products of both reactions have been studied. Reactions 1 and 2 have been found to proceed through an abstraction mechanism, leading to HCl + $C_5H_9(O)$ and HCl + $C_6H_{11}(O)$, respectively. The branching ratio for the abstraction channel was determined at 298 K and 1 Torr, as 0.97 ± 0.10 for reaction 1 and 0.98 ± 0.08 for reaction 2. The results obtained are related to previous studies, and the mechanism and atmospheric implications for both reactions are discussed.

Introduction

Ketones are important trace constituents of the Earth's troposphere. Like other volatile organic compounds (VOCs), ketones are emitted into the atmosphere from anthropogenic and biogenic sources[1] and may also be formed in situ in the atmosphere as products of atmospheric transformation of other VOCs, being intermediate products in the NO_x photo oxidations of hydrocarbons. Although global emissions of VOCs from biogenic sources (mainly vegetation) dominate over anthropogenic sources, in urban areas, anthropogenic ones often dominate. Vegetation has been found to be a significant source for carbonyl compounds including ketones such as 3-pentanone.[2]

In relation to the tropospheric sinks, aliphatic ketones show a weak absorption spectrum in the region 220−370 nm resulting from a dipole-forbidden n−π* transition which may lead to photodissociation, generating organic free radicals in the lower troposphere. Furthermore, reaction with the hydroxyl radical is generally considered as the predominant gas-phase removal process during the day for the majority of the organics (VOCs) emitted into the troposphere. At night, the role of NO_3 radicals may be important as well.[3] In recent years, the oxidation of VOCs by the highly reactive chlorine atom has gained much attention. The main source of tropospheric Cl atoms is the photolysis of photolabile chlorine-containing molecules generated by heterogeneous reactions of sea salt aerosols.[4,5] Evidences for a significant role of Cl atoms in the marine boundary layer (MBL) have been obtained through field measurements of the relative degradation rates of saturated hydrocarbons, which show significant deviations from what can be explained by solely OH radical chemistry.[6] Since Cl reactions are usually very fast, it may also play a role in VOC−NO_x chemistry, in much the same manner as OH. Thus, it is important to obtain knowledge of the kinetics of these chemical reactions in order to evaluate their role in the atmospheric chemistry at global or regional scales.

Accurate estimations of the different atmospheric sinks for a given pollutant also require the knowledge of the temperature dependence of the rate coefficients and chemical mechanisms. Although kinetic rate constants generally decrease when lowering temperature, many exceptions to the classical Arrhenius behavior are found. Thus, for example, Wollenhaupt et al.[7] have recently shown that the rate constant for the OH−acetone reaction in the upper troposphere, at low temperatures, was significantly higher than expected by extrapolating data from results around room temperature, due to a change in the reaction mechanism.

A similar behavior is also possible for Cl−ketones reactions. Thus, in this work, we report a kinetic and mechanistic study at 1 Torr in the temperature range 260−333 K for the reaction of Cl with 3-pentanone (1) and 3-hexanone (2). To the authors' knowledge, only one study has been made for these reactions, Albaladejo et al.,[8] who reported the rate coefficients for reactions 1 and 2 at 298 K in the pressure range 20−200 Torr. Nevertheless, concerning the temperature dependence or the reaction mechanism, no study has been carried out previously. Several studies have been carried out, however, for the reactions of 3-pentanone and 3-hexanone with OH radicals[9−11] and HO_2.[12]

Experimental Section

The experimental system used in this study, Figure 1, has been described in detail previously;[13,14] therefore, only a brief description is given here. All the kinetic and mechanistic experiments in this work were conducted using the absolute technique of discharge flow mass spectrometry (DF-MS). The flow reactor was provided with a jacket for the circulation of the thermostating liquid. To reduce the wall loss of Cl atoms, the inner surfaces of the reactor and the sidearm tube were coated with halocarbon wax. The reactions between the Cl

---

* To whom correspondence may be addressed. Phone: +34 926 29 53 00. Fax: +34 926 29 53 18. E-mail: alfonso.aranda@uclm.es.

10.1021/jp040279w CCC: $27.50 © 2004 American Chemical Society
Published on Web 08/04/2004

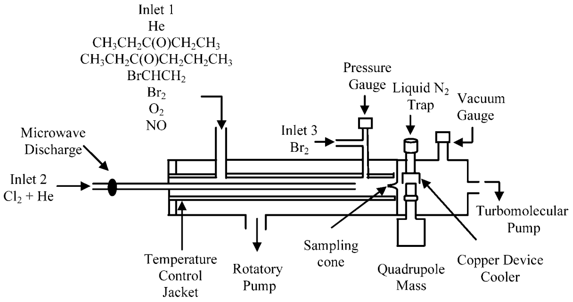

Figure 1. Schematic diagram of the experimental system.

radical and the organic molecules were followed downstream of the end of the axial injector with 3-pentanone and 3-hexanone entering through the sidearm (inlet 1) and Cl atoms through the central injector (inlet 2). Helium was used as the carrier gas in all the experiments.

All the reactants were diluted in helium and stored in bulbs of known volume. 3-Pentanone and 3-hexanone concentrations in the reactor were calculated from their relative flows given by calibrated mass flow controllers. The flows of the helium carrier gas in the reactor and the injector were also regulated and measured with mass flow controllers to get the required concentrations and flow velocities.

Typical concentrations of organic compounds were $(2.5-15) \times 10^{12}$ molecule cm^{-3} with a detection limit of 1.5×10^{10} molecule cm^{-3} for 3-pentanone and 2×10^{10} molecule cm^{-3} for 3-hexanone. Both of them were followed by mass spectrometry at their parent peaks ($m/e = 86$ for 3-pentanone, and $m/e = 100$ for 3-hexanone). Cl atoms were produced by microwave discharge in Cl_2. The absolute concentration of Cl atoms was measured by titration with $BrCHCH_2$ in excess

$$Cl + BrCHCH_2 \rightarrow ClCHCH_2 + Br \qquad (3)$$

$k(3) = (1.43 \pm 0.29) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} [15] with mass spectrometric detection of $ClCHCH_2$ at $m/e = 62$. As it has been described elsewhere,[16] during a kinetic run, the remaining Cl atoms, which have not reacted for any given time of reaction, were scavenged by reaction with Br_2 (added at the end of the reactor, inlet 3), and detected as BrCl at $m/e = 116$

$$Cl + Br_2 \rightarrow BrCl + Br \qquad (4)$$

$k(4) = (2.3 \pm 0.4) \times 10^{-10} \exp[-(135 \pm 60)/T]$ cm^3 molecule^{-1} s^{-1}.[17]

Br_2 was added in excess over the organic compound, ensuring the complete consumption of Cl atoms by Br_2. Typical concentrations for Cl atoms and Br_2 were $(3-6) \times 10^{11}$ and $(4-15) \times 10^{13}$ molecule cm^{-3}, respectively, and detection limit for Br_2 and Cl atoms, were 1×10^{10} and 5×10^{9} molecule cm^{-3}, respectively.

The chemicals used were as follows: He (Praxair, 99.999%), Cl_2 (Praxair, 99.8%), Br_2 (Fluka, ≥99.5%), $CH_3CH_2C(O)CH_2CH_3$ (Aldrich, >99%), $CH_3CH_2C(O)CH_2CH_2CH_3$ (Aldrich, 98%), $BrCHCH_2$ (Aldrich, 98%), $ClCHCH_2$ (Fluka, ≥99.5%), HCl (Aldrich, >99%), NO (Praxair, 99%), and O_2 (Praxair, 99.999%).

Results and Discussion

The experiments were carried out at 1 Torr total pressure within the temperature range, 260−333 K for 3-pentanone and 263−333 K for 3-hexanone, and flow velocities in the range 11−15 m s^{-1}. Preliminary experiments were conducted in which the reactions between Cl_2 (precursor of Cl atoms) and Br_2 (used to produce BrCl) with ketones were evaluated. No reaction was observed within the contact time used in the experiments.

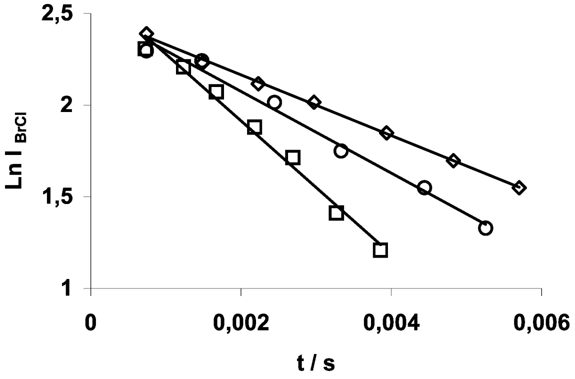

Figure 2. Typical pseudo-first-order decays of BrCl for the Cl + $CH_3CH_2C(O)CH_2CH_3$ (1) reaction at 315 K and 1 Torr: $[CH_3CH_2C(O)CH_2CH_3]$ = 2.98 (◇), 4.54 (○), 7.42 (□), in units of 10^{12} molecule cm^{-3}.

Kinetic measurements were made under pseudo-first-order conditions with ketones concentrations (3-pentanone and 3-hexanone) in excess over Cl radicals

$$Cl + CH_3CH_2C(O)CH_2CH_3 \rightarrow \text{products} \qquad (1)$$

$$Cl + CH_3CH_2C(O)CH_2CH_2CH_3 \rightarrow \text{products} \qquad (2)$$

The kinetic equation applying to such experiments was

$$\ln[Cl]_t = \ln[Cl]_0 - k't$$

where $k' = k[\text{ketone}] + k_w$, with k_w being the heterogeneous wall losses of Cl in the reactor.

For the low pressure and radical concentrations used, Cl self-reaction termolecular does not contribute to the observed temporal concentration profiles. The heterogeneous losses of Cl atoms in the reactor were measured in the absence of organic compound monitoring the formation of BrCl through reaction 4. Br_2 and Cl were introduced through inlets 3 and 2 respectively, like in the experimental kinetic runs, and BrCl was measured for different positions of the injector. K_w was also measured at all the temperatures used in this work (from 260 to 333 K). Within this range, k_w increased slightly with decreasing T. The average values obtained for k_w were 26 ± 7 s^{-1} and 35 ± 8 s^{-1} at 333 and 260 K, respectively.

Typical pseudo-first-order plots for the reaction of 3-pentanone (1) are shown, as an example for both reactions 1 and 2, in Figure 2. After fitting, the obtained values of k' were corrected to take into account the axial and radial diffusion of Cl atoms.[18] The diffusion coefficient of Cl in He was calculated from the volumes of atomic diffusion.[19] The values obtained for the temperature range used (260−333 K) were: $D_{Cl/He}$ = 400−610 cm^2 s^{-1}, giving to maximum corrections due to diffusions of 22 and 31% on k' for reactions 1 and 2, respectively.

The corrected first-order k' values of reactions 1 and 2 at a given temperature were plotted against the reactant concentration and the second-order rate constants were obtained as the slope of least-squares fits of these data. Typical results are shown in Figure 3. Linear behavior and near-zero intercepts are consistent with the proposed kinetic analysis. In Table 1, we summarize the results for all the experimental conditions.

Within the range of temperatures studied, the reaction rate constants are found to increase with increasing temperature for

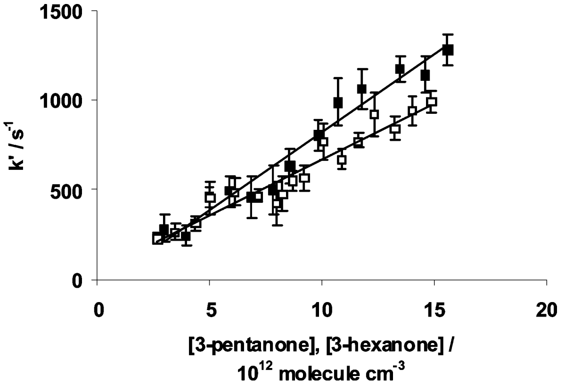

Figure 3. Plots of the diffusion-corrected pseudo-first-order rate constants, k', vs organic compound concentration for data obtained at $p = 1$ Torr and 298 K: 3-pentanone (□); 3-hexanone (■). Errors are 2σ.

TABLE 1: Second-Order Rate Constants for the Reactions Cl + 3-Pentanone (1) and Cl + 3-Hexanone (2) at Different Temperatures and $p = 1$ Torr[a]

3-pentanone		3-hexanone	
$T = 260$ K	5.4 ± 1.6	$T = 263$ K	5.2 ± 1.7
$T = 274$ K	5.6 ± 0.9	$T = 279$ K	6.6 ± 0.9
$T = 288$ K	5.5 ± 0.4	$T = 298$ K	8.3 ± 1.7
$T = 298$ K	5.9 ± 0.5	$T = 315$ K	9.4 ± 1.0
$T = 315$ K	6.0 ± 0.4	$T = 333$ K	10.9 ± 1.3
$T = 333$ K	6.6 ± 0.6		

[a] $k \pm 2\sigma$ in units of 10^{-11} cm^3 molecule^{-1} s^{-1}.

both reactions 1 and 2 and the Arrhenius equation applies to these results as it may be seen in Figure 4. A linear least-squares analysis of the data yields the activation energy, the pre-exponential factor, and affords the calculation of the kinetic rate constants $k(1)$ and $k(2)$ through the following equation at 1 Torr of pressure

$$k(1) = (1.5 \pm 0.7) \times 10^{-10} \exp[(-281 \pm 138)/T]\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}} \quad T = 260{-}333\ \mathrm{K}$$

$$k(2) = (1.6 \pm 0.4) \times 10^{-9} \exp[(-884 \pm 69)/T]\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}} \quad T = 263{-}333\ \mathrm{K}$$

where the quoted uncertainties represent 2σ.

As cited in the Introduction, to the authors knowledge, only one study has been made earlier for reactions 1 and 2. Albaladejo et al.[8] studied these reactions at 298 K in the pressure range of 20−200 Torr by an absolute technique. The coefficients did not show any pressure dependence in the range studied, and the final results are the weighted average of the measurements at three different pressures. The rate coefficients obtained by these authors (in units of cm^3 molecule^{-1} s^{-1}) are $(4.50 \pm 0.32) \times 10^{-11}$ for 3-pentanone and $(6.69 \pm 0.62) \times 10^{-11}$ for 3-hexanone. Our results at 298 K, $k(1) = (5.9 \pm 0.5) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} and $k(2) = (8.3 \pm 1.7) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, are in agreement with the data obtained by Albaladejo et al. [8] if we consider the error limits. Nevertheless, a more recent work[20] reveals that those results[8] could be affected by problems due to regeneration of Cl.

Further experiments were conducted to identify the products and intermediates of reactions at 298 K and 1 Torr by increasing the concentration of the reactants and in absence of Br_2. In these experiments, [3-pentanone] and [3-hexanone] ranged from 8×10^{12} to 1×10^{13} molecule cm^{-3} and [Cl] from 2.5×10^{12} to 5×10^{12} atom cm^{-3}. The studied reactions are expected to proceed through an H-abstraction mechanism

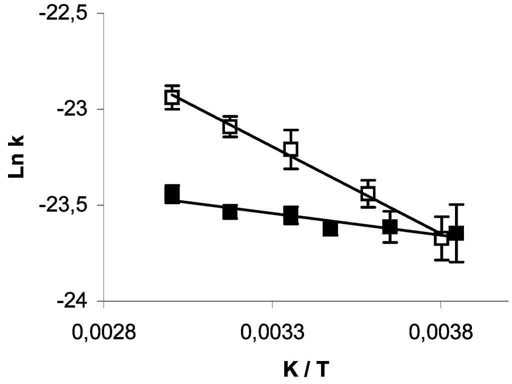

Figure 4. Temperature dependence of the reactions rate constants Cl + 3-pentanone (□) and Cl + 3-hexanone (■) for a total pressure of 1 Torr helium. Errors are 2σ.

$$CH_3CH_2C(O)CH_2CH_3 + Cl \rightarrow C_5H_9(O) + HCl \quad (1a)$$

$$CH_3CH_2C(O)CH_2CH_2CH_3 + Cl \rightarrow C_6H_{11}(O) + HCl \quad (2a)$$

Nevertheless, a mechanism involving an association complex through electrophillic addition of Cl to the carbonyl C atom, favored by the high electron density available within the carbonyl group must be also considered

$$CH_3CH_2C(O)CH_2CH_3 + Cl \rightleftharpoons [ClC_5H_{10}(O)]^* \quad (1b)$$

$$CH_3CH_2C(O)CH_2CH_2CH_3 + Cl \rightleftharpoons [ClC_6H_{12}(O)]^* \quad (2b)$$

In fact, this behavior was suggested to explain the temperature dependence of the rate coefficients of the acetone−OH reaction.[7] Wollenhaupt et al.[7] observed that, at low temperatures, the reaction no longer proceeds via H abstraction and that an association complex could be formed and be sufficiently stabilized to lead to products formation.

For reaction 1, the main signals corresponding to the formation of products, which increased as a function of time, were observed at $m/e = 36$ and 38, which may be assigned to HCl production from the abstraction channel (1a). From these results, radicals $C_5H_9(O)$ should be also produced in reaction 1. Thus, we tried to capture these intermediates through chemical reaction. In this sense, they are expected to react with molecular chlorine[21] and so additional Cl_2 was added through inlet 1 in concentrations up to 3×10^{13} molecule cm^{-3}. Under such conditions, low intensity signals increasing with the time of reaction at $m/e = 120$ and 122 could be observed. They may tentatively be attributed to the subsequent reaction of $C_5H_9(O)$ (formed in (1a) reaction) with Cl_2 molecules giving the chlorinated species $C_5H_9(O)Cl$, considering the two different isomeric species (with ^{35}Cl and ^{37}Cl)

$$C_5H_9(O) + Cl_2 \rightarrow C_5H_9(O)Cl + Cl \quad (5)$$

A similar procedure was followed in relation to reaction 2. Signals increasing with time were obtained at $m/e = 36$ and 38. With additional Cl_2, signals at $m/e = 134$ and 136 were also observed, confirming a mechanism similar to that of reaction 1, that is, the formation of HCl and the $C_6H_{11}(O)$ radicals that we could chemically capture with reaction with Cl_2

$$C_6H_{11}(O) + Cl_2 \rightarrow C_6H_{11}(O)Cl + Cl \quad (6)$$

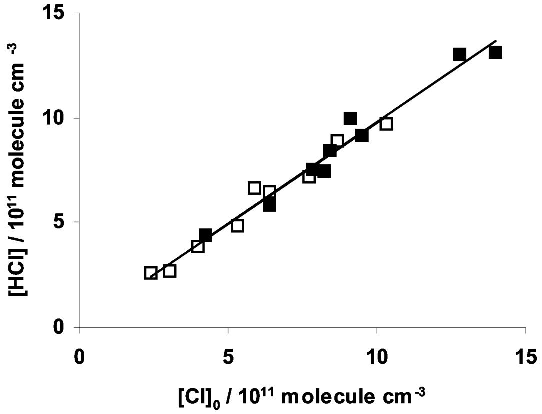

Figure 5. Experimental plots for HCl concentration formed in reactions of Cl + 3-pentanone (☐) and Cl + 3-hexanone (■) vs the initial Cl atom concentration at 298 K and 1 Torr.

These results show that reactions 1 and 2 follow the same mechanism, as expected.

In separate experiments, carried out at 1 Torr and 298 K, we have quantified the yield of the abstraction channel by measuring the concentrations of the direct product HCl in reactions 1 and 2 as in previous works.[16,22] The HCl background and signal were obtained by two different methods. First, with the discharge off and in the presence of Cl_2 and the ketone, the residual signal was measured. Then, with the discharge on, the HCl formed was measured. Second, to ensure that the HCl residual signal was not affected by the discharge itself, Br_2 was added alternatively through inlet 1, together with the ketone, to get the zero (all the chlorine atoms giving BrCl) and through inlet 3 (ketone always through inlet 1) to measure the HCl. Results obtained by these two methods were the same.

The signal of HCl was calibrated by measuring a reference absolute concentration of HCl coming from a freshly prepared storage bulb of known volume. The reaction time was fixed at ca. 15×10^{-3} s for reactions 1 and 2 to ensure the maximum production of HCl from a given initial concentration of Cl atoms. It was verified that for larger times of reaction HCl production remained constant. The quantification of initial Cl atoms concentrations was carried out by means of reaction 3 as described in the Experimental Section. The concentration ranges for reaction 1 were $(5-9) \times 10^{12}$, $(4-13) \times 10^{13}$, and $(2.5-10) \times 10^{11}$ molecule cm^{-3} for 3-pentanone, Br_2, and Cl, respectively. For reaction 2, concentrations were $(4-10) \times 10^{12}$, $(5-14) \times 10^{13}$, and $(4-14) \times 10^{11}$ for 3-hexanone, Br_2, and Cl, respectively. Results obtained for both reactions are presented in Figure 5 as the dependence of HCl concentrations produced in reactions 1 and 2 vs initial concentration of Cl atoms. The ratio $k(\mathrm{HCl})/k = [\mathrm{HCl}]/[\mathrm{Cl}]_0$ can be derived from the slopes of the straight lines in Figure 5. The obtained results at 298 K and 1 Torr were $k(1,\mathrm{HCl})/k(1) = 0.97 \pm 0.10$ and $k(2,\mathrm{HCl})/k(2) = 0.98 \pm 0.08$, where errors are 2σ, showing that the dominant, if not exclusive, pathway for both reactions of Cl with 3-pentanone and 3-hexanone is the abstraction channel at room temperature and 1 Torr.

The linearity in the Arrhenius plots, Figure 4, also suggests that no change of the reaction mechanism occurs within the range of temperature 260−333 K for reactions 1 and 2. For the OH−acetone reaction, temperatures down to 200 K could be studied[7] with arising evident curvature in the Arrhenius plot at 300 K and below. Although we cannot discard such a behavior for reactions 1 and 2 at temperatures below the range our experimental system affords, the results for the reaction of chlorine atoms with acetone[23] show that it proceeds through an abstraction mechanism in the whole range of temperature studied (298 down to 215 K). The same was observed for Cl−cyclohexanone for temperatures from 273 to 333 K.[20] No further data are available for reactions of Cl atoms with ketones as a function of temperature in the low-temperature region, so additional studies are required. Furthermore, the study of Albaladejo et al.[8] shows that the rate coefficients of reactions 1 and 2 are not pressure dependent, which suggests that the H-atom abstraction mechanism also prevails at higher pressures. Thus, the data obtained in this work for the kinetic rate constants, products, and temperature dependence also appleis to atmospheric pressure.

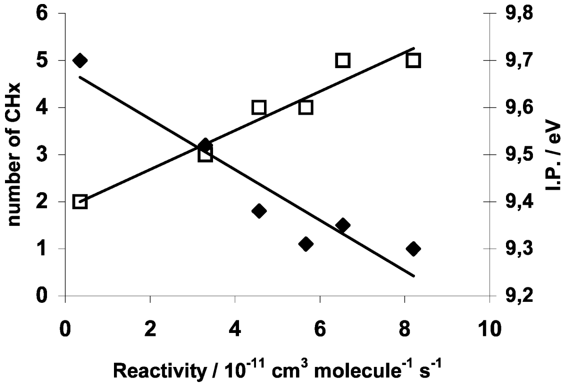

Figure 6. Correlations of the reactivity (kinetic rate constant at room temperature) vs the number of CH_x groups, ☐, and the ionization potential, ◆,[29] for straight-chain aliphatic ketones reactions with Cl. k_{acetone} is from ref 26; $k_{2-\mathrm{butanone}}$, $k_{2-\mathrm{pentanone}}$, and $k_{2-\mathrm{hexanone}}$ are from ref 8; $k_{3-\mathrm{pentanone}}$ and $k_{3-\mathrm{hexanone}}$ are from this work.

Any H atom in the aliphatic chain is susceptible to an oxidant attack. Generally, the radical (OH, NO_3, Cl...) will tend to abstract the most weakly bound hydrogen atom in the molecule.[24] In this sense, Sarzynski and Sztuba[25] have recently obtained the yield for abstraction of hydrogen attached to primary carbon as (29 ± 2)% and (71 ± 3)% for abstraction of hydrogen attached to secondary carbon. Thus, it is expected that reactions occur in a great percentage by H-atom abstraction from an α-secondary carbon atom, in the $CH_3CH_2C(O)CH_2CH_3$ + Cl reaction, and one of the three secondary carbon atom in the $CH_3CH_2C(O)CH_2CH_2CH_3$ + Cl reaction (two in α-position and one in β-position). Unfortunately, the selective detection by mass spectrometry of the different isomeric radicals was not possible. Our data show that the rate coefficients obtained in this work are due to the contributions of the different sites of reaction. In fact, if we take into account the available data in the literature for Cl−ketone reactions, Figure 6, the global rate coefficient clearly increases linearly with the number of CH_x groups, that is, with the inclusion of additional sites of reaction. A similar behavior has been observed for reactions of ketones with OH radical. [9−11]

Concerning the reactivity trend of the different ketones toward electrophillic radicals, it is expected to correlate with the H−C bond dissociation energy.[27] Furthermore, since in the transition state of an H-abstraction process the electron density of the relevant bond is lower than in the original substrate, a certain degree of correlation between the kinetic data and the ionization potential can be expected. This fact has been previously observed for H-abstraction reactions by NO_3 radical[28] and Cl.[27] From the available data for Cl− ketones reactions, see Figure 6, and the results from this work, such a dependence is clearly observed.

Atmospheric Implications. Several studies of the different atmospheric sinks of 3-pentanone and 3 hexanone have been carried out previous to this work. Gierczak et al.[12] studied the possible reaction of HO_2 with different ketones, including 3-pentanone, at 298 K and (1.5−3) Torr with an absolute technique. They did not observe reactive losses of HO_2 in any of the studied reactions (with an upper limit of $<4 \times 10^{-16}$ cm^3 $molecule^{-1}$ s^{-1} for reaction of HO_2 atoms with 3-pentanone) and concluded that those reactions are unlikely to be important loss processes for ketones in the atmosphere. With regards to the OH radical, Atkinson et al.[9,11] studied the reactions of a series of ketones using a relative method at 299 ± 2 K and 0.98 bar with $k = 2.05 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} and 6.95×10^{-12} cm^3 $molecule^{-1}$ s^{-1} for 3-pentanone and 3-hexanone, respectively. Wallington and Kurylo[10] also studied a series of ketones (including 3-pentanone) using an absolute technique over the temperature range 240−440 K and at total pressures between 25 and 50 Torr. They obtained $k = 2.74 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} for the OH−3-pentanone reaction.

Martínez et al.[30] reported the absorption spectra of several aliphatic aldehydes and ketones (including 3-pentanone). It was shown that such ketones absorb actinic radiation in the range 280−340 nm. For 3-pentanone, noontime photolysis rate constants (upper limits) at 40 °N at sea level under cloudless conditions of 3.7×10^{-6} s^{-1} and 13.0×10^{-6} s^{-1} were obtained for 1 January and 1 July, respectively. From the spectra of the different studied ketones,[30] it is expected a similar behavior for 3-hexanone.

From the previous results, an estimation of the gas-phase lifetime for 3-pentanone and 3-hexanone in the marine boundary layer (MBL) may be obtained for their reactions toward tropospheric agents such as OH and Cl and photodissociation. The lifetime can be derived from the values for the rate constant at room temperature and, taking into account the average concentration in remote areas, in the MBL. The atmospheric lifetimes of 3-pentanone and 3-hexanone from their reactions with Cl atoms, ($k(1)$ and $k(2)$ at 298 K), are $\tau = 1/(k[Cl]) =$ 490 and 337 h for 3-pentanone and 3-hexanone, respectively, with $[Cl] = 1 \times 10^4$ atoms cm^{-3}.[31] The gas-phase lifetime of these ketones toward its reaction with OH radicals may be calculated using $[OH] = 5 \times 10^5$ molecule cm^{-3}.[32] For 3-pentanone, with a rate constant of 2.05×10^{-12} cm^3 $molecule^{-1}$ cm^{-3},[11] the lifetime can be determined as 271 h, and for 3-hexanone, with a rate constant of 6.95×10^{-12} cm^3 $molecule^{-1}$ cm^{-3},[9] $\tau = 80$ h. From the photolysis rate constants, the lifetimes range from 21 to 75 h. The calculated lifetimes indicate that photodissociation and gas-phase reactions with OH radicals will dominate over reactions with Cl atoms. Nevertheless we must remember that the photolysis rate constants are upper limits, that is, they were estimated assuming a photodissociation quantum yield of unity. Thus, the real contribution of photolysis is subject to high uncertainty and it may even be of minor importance. On the other hand, the potential role of Cl in the troposphere is also quite uncertain due to the lack of agreement regarding its concentration. Thus, for example, local Cl concentration in the MBL may be as high as 1×10^5 atoms cm^{-3},[33] giving $\tau = 49$ and 34 h for reactions 1 and 2, respectively. Furthermore in the MBL in coastal urban areas, Cl concentrations peak at dawn much earlier than OH. For these reasons, Cl reactions may play a significant role as a reactive sink for ketones in the troposphere.

Acknowledgment. The authors gratefully thank the Spanish Dirección General de Enseñanza Superior e Investigación Científica (BQU 2001-157-4 Contract) and the Consejería de Ciencia y Tecnología (Junta de Comunidades de Castilla-La Mancha) for their finantial support.

References and Notes

(1) Atkinson, R.; Arey, J. *Chem. Rev.* **2003**, *103*, 4605.

(2) König, G.; Brunda, M.; Puxbaum, H.; Hewit, C. N.; Duckham, S. C.; Rudolph, J. *Atmos. Environ.* **1995**, *29*, 861.

(3) Finlayson-Pitts, B. J.; Pitts, J. N., Jr. *Chemistry of the Upper and Lower Atmosphere: Theory, Experiments, and Applications;* Wiley: New York, 2000.

(4) Singh, H. B.; Kasting, J. F. *J. Atmos. Chem.* **1988**, *7*, 261.

(5) Finlayson-Pitts, B. J. *Res. Chem. Intermed.* **1993**, *19*, 235.

(6) Jobson, B. T.; Niki, H.; Yokouchi, Y.; Bottenheim, J.; Hopper, F.; Leaitch, R. *J. Geophys. Res., [Atmos.]* **1994**, *99*, 25355.

(7) Wollenhaupt, M.; Crowley, N. *J. Phys. Chem.* A **2000**, *104*, 6429.

(8) Albaladejo, J.; Notario, A.; Cuevas, C. A.; Jiménez, E.; Cabañas, B.; Martínez, E. *Atmos. Environ.* **2002**, *37*, 455.

(9) Atkinson, R.; Aschmann, S. M.; Carter, W. P. L.; Pitts, J. N., Jr. *Int. J. Chem. Kinet.* **1982**, *14*, 839.

(10) Wallington, T. J.; Kurylo, M. J. *J. Phys. Chem.* **1987**, *91*, 5050.

(11) Atkinson, R.; Aschmann, S. M. *J. Phys. Chem.* **1988**, *92*, 4008.

(12) Gierczak, T.; Ravishankara, A. R. *Int. J. Chem. Kinet.* **2000**, *32*, 573.

(13) Martínez, E.; Aranda, A.; Díaz de Mera, Y.; Rodríguez, D.; López, M. R.; Albaladejo, J. *Environ. Sci. Technol.* **2002**, *36*, 1226.

(14) Díaz de Mera, Y.; Aranda, A.; Rodríguez, D.; López, R.; Cabañas, B.; Martínez, E. *J. Phys. Chem. A* **2002**, *106*, 8627.

(15) Park, J.; Slagle, I. R.; Gutman, D. *J. Phys. Chem. A* **1983**, *101*, 5776.

(16) Rodríguez, D.; Aranda, A.; Díaz de Mera, Y.; Ballesteros, B.; Martínez, E. *Phys. Chem. Chem. Phys.* **2003**, *5*, 514.

(17) Bedjanian, Y.; Laverdet, G.; Le Bras, G. *J. Phys. Chem. A* **1998**, *102*, 953.

(18) Kaufman, F. *J. Phys. Chem.* **1984**, *88*, 4909.

(19) Gilliland, E. R.; Sherwood, T. K.; *Ind. Eng. Chem.* **1934**, *26*, 516.

(20) Martínez, E.; Aranda, A.; Díaz-de-Mera, Y.; Rodríguez, A.; Rodríguez, D.; Notario, A. *J. Atmos. Chem.*, in press.

(21) Tyndall, G. S.; Orlando, J. J.; Wallington, T. J.; Dill, M.; Kaiser, E. W. *Int. J. Chem. Kinet*. **1997**, 29, 43.

(22) Aranda, A.; Díaz de Mera, Y.; Rodríguez, A.; Martínez, E. *J. Phys. Chem. A* **2003**, *107*, 5717.

(23) Orlando, J. J.; Tyndall, G. S.; Vereecken, L.; Peeters, J. *J. Phys. Chem. A* **2000**, *104*, 11578.

(24) Seinfeld, J. H.; Pandis, S. N. *Atmospheric Chemistry and Physics: From Pollution to Climate Change*; John Wiley & Sons: New York, 1998.

(25) Sarzynski, D.; Sztuba, B. *Int. J. Chem. Kinet.* **2002**, *34*, 651.

(26) Atkinson, R.; Baulch, D. L.; Cox, R. A.; Crowley, J. N.; Hampson, R. F, Jr.; Kerr, J. A.; Rossi, M. J.; Troe, J. IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry Web Version, November, 2003.

(27) Papadimitriou, V. C.; Kambanis, K. G.; Lazarou, Y. G.; Papagiannakopoulos, P. *J. Phys. Chem. A* **2004**, *108* (14), 2666.

(28) Wayne, R. P.; Barnes, I.; Biggs, P.; Burrows, J. P.; Canosa-Mas, C. E.; Hjorth, J.; Le Bras, G.; Moortgat, G. K.; Perner, D.; Poulet, G.; Restelli, G.; Siddebottom, H. *Atmos. Environ.* **1991**, *25* (1), 1.

(29) NIST Standard Reference Database Number 69, 2003 U. S. Secretary of Commerce on behalf of the U.S.A. http://webbook.nist.gov/chemistry.

(30) Martinez, R. D.; Buitrago, A. A.; Howell, N. W.; Hearn, C. H.; Joens, F. A. *Atmos. Environ.* **1992**, *26A*, 785.

(31) Wingenter, O. W.; Kubo, M. K.; Blake, N. J.; Smith, T. W.; Blake, D. R.; Rowland, F. S. *J. Geophys. Res.* **1996**, *101*, 4331.

(32) Brauers, T.; Aschmutat, U.; Brandenburger, U.; Dorn, H. P.; Hausmann, M.; Hessling, M.; Hofzumahaus, A.; Holland, F.; Plas-Dülmer, C.; Ehhalt, D. H. *Geophys. Res. Lett.* **1996**, *23*, 2545.

(33) Spicer, C. W.; Chapman, E. G.; Finlayson-Pitts, B. J.; Plastridge, R. A.; Hubbe, J. M.; Fast, J. D.; Berkowitz, C. M. *Nature* **1998**, *394*, 353.