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Kinetic Investigation of the OH Radical and Cl Atom Initiated Degradation of Unsaturated Ketones at Atmospheric Pressure and 298 K

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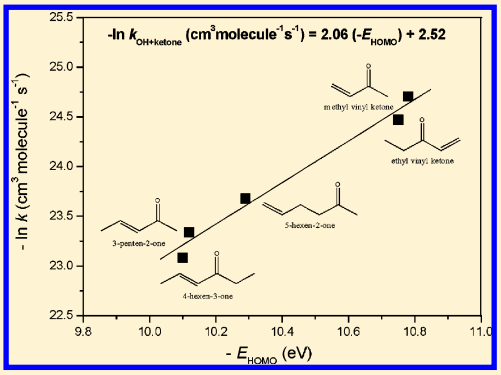
ABSTRACT: Rate coefficients for the reactions of hydroxyl radicals and chlorine atoms with 4-hexen-3-one, 5-hexen-2-one, and 3-penten-2-one have been determined at 298 ± 2 K and atmospheric pressure of air. Rate coefficients for the compounds were determined using a relative kinetic technique with different reference compounds. The experiments were performed in a large photoreactor (480 L) using in situ FTIR spectroscopy to monitor the decay of reactants. From the different measurements the following rate coefficients (in units of cm^3 $molecule^{-1}$ s^{-1}) have been determined: k_1(OH + 4-hexen-3-one) = (9.04 ± 2.12) × 10^{-11}, k_2(OH + 5-hexen-2-one) = (5.18 ± 1.27) × 10^{-11}, k_3(OH + 3-penten-2-one) = (7.22 ± 1.74) × 10^{-11}, k_4(Cl + 4-hexen-3-one) = (3.00 ± 0.58) × 10^{-10}, k_5(Cl + 5-hexen-2-one) = (3.15 ± 0.50) × 10^{-10} and k_6(Cl + 3-penten-2-one) = (2.53 ± 0.54) × 10^{-10}. The reactivity of the double bond in alkenes and unsaturated ketones at 298 K toward addition of OH radicals and Cl atoms are compared and discussed. In addition, a correlation between the reactivity of the unsaturated ketones toward OH radicals and the HOMO of the compounds is presented. On the basis of the kinetic measurements, the tropospheric lifetimes of 4-hexen-3-one, 5-hexen-2-one, and 3-penten-2-one with respect to their reaction with hydroxyl radicals are estimated to be between 2 and 3 h.



1. INTRODUCTION

Large quantities of anthropogenic and biogenic volatile organic compounds (VOCs) are emitted continuously into the atmosphere. Many of these compounds, such as aromatic hydrocarbons, esters, ethers, aldehydes, and ketones play an important role in the chemistry of polluted urban areas.[1]

There are a number of different sources that contribute to the presence of unsaturated ketones, such as 4-hexen-3-one, 5-hexen-2-one, and 3-penten-2-one, in the environment; emissions from mechanical and biological treatment plants,[2] production as intermediate products in the synthesis of perfume, use of insecticides and fungicide,[3] and biomass burning.[4] Field and laboratory studies show that these compounds are also released into the atmosphere from the wounded leaves of a variety of plants.[5−10]

It is well-established that the gas phase degradation of unsaturated ketones in the troposphere is initiated by reactions with OH and NO_3 radicals, O_3, and photolysis,[11−17] whereby reaction with OH radicals is clearly the most important process during the daytime.[11] Thus, the atmospheric reaction with OH radicals plays an important role in determining the contribution of the unsaturated ketones to the formation of tropospheric ozone and other secondary photooxidants. At night, their chemistry will be dominated by reaction with NO_3 radicals[11,13,16] and ozone can contribute to the oxidation of the unsaturated carbonyl compounds during both day and night.[1,11,13,17]

Until recently the chlorine atom initiated oxidation of VOCs has generally only been considered to be of importance in coastal and marine air environments where it has been shown that heterogeneous chemistry involving nitrogen oxides converts inorganic chloride into Cl atom precursors.[18−22] In a recent field study,[22] however, evidence has been presented for Cl chemistry in continental regions far removed from coastal and marine regions where observations of nitryl chloride ($ClNO_2$), a gaseous photolytic Cl atom precursor, were made. These observations suggest that Cl chemistry may possibly be ubiquitous in the atmosphere and play a significantly more important role than previously thought in the oxidizing capacity of the troposphere particularly in the early morning. In urban environments additional sources of Cl atoms due to industrial activities can exist; for example, in the vicinity of brick factories (e.g., heating of ceramic raw materials) concentrations of Cl atoms higher than the concentrations observed in marine coasts have been reported.[23]

Kinetic data and mechanistic information on all the important atmospheric degradation pathways of individual compounds

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are essential components in any attempts to reliably assess the possible contribution of these substances to the severe photochemical air pollution frequently experienced in urban and regional areas. Thus, in addition to knowledge on the kinetics of the dominant atmospheric oxidant OH with the unsaturated ketones, it would now appear that the kinetics of their reactions with Cl atoms is desirable because under some circumstances it is possible that this loss pathway may be quite significant or even dominate.

A kinetic study on the reactions of OH radicals and Cl atoms with 4-hexen-3-one, 5-hexen-2-one, and 3-penten-2-one performed in a photoreactor at 298 K and atmospheric pressure using a relative kinetic technique is presented.

$$CH_3CH{=}CHC(O)CH_2CH_3 + OH \rightarrow \text{products} \quad (k_1) \quad (1)$$

$$CH_3C(O)CH_2CH_2CH{=}CH_2 + OH \rightarrow \text{products} \quad (k_2) \quad (2)$$

$$CH_3CH{=}CHC(O)CH_3 + OH \rightarrow \text{products} \quad (k_3) \quad (3)$$

$$CH_3CH{=}CHC(O)CH_2CH_3 + Cl \rightarrow \text{products} \quad (k_4) \quad (4)$$

$$CH_3C(O)CH_2CH_2CH{=}CH_2 + Cl \rightarrow \text{products} \quad (k_5) \quad (5)$$

$$CH_3CH{=}CHC(O)CH_3 + Cl \rightarrow \text{products} \quad (k_6) \quad (6)$$

There is one previously reported rate coefficient for the reaction of OH radicals with 5-hexen-2-one (k_2) of $(4.49 \pm 1.02) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} obtained by Wang et al.[15] at atmospheric pressure and room temperature in a 100 L Teflon reaction chamber using a relative kinetic technique with three different reference compounds and gas chromatographic detection of the organics. Grosjeans and Williams,[12] using structure−reactivity (SAR) and linear free-energy relationships, have estimated rate coefficients for the reactions of OH radicals with 4-hexen-3-one (k_1) and 3-penten-2-one (k_3) of 4.3×10^{-11} and 4×10^{-11} cm^3 molecule^{-1} s^{-1}, respectively, at 298 K and atmospheric pressure. This work, therefore, is the first experimental kinetic study of the reaction of OH radicals with 4-hexen-3-one and 3-penten-2-one. To the best of our knowledge, this work provides the first kinetic study for the reactions of Cl atoms with $CH_3CH{=}CHC(O)CH_2CH_3$ (k_4), $CH_3C(O)CH_2CH_2CH{=}CH_2$ (k_5), and $CH_3CH{=}CHC(O)CH_3$ (k_6).

In addition, to the reported kinetic data (i) a comparison is made between the OH rate coefficients for the unsaturated ketones and the analogous alkenes and (ii) a correlation between and the HOMO (highest occupied molecular orbital) of the unsaturated ketones and the natural logarithm of the OH rate coefficient is examined. The atmospheric lifetimes of the VOCs studied, with respect to reaction with OH and Cl are calculated with the rate coefficients obtained in this work and compared with the lifetimes of these compounds due to other sinks in the troposphere.

2. EXPERIMENTAL SECTION

All the experiments were performed in a 480 L chamber at 298 ± 2 K in 1000 mbar of synthetic air. The chamber is composed of a cylindrical borosilicate glass vessel (3 m in length and 45 cm inner diameter) closed at both ends by aluminum end flanges. The metal flanges contain ports for the introduction of bath gases and reactants into the chamber. A magnetically coupled Teflon mixing fan is mounted inside the chamber to ensure homogeneous mixing of the reactants. The reactor contains 32 fluorescent lamps (Philips TLA 40 W, $300 \leq \lambda \leq 450$ nm, $\lambda_{max} = 360$ nm) spaced evenly around the outside of the reactor. It can be evacuated by a pumping system consisting of a turbomolecular pump backed by a double stage rotary fore pump to 10^{-3} Torr.

A White-type mirror system mounted internally in the chamber and coupled to a FTIR spectrometer Nicolet Magna 520 equipped with a liquid nitrogen cooled mercury−cadmium−telluride (MCT) detector enables in situ monitoring of the reactants in the infrared range 4000−700 cm^{-1}. The White mirror system was operated with the total optical absorption path length set to 48.11 m and infrared spectra were recorded with a spectral resolution of 1 cm^{-1}. Typically, 64 interferograms were coadded per spectrum over a period of approximately 1 min and 15 such spectra were recorded per experiment. The chamber is described in greater detail elsewhere.[24]

OH radicals were generated by the photolysis of CH_3ONO/NO/air mixtures with the fluorescent lamps,

$$CH_3ONO + h\nu \rightarrow CH_3O + NO \quad (7)$$

$$CH_3O + O_2 \rightarrow CH_2O + HO_2 \quad (8)$$

$$HO_2 + NO \rightarrow OH + NO_2 \quad (9)$$

and chlorine atoms were generated by the photolysis of Cl_2 in air also with the fluorescent lamps:

$$Cl_2 + h\nu \rightarrow 2Cl \quad (10)$$

The initial concentrations of reactants in ppmV (1 ppmV = 2.46×10^{13} molecules cm^{-3} at 298 K) were 4-hexen-3-one, (8−9); 5-hexen-2-one, (9−10); 3-penten-2-one, (9−11); methyl nitrite, (42); nitrogen monoxide, (10); Cl_2, (20); isobutene, (15−21); and 1-butene, (21).

The reactants were monitored at the following infrared absorption frequencies (in cm^{-1}): 4-hexen-3-one at 1113, 1203, 1113, 973.2; 5-hexen-2-one at 3090.6 and 1322.9; 3-penten-2-one at 1251.5; isobutene at 890 and 1-butene at 911.8.

3. MATERIALS

The following chemicals, with purities as stated by the supplier, were used without further purification: synthetic air (Air Liquide, 99.999%), 4-hexen-3-one (Aldrich, 90+%, predominantly trans), 5-hexen-2-one (Aldrich, 99%), 3-penten-2-one (Aldrich, 70%), isobutene (Messer Griesheim, 99%), 1-butene (Messer Griesheim, 99%), nitrogen monoxide (Messer Griesheim, 99%), and Cl_2 (Messer Griesheim, >99.8%). The suppliers do not specify the cis/trans isomer ratio for 3-penten-2-one. A major portion of the 30% impurity in 3-penten-2-one is mesityl oxide (4-methyl-3-penten-2-one).

Methyl nitrite was synthesized[25] by the dropwise addition of 50% H_2SO_4 to a saturated solution of sodium nitrite in methanol and was purified by vacuum distillation until a sample of 99% purity was obtained, confirmed by IR spectroscopy.

4. RESULTS

Rate coefficients for the reactions of OH radicals and Cl atoms with 4-hexen-3-one, 5-hexen-2-one, and 3-penten-2-one were determined by comparing their rate of decay with that of the corresponding decay of the two reference compounds 1-butene and isobutene:

$$X + \text{ketone} \rightarrow \text{products} \quad k_{\text{ketone}} \quad (11)$$

$$X + \text{reference} \rightarrow \text{products} \quad k_{\text{reference}} \quad (12)$$

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In the above equations X is either OH or Cl. Provided that the reference compound and the reactant are lost only by reactions 11 and 12, then it can be shown that

$$\ln\left\{\frac{[\text{ketone}]_0}{[\text{ketone}]_t}\right\} = \frac{k_{11}}{k_{12}} \ln\left\{\frac{[\text{reference}]_0}{[\text{reference}]_t}\right\} \quad \text{(I)}$$

where $[\text{ketone}]_0$, $[\text{reference}]_0$, $[\text{ketone}]_t$, and $[\text{reference}]_t$ are the concentrations of the unsaturated ketone compound under study and the reference compound at times $t = 0$ and t, respectively, and k_{11} and k_{12} are the rate coefficients of reactions 11 and 12, respectively.

The relative rate technique relies on the assumption that both the unsaturated compound and reference organics are removed solely by reaction with OH radicals or Cl atoms.

To verify this assumption, various tests were performed to assess possible additional loss of the unsaturated ketones and reference compounds via (i) dark reaction with the radical precursors methyl nitrite or molecular chlorine, (ii) photolysis in air in the absence of radical precursors, and (iii) wall deposition. Mixtures of the unsaturated ketones and reference compounds with CH_3ONO or Cl_2 were left in the dark in the chamber for the typical time span of the kinetic experiments (10−20 min) and mixtures of the unsaturated ketones and reference compounds were subjected to photolysis with the fluorescent lamps for periods of 30 min without the radical precursor. All of the tests showed that loss due to the three listed processes were negligible for both the unsaturated ketones and the reference compounds compared to the loss that occurred on OH radical or Cl atom photoinduced degradation.

Figures 1−3 show examples of the kinetic data, obtained from experiments on the reactions of OH radicals with the unsaturated ketones measured relative to 1-butene and isobutene, plotted according to eq I. Figure 4 shows examples of the kinetic data obtained from experiments on the reactions of Cl atoms with 5-hexen-2-one and 3-penten-2-one measured relative to isobutene, plotted according to eq I. In all cases each plot represents a minimum of three to four experiments for each reference compound. Reasonable linear relationships were obtained in all cases. The linearity of the plots with zero or near-zero intercepts, combined with the fact that similar results

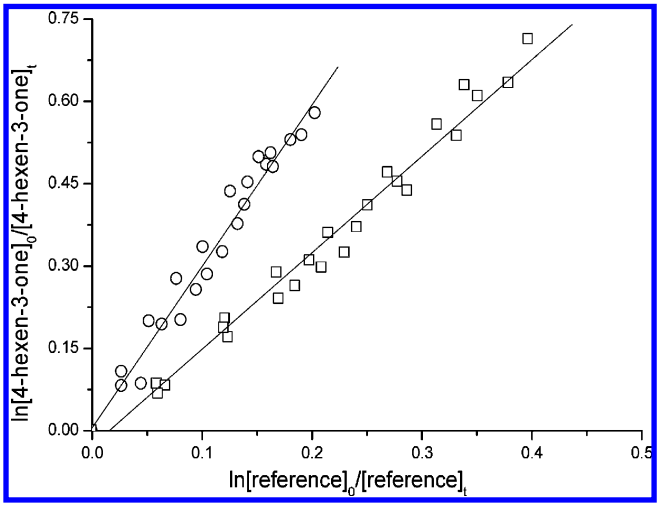

Figure 1. Plot of the kinetic data for the reaction of OH radicals with 4-hexen-3-one measured relative to 1-butene (○) and isobutene (□) at 298 ± 2 K and atmospheric pressure of air.

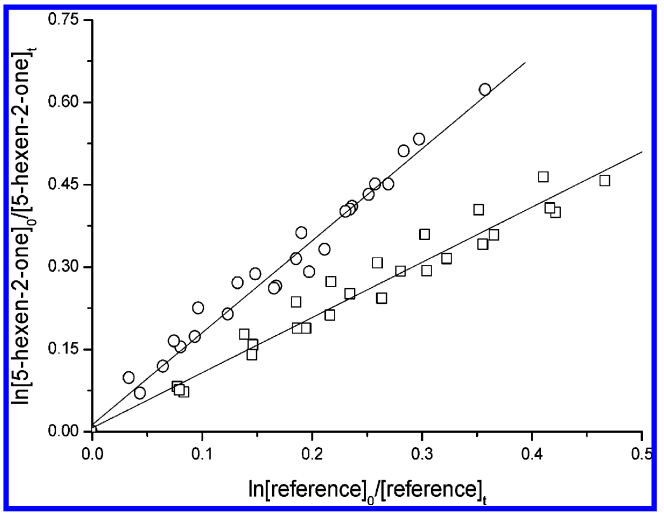

Figure 2. Plot of the kinetic data for the reaction of OH radicals with 5-hexen-2-one measured relative to 1-butene (○) and isobutene (□) at 298 ± 2 K and atmospheric pressure of air.

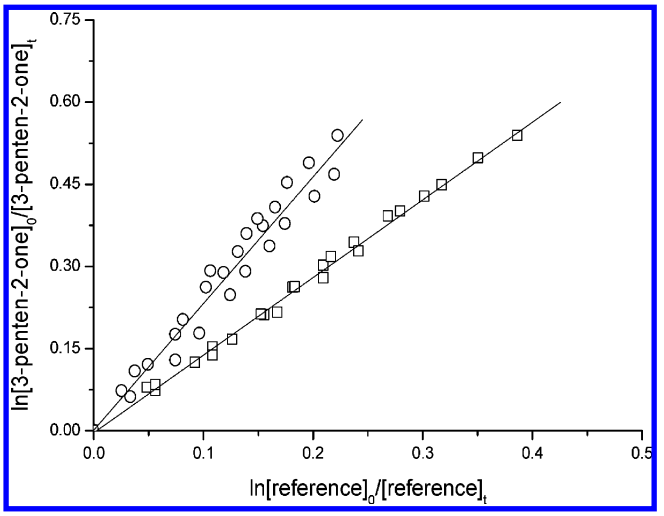

Figure 3. Plot of the kinetic data for the reaction of OH radicals with 3-penten-2-one measured relative to 1-butene (○) and isobutene (□) at 298 ± 2 K and atmospheric pressure of air.

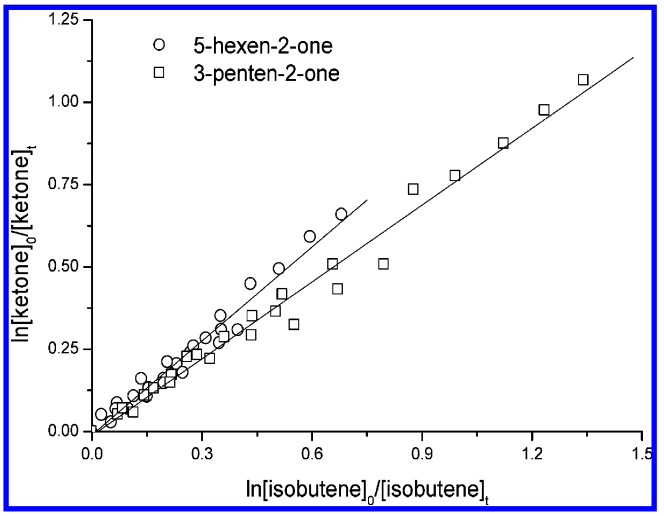

Figure 4. Plot of the kinetic data for the reactions of Cl atoms with 5-hexen-2-one (○) and 3-penten-2-one (□) measured relative to isobutene at 298 ± 2 K and atmospheric pressure of air.

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Table 1. Reference Compound, Measured Rate Coefficient Ratios, $k_{ketone}/k_{reference}$, and Rate Coefficients for the Reactions of OH Radicals and Cl Atoms with 4-Hexen-3-one, 5-Hexen-2-one, and 3-Penten-2-one Measured in 1000 mbar of Air at 298 K

reaction	reference	no. of runs	$k_{ketone}/k_{reference}$	k_{ketone} (cm^3 $molecule^{-1}$ s^{-1})
$CH_3CH{=}CHC(O)CH_2CH_3$ + OH	1-butene	3	2.91 ± 0.09	(9.14 ± 2.10) × 10^{-11}
(4-hexen-3-one)	isobutene	4	1.74 ± 0.05	(8.94 ± 2.05) × 10^{-11}
			average	**(9.04 ± 2.12) × 10^{-11}**
$CH_3C(O)CH_2CH_2CH{=}CH_2$ + OH	1-butene	3	1.66 ± 0.05	(5.21 ± 1.20) × 10^{-11}
(5-hexen-2-one)	isobutene	3	1.00 ± 0.04	(5.14 ± 1.23) × 10^{-11}
			average	**(5.18 ± 1.27) × 10^{-11}**
$CH_3CH{=}CHC(O)CH_3$ + OH	1-butene	3	2.29 ± 0.09	(7.19 ± 1.71) × 10^{-11}
(3-penten-2-one)	isobutene	3	1.41 ± 0.02	(7.25 ± 1.55) × 10^{-11}
			average	**(7.22 ± 1.74) × 10^{-11}**
$CH_3CH{=}CHC(O)CH_2CH_3$ + Cl	1-butene	4	0.99 ± 0.05	(2.97 ± 0.55) × 10^{-10}
(4-hexen-3-one)	isobutene	3	0.89 ± 0.03	(3.03 ± 0.35) × 10^{-10}
			average	**(3.00 ± 0.58) × 10^{-10}**
$CH_3C(O)CH_2CH_2CH{=}CH_2$ + Cl	1-butene	3	1.02 ± 0.02	(3.06 ± 0.47) × 10^{-10}
(5-hexen-2-one)	isobutene	3	0.95 ± 0.03	(3.23 ± 0.36) × 10^{-10}
			average	**(3.15 ± 0.50) × 10^{-10}**
$CH_3CH{=}CHC(O)CH_3$ + Cl	1-butene	3	0.80 ± 0.03	(2.40 ± 0.41) × 10^{-10}
(3-penten-2-one)	isobutene	3	0.78 ± 0.02	(2.65 ± 0.28) × 10^{-10}
			average	**(2.53 ± 0.54) × 10^{-10}**

were obtained for different initial concentrations of the unsaturated ketones and reference organics, supports that complications due to secondary reactions in the experimental systems were negligible.

The $k_{ketone}/k_{reference}$ ratios determined from the slopes of the straight-line plots in Figures 1−4 are listed in Table 1 together with the number of experiments performed, and the absolute values of the rate coefficients, k_{ketone}, calculated from the $k_{ketone}/k_{reference}$ ratios. As stated in the Materials, the sample of 3-penten-2-one used in the experiments has a purity of only 70% and the majority of the impurity is due to mesityl oxide. However, the decay of both 3-penten-2-one and the reference hydrocarbons were monitored at infrared absorption frequencies that did not overlap with those of mesityl oxide, so the measured $k_{ketone}/k_{reference}$ ratios are considered to be free from interferences from mesityl oxide.

The rate coefficients for the reactions of OH and Cl with the unsaturated ketones were placed on an absolute basis using the following values for the reference reactions at 298 K: (3.14 ± 0.63) × 10^{-11} cm^3 $molecule^{-1}$ s^{-1} for OH + 1-butene,[11] (5.14 ± 1.03) × 10^{-11} cm^3 $molecule^{-1}$ s^{-1} for OH + isobutene,[11] (3.00 ± 0.40) × 10^{-10} cm^3 $molecule^{-1}$ s^{-1} for Cl + 1-butene,[26] and (3.40 ± 0.28) × 10^{-10} cm^3 $molecule^{-1}$ s^{-1} for Cl + isobutene.[27]

The errors for the $k_{ketone}/k_{reference}$ ratios given in Table 1 are the 2σ statistical errors from the scatter in the plots shown in Figures 1−4. The errors quoted for k_{ketone} are a combination of the 2σ statistical errors from the linear regression analysis plus an additional 20% error to cover potential uncertainties in the recommended values of the rate coefficients for the reference reactions.

For all the compounds investigated, there is good agreement between the values of k_{ketone} determined for both the OH and Cl reactions using the two reference compounds; therefore, we prefer to quote final values for the rate coefficients at 298 K that are averages of the two individually determined values with errors that encompass the extremes of both determinations:

$$k_1 = (9.04 \pm 2.12) \times 10^{-11}\ cm^3\ molecule^{-1}\ s^{-1}$$

$$k_2 = (5.18 \pm 1.27) \times 10^{-11}\ cm^3\ molecule^{-1}\ s^{-1}$$

$$k_3 = (7.22 \pm 1.74) \times 10^{-11}\ cm^3\ molecule^{-1}\ s^{-1}$$

$$k_4 = (3.00 \pm 0.58) \times 10^{-10}\ cm^3\ molecule^{-1}\ s^{-1}$$

$$k_5 = (3.15 \pm 0.50) \times 10^{-10}\ cm^3\ molecule^{-1}\ s^{-1}$$

$$k_6 = (2.53 \pm 0.54) \times 10^{-10}\ cm^3\ molecule^{-1}\ s^{-1}$$

5. DISCUSSION

OH Kinetics. The rate coefficient k_2 = (5.18 ± 1.27) × 10^{-11} cm^3 $molecule^{-1}$ s^{-1} obtained in this study for the reaction of OH radicals with 5-hexen-2-one is in very good agreement, within experimental error, with the recently reported value of k_2 = (4.49 ± 1.02) × 10^{-11} cm^3 $molecule^{-1}$ s^{-1} by Wang et al.[15] determined relative to the reactions of OH with methyl acrylate, cyclohexane, and isoprene in a 100 L Teflon chamber at 298 ± 1 K in 101 kPa of N_2 using H_2O_2 as the source of OH radicals and CG-FID for the analysis. However, the values of 4.3 × 10^{-11} and 4 × 10^{-11} cm^3 $molecule^{-1}s^{-1}$ estimated by Grosjean and Williams[12] for the reactions of OH radicals with 4-hexen-3-one (k_1) and 3-penten-2-one (k_3), respectively, using structure−reactivity and linear free-energy relationships are factors of 2.1 and 1.8 lower than the values determined experimentally in this study. The SAR method of Kwok and Atkinson[28] gives values (in units of 10^{-11} cm^3 $molecule^{-1}$ s^{-1}) of 3.09, 5.78 (trans-isomer), and 5.89 (trans-isomer) for the reactions of OH with 5-hexen-2-one, 3-penten-2-one, and 4-hexen-3-one, respectively. Although the SAR of Kwok and Atkinson[28] just captures the reactivity trend for the reactions determined in this work, $k_{5\text{-hexen-2-one}}$ (5.18) < $k_{3\text{-penten-2-one}}$ (7.22) < $k_{4\text{-hexen-3-one}}$ (9.04 × 10^{-11} cm^3 $molecule^{-1}$ s^{-1}), it underestimates the measured values in all cases, in particular, for 5-hexen-2-one and 4-hexen-3-one where the difference is about 40%.

Intuitively, one would expect the rate coefficient for the reaction of OH radicals with 4-hexen-3-one to be higher than that of 3-penten-2-one based simply on the extra $-CH_2-$ group in the structure with abstractable H-atoms. However, the difference between the rate coefficient for the reaction of OH with 4-hexen-3-one and that of OH with 3-penten-2-one is

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Table 2. Comparison of the Rate Coefficients k for the Reactions of OH with Unsaturated Ketones and Their Analogue Alkenes and Alkyl Esters[a]

$CH{=}CH_2C(O)CH_3$ (methyl vinyl ketone) k = 1.86[b]	$CH_3CH{=}CHC(O)CH_3$ (3-penten-2-one) k = 7.22[c]	$CH_3CH{=}CHC(O)CH_2CH_3$ (4-hexen-3-one) k = 9.04[c]	$CH_2{=}CHCH_2CH_2C(O)CH_3$ (5-hexen-2-one) k = 5.18[c]
$CH{=}CH_2CH_3$ (propene) k = 2.63[b]	$CH_3CH{=}CH_2CH_3$ (2-butene) k = 6.40[b] (trans), 5.64[b] (cis)	$CH_3CH{=}CH_2CH_2CH_3$ (2-pentene) k = 6.7[b] (trans), 6.5[b] (cis)	$CH_2{=}CHCH_2CH_2CH_3$ (1-pentene) k = 3.14[b]
$CH_2{=}CHC(O)OCH_3$ (methyl acrylate) k = 1.3[d]	$CH_2{=}C(CH_3)C(O)OCH_3$ (methyl methacrylate) k = 4.2[d]	$CH_2{=}C(CH_3)C(O)OCH_2CH_3$ (ethyl methacrylate) k = 4.6[e]	$CH_2{=}CHCH_2C(O)OCH_3$ (methyl-3-butenoate) k = 3.16[f]

[a]The values of k are in units of 10^{-11} cm^3 molecule^{-1} s^{-1}. [b]Atkinson and Arey.[11] [c]This work. [d]Teruel et al.[31] [e]Blanco et al.[32] [f]Unpublished work from the University of Wuppertal.

1.82×10^{-11} cm^3 molecule^{-1} s^{-1}, which is over an order of magnitude higher than the value of 0.7×10^{-12} cm^3 molecule^{-1} s^{-1} quoted by Mellouki et al.[29] for H-atom abstraction by OH radicals from an $-CH_2-$ group in the α-position to the carbonyl group of an alkyl ketone ($RC(O)CH_2R'$).

Intuitively, one would also expect the OH rate coefficients for all of the unsaturated ketones investigated to be less than those of their analogous alkenes based simply on the deactivating effect of the CO group toward electrophilic reactions. However, as can be seen in Table 2 for the unsaturated ketones studied in this work, the analogous alkenes are all less reactive toward OH than the unsaturated ketones. This is especially difficult to understand in the cases of 4-hexen-3-one and 3-penten-2-one where the deactiving carbonyl group is attached directly to the double bond and one would expect the deactivating effect to be greatest. The unsaturated ketone methyl vinyl ketone has also been included in Table 2, and in this case a slight decrease in activity toward OH is observed compared to its analogue alkene propene. This is also the case for ethyl vinyl ketone, which has a reported rate coefficient of 2.36×10^{-11} cm^3 molecule^{-1} s^{-1} at 298 K[30] compared to a rate coefficient of 3.14×10^{-11} cm^3 molecule^{-1} s^{-1} for 1-butene.[11] However, the difference is fairly small and in both cases the rate coefficients more or less agree within the combined reported error limits. Interestingly, the rate coefficients of OH with the unsaturated esters methyl acrylate ($CH_2{=}CHC(O)OCH_3$), methyl methacrylate ($CH_2{=}C(CH_3)C(O)OCH_3$), and ethyl methacrylate ($CH_2{=}C(CH_3)C(O)OCH_2CH_3$) are all somewhat lower than those of OH with their alkene anolgues.

The minimal effect on the OH rate coefficient for methyl and ethyl vinyl ketone compared to their alkene analogues and increase in rate coefficient for 4-hexen-3-one, 5-hexen-2-one, and 3-penten-2-one compared to their alkene analogues is difficult to rationalize. The evidence suggests that the mechanism of the OH addition to the double bond in the unsaturated ketones is possibly different from that for OH addition to alkenes. The mechanism may involve some form of hydrogen bonded complex between the OH and the carbonyl, as has been discussed in the literature for reactions of OH radicals with oxygenated organics,[29,33] which could explain the higher than expected rate coefficients. Such an effect could be augmented by the presence of electron donating alkyl groups, and this may explain the larger than expected rate coefficient for 4-hexen-3-one compared to 3-penten-2-one. However, at present this is only speculation and theoretical calculations on the reactions probably represent a good way of probing the possible effects of hydrogen bonding complexes on the reaction kinetics.

King et al.[34] have shown that it is possible to predict rate coefficients for the reactions of NO_3, OH, and O_3 with monalkenes and conjugated dienes using perturbation frontier molecular orbital (PFMO) theory. The basis of the PFMO approach is that the reactivity of a series of structurally similar organic compounds can be explained and correlated in terms of the frontier molecular orbitals. To a good approximation, King et al.[34] found that the natural logarithm of the room temperature rate coefficient k for the reactions of NO_3, OH, and O_3 with alkenes correlates linearly with the energy of the highest occupied molecular orbital (HOMO), E_{HOMO}, of the alkene for a small range of values of E_{HOMO}. The original correlation of King et al. for alkenes has been updated by Pfrang et al.,[35] and the concept has been shown to be applicable also to the reactions of NO_3, OH, and O_3 with unsaturated alcohols,[36] ethers,[36] esters,[37] and ketones.[37]

The electron density in the π-bond that is attacked by the OH radical should be reflected in the energy of the highest occupied molecular orbital (E_{HOMO}) with the lowest negative value being expected for the compound with the largest rate coefficient. To check the reactivity trend for the unsaturated ketones measured in this work, values of E_{HOMO} have been calculated using the Gaussian 03 package.[38] The geometry optimizations and initial values of energies were obtained at the Hartree−Fock (HF) level, and an ab initio Hamiltonian with a 6-31++ G(d,p) bases set was used. The self-consistent field energies were then calculated by Moller−Plesset perturbation theory (MP4-SCF) using an ab initio Hamiltonian with a 6-311++ G(d,p) basis set. The E_{HOMO} calculated for the unsaturated ketones (4-hexen-3-one, 5-hexen-2-one, 3-penten-2-one, methyl vinyl ketone, and ethyl vinyl ketone) are listed in Table 3. Figure 5 shows a plot of the natural logarithms of the OH rate coefficients plotted as a function of the calculated E_{HOMO} in electronvolts. A linear relationship with a correlation coefficient (r) = 0.99 is obtained. The linear relationship in Figure 5 is well described by

$$-\ln k_{OH+ketone}\ (\text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}) = (2.06 \pm 0.16)(-E_{HOMO}) + (2.52 \pm 0.27) \quad (13)$$

The calculated values of the E_{HOMO} for the unsaturated ketones are totally in agreement with the OH rate coefficient trend observed in this study, i.e., $k_{5\text{-hexen-2-one}} < k_{3\text{-penten-2-one}} < k_{4\text{-hexen-3-one}}$. The good quality of the correlation supports that it

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Table 3. Comparison of the 298 K Rate Coefficients for the Reactions of OH Radicals with Alkenes and Unsaturated Ketones and the Calculated HOMO Energies for These Unsaturated Carbonyls

unsaturated ketone	$10^{11}k_{OH}$ (cm^3 $molecule^{-1}$ s^{-1})	$-E_{HOMO}$ (eV)
$CH_3CH{=}CHC(O)CH_2CH_3$	9.04[a]	10.10
$CH_3C(O)CH_2CH_2CH{=}CH_2$	5.18[a]	10.29
$CH_3CH{=}CHC(O)CH_3$	7.22[a]	10.12
$CH_2{=}CHC(O)CH_2CH_3$	2.36[b]	10.75
$CH_2{=}CHC(O)CH_3$	1.86[c]	10.78

[a]This work. [b]Jiménez et al.[30] [c]Holloway et al.[14]

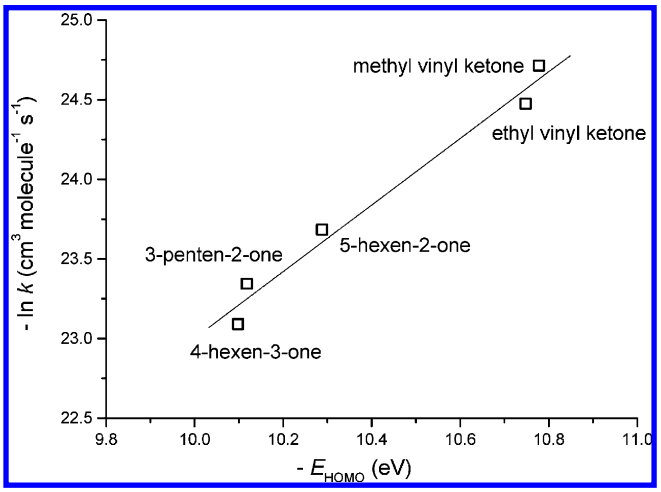

Figure 5. Plot of $-\ln(k_{OH+ketone}/cm^3\ molecule^{-1}\ s^{-1})$ versus the calculated values of $-E_{HOMO}$ for the reactions of OH radicals with unsaturated ketones.

can be reliably used for estimations of rate coefficients for reactions of OH radicals with similar structured unsaturated ketones where data does not yet exist.

Cl Kinetics. To the best of our knowledge, no kinetic data on the reactions of Cl atoms with 4-hexen-3-one, 5-hexen-2-one, and 3-penten-2-one have been reported. The present study is, therefore, the first measurement of the rate coefficients for reactions 4–6, and no direct comparison with literature values can be made. The rate coefficients for all three compounds are very similar and agree with one another within the error limits. Because the rate coefficients are near the gas kinetic collision limit, it is not surprising that no reactivity trend is discernible.

As for the OH reactions, one can compare the rate coefficients obtained here for the reactions of the unsaturated ketones with Cl atoms with those of the corresponding alkenes. In contrast to rate coefficients for the corresponding OH reactions the measured rate coefficients for Cl with 5-hexen-2-one and 3-penten-2-one are approximately 25% and 40% lower than those of their corresponding alkenes 1-pentene (k = 3.97 × 10^{-10} cm^3 $molecule^{-1}$ s^{-1})[27] and (*E*)-2-butene (k = 4.00 × 10^{-10} cm^3 $molecule^{-1}$ s^{-1}),[26] respectively. This reduction in reactivity indicates that for the Cl reactions with the unsaturated ketones the expected electron withdrawing effect of the carbonyl group is operational, which was not the case for the OH reactions. This observation provides additional evidence to support that the addition of OH to the double bond in the unsaturated ketones occurs differently from that of Cl, possibly involving the formation a H-bonded complex. No comparison can be made for 4-hexen-3-one because a rate coefficient for reaction of Cl with the analogous alkene, 2-pentene, is not available.

Atmospheric Implications. Jiménez et al.[30] have shown that photolysis by sunlight is not an important degradation pathway for unsaturated ketones in the troposphere; therefore, the main gas phase degradation for these compounds will be reaction with the oxidants OH and NO_3 radicals, O_3, and possibly Cl atoms. The tropospheric lifetimes, τ, of the studied unsaturated ketones with respect to reaction with OH and NO_3 radicals, Cl atoms, and ozone were calculated using $\tau = 1/(k_x[X])$, where [X] is the concentration of OH, NO_3, O_3, or Cl and k_x is the rate coefficient for reaction of OH, NO_3, O_3, or Cl, respectively, with the unsaturated ketone. For the calculations a 12 h averaged daytime OH radical concentration of 2 × 10^6 radicals cm^{-3},[39] a 24 h average O_3 concentration of 7 × 10^{11} molecules cm^{-3},[40] a night-time average NO_3 concentration of 5 × 10^8 radicals cm^{-3},[41] and an average global Cl concentration of 1 × 10^4 atoms cm^{-3} [42] have been used. The estimated atmospheric lifetimes are listed in Table 4. Where possible, literature rate coefficients have been used in the calculations; however, a rate coefficient for the reaction of NO_3 radicals with 4-hexen-3-one has not been reported in the literature. There are number of SAR methods for estimating rate coefficients for the reactions of NO_3[46−48] radicals and O_3[47,48] with unsaturated compounds. For the reaction of NO_3 radicals with 4-hexen-3-one, the SAR method of Kerdouci et al.[46] yields a rate coefficient of 6.36 × 10^{-15} cm^3 $molecule^{-1}$ s^{-1} whereas that of Pfrang et al.,[48] which is strictly only applicable to unsaturated alkenes, yields a value of 3.89 × 10^{-15} cm^3 $molecule^{-1}$ s^{-1}. Because the rate coefficient for the reaction of NO_3 with 4-hexen-3-one is expected to be very similar to that of NO_3 with 3-penten-2-one, which has a reported rate coefficient of 1.03 × 10^{-14} cm^3 $molecule^{-1}$ s^{-1} [43] at 298 K, the predictive nature of the Kerdouci et al.[46] SAR for NO_3 radical reactions would appear, at least for this particular case, to be better than that of the Pfrang et al.[48] approach.

Table 4. Estimated Tropospheric Lifetimes for the Unsaturated Ketones Studied in This Work with Respect to Their Reactions with OH, Cl, NO_3, and O_3[a]

unsaturated ketone	$10^{11}k_{OH}$	τ_{OH} (h)	$10^{10}k_{Cl}$	τ_{Cl} (h)	$10^{14}k_{NO_3}$	τ_{NO_3} (h)	$10^{18}k_{O_3}$	τ_{O_3} (h)
$CH_3CH{=}CHC(O)CH_2CH_3$ (4-hexen-3-one)	9.04[b]	2	3.00[b]	93	[c]		63.7[f]	6
$CH_3C(O)CH_2CH_2CH{=}CH_2$ (5-hexen-2-one)	5.18[b]	3	3.15[b]	88	2.16[d]	26	9.17[d]	43
$CH_3CH{=}CHC(O)CH_3$ (3-penten-2-one)	7.22[b]	2	2.53[b]	110	1.03[e]	54	29.5[g]	13

[a]The rate coefficients are in units of cm^3 $molecule^{-1}$ s^{-1}. [b]This work. [c]Rate coefficient not known but expected to be similar to that for NO_3 with 3-pentene-2-one. [d]Wang et al.[15] [e]Canosa-Mas et al.[43] [f]Grosjean and Grosjean.[44] [g]Sato et al.[45]

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On the basis of the rate coefficients obtained in this work, the tropospheric lifetimes for unsaturated ketones due to reaction with OH radicals are between 2 and 3 h and thus represent the major gas phase tropospheric sink for these compounds. The OH reaction lifetime is much shorter than the lifetimes between 88 and 110 h estimated for reaction with Cl atoms. However, in marine regions where the chlorine concentration peaks at dawn, i.e., much earlier than OH, and where Cl concentrations of around 1×10^5 atoms cm^{-3} have been observed,[18] the tropospheric lifetimes for these unsaturated ketones studied would be around 10 h or less and, under such circumstances, reaction with Cl will compete with reaction with OH. As stated in the Introduction, there is now evidence for sources of Cl in continental regions far inland from coastal regions;[22] although just how widespread such sources are still remains to be established, it may not always be appropriate to use a global Cl average concentration for estimating lifetimes of VOCs with respect to degradation by Cl atoms. In any event, degradation of VOCs in areas in the close vicinity of Cl sources such as brick ceramic industries[23] will always be competitive with OH induced degradation reactions.

As can be seen in Table 4, the two unsaturated ketones with the carbonyl group attached to the double bond, 3-penten-2-one and 4-hexen-3-one, are relatively reactive toward O_3 whereas 5-hexen-2-one, where the carbonyl group is not attached to the double bond, is much less reactive toward O_3. Thus reactions of O_3 with 3-penten-2-one and 4-hexen-3-one will contribute to some degree in their atmospheric degradation particularly in polluted urban areas. Decay of the unsaturated ketones during the night due to reaction with NO_3 will only be of marginal importance.

The OH radical initiated atmospheric degradation of the studied ketones is expected to result in the formation of mainly aldehydes and α-dicarbonyls, which will be subject to further reaction with OH and also photolysis. Thus, the high reactivity of these unsaturated compounds and also their primary products implies they will be contributors to the ozone and other photooxidant formation in the atmosphere if emitted in large qunatities. The exact nature and yields of the products from the OH, NO_3, Cl, and O_3 initiated photooxidation of the unsaturated ketones studied here, however, still remains to be elucidated.

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Notes

The authors declare no competing financial interest.

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