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Atmospheric Chemistry of 3-Pentanol: Kinetics, Mechanisms, and Products of Cl Atom and OH Radical Initiated Oxidation in the Presence and Absence of NO_X

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Smog chamber/FTIR techniques were used to study the atmospheric chemistry of 3-pentanol and determine rate constants of k(Cl+3-pentanol) = $(2.03 \pm 0.23) \times 10^{-10}$ and k(OH+3-pentanol) = $(1.32 \pm 0.15) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} in 700 Torr of N_2/O_2 diluent at 296 ± 2 K. The primary products of the Cl atom initiated oxidation of 3-pentanol in the *absence* of NO were (with molar yields) 3-pentanone (26 ± 2%), propionaldehyde (12 ± 2%), acetaldehyde (13 ± 2%) and formaldehyde (2 ± 1%). The primary products of the Cl atom initiated oxidation of 3-pentanol in the *presence* of NO were (with molar yields) 3-pentanone (51 ± 4%), propionaldehyde (39 ± 2%), acetaldehyde (44 ± 4%) and formaldehyde (4 ± 1%). The primary products of the OH radical initiated oxidation of 3-pentanol in the *presence* of NO were (with molar yields) 3-pentanone (58 ± 3%), propionaldehyde (28 ± 2%), and acetaldehyde (37 ± 2%). In all cases the product yields were independent of oxygen concentration over the partial pressure range 10−700 Torr. The reactions of Cl atoms and OH radicals with 3-pentanol proceed 26 ± 2 and 58 ± 3%, respectively, via attack on the 3-position to give an α-hydroxyalkyl radical, which reacts with O_2 to give 3-pentanone. The results are discussed with respect to the literature data and atmospheric chemistry of 3-pentanol.

1. Introduction

Concerns regarding energy security and climate change have renewed interest in alternative transportation fuels derived from biogenic sources. The two classes of biofuels currently receiving attention are methyl esters of long chain fatty acids for blending with diesel fuel and alcohols for blending with gasoline. Currently, ethanol is the dominant alcohol biofuel; however, there is interest in moving to larger alcohols to reduce water induced phase separation of alcohol−gasoline blends.[1] The use of alcohols as transportation fuels will result in their release into the atmosphere. Once in the atmosphere, the fate of alcohols will be photochemical oxidation initiated by the OH radical.[2] Prior to any large scale industrial use of larger alcohols, an assessment of their atmospheric chemistry and environmental impact is needed. There is a substantial kinetic and mechanistic database for small alcohols such and methanol and ethanol,[3] and the atmospheric oxidation mechanisms of these species are well understood. However, the kinetic and mechanistic database for larger alcohols is rather sparse and detailed descriptions of their atmospheric oxidation mechanisms are, in general, not available. For example, the reaction of 3-pentanol with OH radicals has been the subject of just one kinetic study and this was conducted at just one temperature (ambient); there have been no product studies of the atmospheric oxidation of 3-pentanol. To improve our understanding of the atmospheric chemistry of alcohols, the kinetics and mechanism of the simulated atmospheric oxidation of 3-pentanol was studied using the smog chamber at Ford Motor Company.

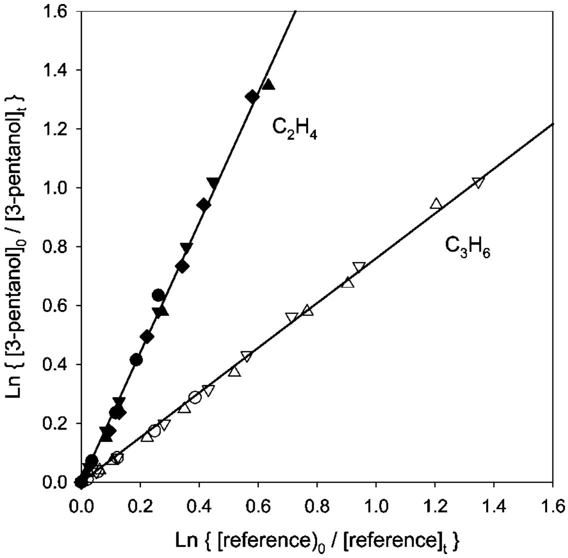

Figure 1. Loss of 3-pentanol versus ethene (filled symbols) and propene (open symbols) in the presence of Cl atoms in 700 Torr air at 296 ± 2 K. Different symbols are results from different experiments.

2. Experimental Section

Experiments were performed in a 140 L Pyrex reactor interfaced to a Mattson Sirius 100 FTIR spectrometer.[4] The reactor was surrounded by 22 fluorescent blacklamps (GE F40T12BLB) that were used to photochemically initiate the experiments. Chlorine atoms were produced by photolysis of molecular chlorine.

$$Cl_2 + h\nu \rightarrow Cl + Cl \qquad (1)$$

OH radicals were produced by photolysis of CH_3ONO in the presence of NO in air.

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$$CH_3ONO + h\nu \rightarrow CH_3O + NO \tag{2}$$

$$CH_3O + O_2 \rightarrow HO_2 + HCHO \tag{3}$$

$$HO_2 + NO \rightarrow OH + NO_2 \tag{4}$$

Relative rate techniques were used to measure the rate constant of interest relative to a reference reaction whose rate constant has been established previously. The relative rate method is a well established technique for measuring the reactivity of Cl atoms and OH radicals with organic compounds.[5] Kinetic data are derived by monitoring the loss of 3-pentanol relative to one or more reference compounds. The decays of 3-pentanol and the reference are then plotted using the expression

$$\ln\left(\frac{[\text{reactant}]_0}{[\text{reactant}]_t}\right) = \frac{k_{\text{reactant}}}{k_{\text{reference}}} \ln\left(\frac{[\text{reference}]_0}{[\text{reference}]_t}\right) \tag{I}$$

where $[\text{reactant}]_0$, $[\text{reactant}]_t$, $[\text{reference}]_0$ and $[\text{reference}]_t$ are the concentrations of 3-pentanol and the reference compound at times "0" and "t", and k_{reactant} and $k_{\text{reference}}$ are the rate constants for reactions of Cl atoms or OH radicals with the 3-pentanol and the reference compound. Plots of $\ln([\text{reactant}]_0/[\text{reactant}]_t)$ versus $\ln([\text{reference}]_0/[\text{reference}]_t)$ should be linear, pass through the origin and have a slope of $k_{\text{reactant}}/k_{\text{reference}}$.

CH_3ONO was synthesized by the dropwise addition of concentrated sulfuric acid to a saturated solution of $NaNO_2$ in methanol. 3-Pentanol was obtained from Sigma-Aldrich at a purity of 98%. Experiments were conducted in 700 Torr total pressure of high purity O_2/N_2 diluent at 296 ± 2 K. Concentrations of reactants and products were monitored by FTIR spectroscopy. IR spectra were derived from 32 coadded interferograms with a spectral resolution of 0.25 cm^{-1} and an analytical path length of 27.1 m. To check for unwanted loss of reactants and reference compounds via heterogeneous reactions, reaction mixtures were left to stand in the chamber for 60 min. With the exception of $CH_3CCl(OH)CH_3$, there was no observable (<2%) loss of any of the reactants or products in the present work. Unless stated otherwise, quoted uncertainties are 2 standard deviations from least-squares regressions.

3. Results and Discussion

3.1. Kinetics of the Cl + 3-Pentanol Reaction.

The rate of reaction 5 was measured relative to reactions 6 and 7

$$Cl + CH_3CH_2CH(OH)CH_2CH_3 \rightarrow \text{products} \tag{5}$$

$$Cl + C_2H_4 \rightarrow \text{products} \tag{6}$$

$$Cl + C_3H_6 \rightarrow \text{products} \tag{7}$$

Reaction mixtures consisted of 7.4−66.3 mTorr 3-pentanol, 100−120 mTorr Cl_2 and either 2.4−8.0 mTorr C_2H_4 or 4.4−7.6 mTorr C_3H_6 in 700 Torr of air diluent. The observed loss of 3-pentanol versus the loss of the reference compounds is plotted in Figure 1. Linear least-squares analysis of the data in Figure 1 gives $k_5/k_6 = 2.20 \pm 0.20$ and $k_5/k_7 = 0.76 \pm 0.08$. Using $k_6 = 9.29 \times 10^{-11}$ [6] and $k_7 = 2.64 \times 10^{-10}$ [7] gives $k_5 = (2.04 \pm 0.19) \times 10^{-10}$ and $(2.01 \pm 0.21) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. We cite a final value which is the average of the individual determinations together with error limits which encompass the extremes of the determinations, $k_5 = (2.03 \pm 0.23) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}.

There have been no previous studies of k_5; however, we can compare our result with the rate constants reported for other alcohols. As shown in Table 1, there is a general trend of increasing reactivity of alcohols with increasing molecular size.[8−11] The reactivity of 3-pentanol measured in the present work is consistent with this trend. Also, as seen from the literature data for 1- and 2-propanol and 1- and 2-butanol in Table 1, secondary alcohols are less reactive than primary alcohols. Inspection of the data in Table 1 shows that the reactivity of 3-pentanol, although indistinguishable from that for 2-pentanol, is significantly less than that for 1-pentanol. Our kinetic data for 3-pentanol are consistent with the available database for the reactions of chlorine atoms with alcohols.

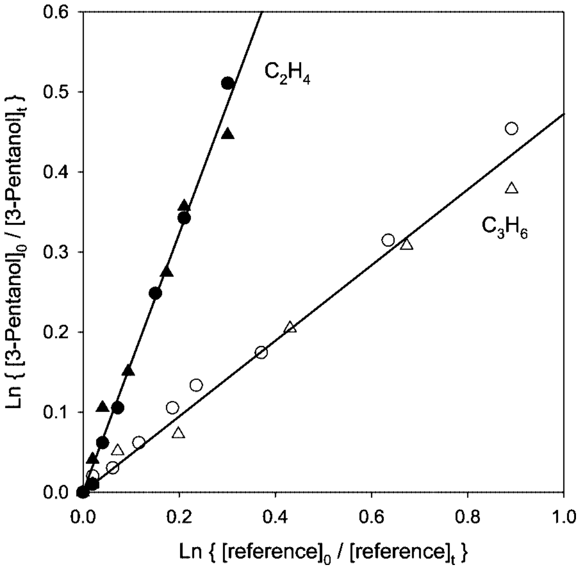

Figure 2. Loss of 3-pentanol versus ethene (filled symbols) and propene (open symbols) in the presence of OH radicals in 700 Torr air at 296 ± 2 K. Different symbols are results from different experiments.

TABLE 1: Summary of the Rate Constants for the Reaction of Cl Atoms with Alcohols at Ambient Temperature Reported in This Work and Selected Previous Studies

	k(Cl) at 298 K (10^{-11} cm^3 molecule^{-1} s^{-1})					
	this work	Garzón et al.[8]	Ballesteros et al.[9]	Wu et al.[11]	Nelson et al.[10]	IUPAC[3]
methanol		5.44 ± 0.34			4.79 ± 0.36	5.5
ethanol		9.93 ± 0.98		9.95 ± 0.7	10.1 ± 0.6	10.0
1-propanol		15.3 ± 1.2		15.0 ± 1.3	14.9 ± 0.7	16.0
2-propanol				7.8 ± 0.7	8.4 ± 0.4	8.6
1-butanol		19.6 ± 1.9		21.7 ± 1.1	20.4 ± 1.4	
2-butanol			12.6 ± 2			
1-pentanol		23.7 ± 2.9		25.8 ± 2.5	25.1 ± 1.3	
2-pentanol			21.8 ± 3.6			
3-pentanol	20.3 ± 2.3					
1-hexanol					29.5 ± 0.9	

TABLE 2: Summary of the Rate Constants for the Reaction of OH Radicals with Alcohols at Ambient Temperature Reported in This Work and Selected Previous Studies

	k(OH) at 298 K (10^{-12} cm^3 molecule^{-1} s^{-1})					
	this work	Wallington et al.[13]	Cavalli et al.[14,15]	Wu et al.[11]	Nelson et al.[10]	IUPAC[3]
methanol					0.90 ± 0.09	0.9
ethanol				3.4 ± 0.25	3.04 ± 0.85	3.2
1-propanol				5.47 ± 0.44	5.64 ± 0.48	5.8
2-propanol				5.31 ± 0.39	5.69 ± 1.09	5.1
1-butanol			8.28 ± 0.85	8.66 ± 0.66	7.80 ± 0.20	8.5
2-butanol						8.7
1-pentanol			11.1 ± 1.1	12.3 ± 1.0	12.0 ± 1.6	
2-pentanol		11.8 ± 0.8				
3-pentanol	13.2 ± 1.5	12.2 ± 0.7				
1-hexanol		12.4 ± 0.7			12.2 ± 2.4	

3.2. Kinetics of the OH + 3-Pentanol Reaction. The rate of reaction 8 was measured relative to reactions 9 and 10:

$$\mathrm{OH + CH_3CH_2CH(OH)CH_2CH_3 \rightarrow products} \quad (8)$$

$$\mathrm{OH + C_2H_4 \rightarrow products} \quad (9)$$

$$\mathrm{OH + C_2H_2 \rightarrow products} \quad (10)$$

Reaction mixtures consisted of 74.3−81.0 mTorr 3-pentanol, 100−153 mTorr CH_3ONO, and either 4.6−7.8 mTorr C_2H_4 or 9.7−13.2 mTorr C_3H_6 in 700 Torr total pressure of air diluent. Figure 2 shows the loss of 3-pentanol plotted versus loss of the reference compounds. Linear least-squares analysis gives $k_8/k_9 = 1.61 \pm 0.15$ and $k_8/k_{10} = 0.47 \pm 0.50$. Using $k_9 = 8.52 \times 10^{-12}$ [12] and $k_{10} = 2.9 \times 10^{-11}$ [3] gives $k_8 = (1.37 \pm 0.13) \times 10^{-11}$ and $(1.36 \pm 0.15) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. Indistinguishable values of k_8 are obtained using the two different references. We cite a final value which is the average of the individual determinations together with error limits which

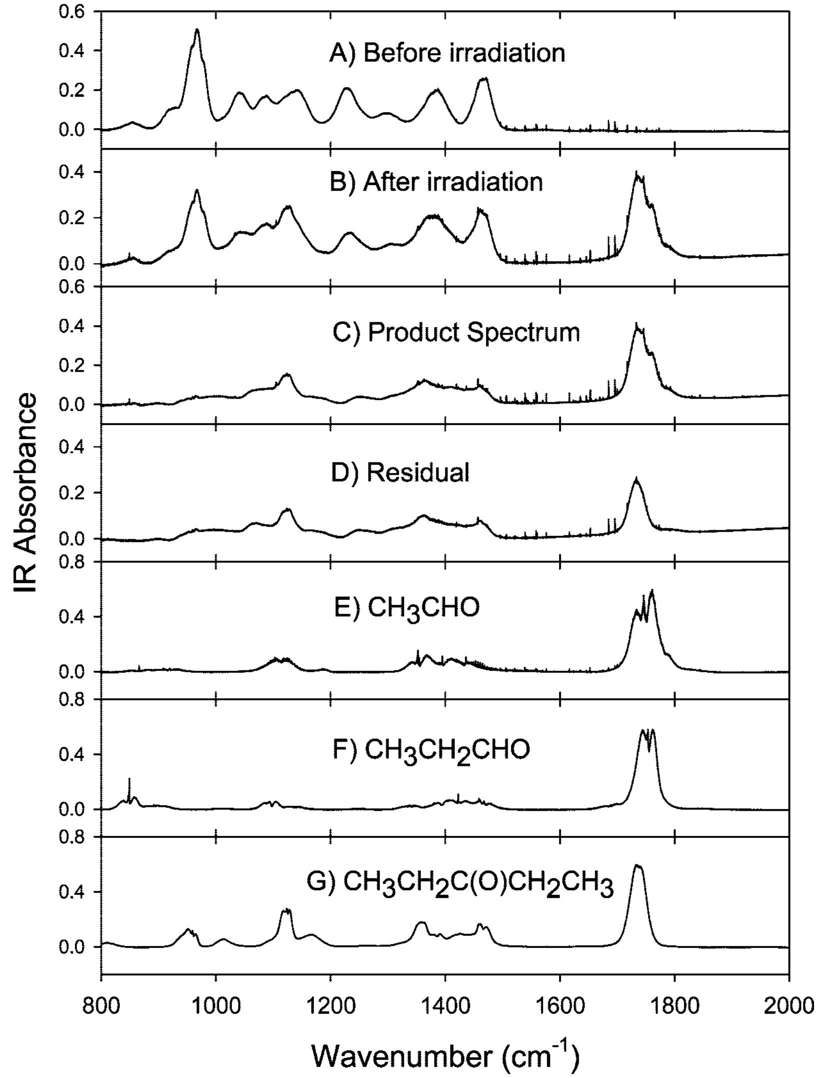

Figure 3. IR spectra obtained before (A) and after (B) a 250 s irradiation of 65.7 mTorr, 3-pentanol and 99 mTorr Cl_2 in 700 Torr air. Panel C shows the product spectrum obtained by subtracting 55% of panel A from panel B. Panel D shows the residual product spectrum after the features attributable to CH_3CHO (E), CH_3CH_2CHO (F), and 3-pentanone (G) have been subtracted from panel C.

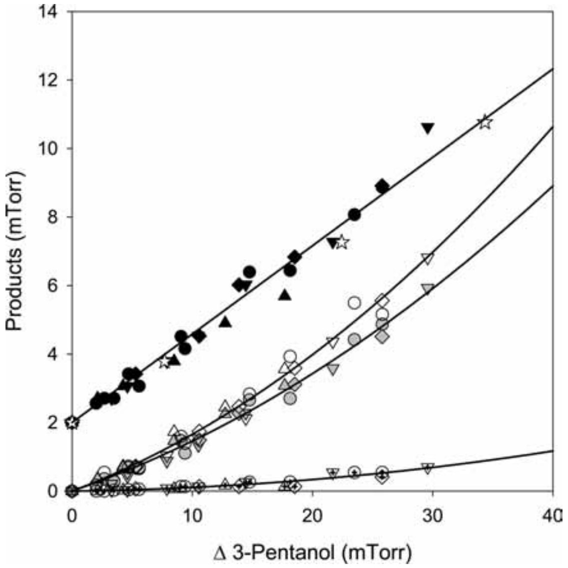

Figure 4. Formation of 3-pentanone (black), propionaldehyde (gray), acetaldehyde (open) and formaldehyde (crossed) versus the loss of 3-pentanol following UV irradiation of 3-pentanol/Cl_2 with 10 Torr O_2 (circles), 50 Torr O_2 (triangles up), 140 Torr O_2 (triangles down), or 700 Torr O_2 (diamonds) in 700 Torr total pressure of nitrogen diluent. Formation of 3-pentanone following the UV irradiation of 3-pentanol/Cl_2 in N_2 is shown with stars. The 3-pentanone data is offset for clarity.

encompass the extremes of the determinations, $k_8 = (1.32 \pm 0.15) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. Wallington et al.[13] measured k_8 using an absolute technique and report $k_8 = (1.22 \pm 0.07) \times 10^{-11}$ cm^{3}molecule^{-1} s^{-1}, which is in agreement, within the experimental uncertainties, with our result.

From inspection of Table 2 we can make two general observations regarding the reactivity of 3-pentanol toward OH radicals measured in the present work compared to the kinetic database for alcohols.[10,11,13−15] First, the magnitude of k_8 is consistent with expectations based upon the trend of increasing reactivity with size of the alcohol. Second, unlike the situation with chlorine atoms described in the previous section, there is no discernible difference in reactivity of primary and secondary alcohols toward OH radicals (e.g., compare 1- and 2- propanol, and 1- and 2-butanol in Table 2) and our results for 3-pentanol show that this holds true for pentanol.

The structure−activity relationship (SAR) method of Kwok and Atkinson[16] is useful for estimating the rate constants for the gas-phase reactions of the OH radical with organic compounds. Bethel et al.[17] have proposed new substituent factors for use with alcohols and diols. The updated SAR method predicts $k(\mathrm{OH}+3\text{-pentanol}) = 1.38 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, which is consistent with the result from the present work.

3.3. Products and Mechanism of Cl Atom Initiated Oxidation of 3-Pentanol in the Absence of NO. The mechanism of Cl atom initiated oxidation of 3-pentanol was investigated by irradiating mixtures of 34−71 mTorr 3-pentanol and 99−1010 mTorr Cl_2 in 0−700 Torr oxygen. Nitrogen was added as needed to provide 700 Torr total pressure. Figure 3 shows spectra acquired before (A) and after (B), a 250 s irradiation of a mixture of 65.7 mTorr 3-pentanol and 99 mTorr Cl_2 in 700 Torr air. The consumption of 3-pentanol in this experiment was 45%. Panel C shows the product spectrum derived by subtracting the IR features of 3-pentanol from the spectrum in panel B. Comparison of the IR features in panel C with reference spectra of acetaldehyde, propionaldehyde, and 3-pentanone in panels E, F, and G shows the formation of these compounds. Panel D shows the IR features that remain after subtraction of the features from acetaldehyde, propionaldehyde, and 3-pentanone. In addition, there are features in the residual spectrum at 3500−3700 cm^{-1}, which are characteristic of alcohols. These residual IR features are ascribed to unidentified product(s). Figure 4 shows the formation of 3-pentanone, acetaldehyde, and propionaldehyde versus the loss of 3-pentanol for experiments with 10 Torr O_2, 50 Torr O_2, 140 Torr O_2 and 700 Torr O_2 in 700 Torr total pressure made up with N_2 in the absence of NO. The data have been corrected for secondary reactions of the products with Cl atoms using the procedure described elsewhere.[18] Inspection of the data in Figure 4 reveals that there was no discernible impact of $[O_2]$ on the product yields. Linear least-squares analysis of the composite 3-pentanone data set gives a molar yield of 26 ± 2%. The yield plots of acetaldehyde and propionaldehyde are curved, suggesting that there are both primary and secondary sources of these compounds. The initial yields of acetaldehyde and propionaldehyde are 13 ± 2% and 12 ± 2%, respectively, and represent primary product yields. Formaldehyde is present in a yield of 2 ± 1%. Given the very small amounts of formaldehyde observed, within the experimental uncertainties, we are not able to exclude the possibility that a significant fraction, perhaps all, of the observed HCHO may come from secondary reactions.

The reaction of Cl atoms with 3-pentanol proceeds via three channels

$$\mathrm{Cl + CH_3CH_2CH(OH)CH_2CH_3 \rightarrow CH_3CH_2C(OH)CH_2CH_3 + HCl} \quad (5a)$$

$$\mathrm{Cl + CH_3CH_2CH(OH)CH_2CH_3 \rightarrow CH_3CH_2CH(OH)CHCH_3 + HCl} \quad (5b)$$

$$\mathrm{Cl + CH_3CH_2CH(OH)CH_2CH_3 \rightarrow CH_3CH_2CH(OH)CH_2CH_2 + HCl} \quad (5c)$$

By analogy to the behavior of other hydroxyalkyl radicals,[3] the α-hydroxyalkyl radical formed via attack at the 3-position is expected to react exclusively with oxygen to form 3-pentanone and HO_2.

$$\mathrm{CH_3CH_2C(OH)CH_2CH_3 + O_2 \rightarrow CH_3CH_2C(O)CH_2CH_3 + HO_2} \quad (11)$$

The β and γ hydroxyalkyl radicals formed from the abstraction of a hydrogen atom at the 2 and 1 positions, respectively, will add oxygen to give hydroxyalkylperoxy radicals. In the absence of NO, the hydroxyalkylperoxy radicals will react with peroxy radicals to give hydroxyalkoxy radicals. As illustrated in Figures 5 and 6, the fate of the hydroxyalkoxy radicals is expected to be reaction with O_2, decomposition, or isomerization via a hydrogen shift through a six-member transition state.

In addition to the above reactions, a variety of other reactions probably occur in the system. In the discussion above, it is assumed that $RO_2 + RO_2$ reactions result in the formation of alkoxy radicals. Typically, such $RO_2 + RO_2$ reactions also proceed via a molecular channel to form ROH and R′CHO.[3] Furthermore, the formation of HO_2 radicals (e.g., via reaction 12) raises the possibility that reaction of RO_2 radicals with HO_2 radicals to form hydroperoxides,[19] ROOH, is important in the system. These possibilities are included in Figures 5 and 6. The isomerization pathways in Figures 5 and 6 give 1,4-hydroxycarbonyls that can undergo reversible cyclization to cyclic hemiacetals which can dehydrate to form reactive dihydrofurans.[20,21]

Further information on the branching ratio for chlorine atom attack on 3-pentanol was obtained by conducting experiments with 3-pentanol and Cl_2 in 700 Torr N_2. Under these conditions, attack of Cl at the 3-position results in the formation of the chlorinated alcohol $CH_3CH_2CCl(OH)CH_2CH_3$.

$$CH_3CH_2CH(OH)CH_2CH_3 + Cl \rightarrow CH_3CH_2C(OH)CH_2CH_3 + HCl \quad (5a)$$

$$CH_3CH_2C(OH)CH_2CH_3 + Cl_2 \rightarrow CH_3CH_2CCl(OH)CH_2CH_3 + Cl \quad (12)$$

α-Chloro-alcohols such as CH_2ClOH, $CHCl_2OH$, CCl_3OH, $CH_3CHClOH$, and $CH_3CClOHCH_3$ decompose heterogeneously in the chamber via elimination of HCl[22-24] to give the corresponding carbonyl compound. In the case of $CH_3CH_2CCl(OH)CH_2CH_3$ this gives 3-pentanone, which then provides a marker for reaction 5a.

$$CH_3CH_2CCl(OH)CH_2CH_3 \rightarrow CH_3CH_2C(O)CH_2CH_3 + HCl \quad (13)$$

The 3-pentanone yield determined in experiments conducted in N_2 is shown in Figure 4 and was indistinguishable from the 3-pentanone yield observed in the presence of oxygen. From the yields of 3-pentanone in the presence and absence of oxygen we conclude that $k_{5a}/k_5 = 0.26 \pm 0.02$. As seen from inspection of Figures 5 and 6, the only primary reaction that gives acetaldehyde is decomposition of the $CH_3CH_2CH(OH)CH(O)CH_3$ radical formed from abstraction of a H atom in the 2-position. Furthermore, the channel giving acetaldehyde (see Figure 5) leads to formation of an equal amount of propionaldehyde. Consistent with expectations the primary yields of acetaldehyde and propionaldehyde, 0.13 ± 0.02 and 0.12 ± 0.02, respectively, were indistinguishable; see Figure 4. Recognizing two factors, (i) the possibility of $RO_2 + RO_2$ and $RO_2 + HO_2$ reactions discussed above which reduce the efficiency with which the peroxy radical $CH_3CH_2CH(OH)CH(OO)CH_3$ is converted into the alkoxy radical $CH_3CH_2CH(OH)CH(O)CH_3$

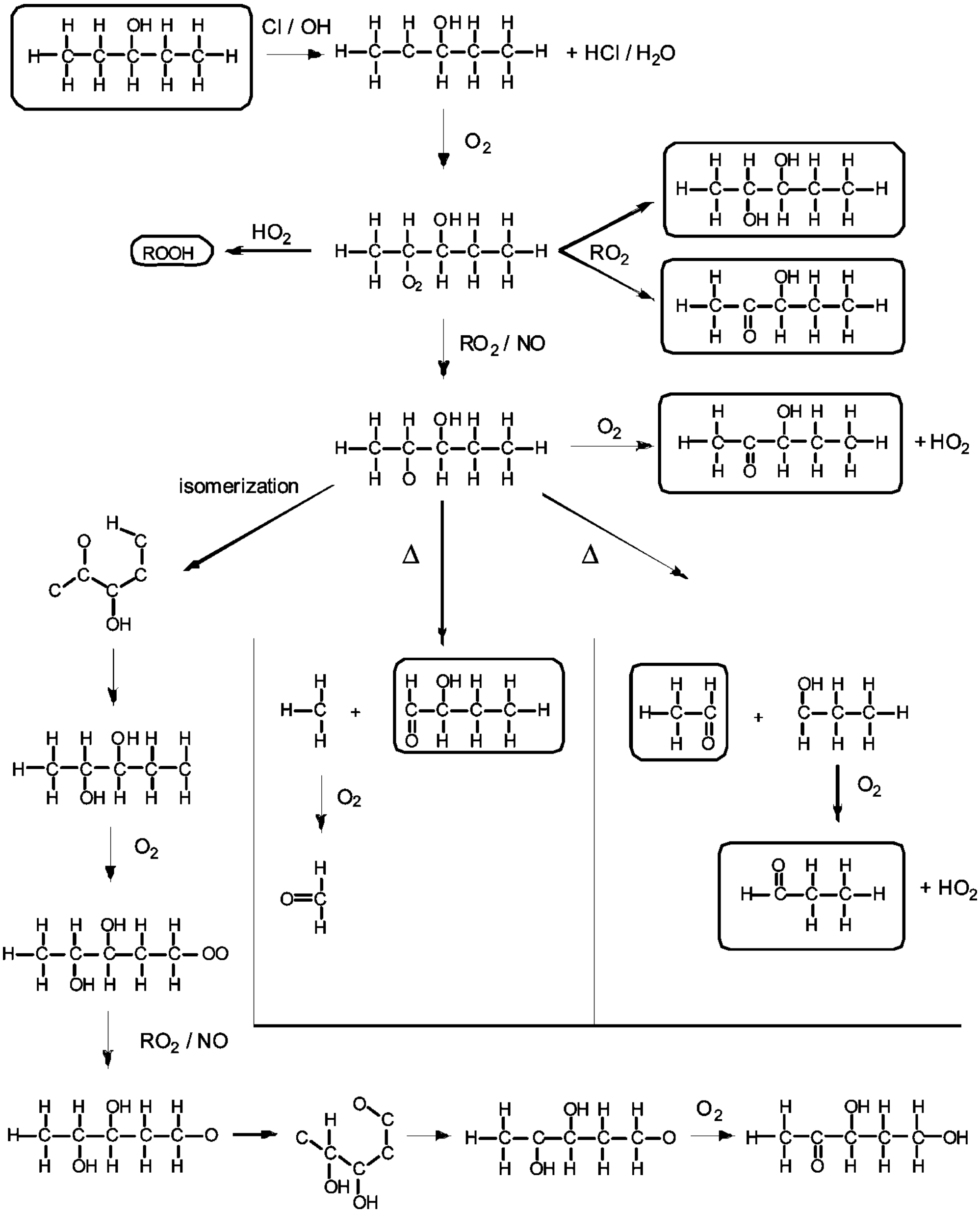

Figure 5. Fate of the β-hydroxyalkyl radical in the Cl atom/OH radical initiated oxidation of 3-pentanol.

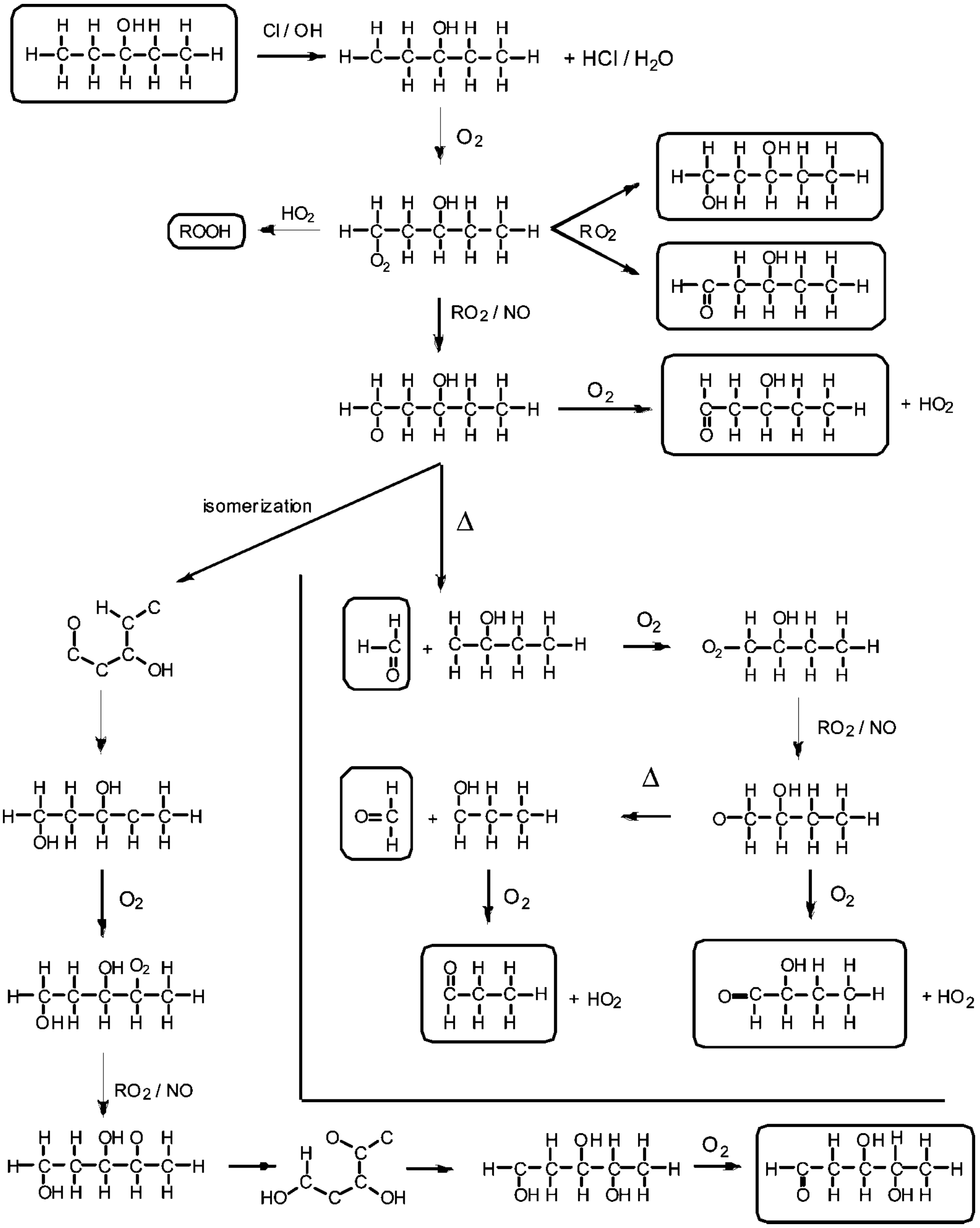

Figure 6. Fate of the γ-hydroxyalkyl radical in the Cl atom/OH radical initiated oxidation of 3-pentanol.

and (ii) the fact that we are not able to exclude the possibility that isomerization and decomposition via methyl elimination are competing fates for the alkoxy radical (see Figure 5), we conclude that $k_{5b}/k_5 \geq 0.13 \pm 0.02$.

3.4. Products and Mechanism of OH Radical Initiated Oxidation of 3-Pentanol. The mechanism of OH radical initiated oxidation of 3-pentanol in the presence of NO_x was investigated by irradiating mixtures consisting of 65−67 mTorr of 3-pentanol, 96−122 mTorr CH_3ONO and 0−50 mTorr NO in 700 Torr air. Figure 7 shows the formation of 3-pentanone, acetaldehyde and propionaldehyde versus the loss of 3-pentanol for experiments in 700 Torr air in the presence of NO. The data have been corrected for losses via secondary reaction of the products with OH radicals.[18] Linear least-squares analyses of the data in Figure 7 give molar yields of 3-pentanone, acetaldehyde, and propionaldehyde of 58 ± 3%, 37 ± 2%, and 28 ± 2%, respectively. Quoted uncertainties are two standard deviations from the regression analyses.

The reaction of OH radicals with 3-pentanol proceeds via three channels

$$OH + CH_3CH_2CH(OH)CH_2CH_3 \rightarrow CH_3CH_2C(OH)CH_2CH_3 + H_2O \quad (8a)$$

$$OH + CH_3CH_2CH(OH)CH_2CH_3 \rightarrow CH_3CH_2CH(OH)CHCH_3 + H_2O \quad (8b)$$

$$OH + CH_3CH_2CH(OH)CH_2CH_3 \rightarrow CH_3CH_2CH(OH)CH_2CH_2 + H_2O \quad (8c)$$

As discussed in section 3.3, reaction 11 is the sole fate of the $CH_3CH_2C(OH)CH_2CH_3$ radical and hence from the 3-pentanone yield we conclude that $k_{8a}/k_8 = 0.58 \pm 0.03$. The only source of acetaldehyde as a primary product is decomposition of the $CH_3CH_2CH(OH)CH(O)CH_3$ radical formed from abstraction of a hydrogen atom in the 2-position, which should lead to equal amounts of acetaldehyde and propionaldehyde. From the yield plots in Figure 4, the yields of acetaldehyde and propionaldehyde as primary products are 37 ± 2% and 28 ± 2%, respectively. Recognizing the possibility of nitrate formation in reaction of the peroxy radical with NO [3] and isomerization of the alkoxy radical, we conclude that $k_{8b}/k_8 \geq 0.28 \pm 0.02$. The observed products account for 86% of the reacted 3-pentanol.

The SAR method is also useful for estimating branching ratios for the various sites of attack of the OH radicals with an organic compound. Using the SAR method of Kwok and Atkinson[16] with the refinements of Bethel et al.[17] gives values of 0.61, 0.35 and 0.02 for k_{8a}/k_8, k_{8b}/k_8 and k_{8c}/k_8, respectively. These values are consistent with those for k_{8a}/k_8 and k_{8b}/k_8 determined experimentally.

3.5. Products and Mechanism of Cl Atom Initiated Oxidation of 3-Pentanol in the Presence of NO. The mechanism of Cl atom initiated oxidation of 3-pentanol in the presence of NO was investigated by irradiating mixtures consisting of 66−74 mTorr 3-pentanol, 100−105 mTorr Cl_2, 27−58 mTorr NO, and 10−140 Torr oxygen in 700 Torr total pressure of nitrogen diluent.

Figure 8 shows the formation of 3-pentanone, acetaldehyde, propionaldehyde, and formaldehyde versus the loss of 3-pentanol for experiments with 10 Torr O_2, 100 Torr O_2, or 140 Torr O_2 in 700 Torr of nitrogen diluent in the presence of NO. The data in Figure 8 have been corrected for losses via secondary reaction of the products with Cl atoms. Data for different O_2 concentrations are indistinguishable. Linear least-squares analysis of the composite data sets gives initial molar yields of 51 ± 4% for 3-pentanone, 44 ± 4% for $CH_3C(O)H$, 39 ± 2% for $CH_3CH_2C(O)H$, and 4 ± 1% for HC(O)H. Quoted uncertainties are two standard deviations from the regression analyses.

It is of interest to compare the products observed in the absence of NO (see section 3.3) and those observed in the presence of NO. The presence of NO ensures rapid removal of RO_2 (converted into RO radicals and, to a small degree, organic nitrates, $RONO_2$) and HO_2 radicals.

$$RO_2 + NO \rightarrow RO + NO_2 \tag{14a}$$

$$RO_2 + NO + M \rightarrow RONO_2 + M \tag{14b}$$

$$HO_2 + NO \rightarrow OH + NO_2 \tag{15}$$

The presence of NO simplifies the mechanistic interpretation of the product yields because it provides a more direct conversion of peroxy into alkoxy radicals via reaction 14a and removes the need to consider $RO_2 + RO_2$ and $RO_2 + HO_2$ reactions. However, the presence of NO adds complexity to the analysis because of the need to consider three additional factors: (i) the possibility that both Cl atoms and OH radicals (formed in reaction 15) initiate the oxidation of 3-pentanol, (ii) the effect of chemical activation of the alkoxy radicals formed in reaction 14a[25] and (iii) the formation of small amounts of organic nitrates in channel 14b.

The increase in initial acetaldehyde yield from 13% to 44% and the increase in initial propionaldehyde yield from 12% to 39% with the addition of NO probably reflects more efficient peroxy to alkoxy radical conversion in the system as a result of the elimination of $RO_2 + RO_2$ and $RO_2 + HO_2$ chemistry. The increase in the yield of 3-pentanone from 26% to 51% with the addition of NO probably reflects a substantial contribution of OH radical initiated oxidation of 3-pentanol. As illustrated in Figures 5 and 6, for each molecule of 3-pentanol that is lost via reaction with chlorine atoms an HO_2 radical is formed. HO_2 radicals react with NO to give OH radicals which will then react with 3-pentanol starting another cycle. For typical initial experimental conditions with [3-pentanol] = 70 mTorr and [NO] = 42 mTorr and using $k(OH+3\text{-pentanol}) = 1.3 \times 10^{-11}$ and $k(OH+NO) = 9.0 \times 10^{-12}$ $cm^3 molecule^{-1}$ s^{-1},[26] it can be calculated that approximately 70% of OH radicals will react with 3-pentanol with the remaining 30% reacting with NO to form HONO. The formation of HONO and HNO_3 (formed from addition of OH to NO_2) was confirmed by examination of the IR product spectra. In addition to gas phase chemistry, HONO and HNO_3 are probably also formed in the chamber via the heterogeneous reaction of NO_2 with H_2O on the chamber walls.[27]

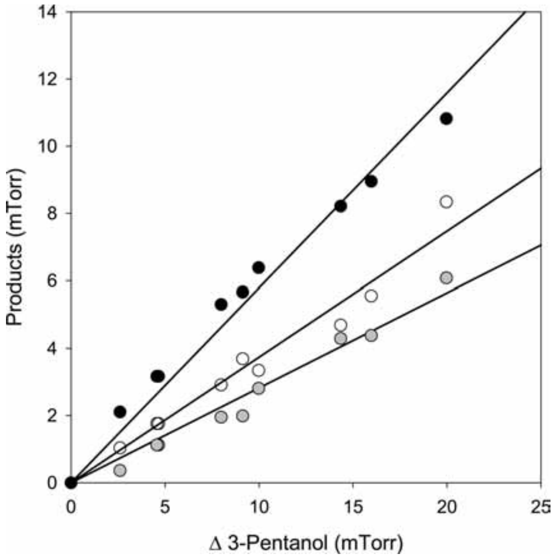

Figure 7. Formation of 3-pentanone (black), propionaldehyde (gray), and acetaldehyde (open) versus loss of 3-pentanol following UV irradiation of 3-pentanol /CH_3ONO mixtures in 700 Torr of air diluent.

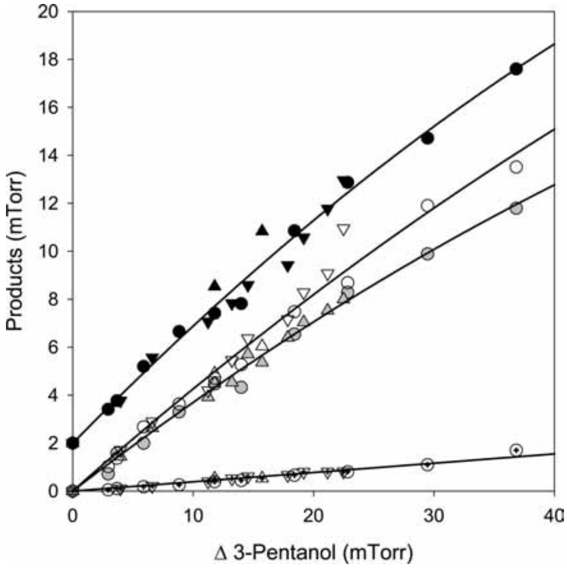

Figure 8. Formation of 3-pentanone (black), propionaldehyde (gray), acetaldehyde (open) and formaldehyde (dotted) versus loss of 3-pentanol following UV irradiation of 3-pentanol/Cl_2/NO mixtures with 10 Torr O_2 (circles), 100 Torr O_2 (triangles), or 140 Torr O_2 (inverted triangles) in 700 Torr of nitrogen diluent. The 3-pentanone data are offset for clarity.

4. Implications for Atmospheric Chemistry

We present a large body of self-consistent data concerning the kinetics and mechanisms of the Cl atom and OH radical initiated oxidation of 3-pentanol, which increases our knowledge of the atmospheric chemistry of this compound. The atmospheric oxidation of 3-pentanol will be initiated by reaction with OH radicals, which occurs with a rate constant of $k_8 = (1.32 \pm 0.15) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} in 700 Torr of air diluent at 296 K. Using an estimate for the 24 h average OH radical concentration in the atmosphere of 10^6 molecules cm^{-3} [2] gives an estimate for the atmospheric lifetime of 3-pentanol of approximately 1 day. The atmospheric oxidation of 3-pentanol gives 3-pentanone as the major product in a yield of 58 ± 3%. The reactivity of 3-pentanone toward OH radicals is approximately 6 times lower than that of 3-pentanol,[28-30] and hence 3-pentanone has an atmospheric lifetime of approximately 1 week. This lifetime is sufficiently long that most of the 3-pentanone will be transported out of urban areas and will not contribute further to local air quality issues. CH_3CHO and C_2H_5CHO are formed in yields of 37 ± 2% and 28 ± 2%. With respect to reaction with OH radicals, CH_3CHO has approximately the same reactivity as 3-pentanol and C_2H_5CHO is approximately 50% more reactive than 3-pentanol. A substantial fraction of the CH_3CHO and C_2H_5CHO products will react in urban areas and contribute to local air quality issues. The present study provides kinetic and mechanistic data that can be used in future computer model studies of urban air chemistry to assess the environmental impact of emissions of 3-pentanol. Such studies are beyond the scope of the present work.

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References and Notes

(1) Mueller, S. A.; Anderson, J. E.; Wallington, T. J. *J. Chem. Educ.*, in press, 2008.

(2) Finlayson-Pitts, B. J.; Pitts, J. N., Jr. *Atmospheric Chemistry: Fundamentals and Experimental Techniques*; John Wiley and Sons: New York, 1986.

(3) Atkinson, R.; Baulch, D. L.; Cox, R. A.; Crowley, J. N.; Hampson, R. F.; Hynes, R. G.; Jenkin, M. E.; Rossi, M. J.; Troe, J. *Atmos. Chem. Phys.* **2006**, *6*, 3625.

(4) Wallington, T. J.; Japar, S. M. *J. Atmos. Chem.* **1989**, *9*, 399.

(5) Atkinson, R. *J. Phys. Chem. Ref. Data* **1989**, Monograph 1.

(6) Wallington, T. J.; Andino, J. M.; Lorkovic, I. M.; Kaiser, E. W.; Marston, G. *J. Phys. Chem.* **1990**, *94*, 3644.

(7) Ezell, M. J.; Wang, W.; Ezell, A. A.; Soskin, G.; Finlayson-Pitts, B. J. *Phys. Chem. Chem. Phys.* **2002**, *1*, 5813.

(8) Garzón, A.; Cuevas, C. A.; Ceacero, A. A.; Notario, A.; Albaladejo, J.; Fernández-Gómez, M. *J. Chem. Phys.* **2006**, *125*, 104305.

(9) Ballesteros, B.; Garzón, A.; Jimenez, E.; Notario, A.; Albaladejo, J. *Phys. Chem. Chem. Phys.* **2007**, *9*, 1210.

(10) Nelson, L.; Rattigan, O.; Neavyn, R.; Sidebottom, H.; Treacy, J.; Nielsen, O. J. *Int. J. Chem. Kinet.* **1990**, *22*, 1111.

(11) Wu, H.; Mu, Y.; Zhang, X.; Jiang, G. *Int. J. Chem. Kinet.* **2003**, *35*, 81.

(12) Calvert, J. G.; Atkinson, R.; Kerr, J. A.; Madronich, S.; Moortgat, G. K.; Wallington, T. J.; Yarwood, G., *The Mechanisms of Atmospheric Oxidation of the Alkenes*; Oxford University Press: Oxford. U.K., **2000**.

(13) Wallington, T. J.; Dagaut, P.; Liu, R.; Kurylo, M. J. *Int. J. Chem. Kinet.* **1988**, *20*, 541.

(14) Cavalli, F.; Barnes, I.; Becker, K. H. *Environ. Sci. Technol.* **2000**, *34*, 4111.

(15) Cavalli, F.; Geiger, H.; Barnes, I.; Becker, K. H. *Environ. Sci. Technol.* **2002**, *36*, 1263.

(16) Kwok, E. S. C.; Atkinson, R. *Atmos. Environ.* **1995**, *29*, 1685.

(17) Bethel, H. L.; Atkinson, R.; Arey, J. *Int. J. Chem. Kinet.* **2001**, *33*, 310.

(18) Meagher, R. J.; McIntosh, M. E.; Hurley, M. D.; Wallington, T. J. *Int. J. Chem. Kinet.* **1997**, *29*, 619.

(19) Wallington, T. J.; Hurley, M. D.; Schneider, W. F.; Sehested, J.; Nielsen, O. J. *Chem. Phys. Lett.* **1994**, *218*, 34.

(20) Martin, P.; Tuazon, E. C.; Aschmann, S. M.; Arey, J.; Atkinson, R. *J. Phys. Chem. A* **2002**, *106*, 11492.

(21) Holt, T.; Atkinson, R.; Arey, J. *J. Photochem. Photobiol A: Chem.* **2005**, *176*, 231.

(22) Wallington, T. J.; Schneider, W. F.; Barnes, I.; Becker, K. H.; Sehested, J.; Nielsen, O. J. *Chem. Phys. Lett.* **2000**, *322*, 97.

(23) Taatjes, C. A.; Christensen, L. K.; Hurley, M. D.; Wallington, T. J. *J. Phys. Chem. A* **1999**, *103*, 9805.

(24) Yamanaka, T.; Kawasaki, M.; Hurley, M. D.; Wallington, T. J.; Schneider, W. F. *Phys. Chem. Chem. Phys.* **2007**, *9*, 4211.

(25) Orlando, J. J.; Tyndall, G. S.; Wallington, T. J. *Chem. Rev.* **2003**, *103*, 4657.

(26) Atkinson, R.; Baulch, D. L.; Cox, R. A.; Crowley, J. N.; Hampson, R. F.; Hynes, R. G.; Jenkin, M. E.; Rossi, M. J.; Troe, J. *Atmos. Chem. Phys.* **2004**, *4*, 1461.

(27) Sakamaki, F.; Hatakeyama, S.; Akimoto, H. *Int. J. Chem. Kinet* **1983**, *15*, 1013.

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

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

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

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