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Oxidation Mechanisms for Ethyl Chloride and Ethyl Bromide under Atmospheric Conditions

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The Cl-atom initiated oxidation of ethyl chloride and ethyl bromide has been investigated as a function of temperature (220−298 K) in an environmental chamber equipped with an FTIR spectrometer. In the absence of NO_x, reaction with O_2 ($CH_3CHClO + O_2 \rightarrow CH_3C(O)Cl + HO_2$, reaction 9) and decompositon via HCl-elimination ($CH_3CHClO \rightarrow CH_3CO + HCl$, reaction 8a) are shown to be competing fates of the CH_3CHClO radical generated in the ethyl chloride system, with $k_9/k_{8a} = 3.2 \times 10^{-24} \exp(2240/T)$ cm^3 molecule^{-1}. The CH_3CHClO radical is also shown to be subject to a chemical activation effect; when produced in the exothermic reaction of CH_3CHClO_2 with NO, about 50% of the nascent CH_3CHClO radicals decompose promptly via HCl elimination, before collisional deactivation can occur. The reaction of Cl with ethyl bromide occurs 70−80% via abstraction from the $-CH_2Br$ group and 20−30% via abstraction from the $-CH_3$ group. The observation of ethene in this system indicates that the $BrCH_2CH_2$ radical (generated via abstraction from the $-CH_3$ group) undergoes Br-atom elimination ($BrCH_2CH_2 \rightarrow CH_2{=}CH_2 + Br$, reaction 37) in competition with its reaction with O_2 ($BrCH_2CH_2 + O_2 \rightarrow BrCH_2CH_2O_2$, reaction 34) At atmospheric pressure, this competition is governed by the rate coefficient ratio, $k_{37}/k_{34} = 1.4 \times 10^{23} \exp(-2800/T)$ molecule cm^{-3}. The chemistry of the CH_3CHBrO radical (generated from abstraction at the $-CH_2Br$ site) is dominated by Br-atom elimination; no evidence for its reaction with O_2 could be found at any temperature.

Introduction

Partially chlorinated and/or brominated alkanes are present in the earth's atmosphere as the result of both natural and anthropogenic activities,[1] and their oxidation mechanisms under atmospheric conditions have been the subject of a number of recent studies.[2−20] Ethyl chloride and ethyl bromide are minor components of the atmospheric halogen burden,[1] arising mostly from natural sources. In addition, these species are good model compounds for larger partially halogenated organics found in the atmosphere (e.g., chlorinated solvents, the HCFCs in use as CFC replacement compounds, and the alkyl bromides being proposed for use as industrial solvents).

The Cl-atom initiated oxidation of ethyl chloride has been extensively investigated near 298 K by scientists at the Ford Motor Company.[2−4] Abstraction of an H-atom occurs at two sites (with abstraction at the $-CH_2Cl$ group dominating), leading to the formation of two peroxy radicals, CH_3CHClO_2 and $ClCH_2CH_2O_2$:

$$Cl + CH_3CH_2Cl \rightarrow CH_3CHCl + HCl\ (82\%) \tag{1a}$$

$$Cl + CH_3CH_2Cl \rightarrow ClCH_2CH_2 + HCl\ (18\%) \tag{1b}$$

$$CH_3CHCl + O_2 + M \rightarrow CH_3CHClO_2 + M \tag{2}$$

$$ClCH_2CH_2 + O_2 + M \rightarrow ClCH_2CH_2O_2 + M \tag{3}$$

Subsequent chemistry of these peroxy species (in the absence of the oxides of nitrogen) yields in part 1-chloroethoxy (CH_3CHClO) and 2-chloroethoxy ($ClCH_2CH_2O$) radicals, as well as a suite of carbonyls, alcohols, and organic hydroperoxides:

$$CH_3CHClO_2 + RO_2 \rightarrow CH_3CHClO + RO + O_2 \tag{4a}$$

$$CH_3CHClO_2 + RO_2 \rightarrow CH_3C(O)Cl + ROH + O_2 \tag{4b}$$

$$CH_3CHClO_2 + RO_2 \rightarrow CH_3CH(Cl)OH + R{=}O + O_2 \tag{4c}$$

$$CH_3CHClO_2 + HO_2 \rightarrow CH_3CH(Cl)OOH + O_2 \tag{5}$$

$$ClCH_2CH_2O_2 + RO_2 \rightarrow ClCH_2CH_2O + RO + O_2 \tag{6a}$$

$$ClCH_2CH_2O_2 + RO_2 \rightarrow ClCH_2CHO + ROH + O_2 \tag{6b}$$

$$ClCH_2CH_2O_2 + RO_2 \rightarrow ClCH_2CH_2OH + R{=}O + O_2 \tag{6c}$$

$$ClCH_2CH_2O_2 + HO_2 \rightarrow ClCH_2CH_2OOH + O_2 \tag{7}$$

where RO_2 represents any organic peroxy radical present in the system.

Surprisingly large yields of HCl and CO_2 observed in these experiments[2−4] were rationalized in terms of a novel HCl elimination from the CH_3CHClO radical, reaction 8a:

$$CH_3CHClO + M \rightarrow CH_3CO + HCl + M \tag{8a}$$

$$\rightarrow CH_3CHO + Cl + M \tag{8b}$$

$$CH_3CHClO + O_2 \rightarrow CH_3C(O)Cl + HO_2 \tag{9}$$

Furthermore, the lack of a dependence of the product (HCl, $CH_3C(O)Cl$) yields on O_2 partial pressure indicated that this

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HCl elimination was the dominant (if not sole) fate of the CH_3CHClO radical over the range of conditions studied.

Similar studies[5−9] on the CH_2ClO radical (generated from the Cl-atom initiated oxidation of methyl chloride) show that HCl elimination does occur, though this is a minor process compared with O_2 reaction 11 under typical atmospheric conditions:

$$CH_2ClO + M \rightarrow HCO + HCl + M \qquad (10a)$$

$$\rightarrow CH_2O + Cl + M \qquad (10b)$$

$$CH_2ClO + O_2 \rightarrow HC(O)Cl + HO_2 \qquad (11)$$

Furthermore, it was shown[7] that the HCl elimination channel (10a), as well as the C−Cl scission reaction 10b were enhanced by a chemical activation effect in the presence of NO. That is, conversion of CH_2ClO_2 to CH_2ClO via exothermic reaction 12 results

$$CH_2ClO_2 + NO \rightarrow CH_2ClO^* + NO_2 \qquad (12)$$

in part in the formation of internally excited CH_2ClO, whose decomposition via reactions 10a and 10b is prompt compared to its deactivation rate.

Theoretical studies of the CH_3CHClO and CH_2ClO reaction systems have also been carried out.[18−20] In accord with the laboratory results, HCl elimination (8a) from CH_3CHClO was found to be the most rapid unimolecular pathway available, occurring with a rate coefficient of about 10^6 s^{-1} at 1 atm, 298 K.[18] Furthermore, the calculated barrier of only about 5 kcal/mol for (8a) makes chemical activation likely in this system. In an earlier study from the same group,[19] Cl-atom elimination was shown to be the lowest energy pathway for CH_2ClO; the HCl-elimination process (10a) was apparently not considered, however. Semiempirical calculations show HCl elimination from CH_2ClO to be possible,[20] though barriers to both reactions 10a and 10b obtained by these methods are considerably higher than has been shown by recent experiments.[7]

The oxidation of ethyl bromide has not yet been studied under atmospheric conditions. However, some data on α-brominated alkoxy radical chemistry are available.[15−17,21] The chemistry of the CH_2BrO and $CHBr_2O$ radicals[15−17] has been shown to be dominated by Br-atom elimination over the temperature range 220−300 K, even in the presence of ≈1 atm of O_2. The CH_3CHBrO radical has been studied indirectly by Bierbach et al.[21] in a study of the Br-atom-initiated oxidation of *trans*-2-butene. While the major CH_3CHBrO reaction pathway was via Br-atom elimination reaction 13, small yields of $CH_3C(O)Br$ indicated that some reaction with O_2, reaction 14, may have been occurring:

$$CH_3CHBrO + M \rightarrow CH_3CHO + Br + M \qquad (13)$$

$$CH_3CHBrO + O_2 \rightarrow CH_3C(O)Br + HO_2 \qquad (14)$$

However, formation of $CH_3C(O)Br$ via this pathway is not consistent with the anticipated rapid elimination of a Br-atom.

In this paper, the Cl-atom-initiated oxidation of ethyl chloride and ethyl bromide is explored over a range of temperature (220−298 K) and O_2 partial pressures (20−650 Torr), both in the absence and presence of NO_x. Product yield data are interpreted in terms of the fate of the α-halogenated alkoxy radicals, CH_3CHClO and CH_3CHBrO, for conditions representative of the troposphere. The mechanism for the Cl-atom reaction with ethyl bromide and the chemistry of the $BrCH_2CH_2$ radical are also investigated.

Experimental Section

All experiments were carried out in a 2-m long, 47-L stainless steel environmental chamber, described previously.[6,7,16,17,22] The cell temperature (which was varied from 220 to 298 K) was controlled by flowing chilled ethanol (from a Neslab ULT-80DD circulating bath) through a jacket surrounding the cell. The chamber is interfaced to a Bomem DA 3.01 Fourier Transform Infrared Spectrometer via a set of Hanst multipass optics, which provided a total observational path length of 32.6 m. Spectra were recorded over the range 800−3900 cm^{-1} at a resolution of 1 cm^{-1}, and were obtained from the co-addition of 200 interferograms (3.5 min acquisition time).

Experiments involved the photolysis of mixtures of Cl_2 ((0.7−10) × 10^{15} molecule cm^{-3}) and either ethyl chloride ((0.8−8) × 10^{15} molecule cm^{-3}) or ethyl bromide ((1.7−7) × 10^{15} molecule cm^{-3}), in mixtures of O_2 (20−620 Torr) and N_2 (100−720 Torr) at total pressures of 700−760 Torr. NO ((4−7) × 10^{14} molecule cm^{-3}) was added to the reaction mixture in some cases. The ratio of $[O_2]/[Cl_2]$ was typically >2000, thus limiting the occurrence of reactions of alkyl (e.g., CH_3CHCl) or acyl (e.g., CH_3CO) radicals with Cl_2 to <1%.[4] Photolyses were conducted with an unfiltered cw Xe-arc lamp, directed along the length of the cell through a quartz window located at one end. Reaction mixtures were photolyzed four to six times (each photolysis period being 30−200 s), and an infrared spectrum was recorded following each photolysis period. Under these conditions, about 20% of the parent alkyl halide was consumed over the course of an experiment.

Reactants (ethyl chloride and ethyl bromide) and products (CO_2, CO, $CH_3C(O)Cl$, $CH_3C(O)Br$, CH_3CHO, CH_3OH, $CH_3C(O)OH$, $CH_3C(O)OOH$, CH_2O, HC(O)OH and its dimer, HC(O)Cl, $BrCH_2CHO$, $ClCH_2CHO$) were quantified by comparison with standard spectra recorded in our laboratory at the same pressure and temperature as the experiment. For CO_2, which showed nonlinear absorbance vs concentration behavior under the conditions employed, concentrations were obtained by interpolation of absorbance versus $[CO_2]$ plots. Standard samples of $CH_3C(O)Cl$ or $CH_3C(O)Br$ were generated in the chamber from the brief photolysis of Cl_2 or Br_2 (≈20 mTorr)/CH_3CHO (≈20 mTorr)/N_2 mixtures at atmospheric pressure. Quantification of the $CH_3C(O)Cl$ and $CH_3C(O)Br$ was possible with the assumption[23] of unit conversion of CH_3CHO to the acetyl halide, e.g.,

$$Cl_2 + h\nu \rightarrow Cl + Cl \qquad (15)$$

$$Cl + CH_3CHO \rightarrow CH_3CO + HCl \qquad (16)$$

$$CH_3CO + Cl_2 \rightarrow CH_3C(O)Cl + Cl \qquad (17)$$

Absorption cross sections for the two halides were found to be 1.3 × 10^{-18} cm^2 $molecule^{-1}$ (acetyl chloride, R-branch maximum at 1827 cm^{-1}) and 1.8 × 10^{-18} cm^2 $molecule^{-1}$ (acetyl bromide, R-branch maximum at 1831 cm^{-1}) at 298 K; both values increased by 20% at 220 K. These $CH_3C(O)Cl$ data are in accord with previous determinations made in our laboratory.[23] Reference spectra for $BrCH_2CHO$ ($ClCH_2CHO$) were generated from the reaction of Br (Cl) with ethene in the presence of O_2, and quantified using cross section data provided by Yarwood et al.[24]

Test experiments were conducted to ensure that no unaccounted-for loss of products or starting materials was occurring. Loss of ethyl chloride and ethyl bromide by photolysis (i.e., in the absence of Cl_2) was found to be negligibly slow. In some cases, reacted mixtures were left sitting in the dark for periods of up to an hour. No gain or loss of any reaction product or starting material was noted.

Chemicals used in these experiments were obtained from the following sources: Cl_2 (Matheson, UHP); ethyl chloride, ethyl bromide, acetaldehyde (all Aldrich, > 99+ %); O_2 (U.S. Welding); N_2, (boil-off from liquid N_2, U.S. Welding); NO (Linde, UHP). Gases were used as received, while liquids were subjected to several freeze−pump−thaw cycles before use.

Results and Discussion

1. Ethyl Chloride. Products observed at all temperatures following the photolysis of Cl_2/CH_3CH_2Cl mixtures in O_2/N_2 diluent were CO_2, $CH_3C(O)Cl$, CO, CH_2O, CH_3OH, HC(O)OH (and its dimer at low temperature), $CH_3C(O)OOH$ (peracetic acid), HC(O)Cl, and $ClCH_2CHO$. Yield data for selected experiments are shown in Table 1. The observed products accounted for about 70−85% of the reacted ethyl chloride, and can be explained from a consideration of reactions 1−8 above, as well as chemistry of the acetyl radical generated in reaction 8a,

$$CH_3CO + O_2 + M \rightarrow CH_3C(O)O_2 + M \tag{18}$$

$$2CH_3C(O)O_2\ (+\ 2O_2) \rightarrow 2CH_3O_2 + 2CO_2 + O_2 \tag{19}$$

$$CH_3C(O)O_2 + HO_2 \rightarrow CH_3C(O)OOH + O_2 \tag{20a}$$

$$\rightarrow CH_3C(O)OH + O_3 \tag{20b}$$

$$CH_3C(O)O_2 + CH_3O_2\ (+\ O_2) \rightarrow CH_3O + CH_3O_2 + CO_2 + O_2 \tag{21}$$

$$CH_3C(O)O_2 + CH_3O_2 \rightarrow CH_3C(O)OH + CH_2O + O_2 \tag{22}$$

$$2CH_3O_2 \rightarrow CH_3OH + CH_2O + O_2 \tag{23a}$$

$$\rightarrow 2CH_3O + O_2 \tag{23b}$$

$$CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2 \tag{24}$$

$$CH_3O + O_2 \rightarrow CH_2O + HO_2 \tag{25}$$

$$CH_2O + HO_2 \leftrightarrow HOCH_2OO \rightarrow \quad \rightarrow HCOOH \tag{26}$$

$$2HO_2 \rightarrow H_2O_2 + O_2 \tag{27}$$

and secondary reactions of $ClCH_2CHO$, which lead to HC(O)Cl. As with other peroxides in our chamber system, H_2O_2, CH_3OOH, and $CH_3CH(Cl)OOH$ were not detected and are presumably lost rapidly at the cell walls. Before considering in more detail the implications of the observed yields and their dependence on temperature and O_2 partial pressure, it is worthwhile to compare our room-temperature yields with previous[2,4] work. Shi et al.[2] and Kaiser and Wallington[4] both reported yields of ≈15% $CH_3C(O)Cl$ from the Cl-atom initiated oxidation of ethyl chloride, similar to our yields which range from 12% at low [O_2] to 19% at high [O_2]. However, Shi et al. observed no dependence of the $CH_3C(O)Cl$ yield on [O_2], in contrast to our data. Shi et al. also report yields for CO_2 (53%), CH_3OH (7%), and CH_2O (30%, if its byproducts CO and HCOOH are included). Again, although Shi et al. observed no dependence of these yields on [O_2], their yields are quite similar to ours.

TABLE 1: Measured Product Yields (%) as a Function of Temperature from the Photolysis of $Cl_2/CH_3CH_2Cl/O_2/N_2$ Mixtures at a Total Pressure of 710 Torr[a]

temperature (K)	298		273		254		237		220	
O_2 pressure (Torr)	20	550	20	620	20	620	20	500	20	620
CO_2	66	52	57	46	51	32	58	24	50	12
$CH_3C(O)Cl$	12	19	12	22	14	34	20	43	26	48
CH_3OH	5	4	4	2	4	2	4	2	3	1
CH_2O[b]	32	28	29	24	23	10	11	4	12	3
peracetic acid	7	7	5	6	5	6	5	5	2	2
$ClCH_2CHO$[b]	17	19	15	14	13	12	11	11	9	9
total C balance	87	87	77	78	71	74	73	74	70	67

[a] Uncertainties in the measured yield data are as follows: for CO_2, ±5%; for $CH_3C(O)Cl$, CH_3OH, CH_2O, and peracetic acid, ±2%; for $ClCH_2CHO$, ±4%; data are shown for the extremes of the range of O_2 partial pressures investigated. [b] The yield of CH_2O includes those of its byproducts, CO and HCOOH (monomer + dimer). See text for details. [c] The yield of $ClCH_2CHO$ includes that of its byproduct, HC(O)Cl.

Since $ClCH_2CHO$ and its byproduct HC(O)Cl are the major products obtained following reaction 1b, the total yield of these species provides a lower limit to the branching ratio k_{1b}/k_1. The sum of the yields of these two species was found to be 18 ± 4% at 298 K, and to decrease to 9 ± 4% at 220 K. Our value of k_{1b}/k_1 at 298 K, though strictly a lower limit, is in agreement with those determined by Shi et al.[2] and Niedzielski et al.,[25] who both obtained values of k_{1b}/k_1 of 0.18 ± 0.02 using a competitive chlorination technique.

As alluded to earlier, products resulting from abstraction at the $-CH_2Cl$ group included $CH_3C(O)Cl$, CO_2, $CH_3C(O)OOH$, $CH_3C(O)OH$, CH_2O, CO, HCOOH, and CH_3OH. No evidence was found for the presence of CH_3CHO under any conditions. Based on an upper limit of 4% to its yield, we can conclude that Cl-atom elimination, reaction 8b, accounts for no more than 10% of the chemistry of the CH_3CHClO radical.

At a given temperature, the $CH_3C(O)Cl$ yield was found to increase with increasing O_2 partial pressure (note that the yields in Figure 1 have been corrected for a very small, ≤1.5%, occurrence of the reaction of CH_3CO with Cl_2 at low [O_2]). On the other hand, the total yield of all products originating from the acetylperoxy radical chemistry (CO_2, CO, HC(O)OH, $CH_3C(O)OOH$, CH_2O, CH_3OH) was found to decrease with increasing O_2 partial pressure. These observations reflect the competition between reactions 8a and 9, which can be expressed as follows:

$$Y(CH_3COCl) = Y(CH_3CHClO) * \{(k_9/k_{8a})\,[O_2]/(1 + (k_9/k_{8a})\,[O_2])\} + C \tag{A}$$

$$Y(CO_2^{corr}) = Y(CH_3CHClO) * \{1/(1 + (k_9/k_{8a})\,[O_2])\} \tag{B}$$

where Y(X) reflects the yield of species X, CO_2^{corr} reflects the yield of CH_3CO radical as described below, and C is used to quantify any O_2-independent formation of CH_3COCl, for example via reaction 4b. Inclusion of the term $Y(CH_3CHClO)$, the fraction of the oxidized ethyl chloride that proceeds via CH_3CHClO formation, serves to normalize the measured product yields to the amount of CH_3CHClO actually generated.

While the occurrence of reaction 9 can be tracked uniquely through the O_2-dependence of the $CH_3C(O)Cl$ yield, reaction 8a leads to the generation of either peracetic acid, acetic acid (not observed, but minor compared to peracetic acid based on measurements of k_{20a}/k_{20b} = 2.5 ± 0.5),[26−30] or CO_2 and a

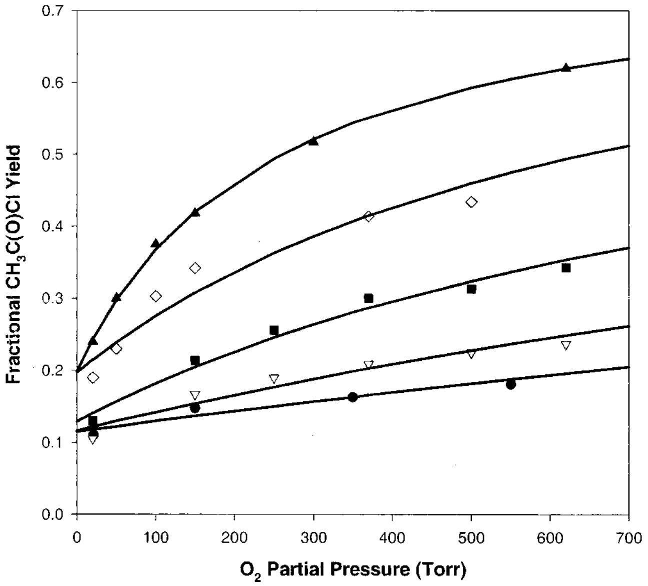

Figure 1. Yield of $CH_3C(O)Cl$ as a function of the O_2 partial pressure from the photolysis of $Cl_2/CH_3CH_2Cl/O_2/N_2$ mixtures at a total pressure of 710 ± 10 Torr: solid circles, 298 K; open triangles, 273 K; solid squares, 254 K; open diamonds, 237 K; solid triangles, 220 K. Lines are fits of equation (A) to the data, see text for details.

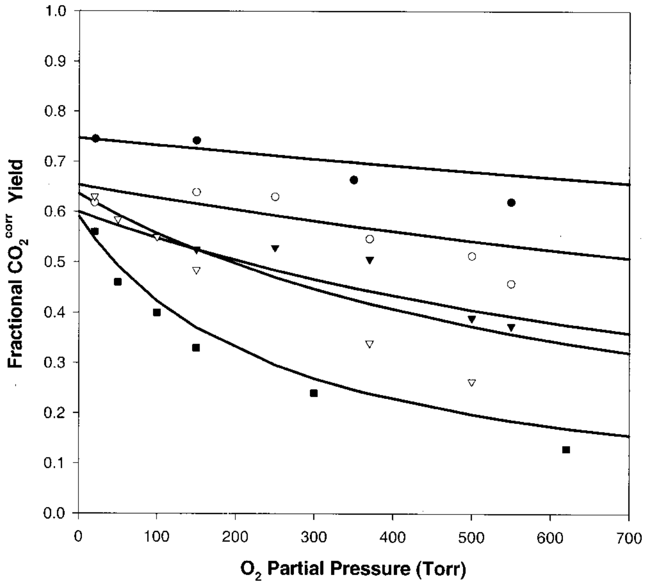

Figure 2. Yield of CO_2^{corr} as a function of the O_2 partial pressure from the photolysis of $Cl_2/CH_3CH_2Cl/O_2/N_2$ mixtures at a total pressure of 710 ± 10 Torr: solid circles, 298 K; open circles, 273 K; solid triangles, 254 K; open triangles, 237 K; solid squares, 220 K. Lines are fits of equation (A) to the data, see text for details.

CH_3O_2 radical (which eventually generates CH_2O, HC(O)OH, CH_3OH, CO, or CH_3OOH). The most accurate method for determining the extent of occurrence of reaction 8a was from the sum of the CO_2 and peracetic acid yields (with the peracetic acid yield multiplied by 1.4 to account for the undetected acetic acid), a quantity referred to as CO_2^{corr}. Plots of CO_2^{corr} versus O_2 as a function of temperature are shown in Figure 2. Although the data exhibit considerable scatter, they do show the expected trend of decreasing CO_2^{corr} with increasing O_2 and decreasing temperature. The sum of the CO, CH_2O, HC(O)OH, and CH_3OH yields were typically 20−40% less than those of CO_2, probably reflecting the (undetected) formation of CH_3OOH.

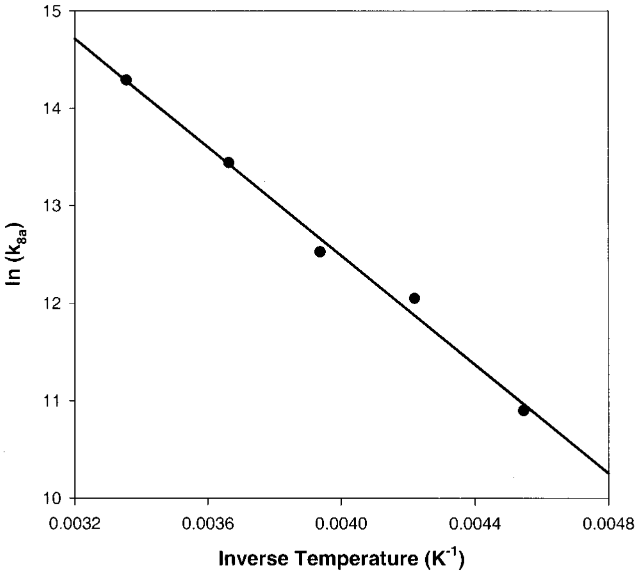

Figure 3. Rate coefficient data for the HCl elimination from CH_3CHClO, reaction 8a, plotted in Arrhenius form.

Fits of the $CH_3C(O)Cl$ and CO_2^{corr} data to the expressions above are shown in Figures 1 and 2. The fitting procedure was as follows. First, all $CH_3C(O)Cl$ and CO_2^{corr} yield data at a given temperature were fit simultaneously, with $Y(CH_3CHClO)$, k_9/k_{8a}, and C as fit parameters. Because the $CH_3C(O)Cl$ yield data were deemed to be the most accurate, a second fit was performed using only the $CH_3C(O)Cl$ data, but with the value of $Y(CH_3CHClO)$ (which is best determined by the CO_2 data at low $[O_2]$) fixed to the value obtained in the first fit. A couple of trends with temperature are evident in the data. First, the value of C was found to increase with decreasing temperature (from 12% at 298 K to 22% at 220 K), probably reflecting an increase in the branching ratio to molecular products in the peroxy radical self-reactions (4) and also the increase in the branching ratio k_{1a}/k_1 with decreasing temperature. As alluded to above, our yield of $CH_3C(O)Cl$ at 298 K and low O_2 is similar to previous reports,[2,4] though no O_2 dependence to the yield was noted in these previous studies.

More importantly, the rate coefficient ratio k_9/k_{8a} was found to increase with decreasing temperature. Fits of the temperature-dependent k_9/k_{8a} data to an Arrhenius expression yielded $k_9/k_{8a} = 3.2 \times 10^{-24} \exp(2240/T)$ cm^3 molecule^{-1}. If one estimates the value of k_9 to be $6 \times 10^{-14} \exp(-550/T)$ cm^3 molecule^{-1} s^{-1}, on the basis of data for the rate coefficient for the reaction of ethoxy radicals with O_2,[31] an estimated expression for k_{8a} can be obtained, $k_{8a} = 1.9 \times 10^{10} \exp(-2790/T)$ s^{-1}, for 1 atm total pressure (see Figure 3). Thus, the three-center HCl elimination is characterized by a relatively low A-factor (compared to values of $10^{13}-10^{14}$ typical of simple alkoxy radical bond cleavage reactions), and a relatively low activation barrier (about 6 kcal/mol). The agreement between our Arrhenius expression for k_{8a} and that obtained in the theoretical analysis of Hou et al.,[18] $k_{8a} = 6.5 \times 10^{10} \exp(-2869/T)$ s^{-1}, is quite remarkable given the uncertainties involved in the two studies. The theoretical studies also show that the reaction is in the pressure fall-off region at atmospheric pressure, reaching its high-pressure limit near 10 atm with an *A*-factor of order 10^{12} s^{-1}.

The low activation barrier to reaction 8a makes it quite likely that this decomposition will be prone to chemical activation;[7,18,30,32] that is, decomposition yields will be larger when the CH_3CHClO radical is generated from the exothermic reaction of CH_3CHClO_2 with NO, than following its generation from the near-thermoneutral peroxy radical self-reaction. Thus, some ethyl chloride experiments were carried out in the presence of NO_x. Major carbon-containing products observed in the photolysis of $Cl_2/C_2H_5Cl/NO/O_2/N_2$ mixtures were CO_2, $CH_3C(O)Cl$, PAN, CH_2O, and CO. As was the case in the absence of NO_x, CH_3CHO was not found in these experiments (yield <4%). Under these conditions, the chemistry of the CH_3CHClO_2 radical is dominated by its reaction with NO,

$$CH_3CHClO_2 + NO \rightarrow CH_3CHClO + NO_2 \qquad (28)$$

and all $CH_3C(O)Cl$ must originate from this reaction, followed by reaction 9. Other major products listed above are obtained pursuant to reactions 8a and 18, with the sum of the CO_2 and PAN yields providing a measure of the occurrence of (8a):

$$CH_3C(O)O_2 + NO\ (+O_2) \rightarrow CH_3O_2 + CO_2 + NO_2 \qquad (29)$$

$$CH_3C(O)O_2 + NO_2 + M \rightarrow CH_3C(O)O_2NO_2 + M \qquad (30)$$

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2 \qquad (31)$$

$$CH_3O + O_2 \rightarrow CH_2O + HO_2 \qquad (25)$$

$$HO_2 + NO \rightarrow OH + NO_2 \qquad (32)$$

Surprisingly, the sum of the yields of CO_2, PAN, and $CH_3C(O)Cl$ was only 65 ± 7%, lower than the 80% yield expected on the basis of the branching ratio k_{1a}/k_1. This discrepancy was also noted by Shi et al.[2] The absence of CH_3CHO in these experiments indicates that reaction 8b does not play a major role in the chemistry of excited CH_3CHClO radicals, and cannot account for the missing carbon. Note also that OH is generated when NO is present; this should have little effect on the observed chemistry, however, since the branching ratio for attack of OH on the two ends of ethyl chloride should be about equal to that for Cl-atom attack.[33]

To explore the extent of the effects of chemical activation, experiments were conducted in the presence of NO_x under conditions most likely to favor reaction of the CH_3CHClO radical with O_2, reaction 9, relative to its decomposition reaction 8a (i.e., under conditions of low temperature, 220 K, and high O_2 partial pressures, 300 Torr). In the NO_x-free experiments discussed above, the ratio $k_9[O_2]/k_{8a}$ was about unity for these conditions. However, in the presence of NO_x, the (CO_2 + PAN) yield exceeded that of $CH_3C(O)Cl$ by about a factor of 3, implying that about half of the nascent CH_3CHClO radicals decompose promptly via (8a), before collisional deactivation occurs. Chemical activation was also predicted by the theoretical study of Hou et al.; they calculate a lifetime of ≈10−100 ps for CH_3CHClO radicals containing 8 kcal/mol of internal energy, about the average amount expected to be imparted in the exothermic reaction 28.[32]

2. Ethyl Bromide. Products observed in the photolysis of $Cl_2/C_2H_5Br/O_2/N_2$ mixtures at all temperatures were CO, CO_2, CH_2O, $CH_3C(O)Br$, CH_3CHO, C_2H_4, $BrCH_2CHO$, and $CH_3C(O)OOH$. On average, these species accounted for 80 ± 10% of the reacted carbon. The apparent yields of CH_2O and C_2H_4 were observed to roll off with time. This roll-off is too rapid to be explained by reaction of these species with Cl, and is very likely due to their rapid reaction with Br-atoms.[34−36] As will be discussed in more detail below, the Cl-atom initiated oxidation of ethyl bromide generates substantial yields of Br (via decomposition of $BrCH_2CH_2$ and CH_3CHBrO radicals); because Br is not reactive with ethyl bromide, its main fate is thus reaction with CH_2O, CH_3CHO, and C_2H_4 products. For quantification, plots of percent yield of these species versus ethyl bromide consumption were constructed, and actual yields were obtained via extrapolation of these plots to zero ethyl bromide consumption. Yields of CH_3CHO and $BrCH_2CHO$ were difficult to quantify because the spectra of these two species are strongly overlapped, and because the apparent yields were small and decreased with increasing reaction time, again likely due to rapid reaction with Br.

By analogy to reaction of Cl with ethyl chloride[2] and ethyl fluoride,[37] abstraction at the $-CH_3$ group (33b) is likely to be minor compared to reaction at the $-CH_2Br$ group (33a):

$$Cl + CH_3CH_2Br \rightarrow CH_3CHBr + HCl \qquad (33a)$$

$$Cl + CH_3CH_2Br \rightarrow BrCH_2CH_2 + HCl \qquad (33b)$$

Products anticipated following the occurrence of the minor channel (33b) include $BrCH_2CHO$, $BrCH_2CH_2OH$, and $BrCH_2CH_2OOH$. Of these species, only $BrCH_2CHO$ could be identified in the product spectra.

$$BrCH_2CH_2 + O_2 + M \rightarrow BrCH_2CH_2O_2 + M \qquad (34)$$

$$BrCH_2CH_2O_2 + RO_2 \rightarrow BrCH_2CH_2O + RO + O_2 \qquad (35a)$$

$$BrCH_2CH_2O_2 + RO_2 \rightarrow BrCH_2CHO + ROH + O_2 \qquad (35b)$$

$$BrCH_2CH_2O_2 + RO_2 \rightarrow BrCH_2CH_2OH + R{=}O + O_2 \qquad (35c)$$

$$BrCH_2CH_2O_2 + HO_2 \rightarrow BrCH_2CH_2OOH + O_2 \qquad (36)$$

Generation of C_2H_4 also likely occurs following reaction 33b, as the result of the decomposition of the $BrCH_2CH_2$ radical,

$$BrCH_2CH_2 + M \rightarrow Br + C_2H_4 + M \qquad (37)$$

which occurs in competition with its reaction with O_2, reaction 34. This reaction sequence is identical to that seen in the reaction of Br with ethene (and other alkenes),[34,36,38,39] in which the effective rate coefficient is dependent on O_2, reflecting a competition between Br/ethene adduct decomposition and its reaction with O_2.

This competition was explored in the present case by examining the ethene yield as a function of O_2 at various temperatures, ranging from 226 to 298 K. As discussed earlier, C_2H_4 yields were taken as the intercepts of plots of ethene yield (molar %) vs ethyl bromide conversion. Ethene yield data, defined in this manner, are shown as a function of O_2 partial pressure and temperature in Figure 4. The data show the expected trends— the ethene yield decreases with increasing O_2 (i.e., with increasing rate of reaction 34), and with decreasing temperature (as the thermal stability of the $BrCH_2CH_2$ adduct increases). From a consideration of the reaction mechanism, it can be seen that the ethene yield is described by the following expression:

$$Y_{C_2H_4} = Y_{BrCH_2CH_2}\,\{1/(k_{34}[O_2]/k_{37} + 1)\} \qquad (C)$$

where $Y_{C_2H_4}$ is the observed C_2H_4 yield, and $Y_{BrCH_2CH_2}$ is the yield of $BrCH_2CH_2$, that is, the branching ratio k_{33b}/k_{33}. Ethene yield data at the three highest temperatures (298, 273, and 250 K) were fit to this expression, with k_{37}/k_{34} and $Y_{BrCH_2CH_2}$ as fit parameters. Retrieved values for k_{33b}/k_{33} and k_{37}/k_{34} are shown in Table 2. The fits (shown as solid lines in Figure 4) show a

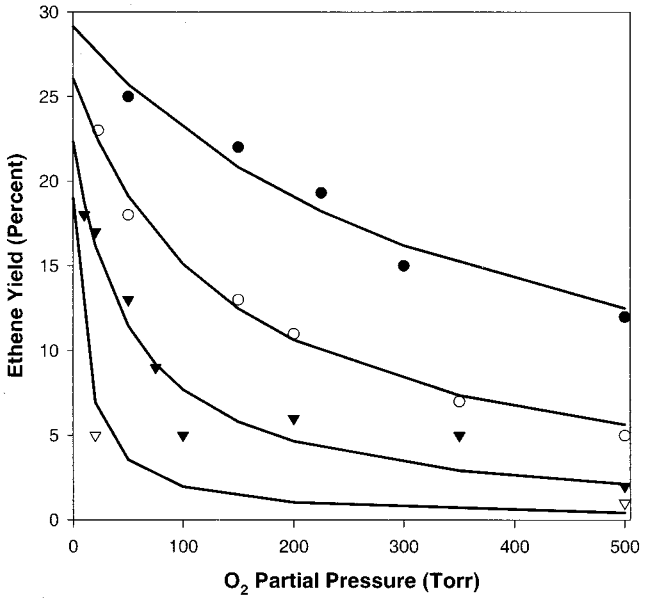

Figure 4. Yield of ethene (molar %) as a function of the O_2 partial pressure from the photolysis of $Cl_2/CH_3CH_2Br/O_2/N_2$ mixtures at a total pressure of 710 ± 10 Torr: solid circles, 298 K; open circles, 273 K; solid triangles, 250 K; open triangles, 226 K. Solid lines are fits of equation (C) to the data, see text for details.

TABLE 2: Data for k_{33b}/k_{33}, k_{37}/k_{34}, and k_{37}, Obtained from an Analysis of Ethene Yield Data from the Cl-Atom-Initiated Oxidation of Ethyl Bromide (see text for details)[a]

temp (K)	k_{33b}/k_{33}	k_{37}/k_{34} (molecule cm^{-3})	k_{37} (s^{-1})
298	0.29	1.2×10^{19}	9.1×10^{7}
273	0.26	4.9×10^{18}	3.7×10^{7}
250	0.22	2.0×10^{18}	1.5×10^{7}
226	0.19	6.0×10^{17}	4.5×10^{6}

[a] Data at 226 K are obtained via extrapolation of higher temperature values.

slight decrease in branching ratio k_{33b}/k_{33} with decreasing temperature, from about 29% at 298 K to 23% at 250 K, and imply a slightly higher fraction of reaction occurring at the $-CH_3$ group than in the case of ethyl chloride (18% at room temperature[2]). As expected, retrieved values of k_{37}/k_{34} decreased with decreasing temperature, reflecting the greater thermal stability of the $BrCH_2CH_2$ radical (i.e., a decrease in k_{37} with temperature, see Table 1). The k_{37}/k_{34} data are described by the following Arrhenius expression, $k_{37}/k_{34} = 1.4 \times 10^{23} \exp(-2800/T)$ molecule cm^{-3}. With a reasonable assumption about the magnitude of k_{34} ($k = 7.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range considered here, by analogy to the rate coefficient for reaction of C_2H_5 with O_2 at 1 atm[37]), an Arrhenius expression for the decomposition reaction 37 can be estimated, $k_{37} = 1 \times 10^{12} \exp(-2800/T)$, see Table 2 and Figure 5.

These data are in reasonable agreement with k_{37} data obtained from studies of the reaction of Br with ethene,[34,36,38] the present data set being about a factor of 1.5−2 lower. While this level of agreement is within the combined uncertainties of the two data sets, it is possible that larger k_{37} values are obtained in the Br/ethene studies due to internal energy in the adduct that may allow for a more rapid decomposition before stabilization can occur. In any event, it is quite clear from studies of both Br + C_2H_4 and of the Cl-atom-initiated oxidation of ethyl bromide that the bond strength of the Br/C_2H_4 adduct is of order 6 kcal/mol, and that this adduct has a lifetime of order 10 ns at 298 K, 1 atm.

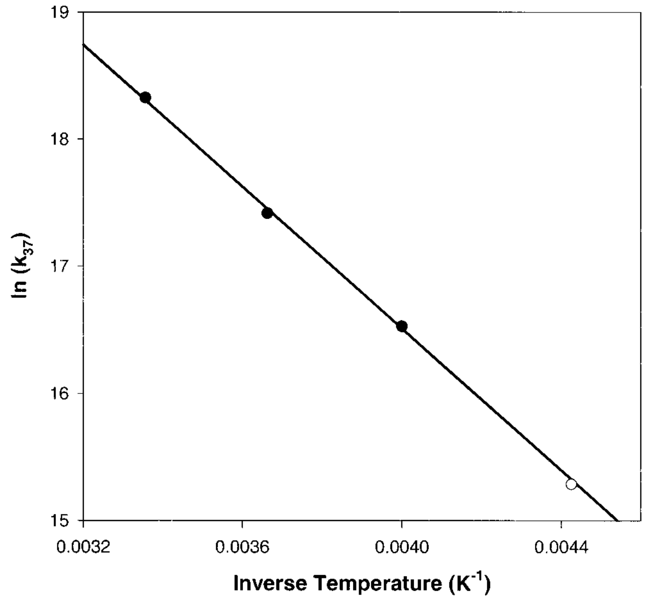

Figure 5. Rate coeffient data obtained for the decomposition of $BrCH_2$-CH_2 radical, reaction 37, plotted in Arrhenius form.

For completeness, a couple of ethene yield determinations were made at 228 K. Ethene yields were found to be quite small, 5% at 20 Torr O_2 partial pressure and 2% at 500 Torr. The "fit" curve for these data shown in Figure 4 was obtained by extrapolation of the temperature-dependent expression for k_{37}/k_{34} to 228 K, with an assumed $Y_{BrCH_2CH_2}$ of 19% (also obtained from an extrapolation of the higher temperature data). The two measured ethene yields are consistent with these extrapolated fit parameters.

The production of an alkene from the atmospheric oxidation of alkyl bromides will not be unique to the case of ethyl bromide. In fact, a similar reaction to reaction 37 has been noted in the case of the bromacetyl radical, $BrCH_2CO$, where Br-atom elimination to form ketene occurs in competition with C−C bond cleavage and addition of O_2 in 1 atm air at 298 K.[40] In addition, propene has recently been observed in the atmospheric oxidation of *n*-propyl bromide,[41] a compound currently being considered for use as an industrial solvent. The elimination of Br-atom from a β-brominated alkyl radical immediately following the initial OH attack on the parent alkyl bromide will serve to decrease the likelihood of the formation of long-lived brominated organics (e.g., bromoacetone from *n*-propyl bromide), and thus lessen the likelihood of Br transport to the stratosphere via these intermediate species. However, it should also be noted that data from Bedjanian et al.[38,39] imply a stronger Br/alkene bond with increasing alkene size, which will serve to decrease the yield of alkene from the correspondingly larger bromoalkanes. More information on the kinetics and energetics of the Br/alkene adducts (from studies of Br + alkene kinetics and alkyl bromide oxidation) is clearly desirable.

On the basis of our measured ethene yields at low O_2 partial pressure, it is apparent that about 70% of the Cl-atom reaction with ethyl bromide occurs via pathway 33a, with this fraction increasing to about 80% near 220 K:

$$Cl + CH_3CH_2Br \rightarrow CH_3CHBr + HCl \qquad (33a)$$

In a NO_x-free environment, products expected following pathway 33a include $CH_3C(O)Br$, $CH_3CH(Br)OOH$, CH_3CHO, and the products obtained from CH_3CO chemistry (CH_2O, CH_3OH, $CH_3C(O)OOH$, $CH_3C(O)OH$, and CO). All these species were indeed observed, except $CH_3CH(Br)OOH$, which is likely to decompose in our chamber system.

$$CH_3CHBr + O_2 + M \rightarrow CH_3CHBrO_2 + M \quad (38)$$

$$CH_3CHBrO_2 + RO_2 \rightarrow CH_3CHBrO + RO + O_2 \quad (39a)$$

$$CH_3CHBrO_2 + RO_2 \rightarrow CH_3C(O)Br + ROH + O_2 \quad (39b)$$

$$CH_3CHBrO_2 + HO_2 \rightarrow CH_3CH(Br)OOH + O_2 \quad (40a)$$

$$\rightarrow CH_3C(O)Br + H_2O + O_2 \quad (40b)$$

$$CH_3CHBrO + M \rightarrow CH_3CO + HBr + M \quad (41a)$$

$$\rightarrow CH_3CHO + Br + M \quad (41b)$$

$$CH_3CHBrO + O_2 \rightarrow CH_3C(O)Br + HO_2 \quad (42)$$

$CH_3C(O)Br$ formation can be via two pathways—via molecular channels of the reaction of the peroxy radical CH_3CHBrO_2 with other peroxy radicals (which would be independent of O_2 partial pressure) and via reaction of the CH_3CHBrO radical with O_2, which may occur in competition with the decomposition of this alkoxy species. $CH_3C(O)Br$ yields were found to be $5.5 \pm 1.0\%$, independent of O_2 (varied from 20 to 500 Torr) and temperature (varied from 226 to 298 K). The small yield of $CH_3C(O)Br$ indicates that the radical-propagating channels of the CH_3CHBrO_2 self- and cross-reactions, (39a), predominate as has been observed for other α-halogenated peroxy radicals.[2,42] Furthermore, there is no evidence for the occurrence of reaction 42, even at temperatures as low as 226 K, and the decomposition reactions (either 41a or 41b) must dominate. The conclusions drawn here regarding the chemistry of the CH_3CHBrO radical are similar to those reached by Bierbach et al.[20] in their study of the Br-atom initiated oxidation of *trans*-2-butene. However, these workers interpreted their observation of a small $CH_3C(O)Br$ yield as evidence for the occurrence of reaction 42. Our demonstration of the independence of the $CH_3C(O)Br$ yield on the O_2 partial pressure clearly shows that this species is obtained from chemistry of CH_3CHBrO_2 radicals, and not from the alkoxy species.

The relative rate of occurrence of the two decomposition reactions 41a and 41b is difficult to assess under the conditions of our experiments, as the rapid reaction of Br with CH_3CHO ($k = 3.2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K)[35] kept observed CH_3CHO levels very low (apparent yield ≈ 1% of the ethyl bromide consumption), and essentially rendered the two decomposition reactions indistinguishable. However, there is some evidence pointing to the occurrence of reaction 41b. First, the very fact that the apparent CH_3CHO yield was observed to fall off rapidly with ethyl bromide conversion is evidence for the production of substantial yields of Br atoms. Furthermore, on the basis of thermodynamic arguments, it is likely that the simple Br-atom elimination reaction 41b is predominant. Using data from the NASA JPL evaluation,[37] the Br-atom elimination is more exothermic than HBr elimination by about 2 kcal/mol. This is in contrast to the situation for CH_3CHClO, in which the HCl elimination channel is about 15 kcal/mol more exothermic than Cl-atom elimination.[18] The *trans*-2-butene experiments of Bierbach et al.[21] also point toward the predominance of Br-atom elimination; they observed CH_3CHO, but only very minor yields of the expected end-products of CH_3CO production (i.e., CH_2O and CH_3OH). Regardless of the nature of the decomposition reaction 41, some conclusions can be drawn regarding its rate. On the basis of our $CH_3C(O)Br$ yield data, we estimate that the rate of decomposition exceeds the rate for reaction with O_2 by a factor of 10, even at 226 K and in the presence of 500 Torr. Thus, with a likely value for k_{42} exceeding 1×10^{-14} cm^3 molecule^{-1} s^{-1},[8,9,31] the rate coefficient for the decomposition reaction must be at least 2×10^6 s^{-1} at 226 K.

Some room-temperature ethyl bromide oxidation experiments were also carried out in the presence of NO. In these experiments, conversion of the peroxy radical CH_3CHBrO_2 to the oxy radical CH_3CHBrO is via the exothermic reaction 43:

$$CH_3CHBrO_2 + NO \rightarrow CH_3CHBrO + NO_2 \quad (43)$$

and complications due to peroxy radical self- and cross-reactions are eliminated. In addition, the presence of NO and NO_2 serves to lower the steady-state Br-atom concentration (through the formation of BrNO and $BrNO_2$, and the subsequent reactions of these species with Br[15,16]), allowing the concentrations of species reactive toward Br-atoms to build up to higher levels than was the case in the NO_x-free experiments described above. In the presence of NO_x, CH_3CHO is clearly observed as a reaction product following reaction of Cl with ethyl bromide, with an initial yield of order 60% (recall that only 70% of the reaction occurs via abstraction at the $-CH_2Br$ group). Thus, in the case of internally excited CH_3CHBrO radicals generated from reaction 43, Br-atom elimination dominates. Finally, we note that no $CH_3C(O)Br$ was observed in these experiments, again confirming the lack of importance of reaction 42 in the chemistry of CH_3CHBrO radicals.

Conclusion

The oxidation mechanisms of both ethyl chloride and ethyl bromide have been studied under tropospherically relevant conditions. Ethyl chloride oxidation proceeds mainly via the CH_3CHClO radical, whose chemistry involves decomposition via HCl-elimination or reaction with O_2. The HCl-elimination reaction was found to possess an energy barrier of about 6 kcal/mol. As a result of this modest barrier, chemical activation plays an important role in the chemistry of internally excited CH_3CHClO radicals generated from the exothermic reaction of the CH_3CHClO_2 radical with NO.

Reaction of Cl-atoms with ethyl bromide occurs mostly (70−80%) at the $-CH_2Br$ group. The CH_3CHBrO radical thus obtained reacts exclusively via Br-atom elimination under tropospheric conditions. $BrCH_2CH_2$ radicals, generated via Cl-atom abstraction at the $-CH_3$ group, react via Br-atom elimination to form ethene or via addition of O_2 to form a peroxy radical. Kinetic parameters obtained for the Br-atom elimination reaction are broadly consistent with those obtained in previous studies of the reaction of Br with ethene. The generation of an alkene is likely to be a general occurrence in the tropospheric chemistry of alkyl bromides.

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