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FT-IR Product Studies of the Cl-Initiated Oxidation of CH_3Cl in the Presence of NO

Merete Bilde[†]

Risø National Laboratory, Roskilde, DK-4000, Denmark

John J. Orlando* **and Geoffrey S. Tyndall**

Atmospheric Chemistry Division, National Center for Atmospheric Research, Boulder, Colorado 80303

Timothy J. Wallington, Michael D. Hurley, and E. W. Kaiser

Ford Motor Company, Dearborn, Michigan 48121-2053

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The Cl-atom initiated oxidation of CH_3Cl has been studied at 296 K using two different FTIR/environmental chamber systems. In the presence of NO, the carbon-bearing products observed are HCOCl, HCHO, and CO, with yields in 700 Torr of air of (56 ± 10), (32 ± 6), and (12 ± 5)%, respectively. This product distribution is different from previous studies conducted in the absence of NO, in which a nearly 100% yield of HCOCl was obtained. The different product distribution observed in the presence of NO is attributed to the formation and subsequent decomposition of chemically activated CH_2ClO radicals, formed in the exothermic reaction of CH_2ClO_2 with NO.

Introduction

The deleterious effect of chlorine chemistry on stratospheric ozone levels is now well documented.[1] The sources of chlorine to the stratosphere include the man-made chlorofluorocarbons and naturally occurring species, the most abundant of which is methyl chloride. The atmospheric oxidation of methyl chloride proceeds via formation of the chloromethoxy radical, CH_2ClO.[2−6] In all previous studies[2−6] of CH_3Cl oxidation, CH_2ClO radicals were produced via Cl-initiated oxidation of CH_3Cl in the absence of NO, i.e., via reactions 1−4

$$Cl_2 + h\nu \rightarrow 2\ Cl \tag{1}$$

$$Cl + CH_3Cl \rightarrow CH_2Cl + HCl \tag{2}$$

$$CH_2Cl + O_2 \rightarrow CH_2ClO_2 \tag{3}$$

$$CH_2ClO_2 + CH_2ClO_2 \rightarrow CH_2ClO + CH_2ClO + O_2 \tag{4}$$

The conclusion of the two most recent studies[5,6] was that three-center elimination of HCl via reaction 5 and reaction with O_2 via reaction 6 are competing fates of the CH_2ClO radicals generated from reaction 4, with $k_6/k_5 = 5.6 \times 10^{-23} \exp(3300/T)$ cm^3 molecule^{-1}.

$$CH_2ClO + M \rightarrow HCO + HCl + M \tag{5}$$

$$CH_2ClO + O_2 \rightarrow HCOCl + HO_2 \tag{6}$$

Semiempirical calculations[4,7] show that HCl elimination will be favored over both Cl-atom and H-atom elimination, although the absolute barrier heights calculated are higher than those experimentally observed.[6]

In general, the self-reactions of peroxy radicals are close to thermoneutral,[8] and the resulting alkoxy radical has little or no excitation. However, because reactions of peroxy radicals with NO are exothermic[8] and occur via the formation of a ROONO complex that is sufficiently long-lived to allow for energy randomization, the alkoxy radicals produced in these reactions can possess internal excitation.[9−12] This internal excitation has been shown to be comparable to, or greater than, the barrier to various unimolecular processes (e.g., C−C bond rupture, elimination of a halogen atom, or HCl elimination), allowing the activated radicals to decompose on time scales that are short, compared to collisional deactivation, and thus leading to product distributions different from those obtained from thermalized radicals.

In light of our new understanding of the potential role of chemical activation in the atmospheric chemistry of alkoxy radicals, particularly for cases in which the activation barrier for decomposition of the alkoxy species is low, we have re-examined the atmospheric fate of CH_2ClO radicals. In this study, the products of the Cl-initiated oxidation of CH_3Cl in the presence of NO are investigated. It will be shown that the product yields obtained in the presence of NO are significantly different from those obtained in the absence of NO,[2,3,5,6] suggesting that an excited alkoxy radical (CH_2ClO^*) is formed in the reaction of CH_2ClO_2 with NO

$$CH_2ClO_2 + NO \rightarrow CH_2ClO^* + NO_2 \tag{7}$$

and that this excited species plays an important role in the atmospheric chemistry of CH_3Cl.

Experimental Section

Experiments were conducted in environmental chambers at Ford and NCAR, each of which is equipped with FT-IR spectrometers as described elsewhere.[13,14] CH_3Cl oxidation is

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* To whom correspondence should be addressed.

[†] Present address: Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213.

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initiated both by Cl-atoms (reaction 2) and by OH, which is generated via reaction of HO_2 radicals with NO.

$$OH + CH_3Cl \rightarrow CH_2Cl + H_2O \qquad (8)$$

The FT-IR system at Ford was interfaced to a 140-L Pyrex reactor. Radicals were generated by the UV irradiation (using 22 black lamps which surround the cell) of mixtures of CH_3Cl, Cl_2, O_2, and NO in 700 Torr total pressure of N_2 at 296 K. Reactant loss and product formation were monitored by FT-IR spectroscopy, with an analyzing path-length of 28 m and a resolution of 0.25 cm^{-1}. Infrared spectra were derived from 32 co-added spectra.

The apparatus at NCAR consisted of a 47-L stainless steel reactor fitted with a quartz window at one end to allow photolysis by means of a filtered xenon arc lamp. Experiments involved the photolysis of CH_3Cl (Matheson), Cl_2 (Matheson, UHP), NO (Linde), O_2 (U.S. Welding, UHP), and N_2 (liquid N_2 boil-off) and were conducted at 296 K. Typical photolysis times were 3 min. A Bomem DA 3.01 FT-IR spectrometer was interfaced to a Hanst-type optical arrangement mounted within the reaction cell, for in situ IR spectroscopic analysis of the gas mixture composition. Reactant loss and product formation were monitored by FT-IR absorption spectroscopy, with an optical path length of 32.6 m and a spectral resolution of 1.0 cm^{-1}. Infrared spectra were derived from 50 co-added interferograms.

CH_3Cl, and its oxidation products HCHO, HCOCl, and CO, were monitored using their characteristic features over the range 1000−2300 cm^{-1}. Reference spectra of HCHO and CO were acquired and calibrated by expanding a known pressure of reference material into the reactor from a calibrated volume. CO quantification was done in the 2060−2220 cm^{-1} region, while HCHO was quantified using the carbonyl stretch centered at 1745 cm^{-1}. HCOCl was identified by means of its characteristic IR features at 1305 and 1784 cm^{-1}. Quantification of the HCOCl yield was achieved using a previously reported cross section, $\sigma(1793\ cm^{-1}) = 1.63 \times 10^{-18}\ cm^2\ molecule^{-1}$.[5,6]

Although $[CH_3Cl]$ was kept high to minimize secondary chemistry, minor corrections to measured product yields needed to be made in some cases. First, stoichiometric conversion of HCOCl to CO on the stainless steel walls of the NCAR chamber,[6] which occurred with a first-order rate coefficient of $k_{het} = 3 \times 10^{-4}\ s^{-1}$, was accounted for as previously documented.[6] Conversion of HCOCl to CO via reaction with Cl-atoms, $k_9 = 7.6 \times 10^{-13}\ cm^3\ molecule^{-1}\ s^{-1}$,[15,16] or with OH, $k_{10} \approx 1 \times 10^{-13}\ cm^3\ molecule^{-1}\ s^{-1}$,[16] was also considered

$$Cl + HCOCl \rightarrow ClCO + HCl \qquad (9)$$

$$OH + HCOCl \rightarrow ClCO + H_2O \qquad (10)$$

$$ClCO \rightarrow Cl + CO \qquad (11)$$

Under conditions used at Ford (very high $[CH_3Cl]$ and thus small fractional conversion), reactions 9 and 10 were insignificant, and no correction was necessary. Computer simulations of the conditions used at NCAR (using ACUCHEM)[17] showed that the chemistry was largely controlled by Cl-atom reactions, and corrections were made for reaction 9 as previously described.[6]

Conversion of HCHO to CO, via reaction with either OH or Cl-atoms, was also considered

$$Cl + HCHO \rightarrow HCO + HCl \qquad (12)$$

$$OH + HCHO \rightarrow HCO + H_2O \qquad (13)$$

with $k_{12} = 7.3 \times 10^{-11}\ cm^3\ molecule^{-1}\ s^{-1}$ and $k_{13} = 1.0 \times 10^{-11}\ cm^3\ molecule^{-1}\ s^{-1}$.[8] As discussed above, Cl-atom chemistry was most important for experiments conducted at NCAR, and corrections were made as follows, i.e., ignoring the small effects of reaction 13:

$$[HCHO]_{corr} = [HCHO]_{obs}\,\{1 - \Delta[CH_3Cl]/[CH_3Cl]\}^{-0.5k_{12}/k_2}$$

$$[CO]_{corr} = [CO]_{obs} - ([HCHO]_{corr} - [HCHO]_{obs})$$

For experiments conducted at Ford, conversions of CH_3Cl were sufficiently small that correction to measured HCHO yields were not required.

Finally, conversion of HCO to HCOCl via reaction with Cl_2 was accounted for. Initial yield calculations were based on the assumption of total conversion of HCO to CO via reaction 14, $k_{14} = 5.5 \times 10^{-12}\ cm^3\ molecule^{-1}\ s^{-1}$.[8]

$$HCO + O_2 \rightarrow HO_2 + CO \qquad (14)$$

However, with $k_{15}/k_{14} = 1.15$,[5] small amounts of HCO were converted to HCOCl via reaction 15 in experiments conducted at low $[O_2]$.

$$HCO + Cl_2 \rightarrow HCOCl + Cl \qquad (15)$$

The observed product yields were quantified with a precision of ±10%. Possible systematic errors associated with the references may contribute an additional 10% to the uncertainty, leading to a total uncertainty of ±15% on the product yields. Uncertainties reported in this paper are two standard deviations unless otherwise stated, and standard error propagation methods are used to calculate combined uncertainties.

Results and Discussion

To investigate the potential formation of chemically activated alkoxy radicals in reaction 7, $Cl_2/CH_3Cl/O_2/N_2/NO$ mixtures in 700 Torr total pressure were irradiated. In the first series of experiments mixtures of 11.5 Torr (Ford) or 0.11 Torr (NCAR) of CH_3Cl, 100 mTorr of Cl_2, 10 mTorr of NO, and 4−400 Torr of O_2 in 700 Torr total pressure of N_2 were subjected to UV irradiation. Three carbon-containing products were identified: HCOCl, HCHO, and CO. In all of the experiments the loss of CH_3Cl was too small (<3%) to be quantified accurately, and the loss of CH_3Cl was thus assumed equal to the sum of the concentrations of the carbon-containing products: $\Delta[CH_3Cl] = \Delta[HCOCl] + \Delta[CO] + \Delta[HCHO]$. Figure 1 shows the yield of HCOCl and the combined yield of CO and HCHO versus the O_2 partial pressure. The dotted lines are included to aid visual inspection of the data trend. The solid lines show the expected yields of CO and HCOCl based upon experiments performed in the absence of NO,[5,6] and are given by $Y(HCOCl) = k_6[O_2]/(k_5 + k_6[O_2])$ and $Y(CO) = 1 - Y(HCOCl)$ with $k_6/k_5 = 3.9 \times 10^{-18}\ cm^3\ molecule^{-1}$.[6] Clearly, there is a difference in product yields from oxidation of CH_3Cl in the presence and absence of NO. At the highest concentrations of O_2, the HCOCl yield is expected to exceed 98%. However, in the presence of NO, only a 60% yield of HCOCl was observed at high $[O_2]$, whereas the combined yield of CO and HCHO was 40% under these conditions. This significant change in the product yields is a strong indication that a fraction of the alkoxy radicals formed in reaction 7 are chemically activated and undergo prompt decomposition to form products other than those expected from reactions 5 and 6 alone. Furthermore, the observation of HCHO suggests that a new reaction channel is opened up, which is inaccessible to the thermalized CH_2ClO radicals.

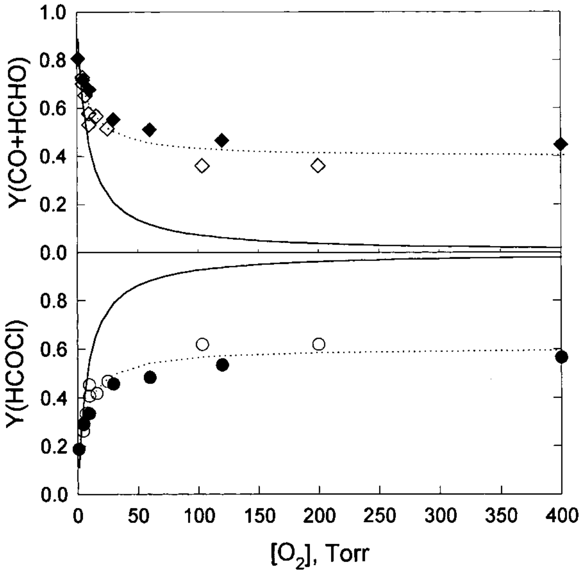

Figure 1. Product yields obtained in the Cl-atom-initiated oxidation of CH_3Cl (0.11 Torr, NCAR; 11.5 Torr, Ford) in the presence of NO (10 mTorr), as a function of the O_2 partial pressure: diamonds, combined yield of CO and HCHO; circles, yield of HCOCl, obtained at NCAR (open symbols) or Ford (filled symbols). The data were corrected for the effects of secondary chemistry, as described in the text. The dotted lines are included to aid visual inspection of the data trend. The solid lines are the expected product yields in the absence of NO.

On the basis of our previous studies of CF_3CFHO^*[9] and $HOCH_2CH_2O^*$[12] radicals, those radicals produced with an energy that is insufficient to overcome any barrier to unimolecular reaction are expected to be thermalized via collisions with molecules of the bath gas

$$CH_2ClO^* + M \rightarrow CH_2ClO + M \qquad (16)$$

whereas those produced above barriers to decomposition are expected to decompose on a subnanosecond time scale (i.e., on a time scale that does not allow for collisional deactivation or for bimolecular chemical reaction to occur). Possible channels for the decomposition of CH_2ClO^* radicals include

$$CH_2ClO^* \rightarrow H + HCOCl \qquad (17a)$$

$$CH_2ClO^* \rightarrow HCl + HCO \qquad (17b)$$

$$CH_2ClO^* \rightarrow Cl + HCHO \qquad (17c)$$

$$CH_2ClO^* \rightarrow H_2 + ClCO \qquad (17d)$$

Using a calculated enthalpy of formation for the thermalized alkoxy radical of ΔH_f (CH_2ClO) = -2.4 kcal mol^{-1},[6] the reaction enthalpies for decomposition of the thermalized radicals via reactions 17a−d are as follows:[8] ΔH_r (17a) = 10.2 kcal mol^{-1}, ΔH_r (17b) = -9.7 kcal mol^{-1}, ΔH_r (17c) = 5.3 kcal mol^{-1}, and ΔH_r (17d) = -2.6 kcal mol^{-1}. Again, on the basis of comparison with previous studies,[9,12] it is reasonable that at least a fraction of the nascent alkoxy radicals will possess sufficient energy to allow Cl-atom or possibly H-atom elimination to occur. The energy barrier to HCl elimination from the thermalized alkoxy radical is 9 kcal mol^{-1} [6] and is thus also accessible. H_2 elimination is 7 kcal mol^{-1} less favorable than HCl elimination; thus, the barrier to this process is likely to be prohibitively high, and its occurrence will not be further considered.

The remainder of this paper will be concerned with the determination of the relative importance of reactions 16 and 17a−c in the chemistry of the CH_2ClO^* radical formed in reaction 7. The following notation will be used throughout: α is the fraction of alkoxy radicals produced with insufficient energy to overcome any barrier to unimolecular reaction and that is thus collisionally thermalized, reaction 16; β is the fraction of activated alkoxy radicals that eliminates a hydrogen atom to form HCOCl, reaction 17a; γ_1 is the fraction of activated alkoxy radicals that eliminates HCl to form HCO (reaction 17b); and γ_2 is the fraction that eliminates Cl atoms to form HCHO (reaction 17c).

There are three potential sources of HCOCl in the system: hydrogen atom elimination from the excited alkoxy radical (reaction 17a), reaction of the thermalized alkoxy radical with O_2 (reaction 6), and reaction of the thermalized alkoxy radical with NO, via reaction 18a

$$CH_2ClO + NO \rightarrow HCOCl + HNO \qquad (18a)$$

$$CH_2ClO + NO \rightarrow HCHO + NOCl \qquad (18b)$$

$$CH_2ClO + NO + M \rightarrow CH_2ClONO + M \qquad (18c)$$

In Figure 1, the yield of HCOCl converges toward 60% at the highest concentrations of O_2. This suggests that essentially all of the thermalized alkoxy radicals are converted to HCOCl via reaction with O_2 and that reaction 18 is unimportant under these conditions. Thus, the yield of HCOCl in the limit of high O_2 provides a value of $\alpha + \beta$ of roughly 60%.

Also, at high [O_2], where reaction 18 is of negligible importance, channel 17c is the only source of HCHO. CO is formed via reaction 17b followed by reaction 14 or via destruction of HCHO, reactions 12−14. Thus, from the combined yield of CO and HCHO at high [O_2], we obtain $\gamma_1 + \gamma_2 \approx 40\%$. That is, approximately 40% of the alkoxy radicals generated in reaction 7 decompose promptly to generate products not observed in previous studies of methyl chloride oxidation carried out under similar conditions, but in the absence of NO.

To determine the individual values of γ_1 and γ_2, the effects of reactions 12 and 13, which convert HCHO to CO, must be minimized. Thus, the yields of CO and HCHO were analyzed in the experiments using 11.5 Torr of CH_3Cl, and 10 mTorr of NO. In these experiments, Cl and OH react almost exclusively with CH_3Cl and the occurrence of reactions 12 and 13 is of minor importance. Figure 2 shows the yields of CO and HCHO versus the O_2 concentration. At the highest [O_2], 100−400 Torr, where the effects of reaction 18 are also minimized, the product yields converge toward 32% for CO and 12% for HCHO. Since there is no (<2%) HCHO formation from the thermalized alkoxy radicals[5,6] and increasing [O_2] from 100 to 400 Torr with constant [NO] has no discernible impact on the product yields, it seems reasonable to interpret the yield of 12% HCHO as the fraction γ_2 of the excited alkoxy radicals that undergo Cl-atom elimination. Similarly, the yield of CO at high concentrations of O_2 can be ascribed to the HCl elimination from the excited alkoxy radical, $\gamma_1 \approx 32\%$.

So far, CO and HCHO have been identified as products of the prompt decomposition of chemically activated CH_2ClO radicals, with a total yield of 40−45%. It is now left to address the origin of the observed HCOCl product. This issue is complicated by the multiple possible sources of this compound: H-atom elimination from chemically activated CH_2ClO (reaction 17a) and the reactions of thermalized CH_2ClO radicals with either O_2 (reaction 6) or NO (reaction 18a).

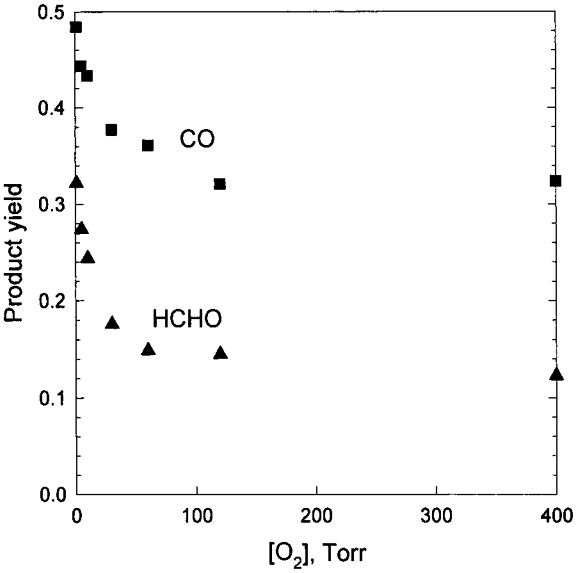

Figure 2. Yields of HCHO (▲) and CO (■) following irradiation of 11.5 Torr of CH_3Cl, 100 mTorr of Cl_2, 10 mTorr of NO, 4−400 Torr of O_2 in 700 Torr total pressure of N_2 plotted versus the partial pressure of O_2.

To assess the relative contributions of these sources, experiments were performed using low O_2 partial pressures to increase the relative importance of loss of thermalized CH_2ClO radicals via HCl elimination, reaction 5. However, under these conditions, the observed product yields are also influenced by the reaction of the thermalized CH_2ClO with NO. Thus, to determine the effects of reaction 18, experiments were conducted at a fixed low O_2 pressure (5 Torr), with the initial NO concentration varied over a wide range (5−110 mTorr). Experiments were conducted both at Ford (with an initial [CH_3Cl] of 11.5 Torr) and at NCAR (initial [CH_3Cl] of 1.1 Torr). In all of the experiments the conversion of CH_3Cl was <0.2% and HCOCl, CO, and HCHO were again the only observed carbon-containing products. Figure 3 shows the corrected yields of HCHO, HCOCl, and CO versus the partial pressure of NO. Experimental data acquired using the setup at NCAR are shown as open symbols, and data acquired at Ford are shown as filled symbols. Clearly, the product yields depend on the partial pressure of NO relative to that of O_2. Since the excited alkoxy radicals are expected to be too short-lived to undergo chemical reactions, it can be concluded that the NO dependency is due to the occurrence of reaction 18. Furthermore, the constant yields reached at the higher NO partial pressure (0.05−0.12 Torr) indicate that the thermalized CH_2ClO radicals are reacting almost exclusively with NO under these conditions.

There are a number of conclusions that can be drawn from the data in Figure 3. First, the HCHO yield is seen to increase from 12% at low NO to about 40% at higher NO, offering clear evidence for the importance of reaction 18b in the system. A more thorough discussion of the impact of reaction 18 is given below. The CO yield at high [NO] reaches a constant value of about 32%. Since there are no apparent sources of CO from the reaction of CH_2ClO with NO, this CO must be coming from the decomposition of chemically activated CH_2ClO via process (17b). This result is wholly consistent with the value of γ_1 = 32%, inferred from the yield of CO in the presence of high O_2 concentrations (see above).

The HCOCl yield is relatively independent of [NO] in this set of experiments, with a value of 25% at high [NO]. Because all thermalized CH_2ClO radicals react with NO under these conditions, the only sources of HCOCl are reactions 17a or 18a. Thus, an upper limit to β (reaction 17a) of 25% can be established. This result can be combined with the estimate that $\alpha + \beta = 60\%$ (inferred from the HCOCl yield at high [O_2], see above). Hence, the value of α (the fraction of CH_2ClO radicals that is thermalized) must fall in the range 35−60%.

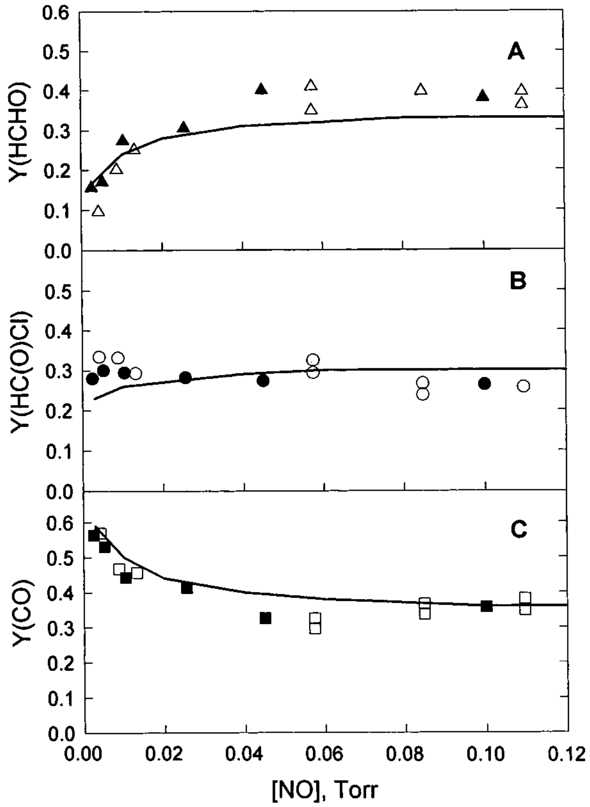

Figure 3. Product yields of (A) HCHO, (B) HCOCl, and (C) CO versus the concentration of NO following UV irradiation of mixtures of 5 Torr of O_2, 1−11 Torr of CH_3Cl, ~100 mTorr of Cl_2 and 5−110 mTorr of NO at 700 Torr total pressure. Experimental data were obtained at NCAR (open squares, triangles, and circles) or Ford (filled squares, triangles, and circles). Solid lines: model results with $k_{18c} = 0$, $k_{18a} = 7 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, and $k_{18b} = 9 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, $\alpha = 56\%$, $\beta = 0\%$, $\gamma_1 = 12\%$, and $\gamma_2 = 32\%$; see text for details.

Further conclusions regarding the values of α and β can only be obtained with a prior knowledge of the overall rate and mechanism of reaction 18, information which is not currently available. However, with reasonable assumptions about this reaction, some computer simulations of the experiments shown in Figure 3 were conducted, as is now described. First, 32% of the alkoxy radicals were assumed to decompose promptly via HCl elimination, γ_1, while 12% were assumed to decompose via Cl-atom elimination, γ_2. Values of $k_5 = 2600$ s^{-1} and $k_6 = 1 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} were assumed, in agreement with the measured[6] ratio of these rate coefficients and consistent with typical rate coefficients for reaction of alkoxy radicals with O_2.[8] Since reaction of CH_3O with NO to form CH_3ONO occurs with a rate coefficient of about 2.5×10^{-11} cm^3 molecule^{-1} s^{-1} at 700 Torr,[8] the same rate coefficient was assumed in the model for reaction 18c.

Two model scenarios were then considered, one in which H-atom elimination was assumed to be important ($\alpha = 34\%$, $\beta = 22\%$), and one in which this process was assumed to be negligible ($\beta = 0$, $\alpha = 56\%$). In the first scenario, the rate coefficient for reaction 18b was adjusted until the proper trend in HCHO production with the initial [NO] was obtained. Best agreement between the model and the experiments was obtained with $k_{18b} = (3.5 \pm 1.0) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. The modeled trends in the data matched those observed fairly well. The drawback to this model scenario is that it seems improbable that as many as 20−25% of the nascent CH_2ClO radicals have internal energy that is above what is likely to be a fairly large barrier to H-atom elimination (probably in excess of 15 kcal/mol).

In the second model scenario, values of $\beta = 0\%$ and $\alpha = 56\%$ were assumed. This model can also be made to fit the data quite well if significant amounts of HCOCl are formed in the reaction of CH_2ClO with NO, reaction 18a. Again assuming that $k_{18c} = 2.5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, k_{18a} must be 4×10^{-11} cm^3 molecule^{-1} s^{-1} for sufficient HCOCl production to occur. While this scenario again fits the observed data quite well, it seems unlikely that reactions 18a through c are all operative with rate coefficients in excess of 2×10^{-11} cm^3 molecule^{-1} s^{-1} (total $k_{18} \approx 1 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}), given that analogous RO + NO reactions are typically in the low 10^{-11} range.[8] A further possibility is that CH_2ClONO is not formed in reaction 18. This reaction probably occurs through the formation of a complex

$$CH_2ClO + NO \rightarrow [CH_2ClONO]^* \rightarrow HCOCl + HNO \quad (18a)$$

$$\rightarrow HCHO + NOCl \quad (18b)$$

$$\rightarrow CH_2ClONO \quad (18c)$$

and it is possible that stabilization of the nitrite does not occur. A similar mechanism has been postulated for the reaction of CF_3O with NO,

$$CF_3O + NO \rightarrow [CF_3ONO]^* \rightarrow CF_2O + FNO \quad (19)$$

for which the yields of CF_2O and FNO have been shown to be unity.[8,18,19] Under the assumption that $k_{18c} = 0$, lower values for k_{18a} and k_{18b} (about 7×10^{-12} and 9×10^{-12} cm^3 molecule^{-1} s^{-1}) are required to model the data (see Figure 3), and a much more reasonable total value for k_{18} is obtained. Note that the exothermicities of reactions 18a, 18b, and 19 are all at least 8 kcal/mol greater than that of reaction 20b, offering a possible reason nitrite formation may not be important in reactions 18 or 19.

$$CH_3O + NO \rightarrow [CH_3ONO]^* \rightarrow CH_3ONO \quad (20a)$$

$$\rightarrow HCHO + HNO \quad (20b)$$

We reiterate that all of the scenarios discussed above are capable of reasonably explaining the observed data, and firmer conclusions regarding the actual values of α and β await further information on the rate and mechanism of reaction 18. In any event, the above discussion has served to identify and quantify the various reactions important in the chemistry of activated CH_2ClO^* radicals (see Figure 4 for a summary). On the basis of previous studies,[12] the alkoxy radicals are expected to be born with a range of excess energies. Because the lowest barrier to decomposition (HCl elimination)[4] is about 8 kcal/mol,[6] at least 40% of the activated radicals must be born with at least this much excess energy. The Cl-atom elimination channel likely has a barrier higher than 8 kcal/mol. Thus, while this high barrier prohibits significant decomposition of thermalized CH_2ClO radicals by this route, highly excited CH_2ClO^* radicals are capable of accessing this reaction channel. (Note that the A-factor for HCl elimination is only 10^9−10^{10} s^{-1} [6] while the A-factors for the Cl-atom elimination channel are likely greater than 10^{13} s^{-1}.)[12]

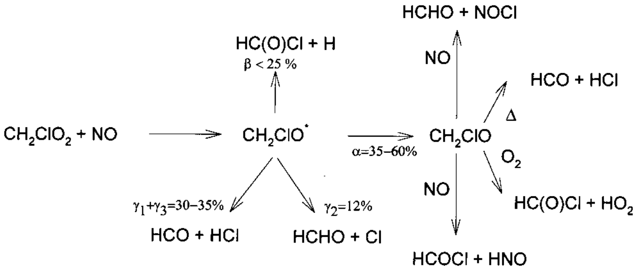

Figure 4. Fate of the excited CH_2ClO^* radicals produced in the reaction of CH_2ClO_2 with NO in 700 Torr total pressure of O_2/N_2 at 296 K: α is the fraction of excited alkoxy radicals which are thermalized by reaction with a third body; β is the fraction which eliminates a hydrogen atom; γ_1 and γ_2 are the fractions which eliminate HCl, and Cl, respectively. Most likely, the value of β is close to zero, and that of α is near 60%; see text for details.

Conclusions and Atmospheric Implications

It has been shown that the products of the oxidation of CH_3Cl are different in the presence of NO from what had previously been observed in its absence. Previous studies[2,3,5,6] showed that the dominant product obtained under atmospheric conditions, but in the absence of NO, is HCOCl. However, the chemically activated CH_2ClO radicals formed in the presence of NO lead to a different product distribution. The observed product yields when low levels of NO are present (in 700 Torr air, at 296 K) are: HCOCl (56%), CO and HCl (32%), and HCHO and Cl (12%). These product yields will be obtained from the OH- or Cl-initiated oxidation of CH_3Cl in the atmosphere in regions where the chemistry of the CH_2ClO_2 radical is dominated by its reaction with NO, such as throughout most of the continental boundary layer. Although studies have only been conducted at 296 K, these product yields should be relatively insensitive to temperature, since the prompt decomposition of the chemically activated CH_2ClO should be largely unaffected by temperature, and the majority of the thermalized CH_2ClO radicals will react with O_2 at all temperatures encountered in the atmosphere.

Chemical activation effects in the atmospheric chemistry of a number of alkoxy radicals have now been demonstrated[9−12] and appear to be a phenomenon general to radicals possessing activation barriers to decomposition of about 12 kcal/mol or less.

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