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# "Research in Chemical Kinetics"

Principal Investigator, F. S. Rowland

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# Research in Chemical Kinetics Related to Atmospheric Chemistry

Department of Energy

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June 1, 1994

## PROGESS REPORT

## RESEARCH PROPOSAL

Progress Report

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# PROGRESS REPORT

## I. Computational Quantum Chemistry Applied to Problems in Atmospheric Chemistry

The advances in the precision and accuracy of electronic structure calculations were already sufficient in the late 1980's to become competitive with many experimental approaches to such questions as the relative stability of isomeric species, and were applied at the University of California Irvine to a study of the possible isomers of $HNO_3$ and $ClONO_2$ because of the potential importance of compounds such as HOONO and ClOONO, if formed in the Earth's atmosphere.[1] A second problem approached by these computational methods has been the structure of the chlorine oxide dimer, ClOOCl, a key intermediate in the $ClO_x$ chain removal of stratospheric ozone in polar regions.[2,3]

These studies have now been continued with a more extended study of the various conformers of ClOONO and HOONO, together with detailed calculations of the infrared spectra associated with each.[4] The earlier calculations provided the appropriate infrared spectra with which Professor Y. P. Lee and colleagues identified the existence of the isomer HOONO in their matrix experiments. The work done here in 1994 identified the probable conformer, under matrix conditions[4], and has again been confirmed by Professor Lee and colleagues. Further calculations directed toward an understanding of the photolysis pathways are proposed for future work.

As the number of chemical species of atmospheric interest grows, some have been identified for which experimental material is meager or non-existent, or the species itself is unknown. In many of these instances, electronic structure calculations provide the best estimate of structural energetics. Our new evaluation for the heat of formation as HOBr of $-14.2\pm1.6$ kcal/mole[5] is significantly different and somewhat more precise than the old value of $-19\pm3$ kcal/mole[6], and a newer value of $-9^{+1}_{-4}$ kcal/mole.[7] Another recent experimental study, not yet published, gives a value of $\geq -13.43\pm0.42$ kcal/mole[8] in excellent agreement with out calculation.

## II. Methyl Halides in Seawater

The major organic chlorine compound in the atmosphere during the first half of the 20th century was methyl chloride, whose sources are believed to be largely natural, and which certainly include emission from the ocean. A probable mechanism for much of this oceanic emission begins with the release of methyl iodide from oceanic biology into the ocean itself. These dissolved gaseous molecules are then available for halide ion displacement reactions by $Cl^{-}_{aq}$, present at 0.5 molar in sea water, to form $CH_3Cl$, and by the much less abundant $Br^{-}_{aq}$ to form $CH_3Br$. Alternatively, if an atmospheric methyl halide is carried into the ocean, it then becomes susceptible to nucleophilic displacement by $H_2O \cdot Cl^{-}_{aq}$, etc., and may therefore have a partial oceanic sink.

The atmospheric chemistry of $CH_3Cl$ is significant with respect to stratospheric ozone depletion because, at 600 pptv by volume, it is the only important natural compound which can deliver chlorine atoms to the stratosphere.[9] The atmospheric chemistry of $CH_3Br$ is also important, even though its concentration is only about 10 pptv, because Br atoms are much more effective per atom in depleting stratospheric ozone than are Cl atoms, especially in the 1990's stratosphere rich in anthropogenic chlorocarbons and their decomposition products. The chemistry of methyl bromide has received major additional attention in the 1990's because one of its major source is its anthropogenic release as a fumigant.[10]

The rates of reaction in both formation and destruction of these methyl halides within the ocean are very pertinent to estimates of the overall lifetimes of these molecules when released to the atmosphere from any source. A substantial set of measurements of aqueous phase methyl halide reactions was carried out earlier under this contract, but reported only in the Ph.D. thesis of Dr. Scott Elliott. These data have now been placed in current context and published. The nucleophilic substitution rates for reactions of $H_2O$ with $CH_3Cl$, $CH_3Br$ and $CH_3I$, and for $Cl^{-}_{aq}$ with the latter two have been published in *Geophysical Research Letters*.[11] The hydrolysis reactions for these halides are roughly one factor of ten slower than $Cl^{-}_{aq}$ attack under all oceanic conditions (the activation energies are similar), so that hydrolysis is always a minor but non-negligible sink for the methyl halide. These hydrolyses are always an oceanic source of methanol. These reactions and consequences have been described in detail in a paper in press with the *Journal of Atmospheric Chemistry*.[12]

## III. Thermal Reactions of $^{38}$Cl Atoms

Our studies of the various chemical processes initiated by thermalized $^{38}$Cl atoms over the past decade have provided substantial information about two general classes of reactions: addition to multiple bonds, and abstraction of hydrogen. The addition of $^{38}$Cl atoms to compounds such as $CH_2{=}CHX$ (X=F, Cl, Br) and then photolysis studies with stable chlorine atoms added to $CH_2{=}CHBr$ and $CF_2{=}CFBr$ have elucidated the mechanism of the "anti-Markovnikoff addition" process. Relatively little favoritism toward one or the other end of an asymmetric olefin exists in the addition step itself, but complete or nearly complete isomerization (e.g. $CH_2CHClBr^* \rightarrow CH_2BrCHCl$) of the excited radical can produce a species which has the appearance of having been the consequence of a strong favoritism toward addition to the less-substituted position. These experiments were described in some detail in last year's progress report, and have now appeared in the Ph.D. thesis of Paul Bredt.[13]

A second aspect of the addition of $^{38}$Cl atoms to olefinic compounds had been concerned with the redistribution of energy within the resultant radical, as evidenced by rates of decomposition to release a detectable radioactive product, e.g. $CH_2{=}CH^{38}Cl$ from $^{38}Cl + (CH_2{=}CH)_xM$, with molecules such as M=Si, X=4; M=Sb, X=3; M=Pb, X=2. These reactions were described in detail in last year's progress report, and are being prepared for publication.

When $^{38}$Cl atoms are formed by $(\eta,\gamma)$ nuclear reactions in pure $CClF_3$, about 95% fail to react while still carrying residual kinetic energy from the nuclear process, and react as thermal $^{38}$Cl atoms with whatever minor components are mixed with $CClF_3$. The abstraction of H from RH leads to the formation of $H^{38}Cl$, which is itself not easy to measure with precision in these gaseous systems because of its tendency to stick on the various walls. However, the absence of the $^{38}$Cl can be accurately measured by its failure to appear in some other, more-readily measured chemical form.

When the abstraction reaction has a high collision efficiency, e.g. ($Cl + C_2H_6 \rightarrow HCl + C_2H_5$), a suitable competitor molecule is $CH_2{=}CHBr$ from which $CH_2{=}CH^{38}Cl$ is observed with high precision. The yield of $CH_2{=}CH^{38}Cl$ is pressure dependent but quite consistent at each pressure. The abstraction reaction rate constant for a previously unmeasured species RH can be readily measured by the separate competitions of RH with $CH_2{=}CHBr$ and R'H with $CH_2{=}CHBr$ when the rate constant for Cl + R'H is well-known from other experimental techniques. Reaction of $^{38}Cl$ with $C_2H_6$ has served as one of the calibration reactions for competitions with $CH_2{=}CHBr$.

When the rate constant for the abstraction reactions drop into the $10^{-13}$ to $10^{-14}$ $cm^3 molecule^{-1}$ range, the abstraction reactions do not seriously diminish the observed yield of $CH_2{=}CH^{38}Cl$ from $CH_2{=}CHBr$ until the (RH)/($CH_2{=}CHBr$) ratio is rather high. One possible remedy for this mismatch in reactivities is a less reactive olefinic competitor, and a detailed study has been made of the formation of $CF_2{=}CF^{38}Cl$ from $CF_2{=}CFBr$ as an alternate competiton reaction.

We reported last year on the approximate reaction rate constants measured for several hydrohalocarbons versus $CF_2{=}CFBr$ as competitor. Most of these hydrohalocarbons were chosen because of their potential technological use as substitutes for chlorofluorocarbons. Our earlier results were not very satisfactory for reasons primarily associated with the much greater purity requirements needed for RH compounds much less reactive than $C_2H_6$, and $CF_2{=}CFBr$ less reactive than $CH_2{=}CHBr$. During the past year, we have obtained very much better purities of the components, and consequently much more satisfactory estimates of rate constants for the hydrohalocarbon competitors. These new values are reported in the proposal for future work because we plan to complete these studies with measurements of the competitive rate constants at different temperatures, and thereby also evaluate the activation energies for these abstraction reactions.

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