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Progress Report on work carried out during the contract period from:

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PRINCIPAL INVESTIGATOR _____ F. S. Rowland _____

MASTER

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"Research in Chemical Kinetics"

F. S. Rowland, Principal Investigator

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RESEARCH IN CHEMICAL KINETICS - UNIVERSITY OF CALIFORNIA, IRVINE

F.S. ROWLAND

Progress Report, Department of Energy, Contract No. EY-76-S-03-0034 P.A.#126

Progress during period January 1, 1978 - September 30, 1978

I.   Stratospheric Chemistry of Chlorinated Molecules

The potential for destruction of stratospheric ozone by the atmospheric release of the chlorofluoromethane molecules CCl_2F_2 and CCl_3F was originally recognized in 1973 in work supported by the predecessor of this contract under the Atomic Energy Commission[1,2] During the period from 1974 to 1977 an increasing percentage of the effort under this contract was devoted to the general problem of halogen effects on stratospheric ozone. These efforts included laboratory investigations of the photochemical properties and chemical reactivity of chlorine compounds pertinent to the atmosphere; field measurements of absolute concentrations of several halogenated compounds in the atmosphere; and some modeling of the distribution of such molecules in the atmosphere. No new activities have been initiated on either field investigations or modeling during 1978, although several studies are still in various stages of completion for publication.

The field investigations initiated in 1977 were very successful in late 1977 and early in 1978, and have provided very useful information on the atmospheric concentrations at that time of the chlorofluoromethanes (CCl_3F and CCl_2F_2), of methylchloroform (CH_3CCl_3) and of methane, CH_4.
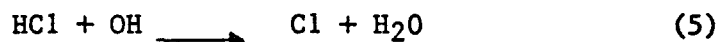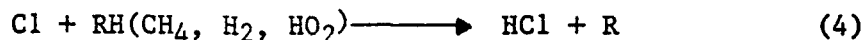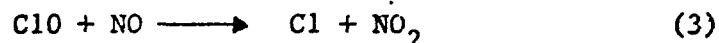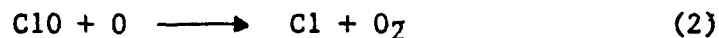
The general outline of the chlorofluorocarbon-ozone problems as stated by us in 1974[1] and 1975[2] has been confirmed by separate reports from the National Academy of Sciences[3-5] and by the National Aeronautics and Space Administration[6] Our earliest prediction of the magnitude of possible ozone loss from continued release of the chlorofluoromethane gases was for an

eventual steady-state loss of 7-13% of the total stratospheric ozone[7].
These estimates were based on the assumption of continued release of
CCl_3F and CCl_2F_2 at the 1972 rates.

Two years later in 1976, the National Academy of Sciences gave their
best estimate of the eventual ozone loss as 7%[3,4] with a possible range from
2% to 20%. In the two succeeding years since the N.A.S. report the only
major changes in the overall understanding of stratospheric chemistry have
involved direct measurements of the rates of reaction of HO_2 radicals with
OH, NO, and O_3. While none of these reactions involve chlorine directly,
the concentrations of OH, HO_2, O_3, NO and NO_2 are all intimately involved in
the chemical reactions of the chlorinated species. The direct measurements
of the reaction of HO_2 with NO completely failed to confirm earlier indirect
measurements, and gave a reaction rate about 50 times faster at stratospheric
temperatures than previously believed.[8] With the new direct measurements of
these three HO_2 reaction rates the predicted losses of ozone have risen
sharply to the current estimates of a steady-state loss of 20%, with a
possible range from 8% to 35%.[9]

Basic Stratospheric Chlorine Chemistry

Chlorinated molecules released at the surface of the earth can, if no
tropospheric removal process affects them earlier, rise into the stratosphere
and be decomposed by solar ultraviolet radiation. Many such compounds,
including CCl_3F and CCl_2F_2, are photodissociated in the 25-40 km altitude
range by u.v. radiation between 190-220 nm. The chlorine atoms released by
such photolysis are then able to participate in a series of chemical reac-
tions (1) - (5), which include the ozone-removing ClO_x chain of (1) and (2).[1-6]

$$Cl + O_3 \longrightarrow ClO + O_2 \qquad (1)$$

$$ClO + O \longrightarrow Cl + O_2 \qquad (2)$$

$$ClO + NO \longrightarrow Cl + NO_2 \qquad (3)$$

$$Cl + RH(CH_4, H_2, HO_2) \longrightarrow HCl + R \qquad (4)$$

$$HCl + OH \longrightarrow Cl + H_2O \qquad (5)$$

The total concentration of some chlorinated molecules is increasing with time in the troposphere, and corresponding increases are expected to follow in the stratosphere with a delay period of 5 - 10 years. The main questions involving atmospheric chlorine chemistry can be considered in five categories:

(a) Removal processes ("tropospheric sinks") for halogenated molecules before they can diffuse to the stratosphere;
(b) Stratospheric decomposition processes;
(c) Chlorine chemistry additional to reactions (1) to (5);
(d) Accurate chemical kinetic data for all important processes under (b) and (c); and
(e) Stratospheric measurements of chlorinated species, and of other molecules with which they interact.

Quantitative predictions of potential depletion of stratospheric ozone by anthropogenic chlorine are dependent upon evaluation of (i) the fraction of each chlorinated molecule which decomposes in the stratosphere; and (ii) the fraction of the chlorine in each compound which is then released into the ClO_x cycle; (iii) the distribution of elemental chlorine among HCl, ClO, Cl, and other chlorinated stratospheric species through application of the quantitative rate data. The validity of such conclusions about stratospheric chlorine chemistry can be tested by the correspondence in the present atmosphere between measured and predicted concentrations of the various chlorinated species. The future predictions are of course critically dependent upon the future release pattern of anthropogenic chlorinated molecules.

Possible Tropospheric Removal Processes

Many chlorinated molecules released at the earth's surface have very
short atmospheric lifetimes (e.g., Cl_2, decomposed by visible solar
radiation) and do not pose any stratospheric problems. On the other hand,
the perhalo chlorofluorocarbons do not absorb visible or near u.v. solar
radiation, and do not undergo atmospheric photodissociation except at
stratospheric altitudes above most of the atmospheric O_2 and O_3 which shield
out solar 190 - 220 nm radiation. Without photoysis at wavelengths longer
than 295nm, these molecules have lifetimes of 50-100 years for photochemical
dissociation. Our measurements of CCl_3F concentrations in the northern and
southern hemispheres in November 1977 to February 1978, are shown in Figure 1
in comparison with the first report by Lovelock for measurements in 1971.
Obviously, CCl_3F is accumulating in the atmosphere, indicative of a long
atmospheric lifetime. In 1976, we calculated that the observed concentra-
tions of CCl_3F were at the level expected for atmospheric release minus
stratospheric destruction alone,[10] with no "missing" CCl_3F which might
indicate some as yet undiscovered tropospheric sink. Calculations by
Jesson et al.,[11] on the other hand, showed a large discrepancy between their
estimates of atmospheric release and amount actually present. In mid-1976
relatively few measurements were available for CCl_3F concentrations in the
tropics and in the southern hemisphere. Jesson et al. relied on Lovelock's
data (Figure 1) as a model for the distribution with latitude of CCl_3F,
while we relied on numerous measurements with other gases which indicated
much more rapid mixing southward, and therefore higher concentrations there.

The observed concentrations with latitude shown in Figure 1 for our
1977-78 data are consistent with other recently measured latitude distribu-
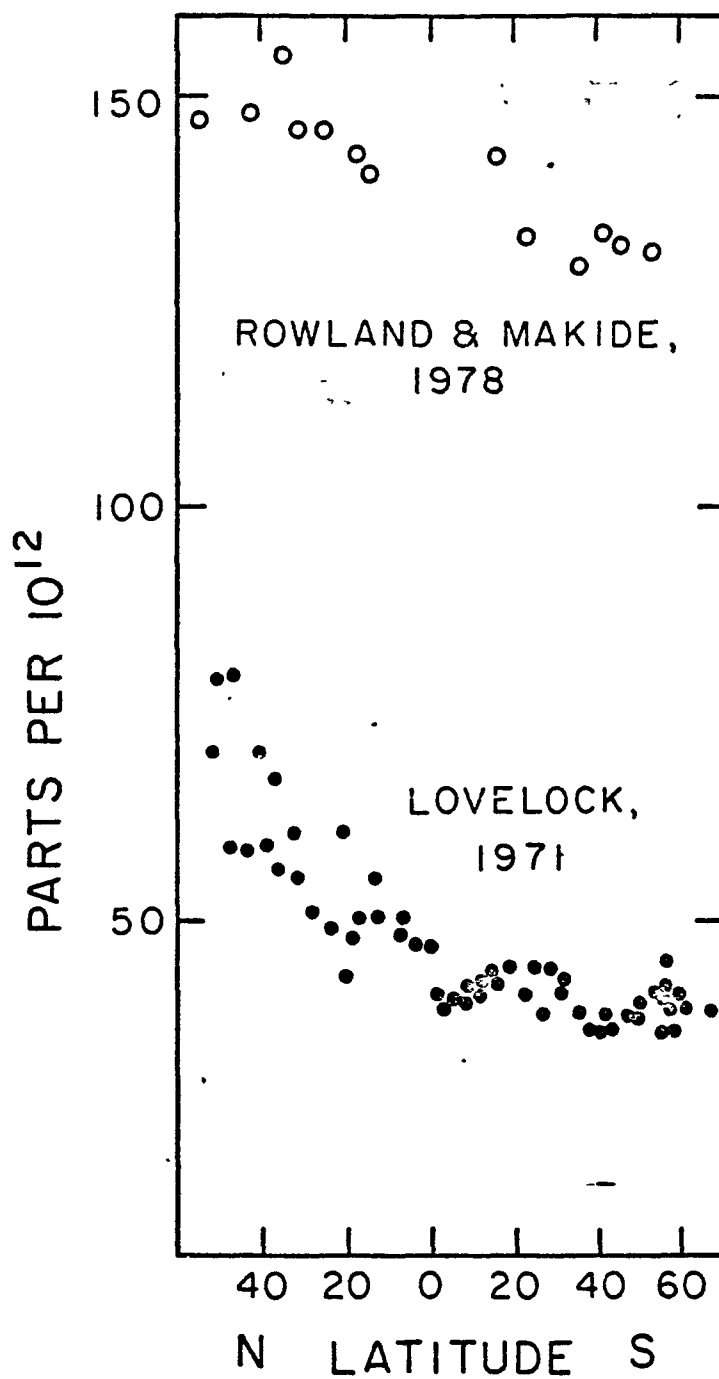tions, and show that the basic assumption made by Jesson et al. of slow

Figure 1

Observed Atmospheric Concentrations of CCl_3F: 1971, Lovelock; 1978, Rowland and Makide

southward mixing was not correct. Our data shown in Figure 1 are consistent

with a mixing coefficient of 0.8 ± 0.1 year $^{-1}$ from the northern to the

southern hemisphere. Our own calculations with both CCl_3F and CCl_2F_2

measured in 1977-78 continue to show excellent agreement with atmospheric

release minus stratospheric destruction alone, and indicate that tropospheric

sinks must be very small or negligible for both CCl_3F and CCl_2F_2.[12]

The other approach toward the possibility of tropospheric sinks for

chlorofluorocarbons is the identification of a particular process, followed

by appropriate measurement and estimate of the magnitude of the removal

process. Several processes have been identified which can lead to

destruction of CCl_3F, for example, but none has proven to be important on a

global scale.[1-6]

Hydrogen-containing saturated chlorocarbon molecules are subject to

tropospheric removal by OH radical attack, illustrated in (6) for the

important compound, methylchloroform, CH_3CCl_3[13]. However, estimates of the

overall

$$OH + CH_3CCl_3 \longrightarrow H_2O + C_2H_2Cl_3 \qquad (6)$$
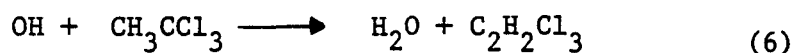
rate of reactions such as (6) in the atmosphere require presently incomplete

worldwide measurements of the concentrations of OH radicals. At present,

estimates of average tropospheric OH concentrations can probably better be

determined by inference from direct measurements of the amount of CH_3CCl_3

accumulated in the atmosphere.[13-18] If a reasonable estimate of the

atmospheric lifetime can be obtained for one C-H containing molecule then the

lifetimes for others can be quickly calculated from the known relative rates

of OH reactions with various RH molecules.[19-21]

We have measured the concentrations of methylchloroform (CH_3CCl_3) in

atmospheric samples collected at latitudes from 55° N to 53° S. The data

are shown in Table 1, and indicate that the north temperate zone concentration is about 1.5 times that found in the south temperate zone.[22] Our absolute concentrations are less than those reported by others by about 20%. [23,24] Our sample flasks and measuring system are both all-metal, without teflon coatings, grease, etc. We believe that the all-metal systems are necessary to avoid contamination for some of the chlorocarbon compounds, and especially for CH_3CCl_3, $CHCl_2F$ and CCl_2FCClF_2.

Stratospheric Decomposition Processes

The ultraviolet absorption cross-sections have now been measured for the most important chlorinated molecules in current technological use . [1-6,25] Measurements of these cross sections at stratospheric temperatures (215-270°K) are considerably more difficult, but have been carried out for the most important molecules such as CCl_2F_2 and CCl_3F. [26,27] The effect of the temperature dependence of photo cross sections upon the overall photodissociation rates of chlorofluorocarbon molecules in the atmosphere is rather minor since the rate-controlling step in the decomposition of such molecules is primarily the upward diffusion of the molecules into more and more intense u.v. radiation fields. The effect of stratospheric temperatures on photolytic cross sections is potentially much more significant for molecules such as $ClONO_2$ and $HOCl$ which are formed in the stratosphere and for which diffusion plays only a minor role during the time between formation and photodestruction.

Most of these measured photo cross sections for chlorocarbons correspond to absorption into a repulsive electronic state which immediately dissociates with the loss of atomic chlorine. The quantum yields for these reactions have been measured to be essentially unity for several compounds, but the quantum yields of many others have not been measured at all. Again, a quantum yield of only 0.5 instead of 0.1 for the decomposition of a chlorofluorocarbon would

TABLE 1

TROPOSPHERIC CONCENTRATIONS OF METHYLCHLOROFORM (CH_3CCl_3), CORRECTED TO JANUARY 1, 1978

Latitude	Sampling Location	Date	Observed	Concentrations (PPT) Corrected to 1/1/78
55.3°N	Ketchikan, Alaska	1/21/78	97.9	97.2
47.6°N	Queets, Washington	1/22/78	94.9	94.2
45.2°N	Nestucca, Oregon	1/22/78	104.2	103.4
43.4°N	Twin Buttes, Idaho	10/31/77	95.0	97.0
43.4°N	Twin Buttes, Idaho	11/ 1/77	95.3	97.3
43.4°N	Twin Buttes, Idaho	11/ 1/77	92.3	94.2
41.6°N	Gold Bluffs, California	1/26/78	101.3	100.4
36.4°N	Emigrant Pass, California	11/29/77	92.7	93.8
35.3°N	Ivanpah, California	11/ 8/77	88.9	90.5
35.2°N	Needles, California	11/ 8/77	89.8	91.5
35.2°N	Katsuura (Chiba), Japan	7/22/78	96.4	90.6
35.1°N	Baker, California	11/8 /77	89.2	90.9
34.8°N	Barstow, California	11/ 8/77	93.0	94.7
34.1°N	Blythe, California	12/ 1/77	89.7	90.6
25.2°N	Key Largo, Florida	2/ 1/78	96.8	95.7
17.8°N	St. Croix, Virgin Islands	2/ 3/78	82.3	81.3
13.7°N	St. Lucia, British West Indies	2/ 5/78	87.2	86.1
16.2°S	Rio Zongo, Bolivia	1/14/78	78.6	78.2
23.5°S	Antofagasta, Chile	1/12/78	66.2	65.9
33.8°S	San Alfonso, Chile	1/11/78	70.4	70.1
36.8°S	Concepcion, Chile	1/ 6/78	66.1	66.0
41.5°S	Puerto Montt, Chile	1/ 8/78	65.0	64.8
45.7°S	Coihaique, Chile	1/10/78	64.5	64.3
45.8°S	Balmaceda, Chile	1/ 9/78	63.7	63.5
53.5°S	Punta Arenas, Chile	1/ 8/78	67.1	66.9

North Temperate Zone average (1/1/78) 94.8±3.8

South Temperate Zone average (1/1/78) 65.2±1.2

not be particularly important because of the dominance of the rate of diffusion in their overall photodecomposition rate.

The residual radicals left by photodecomposition usually react with molecular O_2 within seconds, but detailed reaction mechanisms afterward are poorly known. After the reactions of CCl_2F and $CClF_2$ with O_2, phosgene-type molecules can be identified (i.e., $CClFO$ and CF_2O), indicating that a second Cl atom from the original molecule has been lost during the oxidation. Whether the second Cl is eliminated as Cl or ClO is only of mechanistic interest because of the rapid Cl/ClO interchange through the ClO_x reactions (1) to (3). Photochemical absorption measurements have also been made for $CClFO$ for estimates of the release rate of the third Cl atom form CCl_3F.[1-6]

The further decomposition of $CClFO$ and CF_2O (as well as CCl_2O from CCl_4 decomposition) will form radicals such as $.CF=O$, and ultimately the F atoms appear as HF. Since fluorine is a very scarce element geochemically, the appearance of HF in the stratosphere is an excellent tracer for the decomposition there of molecules such as CCl_3F, CCl_2F_2 and their degradation products. However, the stratospheric photodissociation of CF_2O and $CClFO$ is not too rapid, and there may be quantities of fluorine in these fluorophosgenes comparable to that found as HF.

Relatively little study has yet been given to the residual fragments remaining following decomposition of chlorinated molecules other than CCl_3F and CCl_2F_2. For example, stratospheric OH attack on CH_3CCl_3 by (6) still leaves all three Cl atoms bonded to carbon and not yet participating in the sequence (1) to (6). Since most of these molecules are reasonably reactive, it is likely that much of the clorine of the original compound is released in the stratosphere, but experimental confirmation is lacking in many instances.

Additional Chlorine Chemistry

Many chemical reactions of lesser importance are minor competitors of reactions (1) to (5), while an intensive search has been carried out to determine whether any chemical species or chemical reactions of major importance have been omitted. The formation of chlorine nitrate ($ClONO_2$) by reaction of ClO with NO_2 is an example of such attempts.[28] In 1975 relatively little was known experimentally about either the rate of formation (7), or the rate and

$$ClO + NO_2 + M \longrightarrow ClONO_2 + M \qquad (7)$$

mechanism of photodecomposition. The possible importance of a stratospheric sink molecule ($ClONO_2$ ties up both the ClO_x and NO_x chains) with photolytic absorption in the 300-450 nm range also forced the use of much more detailed stratospheric models because of the errors made with some of the existing models. The major changes have included the use of diurnal models instead of the computationally-simpler "24-hour, half-intensity sun" models, and the inclusion of multiple scattering which is quite important for solar radiation with $\lambda > 300$ nm.[5,6]

Several measurements in good agreement with each other now have been made for the rate of reaction (7), although in each case the measured rate has been for the removal of ClO and not for the formation of $ClONO_2$.[29,30]

The absorption cross sections for $ClONO_2$ have been measured, first at $295^\circ K$ [28] and later at stratospheric temperatures. The mechanism of photodecomposition of $ClONO_2$ has not been conclusively established, but strong evidence has been found that the decomposition process does not simply reverse the formation and release ClO and NO_2. At 302.5 nm the observed products from the photodecomposition of $ClONO_2$ are most consistent with the loss of atomic O leaving residual ClONO.[31] In the stratosphere the photo lifetime of ClONO is very short. While the photochemical decompositon of

ClONO has not been established, the release of Cl + NO_2 + O or ClO + NO + O are both closely equivalent in effect on ozone chemistry to the original ClO + NO_2 from which $ClONO_2$ is formed.

The significance of $ClONO_2$ for estimates of stratospheric ozone depletion has lessened greatly during the past two years. One important reason has been the improvement in both models and measurements which have shown it not to be a major species in the stratosphere. A second reason is that the primary importance of $ClONO_2$ lay in its ability to tie up NO_x in the 20-30 km region. However, the new measurements of HO_2 rate constants described earlier have led to very greatly diminished estimates of the importance of NO_x removal of O_3 (and increased importance for HO_x chains) in the 20-30 km region. Consequently, the estimates of ozone depletion are now quite insensitive to the magnitude of calculated $ClONO_2$ concentrations in this region of the atmosphere.

Another potential stratospheric sink molecule is HOCl, which can be formed by the reaction of ClO with HO_2, as in (8).

$$ClO \ + \ HO_2 \ \longrightarrow \ HOCl \ + \ O_2 \qquad (8)$$
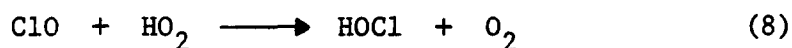
Again, evaluation of the stratospheric importance of HOCl requires measurements of the rate of its formation and of the rates of the various possible decomposition reactions. The key reaction in this case is the rate of photochemical decomposition (9), as well as the nature of the products (e.g., an alternate path might lead

$$HOCl \ + \ u.v. \ \longrightarrow \ OH \ + \ Cl \qquad (9)$$

to HCl + O). The photochemical cross sections for HOCl are most important in the 300 - 450 nm region. While measurements more than 40 years ago indicated strong absorption by HOCl in that region, theoretical arguments have been presented against the existence of a second absorption maximum

around 370 nm[32,33] and even that HOCl absorbs very weakly or not at all beyond 300 nm. An important chemical complication exists because HOCl reacts with itself by the equilibrium in (10), and

$$Cl_2O + H_2O \rightleftharpoons 2HOCl \qquad (10)$$
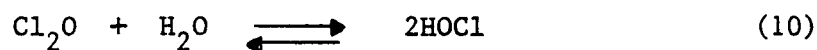
Cl_2O also absorbs in the critical region. Recent measurements with a very long path length u.v. cell have clearly shown that the addition of H_2O to Cl_2O increases the total absorption between 320 -380 nm, and therefore that the photochemical cross sections for HOCl in that region must be greater than 1/2 those of Cl_2O.[34] With these measured cross sections the calculated lifetime against photochemical decomposition for HOCl is less than 30 minutes throughout both the troposphere and stratosphere. Such a rapid removal rate for HOCl prevents any important stratospheric buildup for this molecule for the measured rate of reaction of ClO with HO_2 to form HOCl.

The major stratospheric sink for atomic Cl is HCl, which is known to be formed by reaction of Cl with CH_4, H_2 and HO_2. The possibilities have also been considered that atomic Cl might react with other organic molecules either to form HCl or some other product. The collision efficiency for abstraction of H from CH_4 by Cl is about 10^{-4} and the CH_4 mixing ratio is about 10^{-6} below 40 km. Therefore, any organic species must be present at greater than 10^{-10} mixing ratio and react with efficiencies approaching unity to compete with CH_4 for conversion of Cl to HCl. The reaction of Cl with C_2H_6 is very rapid, but the removal of C_2H_6 by OH in the stratosphere prevents C_2H_6 from attaining a mixing ratio as great as 10^{-10} in the critical region above 25 km. The reaction of Cl with formaldehyde, CH_2O, is also very rapid, and some atmospheric calculations show CH_2O in the 10^{-10} range, so the possibility exists that CH_2O should be added to the

(CH$_4$, H$_2$, HO$_2$) list in equation (4).[35]

Chlorine atom addition to acetylene, C$_2$H$_2$, is also extremely rapid, but the product C$_2$H$_2$Cl is unstable toward loss of the Cl atom and less than 1% of the C$_2$H$_2$Cl molecules survive at 30 km.[36] The eventual fate of C$_2$H$_2$Cl radicals in reaction with O$_2$ is not known, but the likelihood is that photochemical processes will rapidly release the chlorine atom again. Experiments are being carried out under this contract by Charles Yarbrough which are intended to identify these products.

Other Related Reactions

The same chemical reactions occur for cosmic-ray produced radioactive isotopes ^{38}Cl and ^{39}Cl as for the stable Cl atoms discussed throughout.[37] However, ^{38}Cl and ^{39}Cl exist for no more than a few hours before radioactive decay, and cannot readily be transported far from their production site (peak formation at about 30 km altitude). Their chemistry is also limited to reactions occurring on a time scale of a few hours or less, which means that there is rarely time for formation of H^{38}Cl or H^{39}Cl. A few collection experiments were performed in the lower stratosphere about a decade ago, with results consistent with the currently known chemistry expected for atomic chlorine at those altitudes. The predicted distribution of ^{38}Cl and ^{39}Cl with altitude is shown in Figure 2.

The chemistry of bromine in the stratosphere is quite similar to that of chlorine, including the BrO$_y$ chain for removal of O and O$_3$. However, the technological release of bromine compounds to the atmosphere is far less than that of chlorine compounds. The efficiency of the BrO$_x$ chain is comparable to or greater than that of the ClO$_x$ chain in removing ozone, because Br can be converted to HBr only by reaction with HO$_2$ and not with CH$_4$ or H$_2$. Furthermore, all compounds with two Br atoms on the same carbon atom have a tropospheric photochemical sink because they absorb appreciably beyond 300 nm

Figure 2. Calculated Distributions of Stable Chlorine and Radioactive ^{38}Cl among Cl, ClO, HCl and $ClONO_2$
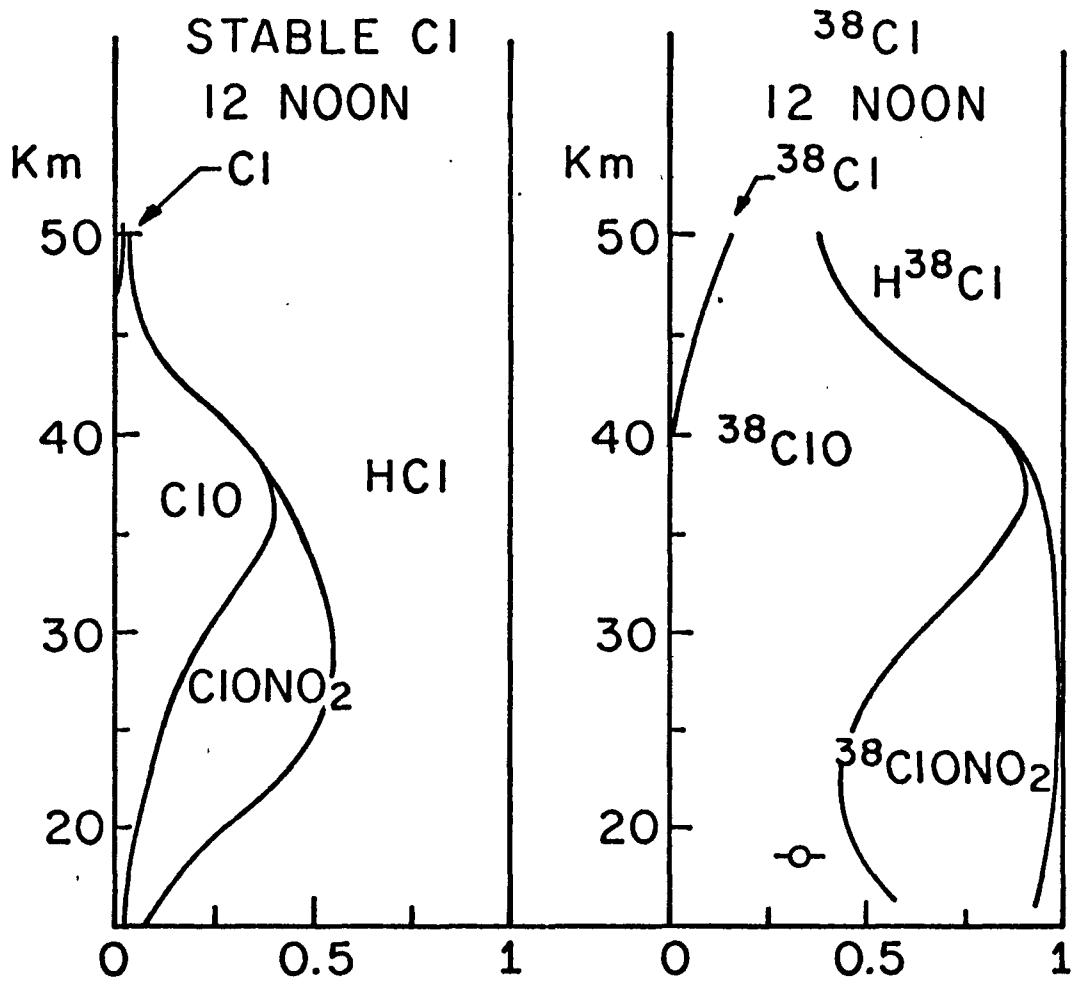
into the near u.v. region. Overall, then, brominated molecules are not expected

to have long atmospheric residence times except for molecules such as $CBrF_3$,

$CBrClF_2$ and $CBrF_2CBrF_2$. The latter two of these may have tropospheric sinks

comparable to their stratospheric sinks.

Chemical Kinetic Data

During the past several years the rate constants at stratospheric

temperatures for reactions (1) to (7) have been measured by several research

groups [1-6] and the remaining discrepancies are not very significant for

stratospheric modeling. During that period, the best value for (1)

decreased by a factor of 2, while that for (5) increased by a similar amount.

However, the multiplicity of experiments provides assurance that no order-of

magnitude errors exist for these reactions of major importance.

The overall chlorine equilibria are affected too by the reaction rates

for reactions not involving chlorine at all. A pertinent example is the

reaction rate for $OH + HO_2 \longrightarrow H_2O + O_2$ for which there is now

disagreement within the range from $2\text{-}5 \times 10^{-11}$ cm^3 molecule^{-1} sec^{-1} in

place of the 20×10^{-11} cm^3 molecule^{-1} sec^{-1} used in 1974. A second example

is the reaction rate for $NO + HO_2 \longrightarrow NO_2 + OH$ discussed earlier.

The chief uncertainties in chlorine chemical kinetic data now focus on

less important reactions for which very little information is available.

The observation of HCl and ClO in reasonable agreement with expected

concentration levels provide strong indication that the major stratospheric

reactions of chlorine are indeed those discussed in the equations above.

All of the reactions considered here are homogeneous gas phase reactions

of neutral species. Although the reactions of many ionic species are very

rapid, the concentrations of ions in the atmosphere are too low for them to

play an important role in stratospheric chlorine chemistry.[38] The possibilities

of heterogeneous reactions on the surfaces of stratospheric aerosols have also

been considered, without any evidence for an important role for such reactions.
These aerosol particles (chiefly H_2SO_4) are most abundant around 20 km
altitude, and have by elemental analysis very low concentrations of chlorine
in them. In the 30-45 km altitude range in which the ClO_x reaction is most
effective in removing ozone, aerosol particles are very scarce and
chemical reactions on their surfaces are much less likely than at 20 km.

Stratospheric Halogen Measurements

Measured stratospheric altitude profiles of CCl_3F and CCl_2F_2 have
regularly confirmed the expected dissociation by solar u. v. [1-6] The stable
products HCl [39,40] and HF [41,42] have both been identified in situ in the
stratosphere, and HCl has been regularly collected on both neutral and basic
filters borne by balloons and aircraft. Both ClO and Cl have been repeatedly
detected with a chlorine resonance lamp detector parachuted through the 43-20
km range of altitudes .[43] ClO has also been detected by microwave spectroscopy.[44]
Furthermore, the observed concentrations of these chlorinated species
have generally been in semi-quantitative agreement with model calculations.
An upper limit has been placed on $ClONO_2$ concentration ,[45] and other possible
chlorinated degradation products have so far not been identified in the
stratosphere. The qualitative and semi-quantitative aspects of stratospheric
chlorine chemistry have thus been widely confirmed, and the stratospheric
measurements have now entered into the stage of detailed quantitative
comparisons. Studies of experimental and atmospheric variability, simultane-
ous measurements of several constituents, confirmation by independent experi-
mental methods--all of these are now proceeding for the various stratospheric
chlorine components.

II. Atmospheric Chemistry of Methane

The major hydrocarbon present in the natural atmosphere is methane, which is found in a concentration of approximately 1.5×10^{-6} (ppm). The sources of atmospheric methane are not thoroughly understood on a quantitative basis, although gaseous evolution from biological material under reducing conditions, (e.g. rice paddies, swamps, enteric fermentation) is clearly very important.[46,47] A major fraction of atmospheric methane must come from biological origin because its ^{14}C content approaches that of living plant material which draws its CO_2 from the atmosphere together with $^{14}CO_2$ from cosmic radiation plus nuclear weapons testing.

The major removal process for atmospheric methane is believed to be reaction with tropospheric hydroxyl radicals, as in (11), and therefore

$$OH + CH_4 \longrightarrow H_2O + CH_3 \qquad (11)$$
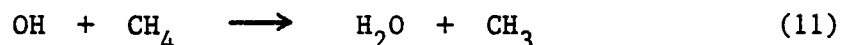
is closely parallel to the removal process for CH_3CCl_3, as described by reaction (6) earlier. After completing measurements for various halocarbons on the atmospheric samples specifically collected for that purpose, we have analyzed additional aliquots from these samples for CH_4, substituting a flame ionization detector for the electron capture detector used following gas chromatographic separation in the halocarbon work.

The CH_4 concentrations of these samples showed a clear interhemispheric gradient between the northern and southern hemispheres, with the north temperate zone concentrations exceeding the south temperate zone concentrations by 7.4%. A good correlation exists between the CH_3CCl_3 and CH_4 concentrations in the same sample, as shown in Figure 3. Such a correlation is expected for two chemical compounds whose chief removal process is in each case reaction with tropospheric OH radicals. However, the existence of a 7.4% gradient between the northern and southern temperate zones places some limits on the maximum atmospheric lifetime

for CH_4. Since the atmospheric lifetimes are interconnected for CH_4 and

CH_3CCl_3 through their common tropospheric sink, independent estimates of the

atmospheric lifetime of CH_4 simultaneously furnish information about the

atmospheric lifetime of CH_3CCl_3 (approximately 2.5 times shorter than that of

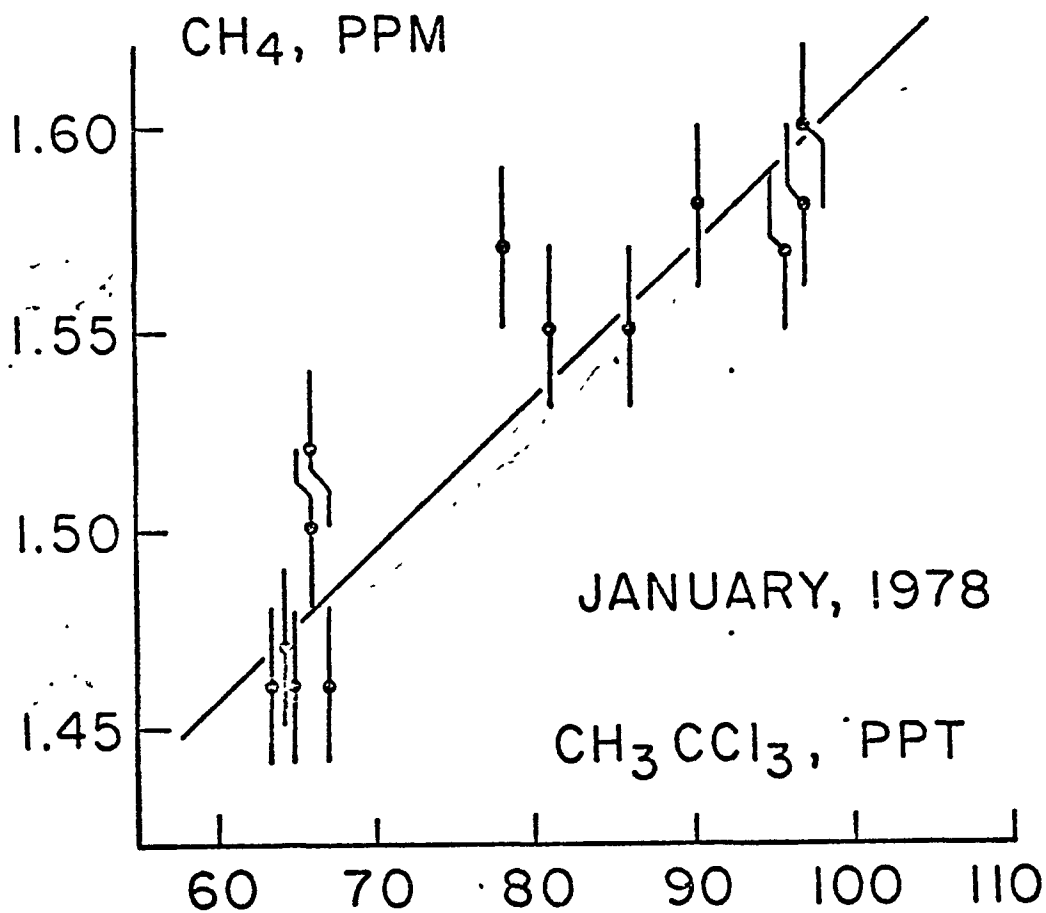CH_4, in the inverse ratio of their reaction rate constants with OH radicals).[48]

Figure 3

Observed Concentrations of CH_4 and CH_3CCl_3, January, 1978

III. Atmospheric Chemistry of Cosmogenic Tritium

Our studies in the atmospheric chemistry of the chlorofluorocarbons have led to corollary calculations on the expected behavior of radioactive isotopes of chlorine (^{38}Cl, ^{39}Cl) as described earlier.[37] We have now extended these to consideration of the expected behavior of other cosmogenic isotopes. Although tritium found in the atmosphere now is overwhelmingly of artificial origin, some measurements were made several decades ago[49-52] prior both to extensive atmospheric testing of nuclear weapons and to commercial applications of tritium. These studies showed the presence in the atmosphere of HT, with specific activity (i.e. HT/H_2) several orders of magnitude higher than for water vapor (HTO/H_2O). This tritium activity was produced by cosmic ray inter- actions, mostly by spallation of ^{14}N and ^{16}O by $> 10^9$ e.v. protons.

As a first task in considering the atmospheric chemistry of tritium in its various possible volatile gaseous forms, we have sought an explanation for the formation of high specific activity HT in the stratosphere. Two earlier sug- gested possibilities have been shown not to be consistent with stratospheric knowledge gained since their suggestion. Far less water vapor exists in the stratosphere ($\sim 3 \times 10^{-6}$) than needed for the 1959 suggestion of energetic tritium atom reaction with it,[52] and the photolysis rate of HO_2 and TO_2 is much too slow for the earlier suggestion that the tritium atoms are recycled by this photochemical route.[51]

A plausible reaction scheme has been found with the important formation reaction involving the tritiated isotopic variants of $H + HO_2 \longrightarrow H_2 + O_2$, using either T or TO_2 as one of the reactants. The rate constant for the reac- tion $H + HO_2$ has just been measured,[53] permitting detailed evaluation of its importance for cosmogenic tritium. The isotopic tritium reactions leading to HT can occur to the level of a few percent in the 45-60 km region, and sufficient tritium is initially formed at these altitudes to account for the observed

fraction of cosmogenic tritium going to HT. These calculations are now being prepared for publication.[54]

IV. Reactions of Energetic and Thermal Radioactive Atoms

The formation of energetic atoms by nuclear recoil offers the opportunity for study of the effects of excess kinetic energy on chemical reactions. While other experimental techniques such as molecular beams are now also furnishing experimental data on such energetic processes, the nuclear recoil method continues to offer particular advantages in the gas phase, especially with more complex molecular targets, and with all condensed phases.

At the same time, the thermalization of such atoms through multiple collisions with inert molecules can be readily accomplished, and offers some strong advantages for study of the thermal reactions of these atoms. The radioactive tracer aspect of thermal ^{38}Cl and ^{18}F atoms permits approaches complementary to macroscopic Cl and F studies. The nuclear activation process can be carried out with molecules such as $CClF_3$[55] and SF_6[56,57] which are easy to handle because of their inert chemical nature, avoiding the difficulties found for example with the photolysis of Cl_2 or F_2 as halogen atom sources. Therefore, most of our experimental investigations of hot atom reactions of ^{38}Cl or ^{18}F with various substrates have been accompanied by thermal studies of the same systems. The experimental advantages of the thermalized nuclear recoil halogen species are sufficiently important that we have recently concentrated more and more on the thorough understanding of the reactions of thermal atomic chlorine and fluorine. Our studies with tritium, on the other hand, have continued to emphasize energetic reactions.

IV A. Atomic ^{18}F Chemistry

The experimental investigation of ^{18}F reactions began in this laboratory a decade ago, and the techniques for hot atom studies were summarized in detail in a progress report in 1973.[56] For mole fractions of SF_6(or NF_3, C_2F_6, CF_4) ≥ 0.95, about 1.5% of all ^{18}F atoms react "hot" with SF_6 to form $SF_5^{18}F$, and almost all of the remaining 98% react thermally with the other components of the system. We have

continued to emphasize thermal reactions of ^{18}F atoms in these studies. Our progress on new systems has been severely hampered all during 1978 by the terminal illness of the original Kaman fast neutron generator. During the winter and spring occasional short periods of operation were obtained, and some supplementary irradiations were carried out which pertained to systems already under study. The running periods with the neutron generator never were long enough for more than exploratory runs with new systems. The purchase by the university of a new Kaman fast neutron generator has solved the equipment problem and it is expected to be in full operation by mid-November.

The reactions of F atoms with ethylene have been approached within the last several years by molecular beams[58], by infrared chemiluminescence,[59] and by our thermal ^{18}F techniques.[57,60] A key question in such experiments has been that of equilibration among the various degrees of freedom of the excited $C_2H_4F^*$ radicals formed by the addition of F to C_2H_4. The observation of a high degree of stabilization of $C_2H_4{}^{18}F^*$ by collision with SF_6 at a pressure of 5 atmospheres requires that $C_2H_4F^*$ must have an average lifetime of $>10^{-10}$ seconds, with even longer lifetimes found for $C_2D_4{}^{18}F^*$ formed by ^{18}F reactions with isotopic C_2D_4. Our RRKM calculations for the $F/C_2H_4/C_2D_4$ systems are in good agreement with the observed lifetimes for both $C_2H_4F^*$ and $C_2D_4F^*$, and imply that randomization of energy must be nearly complete.

These calculations also have been extended to explain the different isotope effects found for $C_2H_4{}^{18}F^*$ and $C_2D_4{}^{18}F^*$ in collisions with SF_6 or NF_3 on the one hand, and CF_4 or C_2F_6 on the other. With either of the two fluorocarbon molecules as the collider gas for the fluoroethyl radicals, the energy loss is quite small, and is less for $C_2D_4{}^{18}F^*$ than for $C_2H_4{}^{18}F^*$. This isotopic variation in energy loss

for such excited radicals (~50 kcal/mole excitation) remains of considerable

interest, and other isotopically related systems are being tested for their

suitability in such comparisons. The primary limitation on these experiments

is the high pressure of parent fluorine compound (SF_6, CF_4, etc.) Needed for

sufficient ^{18}F activity, and the limitation placed thereby to systems which

decompose appreciably on the 10^{-10} sec. time scale. Some larger radicals show

so little decomposition at these pressures that sufficient statistical accuracy

in isotopic experiments cannot be obtained. The reactions of ^{18}F with

$CH_3CH_2CH=CH_2$ furnish an interesting chemical system by itself,[61] and it will be

tested with some deuterated variants.

The observation that RRKM calculations are quite satisfactory for $C_2H_4F^*$

radicals indicates that equilibration of energy throughout the radical is a

reasonable model for the radical at its critical configuration just as the

decomposition to C_2H_3F plus H becomes fully committed. The molecular beam studies

have shown non-randomization of energy between the vibrational and translational

degrees of freedom of C_2H_3F and H. These measurements, however, pertain to the

fully separated fragments and not to $C_2H_4F^*$ at the critical configuration. Both

experimental results are consistent with random equilibration at the $C_2H_4F^*$ stage,

and conversion of energy without full equilibration during the "downhill" energetic

separation of C_2H_3F and H. Similarly, the infrared chemiluminescence experiments

on emission from excited $C_2H_3F^*$ pertain to the vibrational energies of C_2H_3F after

the separation of the fragments.

Thermal ^{18}F reactions have also been carried out with a variety of metallo-

organic target molecules, such as R_4Sn (with $R=CH_3$, C_2H_5, n-Pr, vinyl and allyl).

These studies have been directed toward identification of the important reaction

paths in such systems. In all of these cases, the "abstraction" of an R group by

^{18}F to form $R^{18}F$ has been observed. No stereochemical information has been obtained

about these reactions, so the mechanism may very well correspond to some pathway

$$^{18}F + R_4Sn \longrightarrow R^{18}F + R_3Sn \tag{12}$$

<u>not</u> resembling an abstraction process. The yields of $R^{18}F$ vary from about 1%

with $Sn(allyl)_4$ to 14% with $Sn(vinyl)_4$. The yield increases monotonically with

increasing strength of the C-F bond formed in $R^{18}F$, indicating the great importance

of the thermochemistry of the individual reactions (all of which are highly

exothermic). Pressure studies have now been carried out which test for the possi-

bility that an appreciable fraction of such reactions occur through a radical

addition process similar to the decomposition of $CH_3CH_2\dot{C}HCH_2{}^{18}F^*$ radicals formed

by addition to 1-butene, (e.g. $^{18}F + R_3Sn-CH=CH_2 \longrightarrow R_3Sn-\dot{C}H-CH_2{}^{18}F^*$). The direct

substitution (i.e. pressure-independent) of ^{18}F for R is a major route for this

process.

IV B. Atomic ^{38}Cl Chemistry

Extensive experiments have been performed with $CClF_3$ and CCl_2F_2 as essentially

chemically inert targets for the $^{37}Cl(n,\gamma)^{38}Cl$ nuclear reaction. Both work very

well, and the ^{38}Cl atoms are essentially thermalized in any system containing

$\geq 95\%$ $CClF_3$ or CCl_2F_2. While the two Cl atoms of CCl_2F_2 provide twice as much

^{38}Cl as from $CClF_3$, total ^{38}Cl radioactivity is seldom a limiting problem with a

nuclear reactor source, and $CClF_3$ is the preferred target molecule for study of

thermal ^{38}Cl reactions because the spectrum of hot ^{38}Cl products is simpler.[55]

Thermal ^{38}Cl reactions were studied first with ethylene and with acetylene.

In both cases, the only energetically-available reaction is addition, as in

equation (13). The only available paths for reaction of $C_2H_4{}^{38}Cl^*$ are

$$^{38}Cl + C_2H_4 \longrightarrow C_2H_4{}^{38}Cl^* \tag{13}$$
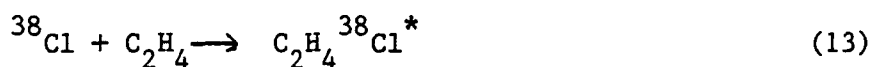
stabilization by collision (14) or loss of ^{38}Cl, as in (15). Reaction (13) has

been studied in competition with abstraction of H from HI, as in (16).

$$C_2H_4{}^{38}Cl* + M \longrightarrow C_2H_4{}^{38}Cl + M \qquad (14)$$

$$C_2H_4{}^{38}Cl \longrightarrow {}^{38}Cl + C_2H_4 \qquad (15)$$
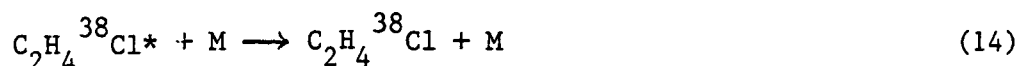
The HI serves also to convert stabilized $C_2H_4{}^{38}Cl$ to $C_2H_5{}^{38}Cl$, as in (17).

About half of the $C_2H_4{}^{38}Cl^*$ radicals are stabilized at a pressure of 800 torr

$$^{38}Cl + HI \longrightarrow H^{38}Cl + I \qquad (16)$$

$$C_2H_4{}^{38}Cl + HI \longrightarrow C_2H_5{}^{38}Cl + I \qquad (17)$$
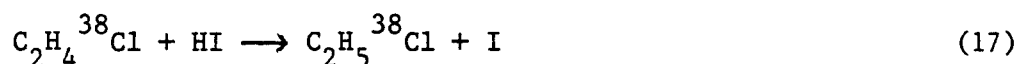
of $CClF_3$. No particular complications are observed in this study of thermal ^{38}Cl atom reactions, and the work was published last year.[62]

The reactions of thermal ^{38}Cl atoms with acetylene are described by a mechanism similar to that given by equations (13) to (17), with the substitution $C_2H_2{}^{38}Cl*Cl$ for $C_2H_4{}^{38}Cl$ throughout. This study was less extensive than that with ethylene, but the observation of acetylene in the earth's atmosphere gave it special environmental significance.[63] Further studies have now been drected toward the possible reactions of $CHCl = \overset{\bullet}{C}H$ radicals in the atmosphere. The experimental procedure still involves the reaction of thermalized ^{38}Cl atoms with C_2H_2, but O_2 is now included in the system as well. The most probable reaction of $C_2H_2{}^{38}Cl$ with O_2 is the formation of the peroxy radical $C_2H_2{}^{38}ClO_2$, and the subsequent molecules formed from this are not readily handled by radio gas chromatography. We are now separating the radioactive products into those soluble in organic and inorganic phases, respectively. The inorganic material is largely $H^{38}Cl$, but we have not yet positively identified any of the organic-soluble ^{38}Cl-labeled compounds. The eventual goal of this analytical treatment is understanding the mechanism for vinylic radical reaction with O_2, and then its application to the atmospheric system.
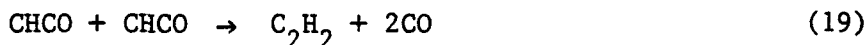
V. Methylene Chemistry

The photolysis of ketene, $CH_2=CO$, has long been used as a source for methylene, CH_2[64,65] and this contract has been concerned for more than a decade with the reactions of both the singlet and triplet forms of methylene. Our experiments were designed to take advantage of the use of tracer-labeled ketene, with $CHT=CO$, $^{14}CH_2=CO$ and $CT_2=CO$ as target molecules, we have accumulated a substantial amount of information about the photochemical reactions of ketene, and of methylene. Much of this information has been published, but some of the experiments have provided detailed information whose full significance is still under investigation.

The generally accepted reaction mechanism for the photolysis of ketene alone includes a series of reactions initiated by triplet methylene, as in reactions (18) to (21). Triplet $^3CH_2$ has been postulated to react with ketene itself by abstraction, as in (18). The observed formation of acetylene and ethane has then been attributed to the subsequent radical

$$^3CH_2 + CH_2CO \rightarrow CH_3 + CHCO \qquad (18)$$
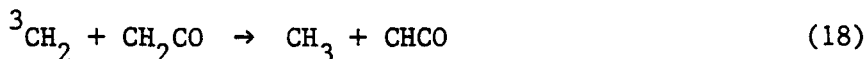
combination reactions (19) to (21).[66] The sequence of reactions (18) to (21)

$$CHCO + CHCO \rightarrow C_2H_2 + 2CO \qquad (19)$$

$$CH_3 + CHCO \rightarrow C_2H_4 + CO \qquad (20)$$

$$CH_3 + CH_3 \rightarrow C_2H_6 \qquad (21)$$

leads to one additional CO per $^3CH_2$ (plus one from the initial photolysis) and equal amounts of acetylene and ethane. Experimental measurements

have indicated the near-equivalence of the yields of acetylene and ethane in both direct and Hg-photosensitized decomposition of ketene. Flash photolysis experiments have shown that $^3CH_2$ can react with $^3CH_2$ to form C_2H_2, and the overall reaction is usually written as in (22).

$$^3CH_2 + {}^3CH_2 \rightarrow C_2H_2 + H_2 \qquad (22)$$
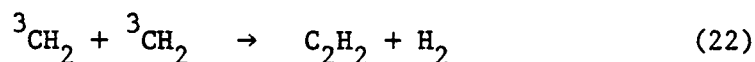
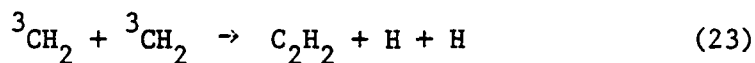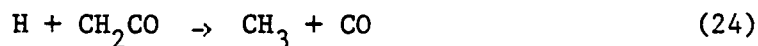However, our own ^{14}C and T tracer experiments indicate that the primary route for $^3CH_2 + {}^3CH_2$ leads to acetylene and <u>atomic</u>, not molecular, hydrogen as in (23). In both steady state and flash photolysis systems the H atoms from (23) then attack ketene

$$^3CH_2 + {}^3CH_2 \rightarrow C_2H_2 + H + H \qquad (23)$$

by the known reaction (24) to form CH_3 radicals. The CH_3 radicals from (24)

$$H + CH_2CO \rightarrow CH_3 + CO \qquad (24)$$

are then available for reaction with $^3CH_2$ in the pure ketene system (as well as with CH_4 or CD_4 present) by reactions (25) and (26). The ethyl

$$^3CH_2 + CH_3 \rightarrow C_2H_5^* \qquad (25)$$

$$C_2H_5^* \rightarrow C_2H_4 + H \qquad (26)$$

radical formed in (25) is so highly excited ($\sim$100 kcal/mole) that it is not collisionally stabilized but immediately decomposes with the loss of H.

The combined mechanism from reactions (23) to (26) plus (21) also leads to a prediction of equal yields of C_2H_2 and C_2H_6, and satisfactorily accounts for the major observations in the steady-state photolysis of pure ketene. The increased yield of H atoms from reaction (23), and therefore of CH_3 radicals from reaction (24), also alters the kinetic description in the

flash photolysis of ketene, and may furnish explanations for some of the
unsolved problems in its flash photolysis. This new analysis of the
mechanism for ketene photolysis has been accepted for publication in the
Journal of Physical Chemistry.[67]

VI. Laboratory Simulation of Chemical Reactions in the
Atmosphere of Jupiter

Infrared investigations of the atmosphere of Jupiter indicate the
presence of phosphine, (PH_3), acetylene, methane and other hydrogenated
gases.[68] Ultraviolet bombardment of this atmosphere causes photodissociation
of these molecules, and various chemical mechanisms have been considered
in explanation of some of the Jovian characteristics. One prominent atmo-
spheric feature of Jupiter is the Great Red Spot, which has been observed
since the invention of the telescope. Several chemical mechanisms have been
proposed as the origin of the chromophore responsible for the orange-red
color, including one which starts with the photolysis of PH_3 by reaction (27),

$$PH_3 + u.v. \rightarrow H + PH_2 \qquad (27)$$
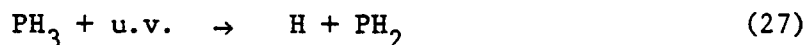
and proceeds in successive steps to form elemental red phosphorus.[69] These
steps include reactions of PH_2 with itself and PH with itself, and are quite
reasonable for the laboratory photolysis of PH_3 in pure state. Elemental red
phosphorus is visibly observable almost immediately in such photolyses.

However, the presence of efficient free radical scavengers such as
acetylene and presumably ethylene makes some of the proposed mechanistic steps
questionable. Our laboratory photolyses of PH_3 scavenged with C_2H_2 or
C_2H_4 have failed to produce red phosphorus, leading instead to a white poly-
meric powder. We have discussed the significance of these results for the

Jovian atmosphere, and have concluded that, if the red color of the Great Red Spot is from red phosphorus, then acetylene and ethylene should probably not be observable there.[70]

More definitive studies will require low temperature photolysis and/or studies of the low temperature reactions with C_2H_2 and C_2H_4 of radicals such as PH_2 and PH. The present results cannot completely eliminate the possibility that these pi-bonded scavengers are not efficient for PH_2 and PH in the $110-150^{\circ}K$ temperature regime characteristic of the photodecomposition layer of Jupiter.

VII. Abstracts of Published Papers, Submitted Papers and Meeting Publications.

The following articles describing work supported by this contract have been published since the submission of our proposal last year. In addition, a general description of the significance of the stratospheric chemistry of the chlorine compounds has been published in the Encyclopedia Britannica 1979 Yearbook of Science and the Future. A translation (into Italian) of one of last year's review articles has been published in Ingegneria Ambientale.

1.   The Mechanism for Ultraviolet Photolysis of Gaseous Chlorine Nitrate
      at 302.5 nm.
      Geophysics Research Letters, 4, 517-520 (1977).

      W.S. Smith, C.C. Chou and F.S. Rowland

The laboratory photolysis of chlorine nitrate ($ClONO_2$) with 302.5 nm ultraviolet light leads to the destruction per quantum of 4 molecules of $ClONO_2$ and the formation of 1 molecule of O_2, 2 of Cl_2 and 2 of N_2O_5. These quantum yields are not consistent with the current assumption that the primary photolysis step for $ClONO_2$ in the stratosphere leads to the formation of ClO plus NO_2. A consistent mechanism exists in which the photolytic step involves the decomposition of $ClONO_2$ to ClONO + $O(^3P)$. The onset of observed absorption of radiation by $ClONO_2$ corresponds approximately to the thermodynamic accessibility of this simple splitting away of an O atom.

The photolysis of ClONO occurs very rapidly in the stratosphere, either to Cl + NO_2 or ClO + NO. The substitution of either Cl + NO_2 + O or ClO + NO + O for ClO + NO_2 as the eventual photolysis products from $ClONO_2$ is not expected to cause appreciable alteration in predictions from stratospheric modeling.

2. Bromine Nitrate, $BrONO_2$, and Its Stratospheric Significance

    Journal of Physical Chemistry, 82, 7-10 (1978)

    John E. Spencer and F.S. Rowland

    Bromine nitrate, $BrONO_2$, has been synthesized and purified, and its ultraviolet and infrared spectra have been measured. The stratospheric photolysis of $BrONO_2$ is about twenty times more rapid than that of the analogous $ClONO_2$. However, since HBr is not as important a sink in the BrO_x-catalytic chain for removal of stratospheric ozone as HCl is for the ClO_x chain, as much as 10-20% of the Br may be present as $BrONO_2$. Measurements of the rate of its formation from $BrO + NO_2 + M$ are necessary for accurate estimate of the stratospheric importance of $BrONO_2$.

3. Stratospheric Photodissociation of Several Saturated Perhalo Chloro-fluorocarbon Compounds in Current Technological Use (Fluorocarbons-13, 113, 114, 115)

    Journal of Physical Chemistry, 82, 7-10 (1978)

    C.C. Chou, R.J. Milstein, W.S. Smith, H. Vera Ruiz, Mario J. Molina, and F.S. Rowland

    Photon absorption cross sections have been measured in the stratospherically-important 1849-2273 Å range for $CClF_3$ (Fluorocarbon-13), CCl_2FCClF_2 (FC-113), $CClF_2CClF_2$(FC-114), and $CClF_2CF_3$ (FC-115). Atmospheric residence times have been calculated for these four compounds, and for CCl_3F(FC-11) and CCl_2F_2 (FC-12), with the assumption that the molecules are removed only by direct solar photolysis or by reaction with $O(^1D)$ atoms. Four different eddy diffusion models were used for stratospheric mixing. Direct photolysis accounts for > 90% of the removal of FC-11, > 80% for FC-12 and FC-113, < 20% for FC-13 and FC-115. Direct photolysis and reaction with $O(^1D)$ atoms are roughly comparable in importance for the removal of FC-114.

The calculated atmospheric residence times range from 40 to 550 years, with especially long calculated residence times for FC-13 and FC-115 which have very low photon absorption cross sections and which are therefore primarily removed from the stratosphere by reaction with $O(^1D)$ atoms.

4. The Chemical Form of Cosmogenic Radioactive ^{38}Cl and ^{39}Cl
    in The Lower Stratosphers
    Geophysical Research Letters, 5, 9-12 (1978)

    F.S. Rowland

The cosmogenic radioisotopes $^{38}Cl(t_{1/2} = 37.3$ min.) and ^{39}Cl ($t_{1/2} = 55.5$ min.) are formed in the stratosphere in detectable quantities, and participate in the stratospheric chlorine cycles. The predominant expected chemical forms for these radioisotopes are ClO and/or $ClONO_2$ throughout the stratosphere. The rates for formation of HCl are sufficiently slow that most ^{38}Cl and ^{39}Cl atoms undergo radioactive decay before ever reacting to form HCl.

The measurement of the fraction of ^{38}Cl and ^{39}Cl in the forms ClO and $ClONO_2$, with a concurrent NO_2 measurement, can be used to measure in situ the stratospheric formation (and destruction) rate for $ClONO_2$. Such experiments could be conducted at altitudes accessible for aircraft experiments.

5. Reactions of Radioactive ^{18}F With Alkenes, Alkynes, and Other
    Substrates "Fluorine Containing Radicals",
    J.W. Root, Editor, American Chemical Society Symposium Series,
    1978, pages 26-58

    F.S. Rowland, Fleet Rust and Joan P. Frank

Radioactive ^{18}F atoms at tracer levels offer several special advantages, and some problems, in comparison with stable ^{19}F atoms for the study of gaseous chemical reactions. Thermal fluorine atoms are exceedingly reactive

with a wide variety of substrates (and surfaces), leading to a variety of experimental difficulties: (a) the reactive, often corrosive, nature of many F atom sources; (b) the rapid abstraction of H from most hydrogeneous substrates, with the formation of HF; (c) the exothermicity of many reactions, especially the formation of HF, with corollary problems of rapid, uncontrolled temperature rises; and (d) the high chemical reactivity of many product molecules, again including HF. The use of ^{18}F atoms at tracer levels avoids several of these difficulties, permitting the systematic study of the reactions of atomic fluorine with many types of substrate molecules, e.g. alkenes and alkynes.

Fluorine atoms react with C_2H_4 to form $C_2H_4F^*$, which can decompose to $C_2H_3F + H$. Pressure-dependent measurements of this decomposition indicate that stabilization occurs about 50% of the time at 80 torr pressure with SF_6. This corresponds to an average lifetime of $\sim 10^{-9}$ seconds. The corresponding pressure for C_2D_4F is only 13 torr. Both lifetimes are consistent with RRKM calculations.

6.   Possible Scavenging Reactions of C_2H_2 and C_2H_4 for Phosphorus-Containing Radicals in the Jovian Atmosphere.

Geophysical Research Letters, 5, 407 (1978)

H. G. Vera Ruiz and F. S. Rowland

The ultraviolet photolysis of PH_3 in the laboratory leads to the formation of elemental red phosphorus, and the occurrence of the same reactions in the atmosphere of Jupiter has been suggested as the source of the chromophore of the Great Red Spot. The inclusion of either C_2H_2 or C_2H_4 as scavenger molecule in the laboratory photolysis at 295°K completely suppresses the formation of red

phosphorus. Experiments are needed on the activation energies for the reactions of PH_2, PH and P_2 with C_2H_2 and C_2H_4 to determine whether the scavenging processes are also effective at Jovian atmospheric temperatures. If the scavenging reactions are effective there, the formation of red phosphorus should occur only in regions with low concentrations of C_2H_2 and C_2H_4.
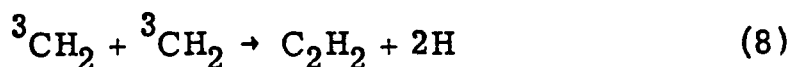
7.   The following article describing work supported by this contract has been accepted for publication since our last proposal.

The Mechanism of Product Formation During the Photolysis of Ketene
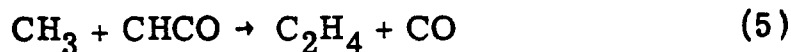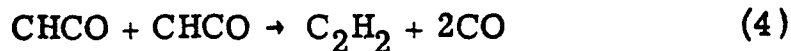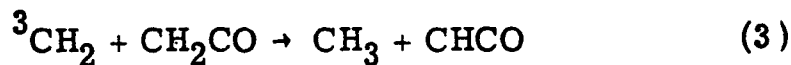
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The photolysis of ketene has been studied with both $^{14}CH_2CO$ and CHTCO, and a new mechanism is suggested for the reactions of triplet methylene in pure ketene. The isotopic experiments are consistent with the set of reactions (6) plus (8) to (11),

$$^3CH_2 + {}^3CH_2 \rightarrow C_2H_2 + 2H \qquad (8)$$

$$H + CH_2CO \rightarrow CH_3 + CO \qquad (9)$$

$$^3CH_2 + CH_3 \rightarrow C_2H_4 + H \qquad (10, 11)$$

$$CH_3 + CH_3 \rightarrow C_2H_6 \qquad (6)$$

and not with the earlier proposal of (3) to (6).

$$^3CH_2 + CH_2CO \rightarrow CH_3 + CHCO \qquad (3)$$

$$CHCO + CHCO \rightarrow C_2H_2 + 2CO \qquad (4)$$

$$CH_3 + CHCO \rightarrow C_2H_4 + CO \qquad (5)$$

The formation of atomic hydrogen rather than molecular hydrogen in (8) has important consequences for interpretation of the flash photolysis of ketene.

The following additional work has been submitted for presentation at the
national meeting of The American Chemical Society in Honolulu, April, 1979.

8.   The Reactions of Thermal 18_F atoms with 1-Butene

          Joan P. Frank, Stanley Tyler and F. S. Rowland

Radioactive ^{18}F atoms (t 1/2=110 mins.) are formed in the gas phase by
the $^{19}F(n, 2n)^{18}F$ nuclear reaction with sulfur hexafluoride. These ^{18}F atoms
are then thermalized by multiple moderator collisions with the inert parent
compound. Once thermalized they can react with minor components which
contain π-bonds such as ethylene, propylene and 1-butene to form energetic
fluoro radicals. These radicals are chemically excited by 40-50 kcal/mole
from C-F bond formation and can undergo decomposition reactions unless
first stabilized by collision. Stabilized free radicals are reacted with scavenger
molecules (e.g. HI) and all volatile products are assayed by radio gas chroma-
tography. The rate constants for decomposition are estimated from experiments
at various pressures in the 200-4000 torr range and lifetimes for the fluoroalkyl
radicals are about 10^{-9} sec. In the SF_6/1-butene/HI system the high yield
products include 1-fluorobutane from C_1-addition followed by stabilization,
2-fluorobutane from C_2-addition followed by stabilization, and vinyl fluoride
from C_2-addition with decomposition. The preference for terminal addition
(C_1) to addition at C_2 is in the ratio 1.42, essentially the same as for addition
to propylene. This is consistent with the characterization of atomic fluorine
as a rather indiscriminate, highly reactive species.

9.   Tropospheric Concentrations of Methylchloroform, CH_3CCl_3, in
      January, 1978, and Estimates of Its Atmospheric Residence Time

      Y. Makide and F.S. Rowland

Ground level samples of ambient air have been collected in stainless steel

flasks in remote locations from $55°N$ latitude to $53°S$ latitude, and returned to

the laboratory for electron capture gas chromatographic measurement of CH_3CCl_3

concentrations. The average concentration of CH_3CCl_3 in the north temperate

zone was $95±4$ ppt (1 ppt = 10^{-12} v/v), while the average for the south temperate

zone was $65±2$ ppt. Samples collected in tropic regions gave concentrations

intermediate between the two temperate zone averages. All samples have been

corrected to January 1, 1978, from the time of collection (November 1977, to

February, 1978) on the basis of 13.5% growth in atmospheric concentration of

CH_3CCl_3 expected during 1977. Comparison of the total CH_3CCl_3 observed in

the atmosphere with estimates of total anthropogenic release indicate an average

atmospheric lifetime of about 6 years. The ratio in concentrations of CH_3CCl_3

between the northern and southern hemispheres, after averaging of tropic and

temperate zones, is about $1.35±0.10$. Comparisons are made between these

results and earlier results indicating a world average concentration of about

100 ppt at approximately the same time.

10.   Interhemispheric Gradient of Atmospheric Methane Between The
       Northern and Southern Hemispheres, 1978

       E.W. Mayer, F.S. Rowland and Y. Makide

Ground level samples of ambient air have been collected in stainless steel

flasks in remote locations from $55°N$ latitude to $53°S$ latitude, and returned to

the laboratory for flame-ionization gas chromatographic measurement of CH_4 concentrations. The average concentration of CH_4 in the north temperate zone was 1.59 ± 0.03 ppm, while the average for the south temperate zone was 1.48 ± 0.03; the gradient between the north and south temperate zones was about 7%. Samples collected in tropic regions gave concentrations consistent with the temperate zone gradient. The existence of an observable north/south gradient requires that the atmospheric lifetime of CH_4 cannot be longer than about 12 years, and is probably considerably less. Other estimates of the atmospheric lifetime of CH_4 have placed it between 4-7 years. Both CH_4 and CH_3CCl_3 are believed to be removed from the atmosphere almost entirely by reaction with tropospheric OH radicals, and the CH_4 and CH_3CCl_3 concentrations in individual samples are strongly correlated. Since the room temperature reaction rates of OH with CH_3CCl_3 are in the ratio of 2.1, the atmospheric lifetime of CH_4 should be more than twice as long as that of CH_3CCl_3.

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