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~~ANNUAL~~  
~~PROGRESS~~ REPORT

DEPARTMENT OF ENERGY  
(DE-FG03-86ER-13469)

RESEARCH IN CHEMICAL KINETICS

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Progress Report on work carried out during the contract period from  
September 1, 1989 to December 31, 1990

MASTER

PRINCIPAL INVESTIGATOR: F. SHERWOOD ROWLAND

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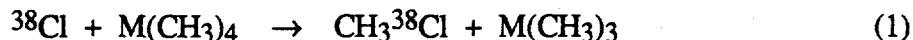
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## PROGRESS REPORT

**DEPARTMENT OF ENERGY  
RESEARCH CONTRACT DE-FG03-86ER13469**

### **1. GAS PHASE SUBSTITUTION REACTIONS OF THERMAL CHLORINE ATOMS WITH TETRAMETHYL METALLO-ORGANIC COMPOUNDS**

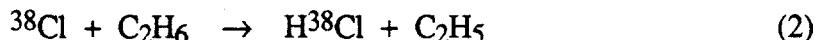
Thermalized  $^{38}\text{Cl}$  atoms have been allowed to react in the gas phase with a series of group IV tetramethyl organometallic compounds to determine the qualitative presence or absence of the substitution reaction (1).<sup>1</sup> Extensive studies of chlorine atom reactions from other sources had never



shown any substitution reactions with hydrocarbons (e.g.  $\text{M}=\text{C}$ ) and, at most, equivocal evidence for the existence of reaction (1) with organometallic compounds. Earlier studies from this laboratory had established that  $\text{CH}_3^{38}\text{Cl}$  is a thermal product from reactions with  $\text{Pb}(\text{CH}_3)_4$ .<sup>2</sup>

We have now carried out a series of experiments with the entire Group IV series ( $\text{M}=\text{C, Si, Ge, Sn, Pb}$ ) and have found that reaction (1) has a very high percentage yield ( $22 \pm 1\%$ ) with  $\text{Pb}(\text{CH}_3)_4$  as the reacting molecule, and a small yield (0.5%) for  $\text{Sn}(\text{CH}_3)_4$ . No  $\text{CH}_3^{38}\text{Cl}$  was observed with  $\text{Ge}(\text{CH}_3)_4$  as the target within the statistical error determined by the background counting rate at the radio gas chromatographic elution time for  $\text{CH}_3^{38}\text{Cl}$ . The upper limit on this percentage yield is  $\pm 0.1\%$ . Similar upper limits can be placed on the yield of reaction (1) from  $\text{Si}(\text{CH}_3)_4$  and  $\text{C}(\text{CH}_3)_4$ . The lack of pressure dependence in reaction (1) with  $\text{Sn}(\text{CH}_3)_4$  as shown by the constancy in  $\text{CH}_3^{38}\text{Cl}$  yield (Figure 1) is consistent with the interpretation that the substitution process is direct, rather than involving an intermediate complex with a lifetime of  $10^{-10}$  seconds or longer, i.e. collision times in the 0.1-4 atmosphere range.

Reaction rate constants have been determined for the substitution reaction through competition with the hydrogen abstraction reaction (2), for which the absolute value of its reaction rate constant has



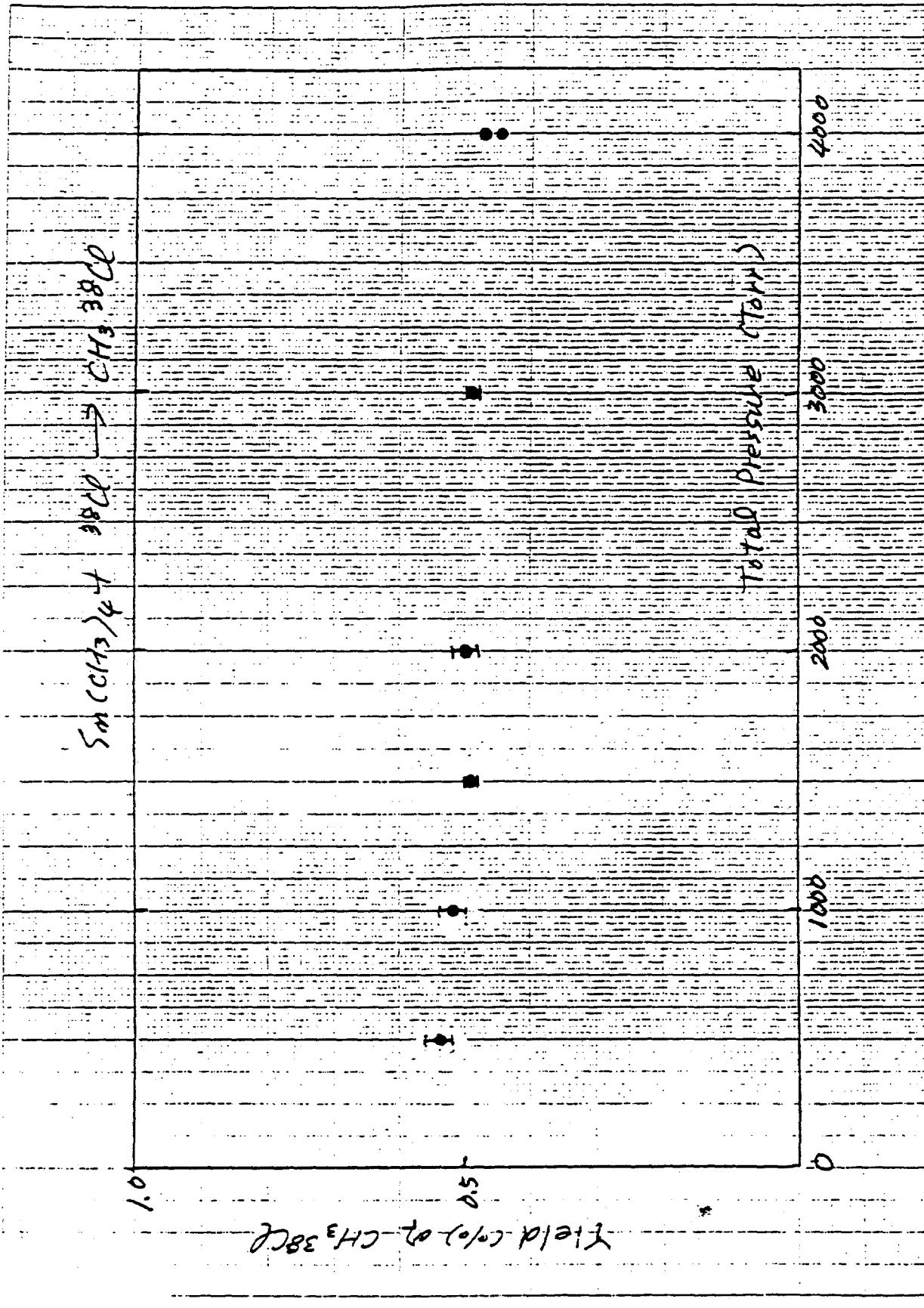
been well-established by other techniques as  $5.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ .<sup>3</sup> This diminution in observed  $\text{CH}_3^{38}\text{Cl}$  yield from (1) in competition with (2) is shown in Figure 2 for  $\text{Pb}(\text{CH}_3)_4$ , and provides the reaction rate constants given in Table 1. An earlier estimate of the reaction rate constant

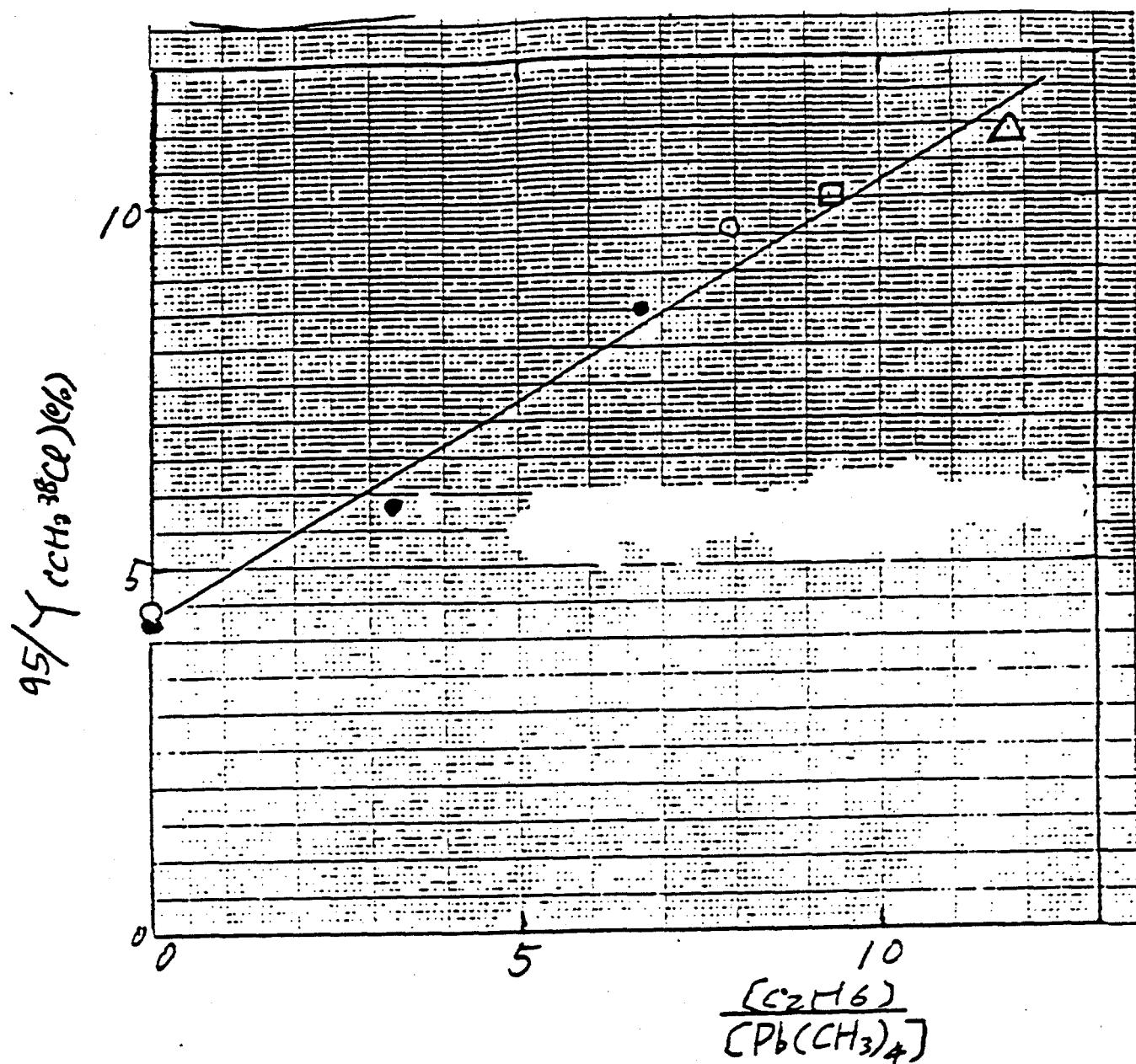
**Table 1 Reaction Rate Constants for Formation of  
 $\text{CH}_3^{38}\text{Cl}$  by Thermal  $^{38}\text{Cl}$  Attack on  $\text{M}(\text{CH}_3)_4$**

$\text{M}(\text{CH}_3)_4$	$k_1 \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$
$\text{C}(\text{CH}_3)_4$	$< 2 \times 10^{-13}$
$\text{Si}(\text{CH}_3)_4$	$< 2 \times 10^{-13}$
$\text{Ge}(\text{CH}_3)_4$	$< 2 \times 10^{-13}$
$\text{Sn}(\text{CH}_3)_4$	$(1.28 \pm 0.15) \times 10^{-12}$
$\text{Pb}(\text{CH}_3)_4$	$(9.67 \pm 0.48) \times 10^{-11}$

for (1) with  $\text{Pb}(\text{CH}_3)_4$  was given as  $3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ , on the basis of competitive reactions of  $^{38}\text{Cl}$  with  $\text{Pb}(\text{CH}_3)_4$  and  $\text{C}_2\text{H}_4$ .<sup>2,4</sup> However, the accepted absolute reaction rate constant for  $^{38}\text{Cl}$  with  $\text{C}_2\text{H}_4$  at that time has since been shown to be in error by more than a factor of 2 and has

FIGURE 1 Percentage yields of  $\text{CH}_3^{38}\text{Cl}$  vs. total sample pressure from the reactions of thermal  $^{38}\text{Cl}$  atoms with  $\text{Sn}(\text{CH}_3)_4$  in excess  $\text{CCl}_3\text{F}_3$ .





**FIGURE 2** Reciprocal yield of  $\text{CH}_3{}^{38}\text{Cl}$  in competition between  $\text{Pb}(\text{CH}_3)_4$  and  $\text{C}_2\text{H}_6$  for thermal  ${}^{38}\text{Cl}$  atoms at various total pressures:

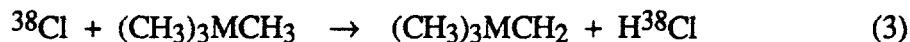
- 500 torr
- 1500 torr
- △ 3000 torr
- 4000 torr

now been revised,<sup>4</sup> raising the rate constant from the  $C_2H_4$  competition to  $(8 \pm 1) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ , in reasonable agreement with the value of  $9.67 \pm 0.48 \times 10^{-11}$  in Table 1.

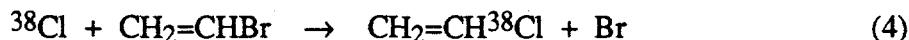
The explanation for the wide variation in rate constants in Table 1 is thermochemical. The approximate strengths of C-M bonds are 57 kcal/mole for Pb, 71 kcal/mole for Sn, 84 kcal/mole for Ge, and 90 kcal/mole for C.<sup>5</sup> When reaction (1) is highly exothermic (C-Cl in  $CH_3Cl$  is about 80 kcal/mole), the substitution reaction proceeds quite readily. The total reactivity of thermal  $^{38}Cl$  with  $Pb(CH_3)_4$  is very high, with reaction occurring on nearly every gas phase collision. The distribution of products between substitution ( $CH_3^{38}Cl$ ) and abstraction ( $H^{38}Cl$ ) is probably strongly influenced by steric accessibility of reaction paths in these collisions.

## 2. ABSTRACTION REACTIONS BY THERMAL CHLORINE ATOMS WITH TETRAMETHYL METALLO-ORGANIC COMPOUNDS

The highest yield reaction of thermal chlorine atoms with  $M(CH_3)_4$  is assumed to be the abstraction reaction (3), although our standard radio gas chromatographic technique does not measure



the yield of  $H^{38}Cl$ .<sup>1</sup> With molecular targets such as  $C_2H_6$ ,  $C(CH_3)_4$ ,  $Si(CH_3)_4$  and  $Ge(CH_3)_4$ , no carbon-bonded  $^{38}Cl$  products are observed. However, the total reactivity of compounds such as  $C_2H_6$  (forming  $H^{38}Cl$ ) can be established in competition with another reaction which leads to a measurable organochlorine yield, as with  $CH_3^{38}Cl$  from  $Pb(CH_3)_4$  in Eq. (1). Similarly, the total reactivity of  $M(CH_3)_4$  compounds can be demonstrated versus another substrate which provides a measurable product whose diminution by competition provides a measured relative reaction rate. These competitions have been carried out versus  $CH_2=CHBr$ , with measurement of its product  $CH_2=CH^{38}Cl$ , as in (4).



The competitive diminutions in  $CH_2=CH^{38}Cl$  versus five RH molecules are all shown in Figure 3 for experiments at 4000 torr. (The reciprocal yield calculations in Figures 2 and 3 are performed on the basis of  $0.95/Y$  rather than  $1.00/Y$  because about 5% of  $^{38}Cl$  formed with  $CCl_3F$  in substantial excess is removed from the system by energetic  $^{38}Cl$  reactions with  $CCl_3F$ .<sup>6</sup> The absolute total reaction rates for these molecules are all summarized in Table 2. The ultimate absolute base for these reaction rates is reaction (2) with  $C_2H_6$ , which permits the evaluation of  $k_4$  at 4000 torr, with calculation of the various  $k_3$  values following by comparison to  $k_4$  as the secondary standard. The absolute reaction rate constant for  $k_3$  with  $Pb(CH_3)_4$  as substrate was evaluated directly from competition with  $C_2H_6$ .

**Table 2** Absolute Reaction Rate Constants for Abstraction of Hydrogen from  $M(CH_3)_4$  Substrates

$M(CH_3)_4$	$k_4 \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$
$C(CH_3)_4$	$(1.27 \pm 0.16) \times 10^{-10}$
$Si(CH_3)_4$	$(1.54 \pm 0.19) \times 10^{-10}$
$Ge(CH_3)_4$	$(1.49 \pm 0.17) \times 10^{-10}$
$Sn(CH_3)_4$	$(2.64 \pm 0.30) \times 10^{-10}$
$Pb(CH_3)_4$	$(3.21 \pm 0.16) \times 10^{-10}$
$C_2H_6$	$(5.7 \times 10^{-11})$ (Standard)

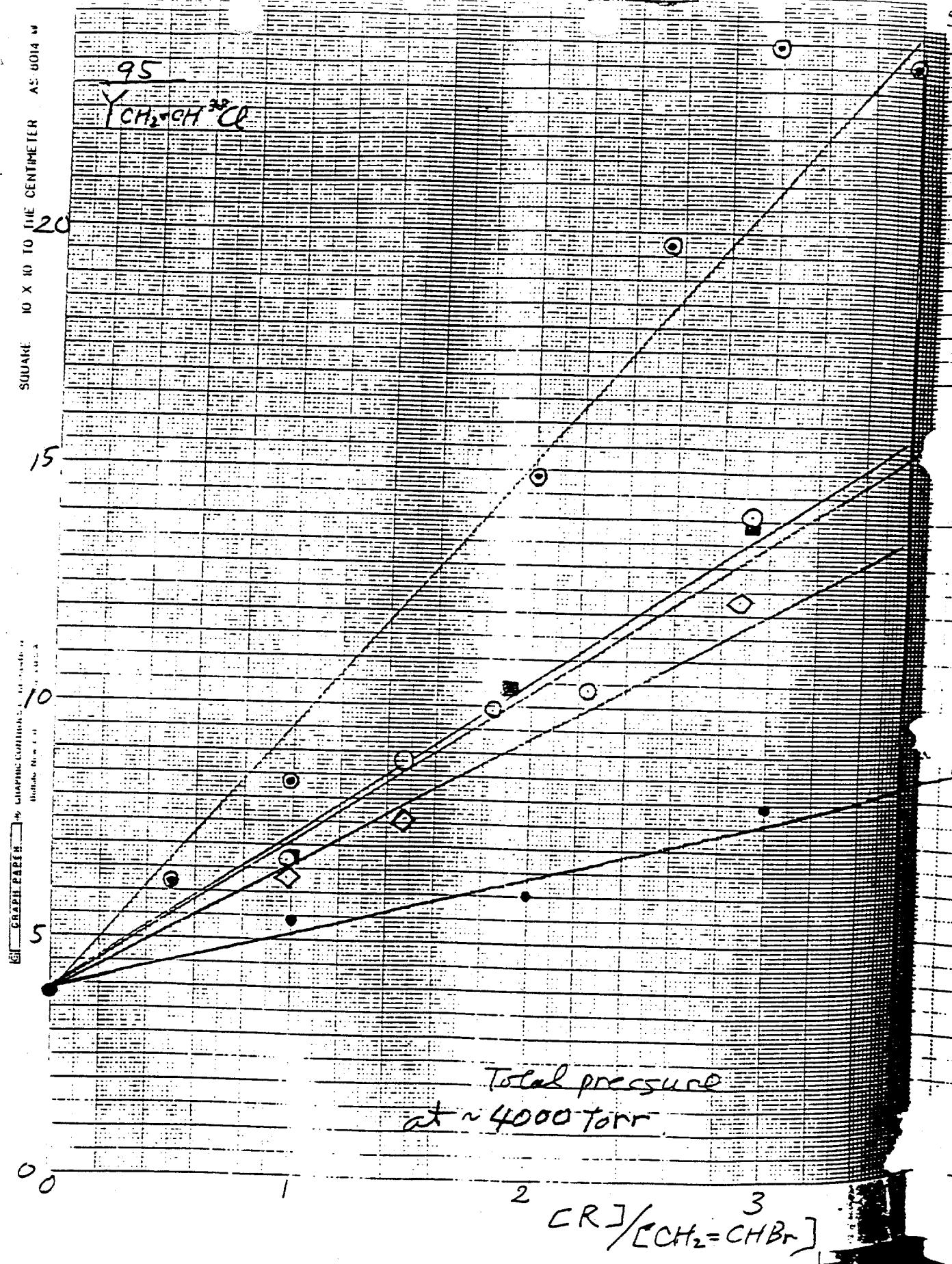


FIGURE 3

Reciprocal yield of  $\text{CH}_2=\text{CH}^{38}\text{Cl}$  in competition between  $\text{M}(\text{CH}_3)_4$  or  $\text{C}_2\text{H}_6$  and  $\text{CH}_2=\text{CHBr}$  for  $^{38}\text{Cl}$  atoms at total pressure of 4000 torr, where  $\text{M} = \text{C, Si, Ge and Sn}$ :

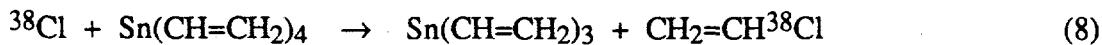
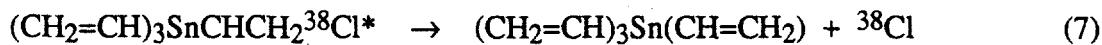
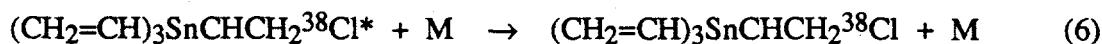
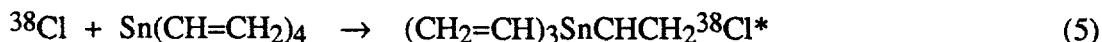
●  $\text{C}_2\text{H}_6$ ; ♦  $\text{C}(\text{CH}_3)_4$ ; ■  $\text{Si}(\text{CH}_3)_4$ ; ○  $\text{Ge}(\text{CH}_3)_4$ ; ○  $\text{Sn}(\text{CH}_3)_4$

The abstraction rate constants with  $C(CH_3)_4$ ,  $Si(CH_3)_4$  and  $Ge(CH_3)_4$  are all within 2.3 to 2.7 times as rapid as with  $C_2H_6$ , which is itself a very rapid reaction. These molecules each have twice as many H atoms as  $C_2H_6$ , and the availability of each of the 12 individual C-H bonds is therefore about 15% to 35% greater per C-H bond in these three  $M(CH_3)_4$  molecules than for the six C-H bonds in  $C_2H_6$ . However, hydrogen abstraction from the 12 C-H bonds in  $Sn(CH_3)_4$  and  $Pb(CH_3)_4$  are, respectively, 2.3 and 2.8 times easier per C-H bond than from  $C_2H_6$ . In contrast to the observations of steadily weakening C-M bond strengths with increasing atomic weight of M, the C-H bond strengths are quite similar and actually strengthen perceptibly in the sequence C, Si, Ge, Sn, Pb.<sup>7</sup> The explanation for increasing yield of  $H^{38}Cl$  with heavier central atoms is not clear, but may be related to an energetically or sterically easier relaxation process for the residual  $(CH_3)_3PbCH_2$  than for  $(CH_3)_3SiCH_2$  radical because of longer C-M bonds (2.29 Å for Pb-C versus 1.87 Å for Si-C and 1.54 Å for C-C). Energetically easier pathways and consequent higher yields were postulated earlier for abstraction reactions from  $CH_4$ ,  $CHF_3$ , etc. by energetic tritium atoms when the residual radical structure from the transition state of the abstraction reaction is more nearly like the fully relaxed radical structure.<sup>8</sup>

## References for Sections 1 and 2

1. F.S.C. Lee and F.S. Rowland *J. Phys. Chem.* **1977**, *81*, 1229
2. M. Kikuchi, *et al.* *J. Phys. Chem.* **1981**, *85*, 84
3. DeMore, *et al.* "Evaluated Reaction Rate Constants for Reactions of Atmospheric Interest", JPL-90-1, **1990**
4. R.S. Iyer, *et al.* *J. Phys. Chem.* **1983**, *87*, 3799
5. D.F. McMillen and D.M. Golden *Ann. Rev. Phys. Chem.* **1982**, *33*, 493
6. F.S.C. Lee and F.S. Rowland *J. Phys. Chem.* **1980**, *84*, 1876
7. F. Watori *Spectrochim. Acta* **1978**, *34A*, 1239
8. E. Tachikawa and F.S. Rowland *J. Am. Chem. Soc.* **1969**, *91*, 559
3. **GAS PHASE THERMAL  $^{38}Cl$  REACTIONS WITH  $M(CH=CH_2)_n$ ; NON-RRKM DECOMPOSITION OF EXCITED RADICALS ( $M=Sn, Si, n=4$ ;  $M=Sb, n=3$ ;  $M=Hg, n=2$ ).**

The thermal reaction of  $^{38}Cl$  with  $Sn(CH=CH_2)_4$  has provided an interesting example of an addition-decomposition sequence (equations 5 to 8) in which the rate constant for  $k_7$  per vinyl group is approximately equal to that for  $CH_2CH_2^{38}Cl^*$  formed by thermal addition to  $C_2H_4$ . The interpretation



of these thermoneutral decomposition reactions has been that the  $(CH=CH_2)_3Sn$  grouping in (7) provides no more degrees of freedom for sequestering the excitation energy from  $^{38}Cl$  addition than the last H in  $C_2H_4^{38}Cl^*$ . The non-participation of the other three ( $CH_2=CH$ ) groups has been attributed to heavy central atom blocking by Sn of internal energy redistribution--an example of "non-RRKM" behavior analogous to that postulated earlier for thermal reactions of  $^{18}F$  and seriously questioned from addition reaction experiments with H atoms. An important component of the kinetic behavior in the  $^{38}Cl/Sn(CH=CH_2)_4$  system is the observation that the yield of  $CH_2=CH^{38}Cl$  from (8) increases from 66% at 4000 torr total pressure to 91% at 130 torr. Competitive experiments with  $C_2H_6$  and  $Sn(CH=CH_2)_4$  simultaneously available as substrates have demonstrated that the additional  $^{38}Cl$  atoms found as  $CH_2=CH^{38}Cl$  at low pressures have been repeatedly free to undergo the substrate competition, as postulated in (7). An isomerization/decomposition from  $(CH_2=CH)_3SnCHCH_2^{38}Cl^*$   $\rightarrow (CH_2=CH)_3SnCH^{38}ClCH_2^*$   $\rightarrow CH_2=CH^{38}Cl$  is excluded by this repetitive competition between substrates. This research was published during the past year [Y. Sakai, R. S. Iyer and F. S. Rowland, *J. Phys. Chem.* 1990, 94, 3368-3370].

Comparable experiments with  $Sb(CH=CH_2)_3$  and  $Hg(CH=CH_2)_2$  as substrates again showed yields of  $CH_2=CH^{38}Cl$  in the range of 60% to 65% at high pressures. In contrast, however, to the observations with  $Sn(CH=CH_2)_4$  substrate, the low pressure yields of  $CH_2=CH^{38}Cl$  were the same as at high pressure. This strong mechanistic difference indicates that thermal  $^{38}Cl$  reactions with  $Sb(CH=CH_2)_3$  and  $Hg(CH=CH_2)_2$  provide no indications of non-RRKM behavior. The difference in RRKM vs. non-RRKM behavior for M=Sb, Hg vs. M=Sn has not been definitely identified in mechanistic terms.

#### 4. QUANTITATIVE PRODUCT IDENTIFICATION FOR REACTIONS OF HYDROXYL WITH $^{14}CS_2$ .

The radiochemical identification of products from the reactions of HO with  $CS_2$  were carried out several years ago with  $^{14}CS_2$  as the substrate. Our measurements of significant product yields for  $^{14}CO$  and  $^{14}CO_2$ , in addition to  $O^{14}CS$ , was at variance with the published data indicating only the pathway to OCS. A preliminary report of our results was published several years ago as part of a Conference proceedings.<sup>1</sup> In the meantime, we have done much further work on the  $^{14}CS_2$  system as well as complementary work with  $CS^{35}S$  as the substrate. Furthermore, very recent experiments by other spectroscopic techniques have now succeeded in identifying CO as a product,<sup>2</sup> confirming the existence of dual pathways for  $HO + CS_2$ .

The gas-phase oxidation of  $CS_2$  initiated by HO radicals in the presence of  $O_2$  has been studied using  $^{14}C$ -labeled  $CS_2$  in a static photolysis system. The radioactive products were analyzed by radio gas chromatography and the rates for the oxidation of  $CS_2$  were determined relative to the rates of removal through reaction with HO of a reference reactant ( $C_3H_8$  or *iso*- $C_4H_{10}$ ). Two separate photochemical methods were used for the generation of HO radicals: (a) the 302 nm photolysis of  $H_2O_2$  and (b) photolysis at 366 nm of  $CH_3ONO-NO-O_2$  mixtures. With  $O_2$  and  $N_2$  as diluent gases and one atmosphere total pressure, rapid removal of  $^{14}CS_2$  was observed when both the HO precursor and  $O_2$  were present in the irradiation mixtures. The oxidation rates increased as the  $O_2$  concentration was increased; with the former source of HO, the observed rate constants at  $T=296$  K were  $0.31 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for  $[O_2] = 20$  torr and  $2.68 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for  $[O_2] = 248$  torr. With the latter source also, the rate constants increased with increasing  $O_2$  concentration and the measured rate constants were consistent with those using the  $H_2O_2$  source. With either source of HO radicals, the radioactive products formed from the oxidation were  $O^{14}CS$ ,  $^{14}CO$  and  $^{14}CO_2$ . The relative yield distributions observed for the formation of these three products in one atmosphere of synthetic air were 50%  $O^{14}CS$ , 40%  $^{14}CO$ , and 10%  $^{14}CO_2$  with the  $H_2O_2$  source, and 70%  $O^{14}CS$ , 20%  $^{14}CO$  and 10%  $^{14}CO_2$  with the  $CH_3ONO-NO-O_2$  source. The mechanistic details causing this difference in the relative product yields from the two HO sources remain unclear. In synthetic air at one atmosphere

pressure and T=296K, the effective rate constants for the oxidation were determined to be  $(2.2 \pm 0.4) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  using the  $\text{H}_2\text{O}_2$  source and  $(2.1 \pm 0.3) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  using the  $\text{CH}_3\text{ONO-NO-O}_2$  source. The data obtained are consistent with an oxidation mechanism involving the formation of an  $\text{HOCS}_2$  adduct which either dissociates back to the reactants or reacts with  $\text{O}_2$  to form the observed products.

Our extensive discussion of the  $^{14}\text{CS}_2$  system has been submitted to the *Journal of Atmospheric Chemistry* and is included here as Appendix A.

## References for Section 4

1. Yang Wenxiang; R.S. Iyer and F.S. Rowland "Radioactive Tracer Study on the Photochemical Reaction of  $^{14}\text{CS}_2$  with OH in the Presence of  $\text{O}_2$ ", *Acta Scientiae Circumstantiae [Huanjing Kexue Xuebao]*, 1988, 8, 131-138
2. Stickel, R.E.; Chin, M.; Daykin, E.P.; Hynes, A.J.; Wine, P.H. "Mechanistic Studies of the OH-Initiated Oxidation of  $\text{CS}_2$  in Oxygen", *EOS*, 1990, 71, 1248

## 5. STATISTICAL ANALYSIS OF GROUND-BASED MEASUREMENTS OF TOTAL OZONE WITH DOBSON SPECTROMETERS

In 1986, exploratory work was conducted under this contract on the statistical analysis of total ozone data as measured at Arosa, Switzerland, from 1931 through 1986 with a Dobson ultraviolet spectrometer. All prior statistical analyses of these data and those from other Dobson stations had shown no significant change in ozone concentrations over the various time periods involved. These analyses were implicitly based upon the assumption originating from one-dimensional atmospheric model calculations that any anthropogenically initiated variations in ozone concentrations would be monotonic in nature and seasonally independent. The usual situation in the north temperate latitudes is that total ozone concentrations reach a maximum in March or April and a minimum in October or November. In addition, the natural variability in ozone concentrations is greatest in the winter period and least in the summer. The earlier statistical analyses, therefore, were designed to emphasize the summer data strongly through weighting--the time period in which any ozone variation would be easier to detect against a much smaller natural variability.

Our statistical analysis of the total ozone data from Arosa was based instead on separate examination for possible trends of the data from each series for particular calendar months. With this difference in technique, significant negative deviations in total ozone were detected in the Arosa data for several winter months. A check on this conclusion was then made with data from two other Dobson stations at approximately the same latitude (47°N) as Arosa: Bismarck, North Dakota and Caribou, Maine. Again, significant wintertime losses in total ozone were detected.

Total ozone data are recorded by international agreement through measurements of the relative amounts of solar radiation penetrating at two ultraviolet wavelengths, the shorter of which is far more likely to be absorbed by atmospheric ozone. Four different wavelength pairs--identified by the letters A, B, C and D--have been officially designated for international use; and since 1957, the prescribed wavelengths of choice are a combination of the A and D wavelengths. The Bismarck and Caribou ozone data were recorded with the AD pairs. The 57-year Arosa data were recorded, however, with the C wavelength pair. Since 1957, the A and D pairs have also been recorded at Arosa.

The Arosa/Bismarck/Caribou analyses were presented at the American Geophysical Union meeting in 1986.<sup>1</sup> Soon thereafter, the just-formed NASA Ozone Trends Panel began a more extensive study of Dobson total ozone data with two members of the Irvine research group (Neil Harris and F. S. Rowland) participating fully. The NASA study relied entirely on ozone data taken with the AD pairs at 30 or more stations and fully confirmed the conclusion that wintertime loss of ozone had occurred in the northern temperate regions.<sup>2-4</sup>

The initial efforts with the Arosa C data were later renewed and have firmly established the wintertime losses at that location. The most important aspect of the Arosa C data is the 57-year data series versus 22-30 year sequences with AD ozone data.

Total column ozone measurements were initiated at Arosa, Switzerland, in the mid-1920s and have continued with only minor interruption since August 1931. Statistical analyses of the 57-year data set taken with the C wavelength pair of the Dobson spectrometer from August 1931 to July 1988 are presented here which show that the rate of change in total ozone since 1970 has been -1.17 Dobson Units/year [-3.5%/decade] in the winter months (December-March), or 22 D.U. by 1988. The rate of change in the summer (June-August) has been -0.31 D.U./year [-0.9%/decade], or -6 D.U. from 1969 through 1988. The trend in ozone concentrations was negative in all twelve calendar months and statistically different from zero at the 2s level or greater in five months.

These results are robust to such factors as choice of time period under consideration, effects of the eleven-year solar cycle and of nuclear bomb testing in the atmosphere in the years leading up to 1963. They corroborate the findings of recent studies which used data from more than twenty Dobson stations, but which are limited to 30 years of measurements taken since 1957 [OTP, 1988; Rowland *et al.*, 1989; WMO-UNEP, 1990; Bojkov *et al.*, 1990]. The magnitude of the effect of the eleven-year solar cycle on total ozone is smaller in the long Arosa series than is found in these other studies.

This research has been submitted for publication in the *Journal of Geophysical Research* and is included as Appendix B.

## References for Section 5

1. Harris, N.R.P.; Rowland, F.S. "Trends in Total Ozone Measurements at Arosa", Abstracts, American Geophysical Union Meeting in San Francisco, 1986
2. Ozone Trends Panel (OTP), 1988. Chapter summaries published in NASA, "Present State of Knowledge of the Upper Atmosphere 1988"
3. World Meteorological Organization (WMO), Global Ozone Research and Monitoring Project-Report No. 18, Vols. I and II, "Report of the International Ozone Trends Panel 1988"
4. F. Sherwood Rowland, Neil R.P. Harris, Rumen D. Bojkov and Peter Bloomfield "Statistical Error Analysis of Ozone Trends--Winter Depletion in the Northern Hemisphere" in Ozone in the Atmosphere, Proceedings of the Quadrennial Ozone Symposium 1988, Rumen D. Bojkov and Peter Fabian, Eds., Deepak Publishing, Hampton, Virginia, 1989, pp 71-75

## **RESEARCH PROPOSAL**

**DEPARTMENT OF ENERGY  
(DE-FG03-86ER-13469)**

### **RESEARCH IN CHEMICAL KINETICS**

Department of Chemistry  
University of California Irvine  
Irvine, California 92717

**Research Proposal for work proposed during the period from  
May 1, 1991 through April 30, 1992**

**PRINCIPAL INVESTIGATOR: F. SHERWOOD ROWLAND**

**RESEARCH PROPOSAL**  
**FOR CONTINUATION OF DEPARTMENT OF ENERGY**  
**RESEARCH CONTRACT DE-FG03-86ERF13469**

**1. CHLORINE ATOM REACTIONS WITH ORGANOMETALLIC COMPOUNDS**

Our program of investigation of thermal  $^{38}\text{Cl}$  reactions with  $\text{M}(\text{CH}=\text{CH}_2)_x$  molecules and comparable metallo-organic compounds containing other unsaturated ligands will continue. The observations of pressure-dependent yields of  $\text{CH}_2=\text{CH}^{38}\text{Cl}$  with  $\text{Sn}(\text{CH}=\text{CH}_2)_4$  are most logically interpreted as a failure of rapid energy transfer past the heavy central atom. The observed mechanistic differences between  $\text{Sn}(\text{CH}=\text{CH}_2)_4$  and  $\text{Hg}(\text{CH}=\text{CH}_2)_2$  make further investigations with molecules such as  $\text{Si}(\text{CH}=\text{CH}_2)_4$  and  $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}_2$  very important in determining the causes of these differences.

**2. CHLORINE ATOM REACTIONS WITH HYDROGEN-CONTAINING CHLOROFUOROCARBONS**

The implementation by the United Nations Environment Program of the Montreal Protocol in September 1987 and its strengthening in London in June 1990 will cause almost all of the manufacture of chlorofluorocarbons (CFCs) to cease by the year 2000. Among the substitutes under investigation for the technological replacement of the CFCs are eight or more hydrogen-containing halocarbons, including  $\text{CH}_2\text{FCF}_3$  designated as HFC-134A, and  $\text{CHCl}_2\text{CF}_3$ , HCFC-123. The major atmospheric sink for these compounds is attack by HO radical in the troposphere, as in (1) for  $\text{CH}_2\text{FCF}_3$ . The life-



times of such molecules in the troposphere has been estimated by measurement of laboratory reaction rates with HO, normalized to the measured reaction rate with  $\text{CH}_3\text{CCl}_3$  whose lifetime has been calculated as 6 to 7 years.

The stratospheric reactions of these substitute molecules are determined largely by the fastest of three reactions: ultraviolet photolysis, reaction with HO, and reaction with Cl. With  $\text{C}_2\text{H}_6$ , for example, the abstraction of H by thermal Cl is a significant stratospheric sink.<sup>1</sup> For most of the proposed HFC and HCFC substitutes, the ultraviolet photochemical cross sections and HO reaction rates have already been measured. However, the thermal Cl atom reaction rates have not yet been measured for any of them. We propose to measure the relative reaction rates of thermal  $^{38}\text{Cl}$  atoms with the various HCFC and HFC substitutes in competition with  $^{38}\text{Cl}$  reaction with  $\text{CH}_2=\text{CHBr}$ , using the procedures developed over the past five years in our laboratory. The initial measurements will be made with  $\text{CH}_2\text{FCF}_3$  and  $\text{CHCl}_2\text{CF}_3$ .

**3. DETERMINATION OF THE CARBON 14 COMPOSITION OF CARBONYL SULFIDE AND SELECTED LIGHT HYDROCARBONS**

**INTRODUCTION**

Many carbon-containing trace gases have become the subject of increasing scientific interest, particularly in relation to atmospheric processes such as the greenhouse effect, climate change, ozone depletion and photochemical oxidation [Ramanathan *et al.*, 1985; Warneck, 1988]. Several of these gases are known to be naturally present in the atmosphere but also to have significant anthropogenic

sources. The relative contribution of different source types can however be extremely difficult to quantify.

Radiocarbon ( $^{14}\text{C}$ ) and stable ( $^{13}\text{C}$ ) isotope ratios, with respect to  $^{12}\text{C}$ , of the more abundant atmospheric trace gases  $\text{CO}_2$  and  $\text{CH}_4$  have been measured [Levin *et al.*, 1985; Lowe *et al.*, 1988; Wahlen *et al.*, 1989; Manning *et al.*, 1990] and found to be of direct relevance in the determination of their respective sources and sinks. In this way, it has been possible to quantify the extent to which anthropogenic emissions perturb their natural atmospheric cycles. Any atmospheric gas derived from living organisms has a  $^{14}\text{C}$  radiocarbon content very close to that of modern biological material such as recent wood. In contrast, if the gas is derived from fossil fuels or volcanic activity, it will contain no radiocarbon. This is because fossil fuel deposits are so old that the originally present  $^{14}\text{C}$ , which has a half life of 5730 years, has decayed. The only fossil fuel for which the  $^{14}\text{C}$  has not decayed to negligible levels is peat, for which 10-25% of the  $^{14}\text{C}$  may still remain. The proportion of total fossil fuel combustion represented by combustion of peat is sufficiently low, however, to make its contribution to  $^{14}\text{C}$  negligible. Lowe *et al.* (1988), Wahlen *et al.* (1989), and Manning *et al.* (1990) used the difference between biospheric and fossil  $\text{CH}_4$  sources to suggest that approximately 32%, 21% and 25%, respectively, of atmospheric  $\text{CH}_4$  comes from fossil sources. The straightforward distribution of atmospheric  $\text{CH}_4$  between  $^{14}\text{C}$ -dead fossil fuels and  $^{14}\text{C}$ -live biological sources is complicated by (a) nuclear bomb testing which took place in the atmosphere during the period 1945-1962 and (b) the release of  $^{14}\text{CH}_4$  as a minor contaminant from the operation of some nuclear power plants [Levin *et al.*, 1985]. In the latter case, the  $^{14}\text{C}$  does not have cosmic ray-induced atmospheric nuclear reactions as its source, so has a far higher  $^{14}\text{C}/^{12}\text{C}$  ratio than is characteristic of biological species which have been equilibrated with the relatively low atmospheric  $^{14}\text{C}/^{12}\text{C}$  ratio. Increased  $^{14}\text{C}/^{12}\text{C}$  ratios due to such contamination of atmospheric  $\text{CH}_4$  is, however, believed not to be of major importance on a global scale but can lead to deceptively high  $^{14}\text{CH}_4$  levels in air samples inadvertently collected in the vicinity of  $^{14}\text{CH}_4$ -leaking nuclear reactors [Levin *et al.*, 1985]. In the atmosphere the neutrons emerging from a nuclear fireball produce the same  $^{14}\text{N}(\text{n},\text{p})$   $^{14}\text{C}$  nuclear reaction which serves to form cosmic ray-induced  $^{14}\text{C}$ . By 1962, such nuclear explosions had raised the atmospheric  $^{14}\text{C}/^{12}\text{C}$  ratio in the northern hemisphere to approximately double the 1950 value. Since large-scale atmospheric testing of nuclear weapons ceased almost three decades ago, this  $^{14}\text{CO}_2/^{12}\text{CO}_2$  atmospheric ratio has declined with an approximate half-life of 7 years. However, if a piece of biological material (e.g. a tree ring), formed from atmospheric  $\text{CO}_2$  in 1962, was now combusted with  $\text{CH}_4$  as a by-product, the  $^{14}\text{C}/^{12}\text{C}$  ratio of the  $\text{CH}_4$  produced would reflect the doubled  $^{14}\text{CO}_2$  content that was present in the atmosphere at its time of photosynthesis. This material would thus register as an impossible "200% biological" on the 0-100% "dead  $^{14}\text{C}$ " to "modern" scale. The extent of such  $\text{CH}_4$  release from biological material photosynthesized in each year is totally unknown. Therefore, any such contribution to current atmospheric  $^{14}\text{C}$  activity would introduce an appreciable uncertainty in the apportionment between biological-live and fossil fuel-dead  $^{14}\text{C}$  sources. The atmospheric lifetime of  $^{14}\text{CH}_4$  is about 10 years [Mayer *et al.*, 1982], thus about 14% of any bomb  $^{14}\text{CO}_2$  that was processed into biological material in 1962 then released to the atmosphere by biomass burning as  $^{14}\text{CH}_4$  that same year, would still be in the atmosphere.

Similar uncertainties can affect the use of  $^{14}\text{C}$  data to attribute the sources of other atmospheric trace gases to fossil fuel use or biology. These atmospheric components may, however, have different chemistry and different lifetimes, such that the importance of each type of uncertainty would be qualitatively different for each gas. As an example, if bomb  $^{14}\text{C}$  had been processed through  $^{14}\text{CO}_2$  into gaseous  $\text{CH}_3^{14}\text{CH}_3$  in 1962, the fact that the average atmospheric lifetime for ethane is 2 months means that none would still remain in the atmosphere in 1991. With sufficient data on a suite of similar gasses such as the aliphatic hydrocarbons, some reduction in the uncertainties introduced by past atmospheric nuclear testing might be obtained. In any event, an observation of the total absence of  $^{14}\text{C}$  in a particular atmospheric gas would clearly preclude that gas from having a current biological origin.

## CARBONACEOUS ATMOSPHERIC COMPONENTS FOR WHICH SOURCES REMAIN EITHER QUANTITATIVELY OR QUALITATIVELY UNCERTAIN

In addition to  $\text{CO}_2$  and  $\text{CH}_4$ , carbonyl sulfide (COS) is another important carbon-containing trace gas. After COS was detected in the atmosphere [Hanst *et al.*, 1975] and on the basis that COS is a relatively inert gas with a solubility in water somewhat lower than that of  $\text{CO}_2$ , Crutzen (1976) suggested that COS could diffuse into the stratosphere, be dissociated by solar ultraviolet radiation and form  $\text{H}_2\text{SO}_4$  aerosol. In fact, COS is considered to be the most important non-volcanic source of stratospheric sulfur since the free tropospheric concentration of COS (500 ppt) has been found to be many times greater than that of any other sulfur gases [Hanst *et al.*, 1975; Sandalls and Penkett, 1977; Torres *et al.*, 1980].

The tropospheric chemistry of COS has proven to be more complicated than originally assumed by Crutzen. Oceanic hydrolysis of COS, accompanied by the release of  $\text{HS}^-$  ions, occurs on a time scale of a fraction of a day indicating that the ocean is an effective sink for COS [Rowland, 1979; Elliot, Lu and Rowland, 1987]. Despite this known hydrolysis sink, the oceanic concentration of COS actually exceeds the value calculated from the known atmospheric concentration and Henry's Law constant [Rasmussen *et al.*, 1982; Ferek and Andreae, 1983; Johnson and Harrison, 1986]. The observation of an excess of dissolved COS, rather than a sink-induced deficit, requires that the hydrolytic sink be more than balanced by an oceanic source. Such an oceanic source has not been clearly identified, but the observation of oceanic carbon-sulfur compounds is usually explained in terms of a biochemical origin.

It has been calculated that sufficient COS from the troposphere is photolyzed below 30 km to account for the background level of sulfate aerosol during non-volcanic periods [Leifer, 1989]. An increase of about  $5\pm 2$  percent per year has been observed in the background levels of this stratospheric sulfuric acid aerosol mass at northern mid-latitudes during the past 10 years, but the lack of adequate information on sulfur sources, including COS, means that it is not known whether the increase is due to anthropogenic emissions or not [Hofmann, 1990].

The sources and sinks of COS have been reviewed by Turco *et al.* (1980) who indicate that as much as 50% of the total global source of COS comes from anthropogenic activities related mainly to fuel processing and consumption. Alternately, Khalil and Rasmussen (1984) estimate that such anthropogenic sources contribute only 10% of global emissions. It is obvious, therefore, that great uncertainty surrounds this question, even regarding the distribution of emissions between biological activity and the burning of sulfur-containing fossil fuels, making it well suited to the application of  $^{14}\text{C}$  techniques.

Average concentrations of COS are remarkably constant. Aircraft measurements made by Torres *et al.* (1980) found essentially no north-south interhemispheric or vertical tropospheric gradient for COS. These observations are consistent with the tropospherically inert nature of COS. In addition, a maximum secular trend of  $\pm 3\%$  per year has been calculated by Johnson (1985) from measurements by different groups during a seven-year period beginning in 1975 [Sandalls and Penkett, 1977]. Recent re-evaluation [Johnson *et al.*, 1990] confirms that the atmospheric observations show no COS increase over the past 15 years, while the north/south gradient appears to be very slightly greater than unity [Bates and Johnson, 1990]. The latter does not appear to be consistent with an important ocean-to-atmosphere source of COS more or less evenly spread over the Earth's oceans, although concentrated sources in specific biological hot-spots could still be invoked. To date, however, the measurements of dissolved COS have shown oceanic excesses above Henry's Law expectations essentially everywhere tested, suggesting a more generally distributed oceanic source.

Reduced sulfur compounds  $\text{CS}_2$ ,  $\text{H}_2\text{S}$ ,  $(\text{CH}_3)_2\text{S}$  (DMS) and  $(\text{CH}_3)_2\text{S}_2$  (DMDS), which are emitted from the decay of terrestrial and oceanic organic matter, may also make a significant contribution to stratospheric  $\text{H}_2\text{SO}_4$  as they are thought to be converted to COS in the troposphere [Sze and Ko, 1979; Jones *et al.*, 1983]. Laboratory studies have definitely shown that COS is an oxidation product from gas phase OH radical attack on  $\text{CS}_2$  in the presence of  $\text{O}_2$ , although the original hypothesis of unit carbon conversion of  $\text{CS}_2$  to COS has been shown to be inaccurate through the observation of another route leading from  $\text{CS}_2$  to CO [Iyer *et al.*, 1990; Stickel *et al.*, 1990]. COS distribution, therefore, would also be influenced by emissions of  $\text{CS}_2$  from industrial sources.

There are many problems associated with an increase in stratospheric aerosol mass. These include perturbation of the lower stratospheric (18-22 km) temperature profile, which would lead to ensuing climatic change [Hofmann, 1990]. Also, recent laboratory studies have shown that heterogeneous reactions similar to those occurring on Antarctic ice clouds can take place on sulfuric acid particles such as volcanic and background aerosols [Tolbert *et al.*, 1988; Mozurkewich and Calvert, 1988]. Stratospheric ozone reductions observed after the 1982 eruption of El Chichón in Mexico are in fact thought to have occurred on volcanic aerosol emissions [Hofmann and Solomon, 1989], showing that an increase in background stratospheric aerosol may cause stratospheric ozone depletion during non-volcanic periods. In addition, photochemistry may be altered by an accompanying increase in solar scattering such that the conversion of COS to  $H_2SO_4$  may even be accelerated [Hofmann, 1990].

## SAMPLE CONSIDERATIONS

Low concentrations of  $^{14}C$  radiocarbon (only a few parts in  $10^{12}$  in even modern samples), along with the low ambient concentrations of atmospheric trace gases such as COS ( $\sim 500$  ppt), make the use of the particularly sensitive measurement technique, accelerating mass spectrometry (AMS), a necessity. Even employing AMS, which is vastly superior to the older  $\beta$ -decay counting method in terms of sample size, the collection of  $75\text{ m}^3$  of clean air would be required in order to obtain even 20  $\mu\text{g}$  of carbon of COS origin. Vogel *et al.* (1989) have made reliable  $^{14}C$  determinations directly on samples containing only a few tens of micrograms of carbon. At their AMS facility at Simon Fraser University (SFU), they found that the total measurement precision for a sample size of 50  $\mu\text{gC}$  was  $\pm 3\%$ , and samples as small as 20  $\mu\text{gC}$  have previously been measured [Nelson *et al.*, 1986]. Vogel *et al.* (1989) quote a precision of better than 1% for measurements using large sample sizes ( $>400\text{ }\mu\text{gC}$ ) but reported no bias in the results obtained for a range of sample sizes (between 50 and 6490  $\mu\text{gC}$ ). This indicates that the Lawrence Livermore AMS instrument will have to be employed at the limits of its detection range but, for the type of measurement proposed here, an accuracy of a few percent is more than adequate. A good indication of the proportion of fossil to biospheric sources only is required rather than an accurate archeological date.

Because of the large amount of air required for the determination of COS, it is proposed initially to measure the atmospheric  $^{14}C/^{12}C$  ratio of the light hydrocarbons ethane and propane. These species are relatively abundant and thus require the collection of smaller, though not trivial, volumes of air. Ethane and propane are present in clean air at levels of approximately 2 and 0.8-1 parts in  $10^9$  (ppb), respectively, in the wintertime northern hemisphere [Hov *et al.*, 1984; Blake and Rowland, 1986; Singh *et al.*, 1988]. They also, of course, have the advantage of containing 2 and 3 carbons per molecule rather than only 1. Ethane would require a whole air sample size of approximately  $10\text{ m}^3$  to allow the collection of 20  $\mu\text{g}$  of carbon, and propane would require approximately  $15\text{ m}^3$ .

The sources of the light hydrocarbons ethane and propane are thought to be mainly fossil, originating from the leakage of natural gas [Derwent and Hov, 1979]. It has, however, been suggested by several authors that natural oceanic sources of both species exist [Swinnerton and Lamontagne, 1977; Bonsang *et al.*, 1988] but, as for COS, quantitative estimates of source strengths are difficult to obtain. Measurement of the  $^{14}C/^{12}C$  isotope ratio for these initial species alone, therefore, would prove of scientific interest. In addition and as indicated earlier, the effects on  $C_2H_6$  or  $C_3H_8$  of the  $^{14}C$  released from the bomb tests may be quantitatively different to their effect on  $CH_4$ . Thus, accurate  $^{14}C/^{12}C$  determinations on these and other carbonaceous atmospheric components could perhaps usefully reduce the uncertainties in the source apportionments derived by this technique which are a result of the atmospheric testing of nuclear weapons.

## EXPERIMENTAL PROCEDURES

Clean air samples will be collected at remote sites in the northern and southern hemispheres. Scripps Oceanographic Institute, San Diego and Niwot Ridge, Colorado, are likely initial sampling sites. Because of the requirement for a remote sample collection, the sampling equipment should be portable. It is, therefore, proposed to collect whole air samples in Aculife-treated aluminum cylinders pumped to high pressure (approximately 2500 psi) employing a Rix oil-free pump, rather than by *in situ* cryogenic trapping.

A system for the measurement of  $^{13}\text{C}/^{12}\text{C}$  stable isotope ratios of ethane and propane in natural gas and sediment gas has been described by Dumke *et al.* (1989). It is proposed to follow this earlier work, which employed cryogenic trapping and gas chromatographic separation, to process the air samples in the laboratory. Once the desired components, ethane, propane and COS, have been separated from the other condensable atmospheric species, they will each be collected, submitted for combustion to  $\text{CO}_2$ , graphitisation and finally  $^{14}\text{C}$  AMS analysis at Lawrence Livermore National Laboratories.

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