

AD-A065 527

RICE UNIV HOUSTON TEX
RESEARCH IN FLUORINE CHEMISTRY.(U)
JAN 79 J L MARGRAVE, R H HAUGE

F/6 7/2

DA-ARO-D-31-124-71-6125
NL

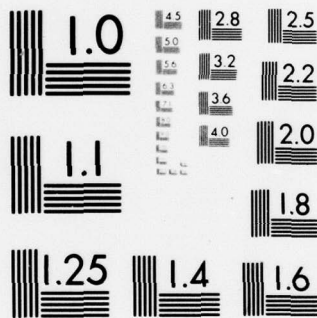
UNCLASSIFIED

ARO-9965.16-C

| OF |
AD
A065527



END
DATE
FILMED
5-79
DDC



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS
BEFORE COMPLETING FORM

5 S.

1. REPORT NUMBER 19 9965.16-C, 12320.4-C 15258.1-C	2. JOINT MILITARY REPORT NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Research in Fluorine Chemistry	5. TYPE OF REPORT & PERIOD COVERED Final Report. 1 Jun 71 - 31 Jul 78	
6. AUTHOR(s) John L. Margrave, R. H. Hauge, R. B. Badachhape, P. Kamarchik, K. R. Kunze, R. L. Pabst, D. L. Perry, P. Meier, S. Gransden, K. Y. San, Delphia Hamill, J. Pederson, M. Garrett, R. Griffey	7. CONTRACT OR GRANT NUMBER(s) DA-ARO-D-31-124-71-G125, Jan DAHC04-74-G-0187, and DAAG29 77 G 0169	
8. PERFORMING ORGANIZATION NAME AND ADDRESS Rice University Houston, Texas 77001	9. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS	
10. CONTROLLING OFFICE NAME AND ADDRESS U. S. Army Research Office P. O. Box 12211 Research Triangle Park, NC 27709	11. REPORT DATE 11 Jan 79	
12. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) 12 14p	13. NUMBER OF PAGES 13	
14. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited. 18 ARO, ARO		15. SECURITY CLASS. (of this report) Unclassified
15a. DECLASSIFICATION/DOWNGRADING SCHEDULE		
16. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
17. SUPPLEMENTARY NOTES The view, opinions, and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.		
18. KEY WORDS (Continue on reverse side if necessary and identify by block number) Silicon Difluoride Nitrides Fluorocarbons Fluorides Fluorine Reactions Fluorine Matrices Organic Compounds Carbenes Inorganic Fluorine Chemistry High Pressure Chemistry		
19. ABSTRACT (Continue on reverse side if necessary and identify by block number) Studies in inorganic fluorine chemistry and high pressure chemistry have been published. The work was divided into the following areas. (1) Preparation and Properties of CFX, (2) Economical Preparation of CFX, (3) High Pressure Studies of CFX, (4) Reactions of Fluorine with Organic Compounds, (5) Fluorination of Nitrides, (6) Hydrolysis of Fluorides, (7) Reactions in Fluorine Matrices at Low Temperatures, (8) New Methods for Preparation of Elemental Fluorine without Electrolysis, and (9) The Chemistry of SiF ₅ .		

305 750

JAM

DD FORM 1 JAN 73 1473

EDITION OF NOV 65 IS OBSOLETE

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

ADA065227
DDC FILE COPY

ROUTING AND TRANSMITTAL SLIP		ACTION	
1 TO DDC	INITIALS	CIRCULATE	
	DATE	COORDINATION	
2	INITIALS	FILE	
	DATE	INFORMATION	
3	INITIALS	NOTE AND RETURN	
	DATE	PER CONVERSATION	
4	INITIALS	SEE ME	
	DATE	SIGNATURE	
REMARKS 3 This report is the final report for two projects sponsored by the Army Research Office. It, therefore, carries two monitor report numbers: 3 9965. 16-C 12320. 4-C 15258. 1-C Do NOT use this form as a RECORD of approvals, concurrences, disapprovals, clearances, and similar actions			
FROM U. S. Army Research Office Post Office Box 12211 Research Triangle Park, NC 27709		DATE 19 Jan 79 PHON	

OPTIONAL FORM 41
AUGUST 1967
GSA FPMR (41CFR) 100-11.206

5041-101-01

* GPO : 1975-555-906

1. PREPARATION AND PROPERTIES OF CFX^{1,2,3,9,11,16}

Characteristics of the grayish to white solid fluorocarbon which has the appropriate stoichiometry C_1F_1 with wide homogeneity ranges have been established and studied as indicated in the recently published review article. The Ph.D. thesis of Dr. Peter Kamarchik¹⁶ and the publications resulting therefrom present studies of the thermal stability of CFX which show, interestingly, that CFX is quite stable in a fluorine atmosphere even at temperatures as high as 800C. In oxygen or nitrogen atmospheres or in vacuum the decomposition rate becomes appreciable at about 500C and the material can be more than 10% decomposed by exposure to temperatures over 600C for a few hours.⁹

In terms of the chemistry of decomposition, it has been found that C_2F_4 is the major gaseous decomposition product. In a high temperature environment C_2F_4 undergoes disproportionation to carbon and CF_4 . Further, since CF_2 groups are probably the migrating entities, the interaction between CF_2 and CF_4 to produce C_2F_6 or other higher perfluorocarbon accounts for the small amounts of polycarbon species detected in the gases when studied by matrix isolation and mass spectrometry.^{9,11,16}

The structure of solid CF_x has been studied by x-ray techniques and there is general agreement about the unit cell dimensions.⁴ Unfortunately, the single crystal data are sparse and an unequivocal structure has not yet been derived. A very recent paper which is in press from Watanabe and associates suggests that there may be still another solid fluorocarbon, C_2F , and this could further complicate interpretation of the C-F phase diagram. Preparations of CFX samples of various stoichiometries for further study are continuing.

ACCESSION for	
DTIC	White Section ☒
DDC	Diff Section ☐
UNANNOUNCED	☐
JUSTIFICATION	
BY	
DISTRIBUTION/AVAILABILITY CODES	
SOL.	AVAIL. and/or SPECIAL
A	

DDC
RECEIVED
MAR 9 1979
D

79 02 27 046

2. ECONOMICAL PREPARATION OF CFX

The current production of CFX is based on the use of elemental fluorine and therefore has an intrinsically high cost because all of the electrochemical methods for preparing fluorine run at least \$2 per pound for the element itself. A preferred synthesis from an economic viewpoint would be as follows:

- 1) $\text{Cd} + 2\text{HF} \rightarrow \text{CdF}_2 + \text{H}_2$
- 2) $\text{CdF}_2 + 2\text{C} \rightarrow 2\text{CF} + \text{Cd}$
- 3) Recycle Cd to get CdF_2 , etc.

The advantages of this proposed synthesis are (1) that relatively cheaper HF which can be prepared directly from fluorite ores would be used and (2) that a metal like zinc or cadmium which one would recycle on a continuous basis would be used as the transporting material to carry fluorine to the carbon for potential reactions.

In addition to the proposed reaction cycle there are several others which one can write but available thermodynamic data are inconclusive enough, especially at elevated temperatures, to allow one to make a clear cut decision.

If CFX could be made cheaply, at prices of 50¢-\$1 per pound then this material would be more attractive than molybdenum disulfide for many uses. Current price of molybdenum disulfide is ~\$2 per pound. Efforts to accomplish these reactions in transpiration experiments and through high pressure experiments are currently underway in the laboratory.

3. HIGH PRESSURE STUDIES OF CFX

Various possibilities for preparation of CFX and transition metal fluorides by using HgF_2 as a fluorinating agent under high pressures were explored. These were, unfortunately, unsuccessful but further studies are in progress. A high pressure fluorinating technique could be extremely attractive for lowering the cost of CFX production since it could be done at relatively low temperatures with efficient use of the available fluorine.

At high pressures, CFX samples become more crystalline and yield excellent powder diffraction patterns from which a unit cell and other structural information have been derived.⁴ Unfortunately, no solvent for CFX is currently known and large single crystals have not been prepared. There are still some unresolved questions about the fluorine positions and the layer-layer interaction parameters.

4. REACTIONS OF FLUORINE WITH ORGANIC COMPOUNDS

The general conditions for preparing reliable and reproducible fluorocarbon coatings on natural rubber, polyethylene, polypropylene, etc. have been established in detail previously.^{5,17,18} The absence of oxygen is essential for getting a really slippery teflon-like coating. Time of exposure to an N_2/F_2 mixture and the exact temperature of exposure also are critical. The optimization of the parameters for such treatments is currently being attempted.

The fluorination of polyvinyl chloride has been extensively¹⁷ studied by ESCA and other techniques to learn how fluorine attacks the polymer. All hydrogens can be replaced by extended fluorination at elevated temperatures but the chlorines remain. In other words, one can convert PVC to Kel-F by direct fluorination.

Differential scanning calorimetry has been used to study the decomposition/oxidation of polyethylene or polypropylene samples with different fluorocarbon coatings applied by direct reaction with F_2 .¹⁸ In the case of polypropylene, the maximum temperature of oxidation resistance is elevated by almost 100C. In addition to thermal stability, the application of a fluorocarbon coating by this technique creates a barrier to vapor diffusion through thin films.

Finally, the freshly prepared fluorocarbon surfaces have been shown to be especially inert toward recombinations⁵ and when the inside of a vessel has a fluorocarbon coating prepared by the techniques developed here, the surface recombination rates of halogen atoms or OH-molecules are reduced by $\sim 10^4$.

A review paper summarizing the current knowledge of direct fluorination techniques applied to organic compounds is in preparation.²⁰

5. FLUORINATION OF NITRIDES

There have been several reports in the literature regarding the existence of a new family of high temperature refractory material, the nitrifluorides. Thus far, these ternary compounds have been reported for transition metals from Group 4 of the Periodic Table -- Ti, Zr, Hf, Th, and U, and some rare earth metals. Because these may not be the most stable nitrifluorides and therefore, perhaps not the most useful, we have begun initial studies on the reaction of fluorine with LaN, AlN, Mg_3N_2 , and other metal nitrides. There would appear to be two possibilities for obtaining a refractory material which might be stable in the presence of fluorine at high temperatures by this technique. (a) a protective film of the refractory binary fluoride could be formed and (b) an even more stable refractory nitrifluoride species involving the +3 metal ions, -3 nitride ions and -1 fluoride ions in some modification of the M_2O_3 -structure or some related structural geometry. Initial studies of $LaN + F_2$ have been carried out and a grayish material which contains both nitrogen and fluorine has been obtained. Its detailed properties are under examination. Structures, thermal stability, the nature of gaseous species formed on decomposition and resistance to fluorine and other oxidizing atmospheres at high temperatures will be determined for various metal nitrifluorides, including some of those previously synthesized -- ZrNF, TiNF, etc.

6. HYDROLYSIS OF FLUORIDES

According to the literature, transition metal oxyfluorides can be prepared by careful hydrolysis of fluorides and most of the rare earth oxyfluorides have been characterized structurally by x-ray diffraction techniques. Little is known about the thermal stability of such materials and there is at least one oxyfluoride which will appear to be potentially important as a refractory container and a protective surface which has not been prepared. This latter compound, AlOF , should have the high thermal stability of aluminum oxide and an enhanced resistance to fluorine imparted by the fluoride coating. Efforts to hydrolyze aluminum fluoride, like the hydrolysis of other fluorides, seem unlikely to yield AlOF because of the great tendency to hydrolyze all the way to oxide and evolve the very stable gaseous HF molecules. A variety of alternate approaches to this problem are under consideration. For example, as an alternative to hydrolysis, it is sometimes easier to fluorinate the oxychloride and AlOCl can be prepared in good yield by literature techniques.

7. REACTIONS IN FLUORINE MATRICES AT LOW TEMPERATURES^{7,8,10,12,14,15,19}

While one often regards the matrix isolation technique as a procedure for isolating reactant A from reactant B with an inert third material C, it is also possible to use a reactive matrix and let the process proceed on a reasonably macroscopic scale. Reactions of elemental fluorine, where fluorine is the matrix material are of current interest. At very low temperatures, F_2 is inert and in fact very similar to an Ne-matrix, i.e., a matrix of pure fluorine is a very nonperturbing environment for most molecules. The low polarizability of fluorine and the high electronegativity mean that fluorine atoms and molecules tend to hold their electrons very tightly and do not distort the surrounding species. Many molecular species show infrared absorption spectra in a fluorine matrix which are within a few wavenumbers of the same frequencies as found for the gaseous molecules under essentially ideal gas conditions. This minimal perturbation of vibrational frequencies by elemental fluorine can be useful and allows one to deduce vibrational frequency values which are very near to the gas phase values but from a somewhat more convenient and controllable matrix environment.

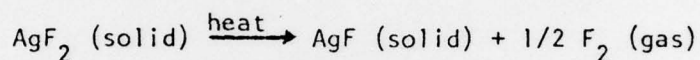
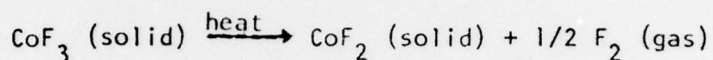
Since the reactivity of the fluorine matrix does increase with increasing temperature and also under the influence of ultraviolet or other radiation, it is clear that one can conveniently carry out the preparation of various fluorides, like those of xenon, etc.; reactions like the fluorination of water to form HOF; the fluorination of chlorides or oxychlorides to form the corresponding fluorides; etc. Studies of various reactions like these are in progress.

One can co-condense molecules like methane, ethane, ethylene, etc. with elemental fluorine without reactions.⁸ These mixtures are, of course, potentially reactive and the reaction may be initiated either by uv photolysis which produces fluorine atoms and immediately thereafter very rapid reactions or by infrared photolysis which apparently leads to excited state species and slow but very definite reactions. We have made extensive studies of the reaction of ethylene and fluorine, and studies of substituted ethylenes reacting with fluorine are planned. From this work, supplemented with studies of the acetylene plus fluorine reaction and the benzene plus fluorine reaction, both with and without photolytic excitation, we hope to elucidate more clearly the fundamental steps in fluorination of multiple bonds in organic molecules. Several theses and

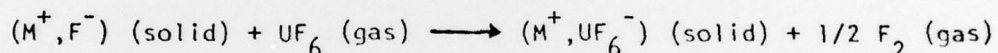
papers regarding this work have been presented^{7,8,10,12,14,15,19} and other manuscripts are in preparation.

8. NEW METHODS FOR PREPARATION OF ELEMENTAL FLUORINE WITHOUT ELECTROLYSIS

The direct production of elemental fluorine is usually accomplished through electrochemical means and there are no ordinary oxidizing agents which will oxidize the fluoride ion to fluorine gas. There are, however, a few unstable salts which contain fluorine and which can be thermally decomposed to produce elemental fluorine and a salt of the carrier element in a lower oxidation stage. For example,



Also, the extremely high electron affinities of PtF_6 , UF_6 , etc. make reactions like



thermodynamically feasible. Both types of reactions are unattractive because one needs to use elemental fluorine to get starting materials like CoF_3 , AgF_2 or UF_6 . The UF_6 reaction is also not reversible.

Various inorganic fluoride systems which could be used in fluorine production cycles are being evaluated in terms of thermodynamics and kinetics. The disadvantages of most of the known materials which can be decomposed to produce fluorine are (1) a fairly high temperature is required (2) the salt is hygroscopic, sensitive to water or oxidation, or otherwise difficult to handle (3) the yield of fluorine per gram of material carried is rather low so that there is a wasted effort in transporting materials which do not in fact lead to production of elementary fluorine. The ideal kind of material would be stable at room temperature but when exposed to the proper degree of heat or light, would provide fluorine and leave a residue of minimum weight and yet a residue which could also be recycled for continuous processing and transport of fluorine.

9. THE CHEMISTRY OF SiF_2 ^{6,12,13}

The characterization of SiF_2 , the long-lived inorganic carbene, is a subject of continuing interest, both in terms of unique synthetic applications of SiF_2 and in terms of electronic properties (singlet or triplet) and the reactions of the reactive unit -- either monomer or dimer -- with electrons paired or unpaired. The radical ion SiF_2^- has been prepared, and detected by ESR and compounds like LiSiF_2 have been prepared in matrices by the reaction of $\text{Li} + \text{SiF}_2$. A summary of evidence from SiF_2 -chemistry relating to the possibility of $>\text{Si}=\text{Si}<$ bonds has been published. Also, a review article has been prepared.

PUBLICATIONS

1. "The Direct Fluorination of Borohydrides and Lithium Aluminum Hydrides: A New Route to Fluoroborates and Fluoroaluminates", *Inorg. Chimica Acta* 10, 9, (1974), (with R. J. Lagow).
2. "Some New Synthetic Approaches to Graphite-Fluorine Chemistry", *J. Chem. Soc.*, 1974, 1268, (with R.B. Badachhape, J.L. Wood and R.J. Lagow).
3. "The Synthesis of Superstoichiometric Poly(Carbon Monofluoride)" *J. Am. Chem. Soc.* 96, 2628, (1974), (with R.B. Badachhape, J.L. Wood, and R.J. Lagow).
4. "X-Ray Powder Diffraction Study of Poly(Carbon Monofluoride), $CF_{1.12}$ ", *Inorg. and Nucl. Chem. Letters*, 10, 1103, (1974), (with R.B. Badachhape and V.J. Mahajan).
5. "Preparation of Non-Reactive Surfaces for Reaction Rate Studies", *Int. J. Chem. Kinetics*, 7, 23, (1976), (with R.B. Badachhape, P. Kamarchik, A.R. Conroy, and G.P. Glass).
6. "The Chemistry of Silicon Difluoride, A Reactive Carbene Analog", *J. Chem. Ed.*, 53, 696, (1976), (with D.L. Perry).
7. "Matrix Isolation IR and EPR Studies of Reaction Intermediates: Lithium Metal Reactions with H_2O , CH_3OH , and NR_3 ", *Proc. Berlin Symposium on Matrix Isolation Spectroscopy*, West Berlin, Germany, June 21-24, (1977), (with R.H. Hauge and P.F. Meier). Also published in *Berichte der Bunsengesellschaft Physikalische Chemie*, 82, 102, (1978).
8. "Reactions of Small Hydrocarbons in Fluorine Matrices", *Proc. Berlin Symposium on Matrix Isolation Spectroscopy*, West Berlin, Germany, June 21-24, (1977), (with R.H. Hauge, S. Gransden and J. Wang). *
9. "A Study of the Thermal Decomposition of the Solid-Layered Fluorocarbon, Poly (Carbon Monofluoride), (1977), *J. Thermal Analysis*, 11, 259-270, (with P. Kamarchik).
10. "Co-condensation Reactions of Uranium Tetrafluoride and Hexafluoride with Alkali Metals and Alkali-metal Fluorides in Low Temperature Argon Matrices" *J. Chem. Soc., Dalton Trans.* 433-440, (1978), (with K.R. Kunze, R.H. Hauge and D. Hamill).
11. "Poly (Carbon Monofluoride) A Solid, Layered Fluorocarbon" *Accts. of Chem. Res.* 11, 296, (1978), (with P. Kamarchik).
12. "Matrix Isolation Infrared and Electron Paramagnetic Resonance Spectroscopic Studies of the Reaction of Lithium with Silicon Tetrafluoride", *Inorg. Chem.* 17, 1364, (1978), (with D.L. Perry, P.F. Meier and R.H. Hauge).

*Abstract in *Berichte der Bunsengesellschaft, Physikalische Chemie*, 82, 104 (1978).

13. Dale L. Perry and John L. Margrave, "Reexamination of the Evidence for Silicon-Silicon Multiply Bonded Intermediates: Possible Existence of $(F_2Si=SiF_2)$ ", *Inorg. Chem.*, 16, 1821, (1977).
14. Delphia Hamill, M.S. Thesis, "Matrix Reactions of Uranium Fluorides as Studied by Infrared Spectroscopy", April 1977. (Rice University)
15. Kenneth R. Kunze, Ph.D. thesis, "Studies in Inorganic Chemistry", Spring, 1978. (Rice University)
16. Peter Kamarchik, Ph.D. thesis, "Studies of the Thermal Decomposition and other High Temperature Reactions of Poly (Carbon Monofluoride)", May, 1976 (Rice University)
17. George Parks, Ph.D. thesis, "X-ray Photoelectron Spectroscopy: Instrumental Development and Chemical Applications", June, 1976 (Rice University)
18. John Pederson, M.A. thesis, in preparation.
19. Paul Meier, Ph.D. thesis, in preparation.
20. R.R. Badachhape, R.H. Hauge and J.L. Margrave, "Direct Fluorination of Organic Compounds", in preparation.