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Inorganic Halogen Oxidizers

Final Report

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Chemistry Division
Arlington, VA 22217

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PREFACE

This is the final report of a research program carried out at Rocketdyne during the time period 19 September 1983 through 30 September 1989. The program was sponsored by the Chemistry Division of the Office of Naval Research with Drs. K. Wynne and H. Guard as Scientific Officers. The program has been directed by Dr. K.O. Christie. The scientific effort was performed mainly by Drs. K.O. Christie, W.W. Wilson, C.J. Schack and Mr. R.D. Wilson.

The purpose of this program was to explore the synthesis and properties of energetic inorganic halogen oxidizers. Although the program was directed toward basic research, applications of the results generated major technological breakthroughs. Thus, the first chemical synthesis of elemental fluorine was achieved, pure fluorine solid-propellant gas generators were developed, and a continuous ion exchange process for the production of advanced NF_4^+ salts was worked out.

Program for the synthesis of NF4+ salts, ARO, ONR, and Rocketdyne
NAO, ONR, and Rocketdyne
Our research effort in inorganic, energetic halogen chemistry was also sponsored by the U.S. Army Research Office. In cases where the two programs overlapped, both agencies ONR and ARO were acknowledged in any resulting publications and reports. Only completed items of research, which have been summarized in manuscript form, are included in this report. Since all of these manuscripts have previously been issued in the form of Technical Reports, only a listing of the titles, authors and the journals, in which they were published, will be given here.

The research under this program has been highly productive. This is reflected by 34 published papers, 2 submitted papers, 1 submitted chapter for a book, 10 issued patents, 6 patent disclosures, 14 papers presented at conferences, 15 invited seminars at American and foreign universities, and above all the bestowment of the 1986 ACS award for "Creative Work in Fluorine Chemistry." A detailed listing of the papers, patents and seminars is given in the following pages.



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MAJOR ACCOMPLISHMENTS UNDER THIS CONTRACT

1. The relative oxidizing power of the strongest, presently known, oxidative fluorinators was systematically evaluated and resulted in the following order of decreasing oxidative power $\text{KrF}^+ > \text{PtF}_6 > \text{F}_2 + \text{Lewis Acid} + \text{activation energy} > \text{CrF}_5 \cdot \text{SbF}_5$.
2. The $\text{ClF}_6^+ \text{ClO}_4^-$ salt was synthesized, but found to be stable only at low temperature. It easily decomposes to ClF_5 and FOClO_3 , thus providing a new synthesis for fluorine perchlorate.
3. A new powerful oxidizer, $(\text{ClF}_2\text{O})_2\text{NiF}_6$, was synthesized and characterized.
4. NF_4BrF_4 and $\text{NF}_4\text{BrF}_4\text{O}$, the first examples of NF_4^+ salts containing halogen fluoride anions, were prepared and characterized.
5. During attempts to prepare CF_3^- , SF_5^- or SF_5O^- substituted NF_4^+ cations, an unusual catalytic decomposition of difluoramino compounds by strong Lewis acids was discovered and elucidated.
6. The estimate of the N-F bond length in NF_4^+ was revised using its general valence force field.
7. The gas-phase structure of CF_3N_3 was determined.
8. A correlation between ^{19}F NMR chemical shifts and O-F bond length was established for hypofluorites.
9. The structure and ion motion of the oxonium cation in its MF_6^- salts was studied by x-ray and neutron diffraction and vibrational spectroscopy.
10. $(\text{O}_2^+)_2\text{NiF}_6^{2-}$ and $(\text{O}_2^+)_2\text{MnF}_6^{2-}$, the first examples of dioxygenyl salts of doubly charged anions, were prepared and characterized.
11. A paper study on the existence of positive fluorine was carried out.

12. The reaction chemistry of CrF_5 was studied and the new salts NF_4CrF_6 , NOCrF_6 and $(\text{NO})_2\text{CrF}_6$ were prepared and characterized.
13. An improved synthesis of CrF_4O was discovered and its properties and reaction chemistry were studied.
14. The possible syntheses of numerous new oxidizers, such as OF_3^+ salts, FOBrO_3 , $\text{O}_2^+\text{ClO}_4^-$, and ClF_5O , were explored.
15. The first chemical synthesis of elemental fluorine was accomplished. Until then, the only method for the preparation of fluorine was by electrolysis, and the chemical synthesis of elemental fluorine had been pursued unsuccessfully for at least 173 years. This breakthrough discovery has received widespread attention in the scientific community.
16. An improved, one step, high yield synthesis of BrF_4O^- salts and BrF_3O from BrF_5 and oxo anions was discovered.
17. The structure of HNF_2 and DNF_2 in their condensed phase and alkali metal fluoride adducts were studied. The reaction chemistry of HNF_2 with inorganic hypofluorites was explored.
18. The self-association in HNF_2 and HOF was studied and it was concluded that N and O are better proton acceptors than F.
19. The principle of the chemical F_2 synthesis was applied to other systems and resulted in the development of novel, solid propellant based, pure fluorine gas generators.
20. A new synthesis of N_2O_5 was discovered and the NO_2^+ cation in N_2O_5 was shown to be nonlinear.
21. A thorough study of bromine nitrate chemistry was carried out and it was shown that the previously reported $\text{Br}(\text{ONO}_2)_3$ is actually $\text{NO}_2^+[\text{Br}(\text{ONO}_2)_2]^-$.
22. The alkali metal fluorides were found to catalyze the decomposition of ClF_5 to $\text{ClF}_3 + \text{F}_2$ at room temperature.

23. The $\text{Ni}(\text{BiF}_6)_2$ salt and its acetonitrile adducts were prepared and their structures determined by x-ray diffraction.
24. An oxidizer- and acid-resistant anion exchange medium based on graphite salts was developed and successfully applied to the syntheses of advanced NF_4^+ salts. A simple, one step, high yield process for the production of pure NF_4BF_4 from NF_4SbF_6 was developed.
25. A systematic study of fluorine-oxygen exchange reactions in halogen and xenon fluorides was carried out resulting in improved synthesis of numerous oxyfluorides and new compounds, such as LiIF_4O , NaIF_4O , NOIF_4O , and $[\text{FO}_2\text{XeFXeO}_2\text{F}]^+\text{AsF}_6^-$. The usefulness of the nitrate anion as a low-cost, efficient F-O exchange reagent was demonstrated.
26. After two decades of efforts and collaboration with six different groups of crystallographers in the U.S., England, Germany, Denmark and France, we have succeeded in determining the crystal structure of the NF_4^+ cation.
27. It was found that CH_3CN , a very common solvent in fluorine chemistry, reacts slowly with the fluoride anion to give the bifluoride and acetonitrile anions.
28. The reaction chemistry of BrF_5 with the Azide, Nitrite and Sulfate Anions was studied.
29. An improved synthesis of IF_5O from IF_7 and PF_3O was discovered.

PAPERS PUBLISHED IN REFEREED JOURNALS

1. "Coordinatively Saturated Fluoro Cations. Oxidative Fluorination Reactions with KrF^+ Salts and PtF_6 ," by K.O. Christe, W.W. Wilson, and R.D. Wilson, *Inorg. Chem.*, 23, 2058 (1984) (other support, ARO).
2. "Positive Fluorine - Reality or Misconception?," by K.O. Christe, *J. Fluorine Chem.*, 25, 269 (1984) (other support, ARO).
3. "Some Interesting Observations in Chlorine Oxyfluoride Chemistry," by K.O. Christe and W.W. Wilson, *J. Fluor. Chem.*, 26, 257 (1984) (other support, ARO).

4. "The Gas-Phase Structure of Azidotrifluoromethane. An Electron Diffraction, Microwave Spectroscopy, and Normal Coordinate Analysis," by K.O. Christe, D. Christen, H. Oberhammer, and C.J. Schack, *Inorg. Chem.*, 23, 4283 (1984) (other support, ARO).
5. "Structure and Vibrational Spectra of Oxonium Hexafluoroarsenates (V) and -Antimonates (V)," by K.O. Christe, P. Charpin, E. Soulié, R. Bougon, J. Fawcett and R. Russell, *Inorg. Chem.*, 23, 3756 (1984) (other support, ARO).
6. "Synthesis and Characterization of Bis[difluoromonoxychlorine (V)] Hexafluoronickelate (IV), $(\text{ClF}_2\text{O})_2\text{NiF}_6$," by W.W. Wilson and K.O. Christe, *Inorg. Chem.*, 23, 3261 (1984).
7. "Extended Correlation Between O-F Bond Energies and ^{19}F NMR Chemical Shifts in Fluoroxy Compounds," by E. Ghibaudi and A.J. Colussi, and K.O. Christe, *Inorg. Chem.*, 24, 2869 (1985).
8. "Lewis Acid Induced Intramolecular Redox Reactions of Difluoramino Compounds," by W.W. Wilson, C.J. Schack, and R.D. Wilson., *Inorg. Chem.*, 24, 303 (1985) (other support, ARO).
9. "Synthesis and Characterization of NF_4CrF_6 and Reaction Chemistry of CrF_5 ," by R. Bougon, W.W. Wilson, and K.O. Christe *Inorg. Chem.*, 24, 2286 (1985) (other support, ARO)
10. "Dioxygenyl Salts Containing Doubly Charged Mononuclear Counterions," by R. Bougon, K.O. Christe and W.W. Wilson, *J. Fluorine Chem.*, 30, 237 (1985).
11. "Chlorylfluoride," by K.O. Christe, R.D. Wilson and C.J. Schack, *Inorg. Syntheses*, 24, 3 (1986) .
12. "Perfluoroammonium Salts," by K.O. Christe, W.W. Wilson, C.J. Schack, and R.D. Wilson, *Inorg. Syntheses*, 24, 39 (1986) (other support, ARO).
13. "Tungsten Tetrafluoride Oxide," by W.W. Wilson and K.O. Christe, *Inorg. Syntheses*, 24, 3 (1986).

14. "Cesium Hexafluoromanganate (IV)," by W.W. Wilson and K.O. Christe, *Inorg. Syntheses*, 24, 48 (1986).
15. "Synthesis and Characterization of $\text{NF}_4^+\text{BrF}_4^-$ and $\text{NF}_4^+\text{BrF}_4\text{O}^-$," by K.O. Christe and W.W. Wilson, *Inorg. Chem.*, 25, 1904 (1986).
16. "Estimation of the N-F Bond Distance in NF_4^+ from its General Valence Force Field," by K.O. Christe, *Spectrochim Acta, Part A.*, 8, 939 (1986) (other support, ARO).
17. "Synthesis and Characterization of CrF_4O , $\text{KrF}_2\cdot\text{CrF}_4\text{O}$ and $\text{NO}^+\text{CrF}_5\text{O}^-$," by K.O. Christe, W.W. Wilson and R. Bougon, *Inorg. Chem.*, 25, 2163 (1986).
18. "On the Existence of a $\text{CrF}_4\text{O}\cdot\text{SbF}_5$ Adduct," by W.W. Wilson and K.O. Christe, *J. Fluorine Chem.*, 35, 531 (1987) (other support, ARO).
19. "Preparation and Characterization of $\text{Ni}(\text{SbF}_6)_2$," by K.O. Christe, W.W. Wilson, R.A. Bougon, and P. Charpin, *J. Fluorine Chem.*, 34, 287 (1986) (other support, ARO).
20. "Self-Association in HOF and HNF_2 . Which Atoms are Better Proton Acceptors, Fluorine, Oxygen, or Nitrogen?," by K.O. Christe, *J. Fluorine Chem.*, 35, 621 (1987).
21. "New, One Step Syntheses of BrF_3O and BrF_4O^- Salts and the Preparation and Characterization of RbBrF_4O and NaBrF_4O ," by W.W. Wilson and K.O. Christe, *Inorg. Chem.*, 26, 916 (1987) (other support, ARO).
22. "On the Condensed Phases of Difluoramine and its Alkali Metal Fluoride Adducts," by K.O. Christe and R.D. Wilson, *Inorg. Chem.*, 26, 920 (1987).
23. "Chemical Synthesis of Elemental Fluorine," by K.O. Christe, *Inorg. Chem.*, 25, 3721 (1986) (other support, ARO).
24. "Dinitrogen Pentoxide. New Synthesis and Laser Raman Spectrum," by W. W. Wilson and K.O. Christe, *Inorg. Chem.*, 26, 1631 (1987).
25. "Bromine Nitrates," by W.W. Wilson and K.O. Christe, *Inorg. Chem.*, 26, 1573 (1987).

26. "Convenient Synthesis of Xenon Oxide Tetrafluoride," by K.O. Christe, and W.W. Wilson, *Inorg. Chem.*, 27, 1296 (1988).
27. "Preparation and Characterization of $\text{Ni}(\text{BiF}_6)_2$ and of the Ternary Adducts $[\text{Ni}(\text{CH}_3\text{CN})_6](\text{BiF}_6)_2$ and $[\text{Ni}(\text{CH}_3\text{CN})_6]\text{SbF}_6)_2$. Crystal Structure of $[\text{Ni}(\text{CD}_3\text{CN})_6](\text{SbF}_6)_2$," by R. Bougon, P. Charpin, K.O. Christe, J. Isabey, M. Lance, M. Nierlich, J. Vigner, and W.W. Wilson, *Inorg. Chem.*, 27, 1389 (1988), (other support, ARO).
28. "Solid Propellant Based Pure Fluorine Gas Generators," by K.O. Christe and R.D. Wilson, *Inorg. Chem.* 26, 2554 (1987), (other support, ARO).
29. "New Syntheses and Properties of XeO_2F_2 , $\text{Cs}^+\text{XeO}_2\text{F}_3^-$, and $\text{NO}_2^+[\text{XeO}_2\text{F}_3 \cdot n\text{XeO}_2\text{F}_2]^-$," by K.O. Christe and W.W. Wilson, *Inorg. Chem.* 27 (1988) 3763.
30. "Synthesis and Properties of $\text{XeO}_2\text{F}^+\text{AsF}_6^-$ and $[\text{FO}_2\text{XeFXeO}_2\text{F}]^+\text{AsF}_6^-$," by K.O. Christe and W.W. Wilson, *Inorg. Chem.* 27 (1988) 2714.
31. "Crystal Structure of NF_4^+ Salts," by K.O. Christe, M.D. Lind, N. Thorup, J. Fawcett, and R. Bau, *Inorg. Chem.* 27 (1988) 2450, (other support, ARO).
32. "Reactions of Chlorine Fluorides and Oxyfluorides with the Nitrate Anion and Alkali Metal Fluoride Catalyzed Decomposition of ClF_5 ," by K.O. Christe, W.W. Wilson and R.D. Wilson, *Inorg. Chem.* 28 (1989) 675, (other support, ARO).
33. "Reactions of BrF_3 with the Azide, Nitrite and Sulfate Anions," by K.O. Christe, W.W. Wilson and C.J. Schack, *J. Fluorine Chem.* 43 (1989) 125, (other support, ARO).
34. "Fluorine-Oxygen Exchange Reactions in IF_5 , IF_7 and IF_5O ," by K.O. Christe, W.W. Wilson, and R.D. Wilson, *Inorg. Chem.* 28 (1989) 904, (other support, ARO).

PAPERS SUBMITTED TO REFEREED JOURNALS

35. "Anion Exchange in NF_4^+ Salts Using Graphite Salts as an Oxidizer- and Acid-Resistant anion Exchange Medium," by K.O. Christe and R.D. Wilson, (other support, ARO).
36. "Reaction of the Fluoride Anion with Acetonitrile," by K.O. Christe and W.W. Wilson, J. Fluorine Chem., (other support, ARO).

BOOKS AND SECTIONS THEREOF SUBMITTED FOR PUBLICATION

37. "Preparation of Halogen Oxyfluorides," by K.O. Christe, Chapter for Inorganic Reactions and Methods, Verlag Chemie.

ISSUED PATENTS

38. "Perfluoroammonium Salt of Heptafluoroxenon Anion," by K.O. Christe and W.W. Wilson U.S. 4,428,913 (1984) (other support, ARO).
39. "Perfluoroammonium Salts of Fluoroxenon Anions," by K.O. Christe and W.W. Wilson, U.S. 4,447,407 (1984) (other support, ARO).
40. "Synthesis of Pentafluorotellurium Hypofluorite," by C.J. Schack, W.W. Wilson and K.O. Christe, U.S. 4,462,975 (1984) (other support, AFOSR).
41. "Method for Introducing Fluorine into an Aromatic Ring," by K.O. Christe and C.J. Schack, U.S. 4,476,377 (1984) (other support, AFOSR).
42. "Pentafluorotelluriumoxide Fluorocarbons," by C.J. Schack and K.O. Christe, U.S. 4,508,662 (1985) (other support, AFOSR).
43. "Multi-(OTeF_2)-Substituted Fluorocarbons," by C.J. Schack and K.O. Christe, U.S. 4,578,225 (1986) (other support, AFOSR).
44. "Process for Preparing Pentafluorotellurium Hypofluorite," by C.J. Schack and K.O. Christe, U.S. 4,594,232 (1986) (other support, AFOSR).

45. "Synthesis of R_fOTeF_5 ," by C.J. Schack and K.O. Christe, U.S. 4,675,088 (1987) (other support, AFOSR).
46. "Pure Fluorine Gas Generator," by K.O. Christe, U.S. 4,711,680 (1987) (other support, ARO).
47. "Process for the Production of Advanced NF_4^+ Salts," by K.O. Christe, U.S. 4,683,129 (1987) (other support, ARO).
48. "Method for the Selective Separation of Gases," by K.O. Christe, U.S. 4,695,296 (1987) (other support, ARO).

PATENT DISCLOSURES

49. "Improved Synthesis of $XeOF_4$," by K.O. Christe and W.W. Wilson.
50. "Improved Process for the Preparation of Pure N_2O_5 ," by K.O. Christe and W.W. Wilson, (other support, ARO).
51. "Improved Synthesis of BrF_3O and BrF_4O^- Salts," by K.O. Christe and W.W. Wilson.
52. "Chemical Synthesis of Elemental Fluorine," by K.O. Christe, (other support, ARO).
53. "Stable ClF_2^+ Salt Containing Energetic Counterions," by K.O. Christe and W.W. Wilson.
54. "Energetic NF_4^+ Salt," by K.O. Christe and W.W. Wilson.

INVITED PRESENTATIONS AT TOPICAL OR SCIENTIFIC/TECHNICAL SOCIETY CONFERENCES

55. "Lewis Acid Induced Intramolecular Redox Reactions of Difluoroamino Compounds," by K.O. Christe, W.W. Wilson, C.J. Schack, International Chemical Congress of Pacific Basin Societies, Honolulu, Hawaii (December 16-21, 1984) (other support, ARO).
56. " CrF_5 Chemistry and Synthesis of NF_4CrF_6 ," by R.A. Bougon, W.W. Wilson, and K.O. Christe, Seventh Winter Fluorine Conference, Orlando, Florida (February 3-8, 1985) (other support, ARO).

57. "High Energy Fluorine Compounds," by K.O. Christe, State of the Art Symposium of Fluorine Chemistry: One Hundred Years and Beyond. Future trends in Fluorine Chemistry, paper presented at 191st National ACS Meeting, New York City, (April 13-18, 1986) (other support, ARO).
58. "Synthesis and Characterization of CrF_4O , $\text{KrF}_2 \cdot \text{CrF}_4\text{O}$ and $\text{NO}^+ \text{CrF}_5\text{O}^-$," by W.W. Wilson, R.A. Bougon and K.O. Christe, paper presented at 191st National ACS Meeting, New York City, (April 13-18, 1986) (other support, ARO).
59. "Chemical Generation of Elemental Fluorine," by K.O. Christe, main lecture presented at the Centenary of the Discovery of Fluorine, International Symposium, Paris, France (August 25-29, 1986) (other support, ARO).
60. "Reactions of Oxo Anions with Halogen and Noble Gas Fluorides," by W.W. Wilson and K.O. Christe, paper presented at the Centenary of the Discovery of Fluorine, International Symposium, Paris, France (August 25-29, 1986) (other support, ARO).
61. "Reactions of BrF_5 with the Nitrate Anion," by W.W. Wilson and K.O. Christe. Eighth Winter Fluorine Conference, St. Petersburg, Florida, January 25-30, 1987.
62. "Some New Results in Nitrogen-Fluorine Chemistry," by K.O. Christe, R.D. Wilson, M.D. Lind, and N. Thorup, Eighth Winter Fluorine Conference, St. Petersburg, Florida, January 25-30, 1987.
63. "Preparation and Characterization of $\text{Ni}(\text{SbF}_6)_2$ and $\text{Ni}(\text{BiF}_6)_2$," by R. Bougon, P. Charpin, J. Isabey, M. Lance, K. Christe and W. Wilson, Eighth Winter Fluorine Conference, St. Petersburg, Florida, January 25-30, 1987.
64. "Xenon Oxyfluoride Chemistry," by K.O. Christe and W.W. Wilson, Third Chemical Congress of North America, Toronto, Canada, June 5-10, 1988.
65. "The Nitrate Anion. A Useful Reagent for Fluorine-Oxygen Exchange," by W.W. Wilson and K.O. Christe, 12th International Symposium on Fluorine Chemistry, Santa Cruz, CA (August 1988).

66. "Ion Exchange Process for the Production of Advanced NF_4^+ Salts," by K.O. Christe and R.D. Wilson, 12th International Symposium on Fluorine Chemistry, Santa Cruz, CA (August, 1988) (other support, ARO).
67. "Some Structural Studies at Rocketdyne and Their Relationship to the VSEPR Rules," by K.O. Christe, keynote lecture at the Chemistry Symposium to honor Prof. R.J. Gillespie, McMaster University, Hamilton, Ontario (June 1989).
68. "Recent Advances in the Synthesis of New Energetic Materials," by K.O. Christe and W.W. Wilson, plenary lecture at the Ninth European Fluorine Symposium, Leicester, England (September 1989).

INVITED SEMINARS ON WORK DONE UNDER THIS CONTRACT WERE GIVEN AT THE FOLLOWING UNIVERSITIES:

- | | |
|--|---|
| 1984: University of Utah, Salt Lake City | University of British Columbia,
Vancouver, Canada |
| 1985: University of California, Santa Barbara
University of Gottingen, Germany
Freie Universitat Berlin, Germany
University of Stuttgart, Germany
University of Marburg, Germany | University of Dortmund, Germany
University of Hannover, Germany
University of Bochum, Germany
University of Ulm, Germany |
| 1987: University of Alabama, Tuscaloosa
Stanford University | Clemson University |
| 1988: University of California, Berkeley | |

AWARDS

1986 ACS, Fluorine Division Award for "Creative Work in Fluorine Chemistry."

LIST OF SCIENTIFIC PERSONNEL WHO HAVE CONTRIBUTED TO THIS PROGRAM

Dr. Karl O. Christe (principal investigator)	Rocketdyne
Dr. William W. Wilson	Rocketdyne
Dr. Carl J. Schack	Rocketdyne
Mr. Richard D. Wilson	Rocketdyne
Drs. Roland Bougon and P. Charpin	CEN Saclay, France
Dr. M.D. Lind	Science Center, Rockwell International
Prof. R. Bau	University of Southern California
Prof. N. Thorup	Technical University of Denmark
Prof. M. Jansen	Universitat Hannover, W. Germany
Profs. H. Oberhammer and D. Christen	Universitat of Tübingen, W. Germany
Profs. Colussi and Ghibaudi	University of La Plata, Argentina
Prof. J. Winfield	University of Glasgow, Scotland
Prof. W. Sawodny	Universitat of Ulm, Germany
Profs. D. Russell and J. Fawcett	University of Leicester, England
Prof. G. Schrobilgen	McMaster University, Canada

