

1990

The CFC Problem, Report of the Situation in France and Evolution

C. Brian
Dehon Service

Follow this and additional works at: <http://docs.lib.purdue.edu/iracc>

Brian, C., "The CFC Problem, Report of the Situation in France and Evolution" (1990). *International Refrigeration and Air Conditioning Conference*. Paper 111.
<http://docs.lib.purdue.edu/iracc/111>

This document has been made available through Purdue e-Pubs, a service of the Purdue University Libraries. Please contact epubs@purdue.edu for additional information.

Complete proceedings may be acquired in print and on CD-ROM directly from the Ray W. Herrick Laboratories at <https://engineering.purdue.edu/Herrick/Events/orderlit.html>

NEW CHEMICAL ALTERNATIVE REFRIGERANTS¹

by

James L. Adcock, Shyam B. Mathur,
W. Alexander Van Hook and Bao-Huai Wang

of the

Department of Chemistry
The University of Tennessee
Knoxville TN 37996-1600

ABSTRACT

Three new fluorinated compounds have been synthesized by Aerosol Direct Fluorination and characterized. Sufficient quantities were prepared for extensive thermophysical property measurements. The compounds, $\text{CF}_3\text{-O-CF}_2\text{CF}_2\text{H}$, *cyclo*- $\text{CF}_2\text{CF}_2\text{CF}_2\text{O}$ - and $\text{CF}_3\text{-O-CF}_2\text{-O-CF}_3$, have normal boiling points of -4.2°C , -29.9°C and -9.8°C and critical temperatures of 114.6°C , 88.7°C and 99.2°C respectively. These and other properties including liquid densities, PVT measurements and heats of vaporization place these compounds intermediate in properties between R-11 and R-12. They therefore could function as replacement working fluids in many applications requiring properties in this range. None of the materials contains chlorine and therefore all have zero ozone depletion potential. It is anticipated, but not yet proven, that structural features in these compounds will lead to reduced atmospheric lifetimes and thus to reduced greenhouse warming potential.

Copyright, March 1990
The University of Tennessee
Knoxville, Tennessee 37996

INTRODUCTION

Amelioration of the Ozone Depletion Potential of chemical alternatives to chlorofluorocarbons entails the use of several potentially conflicting strategies. The removal of chlorine from the molecules solves the ozone problem but potentially creates several undesired complications. Among these the loss of hydrocarbon lubricants compatibility, requiring a more expensive lubricant, a decrease in refrigerant efficiency and if fluorine replaces chlorine a substantial increase in atmospheric lifetime which carries the potential of serious *greenhouse warming* effects. The key to amelioration is to reduce atmospheric lifetimes. Present approaches entail the incorporation of more hydrogen in the molecules which subjects them to attack by atmospheric hydroxyl radical. This approach increases flammability, decreases stability, and may increase toxicity and reduce efficiency. Are there other approaches? Possibly!

Our research into a "second generation" of chemical alternatives investigates this other possibility. Will the incorporation of certain structural features in otherwise stable molecules predispose these molecules to decompose once a single chemical event has occurred. We have developed a set of molecules which we can show by thermophysical measurements could function as working fluids in heating/cooling cycles. These molecules are necessarily more complex than the present CFC's but possess a similar set of physical constants. They could be made to work! Will these molecules possess a reduced atmospheric lifetime? This we have yet to determine. The following compounds represent our first attempts.

The syntheses of F-methyl 2-hydril-F-ethyl ether, F-dimethoxymethane and F-oxetane (F-trimethyleneoxide, "F-" denotes perfluorinated) outlined in the experimental all have structural features which we believe will result in reduced atmospheric lifetimes. Decomposition of F-methyl 2-hydril-F-ethyl ether could occur rapidly on hydrogen abstraction by atmospheric hydroxyl radical giving tetrafluoroethylene and trifluoromethoxy radical. F-dimethoxymethane is a stable molecule, however, photolysis in the upper atmosphere could result in an "un-zipping" of this methylene diether. The third compound F-oxetane, F-trimethyleneoxide, is also quite stable. However it has a strained ring and will probably undergo photolytically induced cleavage. Since F-oxetane is formally an addition product of carbonyl fluoride and tetrafluoroethylene and it will likely fission into these two molecules both of which would be rapidly removed from the atmosphere by hydrolysis and hydroxyl radical attack.

EXPERIMENTAL

Synthesis:

Synthesis of F-methyl 2-hydril-F-ethyl ether was accomplished in an overall yield of near 40% by a two step process involving aerosol direct fluorination² of 2-chloroethyl methyl ether followed by replacement of the chlorine on the perhalogenated ether with hydrogen. The accumulated sample was shown by capillary gas chromatography to be better than 99% pure.

Dimethoxymethane, the acetal of formaldehyde, is a hydrolytically unstable hydrocarbon but when perfluorinated in the low acid conditions of the aerosol fluorination process produces the perfluorinated analog in sixty percent yield. The accumulated sample was shown by capillary gas chromatography to be better than 99% pure after a simple base wash and distillation. The perfluorinated molecule is very stable.

Oxetane, trimethyleneoxide, was prepared by the method of C. R. Noller.³ Aerosol direct fluorination of the hydrocarbon species produced the perfluorinated cyclic ether in 59% yield and with no detectible impurities (by capillary glc) after base wash and simple distillation.

Measurements:

Each of the above materials was characterized by ^{19}F NMR and FTIR. Seventy-five grams of each material was accumulated, assayed for purity and subjected to extensive thermophysical measurements: PVT, density, normal boiling point, and critical temperature. Density measurements were made with a Mettler/Par DMA 601HT vibrating tube densitometer. The densitometer temperature was controlled (± 0.002 deg) by a circulating thermostat at a flow as high as $8 \text{ dm}^3/\text{min}$ and monitored next to the sample chamber with a thermistor. The thermistor had in turn been calibrated against an Hewlett-Packard quartz and a Pt resistance thermometer. A description of the apparatus to measure the vapor pressure, and compressibility of liquids is described in the literature.⁴

RESULTS

The preliminary results we have obtained are contained in the tables that follow. To confirm the accuracy of our measurements, commercial samples of R-11 (CFCl_3) and R-22 (CF_2HCl) were subjected to the same battery of measurements. The comparison was usually better than one part in one thousand.

Liquid densities of R-11 and R-22 were measured and a comparison made with literature values^{5,6} in Table 1. Measurements for the three experimental compounds are tabulated in Table 2. Experimental vapor pressures of R-11 and R-22 from 30°C to the critical temperature measurements are tabulated in Table 3. Comparisons at 10°C intervals are tabulated against literature values in Tables 4 and 5.^{5,7,8} These comparisons give us considerable confidence in the values obtained for the experimental compounds. The respective vapor pressure equations are given with the coefficients and their statistical uncertainty are given in Table 6. The variance between the experimentally determined and the values calculated by the equation (σ^2) are shown as well. A summary of the thermophysical properties calculated from the vapor pressure relationship and the Clapeyron-Clausius Equation are tabulated in Tables 7 and 8. From this set of data it can be seen that the physical constants for the experimental compounds are quite similar to existing refrigerant working fluids.⁹

TABLE 1
DENSITY MEASUREMENTS COMPARED WITH REFERENCE

R-11, CFCl_3

T/K	P/MPa	$X_{\text{expt}}/\text{g}\cdot\text{cm}^{-3}$	$X_{\text{ref5}}/\text{g}\cdot\text{cm}^{-3}$	$X_{\text{ref6}}/\text{g}\cdot\text{cm}^{-3}$
303.15	0.12646	1.4617	1.4643	1.463
313.15	0.17535	1.4377	1.4400	1.439
323.15	0.23748	1.4129	1.4150	1.414
333.15	0.31495	1.3873	1.3893	1.389
343.15	0.41003	1.3607	1.3626	1.363
353.15	0.52504	1.3331	1.3349	1.335
363.15	0.66253	1.3045	1.3060	1.306
373.15	0.82513	1.2749	1.2758	1.276
471.05(Tc)				

TABLE 1 cont.

DENSITY MEASUREMENTS COMPARED WITH REFERENCE

T/K	P/MPa	R-22, CF ₂ C1H	
		X _{expt} /g·cm ⁻³	X _{refs} /g·cm ⁻³
303.15	1.2047	1.1706	1.1708
313.15	1.5508	1.1285	1.1286
323.15	1.9636	1.0828	1.0823
333.15	2.4518	1.0350	1.0303
343.15	3.0261	0.9866	0.9697
369.45(Tc)			

TABLE 2

SATURATED LIQUID DENSITIES OF THE COMPOUNDS

CF ₃ OCF ₂ CF ₂ H			CF ₃ OCF ₂ OCF ₃		
T/K	P/MPa	X/g·cm ⁻³	T/K	P/MPa	X/g·cm ⁻³
303.15	0.33696	1.3973	303.15	0.42432	1.4116
308.15	0.39338	1.3755	308.15	0.49200	1.3875
313.15	0.45660	1.3540	313.15	0.56750	1.3623
318.15	0.52719	1.3326	318.15	0.65148	1.3363
323.15	0.60586	1.3113	323.15	0.74463	1.3098
328.15	0.69261	1.2898	328.15	0.84762	1.2829
333.15	0.78864	1.2682	333.15	0.96125	1.2559
338.15	0.89440	1.2463	338.15	1.0864	1.2289
343.15	1.0106	1.2240	343.15	1.2239	1.2022
348.15	1.1378	1.2013	372.35(Tc)		
353.15	1.2770	1.1782			
358.15	1.4288	1.1546			
387.75(Tc)					

cyclo-CF₃CF₂CF₂-0-

T/K	P/MPa	X/g·cm ⁻³
303.15	0.79907	1.3496
308.15	0.91454	1.3249
313.15	1.0418	1.2989
318.15	1.1816	1.2718
323.15	1.3349	1.2438
328.15	1.5027	1.2152
333.15	1.6856	1.1861
361.85(Tc)		

TABLE 3

VAPOR PRESSURE MEASUREMENTS

R-11, CFC1 ₃				R-22, CF ₂ C1H			
T/K	P/MPa	T/K	P/MPa	T/K	P/MPa	T/K	P/MPa
304.25	0.13134	407.16	1.6071	303.11	1.2048	346.22	3.2222
310.44	0.16088	418.69	1.9666	309.20	1.4046	350.42	3.5037
316.83	0.19653	430.46	2.3945	311.28	1.4837	353.19	3.7008
325.92	0.25715	439.06	2.7537	315.85	1.6562	356.03	3.9129
335.24	0.33299	447.95	3.1605	319.73	1.8135	358.61	4.1140
344.78	0.42698	456.87	3.6106	323.09	1.9645	361.66	4.3597
354.58	0.54345	462.32	3.9153	326.02	2.0952	364.57	4.6080
364.47	0.68180	466.14	4.1550	329.98	2.2887	366.06	4.7391
374.59	0.85204	468.01	4.2705	333.97	2.4944	367.54	4.8719
385.21	1.0598	469.87	4.3950	338.05	2.7215	368.92	5.0044
396.03	1.3083	471.05(Tc)		342.13	2.9637	369.45(Tc)	

TABLE 4

VAPOR PRESSURE MEASUREMENTS COMPARED WITH REFERENCE

R-11, CFC1₃

T/K	P _{expt} /MPa	P _{ref5} (EQN)/MPa	P _{ref5} (TABLE)/MPa
303.15	0.12646	0.12701	0.12630
313.15	0.17535	0.17573	0.17483
323.15	0.23748	0.23774	0.23655
333.15	0.31495	0.31525	0.31361
343.15	0.41003	0.41060	0.40828
353.15	0.52504	0.52625	0.52289
363.15	0.66253	0.66479	0.65991
373.15	0.82513	0.82893	0.82192
383.15	1.0157	1.0215	1.0116
393.15	1.2372	1.2456	1.2318
403.15	1.4931	1.5042	1.4855
413.15	1.7867	1.8008	1.7759
423.15	2.1221	2.1390	2.1066
433.15	2.5036	2.5226	2.4812
443.15	2.9359	2.9558	2.9039
453.15	3.4242	3.4430	3.3787
463.15	3.9744	3.9896	3.9102
471.05(Tc, expt)	4.457(Pc, expt)		
471.15(Tc, ref)	4.474(Pc, EQN)	4.410(Pc, TABLE)	

TABLE 5
VAPOR PRESSURE MEASUREMENTS COMPARED WITH REFERENCE

R-22, CF ₂ C1H			
T/K	P _{expt} /MPa	P _{ref4} (EQN)/MPa	P _{ref4} (TABLE)/MPa
303.15	1.2047	1.2012	1.1921
313.15	1.5508	1.5456	1.5340
323.15	1.9636	1.9579	1.9432
333.15	2.4518	2.4463	2.4279
343.15	3.0261	3.0206	2.9975
353.15	3.6990	3.6928	3.6633
363.15	4.4862	4.4800	4.4413
369.30(Tc,ref)	5.033(Pc,EQN)	4.988(Pc, TABLE)	
369.45(Tc,expt)	5.049(Pc,expt)		

TABLE 6
VAPOR PRESSURE EQUATIONS*



$$\ln(P) = 245.5559 - 8991.46/T + 0.05994252*T - 38.69449*\ln(T)$$

(±27.0) (±778) (±0.00690) (±4.64)

$$\sigma^2 = 3.84E-7$$



$$\ln(P) = 202.4236 - 8114.230/T + 0.04523931*T - 30.91298*\ln(T)$$

(±4.87) (±143) (±0.0012) (±0.83)

$$\sigma^2 = 3.78E-8$$



$$\ln(P) = 227.1457 - 8218.118/T + 0.05538288*T - 35.56644*\ln(T)$$

(±11.5) (±328) (±0.00301) (±1.99)

$$\sigma^2 = 1.92E-8$$

*Where p is pressure in Pascals; T is temperature in Kelvins.

TABLE 7

CALCULATED THERMOPHYSICAL PROPERTIES

Compound	M	T _b °C	T _c °C	P _c MPa	ΔH _{vap} kJ/mol	ΔH _{vap} kJ/Kg
	dlt	±0.5°	±0.5°	±2%	±1.5%	±1.5%
CF ₃ OCF ₂ CF ₂ H	186.03	-3.1°	114.6°	2.64	23.70	127.4
CF ₃ OCF ₂ OCF ₃	220.02	-10.0°	99.2°	2.33	23.07	104.8
-CF ₂ CF ₂ CF ₂ O-	166.02	-27.8°	88.7°	3.09	20.97	126.3
R-11, CFC1 ₃	137.37	23.3°	197.9°	4.46	25.050	182.36
R-22, CF ₂ C1H	86.47	-40.6°	96.3°	5.05	20.093	232.37

* Experimentally measured

TABLE 8

CLAPEYRON-CLAUSIUS EQUATION AND PARAMETERS FOR THE COMPOUNDS

$$\ln(P) = A/T + B \quad A = -\Delta H_v/R$$

Where P is pressure in Pascals, T is temperature in Kelvins

PARAMETERS FOR THE EQUATIONS

COMPOUNDS	A/K	B	σ ²
R-11, CFC1 ₃	-3013.043 ±3.6	21.69709 ±0.01	4.1E-5
R-22, CF ₂ C1H	-2416.722 ±4.0	21.96969 ±0.01	1.1E-5
CF ₃ -0-CF ₂ -0-CF ₃	-2774.611 ±3.7	22.10732 ±0.01	1.1E-5
CF ₃ -0-CF ₂ CF ₂ H	-2850.611 ±1.8	22.13372 ±0.005	3.0E-6
cyclo-CF ₂ CF ₂ CF ₂ -0-	-2522.188 ±2.5	21.91001 ±0.008	2.4E-6

CALCULATED HEAT OF VAPORIZATION OF THE COMPOUNDS

COMPOUNDS	ΔH _{v,expt}		ΔH _{v,ref} ⁹	
	kJ/mol	kJ/kg	kJ/mol	kJ/kg
R-11, CFC1 ₃	25.050	182.36	24.772	180.33
R-22, CF ₂ C1H	20.093	232.37	20.192	233.51
CF ₃ -0-CF ₂ -0-CF ₃	23.068 0.277	104.84 1.26		
CF ₃ -0-CF ₂ CF ₂ H	23.700 0.284	127.41 1.53		
cyclo-CF ₂ CF ₂ CF ₂ -0-	20.970 0.252	126.31 1.52		

Acknowledgement: This work was supported in part by the United States Environmental Protection Agency, The Electric Power Research Institute and The University of Tennessee whose support is gratefully acknowledged.

REFERENCES

1. First presented at the Symposium, "GLOBAL CLIMATE CHANGE AND REFRIGERANT PROPERTIES," Session No. 33, Paper 33d, 1990 Spring National Meeting, American Institute of Chemical Engineers, Orlando, Florida, March 18-22, 1990.
2. "Aerosol Direct Fluorination: A Developing Synthesis Technology, An Entry Level Mechanistic Tool, A Short Review," J. L. Adcock and M. L. Cherry, Industrial & Engineering Chemistry Research, 1987, 26, 208-215.
3. "ORGANIC SYNTHESSES, COLLECTIVE VOLUME 3", pp 835-6.
4. Zorawar S. Kooner and W. A. Van Hook, J. Phys. Chem., 1986, 90, 4860-4865.
5. "Thermophysical Properties of Refrigerants" tables for R-11 and R-22 published by ASHRAE.
6. "Thermophysical Properties of Freons", Methane Series, Part 2 by V. V. Altunin, V. Z. Geller, E. A. Kremenevskaya, I. I. Perelshtein and E. K. Petrov, Hemisphere Publishing Corporation.
7. "Thermophysical Properties of Refrigerants" published by American Society of Heating, Refrigerating and Air-Conditioning Engineers, Inc., c 1969.
8. "Thermophysical Properties of Refrigerants" published by American Society of Heating, Refrigerating and Air-Conditioning Engineers, 2d ed, 1976.
9. "HANDBOOK OF CHEMISTRY AND PHYSICS", 54th Edition, Chemical Rubber Company Press 1974, pages E-28 and E-29.