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Project Summary

New Chemical Alternatives for the Protection of Stratospheric Ozone

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Chlorofluorocarbons (CFCs) and their brominated analogs (halons) are recognized as potent contributors to depletion of the Earth's stratospheric ozone layer. By international agreement, such chemicals are to be phased out of the worldwide market. Additionally, certain partially halogenated CFCs (or hydrochlorofluorocarbons, HCFCs) have likewise been recognized as stratospheric ozone depleters and are also to be phased out of production by developed countries in a step-wise progression over the period 1996 to 2030.

Because of the enormous commercial importance of the CFCs, HCFCs, and halons, and because few chemicals were readily available or had been proven acceptable for use in the numerous applications in which the ozone-depleting substances were employed, the U. S. Environmental Protection Agency and the Electric Power Research Institute sponsored a study of additional potential alternative chemicals.

This study focused on the investigation of fluorinated derivatives of propane and butane to determine if synthesis routes of such compounds were feasible and economical, and to measure the physical properties needed to evaluate the compounds as alternatives. This work resulted in the investigation of 25 compounds including 15 hydrofluorocarbons (HFCs), 9 HCFCs, and 1 hydrofluoroether (HFE). Several of the compounds studied had not been previously synthesized and, for many of those which had been reported in the literature, this study resulted in improved synthesis methods. Also, most compounds which had a prior literature reference had only a boiling point measurement. This study, in addition to the synthesis effort, resulted in a sizeable body of thermophysical property data for each chemical.

This Project Summary was developed by the National Risk Management Research Laboratory's Air Pollution Prevention and Control Division, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Twenty-four fluorinated propane and butane derivatives and one fluorinated ether were evaluated as possible alternatives for CFCs and long-lived HCFCs. Boiling points for these chemicals range from -34.6 to 76.7°C. Therefore, these chemicals provide potential alternatives for a broad range of applications, e.g., as refrigerants, foam blowing agents, and solvents. Emphasis is on hydrogen-containing compounds that are expected to have finite atmospheric lifetimes which reduce their global warming potential. Sixteen of the chemicals investigated contain no chlorine or bromine and therefore have zero ozone depletion potential. The remaining nine chlorine-containing chemicals were selected for investigation before regulatory restrictions were imposed on HCFCs. Nevertheless, the low chlorine content of the nine HCFCs studied, coupled with a finite atmospheric lifetime, may in some cases yield an alternative with a negligible ozone depletion potential.

Selection and evaluation of the compounds as alternatives require: (1) a knowledge of appropriate physical properties and (2) possible synthesis routes. Both of these requirements were investigated in this research. This study emphasized synthesis routes using relatively inexpensive commercially available starting materials and established synthesis procedures (chlorination, hydrogenation, and addition of hydrogen fluoride) which are carried out industrially. This is important in order for a chemical to be an economically viable alternative for other than a small specialty market.

Experimental Procedure

Except for one hydrofluoroether (HFE-125), which was obtained commercially with 98% purity and then repurified, all samples employed for property measurements were synthesized with at least 99.5% purity. Synthesized chemicals were identified and their purity checked by a combination of nuclear magnetic resonance spectrometry, high pressure Fourier transform infrared spectrometry, gas chromatography, and mass spectrometry. Melting point, boiling point, vapor pressures below the boiling point, critical temperature, critical density, liquid densities, and heat of vaporization at the boiling point were measured for all 25 compounds. For four compounds (HFE-125, HFC-227ea, HFC236ea, and HFC-245cb), the vapor pressure was measured as a function of temperature to within 1% accuracy from below the boiling point to the critical temperature.

Vapor density in the liquid-vapor coexistence region and vapor pressure between the boiling point and the critical point were estimated by a modified corresponding states technique. The reference fluid for the modified corresponding states calculations was commercially available HFC-134a (1,1,1,2-tetrafluoroethane), and the equation of state used for the reference fluid was the modified Benedict-Webb-Rubin equation. Heats of vaporization between the boiling point and critical point were calculated from the heat of vaporization at the boiling point, the boiling point temperature, and the critical temperature. Ideal gas heat capacities and vapor-phase thermal conductivities were estimated by functional group additivity methods.

Results

Table 1 lists the 25 compounds investigated by ASHRAE (American Society of Heating, Refrigerating and Air-Conditioning Engineers) refrigerant code designation and by chemical formula.

Table 1. *Compounds Investigated by ASHRAE Refrigerant Designation and Chemical Formula*

Compound (ASHRAE Code)	*Chemical Formula*
HFE-125	CF_3OCF_2H
HFC-227ea	CF_3CHFCF_3
HFC-227ca	$CF_3CF_2CF_2H$
HFC-236fa	$CF_3CH_2CF_3$
HFC-236ea	CF_3CHFCF_2H
HFC-236cb	$CF_3CF_2CFH_2$
HFC-236ca	$CF_2HCF_2CF_2H$
HFC-245fa	$CF_3CH_2CF_2H$
HFC-245ca	$CHF_2CF_2CFH_2$
HFC-245cb	$CF_3CF_2CH_3$
HFC-254cb	$CF_2HCF_2CH_3$
HFC-329ccb	$CF_3CF_2CF_2CF_2H$
HFC-338eea	$CF_3CFHCFHCF_3$
HFC-338cca	$CHF_2CF_2CF_2CF_2H$
HFC-338ccb	$CF_3CF_2CF_2CFH_2$
HFC-347ccd	$CF_3CF_2CF_2CH_3$
HCFC-225ba	$CF_3CFClCFHCl$
HCFC-225da	$CF_3CHClCF_2Cl$
HCFC-226da	$CF_3CHClCF_3$
HCFC-226ea	CF_3CHFCF_2Cl
HCFC-234da	$CF_3CHClCFHCl$
HCFC-235ca	$CF_3CF_2CH_2Cl$
HCFC-243da	$CF_3CHClCH_2Cl$
HCFC-244ca	$CF_2HCF_2CH_2Cl$
cy-HCFC-326d	*cy-*$(CF_2)_3CHCl$

Table 2 lists the 25 compounds studied along with their boiling point (T_b), melting point (T_m), heat of vaporization at the boiling point (ΔH_{vap}), critical temperature (T_c), critical pressure (P_c), critical density (d_c), and liquid heat capacity at 40°C ($C_{p,l}$).

Conclusions

From the data acquired in this study, it appears that several of the chemicals synthesized are worthy of consideration as alternatives to the ozone-depleting CFCs and HCFCs. Table 3 presents selected apparent best candidate alternatives from this study based on a comparison of their thermophysical properties with those of commercially important CFCs and HCFCs and the fact that these candidates have zero ozone depletion potentials. Also, preference was given to fluorinated propanes over fluorinated butanes on the premise that the latter would likely be more expensive to produce (cost generally correlates with total fluorine content) and that, for insulation foam production, the butane derivatives would likely have higher vapor thermal conductivities than the propane derivatives. These presumptions are somewhat tenuous, however, and the possibility that certain of the fluorinated butanes may be excellent candidates should not be discounted.

No fluorinated propane derivatives with as low a boiling point as that of CFC-12 (dichlorodifluoromethane, T_b = -29.8°C) were found. After some searching, HFC-245cb was synthesized with a boiling point of -18.3°C. Its critical temperature of 108.5°C compares well with the critical temperature of CFC-12 (112°C). Therefore, HFC-245cb might be an alternative for CFC-12 for some applications as would HFC-227ca and -227ea with boiling points of -16.3 and -18.3°C, and critical temperatures of 106.3 and 102.8°C, respectively.

HFE-125, with a boiling point of -34.6°C and critical temperature of 80.7°C, appears to be the best candidate alternative for CFC-115(1,1,1,2,2-pentafluorochloroethane, T_b = -39.2°C, T_c = 79.9°C) and HCFC-22 (difluorochloromethane, T_b = -40.6°C, T_c = 96.15°C).

HFC-245ca and -245fa with boiling points of 25.0 and 15.3°C and critical temperatures of 178.4 and 157.5°C, respectively, are promising candidates to replace CFC-11 (fluorotrichloromethane, T_b = 23.8°C, T_c = 198.1°C), HCFC-123 (1,1,1-trifluoro-2,2-dichloroethane, T_b = 27.9°C, T_c = 183.8°C), and HCFC-141b (1-fluoro-1,1-dichloroethane, T_b = 32.2°C, T_c = 204.2°C) as a refrigerant in low pressure chillers and/or as a blowing agent in the manufacture of polyisocyanurate insulation foam. All HFC-245 isomers possess a hydrogen content sufficient to possibly render them borderline flammable. Therefore, the flammabilities of these chemicals should be evaluated.

A number of CFC-114 (1,1,2,2,-tetrafluoro-1,2,-dichloroethane, T_b = 3.7°C, T_c = 145.7°C) alternatives are possible from the chemicals synthesized. HFCs-236ea, -236fa, and -236cb with boiling points of 6.5, -1.1, and -1.4°C, respectively, and HFC-254cb with a boiling point of -0.8°C are especially attractive. However, the relatively high hydrogen-to-fluorine atom ratio of HFC-254cb poses a flammability concern for this compound.

Table 2. Boiling Point, Melting Point, Critical Properties, Heat of Vaporization at the Boiling Point, and Liquid-Phase Heat Capacity for the 25 Compounds Studied.

Compound	T_b (ºC)	T_m (ºC)	ΔH_{vap} (kJ/mol)	T_c (ºC)	P_c (kPa)	d_c (kg/m³)	$C_{p,l}$ @ 40ºC (kJ/kg ºC)
HFE-125	-34.6	-156.1	21.92	80.7	3253	584	1.327
HFC-227ea	-18.3	-126.8	22.29	102.8	2943	580	1.258
HFC-227ca	-16.3	-140.3	23.69	106.3	2874	594	1.254
HFC-236fa	-1.1	-94.2	25.66	130.6	3177	556	1.371
HFC-236ea	6.5	-146.1	26.83	141.1	3533	571	1.304
HFC-236cb	-1.4	-105.4	25.25	130.1	3118	545	1.438
HFC-236ca	12.6	-123.3	26.59	155.2	3405	558	NA
HFC-245fa	15.3	-102.1	27.96	157.5	3623	529	1.422
HFC-245ca	25.0	-73.4	29.21	178.4	3855	529	1.454
HFC-245cb	-18.3	-81.1	23.59	108.5	3264	499	1.457
HFC-254cb	-0.8	-121.1	24.86	146.1	3753	467	1.590
HFC-329ccb	15.1	-122.3	26.71	140.2	2391	600	1.223
HFC-338eea	25.4	-91.5	27.79	148.5	2475	581	NA
HFC-338cca	42.5	-91.0	31.13	186.4	2792	578	1.333
HFC-338ccb	27.8	-119.4	26.36	160.5	2552	562	1.342
HFC-347ccd	15.1	-124.9	25.82	144.2	2570	532	1.383
HCFC-226da	14.1	-119.6	24.64	158.2	3024	591	1.207
HCFC-226ea	17.6	-134.0	26.26	158.3	2939	584	1.205
HCFC-235ca	28.1	-85.0	27.57	170.3	3084	550	1.275
HCFC-244ca	54.8	-101.8	31.07	221.0	3714	525	1.160
HCFC-225da	50.8	-130.3	25.89	206.2	3006	589	1.087
HCFC-225ba	51.9	-132.7	29.38	212.9	3074	586	1.087
HCFC-234da	70.1	-98.0	31.70	242.5	3353	552	1.176
HCFC-243da	76.7	-71.6	30.86	251.9	3496	514	1.234
cy-HCFC-326d	38.1	-94.8	28.69	196.9	2749	515	1.158

NA = not available

Table 3. Selected Possible Alternatives for Commercially Important CFCs and HCFCs

CFC or HCFC To Be Replaced	ASHRAE Code of Alternative	Chemical Formula of Alternative	Chemical Name of Alternative
CFC-11, HCFC-123, HCFC-141b	HFC-245ca	$CF_2HCF_2CFH_2$	1,1,2,2,3-pentafluoropropane
	HFC-245fa	$CF_3CH_2CF_2H$	1,1,1,3,3-pentafluoropropane
CFC-12	HFC-227ea	CF_3CHFCF_3	1,1,1,2,3,3,3-heptafluoropropane
	HFC-227ca	$CF_3CF_2CF_2H$	1,1,1,2,2,3,3-heptafluoropropane
	HFC-245cb	$CF_3CF_2CH_3$	1,1,1,2,2-pentafluoropropane
CFC-114	HFC-236ea	CF_3CHFCF_2H	1,1,1,2,3,3-hexafluoropropane
	HFC-236fa	$CF_3CH_2CF_3$	1,1,1,2,2,2-hexafluoropropane
	HFC-236cb	$CF_3CF_2CFH_2$	1,1,1,2,2,3-hexafluoropropane
	HFC-254cb	$CF_2HCF_2CH_3$	1,1,2,2-tetrafluoropropane
CFC-115, HCFC-22	HFE-125	CF_3OCF_2H	pentafluorodimethylether

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***N. Dean Smith** is the EPA Project Officer (see below).*
The complete report, entitled "New Chemical Alternatives for the Protectin of Stratospheric Ozone," (Order No. PB95-260220; Cost: $27.00, subject to change) will be available only from:
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