

## Calculated Chemical Contributions to Extinguishment by Halocarbons

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### ABSTRACT

Sheinson and Driscoll [1] and Sheinson, Penner-Hahn, and Indritz [2] have presented a method to quantify suppression action pathways for extinguishing agents. We have taken this method, recast the calculation in a slightly different form, and have determined the relative physical and chemical contributions for a large number of halocarbons using extinguishment concentrations determined with the NEMERJ Standard cup burner [3] and vapor-phase heat capacities. Trends, expected and unexpected, are discussed.

### INTRODUCTION

Some researchers believe that extinguishment by all agents is dominated by heat absorption, and that many of the effects attributed to chemical mechanisms may be thermodynamic rather than kinetic (4). These conclusions, however, are not accepted by most researchers, who believe that the “radical trap” mechanism explains fire extinguishment by the halons and other highly effective agents.

A number of approaches can be used to estimate the physical and chemical contributions to extinguishment by an agent (see, e.g., [5]). Here, we estimate the purely physical component of agent effectiveness by comparing the amount of agent required to raise the heat capacity of an enclosed atmosphere to the concentration required for extinguishment by cooling alone compared to the measured extinguishment concentration. The flame-spread rate for burning material is a strong inverse function of the heat capacity per mole of oxygen of the oxidizing atmosphere. As a result, if the heat capacity of an atmosphere is raised to approximately 209 J/mol-K per mole of O<sub>2</sub> present, combustion is not supported [6, 7]. This criterion can be used to calculate the concentration of a given agent required to suppress a fire by heat absorption only. The difference between the calculated and actual concentrations can then be attributed to suppression mechanisms other than purely physical (i.e., chemical suppression).

### METHODOLOGY

When a total-flooding agent is discharged into an enclosed volume and the pressure is maintained constant by leakage, the oxygen concentration decreases. Regardless of the agent used, the O<sub>2</sub> concentration (C<sub>O2</sub>) and the agent concentration (C<sub>a</sub>), both in mole or volume percent (mol % and vol %), are related by Equation 1. This equation assumes ambient air containing 21 vol % O<sub>2</sub> (i.e., before addition of agent, C<sub>O2</sub> = 21 vol %).

$$C_a = -4.7619(C_{O_2}) + 100 \quad [1]$$

Three calculations are required to determine the agent concentration,  $C_a$ , required to raise the total heat capacity of an enclosed area to 209 J/mol-K/mole of  $O_2$ . (The heat capacity assumed affects values calculated but does not affect the rank ordering of agents.) (1) The mole or volume percent (identical for mixtures of ideal gases) of agent required to impart a heat capacity of 209 J/mol-K/mole of  $O_2$  at 298K and constant pressure while maintaining a constant oxygen concentration (e.g., 20 mol %) is calculated. In other words, the oxygen concentration is held constant at 20 mol % and the nitrogen/argon ( $N_2/Ar$ ) concentration is decreased as agent is added. (2) A second calculation is made assuming a different constant  $O_2$  concentration (e.g., 16 mol %). (3) These data are then used to calculate, for each agent, the equation of the line that represents an atmosphere where combustion cannot be sustained. A sample calculation is given below for HFC-125 (pentafluoroethane,  $CHF_2CF_3$ ).

At 298K and 1 atmosphere pressure, the vapor-phase heat capacity ( $C_p$ ) of HFC-125 is 96.1 J/mol K. Under normal conditions, the composition of ambient air is approximately 21 mol % oxygen, 78 mol % nitrogen, and 1 mol % argon. The heat capacity of oxygen ( $O_2$ ) is 29.37 J/mol-K, that of nitrogen ( $N_2$ ) is 29.15 J/mol K, and that of argon (Ar) is 20.800 J/mol-K [8]. The average heat capacity of  $N_2/Ar$  in the ratio found in air (78 mol %/1 mol %) is calculated as 29.04 J/mol-K. Thus, the heat capacity of a mixture of HFC-125,  $O_2$ , and  $N_2/Ar$  is given by  $f_{125}(96.1) + f_{O_2}(29.37) + f_{N_2/Ar}(29.04)$  J/mol-K, where  $f_a$  is the mole fraction of component a. This must be set equal to the heat capacity of 209 J/mol-K/mole of  $O_2$ . Thus for 1 mole of mixture,  $f_{125}(96.02) + f_{O_2}(29.37) + f_{N_2/Ar}(29.04) = 209f_{O_2}$ . If  $f_{O_2}$  is maintained at 0.20, this gives Equation 2, whose solution yields  $f_{125} = 0.1892$  (18.92 mol %). The same procedure for an oxygen concentration of 16 mol % gives  $f_{125} = 0.0648$  (6.48 mol %).

$$f_{125}(96.1) + 0.20(29.37) + (1-0.20-f_{125})(29.04) = 209(0.20) \quad [2]$$

The relation between the HFC-125 and  $O_2$  concentrations ( $C_{125}$  and  $C_{O_2}$ ) is linear and can be written in the form  $y = mx + b$ , where  $y$  is  $C_{125}$ ,  $x$  is  $C_{O_2}$ ,  $m$  is the slope of the line, and  $b$  is the  $y$  intercept. The two ( $x, y$ ) data pairs calculated earlier are (20, 18.92) and (16, 6.48). The slope is given by  $m = (18.92-6.48)/(20-16) = 3.11$  and they-intercept is  $b = 6.48 - (3.11)(16) = -43.31$ . Thus, the equation relating the concentration of HFC-125 to the concentration of  $O_2$  for an atmosphere that will not support combustion due to its heat capacity is

$$C_{125} = 3.11(C_{O_2}) - 43.31 \quad [3]$$

This line defines a family of mixtures containing HFC-125,  $O_2$ , and  $N_2/Ar$ . Only one mixture on this line can be formed by discharging HFC-125 into an enclosed volume. That unique mixture is the intersect of the HFC-125 line described by Equation 3 and the oxygen depletion line defined by Equation 1 with  $C_a = C_{125}$ . The intersection of these two lines is found from the simultaneous Equations 1 and 3. For HFC-125,  $C_{O_2} = 18.21$  mol % and  $C_{125} = 13.33$  mol %.

## RESULTS AND ANALYSIS

Table 1 contains cup burner extinguishment concentrations for n-heptane fuel and heat capacity data for a series of halocarbon compounds. The cup burner values were taken from the original data as reported in Reference 3 with, in some cases, one fewer decimal place. The heat capacity data are from DuPont or the NMERI/CGET Chemical Options Database, which is compiled from a variety of sources. In all cases, agreement between DuPont and NMERI/CGET values was good; however, where both data were available, the DuPont data were used.

**TABLE 1. CUP BURNER AND HEAT CAPACITY DATA**

CAS No.	Halocarbon No.	Formula	Cup Burner, vol (mol) %	Cp at 298K, J/mol-K
353-59-3	BCFC-12B1	CBrClF <sub>2</sub>	3.22	74.7
75-61-6	BFC-12B2	CBr <sub>2</sub> F <sub>2</sub>	2.17	77.8
75-63-8	BFC-13B1	CBrF <sub>3</sub>	2.9	69.8
56-23-5	cc-10	CCl <sub>4</sub>	7.61	83.4
75-69-4	CFC-11	CCl <sub>3</sub> F	7.75	78.1
76-13-1	CFC-113	CCl <sub>2</sub> FCClF <sub>2</sub>	6.19	121.4
354-58-5	CFC-113a	CCl <sub>3</sub> CF <sub>3</sub>	6.19	120.5
76-14-2	CFC-I 14	CClF <sub>2</sub> CClF <sub>2</sub>	6.41	116.3
374-07-2	CFC-114a	CCl <sub>2</sub> FCF <sub>3</sub>	6.41	115.9
76-15-3	CFC-115	CClF <sub>2</sub> CF <sub>3</sub>	6.28	110.9
75-71-8	CFC-12	CCl <sub>2</sub> F <sub>2</sub>	7.64	72.4
75-72-9	CFC-13	CClF <sub>3</sub>	7.22	66.9
76-16-4	FC-I 16	CF <sub>3</sub> CF <sub>3</sub>	7.8	106.4
75-73-0	FC-14	CF <sub>4</sub>	13.79	61
76-19-7	FC-218	CF <sub>3</sub> CF <sub>2</sub> CF <sub>3</sub>	6.11	149
355-25-9	FC-3-1-10	CF <sub>3</sub> CF <sub>2</sub> CF <sub>2</sub> CF <sub>3</sub>	5	191
115-25-3	FC-C3 18	-CF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> -	7.19	159
23 14-97-8	FIC-1311	CF <sub>3</sub> I	3.02	70.88
754-34-7	FIC-217ca11	CF <sub>3</sub> CF <sub>2</sub> CF <sub>2</sub> I	3.04	197
354-06-3	HBCFC-123aB1α	CBrF <sub>2</sub> CHClF	3.17	103
354-04-1	HBFC-123aB2	CHBrFCBrF <sub>2</sub>	2.01	106
1868-53-7	HBFC-21B2	CHBr <sub>2</sub> F	1.77	65
15 11-62-2	HBFC-22B1	CHBrF <sub>2</sub>	4.41	59.6
630-20-6	HCC-130a	CCl <sub>3</sub> CH <sub>2</sub> Cl	<sup>b</sup> 7.96	104.2
75-34-3	HCC-150a	CH <sub>3</sub> CHCl <sub>2</sub>	8.6	76.3
67-66-3	HCC-20	CHCl <sub>3</sub>	10.5	65.4
78-87-5	HCC-270da	CH <sub>3</sub> CHClCH <sub>2</sub> Cl	<sup>b</sup> 4.6	96.7
142-28-9	HCC-270fa	CH <sub>2</sub> ClCH <sub>2</sub> CH <sub>2</sub> Cl	<sup>b</sup> 5.46	93.8
75-29-6	HCC-280da	CH <sub>3</sub> CHClCH <sub>3</sub>	3.2	85.6
540-54-5	HCC-280fa	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> Cl	3.32	82.9
75-09-2	HCC-30	CH <sub>2</sub> Cl <sub>2</sub>	14.1	50.9
354-14-3	HCFC-121	CCl <sub>2</sub> FCHCl <sub>2</sub>	<sup>b</sup> 7.77	114.1
354-15-4	HCFC-122a	CCl <sub>2</sub> FCHClF	6.3	109.7
306-83-2	HCFC-123	CHCl <sub>2</sub> CF <sub>3</sub>	<sup>b</sup> 7.1	102.5
354-23-4	HCFC-123a	CHClFCClF <sub>2</sub>	<sup>b</sup> 8.3	104.3

2837-89-0	HCFC-124	CHClFCF <sub>3</sub>	6.7	98.9
1649-08-7	HCFC-132b	CH <sub>2</sub> ClCClF <sub>2</sub>	7.85	94.2
75-88-7	HCFC-133a	CH <sub>2</sub> ClCF <sub>3</sub>	7.59	89.1
430-57-9	HCFC-141	CHFClCH <sub>2</sub> Cl	18.72	82.1
1717-00-6	HCFC-14 lb	CH <sub>3</sub> CCl <sub>2</sub> F	<sup>b</sup> 12.5	88.7
75-45-6	HCFC-22	CHClF <sub>2</sub>	11.6	57.1
593-70-4	HCFC-31	CH <sub>2</sub> ClF	<sup>b</sup> 20	47.3
354-33-6	HFC-125	CHF <sub>2</sub> CF <sub>3</sub>	9.41	96.1
359-35-3	HFC-134	CHF <sub>2</sub> CHF <sub>2</sub>	11.2	83.7
811-97-2	HFC-134a	CH <sub>2</sub> FCF <sub>3</sub>	10.47	86.3
2252-84-8	HFC-227 <sup>ca</sup>	CHF <sub>2</sub> CF <sub>2</sub> CF <sub>3</sub>	6.5	137.7
431-89-0	HFC-227 <sup>ea</sup>	CF <sub>3</sub> CHFCF <sub>3</sub>	6.3	136.6
75-46-7	HFC-23	CHF <sub>3</sub>	12.6	51.1
431-63-0	HFC-236 <sup>ea</sup>	CF <sub>3</sub> CHFCHF <sub>2</sub>	6.6	128.1
690-39-1	HFC-236 <sup>fa</sup>	CF <sub>3</sub> CH <sub>2</sub> CF <sub>3</sub>	5.6	126
1814-88-6	HFC-245 <sup>cb</sup>	CF <sub>3</sub> CF <sub>2</sub> CH <sub>3</sub>	8.2	120.2
40723-63-5	HFC-254 <sup>cb</sup>	CHF <sub>2</sub> CF <sub>2</sub> CH <sub>3</sub>	<sup>b</sup> 10.1	107.6
62126-90-3	HFC-272 <sup>ea</sup>	CH <sub>2</sub> FCHFCH <sub>3</sub>	<sup>b</sup> 5.6	88.8
75-10-5	HFC-32	CH <sub>2</sub> F <sub>2</sub>	8.75	42.7

<sup>a</sup>Reliability uncertain.

<sup>b</sup>Limited confidence.

<sup>c</sup>Estimated.

Table 2 gives the extinguishment concentrations calculated based on heat capacity alone, the observed extinguishment concentrations, and the ratio of the calculated concentration to that observed (termed the “extinguishment ratio” throughout this paper).

TABLE 2. EXPERIMENTAL AND CALCULATED EXTINGUISHMENT CONCENTRATIONS

Halocarbon No.	Formula	Extinguishment Concentration vol %		Extinguishment Ratio
		Calculated	Observed	Calc/Obs
HBFC-21B2	CHBr <sub>2</sub> F	18.52	1.77	10.47
BFC-12B2	CBr <sub>2</sub> F <sub>2</sub>	15.96	2.17	7.36
HBFC-123aB2	CHBrFCBrF <sub>2</sub>	12.24	2.01	6.09
BFC-13B1	CBrF <sub>3</sub>	17.47	2.9	6.02
FIC-1311	CF <sub>3</sub> I	17.25	3.02	5.71
BCFC-12B1	CBrClF <sub>2</sub>	16.52	3.22	5.13
HCC-280da	CH <sub>3</sub> CHClCH <sub>3</sub>	14.72	3.2	4.60
HCC-280fa	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> Cl	15.13	3.32	4.56
HBFC-22B1	CHBrF <sub>2</sub>	19.87	4.41	4.51
HBCFC-123aB1a	CBrF <sub>2</sub> CHClF	12.55	3.17	3.96
HFC-32	CH <sub>2</sub> F <sub>2</sub>	25.71	8.75	2.94
HCC-270da	CH <sub>3</sub> CHClCH <sub>2</sub> Cl	13.26	4.6	2.88
HFC-272ea	CH <sub>2</sub> FCHFCH <sub>3</sub>	14.27	5.6	2.55
CFC-13	CClF <sub>3</sub>	18.09	7.22	2.51
HCC-270fa	CH <sub>2</sub> ClCH <sub>2</sub> CH <sub>2</sub> Cl	13.61	5.46	2.49
FIC-217caI1	CF <sub>3</sub> CF <sub>2</sub> CF <sub>2</sub> I	6.98	3.04	2.30
CFC-12	CCl <sub>2</sub> F <sub>2</sub>	16.95	7.64	2.22
CFC-11	CCl <sub>3</sub> F	15.91	7.75	2.05
cc-10	CCl <sub>4</sub>	15.05	7.61	1.98
HCFC-124	CHClFCF <sub>3</sub>	13.00	6.7	1.94
HCC-150a	CH <sub>3</sub> CHCl <sub>2</sub>	16.23	8.6	1.89
HCFC-122a	CCl <sub>2</sub> FCHClF	11.87	6.3	1.88
CFC-115	CClF <sub>2</sub> CF <sub>3</sub>	11.76	6.28	1.87
HCFC-133a	CH <sub>2</sub> ClCF <sub>3</sub>	14.23	7.59	1.87
HFC-236fa	CF <sub>3</sub> CH <sub>2</sub> CF <sub>3</sub>	10.50	5.6	1.87
HFC-23	cHF <sub>3</sub>	22.43	12.6	1.78
HCFC-123	CHCl <sub>2</sub> CF <sub>3</sub>	12.60	7.1	1.77
HCFC-22	CHClF <sub>2</sub>	20.56	11.6	1.77
CFC-113a	CCl <sub>3</sub> CF <sub>3</sub>	10.92	6.19	1.76
CFC-114	CClF <sub>2</sub> CClF <sub>2</sub>	11.27	6.41	1.76
CFC-114a	CCl <sub>2</sub> FCF <sub>3</sub>	11.31	6.41	1.76
HCC-20	CHCl <sub>3</sub>	18.43	10.5	1.76
CFC-113	CCl <sub>2</sub> FCClF <sub>2</sub>	10.85	6.19	1.75

HCFC-132b	CH <sub>2</sub> ClCClF <sub>2</sub>	13.56	7.85	1.73
HCC-30	CH <sub>2</sub> Cl <sub>2</sub>	22.50	14.1	1.60
HFC-236ea	CF <sub>3</sub> CHFCHF <sub>2</sub>	10.34	6.6	1.57
FC-116	CF <sub>3</sub> CF <sub>3</sub>	12.19	7.8	1.56
HCC-130a	CCl <sub>3</sub> CH <sub>2</sub> Cl	12.42	7.96	1.56
HFC-227ea	CF <sub>3</sub> CHF <sub>2</sub> CF <sub>3</sub>	9.76	6.3	1.55
HCFC-123a	CHClFCClF <sub>2</sub>	12.41	8.3	1.50
HFC-227ca	CHF <sub>2</sub> CF <sub>2</sub> CF <sub>3</sub>	9.69	6.5	1.49
FC-218	CF <sub>3</sub> CF <sub>2</sub> CF <sub>3</sub>	9.02	6.11	1.48
HCFC-121	CCl <sub>2</sub> FCHCl <sub>2</sub>	11.47	7.77	1.48
FC-3-1-10	CF <sub>3</sub> CF <sub>2</sub> CF <sub>2</sub> CF <sub>3</sub>	7.18	5	1.44
HFC-125	CHF <sub>2</sub> CF <sub>3</sub>	13.33	9.41	1.42
FC-14	CF <sub>4</sub>	19.50	13.79	1.41
HFC-134a	CH <sub>2</sub> FCF <sub>3</sub>	14.62	10.47	1.40
HFC-134	CHF <sub>2</sub> CHF <sub>2</sub>	15.01	11.2	1.34
HFC-245cb	CF <sub>3</sub> CF <sub>2</sub> CH <sub>3</sub>	10.95	8.2	1.34
HFC-254cb	CHF <sub>2</sub> CF <sub>2</sub> CH <sub>3</sub>	12.08	10.1	1.20
HCFC-31	CH <sub>2</sub> ClF	23.80	20	1.19
FC-C318	-CF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> -	8.50	7.19	1.18
HCFC-141b	CH <sub>3</sub> CCl <sub>2</sub> F	14.28	12.5	1.14
HCFC-141	CHFCICH <sub>2</sub> Cl	15.25	18.72	0.81

The data in Table 2 are presented in order of decreasing extinguishment ratio. One would expect this would give an order of decreasing chemical contribution to extinguishment, and inspection of the table indicates that this is generally true. If the assumed heat capacity of 209 J/mol-K/mole of O<sub>2</sub> is correct, a Calc/Obs value of 1.00 indicates no chemical contribution and, except for HCFC-141, 1.00 appears to be a lower limit. Bromine and iodine-containing compounds appear toward the top of the table, and compounds whose extinguishment mechanism is believed to be primarily physical appear toward the bottom. As expected, dibromide compounds are exceedingly effective. FIC-217caII appears to be out of line; however, the heat capacity of this compound has been estimated [9], and appears to be high. This would make the predicted extinguishment concentration based on heat absorption alone low and would give a low value for the extinguishment ratio.

The large apparent chemical contributions to extinguishment by HCC-280fa (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>Cl) and HCC-280da (CH<sub>3</sub>CHClCH<sub>3</sub>) are surprising. In these flammable compounds, the large number of hydrogen atoms may serve as highly effective free radical scavengers (e.g., Reaction 1). Data for the hydrochlorocarbons (HCCs) indicates that the chemical contribution increases as the atom ratio of hydrogen to chlorine increases (Table 3)



TABLE 3. HCC EXTINGUISHMENT RATIO AS FUNCTION OF H/Cl ATOM RATIO

Halocarbon No.	Formula	W/Cl Atom Ratio	Calc/Obs Extinguishment Ratio
HCC-280da	CH <sub>3</sub> CHClCH <sub>3</sub>	7.00	4.60
HCC-280fa	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> Cl	7.00	4.56
HCC-270da	CH <sub>3</sub> CHClCH <sub>2</sub> Cl	3.00	2.88
HCC-270fa	CH <sub>2</sub> ClCH <sub>2</sub> CH <sub>2</sub> Cl	3.00	2.49
HCC-150a	CH <sub>3</sub> CHCl <sub>2</sub>	2.00	1.89
HCC-20	CHCl <sub>3</sub>	0.33	1.76
HCC-30	CH <sub>2</sub> Cl <sub>2</sub>	1.00	1.60
HCC-130a	CCl <sub>3</sub> CH <sub>2</sub> Cl	0.50	1.56

Trends in extinguishment ratio based on the H/F atom ratio in the hydrofluorocarbons (HFCs) is much less clear (Table 4). No trends are immediately apparent even when the data are grouped into methane and ethane derivatives. HFC-32, which is flammable, appears to be particularly anomalous. Its effectiveness does not appear to be due to exceeding the upper flammability limit since the flammability limits for HFC-32 are 12.7 vol % to 33.4 vol % [10]; whereas the cup burner extinguishment concentration is 8.75 vol %. On the other hand, the extreme position of HFC-272ea may well be due to operation of the same mechanism proposed above for the HCCs.

TABLE 4. HFC EXTINGUISHMENT RATIO AS FUNCTION OF H/F ATOM RATIO

Halocarbon No.	Formula	H/F Atom Ratio	Calc/Obs Extinguishment Ratio
HFC-32	CH <sub>2</sub> F <sub>2</sub>	1.00	2.94
HFC-272ea	CH <sub>2</sub> FCHFCH <sub>3</sub>	3.00	2.55
HFC-236fa	CF <sub>3</sub> CH <sub>2</sub> CF <sub>3</sub>	0.33	1.87
HFC-23	CHF <sub>3</sub>	0.33	1.78
HFC-236ea	CF <sub>3</sub> CHFCHF <sub>2</sub>	0.33	1.57
HFC-227ea	CF <sub>3</sub> CHFCF <sub>3</sub>	0.14	1.55
HFC-227ca	CHF <sub>2</sub> CF <sub>2</sub> CF <sub>3</sub>	0.14	1.49
HFC-125	CHF <sub>2</sub> CF <sub>3</sub>	0.20	1.42
HFC-134a	CH <sub>2</sub> FCF <sub>3</sub>	0.50	1.40
HFC-134	CHF <sub>2</sub> CHF <sub>2</sub>	0.50	1.34
HFC-245cb	CF <sub>3</sub> CF <sub>2</sub> CH <sub>3</sub>	0.60	1.34
HFC-254cb	CHF <sub>2</sub> CF <sub>2</sub> CH <sub>3</sub>	1.00	1.20

For the hydrochlorofluorocarbons (HCFCs), any relationship of the extinguishment ratio to the  $H/Cl$  and  $H/halogen$  atom ratios appears to be totally random (Table 5). There is a very weak indication that extinguishment ratio may decrease (!) as the number of chlorine atoms relative to the number of fluorine atoms increases, though the data are ambiguous and variations in hydrogen content and number of carbon atoms undoubtedly obscure any trends. Of particular interest are the small values of the extinguishment ratio for the isomers of HCFC-141. In the case of HCFC-141b, the extinguishment concentration (12.5 vol %) is well within the flammability envelope (5.6 to 17.7 vol % [11]). The effect of hydrogen content on extinguishment ratio, which appears to be so clear for the HCCs, deserves further investigation.

TABLE 5. HCFC **EXTINGUISHMENT** RATIO AS FUNCTION OF ATOM RATIOS

Halocarbon No.	Formula	H/Cl Atom Ratio	H/Halogen Atom Ratio	Cl/F Atom Ratio	Calc/Obs Extinguishment Ratio
HCFC-124	CHClFCF <sub>3</sub>	1.00	0.20	0.25	1.94
HCFC-122a	CCl <sub>2</sub> FCHClF	0.33	0.20	1.50	1.88
HCFC-133a	CH <sub>2</sub> ClCF <sub>3</sub>	2.00	0.50	0.33	1.87
HCFC-22	CHClF <sub>2</sub>	1.00	0.33	0.50	1.77
HCFC-123	CHCl <sub>2</sub> CF <sub>3</sub>	0.50	0.20	0.67	1.77
HCFC-132b	CH <sub>2</sub> ClCClF <sub>2</sub>	1.00	0.50	1.00	1.73
HCFC-123a	CHClFCClF <sub>2</sub>	0.50	0.20	0.67	1.50
HCFC-121	CCl <sub>2</sub> FCHCl <sub>2</sub>	0.25	0.20	4.00	1.48
HCFC-31	CH <sub>2</sub> ClF	2.00	1.00	1.00	1.19
HCFC-141b	CH <sub>3</sub> CCl <sub>2</sub> F	1.50	1.00	2.00	1.14
HCFC-141	CHFC <sub>2</sub> CH <sub>2</sub> Cl	1.00	1.00	2.00	0.81

For fully halogenated compounds, with the exception of the perfluorocarbons, the data show a clear reduction in extinguishment ratio as the chlorine content increases when grouped into methane and ethane derivatives (Table 6). This appears to contradict the general opinion that chlorine provides a small, but significant, chemical contribution to extinguishment. The CFCs have high extinguishment ratios and relatively high extinguishment efficiencies relative to most other agents that operate by primarily physical mechanisms. Work has shown that some CFC blends are actually as good as or better than Halon 1211 in field testing [12].

Comparison of data for isomers indicates that an increase in the number of CF<sub>3</sub> groups gives an increase in the extinguishment ratio, indicative of increased chemical contribution (Table 7), though some differences are small. The sole exception is CFC-114 and CFC-114a, which have identical extinguishment ratios. This observation indicates a chemical participation by •CF<sub>3</sub> free radicals, the primary subject of another paper in this conference [13]. This may explain why FC-C318 (cyclic C<sub>4</sub>F<sub>8</sub>), which contains no CF<sub>3</sub> groups, has the smallest extinguishment ratio (indicating the smallest chemical contribution) of any of the perfluorocarbons in Table 2.

TABLE 6. EXTINGUISHMENT RATIO FOR FULLY HALOGENATED COMPOUNDS AS FUNCTION OF Cl/F ATOM RATIO

Halocarbon No.	Formula	Cl/F Atom Ratio	Calc/Obs Extinguishment Ratio
Methanes			
FC-14	CF <sub>4</sub>	0	1.41
CFC-13	CClF <sub>3</sub>	0.33	2.51
CFC-12	CCl <sub>2</sub> F <sub>2</sub>	1.00	2.22
CFC-11	CCl <sub>3</sub> F	3.00	2.05
CC-10	CCl <sub>4</sub>	∞	1.98
Ethanes			
FC-116	CF <sub>3</sub> CF <sub>3</sub>	0	1.56
CFC-115	CClF <sub>2</sub> CF <sub>3</sub>	0.20	1.87
CFC-I 14a	CCl <sub>2</sub> FCF <sub>3</sub>	0.50	1.76
CFC-114	CClF <sub>2</sub> CClF <sub>2</sub>	0.50	1.76
CFC-113a	CCl <sub>3</sub> CF <sub>3</sub>	1.00	1.76
CFC-I 13	CCl <sub>2</sub> FCClF <sub>2</sub>	1.00	1.75

TABLE 7. DATA FOR ISOMERS WITH DIFFERENT NUMBERS OF CF<sub>3</sub> GROUPS

Halocarbon No.	Formula	Number of CF <sub>3</sub> Groups	Calc/Obs Extinguishment Ratio
HFC-236fa	CF <sub>3</sub> CH <sub>2</sub> CF <sub>3</sub>	2	1.87
HFC-236ea	CF <sub>3</sub> CHFCHF <sub>3</sub>	1	1.57
HCFC-123	CHCl <sub>2</sub> CF <sub>3</sub>	1	1.77
HCFC-123a	CHClFCClF <sub>2</sub>	0	1.50
CFC-113a	CCl <sub>3</sub> CF <sub>3</sub>	1	1.76
CFC-113	CCl <sub>2</sub> FCClF <sub>2</sub>	0	1.75
HFC-227ea	CF <sub>3</sub> CHF <sub>2</sub> CF <sub>3</sub>	2	1.55
HFC-227ca	CHF <sub>2</sub> CF <sub>2</sub> CF <sub>3</sub>	1	1.49
HFC-134a	CH <sub>2</sub> FCF <sub>3</sub>	1	1.40
HFC-134	CHF <sub>2</sub> CHF <sub>2</sub>	0	1.34

It has been proposed by others in the past that •CF<sub>3</sub> free radicals can act chemically as fire suppressants. Ab initio molecular orbital calculations indicate that fire suppression by perfluoromethylamines is due, in part, to reactions of the trifluoromethyl radical, which can be

easily released from perfluoroalkyl-amine by dissociation of C-N bonds (Reference 14). The proposed Reactions 2 through 4 are similar to those proposed for bromine in the case of the halons.



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