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# Temperature-Dependent Electron Capture Detector Response to Common Alternative Fluorocarbons

Sonia R. Sousa and Stephen E. Bialkowski*

*Department of Chemistry and Biochemistry, Utah State University, Logan, Utah 84322-0300*

**The relative electron capture detector (ECD) response to alternative fluorocarbons (AFCs) using gas chromatography are found to be at least 1 order of magnitude lower than that for CFC-12. Detection limits for the chlorofluorocarbons CFC-12, HCFC-22, HCFC-123, and HCFC-124 are found to be 2.5, 90, 30, and 90 pg, respectively. Those for the hydrofluorocarbons are significantly poorer; 14 and 45 ng for HFC-125 and HFC-134a, respectively. HFC-152a was not detected using ECD. Since atmospheric concentrations of these compounds are in the low part-per-trillion level, GC-ECD is apparently not sensitive enough to be used for AFC analysis without substantial preconcentration. Two columns are evaluated for the AFC separation. The Poraplot Q WPLOT column showed good separation ability, though column bleed limits detection performance. A Carboxen 1004 packed column exhibits much lower interference. But separations are time consuming and peak broadening adversely affects limits of detection. Mechanisms for the ECD response are proposed based on thermodynamics and temperature-dependent ECD responses. CFC-12, HCFC-123, and HFC-125 apparently undergo ion-forming dissociative electron capture. The electron capture process for HCFC-22 and HFC-134a appear to form molecular ions. Both mechanisms appear to be operative for HCFC-124 electron capture. Dissociative electron capture rate constants for HCFC-123, HCFC-124, and HFC-125 are estimated to be $3.5 \times 10^{-10}$, $1.0 \times 10^{-10}$, and $5.6 \times 10^{-13}$ $cm^3\ s^{-1}$, respectively at 300 °C.**

The production and use of most volatile chlorocarbons is restricted by international agreement because of their contribution to stratospheric ozone depletion.[1−4] The program for the phase-out of use of these compounds in the United States is Title VI of the Clean Air Act Amendments of 1990.[5] To circumvent problems associated with banning these substances, hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs) have been introduced as substitutes. These are collectively referred to as the alternative fluorocarbons (AFCs). The AFC compounds have physical properties similar to CFCs, but the incorporation of hydrogen allows for relatively rapid atmospheric reaction with OH and O ($^1$D). Faster tropospheric reactions predictably result in lower atmospheric lifetime and correspondingly lower fractions entering the stratosphere.[6−8] Production of HFC compounds is unregulated. HCFC compounds are classified as class II substances in the Clean Air Act since they contain chlorine. Production of the later is scheduled to halt by the year 2030.

Predictions regarding the environmental fate of the AFC compounds were summarized by the Alternative Fluorocarbon Environmental Acceptability Study (AFEAS).[8,9] Progress toward understanding the chemistry and toxicology of the degradation products was reviewed.[10] Products thought to occur with the largest yields are the carbonyl and acetyl halides.[11,12] Acid, hydroxide, peroxide, and nitrate degradation products will probably not prevail in high concentration since they are soluble and hydrolyze. Carbonyl halides, CFClO, $CF_2O$, and $CCl_2O$, have been observed in the stratosphere.[13,14] Dissolution is thought to be the main loss mechanism for carbonyl compounds.[8] However, laboratory measurements indicate that the carbonyl halides are not very soluble.[15] Atmospheric lifetimes are estimated to be from 5 to 30 years for $CF_2O$, CFClO, $CF_3C(O)F$, and $CF_3C(O)Cl$ and up to 1500 years for HFCO.[10] It has been suggested that some fluorocarbon radicals, considered as benign to the ozone layer, may actually destroy it through catalytic processes.[16] AFC compounds are effective absorbers of infrared radiation, and increased use may contribute to global warming.[7]

The underlying assumption to the fates of the AFC compounds is that atmospheric chemistry models are accurate enough to predict atmospheric fate based on laboratory measurements. A

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more direct approach is to measure concentrations in situ. There have been relatively few reports of measured atmospheric abundance of AFCs given the potential impact.[17−23] HCFC-22 ($CHF_2Cl$), a refrigerant, has been in use the longest and has received the most attention.[17−20] HCFC-142b ($CH_3CFCl_2$), used since 1988 as a foam blowing agent and a solvent, has also been measured.[17,21,22] Atmospheric concentration trends for the popular refrigerant HFC-134a ($CF_3CH_2F$) have recently been reported.[23] For the most part, these reports indicate higher than expected concentrations.

With the exception of a single passive infrared absorption report,[19] AFC compounds have been detected using gas chromatography with mass spectrometry (GC/MS) operating in mass-selective detection mode. Air samples are collected in either stainless steel or aluminum cylinders and stored for later laboratory analysis. Analysis samples are concentrated prior to GC/MS analysis. Detection requires preconcentration of nearly 1 L of whole-air sample. Preconcentration has been performed using cryogenic trapping techniques. There are problems with this method such as supplying the liquid nitrogen, the cost, and the band broadening that occurs when large volumes of sample are desorbed and introduced into the column. Several researchers have reported the use of "microtraps" with carbonaceous adsorbents to address these problems.[24−26] Simmonds et al.[26] reported on an automated GC/MS instrument for field measurements using both glass bead and carbonaceous adsorbent "microtraps" to concentrate the AFC compounds. Since selective-ion monitoring was not used, several liters of air are required for concentration prior to GC/MS analysis. Problems with this method are that large numbers of potential interferents have to accounted for in the MS data analysis and that the large sample volumes are subject to problems associated with the use of adsorbent traps. The large size of the instrument and the requirement for liquid nitrogen prevent use of this method for true field measurements.

Sturges and Elkins[24] reported on the use of electron capture detection (ECD) with ambient temperature traps for preconcentration. This method has potential for field monitoring due to the relatively small size, the cost, and no need for cryogenics. Speciation would have to be totally accomplished with chromatography, though some selectivity may be attained with the ECD. Sturrock et al.[27] have evaluated several wide-bore capillary columns for use in AFC analysis. Although no single column was perfect, the solid stationary phase columns tested were apparently capable of performing adequate separation of volatile AFC compounds.

The purpose of this study is to evaluate the potential for using the ECD to detect AFCs. The ECD response to the common AFCs are measured relative to that of CFC-12, which is used as an internal standard. We also examine the utility of a Poraplot-Q WPLOT and Carboxen 1004 packed column in the separation of the AFCs when ECD is used. No attempt was made to enhance the ECD signals using oxygen doping.[28,29] This technique has been shown to increase detection limits for some AFC compounds.[24] On the hand, ECD response is known to be affected by detector temperature. We perform a temperature-dependent response study. The temperature-dependent response results allows deduction of the electron capture mechanism and molecular ion thermodynamics.

## EXPERIMENTAL SECTION

**Apparatus.** A Hewlett-Packard Model 5890a gas chromatograph equipped with both a Model G1223A $^{62}Ni$ $\beta$ source, electron capture detector (ECD) and a Model 19231D/E flame ionization detector (FID) is used in this study. The ECD is a potentially hazardous radioactive source and a semiannual wipe test is required to assess its stability. The ECD and FID are used at temperatures of 300 and 250 °C, respectively, except for the ECD temperature-dependent response study described below. The ECD makeup flow rate is 20 mL $min^{-1}$ nitrogen. Gas samples are introduced either by direct injection using the standard splitless injector or by volumetric injection using a Valco, T series, six-port valve with a 10 $\mu$L volume injection loop. The direct injector is maintained at 200 °C for all experiments. The six-port injection valve is mounted in the gas chromatograph oven. Ultrapure nitrogen (Whitmore Oxygen) is used as the carrier and make-up gas. Oxygen trap (Oxy-trap Alltech) and a molecular sieve 40/50 mesh (Hewlett-Packard) are used to purify the gas supply. Carrier and make-up gas flow rate are measured with the Hewlett-Packard electronic flow sensing.

Separations are performed using two columns. The first is a 30 m, 0.53 mm internal diameter WPLOT Poraplot Q (J&W Scientific, CA) column. The stationary phase of the Poraplot Q is a styrene−divinylbenzene copolymer similar in characteristics to the Porapak phase used in packed columns. The second column is a Carboxen 1004 packed column (Supelco). This stainless steel column has a length of 2 m, with 0.75 mm internal diameter. Carrier flow rates are experimentally derived using a Van Deemter plot of data obtained under isothermal conditions. The carrier flow rates used in this study are 5.6 mL $min^{-1}$ for the Poraplot Q column and 9.6 mL $min^{-1}$ for the Carboxen 1004 column. These carrier flow rates are used for isothermal conditions and for the starting temperature with temperature program conditions. Separation of the compounds tested could be achieved isothermally and with temperature programming on the Poraplot Q column. In order to achieve the separation of HFC-125, HCFC-22, and HCFC-124, on the Carboxen 1004 column, a temperature program is used: 80 (1 min) and then 20 °C $min^{-1}$ ramp to the final 220 °C. Resolution was still poor in this case. Analysis time was ~12 min with the temperature program. Quantitative detector response and retention time data are obtained using 200 °C isothermal conditions by injecting each AFC compound in a mixture with CFC-12.

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Table 1. Physical Properties of AFC and CFC Species Used in This Study

| trade name | formula | bp (°C) | molecular mass |
|---|---|---|---|
| CFC-12 | $CCl_2F_2$ | −29.8 | 120.91 |
| HCFC-22 | $CHClF_2$ | −40.8 | 86.7 |
| HCFC-123 | $CF_3CHCl_2$ | 27.6 | 152.90 |
| HCFC-124 | $CF_3CHClF$ | −11.0 | 136.48 |
| HFC-125 | $CF_3CHF_2$ | −48.5 | 119.98 |
| HFC-134a | $CF_3CH_2F$ | −26.2 | 102.0 |
| HFC-152a | $CH_3CHF_2$ | −25.0 | 66.03 |

**Temperature-Dependent ECD Response.** Data for the temperature-dependent ECD response to the tested AFC and CFC compounds is obtained by monitoring the relative response of standardized gas mixtures while varying the ECD temperature from 200 to 350 °C in increments of 30 °C. Separation is performed with the Poraplot Q column under isothermal conditions. Carrier and make-up gas flow rates are also the same as those used in the separation and relative response studies.

**Data Analysis.** The data are acquired with either a Sergent-Welch Model XKR chart recorder or a PC computer with a Metrabyte Model DAS-HRES, 16-bit analog-to-digital converter board. The data collection software is written in Turbo-C (Borland). The data acquisition software records the chromatogram and writes files that may be subsequently analyzed. Chromatogram data are processed using Quattro-Pro (Borland). A 30-point moving average smoothing filter is often used to improve the signal-to-noise ratio (SNR). Peak areas are estimated using triangulation based on peak tangents. Three or more replicate measurements were used to estimate the detector response of each compound. A relative ECD response is defined as the ratio of the peak area of the compound of interest relative to that of CFC-12 at equal injected amounts.

**Reagents and Sample Preparations.** HCFC-22, HCFC-123, HCFC-124, HFC-125, HFC-134a, and HFC-152a were received as a gift-in-kind from AFEAS, furnished by Allied, DuPont, and ICR. The physical and chemical properties of the AFCs and CFCs studied in this paper are given in Table 1. CFC-12 and HCFC-134a was purchased from PCR. A primary CFC-12 standard 10.5 ppm (v/v) in Ar (Matheson) is used as an internal standard for the mixtures. All these compounds are the highest purity available (at least 99%) and used without further purification. The samples are prepared by volumetric dilution of the standards with ultrapure argon (99.999%, Matheson, CA) in two calibrated glass flasks. The flask pressure is maintained at $9.2 \times 10^4$ Pa under Ar. Glass beads are added in order to enhance mixing upon shaking.

## RESULTS

**Separation of the AFC on Poraplot Q and Carboxen 1004.** On Poraplot Q, separation of CFC-12, HCFC-22 and -124, and HFC-125 is obtained with the isothermal temperature of 100 °C. Figure 1 shows a typical chromatogram obtained using the Poraplot Q WPLOT column under isothermal conditions. The elution time order of HFC-125 < HCFC-22 < CFC-12 < HCFC-124 < HCFC-123 follows the boiling points of these substances. Separation of these substance takes ~10 min. However, HCFC-123 is more strongly adsorbed and does not elute in reasonable times at 100 °C. Increasing the temperature decreases the HCFC-123 elution time, but the lower molecular weight substances are not resolved. In addition, significant column bleed occurs at the higher temperatures. A program with an initial temperature of 45 °C for 5 min followed by a 9 °C min$^{-1}$ ramp to 180 °C final temperature was found to produce satisfactory resolution of all components within 16 min. The program also helped reduce detector noise due to column bleed over the majority of this time. Retention times for this temperature program are given in Table 2.

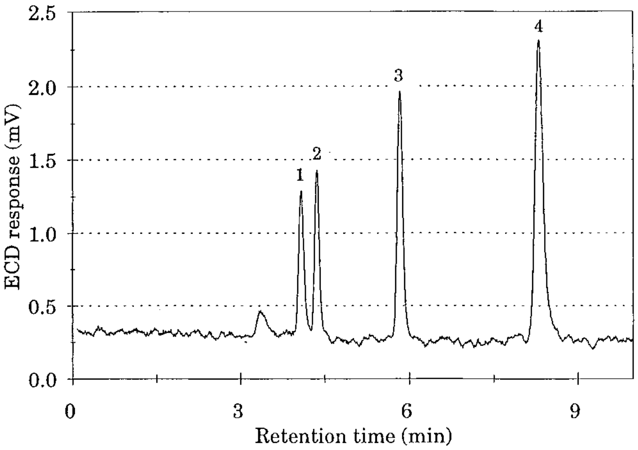

Figure 1. Chromatographic analysis of a mixture of AFC-22, -124, and -125 and CFC-12 on the Poraplot Q with ECD detection and temperature programming. (1) HFC-125; (2) HCFC-22; (3) CFC-12; (4) HCFC-124.

Table 2. Retention Times (Minutes) and Relative ECD Response (300 °C) of the Fluorocarbons Used in This Study[a]

| | retention time | | |
|---|---|---|---|
| compound | Poraplot Q | Carboxen 1004 | rel ECD response |
| CFC-12 | 5.8 | 10.0 | 1 |
| HCFC-22 | 4.7 | 3.5 | $(2.0 \pm 0.3) \times 10^{-2}$ |
| HCFC-123 | 14.3 | 123 | $(1.1 \pm 0.2) \times 10^{-1}$ |
| HCFC-124 | 8.3 | 14.5 | $(3.2 \pm 0.2) \times 10^{-2}$ |
| HFC-125 | 4.0 | 2.1 | $(1.8 \pm 0.1) \times 10^{-4}$ |
| HFC-134a | 4.4 | 2.8 | $(4.7 \pm 0.1) \times 10^{-5}$ |
| HFC-152a | 4.6 | 3.4 | not detected |

[a] Initial Poraplot Q flow rate was 5.6 mL min$^{-1}$. The temperature program was used. Carboxen 1004 flow rate was 9.6 mL min$^{-1}$. Column temperature was 200 °C. An FID was used to obtain the retention time for HFC-152a.

Carboxen 1004 is a porous carbonaceous stationary phase with a high affinity for smaller molecules.[33] All compounds tested on this column are strongly adsorbed, and elevated temperatures are needed to get elution in reasonable times. The elution time order is HFC-125 < HFC-152a < HFC-134a < HCFC-22 < CFC-12 < HCFC-124 < HCFC-123. HCFC-123 is strongly retained even at 225 °C. A temperature program found to resolve HFC-125, HCFC-22, and HCFC-124 is 80 °C for 1 min with a 20 °C min$^{-1}$ ramp to a final temperature of 220 °C. Column bleed is significantly less than found for the Poraplot Q WPLOT column even at the highest temperature (220 °C). The Carboxen 1004 column is not expected to perform as well as the Poraplot Q. The column geometry is less favorable for separation being much shorter, wider, and having a more heterogeneous stationary phase than the WPLOT Poraplot Q.

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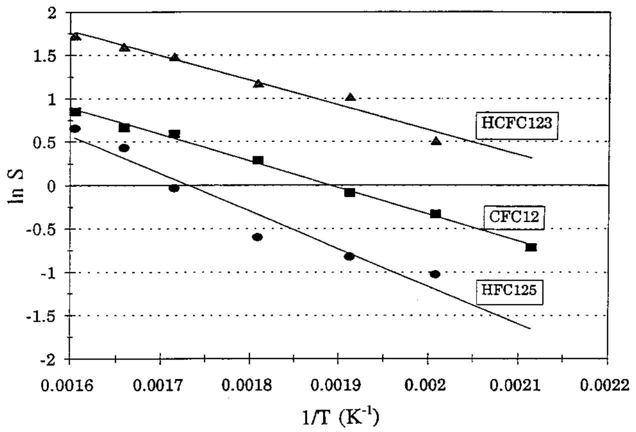

Figure 2. Detector response as a function of inverse temperature from 200 to 350 °C for CFC-12, HCFC-125, and HCFC-123. Injection of 1 $\mu$L of 10.5 ppm (v/v).

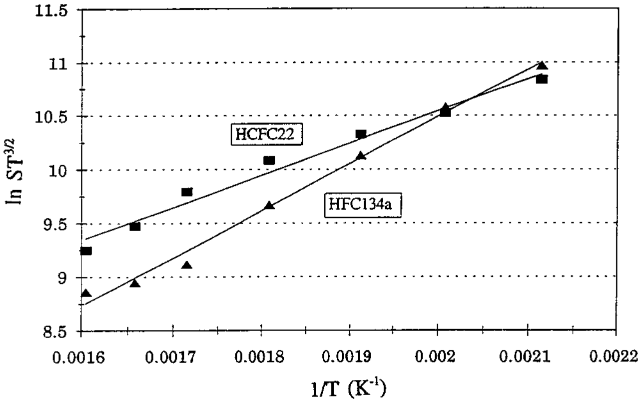

Figure 3. Detector response as a function of inverse temperature from 200 to 350 °C for HCFC-22 and HCFC-134a. Injection of 1 $\mu$L of 42 parts-per-thousand (v/v).

**Relative ECD Response.** Table 2 shows the relative responses of ECD to the AFCs. The relative response is calculated as the peak area ratio of the AFC to that obtained for CFC-12 with equal mole injections. CFC-12 was used as an internal standard to avoid errors due to variation in injection volume. Listed uncertainties are $\pm\sigma$ obtained from replicate measurements.

It is easy to see that the ECD has a much lower response to the AFCs than to CFC-12. The relative response apparently decreases with substitution of hydrogen for chlorine on the molecule, as in the response of HCFC-22 ($CHF_2Cl$) relative to CFC-12 ($CF_2Cl_2$). This trend has been reported in the past.[30] The major trend gleaned from this table is that the relative ECD response decreases with increasing number of hydrogen atoms on the molecule.

**Temperature-Dependent ECD Response.** Data representing the temperature-dependent ECD response are illustrated in Figures 2–4. Each datum represented in the plots is the peak area of the species on the chromatograms. The data are plotted in Arrhenius fashion, i.e., the natural logarithm of the relative peak area as a function of the inverse temperature. Slopes obtained by linear regression are proportional to the activation energy for ion fragmentation or the enthalpy of molecular anion formation. A negative Arrhenius plot slope indicates a dissociative ion fragmentation electron attachment mechanism, whereas a positive slope indicates electron attachment by the resonance mechanism.[31,32]

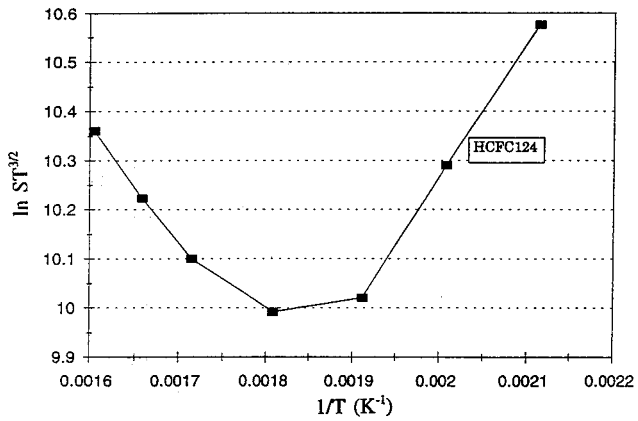

Figure 4. Detector response as a function of inverse temperature from 200 to 350 °C for HCFC-124. Injection of 1 $\mu$L of 1.3 parts-per-thousand (v/v).

As seen in Figure 2, CFC-12 and HFC 125 have negative slopes, indicating that electron attachment occurs by the dissociative mechanism. HCFC-22 and HFC-134a have positive slopes, shown in Figure 3, indicating the electron attachment is due to a reasonable molecular electron attachment mechanism. A complex Arrhenius plot trend for HCFC-124 can be seen in Figure 4. Assuming the trends at the extreme temperatures are lines, the ECD response for this species may be a combination of both molecular ion formation and dissociative mechanisms. In this case, dissociative electron capture occurs at temperatures greater than ~280 °C, and electron attachment is a resonance mechanism at lower temperatures.

## DISCUSSION

**A. Separation of the AFCs on Poraplot Q and Carboxen 1004.** Several types of columns have been evaluated for resolving the AFCs, and no single column is entirely satisfactory.[27] Alumina suffers from a major drawback of inducing a dehydrogenation reaction of smaller HCFCs. Since the degree of the HCl elimination reaction is a function of column temperature and elution time, this stationary phase is not satisfactory for HCFC analysis. It was also shown that the Poraplot Q WPLOT produces good separation of the AFCs.[27] A resolution greater than 1 is observed for all of these compounds. Higher temperatures are required for the timely elution of HCFC-123. Unfortunately, severe column bleeding is observed at temperatures above 200 °C. A temperature program is used to maintain separation between HFC-125 and HCFC-22 while producing timely elution of HCFC-123. The lower, beginning temperature produces band broadening.

Carbonaceous molecular sieves are used as adsorbent for their suitability as concentrating traps for AFCs.[25] Favorable Kovats indices for AFC separation on hexafluoropropylene-modified carbonaceous phase,[33] and the reported high affinity of carbonaceous phases toward fluorocarbons, prompted us to test the relatively new Carboxen 1004 packed column stationary phase as a potential column for AFC separation.[33] Another reason for testing this column is that column bleed could be lower than that observed for the polymer phases, thus lowering detection limits. In fact, negligible column bleed was observed, even at the highest operating temperatures. This suggests that temperature programming could be used to separate all the components of interest: AFC-125, -152a, -22, -12, -124, and -123. We observed poor resolution from the attempt to separate the AFCs. The highest

$R$ value obtained was 0.56. HFC-123 is strongly retained on this column, rendering quantitative analysis impractical. This has been observed using Carboxen 1000 and 1003 adsorbents trap.[25] Temperatures in excess of 260 °C are necessary to desorb HCFC-123. These results can be justified by the fact that all these stationary phases have a large surface area, 1200 and 750 $m^2/g$ for the Carboxen 1000 and the Carboxen 1004, respectively, and strong interactions between the solute and the adsorbate have been shown to occur.[25] In the end, our attempt to obtain better detection limits was not successful. Detection limits were not improved because the peaks were much broader than those obtained using the Poraplot WPLOT column.

**B. Mechanisms for AFC ECD Response.** The instrumental response of an ECD is directly related to the number of electrons removed from the gas by capture processes.[31] Although several individual factors like the cross section for electron collision, electron affinity, unimolecular ion reactions, and cation/anion reactions are all important in interpreting absolute response, it is easier to interpret the response by simpler general mechanisms prior to describing the details. The temperature-dependent response can yield definitive information in this regard.

A general mechanism for alkyl halide electron capture is[32]

$$\mathrm{AX} + e^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{AX}^- \xrightarrow{k_2} \mathrm{A} + \mathrm{X}^- \qquad (1)$$

where X is a halogen. Halide, $X^-$, production is not energetically favorable for fluorine and may be unfavorable for chlorine as well. When the rate of halide production, the $k_2$ process, is slow on the time scale of the ECD measurement, electron capture is essentially an equilibrium between the molecule and the molecular anion, $AX^-$. The ECD response is proportional to the ratio of forward, $k_1$, to reverse $k_{-1}$, rate constants comprising the equilibrium constant $K = [AX^-]/[AX][e^-]$. In the linear operating range of the detector, electron concentrations are much greater than that of the ion or molecule. The ECD response is proportional to $[AX^-] = K[AX][e^-]$. Thus, larger $K$ result in greater relative signals. Large ECD responses are often observed for species that stabilize the captured electron in resonant orbitals, e.g., alkyl fluorocarbon and aromatic compounds.

Equilibrium allows connection to the thermodynamics of molecular ion formation. The enthalpy for electron attachment may be estimated from the slope of Arrhenius plots of $\ln[ST^{3/2}]$ vs inverse temperature,[31,32] where $S$ is the ECD signal. The electron attachment mechanism is indicated for a positive Arrhenius plot slope. In this case $d\ln[ST^{3/2}]/d(1/T) = -\Delta H/k$, where $k$ is Boltzmann constant.

When the rate for halide production from the molecular anion is fast, the free electron is efficiently captured by dissociative halide production.[31] In this case, the rate-limiting step is often the rate at which halide ions are produced, essentially, $k_2$. An Arrhenius plot of $\ln[S]$ versus inverse temperature is more appropriate.[32] The dissociative electron attachment mechanism is indicated by a negative Arrhenius plot slope. In this case $d\ln[S]/d(1/T) = E_A/k$, where $E_A$ is the activation energy for halide production.

ECD is particularly sensitive to chlorofluorocarbons. This may be due to favorable thermodynamics for chloride ion formation. In the case of CFC-12, a thermodynamically favorable mechanism is the multiple-step process

$$\mathrm{CF_2Cl_2} + e^- \rightleftharpoons \mathrm{CF_2Cl_2^-} \qquad \Delta H° = -5.4\ \mathrm{kcal/mol} \quad (2)$$

$$\mathrm{CF_2Cl_2^-} \rightarrow \mathrm{CF_2Cl\cdot} + \mathrm{Cl^-} \qquad \Delta H° = +3.1\ \mathrm{kcal/mol} \quad (3)$$

$$\mathrm{CF_2Cl\cdot} + e^- \rightleftharpoons \mathrm{CF_2Cl^-} \qquad \Delta H° = -37\ \mathrm{kcal/mol} \quad (4)$$

$$\mathrm{CF_2Cl^-} \rightarrow \mathrm{CF_2} + \mathrm{Cl^-} \qquad \Delta H° = +2.5\ \mathrm{kcal/mol} \quad (5)$$

Overall, the heat of reaction to produce two chlorides is −34.5 kcal/mol. However, the first dissociation, eq 3, is significantly endothermic relative to $kT$ (~1.1 kcal/mol at 300 °C). If energy from electron capture in eq 2 is lost by collision faster than chloride dissociation, this step may limit the overall rate for efficiency electron capture. The negative slope obtained in the Arrhenius plot shown in Figure 2 is consistent with a forward reaction rate-limiting step. The slope indicates an Arrhenius activation energy of $E_A = 6$ kcal/mol over the limited temperature range of this study. The activation energy is based on the assumption that $k_2 \gg k_1$ and is thus the activation energy for eq 3. This value is in reasonable agreement with values of $E_A$ between 3.4 and 3.6 kcal/mol reported previously.[34]

HCFC-123 ($CF_3CHCl_2$) exhibits ~1 order of magnitude lower ECD response than CFC-12. Both molecules possess the same number of chlorine atoms. In fact, based on the number of fluorine atoms, HCFC-123 might be predicted to have an ECD response greater than that of CFC-12. The overall lower ECD sensitivity, compared to CFC-12, may be explained by the fact that the electron-withdrawing, and thus bond-weakening, effect of fluorine at the labile C−Cl bond is reduced in HCFC-123 because the fluorines are on an adjacent carbon atom. This lowers the relative ECD response compared to chlorofluorocarbons with the same number of chlorine atoms by strengthening the C−Cl bond energy. In fact, a higher activation energy is expected due to the increased bond strength.

The Arrhenius plot for the ECD response is shown in Figure 2. As with CFC-12, the negative slope is indicative of dissociative electron capture. If loss of the first chloride is the rate-limiting step for electron capture, the lower response may be attributed to the fact that the first C−Cl bond strength could be higher than that in CFC-12 due to hydrogen and carbon substituents on the carbon with chlorine. For example, the first C−Cl bond enthalpy increases with number of hydrogens in the $CH_xCl_{4-x}$ chloromethane series. The higher C−Cl bond strength would increase the minimum activation energy for molecular ion dissociation producing chloride ion, thereby decreasing the ECD response at a given temperature.

The regression slope indicates an activation energy of $E_A = 7.3$ kcal/mol. Assuming that the activation energy is the energy required for loss of the first chloride, the heat of formation of the $CF_3CHF$ radical may be estimated from the dissociative capture mechanism

$$\mathrm{CF_3CHCl_2} + e^- \rightarrow \mathrm{CF_3CHCl\cdot} + \mathrm{Cl^-} \qquad \Delta H = +7.3\ \mathrm{kcal/mol} \quad (6)$$

where the apparent heat of reaction is that determined from the

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[34] Smith, D.; Adams, N. G.; Alge, E. *J. Phys. B: At. Mol. Phys.* **1984**, *17*, 461−472.

Arrhenius plot activation energy. Based on this, and the heats of formation of HCFC-123 and chloride, the heat of formation of the $CF_3CHF$ radical is $\sim -114$ kcal/mol.

The enthalpy for chloride ion production from HCFC-22 ($CHClF_2$) electron capture is slightly endothermic

$$CHF_2Cl + e^- \rightarrow CHF_2\cdot + Cl^- \qquad \Delta H^\circ = 0.5\ \text{kcal/mol} \quad (7)$$

An ECD response on the same order of magnitude as CFC-12 might be expected on the basis of reaction enthalpy alone. However, as shown in Table 2, the relative ECD response to this compound is a factor of 50 less than that for CFC-12. In addition, the Arrhenius plot shown in Figure 3 exhibits a positive slope, indicating that molecular electron attachment is not followed by chloride ion formation. The activation energy for chloride ion production is apparently greater than the electron affinity of HCFC-22. In this case, the slope of the Arrhenius plot ($\ln[ST^{3/2}]$ vs $1/T$) is related to the enthalpy for molecule electron capture. The positive slope indicates an enthalpy for electron capture of $\Delta H = -6.1$ kcal/mol. This places the heat of formation for the $CHClF_2^-$ ion at $\Delta H = \sim -121.7$ kcal/mol.

HCFC-124 ($CF_3CH_2Cl$) has a relative response similar to HCFC-22 at 300 °C. However, the Arrhenius plot in Figure 4 shows a complex thermal behavior for electron capture. The slope is negative slope at high temperatures and becomes positive at low temperatures. This behavior is indicative of the electron capture mechanism of eq 1, but with competition between the back reaction producing the neutral and an electron, and stable anion formation by dissociation of the molecular ion.[31] At low temperatures, the temperature-dependent response is that for molecular ion formation. As the detector cell temperature is increased, more energy is available; thus the production of a stable ion, perhaps $Cl^-$, increases.

ECD response to the HFCs should not be due to a dissociative mechanism. Because of the relatively high C−F bond strength, electron capture cannot lead to stabilization via fluoride ion formation.[35] As shown in Table 2, ECD response to HFC compounds decreases in the order: HFC-125 ($CF_3CF_2H$) > HFC-134a ($CF_3CFH_2$) ≫ HFC-152a ($CH_3CHF_2$). The response is clearly related to the number of fluorides on the substituted ethane. HFC-125 and HCFC-134a have trifluoromethyl groups, which may help stabilize the captured electron relative to over HFC-152a.

ECD response to HFC-125 ($CF_3CHF_2$) is nearly 4 orders of magnitude lower than that for CFC-12. The Arrhenius plot shown in Figure 2 indicates an activation energy, $E_A = 8.6$ kcal/mol for electron stabilization, even in the lower temperature range. It is doubtful that electron stabilization occurs by a direct (two-center) dissociative mechanism because the ion-forming reactions are highly endothermic;

$$\begin{aligned} CF_3CF_2H + e^- &\rightarrow CF_3^- + CHF_2^\bullet && \Delta H^\circ = 49.9\ \text{kcal/mol} \\ CF_3CF_2H + e^- &\rightarrow CF_3CF_2^- + H^\bullet && \Delta H^\circ = 61.1\ \text{kcal/mol} \\ CF_3CF_2H + e^- &\rightarrow CF_3^\bullet + CHF_2^- && \Delta H^\circ = 124.6\ \text{kcal/mol} \end{aligned} \quad (8)$$

Table 3. Heats of Formation (kcal/mol) of Halocarbons and Atoms at Standard State (298.15 K)[a]

| | $\Delta H_f^\circ$ | | | $\Delta H_f^\circ$ | |
|---|---|---|---|---|---|
| molecule | neutral | anion | fragment | neutral | anion |
| $CF_2Cl_2$ | −117.90 | −123.33 | $CF_3$ | −111.7 | −154.9 |
| $CHF_2Cl$ | −115.6 | | $CHF_2$ | −59.2 | −27.7 |
| $CF_3CHCl_2$ | −177.0 | | $CH_2F$ | −7.8 | |
| $CF_3CHFCl$* | −207.8 | | $CH_3$ | 34.8 | 139 |
| $CF_3CHF_2$ | −264.0 | | $CF_2Cl$ | −66.0 | −103.0 |
| $CF_3CH_2F$ | −214.1 | | $CF_3CF_2$ | −213.0 | −255.0 |
| $CH_3CHF_2$ | −119.7 | | $CF_3CHF$ | −162.7 | |
| $CF_2CF_2$ | −157.4 | | $CF_2$ | −44.6 | −102.0 |
| $CHFCF_2$ | −117.4 | | CHF | 39.0 | <27.0 |
| HF | −65.13 | | H | 52.1 | 33.2 |
| | | | F | 18.36 | −59.5 |
| | | | Cl | 29.0 | −55.9 |

[a] Heats of formation are from ref 43, the NIST WWW CKMech database, or the JANAF tables except for (*), which are estimated using HyperChem with the semiempirical AM1 method.

A four-center HF elimination step

$$CF_3CF_2H + e^- \rightarrow CF_2CF_2^- + HF \quad (9)$$

may be possible. The neutral reaction

$$CF_3CF_2H \rightarrow CF_2CF_2 + HF \qquad \Delta H^\circ = 41.5\ \text{kcal/mol} \quad (10)$$

requires relatively less energy to proceed. If the electron affinity of $C_2F_4$ is sufficiently high, then this reaction might be responsible for the positive activation energy. Perfluoro-2-butene and 1-(trifluoromethyl)-1-difluoroethane apparently form very stable molecular anions,[36] indicating a high electron affinity. The electron affinity for $C_2F_5$ and $C_2F_3$ are in the −41 to −55 kcal/mol range. On the other hand, positive electron attachment activation energies have been observed for some compounds.[34,37,38] It is possible that the measured activation energy is that required for molecular electron capture. In fact, positive activation energies are observed for perfluoromethylcyclohexane molecular electron capture.[38,39] (See Table 3.)

HFC-134a has an ECD response that is nearly 5 orders of magnitude less than that for CFC-12. In addition, the Arrhenius plot exhibits a positive slope, indicating a direct electron attachment mechanism

$$CF_3CH_2F + e^- \rightleftharpoons CF_3CH_2F^- \quad (11)$$

The slope of the Arrhenius plot indicates an enthalpy for electron attachment of $\Delta H = -10.3$ kcal/mol. The heat of formation of the molecular anion is thus estimated to be $\Delta H_f = -223$ kcal/mol at 300 K.

A question arises regarding why the ECD response is so much lower for the HFC than for CFC-12. The −10.3 kcal/mol electron

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attachment enthalpy for HFC-134a is significant compared to $kT$ at 300 °C. One plausible explanation for the low relative response is that the molecular anions react with $N_2^+$, present in the ECD detector, producing free electrons. This type of reaction has been observed for larger fluoroalkanes.[38]

**C. Detection Limits.** Detection limits are estimated based on signals produced for the relatively high injection amounts and the baseline noise of a chromatogram. The noise is primarily due to column bleed. A SNR of 3 is used to estimate the detection limit. The detector is assumed to respond linearly down to the detection limit. The 10 $\mu$L sample loop was used to inject 9.9 ppm (v/v) primary CFC-12 standards onto the Poraplot column at 100 °C. The resulting ECD peak and baseline were analyzed with the spread sheet program. SNRs based on both the peak height to baseline noise standard deviation and the integrated area to integrated baseline standard deviation were obtained. SNRs of 510 and 80 were obtained for peak height and peak area measurements, respectively. These correspond to SNR = 3, CFC-12 mass detection limits of 2.5 pg for peak height and 16 pg for peak area using the ECD. Although integrated peak area is normally expected to yield higher SNR, excessing baseline drift and noise due the column resulted in lower SNR, even for this ideal case. If baseline drift were perfectly reproducible, the minimum extrapolated detection obtained from the noise alone would be 14 fg.

Based on the LOD for CFC-12, and the relative responses of the AFC, mass detection limits for HCFC-22, -123, and -124 are 90, 30, and 90 pg, respectively. The HFC mass detection limits are considerably higher, 14 and 45 ng for HFC-125 and -134a, respectively. These results are worse than those of Vidal-Madjar et al.[40] Their ECD mass detection limits for CFC-11 are 75 fg in pulsed detector mode, 250 ft in dc mode, corrected for a SNR of 3. A mass detection limit for CFC-12 of 1.6 pg for dc detector mode is estimated based on their data. However, these detection limits were extrapolated by assuming constant baseline noise. Our detection limits for HCFC-123 and HFC-134a are comparable to those of Sturges and Elkins.[24] Mass detection limits of 12 and 410 pg for HCFC-123 and HFC-134a, respectively, may be obtained from the pulsed mode ECD concentration detection limits reported in the later paper. Although it is possible to enhance ECD sensitivity to halocarbon species with hydrogen, using oxygen in the makeup gas of the ECD detector,[29] the noise level is also enhanced. Sturges and Elkins found that detection limits for HCFC-123 were better without oxygen due to the increased noise level associated with oxygen.

**D. Electron Capture Rates and Atmospheric Fat.** The ECD can be used to measure the relative dissociative electron capture rate constant using a calibration compound for which the electron capture rate constant is known.[32] The conditions have to be such that the compound concentration is not significantly depleted by the dissociative electron capture reaction itself. The later is created by using a fast pulse rate. The measured response should be proportional to the rate constants. Although the Hewlett-Packard ECD detector operates in a variable pulse rate mode, the relative AFC signals were adjusted by changing the relative concentration such that maximum signals were about the same as that for CFC-12. Thus, the detector pulse rates were similar for the all compounds. Dissociative capture rate constants may be estimated in this case.

Smith et al. reported a rate constant of $3.2 \times 10^{-9}$ cm$^3$ s$^{-1}$ for dissociative electron capture by CFC-12 ($CCl_2F_2 + e^- \rightarrow CClF_2 + Cl^-$) at 300 K.[34] Based on this rate constant, and the relative response of the AFCs found to capture electrons by a dissociative process in Table 2, reaction rate constants for HCFC-123, HCFC-124, and HFC-125 are $3.5 \times 10^{-10}$, $1.0 \times 10^{-10}$, and $5.6 \times 10^{-13}$ cm$^3$ s$^{-1}$, respectively, at 300 °C. These rate constants can be extended to other temperatures with the activation energies. These rate constants probably describe the decomposition after capturing a free electron since the temperature-dependent response studies indicate dissociative electron capture for these compounds.

The CFC and AFC compounds may react with free electrons present in the atmosphere, thus initiating the destruction of these compounds. In fact, the role of electron capture-initiated decomposition has been reported to be a major decomposition route in considerations regarding the fate of long-lived halogenated compounds.[36,41] Although ions are found throughout the atmosphere, electron densities are significant only above 50−60 km. To predict the destruction of the AFCs in the mesosphere, the mechanism by which the molecule captures the electron needs to be considered. Compounds such as CFC-12, HCFC-123, HCFC-124, and HFC-125, which apparently undergo rapid dissociative electron capture, would readily decompose in an electron-rich environment.

The fate of compounds that apparently form stable molecular anions is more complicated since electron capture does not alone lead to decomposition. The reaction of the molecular ion with cations, in this case $N_2^+$, produced by $\beta$ collisions, complicates the assessment of the degree to which electron capture will decompose the molecule. Culbertson and Grimsrud have shown that a large fraction of the perfluoromethylcyclohexane anion is converted back to the neutral through reaction with cations present in an ECD.[38] They proposed that the atmospheric chemistry of species that form stable molecular anions is determined by the recombination of the anions with positive ions by

$$M^- + p^+ \rightarrow M + p \tag{12}$$

$$M^- + p^+ \rightarrow P + \text{neutrals} \tag{13}$$

where $p^+$ is a positive ion. Equation 12 indicates that the molecule is regenerated to the original molecule. In eq 13, molecular ion reaction produces new product compound and, thus, degradation. For compounds such as HCFC-22, HCFC-124 (at low temperatures) and HFC-134a, recombination with positive ions could convert the molecular anion to the original molecule or result in new species. The branching ratio to produce the parent neutral can be high.[38]

Contributions to the atmospheric decomposition of species that decompose upon capturing an electron may be extremely low. The lifetime of $SF_6$ due to dissociative electron capture has been estimated as being greater than 600−800 years.[42] The rate constant for $SF_6$ is much greater than that of the AFC compounds studied here. The estimated rate constants for HCFC-123 and

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HCFC-124 are on the order of $10^{-10}$ cm$^3$ s$^{-1}$ while HFC-125 is on the order of $10^{-13}$ cm$^3$ s$^{-1}$. By comparison, the electron attachment rate constant for $SF_6$ is $3.1 \times 10^{-7}$ cm$^3$ s$^{-1}$ at 300 K. Assuming that the atmospheric lifetime is inversely proportional to the rate constant, the lifetime of AFC compound would be from 3 to 6 orders of magnitude greater than that of $SF_6$, or from $10^6$ to $10^9$ years if electron capture were the only decomposition route. The tropospheric lifetime of the AFC compounds based on OH and O($^1$D) are estimated to be between ~2 years, for HCFC-123, and ~20 years, for HCFC-22.[6,8] Clearly, dissociative electron capture decomposition plays a minor role at best in the decomposition of the AFC species.

## CONCLUSION

The maximum atmospheric concentration of the AFC compounds may only on the order of a few parts-per-trillion (ppt). Assuming that atmospheric concentrations of these species have reached steady state due to vertical and horizontal mixing, that steady-state concentrations are inversely proportional to atmospheric lifetime, $\tau$, and that AFC release rates will equal the past CFC-11 rates

$$C_{\mathrm{AFC}} = C_{\mathrm{CFC-11}}(\tau_{\mathrm{AFC}}/\tau_{\mathrm{CFC-11}})$$

The atmospheric lifetime of CFC-11 is ~60 years. AFC concentrations can be found from estimates of atmospheric lifetimes based on the reaction with OH, O ($^1$D), and vertical migration.[29] Future global concentrations for AFCs are as follows (ppt, v/v): HCFC-22, 90; HCFC-123 10; HCFC-124, 40; HFC-125, 170; HFC-134a, 110; and HFC-152a, assuming that the AFCs will be used in the same capacities and amounts of CFC-11. By comparison, Irion et al.[20] found 1993 CFC-22 concentrations to be ~115 ppt (v/v) and increasing at ~6.6% year$^{-1}$. HCFC-22 has not been in use for as long as the CFCs though its concentration is relatively high. However, Montzka et al.[18] found that global averaged concentrations are consistent with an atmospheric lifetime of 13.6 years, which is, in fact, significantly shorter than most model predictions based on the reaction rate constants used to obtain the estimates given above.[6] HCFC-22 is apparently vented at greater rates than have the CFC compounds. Thus, our simple estimation calculation above is conservative in that real future concentrations will probably be higher.

Table 4. Mass Detection Limit Estimates Based on a Signal-to-Noise Ratio of 3 for 300 °C ECD with Poraplot Q Column

| compound | LOD (pg) | concn LOD for 1 L sample |
|---|---|---|
| CFC-12 | 2.5 | 0.2 ppt (v/v) |
| HCFC-22 | 90 | 9.7 ppt (v/v) |
| HCFC-123 | 30 | 1.8 ppt (v/v) |
| HCFC-124 | 90 | 6.1 ppt (v/v) |
| HFC-125 | 14 | 1.1 ppb (v/v) |
| HFC-134a | 45 | 4.1 ppb (v/v) |
| HFC-152a | nd[a] | nd[a] |

[a] nd, not detected.

Our mass detection limits indicate that the ECD may be adequate for quantitation of the HCFC compounds if preconcentration is used. Shown in Table 4 are concentration detection limits for the AFC compounds for a 1 L sample size, assuming complete recovery from preconcentration. Concentration detection limits in the low ppt range should be adequate. These indicate that from 10 to 100 L samples would have to be used to reach the limit of quantitation (10$\sigma$) for the HCFCs. The present atmosphere contains less of the newer HCFC compounds, so preconcentration of over 100 L is needed for quantitation. There is an apparent need for better selective detection if the AFC concentrations are to be monitored to in our changing atmosphere.

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