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**High Voltage Research (Breakdown
Strengths of Gaseous and Liquid
Insulators) and Environmental
Effects of Dielectric Gases**

**Semiannual Report
(October 1, 1979—March 31, 1980)**

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Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road, Springfield, Virginia 22161
NTIS price codes—Printed Copy: A06; Microfiche A01

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Contract No. W-7405-eng-26

Health and Safety Research Division

Atomic, Molecular and High
Voltage Physics Group

HIGH VOLTAGE RESEARCH (BREAKDOWN STRENGTHS OF
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Date Published: August 1980

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ABSTRACT

The electron attachment rates for 1,1-C₂Cl₂H₄ in Ar and for 1,1-C₂Cl₂H₄ in N₂ were measured as functions of E/P for several temperatures from 298 to 473 K. From these data in Ar the attachment cross section has been calculated as a function of electron energy for 1,1-C₂Cl₂H₄ and the data in N₂ are being similarly processed. The measurements of electron attachment rates for n-C₆F₁₄ in Ar were extended to higher pressures.

The calculation of field-induced detachment transition probabilities, addressing the possible role of field detachment in breakdown, has been completed and presented at the Second International Symposium on Gaseous Dielectrics.

To address the lack of standardized lab test techniques for gaseous dielectrics we calculated the potentials and field lines for hyperboloidal electrodes. These are suggested because the electrode shape and fields are known, and field nonuniformity can be varied by varying one parameter.

Continuing basic studies of dipolar gases as potential moderators in dielectric mixtures, we calculated for each of CHF₃, 1,1,1-CH₃CF₃, and CH₃CN both the average momentum transfer cross section over a 298 K maxwellian electron distribution, as well as the momentum transfer cross section as a function electron energy. These calculations were made from measurements of drift velocity vs E/P.

To test further the effect of dipole moment on breakdown inhibition we tested a gas, CH₃CN, with a dipole moment (3.92 debye) larger than others previously used. Its breakdown strength was found to be much

higher than those of the earlier dipolar gases (~ 0.8 times that of SF_6). Some preliminary breakdown measurements were made on mixtures of CH_3CN as a moderator with the electron attaching components SF_6 and $\text{c-C}_4\text{F}_8$, and some mixtures had dielectric strengths greater than those of the respective components.

Breakdown tests were also performed on two other new gases, viz. $(\text{CF}_3)_2\text{S}$ and 3,3,3- $\text{C}_3\text{H}_3\text{F}_3$. The $(\text{CF}_3)_2\text{S}$ was found superior to SF_6 .

An initial study of the fragmentation of $\text{n-C}_6\text{F}_{14}$ under electron impact revealed at least nine negative ions at low energies. Unlike other perfluorocarbons studied previously whose parent ions formed at thermal energies, the parent ion $\text{n-C}_6\text{F}_{14}$ formed around 0.4 eV.

Binary mixtures of SF_6 with $\text{c-C}_4\text{F}_8$ and 2- C_4F_8 were studied for carbon inhibition by sparking them and monitoring CF_4 and solid products. Carbon inhibition was optimum for proportions approximately 70% SF_6 and 30% perfluorocarbon.

Quadrupole mass spectrometer analysis of sparked SF_6 continued with negative spark, various electrode to aperture distances and various pressures. Ions of both polarities are seen, and only the negative ions consist of both fast and slow species. From ion arrival time spectra, energy spectra were calculated. To better explain the results we have added a time-of-flight analyzer in the system, a retarding grid capability, and an isolated aperture.

Mixtures of SF_6 , $\text{c-C}_4\text{F}_8$, and N_2 were further tested under impulse conditions, at different pressures. The initial introduction of small proportions of $\text{c-C}_4\text{F}_8$ to the mixtures greatly affects the choice of

pressure range for corona stabilized breakdown, which could be quite advantageous in applications.

In cylindrical geometry breakdown tests, CHF_3 was used as a moderator in binary mixtures with the electron attaching gases SF_6 , $\text{c-C}_4\text{F}_8$, and $\text{2-C}_4\text{F}_8$. Electrode surface roughness varied (smooth to 0.051 cm grooves), as did pressure (from atmospheric to industrial values). Nitrogen was also tested as a moderator at higher pressure with these attachers and electrode conditions. CHF_3 was found to be generally better than N_2 as a moderator, especially with a highly electron attaching fluorocarbon or with rough surfaces.

The possible effects of bubbles and dipole moment are under study in the liquid breakdown tests. It was found that SF_6 at various pressures above the liquid $\text{n-C}_6\text{F}_{14}$ had no significant effect on the liquid breakdown strength. Three isomers of liquid $\text{C}_6\text{H}_4\text{F}_2$ were tested since they are similar except for dipole moment. Preliminary results show that higher breakdown strengths result with lower dipole moment in these liquids.

I. BASIC STUDIES OF GASEOUS DIELECTRICS

A. Temperature Dependence of Electron Attachment to Halocarbons

In collaboration with Drs. D. L. McCorkle and I. Szamrej of the Department of Physics of the University of Tennessee, Knoxville, an investigation has been undertaken of the temperature dependence of electron attachment to dielectric halocarbons. Specific results have been obtained for 1,1- $\text{C}_2\text{Cl}_2\text{H}_4$ using the electron swarm method.

Electron attachment rate constants, α_w , were measured for small concentrations of 1,1- $\text{C}_2\text{Cl}_2\text{H}_4$ in mixtures with argon and nitrogen as a function of the pressure-reduced-electric field, E/P_{298} , and gas temperature, T , from 298 to 473 K. In Figs. 1 and 2 are shown α_w for 1,1- $\text{C}_2\text{Cl}_2\text{H}_4$ in mixtures with N_2 and Ar, respectively, as a function of mean electron energy for several gas temperatures. The rate constants in Ar show a pronounced maximum at ~ 1.0 eV and the energy at which this maximum occurs decreases with increasing gas temperature. Also, the magnitude of the rate constants increases with increasing temperature. By comparing the data in Figs. 1 and 2 it is seen that the α_w for 1,1- $\text{C}_2\text{Cl}_2\text{H}_4$ are more pronounced in mixtures with N_2 than in those with Ar. Due to electric-field limitations, the rate constants in N_2 could be measured only to a mean electron energy of ~ 0.8 eV. The measured rates were found to be independent of 1,1- $\text{C}_2\text{Cl}_2\text{H}_4$ concentration and the Ar or N_2 pressure.

The attachment rate constants were measured at room temperature (~ 298 K) also and fall $\sim 20\%$ below those at 323 K. The room temperature data, however, were considered too uncertain due to the absorption of

Fig. 1. Electron attachment rate constant vs mean electron energy for 1,1- $\text{C}_2\text{Cl}_2\text{H}_4$ in N_2 at several temperatures.

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Fig. 2. Electron attachment rate constant vs mean electron energy for 1,1-C₂Cl₂H₄ in Ar at several temperatures.

the 1,1-C₂Cl₂H₄ molecules to the walls of the chamber. For this reason these data are not plotted in the figure.

Using an unfolding procedure described previously¹, and the α_w measured in mixtures with Ar (Fig. 2), the electron attachment cross sections, $\sigma_a(\epsilon)$, at five temperatures from 333 to 473 K were determined. These are shown in Fig. 3. Each cross section shows a pronounced maximum at ~ 1.2 eV and a shoulder at ~ 0.8 eV. The energy positions of the maximum and the onset of $\sigma_a(\epsilon)$ shift to lower energy with increasing gas temperature. The unfolding of $\sigma_a(\epsilon)$ for 1,1-C₂Cl₂H₄ using the electron attachment data in mixtures with N₂ is in progress.

Although the analysis of these results is as yet incomplete, several tentative conclusions can be reached. We find good correlation between the positions of the maximum and the shoulder in the $\sigma_a(\epsilon)$ that we obtained, and the positions of the maxima in the Cl⁻ current obtained, in electron-impact studies using mass analysis². Johnson et al.² found a maximum in the Cl⁻ current at 1.1 eV and a shoulder at 0.8 eV. A smaller peak was also observed² in the Cl⁻ current at 0.20 eV. The agreement between the electron swarm and the electron beam data suggests that the electron attachment rates we observe in the swarm are due to the same dissociative attachment process yielding Cl⁻ which Johnson et al.² detected in their electron beam studies.

The maximum at 1.2 eV and the shoulder at ~ 0.8 eV in the $\sigma_a(\epsilon)$ can be interpreted in two ways. Firstly, they can be due to excitation and subsequent dissociation from the ground state of the 1,1-C₂Cl₂H₄ molecule to two separate repulsive negative-ion states of this molecule. These two final states would be closely separated in energy by ~ 0.4 eV.

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Fig. 3. Electron attachment cross section vs electron energy in 1,1-C₂Cl₂H₄ at several temperatures.

The second possibility involves two initial vibrational states of the ground electronic state of the neutral molecule and one final repulsive state of the anion. The two vibrational states are thought to be associated with the C-Cl stretching vibration and are separated in energy by 0.08 eV. The fractional concentration of neutral molecules in the $\nu=1$ vibrational level increases from 6 to 14% when the temperature is increased from 323 to 473 K. In this interpretation, the maximum in $\sigma_a(\epsilon)$ at ~ 1.2 eV and the shoulder at 0.8 eV would be due to transitions to a repulsive negative-ion state from the $\nu=0$ and $\nu=1$ levels, respectively, of the ground electronic state of the 1,1- $\text{C}_2\text{Cl}_2\text{H}_4$ molecule. The $\sigma_a(\epsilon, T)$ which we determine at each temperature, then, would represent a weighted (by the fractional concentration of the molecules in each vibrational state) sum of cross section contributions from the $\nu=0$ and $\nu=1$ initial states.

A complete analysis is currently in progress.

B. Electron Scattering Cross Sections at Subexcitation Energies for Dipolar Molecules

Electron scattering cross sections for the dipolar molecules CH_3CN , 1,1,1- CH_3CF_3 , and CHF_3 have been estimated using electron drift velocity data at thermal energies. Figure 4 shows the measured[#] drift velocity, w , as a function of E/P for CHF_3 and 1,1,1- CH_3CF_3 . From the data in Figure 4 the slope S ($\equiv \frac{w}{E/P}$) of the w vs E/P plot in the region where w varies linearly with E/P was determined and is given in table 1.

[#]These measurements were made by D. V. Maxey.

Fig. 4 Measured electron drift velocities for CHF_3 and for $1,1,1\text{-CH}_3\text{CF}_3$ vs E/P .

Table 1 Values of D , A_I , $\langle \sigma_m(v) \rangle_{\text{exp}}$, and S for CHF_3 , $1,1,1\text{-CH}_3\text{CF}_3$ and CH_3CN

Compound	D (debye)	A_I ($\text{cm}^4 \text{ s}^{-2}$)	$\langle \sigma_m(v) \rangle_{\text{exp}}$ (10^{-14} cm^2)	S (a) ($10^4 \text{ cm}^2 \text{ torr V}^{-1} \text{ s}^{-1}$)
CHF_3	1.65	5.83	12.9	13.3(b)
1,1,1- CH_3CF_3	2.32	9.95	22.0	7.8(b)
CH_3CN	3.92	19.69	43.6	3.94(c)

(a) $T \approx 298 \text{ K}$

(b) Determined from recent w vs E/P measurements by D. V. Maxey for E/P
 $\lesssim 1.2 \text{ Vcm}^{-1} \text{ torr}^{-1}$.

(c) Reference 4.

The slope for CH_3CN has been determined in earlier studies and is also given in Table 1. Using the measured values of S we determined the average value, $\langle\sigma_m(v)\rangle_{\text{exp}}$ of the momentum transfer cross section, $\sigma_m(v)$, over a maxwellian ($T=298\text{ K}$) function and also $\sigma_m(v)$ itself as a function of electron velocity from the formulae^{3,4}.

$$\langle\sigma_m(v)\rangle_{\text{exp}} = 17.176 \times 10^{-9} S^{-1} \quad (1)$$

$$\sigma_m(v) = \frac{A_I}{v^2} = \frac{7.7574 \times 10^5 S^{-1}}{v^2} \quad (2)$$

The estimates of σ_{III} for CH_3CN , 1,1,1- CH_3CF_3 and CHF_3 are given in Fig. 5 vs. energy where they are compared with the total scattering cross section $N_2(\sigma_T)$ of N_2 . These cross sections are very useful in understanding the role of polar gases as electron slowing-down components of multi-component gaseous dielectrics⁵.

Fig. 5. Cross sections for electron attachment and scattering.

- = electron attachment cross section, $SF_6(\sigma_a)$, for SF_6 .
 $N_2(\sigma_T)$ = total electron scattering cross section for N_2 .
 $\sigma_{D=1}$ = the theoretical electron-electric dipole scattering cross section for $D=1$ debye.
 σ_{CHF_3} , $\sigma_{1,1,1-CH_3CF_3}$ and σ_{CH_3CN} = the electron-electric dipole scattering cross sections determined using Eq.(2) and the experimental values of A_I given in Table 1.

C. Field-induced Detachment from Mononegative Ions

Our calculation of the transition probability per unit time of an electron from a singly charged atomic or molecular negative ion to the continuum under the influence of a static electric field as a function of the angular momentum quantum number, l , the magnetic quantum number, m , the electron affinity, EA, and the "size" of the anion, has been completed. The results and their implications to gaseous dielectrics have been presented and discussed at the Second International Symposium on Gaseous Dielectrics (see H. C. Schweinler and L. G. Christophorou, *Proceedings Second International Symposium on Gaseous Dielectrics*).

D. Hyperboloidal Electrodes with Applications to Dielectric Testing in Nonuniform Electric Fields

In Appendix A are given the results of a calculation by Ferrell et al. of the equipotentials and electric field lines for hyperboloidal electrodes. The possible application of the results of these calculations to dielectric breakdown testing is indicated.

E. Electron Attachment to Perfluoro-n-hexane

The measurement[§] of the electron attachment rate for perfluoro-n-hexane ($n\text{-C}_6\text{F}_{14}$) in argon has been extended to high pressures (2260 kPa).

[§]These measurements have been conducted by S. Ghemati, a graduate student from the University of Tennessee.

Figure 6 shows the electron attachment rate as a function of the total pressure for various E/P values for n-C₆F₁₄ in argon. Note that above about 800 kPa, the electron attachment rate is nearly constant. For lower E/P values (and therefore low electron energies) there appears to be a larger pressure dependent component than for higher E/P values (e.g., for E/P = 0.006 $(\alpha w)_{67 \text{ kPa}} \approx 0.5 (\alpha w)_{2260 \text{ kPa}}$; for E/P = 0.06 $(\alpha w)_{67 \text{ kPa}} \approx 0.8 (\alpha w)_{2260 \text{ kPa}}$).

Figure 7 shows the electron attachment rate, αw , of n-C₆F₁₄ in different pressures of argon as a function of the mean electron energy, $\langle \epsilon \rangle$. A well defined peak at $\langle \epsilon \rangle \approx 1 \text{ eV}$ is evident.

F. Dipolar Gases

Our experimental, theoretical, and synthesis work on dipolar gases continued in view of the significant role of such systems as electron thermalizing components in multi-component gas dielectrics. Efforts are under way to explore the possibility of synthesizing some such components with desirable properties.

Fig. 6. Measured electron attachment rate for $n\text{-C}_6\text{F}_{14}$ in Ar as a function of total pressure for various values of E/P .

Fig. 7. Measured electron attachment rate for $n\text{-C}_6\text{F}_{14}$ as a function of mean electron energy for various values of total pressure.

II. DIRECT CURRENT BREAKDOWN STRENGTHS OF GASES/MIXTURES

A. Direct Current Breakdown Strengths - Unitary Gases

As indicated in previous publications,⁵⁻⁷ gases with large permanent electric dipole moments (D) such as CHF_3 ($D=1.65$ debye), $1,1,1\text{-CH}_3\text{CF}_3$ ($D=2.32$ debye) and CH_2F_2 ($D=1.97$ debye) show considerable synergistic behavior when mixed with the highly electron attaching gases SF_6 and $\text{c-C}_4\text{F}_8$. This behavior has been explained on the basis of enhanced electron scattering by the dipolar gases.

To investigate further the effect of highly dipolar gases on breakdown, CH_3CN (acetonitrile) ($D=3.92$ debye) was investigated at a temperature of 339 K and pressure of 20 kPa. The breakdown voltages of CH_3CN were measured in a small chamber with 0.953 cm dia. sphere-sphere electrode geometry. The results are presented in Fig. 8 along with comparable data for SF_6 and $\text{c-C}_4\text{F}_8$. Mixtures are also represented and will be discussed later. An elevated temperature of 339 K was required since the boiling point of CH_3CN is 354.6 K. Acetonitrile was chosen for study because of its large dipole moment, but its practical use as a dielectric gas would be severely limited due to its toxicity and low vapor pressure. Our measurements indicate that the dielectric strength of CH_3CN lies below that of SF_6 . An estimate of its relative breakdown strength is ~ 0.8 . Note in Fig. 8 that the abscissa is Nd , where N is the number density (molecules cm^{-3}) and d is the electrode gap spacing (cm). For these measurements the number density was held constant at $4.34 \times 10^{18} \text{ cm}^{-3}$. The compressibility of CH_3CN was determined from reference 8.

Fig. 8 Breakdown voltages for the dipolar gas CH_3CN ($D=3.92$ debye) and its mixtures with SF_6 and $\text{c-C}_4\text{F}_8$.

Two additional unitary gases have been investigated during this reporting period. The breakdown voltages of hexafluorodimethylsulfide, $(\text{CF}_3)_2\text{S}$, and trifluoropropene, 3,3,3,- $\text{C}_3\text{H}_3\text{F}_3$, were measured in a small chamber using 0.953 cm dia. stainless steel sphere-sphere electrode geometry. Figure 9 compares the breakdown voltages V_s for these compounds with that of SF_6 studied under the same conditions. Since the electrode geometry is non-uniform, an accurate $(V_s)^R$ (ratio of $(E/N)_{\text{lim}}$ of a gas to that of SF_6) for these compounds cannot be obtained. However, estimates of $(V_s)^R$ at the lower gap spacings give 1.5 for $(\text{CF}_3)_2\text{S}$ and 0.8 for 3,3,3,- $\text{C}_3\text{H}_3\text{F}_3$.

Fig. 9 Breakdown voltages for $(\text{CF}_3)_2\text{S}$ and $3,3,3\text{-C}_3\text{H}_3\text{F}_3$ compared with SF_6 .

A compilation of most of the relative strengths of the unitary compounds investigated over the past five years at ORNL appears in Tables 2 and 3. Table 2 gives the $(E/N)_{lim}$ value and $(V_S)^R$ relative to SF_6 of 1 for a number of gases. Except where noted, these gases were studied at our laboratory using Pearson-Harrison profile electrodes (plane-plane, stainless steel) at 66.7 kPa pressure. The temperature range varied from 292 to 298 K in general. The number densities were calculated for $T=295$ K assuming the ideal gas law relation. The $(E/N)_{lim}$ was determined as the straight line slope of the V_S versus Nd plots for the individual gases. The uncertainty in this quantity ranges from approximately 3% for gases like SF_6 and N_2 to about 5% for perfluorocarbon gases. The relative breakdown strength is the ratio of the $(E/N)_{lim}$ for a particular gas to that of SF_6 .

In Table 3 are presented the relative breakdown strengths of a number of compounds studied on a variety of electrode geometries, most of which fall into the category of "near" uniform field conditions. At very small gap spacings the electric field between spherical surfaces approximates a uniform field. However, as the gap increases the field becomes more non-uniform and the V_S versus Nd plot becomes nonlinear. For this reason a slope or $(E/N)_{lim}$ is not well defined by this method. A rough estimate of $(V_S)^R$ can be made by comparing slopes of V_S values at the smaller gaps. The $(V_S)^R$ were determined in this manner for the gases in Table 3, and the reader is cautioned that these are only approximate values.

Table 2 Breakdown Strengths of Unitary Gases; Plane-Plane Electrodes ⁺

Gas	Name	$(E/N)_{lim}$ (10^{-15} Vcm ²)	$(V_s)^R$ #
SF ₆	Sulfur Hexafluoride	3.59	1.0
Ar	Argon	0.25	0.07
CCl ₂ F ₂	Difluorodichloromethane (Freon 12)	3.72	1.04 ^a
CF ₃ H	Trifluoromethane (Genetron 23)	0.98	0.27
CF ₄	Carbon Tetrafluoride (Freon 14)	1.41	0.39
CO ₂	Carbon Dioxide	1.09	0.30 ^b
C ₂ ClF ₅	Chloropentafluoroethane (Genetron-115)	4.09	1.14
1,1,1-C ₂ Cl ₃ F ₃	1,1,1-trichlorotrifluoro- ethane	8.88	2.47 ^s
1,1,2-C ₂ Cl ₃ F ₃	1,1,2-trichlorotrifluoro- ethane	8.66	2.41 ^s
1,1,1-C ₂ F ₃ H ₃	1,1,1-trifluoroethane	1.46	0.41
C ₂ F ₆	Hexafluoroethane (Freon 116)	2.86	0.80
1-C ₃ F ₆	1-Hexafluoropropene	3.32	0.92
n-C ₃ F ₈	Perfluoro-n-propane	3.22	0.90
2-C ₄ F ₆	Hexafluoro-2-butyne	8.08	2.25
c-C ₄ F ₈	Octafluorocyclobutane (Freon C318)	4.49	1.25
2-C ₄ F ₈	Perfluoro-2-butene	5.95	1.66
n-C ₄ F ₁₀	Perfluoro-n-butane	4.72	1.31
H ₂	Hydrogen	0.64	0.18 ^b
N ₂	Nitrogen	1.28	0.36
N ₂ O	Nitrous Oxide	1.57	0.44
Ne	Neon	0.02	0.006

⁺Pearson-Harrison profile stainless electrodes. P=66.7 kPa, T=295 K
except as noted.

$(V_s)^R$ = Ratio of $(E/N)_{lim}$ for the respective gas to that of SF₆ under
identical conditions.

^sP=20 kPa

^aJ.D. Chalmers and D.J. Tedford, Proc. IEE 118(12), 1893 (1971).

^bH.Winkelkemper, Z. Krasucki, J. Gerhold, T. W. Dakin, Electra 52,
67 (1977).

Table 3 Approximate Relative Breakdown Strengths of Unitary Gases

Gas	Name	$(V_s)^R$ ⁺	Pressure (kPa)	Electrode Geometry
CF ₂ H ₂	Difluoromethane	0.3	101	a
CO	Carbon Monoxide	0.4	203	b
COS	Carbonyl Sulfide	0.9	66.7	c
C ₂ F ₆ S	Hexafluorodimethyl-sulfide	1.5	66.7	c
C ₂ H ₃ N	Acetonitrile	0.8	20	d
3,3,3-C ₃ F ₃ H ₃	3,3,3-trifluoropropene	0.8	66.7	c
c-C ₄ F ₆	Hexafluorocyclobutene	1.6	66.7	d
1,3-C ₄ F ₆	1,3-Hexafluorobutadiene	1.2-1.3	37.3	b
c-C ₆ F ₁₀	Perfluorocyclohexene	1.9-2.2	11.1	b
c-C ₆ F ₁₂	Mixture 1,2-and 1,3-perfluorodimethylcyclobutane	2.3-2.4	18.7	b
c-C ₇ F ₁₄	Perfluoromethylcyclohexane	2.1	7.73	b
1-C ₇ F ₁₄	Perfluoroheptene-1	1.2	20.3	b

⁺ $(V_s)^R$ = Ratio of $(E/N)_{lim}$ for the respective gas to that of SF₆

under identical conditions, approximate values only.

^a $(V_s)^R$ estimated from E.E. Charlton and F.S. Cooper, *General Electric*

Review 40, 438 (1937); 5.08 cm rad spherical surfaces.

^b1.91 cm dia. stainless sphere-plane.

^c0.953 cm dia. stainless sphere-sphere.

^d0.953 cm dia. stainless sphere-sphere; T=339 K.

^e3.81 cm dia. stainless sphere-sphere.

B. Direct Current Breakdown Strengths - Gas Mixtures

Figure 8 showed the breakdown voltages for mixtures of CH_3CN with $\text{c-C}_4\text{F}_8$ and SF_6 at constant N . The mixtures were studied at $T=339$ K due to the low vapor pressure of CH_3CN . The V_s of the 31% $\text{c-C}_4\text{F}_8$ /69% CH_3CN mixture was close to that of 100% $\text{c-C}_4\text{F}_8$ at the lower gaps but exceeded it at higher gaps. The breakdown voltage of a 26% SF_6 /74% CH_3CN mixture was higher than that of pure SF_6 over the full range of gaps. Both mixtures exhibit exceptionally high synergism in that the mixture has a breakdown voltage much higher than either single component alone. This finding correlates well with our previous observations^{6,7} that dipole scattering enhances thermalization of electrons resulting in more efficient attachment by the scavenger. The dipole moment of CH_3CN is 3.92 debye ($1 \text{ debye} = 3.33564 \times 10^{-30} \text{ Cm}$) which is the highest of any compound we have studied thus far. Our results on the mixtures containing the polar gases CH_2F_2 , CHF_3 , 1,1,1- CH_3CF_3 , and CH_3CN with the attaching gases $\text{c-C}_4\text{F}_8$ and SF_6 indicate that compounds with a large dipole moment ($\gtrsim 3$ debye) can be beneficial in forming improved dielectric systems.

Binary mixtures of $(\text{CF}_3)_2\text{S}$ and 3,3,3- $\text{C}_3\text{H}_3\text{F}_3$ each with SF_6 and $\text{c-C}_4\text{F}_8$ have been examined on a preliminary basis. Initial results suggest that more extensive studies should be undertaken on plane-plane geometry.

III. ENVIRONMENTAL EFFECTS STUDIES AND DECOMPOSITION ANALYSES

A. Initial Fragmentation of Gaseous Dielectrics upon Electron Impact

Electron impact fragmentation (in the energy range 0-8 eV) of the saturated perfluorocarbon (PFC), $n\text{-C}_6\text{F}_{14}$ (perfluoro *n*-hexane) was studied during this reporting period. The data are presented in Table 4 and Figure 10. Nine fragment negative ions were identified in addition to the parent ion. These include $\text{C}_6\text{F}_{13}^-$, $\text{C}_6\text{F}_{12}^-$, $\text{C}_5\text{F}_{11}^-$, $\text{C}_5\text{F}_{10}^-$, C_5F_9^- , C_4F_9^- , C_4F_7^- , C_3F_7^- , and F^- . The parent ion $\text{C}_6\text{F}_{14}^{-*}$ is not stable and autodetaches in $\sim 40 \mu\text{s}$. Unlike the lower molecular weight perfluorocarbon compounds (see ref. 9) the parent ion is formed at 0.4 eV, whereas the other parent ions exhibited maxima at thermal electron impact energy. As observed from the number of fragment ions several competing decomposition channels exist. For example interaction of an electron of 0.5 eV energy with $n\text{-C}_6\text{F}_{14}$ can result in the formation of any of ten different negative ions. With the exception of F^- the negative ions are formed in two electron energy regions 0-1 eV and 1.5-2.0 eV. The appearance of ions in the higher energy region suggests the formation of a higher excited short-lived (i.e. $\tau < 10^{-6} \text{ s}$) state of $\text{C}_6\text{F}_{14}^{-*}$, which is unstable with respect to autodissociation as well as autodetachment.

In Figure 11 is shown a comparison of the parent ion peak shape with SF_6^{-*} . [The SF_6^{-*} resonance is shifted and normalized to $\text{C}_6\text{F}_{14}^{-*}$ at the peak for comparison of peak shape.] Since the SF_6^{-*} shape is instrumental, it is seen that the $\text{C}_6\text{F}_{14}^{-*}$ may possess additional unresolved resonances states. Also included in Figure 11 is the total ion intensity

Table 4 Negative Ion Formation Due to Electron Impact on n-C₆F₁₄

Negative Ion	% of Total Ion Intensity	Energy of Maximum Ion Intensity (eV) [†]	FWHM [#] (eV)
C ₆ F ₁₄ ^{-*}	70	0.4	1.15
C ₆ F ₁₃ ⁻	1.3	1.8	1.9
C ₆ F ₁₂ ⁻	4.3	0.1	0.65
C ₅ F ₁₁ ⁻	0.9	1.9	3.0
C ₅ F ₁₀ ⁻	0.5	0.05	0.65
C ₅ F ₉ ⁻	0.7	0.5	1.0
C ₄ F ₉ ⁻	8.8	1.6	1.7
C ₄ F ₇ ⁻	0.7	0.9	0.8
C ₃ F ₇ ⁻	11.2	1.5	2.1
F ⁻	1.6	0.1 3.3	0.8 2.5

[†]Energy scale calibration determined from SF₅⁻/SF₆ resonance at 0.37 eV, error ±0.05 eV.

[#]Full width at half-height of the respective ion yield as a function of electron energy.

Fig. 10. Negative ion intensity as a function of electron impact energy for the compound, $n\text{-C}_6\text{F}_{14}$.

Fig. 11. Comparison of parent ion, $C_6F_{14}^{-*}$, resonance with the total ion intensity (sum of curves in Fig. 10) and the SF_6^{-*}/SF_6 resonance (shifted to 0.4 eV and normalized for comparison of energy dependence). Data was taken without RPD.

as a function of electron energy. This curve suggests appreciable attachment out to 3 eV. However, according to figure 11 the attachment is strongly peaked at ~ 0.5 eV. The data reported here was taken without the retarding potential difference method (RPD). The SF_5^-/SF_6 resonance at 0.37 eV was used to establish the energy scale.

B. Analyses of Final Decomposition Products

The work on carbon inhibiting mixtures was continued by considering mixtures of SF_6 with other PFC's ($2-C_4F_8$ and $c-C_4F_8$). The percent perfluoromethane production is plotted as a function of SF_6 concentration in $2-C_4F_8$ and $c-C_4F_8$ in figure 12. The data are strikingly similar to the data obtained for the $SF_6/2-C_4F_6$ system¹⁰ (see Appendix B). Again, the optimum mixture appears to occur for 70% SF_6 in PFC. Visual inspection of electrodes and the gas cell walls showed a disappearance of black deposit as the "optimum" mixture is reached. Although details of the reaction mechanisms are not known, the effectiveness of SF_6 in perfluorination is observed in these systems and detection of perfluoromethane is shown to be a useful indicator of carbon suppression. This relationship is discussed in Appendix B. At concentrations of 70% or more SF_6 in PFC no carbon is observed for the systems $SF_6/2-C_4F_6$, $SF_6/c-C_4F_8$ and $SF_6/2-C_4F_8$. Measurements such as these can aid in optimizing dielectric gas mixtures so that carbon deposits may be eliminated while maintaining high dielectric strengths (higher than SF_6 alone for the systems studied here).

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Fig. 12. Percent CF_4 production as a function of SF_6 content in the mixtures $\text{SF}_6/2\text{-C}_4\text{F}_8$ and $\text{SF}_6/c\text{-C}_4\text{F}_8$ at a total pressure of 0.1333 MPa.

C. Toxicity Studies

Interactions have been established with P. J. Walsh, C. E. Easterly and G. D. Griffin of the Health Effects and Epidemiology Group at ORNL to initiate a cooperative effort for the study of toxicity of dielectric gases/mixtures and the toxicity of decomposition products of sparked gases. Some preliminary conclusions based on literature data have been outlined by Griffin et al. at the Second International Symposium on Gaseous Dielectrics (See Appendix C).

D. Quadrupole Mass Spectrometric Studies of Sparked SF₆

Investigations of the ions produced in sparked SF₆ are continuing. Modifications to the mass spectrometer since the last report are detailed in the "Apparatus" section of this report.

For all of the work quoted in this report, the high voltage pulse polarity was negative. The spark pulse width was 2.7 μ s and the repetition frequency was 27 Hz, unless otherwise noted. The electrode-to-aperture distance, d , was varied over the range from 1.0 to 4.5 mm, and the ion source pressure, P , was in the range from 2.6 to 13.3 kPa, though most data was taken at 5.3 kPa. The ion source temperature was maintained above 80°C to prevent formation of solid deposits which would block the aperture.

The negative and positive ion mass spectra for sparked SF₆ are shown in Figure 13. Positive ions produced in the ion source should not be detected from a negative high voltage pulse since the electric field

Fig. 13. Positive and negative ion mass spectrum in sparked SF_6 for
 $P = 5.3$ kPa and $d = 1.0$ mm.

should draw positive ions towards the high voltage electrode and away from the aperture. This topic will be discussed later. It is interesting to note the presence of a weak signal for SOF^+ at 67 amu in the positive ion spectrum.

Figure 14 is a graph of F^- intensity, I , versus d over the pressure range from 2.7 to 13.3 kPa. Each curve is an average of 6 runs. The relative standard deviations varied from 2% in the flat part of the curves to 20% in the rapidly falling part of the curve. The magnitude of the latter is probably due to uncertainties in d caused by backlash in the linear motion feedthrough. This I vs. d behavior was similar for F_2^- and the positive ions observed.

The lower part of figure 15 shows the I vs. d curve for SF_6^- at $P = 5.3$ kPa. The appearance of a second maximum at larger values of d is evident. The behavior of SF_5^- is similar, except that the second maximum occurs at slightly lower values of d . This anomalous behavior of SF_6^- and SF_5^- ions was observed many times but was not always exactly reproducible. Sometimes, rather than a distinct peak, only a shoulder on the rapidly falling part of the first maximum was observed.

The arrival time spectra for SF_6^- in the upper part of Figure 15 was obtained using the time-of-flight analyzer system discussed in the apparatus section of this report. The start of the arrival time spectrum was synchronized with the rise of the negative high voltage spark pulse. For $d = 1.5$ mm, the ion arrival times separate into two distinct groups, hereafter referred to as the "fast" and "slow" groups. This behavior was repeated for SF_5^- , F^- , and F_2^- , although for F_2^- there was considerable overlap of the two groups. None of the positive ions showed

Fig. 14. Plot of F^- intensity as a function of d at various values of P .

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Fig. 15. (a) arrival time spectrum at $d = 1.5$ mm, (b) arrival time spectrum at $d = 27$ mm, and the I vs d curve for SF_6^- at $P = 5.3$ kPa.

a fast peak; only slow positive ions were detected. As d was increased, corresponding to the rapidly falling part of the I vs. d curves, the fast and slow group intensities decreased together. For SF_6^- and SF_5^- , however, the slow peak reappeared for values of d corresponding to the second peak in the I vs. d curve.

The slow group arrival time was found to be a strong function of the quadrupole pole zero voltage, PZ , and the voltage on the first lens, $L2$. There was only a slight effect of these voltages on the arrival time of the fast group. Increasing PZ from +4.1 V to +44.2 V considerably shortened the arrival time for slow SF_6^- . Increasing $L2$ from +14.8 to 60 V had a similar, though less pronounced, effect.

The fine adjustment of the mass setting controls had no effect on the arrival time spectra within about ± 0.2 amu of the peak ion intensity setting. Decreasing the resolution setting was found to have an important effect, however. At low resolution settings the single slow SF_6^- peak was split into several poorly resolved peaks as much as 30 μs removed from the normal 115 μs location. This problem was eliminated by setting the resolution as high as possible without losing an appreciable fraction of ion intensity. Varying the spark repetition rate from 6 to 889 Hz was found to have no effect on the arrival times of SF_5^- and F^- , although the relative intensities of fast and slow SF_5^- were altered somewhat. Varying the spark pulse width from 0.2 to 100 μs changed neither the arrival times nor the shapes of the distributions (provided the pulse width was shorter than the group arrival time, otherwise the ion signal would be obscured by noise from the spark). This indicates that the ions observed are associated only with the start of the spark (within the 0.25 μs resolution

of the F^- arrival time spectrum), and are not coming from the latter stages of the spark.

Again referring to the SF_6^- arrival time spectrum at $d = 1.5$ mm in Fig. 15, there is a small peak around $10 \mu s$. This peak, if actually from SF_6^- ions, would indicate ion translational energies in excess of 500 eV. Since this seemed excessive, a careful check of background signal at $10 \mu s$ arrival times across the mass range under study was undertaken. The solid line in Fig. 16 is a plot of the signal with $10 \mu s$ arrival time as a function of the quadrupole mass filter setting. The maximum at mass 19 corresponds to the fast peak for F^- . The signal then decreases rapidly until it reaches a much smaller maximum at mass 38 (F_2^-). The signal then drops to a nearly constant level until it begins a gradual decline at ~ 140 amu. The dotted line represents the signal with a $30 \mu s$ arrival time, corresponding to the slow group in the F^- arrival time spectrum. This shows the good mass resolution for low energy ions. The $10 \mu s$ signal is most likely due to incompletely filtered F^- ions. These ions at $10 \mu s$ would have translational energies on the order of 75 eV, and would only spend about 9 radio frequency cycles in the quadrupole mass filter. Adequate resolution typically requires around 100 cycles in the field.

In order to obtain a rough indication of the translational energies of the ions in the fast and slow groups, a fine grid was attached to the front of the mesh cylinder on the first lens, L2. Further details are given in the apparatus section of this report. The voltage on L2 could be varied, providing a retarding grid arrangement. Figure 17 shows the arrival time spectra for F^- at various L2 voltages. At the normal L2

Fig. 16. Plot of $10 \mu s$ and $30 \mu s$ arrival time signal versus quadrupole mass filter setting.

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Fig. 17. F^- arrival time spectra at $d = 1.0$ mm and $P = 5.3$ kPa for various $L2$ voltages.

voltage of +14.8 V, a fast peak and three separate slow peaks (at 30, 35, and 40.5 μ s) are observed. When L2 is lowered to 0 V, or slightly negative, the 40.5 μ s peak disappears. At -4 V, the 35 μ s peak is not present. Below -12 V, the 30 μ s is eliminated. But even at -60 V, a large fraction of ions in the fast peak is still able to surmount the potential barrier. The voltages required to cut-off these peaks cannot be directly converted to ion energies since no calibration has been done. For SF_6^- , SF_5^- , and F_2^- , which show only a single though broader slow peak, a voltage on L2 of -1 V is sufficient to cut-off the slow peak entirely. The fast peak behavior is the same as for the fast F^- . All the positive ions, which have only a slow peak, are cut-off entirely when L2 is made positive.

Figure 18 shows the arrival time spectra for F^- at $P = 5.3$ kPa, but for various values of d . As d is increased, the fast peak is delayed and becomes broader. The slow peaks are not affected until $d = 2.0$ mm where the fast and slow peaks start to overlap. This value of d corresponds to the falling-off part of the F^- I vs d curve.

The ion arrival time spectra were converted to ion translational energy spectra. This involved the transformation of both the horizontal and vertical axes of the arrival time spectra. A computer program was developed to calculate the arrival time of an ion as a function of its initial kinetic energy. The calculation assumes that the ions come from the aperture starting with some variable kinetic energy. The ion is then accelerated through 12 regions in the mass spectrometer, with the transit time for each region dependent on the initial translational energy of the ion and the potentials of the two mass spectrometer elements serving as the boundaries of this region. This program also assumes that all the

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Fig. 18. Arrival time spectra for F^- at $P = 5.3$ kPa and various values of d .

ions leave the aperture at the same instant, and that any time spent in the ion source is negligible compared to the transit time through the rest of the system.

The arrival time and translational energy spectra for SF_6^- and F^- are given in Figs. 19 and 20, for $d = 1.0$ mm and $P = 5.3$ kPa. The time-to-energy transformation, and in particular the intensity factor, become less accurate at lower energies. Below 1 eV, the estimated accuracy of the intensity correction is $\pm 30\%$. No corrections for variations in the mass spectrometer transmission efficiency have been made. Holme et al.¹¹ report that the transmission efficiency of a quadrupole mass filter is fairly constant for ion energies above 10 eV, but begins to fall off below this energy. For this experiment the effect amounts to a 50% relative transmission efficiency for ions with an initial energy of ~ 0 eV increasing to 100% at 6 eV.

The results of the ion energy spectra are listed in Table 5. The value of 3.5 eV for the maximum in the F_2^- fast peak is suspect because of the low intensities observed. In general, the energy corresponding to the fast peak maximum decreases as the ion mass increases. It is also evident that F^- exhibits three distinct low energy peaks.

In figure 21 is plotted the maximum observed F^- translational energy as a function of d and P . The dependence on P appears linear over the pressure range studied. Linear extrapolation predicts that fast F^- ions would be thermalized at pressures above 13 kPa for $d = 1.5$ mm.

If the electric fields near the aperture are uniform, then the fast peak maxima for SF_6^- , SF_5^- , and F^- correspond to ions produced (or making their last collision with SF_6) at a distance of 5.9, 8.2, and 12.6 μm ,

Fig. 19. SF_6^- arrival time and translational energy spectra for $d = 1.0$ mm and $P = 5.3$ kPa.

Fig. 20. F^- arrival time and translational energy spectra for $d = 1.0$ mm and $P \approx 5.3$ kPa.

Fig. 21. Plots of F⁻ maximum translational energy as a function of d and P.

Table 5 Ion Energy Distribution Data		
Ion	Fast Peak Maximum (eV)	Slow Peak Maximum (eV)
SF_6^-	16	0
SF_5^-	22	0
F_2^-	3.5	0
F^-	34	3.3, 1.1, 0

respectively, from the aperture. This is well within the diameter of the pinhole aperture (20 μm). Ions produced in the aperture, with a thickness of 25 μm , will have only thermal energies, assuming they are formed with essentially no kinetic energy. Positive ions formed before the aperture would be accelerated toward the high voltage electrode, while those formed in the aperture could still enter the mass spectrometer. Ions produced after the aperture (up to a distance of about 6 mm) may still be detected, but the arrival times will be longer than those for thermal ions produced in the aperture.

The single low energy peaks for SF_6^- and SF_5^- and the multiple peaks for F^- might be explained on the basis of the electron attachment cross sections of SF_6 .¹² Both SF_6^- and SF_5^- exhibit essentially single maxima at low electron energies. The SF_6^- ions are produced without any kinetic energy, and the SF_5^- could only be produced with very little kinetic energy. However, F^- exhibits maxima at 2.6, 5.1, 8.7, and 11.3 eV, suggesting that it may be formed with a wide range of kinetic energies. Because SF_6^- and SF_5^- can only be formed at very low electron energies, the second peak in the I vs d plots for SF_6^- and SF_5^- indicates a sharp

increase in population of thermal electrons for $d \sim 2.6$ mm. This d may represent a thermalization range for high energy electrons produced at breakdown.

Although the aforementioned rationale of the results is preliminary and incomplete, it indicates that the negative ions observed from sparked SF_6 under the conditions attained are characteristic of electron impact processes. At higher pressures, above ~ 13 kPa, these fast ions will probably not be observed. Studies at these higher pressures are in progress.

IV. IMPULSE STUDIES

In this period we have tested a variety of mixtures of 2-C₄F₈, (perfluoro-n-butene) SF₆ and N₂. The electrode geometry used in all cases was plane-"point" (30° cone terminated by a 1 mm radius hemisphere). Figure 22 shows the V₅₀ values for positive polarity lightning impulse on SF₆ and 20% 2-C₄F₈/80% SF₆. The depressed V₅₀ values for 20% 2-C₄F₈/80% SF₆ are in the region of the corona stabilization peak for pure SF₆. A comparison of these data with the relative V_S values for D.C. positive polarity (Fig. 23) indicates that for lightning impulse the corona stabilization peak is greatly depressed for the mixture but not for pure SF₆. Note that the D.C. corona stabilization peaks at lower pressures for the 20% 2-C₄F₈/80% SF₆ mixture than for pure SF₆.

Figure 24 shows the negative polarity V₅₀ values for 20% 2-C₄F₈/80% SF₆ and pure SF₆. The mixture shows an increase in the V₅₀ values associated with a decrease in the pressure at which the corona stabilization peak occurs.

Figures 25 and 26 show the V₅₀ values for mixtures of 40% SF₆/60% N₂, 5% 2-C₄F₈/35% SF₆/60% N₂, 20% 2-C₄F₈/20% SF₆/60% N₂ and 40% 2-C₄F₈/60% N₂ for positive and negative polarity, respectively, as a function of the total pressure. In both polarities, the introduction of 2-C₄F₈ leads to a dramatic effect on the V₅₀ values of the mixtures.

For positive polarity (Fig. 25) the corona stabilization peak is immediately depressed from 40% SF₆/60% N₂ for a 5% substitution of 2-C₄F₈ for SF₆. Furthermore, almost no change in the V₅₀ values occurs with increasing 2-C₄F₈ substitution. For negative polarity (Fig. 26) 5% 2-C₄F₈ produces a large increase in V₅₀ values. The increase is asso-

ciated however, with a lowering of the corona stabilization peak. The corona stabilization peak for negative polarity occurs at higher pressures than does the peak for positive polarity¹³.

From these results, it is clear that introduction of 2-C₄F₈ in mixtures with SF₆ strongly affects the pressures at which the corona stabilization peak occurs in non-uniform fields.

Fig. 22 V_{50} vs P for positive polarity 1.2 μ s/50 μ s impulse for 100% SF₆ (●) and 20% 2- C₄F₈/80% SF₆(○).

Fig. 23. V_S vs P for positive polarity 100% SF_6 (•) and 20% 2- C_4F_8 /80% SF_6 (o)

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Fig. 24 V_{50} vs P for negative polarity 100% SF_6 (•) and 20% $\text{2-C}_4\text{F}_8$ /80% SF_6 (o).

Fig. 25. V_{50} vs P for positive polarity 60% N_2 with 40% SF_6 (•), 5% 2- C_4F_8 /35% SF_6 (○), 20% 2- C_4F_8 /20% SF_6 (▲) and 40% 2- C_4F_8 (□).

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Fig. 26. V_{50} vs P for negative polarity 60% N_2 with 40% SF_6 (●), 5% 2- C_4F_8 /35% SF_6 (○), 20% 2- C_4F_8 /20% SF_6 (▲) and 40% 2- C_4F_8 (□).

V. BREAKDOWN STRENGTHS OF BINARY MIXTURES WITH CONCENTRIC CYLINDER GEOMETRY

A. Binary Mixtures with CHF_3 as Moderating Gas

In the last report we reported the dielectric strength of the binary mixtures of electron attaching gases with the dipolar gas 1,1,1- $\text{C}_2\text{F}_3\text{H}_3$ ($D=2.32$ debye). During this period, the dipolar gas CHF_3 , which has a lower dipole moment (1.65 debye), has been tested.¹⁴ Figure 27 shows the breakdown voltages of binary mixtures of CHF_3 with the attaching gases SF_6 , $\text{c-C}_4\text{F}_8$ and $2-\text{C}_4\text{F}_8$ with a 0.75 cm radius inner cylindrical electrode at negative polarity at a total pressure of 101.3 kPa. The CHF_3 has a lower breakdown voltage than N_2 as a unitary gas and SF_6/CHF_3 is inferior to SF_6/N_2 as a binary mixture. However, CHF_3 works better with fluorocarbons in that fluorocarbon/ CHF_3 mixtures give higher breakdown voltages than the corresponding fluorocarbon/ N_2 mixtures.

The effects of surface roughness on these mixtures are also shown in Fig. 27. The breakdown voltages of all the mixtures have been lowered by roughness, but some mixtures show more resistance to surface roughness. For example, 20% CHF_3 /80% SF_6 is almost insensitive to this surface roughness. In general, fluorocarbon/ CHF_3 mixtures seem less sensitive to surface roughness than fluorocarbon/ N_2 mixtures.

The effects of higher pressure on these mixtures are also being studied. Figure 28 shows the breakdown voltages of these binary mixtures with the same electrodes at a total pressure of 0.446 MPa. The binary mixtures are limited to a percentage of 50% fluorocarbon because the vapor pressures of the fluorocarbons $\text{c-C}_4\text{F}_8$ and $2-\text{C}_4\text{F}_8$ at room temperature are $\lesssim 250$ kPa. As seen by comparison of Figs. 27 and 28, the strengths of these binary mixtures do not increase proportionally with the pressure.

Fig. 27 D.C. breakdown voltages for binary mixtures of CHF₃ with each of the electron attaching gases SF₆, 2-C₄F₈, and c-C₄F₈ at negative polarity on the 0.75 cm electrode at 101.3 kPa total pressure, including surfaces both smooth and grooved to 0.051 cm depth.

Fig. 28 D.C. breakdown voltages for binary mixtures of N_2 with each of the electron attaching gases SF_6 , $2\text{-C}_4\text{F}_8$, and $\text{c-C}_4\text{F}_8$ at negative polarity on the 0.75 cm electrode at 0.446 MPa total pressure, including surfaces both smooth and grooved to 0.051 cm depth.

Also, the breakdown voltages of $c\text{-C}_4\text{F}_8/\text{CHF}_3$ and $2\text{-C}_4\text{F}_8/\text{CHF}_3$ mixtures do not differ so much at higher pressure as they do at lower pressure, and when surface roughness is introduced there is no significant difference between these two fluorocarbon/ CHF_3 mixtures. This indicates that CHF_3 works better with $c\text{-C}_4\text{F}_8$ than with $2\text{-C}_4\text{F}_8$ under high pressure and surface roughness conditions. These roughness conditions drastically lower the breakdown strengths of the SF_6/CHF_3 mixtures. For example, the breakdown strength of the 20% CHF_3 /80% SF_6 mixture, which is insensitive to surface roughness at lower pressure, drops significantly under these roughness conditions at the higher pressure.

B. Binary Mixtures with N_2 as Moderating Gas

Figure 29 shows the breakdown voltages of SF_6/N_2 , $c\text{-C}_4\text{F}_8/\text{N}_2$ and $2\text{-C}_4\text{F}_8/\text{N}_2$ mixtures with the same cylindrical electrodes at 0.446 MPa. It is seen by comparing N_2 mixtures and CHF_3 mixtures that N_2 works better with SF_6 , but not so well with fluorocarbons. The SF_6/N_2 curve at higher pressure does not saturate so fast with substitution of SF_6 for N_2 as the familiar characteristic saturation curve of SF_6/N_2 at 101.32 kPa. With the introduction of surface roughness, all breakdown voltages are reduced significantly, as expected. However, the SF_6/CHF_3 mixtures, which are inferior to SF_6/N_2 mixtures with the smooth electrode, become superior to SF_6/N_2 mixtures under these roughness conditions.

There is no significant difference between the breakdown voltages of the fluorocarbon/ N_2 and fluorocarbon/ CHF_3 mixtures. However, pure CHF_3 , which has a lower breakdown voltage than N_2 with smooth electrodes, has a higher breakdown voltage than N_2 with surface roughness. The CHF_3 also works better with electron attaching gases under high pressure and surface roughness conditions than does N_2 .

Fig. 29 D.C. breakdown voltages for binary mixtures of CHF_3 with each of the electron attaching gases SF_6 , $2\text{-C}_4\text{F}_8$, and $\text{c-C}_4\text{F}_8$ at negative polarity on the 0.75 cm electrode at 0.446 MPa total pressure, including surfaces both smooth and grooved to 0.051 cm depth.

VI. LIQUID DIELECTRICS

Various authors have postulated that dielectric breakdown in liquids is caused by the presence of bubbles.^{15,16} However, the source, composition and role of these bubbles in the breakdown process is unclear. Perhaps the bubbles are gaseous by-products of electrical stress or of previous breakdowns and have a lower breakdown threshold than the liquid itself. We investigated the effect of placing an insulating gas at different pressures in the test cell above a sample of the liquid. An elevated breakdown threshold under these conditions would imply that the insulating gas inhibits the bubbles from affecting breakdown (by increasing their dielectric strength). Experiments of this type have been performed by Yamashita, Amano, and Mori¹⁶ using SF₆ in transformer oil. They found that partial discharge was inhibited but that breakdown itself still occurred at the same level. Similar findings were reported by Walsh.¹⁷

The data in Table 6 show the results of our placing SF₆ at different pressures over a sample of liquid n-C₆F₁₄. The addition of the gas elevated the mean threshold by ~7% (from 0.75 to 0.81 MV/cm) at 250 torr but less than 3% more at higher pressures. Considering the scatter in the data, there is actually no significant difference among all of these data. The lack of a dramatic effect on the breakdown voltage in these experiments led us to pursue other areas which possess more promise.

Table 6 Breakdown Strength vs Pressure for n-C₆F₁₄ and SF₆
(Electrode Separation = 0.10 mm)

	no SF ₆	SF ₆ at: 250 torr	500 torr	1000 torr
Mean (MV/cm)	0.75	0.81	0.81	0.85
Scatter (%)	13.40	13.10	14.00	8.40

The scarcity of dielectric research on fluorinated hydrocarbon liquids led us to focus our efforts on these compounds to determine the effect on breakdown of the number and arrangement of the fluorine atoms in the molecules. The three isomers of difluorinated benzene are shown in Fig. 30. Note that each compound has the same number of fluorine atoms, but these are located at different positions in the basic structure. It is the various arrangements that give rise to the indicated differences in the dipole moment of the molecule.

Fig. 30. Structure and dipole moments¹⁸ of the difluorinated benzenes.

Results of breakdown experiments for these liquids are shown in Table 7 for several electrode separations. At a gap of 0.10 mm, the para-C₆H₄F₂ and meta-C₆H₄F₂ possess the same breakdown strength (0.51 MV/cm), which was much larger than that of the ortho-C₆H₄F₂. In all other cases, the breakdown strength decreased as the dipole moment increased. For example, for the 0.30 mm gap, there was a 26% decrease between the para and meta and further 29% decrease between the meta and ortho isomers. The dramatic differences in breakdown strength present in these data are of great interest since this finding must be attributed to the properties of the liquids. However, further investigation is warranted to determine if the effect is due solely to the dipole moment.

Table 7 Breakdown Strengths of p-, m-, and o-C₆H₄F₂ at Various Electrode Separations

Liquid	Separation (mm)	0.10	0.20	0.30	0.40	0.50
p-C ₆ H ₄ F ₂	Mean (MV/cm)	0.52	0.36	0.34	0.27	0.28
	Scatter (%)	8.0	5.2	6.5	18.0	13.1
m-C ₆ H ₄ F ₂	Mean (MV/cm)	0.52	0.32	0.25	-	0.21
	Scatter (%)	10.2	9.6	5.9	-	9.8
o-C ₆ H ₄ F ₂	Mean (MV/cm)	0.2	0.16	0.18	-	0.17
	Scatter (%)	9.8	6.2	2.9	-	12.5

VII APPARATUS

A. Impulse Generator

The new (4 kJ 400 kV) impulse generator from Haefely has been installed, tested and is in routine operation. Besides increasing the maximum voltage and energy available for impulse studies, the new impulse generator allowed a significant improvement in the speed of data acquisition.

B. Automation of the Time-of-Flight Mass Spectrometer (TOFMS)

A modular instrument computer (MINC) system (manufactured by Digital Electronics Corporation), has been acquired for automation of the TOFMS used for initial fragmentation studies. The system consists of the MINC computer, RX02 disc drive and VT105 CRT terminal. The purpose of the automation is two-fold: (1) it provides mass data storage and data manipulation facilities for averaging large amounts of data and speeds data analyses and (2) it provides for a control of the electron gun to permit optimal utilization of the retarding potential difference (RPD) method which increases electron energy resolution, thereby improving the quality of the data. In the past the acquisition of RPD data normally required very intense signals and stable source conditions. By pulse counting, signals need not be so large and the electron energy can be swept quickly.

Interfacing of the MINC system to the TOFMS has been undertaken by D. V. Maxey of the Atomic, Molecular and High Voltage Physics Group. The system is expected to be operational within the next reporting period.

C. Time-of-Flight Analysis for Quadrupole Mass Spectrometer

A multichannel analyzer system (Nuclear Data Series 1100) with a time-of-flight module (Nuclear Data ND541TOF) has been added to the quadrupole mass spectrometer. This enables us to determine the temporal relationship between the initiation of a spark and the arrival of a mass-selected ion at the detector. The distribution of ion arrival times for many sparks is obtained. Some of these arrival time spectra have been presented in Section III.

The analyzer has a capacity of 256 or 512 channels, with a maximum resolution of 0.125 μ s per channel (decreasing to 64 μ s per channel in binary increments). So far, the ion arrival times observed have been characteristic of the transit times for these ions through the mass spectrometer, and not of effects within the ion source itself. Thus, the ions we observe under our present conditions spend less than 0.25 μ s in the ion source.

D. Retarding Grid Energy Analyzer

Indications from the ion arrival time studies that the SF_6^- , SF_5^- , F_2^- , and F^- distributions each contained two distinct groups in arrival times prompted us to devise a means of verifying this interesting effect. Accordingly, we installed a fine mesh grid over the front of the wire mesh basket attached to lens 2 (see Fig. 31). Under normal operating conditions, this lens is maintained at a potential of +14.8 V (for negative ions). However, the mass spectrometer electronics allows this voltage to be varied from +60 V to -60 V. Since the aperture was at ground potential, any negative voltage on this grid represented a retarding potential. Therefore, only ions with translational energies

Fig. 31 Cross sectional view of the mass spectrometer

1. tungsten electrodes
2. pinhole aperture
3. new 3 element retarding grid analyzer
4. auxiliary ionizer cylindrical mesh with old retarding grid attached to the front
5. lens stack (L2 through L6)
6. quadrupole mass filter (20 cm long)
7. Faraday plate ion collector
8. Channeltron electron multiplier

(expressed in eV) greater than the grid potential (expressed in volts) would be transmitted (for singly charged ions). In this manner, it was shown that the "fast" ion group had significant intensity at energies greater than 60 eV, since -60 V on the grid was not sufficient to stop all these ions. The "slow" ion groups could be stopped by potentials of less than several volts.

A new retarding grid assembly has just been fabricated (see Fig. 31). This grid is independent of the original mass spectrometer electronics, so that potentials up to several hundred volts may be applied. Furthermore, it is now possible to adjust the retarding potential without changing the focal properties of the lens stack.

E. Floating Aperture

In the original version of the quadrupole mass spectrometer, the pinhole aperture between the spark ion source and the mass spectrometer inlet chamber was maintained at ground potential by its mounting arrangement. This has been changed to the new arrangement shown in Fig. 32. The aperture disc is now captured between two stainless steel plates and sealed with a gold wire gasket. This assembly is fitted into a Macor machinable ceramic insulator, sealed with a Viton o-ring and retained by a threaded ring. This unit is fitted into the main stainless steel flange, sealed with another Viton o-ring and retained with another threaded ring. Electrical contact with the aperture mounting plate is made with an electrically insulated spring loaded contact probe which is connected to a BNC type electrical feedthrough.

This new arrangement allows us to apply a potential to the aperture, so that ions resident in the source after the spark has terminated may be

Fig. 32 New design of pinhole aperture (see text)

1. pinhole aperture (electroformed Nickel)
2. aperture retaining plate (stainless steel)
3. aperture mounting plate (stainless steel)
4. inner retaining ring (stainless steel)
5. outer retaining ring (stainless steel)
6. insulator (corning "Macor" glass-ceramic)
7. Viton o-ring
8. Viton o-ring
9. spring loaded contact probe
10. main flange (stainless steel)
11. BNC electrical feedthrough

drawn out into the mass spectrometer. It is hoped that studies where the aperture is pulsed at varying time intervals after a spark will give us information about the lifetime of ions under practical conditions, and about ions produced by subsequent ion-molecule reactions.

F. High Voltage Pulser

The electrical connections between the high voltage pulser (Cober Electronics model 605P) and the ion source are shown in Fig. 33. The spark current is limited by the 205 Ω resistor (40 82 Ω , 2W carbon composition resistors in a series-parallel combination). The electrode high voltage is monitored at point (a) with a Tektronix model P6015 high voltage probe. The electrode current is monitored with a Pearson Model 411 current pulse transformer. The 1 Ω series resistor may be used to monitor the current flowing to the low voltage electrode; otherwise, these two points are shorted together. Both electrodes may be floated above ground potential by applying a D.C. potential at this point; otherwise it is grounded. Current to the aperture may be monitored at point (e); otherwise this point is normally grounded. The aperture may be floated above ground potential by removing the 10 Ω resistor and applying the appropriate potential.

Figure 34 shows the voltage and current waveforms associated with the spark. Under normal operating conditions (SF_6 pressure 5.3 kPa, electrode gap 0.5-1.0 mm, pulse repetition rate 27 Hz, and pulse width 2.7 μsec) the average breakdown voltage is -2.7 kV, though there may be considerable fluctuation (2.5 to 3.7 kV). The maximum in the voltage waveform corresponds to the start of the abrupt rise in cathode current, which rapidly peaks as high as 60 A and then returns in 50 ns to a steady current of 6.8 A. At this time, the spark voltage has collapsed to 40 or 50 V. Simultaneous

Fig. 33 Connection of high voltage pulse power supply to the electrodes

- a) monitoring point for electrode high voltage
- b) output of current pulse transformer
- c and d) output of current sensing resistor for low voltage
electrode (both outputs normally grounded)
- e) aperture current monitoring point (normally grounded)

Fig. 34 Spark waveforms

- a) cathode voltage (without breakdown)
- b) cathode voltage (with breakdown)
- c) cathode current
- d) aperture current

with the abrupt rise in the cathode current is a 150 - 200 mA current pulse to the aperture.

VIII. SECOND INTERNATIONAL SYMPOSIUM ON GASEOUS DIELECTRICS

The conference was held March 9-13, 1980, at the Hyatt Regency Hotel in Knoxville, with 118 registrants from the United States and twelve other countries attending. Over fifty papers were presented. Results of the post-conference questionnaire indicate that the meeting provided an excellent forum for discussion of the most recent developments in gaseous dielectrics and that interaction between both basic and applied groups was valuable.

Working copies of the papers were distributed at the conference to the participants. All papers, along with the discussion, will be published by Pergamon Press in August, 1980.

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Appendix A

A Solution to Laplace's Equation for Hyperboloidal Electrodes
with Applications to Dielectric Testing in Nonuniform Electric Fields

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*Gaseous Dielectrics II: (Proceedings of the Second
International Symposium on Gaseous Dielectrics, Knoxville,
Tennessee, March 9-13, 1980) to be published by Pergamon
Press.*

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A SOLUTION TO LAPLACE'S EQUATION FOR HYPERBOLOIDAL ELECTRODES WITH
APPLICATIONS TO DIELECTRIC TESTING IN NONUNIFORM ELECTRIC FIELDS*

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ABSTRACT

Equipotentials and electric field lines for hyperboloidal electrodes are calculated. Application of these results to dielectric breakdown near sharp points is discussed.

I. INTRODUCTION

It is safe to say that nonuniform electric fields are the rule rather than the exception in most applications of high voltages in engineering. To assess the effects of such fields on the conditions influencing dielectric breakdown of insulating materials, it is useful to have electrode configurations which produce well understood nonuniformities (1). In principle, the field lines associated with an arbitrary arrangement of charged conductors can always be determined by numerical methods. The reduction of data, however, often requires an integration of the Townsend breakdown equation (2) so that analytic solutions for the field lines are especially convenient. We have found that an analytic solution of Laplace's equation can be obtained for conducting surfaces which are hyperboloids of revolution. In Section II we construct this solution and in Section III discuss some of its properties which are relevant to dielectric testing.

II. SOLUTION TO LAPLACE'S EQUATION

II.1 Description of the Geometry

The locus of a hyperbola of two sheets is given by the equations

$$\frac{z^2}{a^2} - \frac{y^2}{b^2} = 1 \quad (2.1)$$

$$b^2 = c^2 - a^2. \quad (2.2)$$

The foci are located at $\pm c$, and the closest distance of approach of the two sheets is $2a$ (see Fig. 1). If we define the angle α by

$$a = c \cos \alpha \quad (2.3)$$

$$b = c \sin \alpha, \quad (2.4)$$

then the hyperbolae are asymptotic to the lines $z = \pm y \cot \alpha$. If c is held constant but a is made smaller, the hyperbolae retain the same focal points; but the asymptotes get closer to the z -axis. A family of such hyperbolae is shown in Fig. 1. The set of ellipses orthogonal to the hyperbolae is given by the equation

$$\frac{z^2}{\cosh^2 \eta} + \frac{y^2}{\sinh^2 \eta} = c^2. \quad (2.5)$$

If the hyperbolae and ellipses are rotated around the z -axis, families of hyperboloids and ellipsoids of revolution result. The equations above describe the geometry of the three dimensional figures if y is replaced by ρ where $\rho^2 = x^2 + y^2$, where x, y, z are the ordinary Cartesian coordinates.

II.2 Laplace's Equation

In the three dimensional geometry, Laplace's equation can be written in prolate spheroidal coordinates (ϕ, ξ, ζ) where ϕ is the azimuthal angle, $\xi = \cos \alpha$, and $\zeta = \cosh \eta$. These coordinates are orthogonal and related to the Cartesian coordinates by

$$x = c \sinh \eta \sin \alpha \cos \phi \quad (2.6)$$

$$y = c \sinh \eta \sin \alpha \sin \phi \quad (2.7)$$

$$z = c \cosh \eta \sin \alpha \quad (2.8)$$

where

$$\eta \geq 0 \quad (2.9)$$

$$0 \leq \alpha \leq \pi \quad (2.10)$$

$$0 \leq \phi \leq 2\pi. \quad (2.11)$$

The metrical scale factors are given by

$$h_\alpha^2 = h_\eta^2 = c^2 (\sinh^2 \eta + \sin^2 \alpha) \quad (2.12)$$

$$h_\phi^2 = c^2 \sinh^2 \eta \sin^2 \alpha \quad (2.13)$$

so that Laplace's equation for the electrostatic potential ϕ takes the form

$$\nabla^2 \phi = \frac{1}{c^2 (\sinh^2 \eta + \sin^2 \alpha) \sinh \eta} \frac{\partial}{\partial \eta} \left(\sinh \eta \frac{\partial \phi}{\partial \eta} \right) + \quad (2.14)$$

$$\frac{1}{c^2 (\sinh^2 \eta + \sin^2 \alpha) \sin \alpha} \frac{\partial}{\partial \alpha} \left(\sin \alpha \frac{\partial \phi}{\partial \alpha} \right) + \frac{1}{c^2 \sinh^2 \eta \sin^2 \alpha} \frac{\partial^2 \phi}{\partial \phi^2} = 0.$$

ORNL-DWG 80-8949

Fig. 1. Hyperbolae with family of orthogonal ellipses. It is conventional to label as shown the parts of the hyperbolae which lie in the quadrants symmetric with respect to rotations of 180° about the z -axis. Equation (2.1), however, is invariant with respect to this labeling.

In terms of ξ and ζ , this is

$$\frac{\partial}{\partial \xi} \left[(1 - \xi^2) \frac{\partial \Phi}{\partial \xi} \right] + \frac{\partial}{\partial \zeta} \left[(\zeta^2 - 1) \frac{\partial \Phi}{\partial \zeta} \right] + \frac{\zeta^2 - \xi^2}{(\zeta^2 - 1)(1 - \xi^2)} \frac{\partial^2 \Phi}{\partial \zeta^2} = 0. \quad (2.15)$$

We take the upper sheet of the hyperboloid defined by $\xi = \xi_0 > 0$ to be a perfectly conducting electrode with potential V and the lower sheet defined by $\xi = -\xi_0$ to be a grounded perfect conductor.

II.3 Solution

Because of the axial symmetry of the problem, Φ is independent of ϕ . The hyperboloidal sheets defined by $-\xi_0 \leq \xi \leq +\xi_0$ are equipotentials; hence Φ is independent of ζ . Equation (2.15) reduces to the ordinary differential equation

$$\frac{d}{d\xi} (1 - \xi^2) \frac{d\Phi}{d\xi} = 0 \quad (2.16)$$

whose solution is

$$\Phi = \frac{V}{2} \left[1 + \frac{\ln \frac{1+\xi}{1-\xi}}{\ln \frac{1+\xi_0}{1-\xi_0}} \right]. \quad (2.17)$$

Equation (2.17) may also be written in the form

$$\Phi = \frac{V}{2} \left[1 + \frac{\tanh^{-1} \xi}{\tanh^{-1} \xi_0} \right]. \quad (2.18)$$

Taking $\Phi = \text{const.}$, the equipotential surfaces are

$$\frac{z^2}{\beta^2 c^2} - \frac{\rho^2}{(1 - \beta^2) c^2} = 1, \quad (2.19)$$

where

$$\beta = \tanh \left[\left(\frac{2\Phi}{V} - 1 \right) \tanh^{-1} \xi_0 \right]. \quad (2.20)$$

In the Cartesian coordinates, the potential is expressed by

$$\Phi = \frac{V}{2} \left\{ 1 + \frac{1}{\ln \left(\frac{1+\xi_0}{1-\xi_0} \right)} \ln \left[\frac{1 + \sqrt{\frac{1}{2} \left(\frac{z^2}{c^2} + \frac{\rho^2}{c^2} + 1 \right)} - \frac{1}{2} \sqrt{\left(\frac{z^2}{c^2} + \frac{\rho^2}{c^2} + 1 \right) - \frac{4z^2}{c^2}}}{1 + \sqrt{\frac{1}{2} \left(\frac{z^2}{c^2} + \frac{\rho^2}{c^2} + 1 \right)} - \frac{1}{2} \sqrt{\left(\frac{z^2}{c^2} + \frac{\rho^2}{c^2} + 1 \right) - \frac{4z^2}{c^2}}} \right] \right\}. \quad (2.21)$$

The electric field is tangent to the ξ -direction and is given by

$$\begin{aligned} E_{\xi} &= -\frac{1}{h_{\alpha}} \frac{\partial \phi}{\partial \alpha} \\ &= \frac{V}{2} \left[c \left(\zeta^2 - \xi^2 \right)^{1/2} \tanh^{-1} \xi_0 \sqrt{1 - \xi^2} \right] \end{aligned} \quad (2.22)$$

which could also be written in Cartesian coordinates, but the result is not very illuminating.

II.4 Hyperboloid of One Sheet Opposite a Plane

In Fig. 1, the hyperboloids form the equipotentials and the ellipses the field lines for the potential problem involving a hyperboloid of two sheets. Note, however, that the x,y -plane constitutes an equipotential. Thus, if we remove the lower sheet and replace the x,y -plane by a perfect conductor, we have a problem whose potential also satisfies Eq. (2.16). If the x,y -plane is grounded and the upper sheet is held at the potential V , then the potential in between is given by

$$\phi = V \frac{\ln \left(\frac{1+\xi}{1-\xi} \right)}{\ln \left(\frac{1+\xi_0}{1-\xi_0} \right)} = V \frac{\tanh^{-1} \xi}{\tanh^{-1} \xi_0}. \quad (2.23)$$

The equipotentials and field lines for this case can be developed following the methods laid out in Section II.3.

III. APPLICATIONS

Hyperboloidal electrodes are suited for creating well defined geometrical regions in which corona activity can be studied. Suppose it is determined that the onset for corona occurs when a hyperboloidal electrode given by $\xi = \xi_0$ is raised to a potential V with respect to the x,y -plane. We can replace this electrode with a confocal hyperboloid defined by $\xi = \xi_1 > \xi_0$. If we raise this new electrode to a potential V_1 given by

$$V_1 = V \frac{\tanh^{-1} \xi_1}{\tanh^{-1} \xi_0}, \quad (3.1)$$

then the field in the region $\xi \leq \xi_0$ is identical to that produced by the electrode defined by $\xi = \xi_0$. Hence, we can expect the corona to be confined to the region $\xi_0 \leq \xi \leq \xi_1$. Figure 2 shows a diagram of the situation.

It is clear from Eq. (2.21) that the coordinates x,y,z appear everywhere divided by the length c . This includes the parameter ξ_0 which is equal to the ratio of a to c . The focal length c is the natural scale factor. Suppose we measure the potential at the point (x,y,z) for a hyperboloid specified by the parameters a and c which is raised to the potential V . Now suppose that we replace this hyperboloid with another characterized by the parameters $2a$ and $2c$ which carries the potential V . By virtue of Eq. (2.21) we should expect to measure at the point

Fig. 2. Corona confined to high field region.

$(2x, 2y, 2z)$ the same potential which we formerly measured at the point (x, y, z) . We conclude that experiments carried out with electrodes scaled by the dimension c should have identical results.

Among the various arrangements of electrodes for producing nonuniform fields, the hyperboloidal electrodes stand out because the potential field can be expressed in closed form in terms of simple functions. This is particularly important in the limit $\alpha \rightarrow 0$ for which each sheet of the hyperboloid approaches a sharp point.

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* Research sponsored by the Division of Electric Energy Systems, U. S. Department of Energy, under contract W-7405-eng-26 with the Union Carbide Corporation.

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Appendix B

Carbon inhibition in sparked perfluorocarbon/SF₆ mixtures

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J. Phys. D: Applied Physics (to be published).

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Carbon inhibition in sparked perfluorocarbon/SF₆ mixtures

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Abstract

Decomposition products from sparked 2-C₄F₆ (2-perfluorobutyne)/SF₆ mixtures have been identified. These include the perfluorocarbons, CF₄, C₂F₄, C₂F₆, C₃F₈, C₄F₈, C₄F₁₀, C₅F₁₂ and C₆F₁₄ and two isomers of S₂C₂F₄. Saturated perfluorocarbon products are shown to increase in abundance with increasing concentration of SF₆ in 2-C₄F₆ up to ~70% SF₆ in 2-C₄F₆. The most abundant decomposition product, perfluoromethane (CF₄), was measured quantitatively for varying concentrations of SF₆ in 2-C₄F₆ and found to show a maximum for the (70%) SF₆/(30%) 2-C₄F₆ composition. The data suggest that the suppression of solid carbon deposits is effected by conversion of carbon to gaseous products (mostly saturated perfluorocarbons). Comparisons are made with sparked 2-C₄F₆/N₂ mixtures which show no evidence of carbon inhibition. These results indicate that proper tailoring of SF₆/perfluorocarbon mixtures can effectively inhibit carbon formation.

1. Introduction

Recently advances have been made in the development of gas mixtures for use as high voltage insulation which utilize perfluorocarbon (PFC) compounds as a gas component(s) (e.g., see James et al. 1978, Pace et al. 1978, Christophorou et al. 1979a, b, 1980). In general when a PFC compound is sparked, deposits rich in carbon are formed on surfaces.⁺ We have observed that when SF_6 is used as an additive to $2\text{-C}_4\text{F}_6$ (2-perfluorobutyne) carbon formation is largely inhibited without seriously compromising the insulating integrity of the gas mixture. It has been brought to our attention recently that Mears and Orfeo (1978) have observed carbon inhibition when SF_6 is added to other fluorocarbon gases. The observations of Mears and Orfeo were only visual, however, with no data reported either on the decomposition products or on the mechanism of carbon suppression. In this paper quantitative data are presented on the decomposition products of the $\text{SF}_6/2\text{-C}_4\text{F}_6$ system which show the effect of SF_6 on conversion[‡] of carbon to gaseous products. The potential practical significance of these findings is stressed.

2. Experimental Conditions

Except where noted, all gases were sparked under the following conditions: stainless steel spherical electrode geometry; spark gap = 0.5 mm; total pressure = 133.3 kPa; energy per spark = 0.5 J; total number of sparks = 2000. The spark cell (a 6.99-cm Varian cross) was evacuated to $\sim 3 \times 10^{-4}$ Pa before each run. The grounded electrode was

⁺In analyses of the black deposits formed from sparked $2\text{-C}_4\text{F}_6$, fluorine was detected (Christophorou et al., 1978), indicating the presence of perfluorocarbon polymer in addition to free carbon.

[‡]By "conversion" we mean reaction either with carbon or with carbon precursors.

attached to a linear motion vacuum feedthrough to permit the setting of the electrode gap after gas had been admitted into the spark cell. For gas mixtures the mixing time was at least 20 minutes.

The gases were sparked by capacitive discharge, with ~ 3 s between breakdowns. Sparks were counted by detecting the light emitted in the discharge. Following the sparking, the sample was transferred to a stainless steel cell and backfilled with helium to facilitate injection into a gas chromatograph (GC).

Two gas chromatographic systems were utilized. Identification of breakdown products was made on a gas chromatograph/mass spectrometer (GC/MS) system. Quantitative measurements were made on a GC with a thermal conductivity detector. Both GCs had columns packed with silica gel.

The gas $2\text{-C}_4\text{F}_6$ was obtained from Columbia Organic Chemicals Corporation, Inc.

3. Results

3.1. *Decomposition products of sparked $2\text{-C}_4\text{F}_6/\text{SF}_6$ mixtures*

Identification of arc decomposition products were made by GC/MS. Following sample injection, frequent mass scans were made documenting the elution of the various components of the sample. A plot of the ion intensity versus scan number (the scan number is proportional to the retention time) yields a reconstructed gas chromatogram. Frame I of figure 1 shows a typical gas chromatogram for the sparked mixture (60%) $2\text{-C}_4\text{F}_6$ /(40%) SF_6 . In addition to the starting components $2\text{-C}_4\text{F}_6$ and SF_6 , the products CF_4 and C_3F_8 were readily observed. The

"air peak" is due to air that is admitted during the injection. To increase detection sensitivity for other products which might be produced, similar chromatograms were developed for the intensity of specific ions characteristic of a limited number of compounds. Frames II-VI of figure 1 show chromatograms for the ions CF_3^+ ($m/e = 69$), S_2CF^+ ($m/e = 95$), C_2F_4^+ ($m/e = 100$), SF_5^+ ($m/e = 127$) and C_3F_7^+ ($m/e = 169$), respectively. The ion chromatogram (IC) of CF_3^+ (frame II of figure 1) reveals the presence of the products C_2F_6 and C_2F_4 which unfortunately have retention times too close to that of SF_6 for adequate separation chromatographically. The compound C_4F_{10} is also observed despite the high background in the total ion chromatogram (TIC). Similarly, the products C_5F_{12} and C_6F_{14} were detected in the C_3F_7^+ IC (frame VI of figure 1). Additionally, the $m/e = 95$ (believed to be S_2CF^+) shows the presence of two isomers of the compound $\text{S}_2\text{C}_2\text{F}_4$.* Note that absolute intensities are not given; they vary widely among the ICs in figure 1. To summarize: the products CF_4 , C_2F_6 , C_2F_4 , C_3F_8 , C_4F_8 , C_4F_{10} , C_5F_{12} , C_6F_{14} and $\text{S}_2\text{C}_2\text{F}_4$ were identified.

In figure 2 we show the CF_3^+ ICs for several concentrations of 2- C_4F_6 in SF_6 . For comparison the CF_3^+ IC for an "unsparked" sample of a 50/50 mixture of 2- $\text{C}_4\text{F}_6/\text{SF}_6$ is shown in frame I of figure 2. As indicated by the dashed line, the intensity of CF_4 relative to the starting PFC component 2- C_4F_6 increases dramatically as the 2- C_4F_6 concentration decreases from 80 to 20% in the mixture. The abundances of the other low molecular weight saturated PFC products (C_2F_6 , C_3F_8 and C_4F_{10}) behave in a similar

* Mass spectra taken at the maxima of the two peaks marked $\text{S}_2\text{C}_2\text{F}_4$ in figure 1 were identical except for the presence of a CF_3^+ line in the mass spectrum of the $\text{S}_2\text{C}_2\text{F}_4$ peak.

manner except for C_2F_4 , whose amount does not seem to be influenced by the composition of the starting mixture. One might expect that the PFC products would decrease in abundance as the amount of $2-C_4F_6$ was decreased, but in reality the opposite is observed. The data suggest that increase in SF_6 content increases the production of lower PFCs particularly CF_4 . This increase in formation of gaseous PFCs coincides with the visual observation of a significant decrease in carbon deposits in such mixtures (Christophorou et al. 1979b).

To substantiate further these findings, quantitative measurements were made of the concentration of CF_4 produced from sparked $2-C_4F_6/SF_6$ mixtures. In figure 3 the percentage of CF_4 is plotted as a function of the percentage of SF_6 in the mixture. The GC response factors for CF_4 were determined for each sparked $2-C_4F_6/SF_6$ mixture by preparing a similar unsparked concentration of $2-C_4F_6/SF_6$ with a known admixture of CF_4 . The error bars ($\pm 12\%$) represent the sum of the standard deviation of several runs ($\pm 10\%$) and the error ($\pm 2\%$) in determining the relative area. The amount of CF_4 in the unsparked sample was negligible in this work. At 0% SF_6 (i.e., 100% $2-C_4F_6$), the CF_4 product amounts to 0.24%, presumably resulting from direct decomposition of $2-C_4F_6$. As SF_6 is increased from 20 to 70%, the CF_4 content rises by about one order of magnitude. From 70-100% SF_6 in $2-C_4F_6$, the perfluoromethane concentration decreases linearly to zero. Visual inspection of the electrodes and walls of the spark cell indicated no trace of black deposits at $\geq 70\%$ SF_6 in $2-C_4F_6$. At 20% SF_6 in $2-C_4F_6$ there was no change in CF_4 content from that of the 0% case. This is probably due to a decrease in CF_4 produced directly from $2-C_4F_6$ coupled with an increase due to CF_4 produced from carbon conversion (by SF_6 addition).

3.2. *Decomposition products of sparked 2-C₄F₆/N₂ mixtures*

To scrutinize further the results of the preceding section, SF₆ was replaced with N₂ as the additive in 2-C₄F₆. Carbon suppression is not observed for this mixture. Measurements were made of perfluoromethane produced from sparked 2-C₄F₆/N₂ mixtures, and the data are also shown in figure 3. The amount of CF₄ product decreases linearly as the amount of 2-C₄F₆ decreases, indicating that it is simply proportional to the amount of the PFC in the starting mixture. There is no apparent influence of the N₂ additive on the decomposition. To confirm this, several sparked mixtures of the 2-C₄F₆/N₂ system were analyzed by GC/MS. Two of these [(20%) 2-C₄F₆/(80%) N₂ and (60%) 2-C₄F₆/(40%) N₂] are presented in figure 4 and are compared to the corresponding 2-C₄F₆/SF₆ mixture. As in figure 2 these are ICS for m/e = 69. Inspection of the gas chromatograms reveal no "new" products (as compared to a sparked sample of 100% 2-C₄F₆). The data in figure 4 show, also, that very small amounts of CF₄ and other lower PFCs are produced for an N₂ additive.

3.3. *Dependence of breakdown product yields on energy input*

For the "optimum" mixture [(70%) SF₆/(30%) 2-C₄F₆] the number of sparks was varied and the energy/spark was decreased by a factor of ten. All data in figures 1 to 3 are for an energy input of 5 J/spark or a total energy of 10 kJ (2000 sparks). The energy/spark was determined by integrating the product of the voltage and current waveforms; this agreed with the value determined from $E = 1/2 CV^2$, where the capacitance C was 0.1 μF. The percent of CF₄ produced in sparked (70%) SF₆/(30%) 2-C₄F₆ mixtures varied proportionately with the number of sparks (up to 2000). When the energy input was decreased to 0.5 J/spark, the amount of CF₄ also decreased (within the error limits) proportionately.

4. Discussion and Conclusions

From the data presented in Section 3, it can be concluded that the addition of SF_6 in $2\text{-C}_4\text{F}_6$ has the effect of increasing substantially the amount of perfluoromethane product, apparently from a conversion of carbon. The amount of CF_4 produced from carbon conversion in the $\text{SF}_6/2\text{-C}_4\text{F}_6$ mixtures can be determined by subtracting the amount produced in the $\text{N}_2/2\text{-C}_4\text{F}_6$ mixtures from that for the $\text{SF}_6/2\text{-C}_4\text{F}_6$ mixtures at each percentage value of $2\text{-C}_4\text{F}_6$. These data are plotted in figure 5 and give the percent of CF_4 produced from carbon conversion by SF_6 . The peak at 70% SF_6 in $2\text{-C}_4\text{F}_6$ represents the optimum carbon inhibiting mixture. If it is assumed that the amount of carbon produced is proportional to the amount of $2\text{-C}_4\text{F}_6$,* the amount of carbon is decreasing linearly from a maximum (at 0% SF_6) to zero (at 100% SF_6). However, while the carbon content is decreasing, the amount of SF_6 is increased, thereby increasing the amount of carbon scavenged. At 70% SF_6 and above, the percentage of CF_4 represents effectively all the converted carbon which decreases linearly to zero. The inset of figure 5 shows the extrapolation to 0% SF_6 giving an estimate of the amount of carbon formed from the sparked 100% $2\text{-C}_4\text{F}_6$ gas.

The mechanism for carbon suppression is still not clear. It does appear that either SF_6 or a highly reactive product of SF_6 is responsible for the perfluorocarbon products. In our experiments on SF_6 breakdown, we have observed that the compound SF_4 is produced in sparked SF_6 .

* This statement is based on the finding that the gaseous products (e.g., CF_4 produced from sparked $2\text{-C}_4\text{F}_6/\text{N}_2$ shown in figure 3) decrease in proportion to the decrease in $2\text{-C}_4\text{F}_6$.

However, the amount of SF_4 detected decreased with the time elapsed between the preparation of the sparked sample and the subsequent injection into the GC. This is probably due to the reaction of SF_4 with the container walls. To determine whether SF_4 had any effect on carbon conversion, small amounts (2 and 10%) of SF_4 were added to $2\text{-C}_4\text{F}_6$ and the $2\text{-C}_4\text{F}_6/\text{SF}_4$ mixture sparked. There was no indication either of carbon suppression or of CF_4 formation. Only small amounts of SF_4 were added since the results of sparking $2\text{-C}_4\text{F}_6/\text{SF}_6$ mixtures showed very little decomposition of SF_6 . Of course the ineffectiveness of SF_4 does not preclude the possibility that some other highly reactive species is produced from SF_6 which efficiently attacks the carbon. It is possible that the SF_6 in the hot arc reacts directly to form CF_4 and other saturated PFCs. The question remains open at present.

To summarize, the compounds CF_4 , C_2F_6 , C_2F_4 , C_3F_8 , C_4F_8 , C_4F_{10} , C_5F_{12} , C_6F_{14} and two isomers of $\text{S}_2\text{C}_2\text{F}_4$ have been identified in arc decomposition of $2\text{-C}_4\text{F}_6/\text{SF}_6$ mixtures. The saturated PFCs primarily CF_4 , are formed as a result of SF_6 addition and coincide with a decrease in carbon deposits. The optimum mixture from the standpoint of carbon suppression appears to be (30%) $2\text{-C}_4\text{F}_6$ /(70%) SF_6 . It will be interesting to see in future experiments on other fluorocarbon dielectrics whether SF_6 behaves in a similar manner.

The findings reported herewith strongly suggest that in the use of PFC/ SF_6 mixtures as high voltage insulants, the analyses of gaseous products, particularly perfluoromethane, can offer a diagnostic tool

for evaluating the extent of carbon suppression. This is of utmost importance for the optimum tailoring of dielectric mixtures using perfluorocarbon component gases which have been found by us to have excellent dielectric strengths.

Acknowledgements

The GC/MS analyses were performed in collaboration with the Analytical Chemistry Division of Oak Ridge National Laboratory. This research was sponsored by the Division of Electric Energy Systems of the U. S. Department of Energy under contract (W-7405-eng-26) with Union Carbide Corporation.

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Figure Captions

Figure 1. Ion intensity versus scan number (proportional to retention time) for a sparked sample of (60%) $2\text{-C}_4\text{F}_6$ /(40%) SF_6 injected into a GC/MS. (See text for details of sample preparation). (I) Total ion intensity. (II) Ion intensity for $m/e = 69$ (CF_3^+). (III) Ion intensity for $m/e = 95$ (S_2CF^+). (IV) Ion intensity for $m/e = 100$ (C_2F_4^+). (V) Ion intensity for $m/e = 127$ (SF_5^+). (VI) Ion intensity for $m/e = 169$ (C_3F_7^+).

Figure 2. Intensity of CF_3^+ ($m/e = 69$) versus scan number for various $2\text{-C}_4\text{F}_6/\text{SF}_6$ mixtures injected into a GC/MS. (See text for details of sparked sample preparation.) (I) Unsparked (50%) $2\text{-C}_4\text{F}_6$ /(50%) SF_6 . (II) Sparked (80%) $2\text{-C}_4\text{F}_6$ /(20%) SF_6 . (III) Sparked (60%) $2\text{-C}_4\text{F}_6$ /(40%) SF_6 . (IV) Sparked (40%) $2\text{-C}_4\text{F}_6$ /(60%) SF_6 . (V) Sparked (20%) $2\text{-C}_4\text{F}_6$ /(80%) SF_6 .

Figure 3. Concentration (in %) of CF_4 produced in spark-induced breakdown of $2\text{-C}_4\text{F}_6/\text{X}$ (where X is SF_6 or N_2) as a function of the concentration (in %) of X. Spark conditions are given both in the figure and in more detail in the text.

Figure 4. CF_3^+ ($m/e = 69$) ion intensity as a function of retention time for sparked $2\text{-C}_4\text{F}_6/\text{X}$ mixtures (where X is SF_6 or N_2). (a) (20%) $2\text{-C}_4\text{F}_6$ /(80%) X. (b) (60%) $2\text{-C}_4\text{F}_6$ /(40%) X. (See text for details of sample preparation.)

Figure 5. Abundance (in %) of CF_4 as a function of concentration (in %) of SF_6 in $2\text{-C}_4\text{F}_6$; the CF_4 is formed by carbon conversion in sparked-induced breakdown of the $2\text{-C}_4\text{F}_6/\text{SF}_6$ mixtures. The inset shows an extrapolation of the same data to zero SF_6 concentration, yielding an estimate of the carbon production in sparked 100% $2\text{-C}_4\text{F}_6$.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

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Fig. 5

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Appendix C

Assessment of Potential Health Effects of Dielectric Gases

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Gaseous Dielectrics II: (Proceedings of the Second International Symposium on Gaseous Dielectrics, Knoxville, Tennessee, March 9-13, 1980) to be published by Pergamon Press.

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ASSESSMENT OF POTENTIAL HEALTH EFFECTS OF DIELECTRIC GASES*

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ABSTRACT

Potential health effects of certain fluorinated hydrocarbons considered for gaseous dielectric applications have been examined. Toxicological data are lacking for some of the chemicals of interest. The most extensive studies relate to sulfur hexafluoride and octafluorocyclobutane, both of which appear to be rather non-toxic, for acute exposure situations. Mutagenicity studies with fruit flies have identified octafluorocyclobutane and perfluorobutene-2 as producing sex-linked recessive mutations in this organism. Certain products generated by electric discharge through the dielectric gas mixtures and trace contaminants produced during the manufacturing process may be more toxic than the parent compounds.

INTRODUCTION

Assessment of the potential health impacts of chemicals requires an exposure assessment and a health risk assessment. Concern over the increasing number of chemicals to which humans are exposed has generated extensive efforts to test chemicals for effects in different biological systems. Health risk assessments must usually be based upon extrapolation from such systems. Balanced against concerns about chemical hazards, however, is the realization that chemicals are an essential part of the technological society of the present day, and attempts to eliminate all chemical hazards are, by their very nature, unrealistic. The case of certain fluorinated hydrocarbons, which appear to have very great potential as gaseous dielectric compounds, but which may also pose certain health hazards, illustrates this dilemma. These compounds, when used in high voltage transmission systems, may result in large energy and monetary savings. The question that needs to be addressed is, on the basis of human health considerations, what degree of regulation must accompany the different potential uses of the various dielectric materials. In this paper, we will consider studies that have investigated various biological effects of some gaseous dielectrics and their breakdown products, and, based on the paucity of information available, we will suggest new studies that should be conducted to derive a reasonable estimate of the degree of control that may be necessary.

* Research sponsored by the Office of Health and Environmental Research, U.S. Department of Energy under contract W-7405-eng-26 with the Union Carbide Corp.

DISCUSSION

Although there are a number of chemicals that may be suitable for use as dielectric gases, this paper is limited to a consideration of those gases being used by the Atomic, Molecular and High Voltage Physics Group of the Health and Safety Research Division at Oak Ridge National Laboratory. More specifically, we will consider the following chemicals: octafluorocyclobutane (C_4F_8); perfluorobutene-2

(2- C_4F_8); perfluoro-2-butyne (2- C_4F_6); hexafluorocyclobutene (C_4F_6); perfluorocyclohexane (C_6F_{10}); and sulfur hexafluoride (SF_6). We will first consider what few studies are available examining the biological effects of these compounds. A brief discussion of possible effects from breakdown products likely to arise from these parent compounds will follow. Finally, data gaps and recommendations for further studies will be identified.

Toxicity of Parent Compounds

Toxicity studies for some of the parent compounds are incomplete or are lacking altogether. Available data relate primarily to acute exposure conditions; very few chronic exposure studies have been done. Most of the available information is on octafluorocyclobutane and sulfur hexafluoride. Occupational exposure guidance in the form of threshold limit value (TLV's) is available for some of the compounds. Also available are some data on concentrations lethal to some or all test species for certain exposure times. Data of this nature on some of the compounds of interest are presented in Table 1.

TABLE 1 Toxicity of Certain Fluorinated Compounds

Chemical	Toxic Effects	Route of Administration-Species	Length of Exposure	Reference
Carbon Tetrafluoride	LC-Lo = 895,000 ppm	Inhalation - Rat	15 min	2
Octafluorocyclobutane (C_4F_8)	None = 800,000 ppm	Inhalation - Rat	4 hrs	3
Perfluorobutene -2 (C_4F_6)	LC ₅₀ = 170,000 ppm	Inhalation - Fly	6 min	10
Hexafluorocyclobutene (C_4F_6)	LC-Lo = 50,000 ppm	Inhalation - Mouse	Not Reported	2
Perfluoro-2-butyne (C_4F_6)	LC ₅₀ = 91 ppm	Inhalation - Rat	4 hrs	21
Octafluorocyclopentane (C_5F_8)	LC-Lo = 30,000 ppm	Inhalation - Mouse	Not Reported	2
Decafluorocyclohexane (C_6F_{10})	LC-Lo = 8,000 ppm	Inhalation - Mouse	Not Reported	2
Perfluoromethylcyclohexane (C_7F_{14})	LC-Lo = 825 ppm	Inhalation - Mouse	14 hrs	2
Sulfur Hexafluoride (SF_6)	TLV = 1,000 ppm	--	--	2

The fact that some of the chemicals listed above do not occur in this table should not be construed as indicating these compounds have no toxic or lethal effects; absence generally indicates lack of data. To provide some comparison of the toxicity indices in Table 1 with more familiar chemicals, the TLV's for NH_3 and H_2S are 25 and 10 ppm,[†] respectively, while the LC_{50} 's for NH_3 and H_2S are 2000 ppm (4 hr exposure-rat) and 713 ppm (1 hr exposure-rat), respectively. The LC-Lo values are poor toxicity indicators, since individual animal susceptibility can vary greatly, and be a result of many different factors. It can be seen, however, that all of the compounds in Table 1 with the exception of perfluoro-2-butyne, are relatively non-toxic in terms of overt lethality. The activity of perfluoro-2-butyne is not surprising since, from a chemical standpoint, the acetylenic bond should be quite reactive. Lu et al. (1) also noted a toxic effect in dogs from perfluoro-2-butyne.

Sulfur hexafluoride, even in high concentrations, seems to be relatively non-toxic for acute exposure situations. Rats exposed to 80% SF_6 and 20% oxygen for 16-24 hrs showed no ill effects from the exposure (2). Clayton (3) found no mortality in rats exposed to SF_6 (170,000 ppm) for 18 hrs. Troshikhin and Issakyan (4) observed increased respiration rate in rats exposed to 80% SF_6 + 20% O_2 . This observation suggests SF_6 , in acute high exposure conditions, may act as a simple asphyxiant. The concentrations of SF_6 necessary to cause this effect, however, are so high it is unlikely humans will be exposed to these concentrations.

Studies by Clayton (3) indicated that rats exposed to 80% octafluorocyclobutane and 20% oxygen for 4 hrs showed no toxic effects. Acute exposures of mice to the same atmosphere had no effect (3). Chronic exposure conditions (as many as ninety exposures of 6 hrs each to a 10% octafluorocyclobutane atmosphere) showed no toxic effects in rats, mice, rabbits or dogs (3). Clayton et al. (5) carried out rather thorough acute and chronic toxicity studies of octafluorocyclobutane using a variety of species including rats, mice and dogs. Parameters measured included weight gain, cardiac variables, hematology and pathology of various organs. By all these parameters this chemical appeared to be innocuous.

In contrast to these results, Friedman et al. (6) found that octafluorocyclobutane (48% in air) caused apnea (cessation of breath) and cardiac arrest in anesthetized rats. A slowing of the heart rate and a decrease in respiration rate, along with other changes in respiration parameters, was noted. It is important to note that the purity of the gas used was not given. The effect that general anesthesia had on the overall results of this study is also difficult to determine. This same research group (7) studied the effect of octafluorocyclobutane on monkeys. No cardiac arrhythmia, change in heart rate or change in

[†]Abbreviations used in this paper are:

- ppm - parts per million
- pph - parts per hundred
- ALC - Approximate Lethal Concentration
- LC_{50} - A calculated concentration of a substance in air, exposure to which for a specified length of time is expected to cause the death of 50% of an entire experimental population.
- LC-Lo- The lowest concentration of a substance in air, other than LC_{50} , which has been reported to cause death in humans or animals.

aortic blood pressure was found when rhesus monkeys were exposed for 5 min to 10 or 20% concentrations of the chemical in air.

Although the studies are few in number and the results somewhat at variance, a preliminary conclusion about the toxicity of octafluorocyclobutane is that the chemical appears to be relatively non-toxic. It seems unlikely that the general population or even occupational workers would be exposed to levels approaching the high concentrations at which biological effects are seen.

The mutagenic effects of chronic exposure to some of the parent fluorinated gaseous dielectrics has also been studied. The mutagenic potential of chemicals is receiving increasing attention, since most carcinogens have been shown to be mutagens and since mutations to germ cells can result in teratogenesis. Fuerst and Stephens (8) found that perfluorobutene-2 produced a mutation rate of 0.92% in *Neurospora crassa* when the micro-organisms were exposed to the gas for 18 hrs at 4° C. This was compared to control rates of 0%. Foltz and Fuerst (9) found that octafluorocyclobutane did not cause an increase in recessive lethal mutation frequencies in *Drosophila melanogaster* (fruit flies) when the flies were exposed to a gaseous atmosphere of the chemical for 10 min. A 0.38% incidence of phenotypic (non-lethal) mutations was found in Maxy-strain female flies compared with control rates of 0.008%. Tumors were observed in flies treated with octafluorocyclobutane. In contrast, perfluorobutene-2 did cause statistically significant increases in recessive lethal mutation rates when flies were exposed to the gas for 6 min (1.30% compared to control rates of 0.23%).

In further work from this same group, the mutagenicity of perfluorobutene-2 was more carefully investigated in the fruit fly system (10). Exposure to increasing concentrations of perfluorobutene-2 for 6 min resulted in increasing recessive mutation rates in fruit flies. These data are shown in Table 2.

TABLE 2 Mutagenicity of Perfluorobutene-2 to
Drosophila Melanogaster

Gas	Flow Rate (ml/min)	Recessive Mutation Rate (%)
Air	--	0.21
Perfluorobutene-2	7	0.42 ± 0.03
Perfluorobutene-2	13	1.78 ± 0.02
Perfluorobutene-2	22	1.43 ± 0.05 ^a

Exposure 1 min, followed by 6 min, in sealed chamber

^aGas is toxic at this concentration = LC₃₀

When mixtures of perfluorobutene-2 and various components of air such as oxygen, nitrogen, and carbon dioxide were used to treat the flies, all mixtures increased recessive sex-linked mutation frequencies significantly above control levels, although treatment with 10% oxygen also increased mutation frequencies above control levels.

These studies suggest that some of the fluorinated gaseous dielectrics, particularly perfluorobutene-2, may pose a mutagenic hazard. Of course, it is important to determine whether the effect observed is due to the main gaseous component or some contaminant in the gas mixture. If a highly reactive trace contaminant is present, it could account for the mutation frequencies observed. Foltz and Fuerst (9) give the minimum purity of the octafluorocyclobutane and of perfluorobutene-2 used as 99.5%. In addition to this potential confounding factor, there is also the very real and significant problem of species specificity. The evidence for mutation in one species is enough to suggest that some further experiments in *in vitro* mammalian cell mutagenesis systems be carried out. From a biological viewpoint, it is very difficult to understand how octafluorocyclobutane could be a mutagen, since it would seem to lack the necessary chemical reactivity to interact with DNA.

Toxicity of breakdown products and contaminants

Aside from the potential health effects subsequent to using a pure gaseous dielectric, chemical constituents in the form of impurities may also be important. These impurities primarily derive from the manufacturing process, and chemical rearrangement under electrical discharge.

Of the dielectric gases presented by Sauers et al. (11), only the following four-carbon fluorides will be considered based on stability considerations relative to low energy electrons (0-12 eV): $c\text{-C}_4\text{F}_6$, $2\text{-C}_4\text{F}_6$, $c\text{-C}_4\text{F}_8$ and $2\text{-C}_4\text{F}_8$. In the absence of chemical analyses of bulk industrial quality fluorocarbons, insight into potential impurities is attained by examination of production reactions.

Manufacturing processes were identified for each fluorocarbon (12,13) and the last stages in one process for each fluorocarbon are presented (general reactions only are indicated).

PERFLUOROBUTENE-2

2-C₄F₈

Each of the above final products may have several alternate means for production, however, it is interesting to note that within the last processing steps presented above, each fluorocarbon gas has toxic precursors (see Table 3) or co-products. It is likely that a small portion of these toxic materials is present in most gas samples.

TABLE 3 Toxicity of precursors or co-products of fluorocarbon gases

Main Gas	Precursor or co-product	Inhalation Toxicity of Precursor or Co-product		Reference
c-C ₄ F ₆	1,2-Dichlorohexafluoro-cyclobutane	Mouse	LC-Lo: 21 pph/0.5 min	2
		Rat	LC ₅₀ 16 ppm/4hr	2
2-C ₄ F ₆	Dichlorohexafluorobutene	Mouse	LC ₅₀ 26 ppm/4hr	
2-C ₄ F ₈		Dog	LC ₅₀ 182 ppm/4hr	
		Monkey	LC ₅₀ 54 ppm/3hr	
		Rabbit	LC-Lo 500 ppm/1hr	
c-C ₄ F ₈	Perfluoroisobutylene	Rat	LC-Lo 0.8 ppm/4hr	2

Current trends in gaseous dielectric research indicate that it is likely most dielectric gases of the future will be mixtures. Examination of the permanent products due to electrical discharge is important in order to determine if any hazardous material is produced. Products of the present standard gas, SF₆, have been examined thoroughly (14) and will not be reiterated.

The results of sparking mixtures of 2-C₄F₆ and SF₆ were presented in an earlier paper (11). Although relative concentrations are not precisely known, identification of the major products yield CF₄, C₂F₄, C₂F₆, C₃F₈, C₄F₁₀, C₅F₁₂, C₆F₁₄, and S₂C₂F₄. These product fluorocarbons have been examined for their reported toxicities which are presented in Table 4. It appears that for these mixtures (fluorocarbon + SF₆), initial impurities may be of more importance than breakdown products.

TABLE 4 Toxicity of breakdown products from a mixture of 2-C₄F₆ and SF₆

Product	Comments	Inhalation Toxicity for Rat	Reference
CF ₄	--	LC-Lo: 89%/15 min	2
C ₂ F ₄	--	LC ₅₀ : 4%/4hr	3
C ₂ F ₆	--	ALC: 20%/2hr	3
C ₃ F ₈	No Data	--	-
c-C ₄ F ₈ ^a	No toxic effects observed-80%/4hr	--	3
2-C ₄ F ₈ ^a	Fruit fly-6 min exposure	LC ₁₀ : 170,000 ppm	10
iso-C ₄ F ₈ ^a		LC-Lo: 0.8 ppm/4hr	2
C ₄ F ₁₀	No anesthesia-80% in air	--	22
C ₅ F ₁₂	No anesthesia-80% in air	--	22
C ₆ F ₁₄	No Data	--	-
S ₂ C ₂ F ₄	No mortality observed from 2 exposed rats-5ppm/4hr	--	3

^aIsomers not identified in reference 11.

It is suggested that examination be made of impurities in commercial grade of gases once dielectric stability properties appear satisfactory. In addition, the potential of impurities to concentrate should be studied, since this process for the anesthetic halothane has been observed (15), refuted (16, 17, 18), and then convincingly shown (19). This concentration phenomenon, primarily resulting from distillation of multicomponent mixtures, has also been observed for the case of the impurity dichlorohexafluorobutene in the dielectric gas 2-C₄F₆ (20).

It is not inconceivable that the mutagenic effect of 2-C₄F₈ (Table 2) is due to a contaminant in the primary gas since one of the precursor gases is dichlorohexafluorobutene.

Still undetermined are the breakdown products of a "normal" industrial mixture of dielectric gases with their less-than-laboratory grade purity components and likelihood of significant air contamination. The screening of a dielectric gas for possible commercial use should include identification of breakdown species as well as an actual sample of the breakdown products which can then be used in rapid biological screening techniques for toxicity and mutagenesis.

SUMMARY

The foregoing brief discussion has been an attempt to survey the literature available on the toxicity of fluorinated gaseous dielectric compounds. It is clear that the majority of these chemicals have not been adequately investigated, although the current meagre data available seems to justify a fair amount of optimism that these compounds will be relatively non-toxic for humans. From a chemical reactivity standpoint, most of the saturated fluorinated gases considered seem rather inert, and it is hoped that this lack of reactivity will carry over into the biological realm. It is important to realize, however, that an apparently unreactive chemical structure is no guarantee of biological safety, since

enzymatic mechanisms in cells are capable of converting unreactive compounds to highly reactive species. For this reason, it is important that the effect of these compounds and their metabolic products upon cellular systems be studied.

It is somewhat easier to understand the toxic effects exerted by the unsaturated fluorinated hydrocarbons in light of their chemical reactivity. The toxicity spectrum here ranges from quite mild to strongly toxic, and clearly the more toxic members will require much stricter exposure control compared to less toxic compounds.

Most of the acute effects of the fluorinated chemicals discussed in this paper seem to be mild and/or transient, and do not suggest a severe human hazard. A possibly more disturbing finding is the evidence of mutagenicity of some of these chemicals. This observation needs to be studied in a variety of systems using gases of known composition to determine: (1) whether the mutagenicity is due to a contaminant or the main gaseous component; and (2) if the mutagenicity is a peculiarity of the fruit fly system or is a common characteristic with other mutagenesis systems. At present, too little information exists to even speculate whether these compounds, if indeed mutagenic, are also carcinogenic, but further mutagenicity tests may provide evidence for either rejecting or initiating carcinogenicity trials.

In terms of human exposure potential, it appears that the general public would not experience significant exposure to these compounds. Even in the case of occupational exposure, it seems unlikely that any workers will be exposed to the high concentrations used in the animal toxicity experiments. Unless low concentrations of these gases are mutagenic, the risk to human health may be low.

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