EFFECT OF TEMPERATURE ON THE UNIFORM FIELD BREAKDOWN STRENGTH
OF ELECTRONEGATIVE GASES*

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ABSTRACT

In general, the electron attachment rate constant, k_a ($\langle\epsilon\rangle$,T), as a function of the mean electron energy $\langle\epsilon\rangle$ and temperature T for electronegative gases which attach electrons *nondissociatively* decreases greatly with T from room temperature to T $\lesssim$ 600K, while that for electronegative gases which attach electrons *dissociatively* increases with increasing T. Based on recent studies in our laboratory on k_a ($\langle\epsilon\rangle$,T), we investigated the variation with T (~295-575K) of the uniform field breakdown strength, $(E/N)_{\ell im}$, for three classes of electronegative gases: (a) gases such as $c-C_4F_8$ (and $c-C_4F_6$, $1-C_3F_6$) which attach strongly low-energy ($\lesssim$ 1 eV) electrons nondissociatively and for which k_a ($\langle\epsilon\rangle$,T), decreases precipitously with T above ambient; (b) gases such as C_2F_6 and CF_3Cl which attach electrons exclusively dissociatively and whose k_a ($\langle\epsilon\rangle$,T) increases with T; and (c) gases such as C_3F_8 and $n-C_4F_{10}$ which attach electrons both nondissociatively and dissociatively over a common low-energy range and whose k_a ($\langle\epsilon\rangle$,T) first decreases and then increases with T above ambient. The $(E/N)_{\ell im}$(T) has been found to <u>decrease</u> significantly with T for (a), to <u>decrease</u> slowly with T for (c), and to <u>increase</u> slightly with T for (b). These changes in $(E/N)_{\ell im}$ follow those in k_a ($\langle\epsilon\rangle$,T). A similar behavior is expected for other electronegative gaseous dielectrics in the respective three groups.

KEYWORDS

Electronegative gases; breakdown strength; electron attachment; effect of temperature.

INTRODUCTION

The crucial role of electron attachment in determining the dielectric strength of gases has long been recognized (e.g., see Meek and Craggs, 1978; Christophorou and Hunter, 1984) and has recently been quantified (Christophorou, 1980a, 1982, 1984; Christophorou and coworkers, 1981b). Recent studies (Christophorou, 1980b; Christophorou and coworkers, 1984, 1987) have also shown that the electron attachment rate constant k_a (or cross section σ_a) of electronegative gases can be a strong function of the temperature T over a wide range of mean electron energies $\langle\epsilon\rangle$. Thus it has been found that the $k_a(\langle\epsilon\rangle)$ for nondissociative electron attachment to molecules decreases (Christophorou and coworkers, 1984, 1987; Spyrou and Christophorou, 1985a; Hunter and coworkers, 1983; Christodoulides and coworkers, 1987; Datskos and Christophorou, 1987a,b) greatly with increasing T over a wide range of $\langle\epsilon\rangle$ for temperatures within a few hundred degrees above ambient. Similarly, it has been found that the rate constant for dissociative electron attachment increases (Christophorou, 1980b; Christophorou and coworkers, 1984, 1987; Spyrou and Christophorou, 1985b,c; Datskos and Christophorou, 1987a) with T above ambient, but this increase is normally smaller compared to the decrease of k_a in the case of nondissociative electron attachment over a comparable temperature range (~295-575K). For gases for which both dissociative and nondissociative electron attachment occurs over a common energy range, the total electron attachment rate constant was found (Spyrou and Christophorou, 1985c; Datskos and Christophorou, 1987a) to first decrease and then increase with increasing T above ambient, showing a rather delicate dependence of the electron attachment properties of gaseous dielectrics on T for T $\lesssim$ 700K.

In this paper we report on the effect these influences of T on $k_a(\langle\epsilon\rangle)$ have on the uniform field breakdown strength of electronegative gases.

EXPERIMENTAL DETAILS

The experimental procedure and breakdown chamber employed to measure the dc breakdown voltage have been partly described previously (Christophorou and coworkers, 1977, 1981a). The temperature could be measured to $\pm1^\circ C$ over the range ~25-300°C investigated. For each gas studied, the breakdown measurements began at room temperature and with a gas pressure of 69.3 kPa (1.7×10^{19} molecules cm^{-3}). The measurements continued at selected higher values of T between room temperature and 575K using the same gas. Following the measurements at 575K the gas temperature was decreased by 150 degrees or the gas was cooled down to room temperature and the breakdown measurements were repeated. For all gases studied the data reproduced the earlier values showing that no irreversible changes in the gas composition due to heating occurred. No thermal decomposition is expected for any of the gases studied in the temperature range investigated. We found, however, that when SF_6 was heated to T $\gtrsim$ 420K, it reacted with the metal surfaces, especially with the small copper gaskets we used to seal vacuum flanges.

At each value of T where measurements were made, ten breakdown measurements were conducted for each value of the electrode gap d which was varied from 1.905 to 10.795 mm in steps of 1.27 mm. The measurements were corrected for compressibility (Biasiutti, 1985). The purity of the gases used was >99%.

In Fig. 1 is plotted the uniform field dc breakdown voltage V_s as a function of Nd (product of the gas number density N and the electrode gap d) for c-C_4F_8 at various temperatures. These measurements are representative of those obtained for this and the rest of the gases investigated. From such measurements the ratio $(V_s)_T/(V_s)_{Room}$ (ratio of the values of V_s at a temperature T above room temperature and at room temperature) were determined as a function of T and are shown in Fig. 2. We found, however, that the $V_s(T)$ vs Nd measurements could best be presented as the measured $(E/N)_m$ vs Nd for various values of $T(\leq 575K)$. An example of such plots is shown in Fig. 3 for c-C_4F_8. For each value of T and each gas studied the plots $(E/N)_m$ vs Nd were fitted to the expression

$$(E/N)_m = (E/N)_{\ell im} + A/Nd$$

(where A is a constant) and the limiting value, $(E/N)_{\ell im}$, of E/N was obtained. The values of $(E/N)_{\ell im}$ at various T are listed in Table 1 and are plotted in Fig. 4 for c-C_4F_8. n-C_4F_{10}. C_3F_8. 1-C_3F_6 and in Fig. 5 for C_2F_6 and CF_3Cl.

TABLE 1 $(E/N)_{\ell im}(T)$ for CF_3Cl. C_2F_6. C_3F_8. n-C_4F_{10}. c-C_4F_8. and 1-C_3F_6

CF_3Cl		C_2F_6		C_3F_8		n-C_4F_{10}		c-C_4F_8		1-C_3F_6	
T^a	$(E/N)_{\ell im}^b$	T	$(E/N)_{\ell im}$	T	$(E/N)_{\ell im}$	T	$(E/N)_{\ell im}$	T	$(E/N)_{\ell im}$	T	$(E/N)_{\ell im}$
294	1.928	298	2.742	297	3.524	298	4.854	295	4.354	297	3.496
400	1.927	373	2.746	348	3.517	324	4.868	324	4.239	324	3.469
450	1.941	423	2.751	373	3.505	348	4.857	373	4.073	373	3.446
500	1.958	473	2.759	398	3.499	373	4.815	423	3.830	423	3.389
550	1.989	523	2.763	423	3.488	398	4.777	473	3.622		
573	1.995	573	2.771	448	3.482	423	4.738	523	3.542		
				473	3.476	448	4.708	573	3.535		
				497	3.470	476	4.665				
				523	3.467	499	4.637				
				573	3.463	527	4.594				
						549	4.571				
						574	4.546				

^{a} in K.

^{b} in 10^{-16} V cm^2.

Fig. 1. V_s versus Nd at various T for c-C_4F_8.

Fig. 2. $(V_s)_T/(V_s)_{Room}$ versus T for c-C_4F_8.
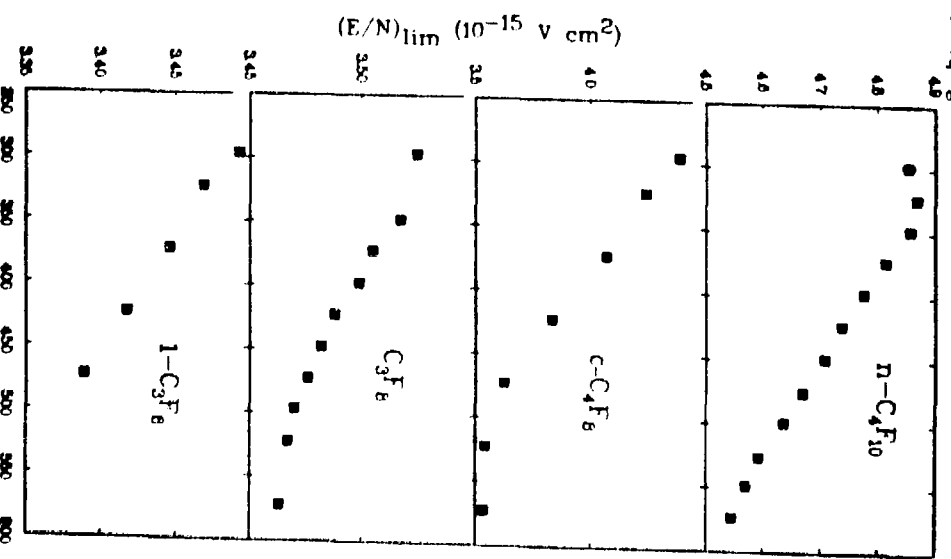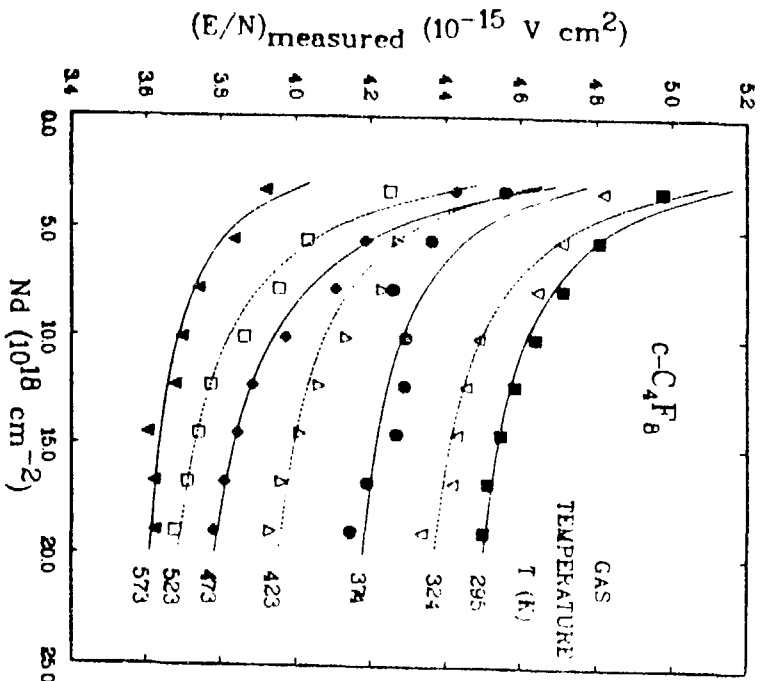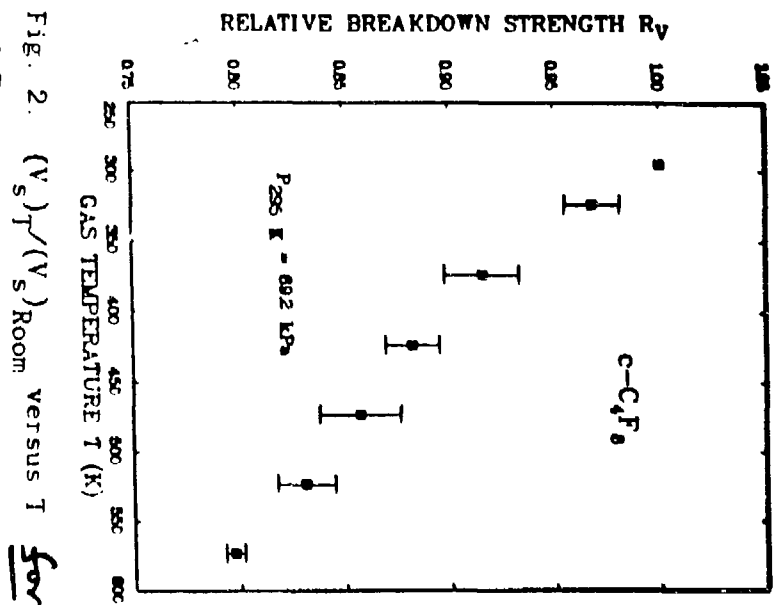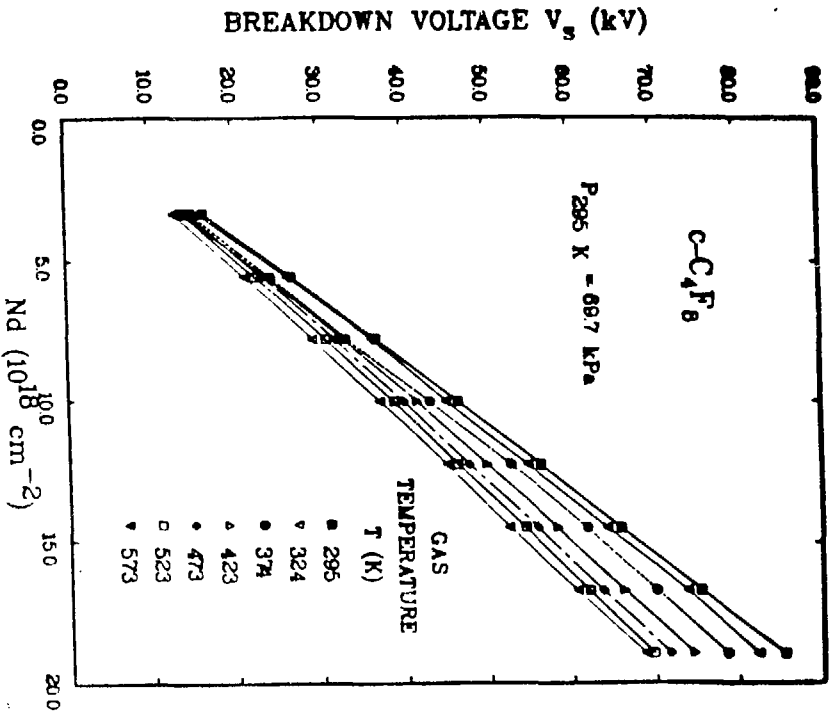

Fig. 3. $(E/N)_{measured}$ versus Nd at various T for c-C_4F_8.

Fig. 4. $(E/N)_{0lim}$ versus T for n-C_4F_{10}, c-C_4F_8, C_3F_8, and 1-C_3F_6.

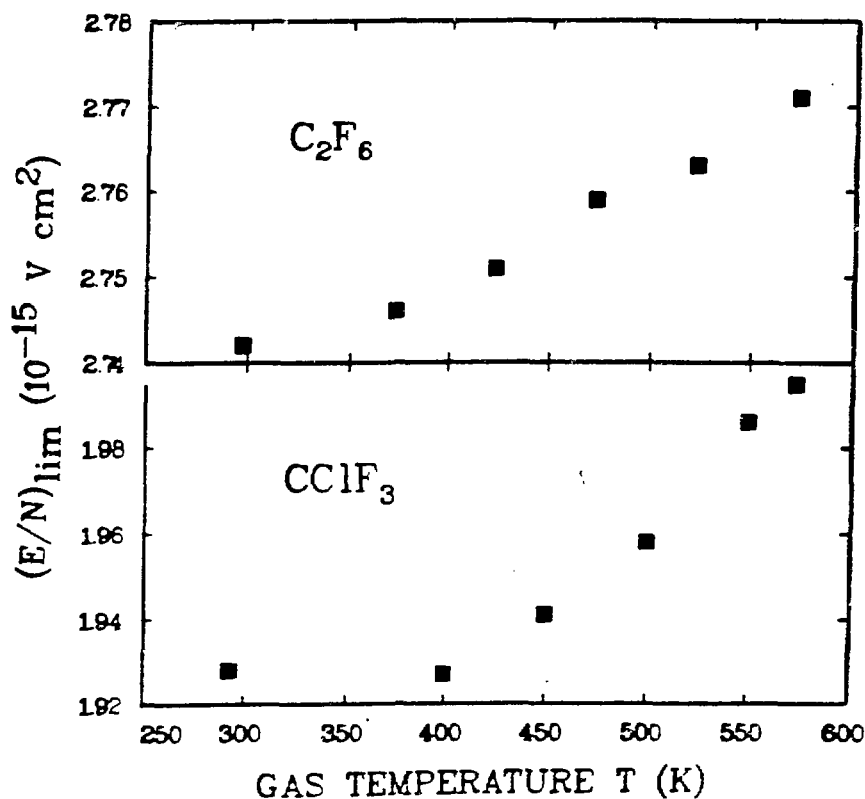Fig. 5. $(E/N)_{\ell im}$ versus T for C_2F_6 and $CClF_3$.

DISCUSSION

Variation of the Electron Attachment Rate Constant/Cross Section with Temperature

In Figs. 6, 7, and 8 are given, respectively, examples of electronegative gases in groups (a), (b), and (c). In the energy range indicated in Figs. 6 to 8, $c-C_4F_8$ (and $1-C_3F_6$) attach electrons almost exclusively nondissociatively, CF_3Cl (and C_2F_6) exclusively dissociatively, and $n-C_4F_{10}$ (and C_3F_8) both dissociatively and nondissociatively. From the data in Figs. 6 to 8 the total electron attachment cross sections $\sigma_a(\epsilon,T)$ were estimated and used to determine the energy integrated attachment cross sections $\int\sigma_a(\epsilon,T)d\epsilon$. These are shown in Fig. 9. The data in Figs. 6 to 9 clearly demonstrate the delicate dependence of electron attachment on the gas temperature and help explain (see below) the observed variation of V_s (or $(E/N)_{\ell im}$) with T.
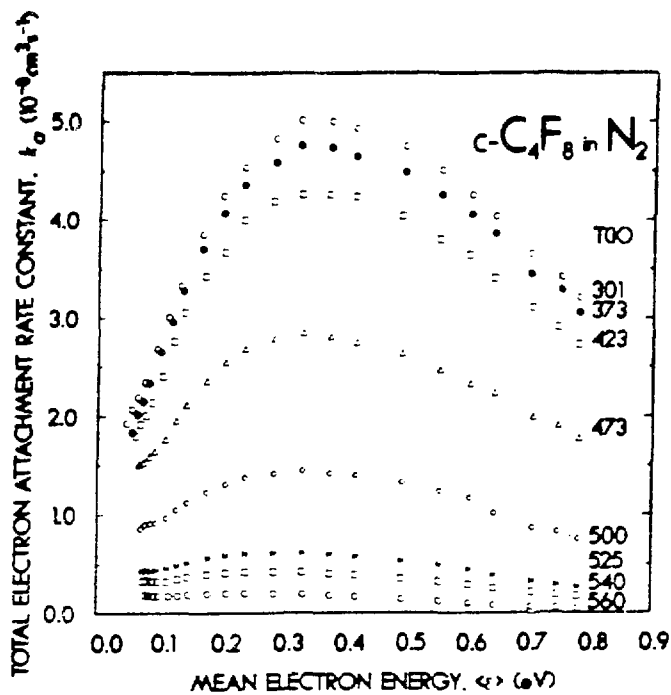
Fig. 6. $k_a(\langle\epsilon\rangle,T)$ for c-C_4F_8
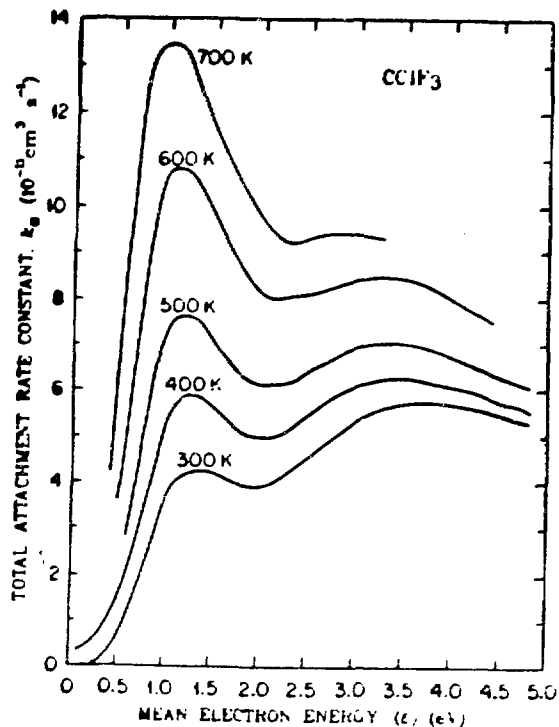(Christodoulides and coworkers, 1987).

Fig. 7. $k_a(\langle\epsilon\rangle,T)$ for CF_3Cl
(Spyrou and Christophorou, 1985b).

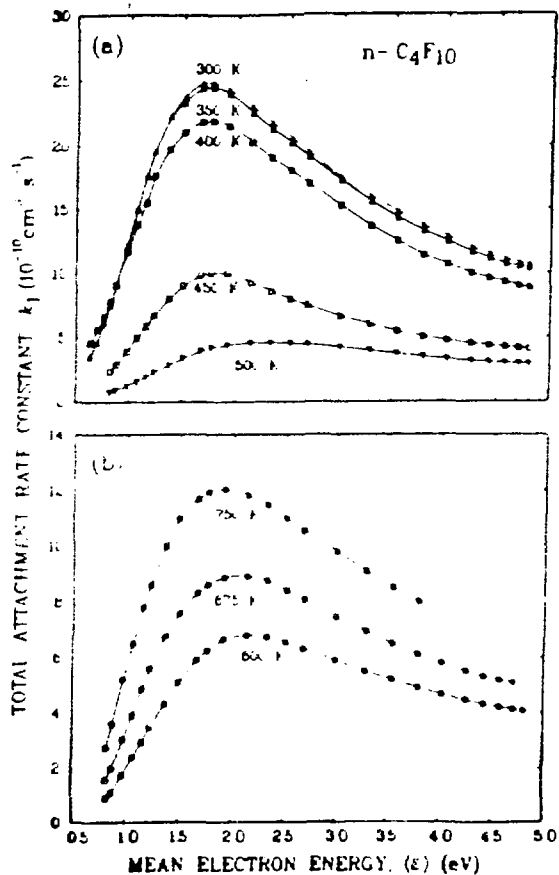Fig. 8. $k_a(\langle\epsilon\rangle,T)$ for n-C_4F_{10}
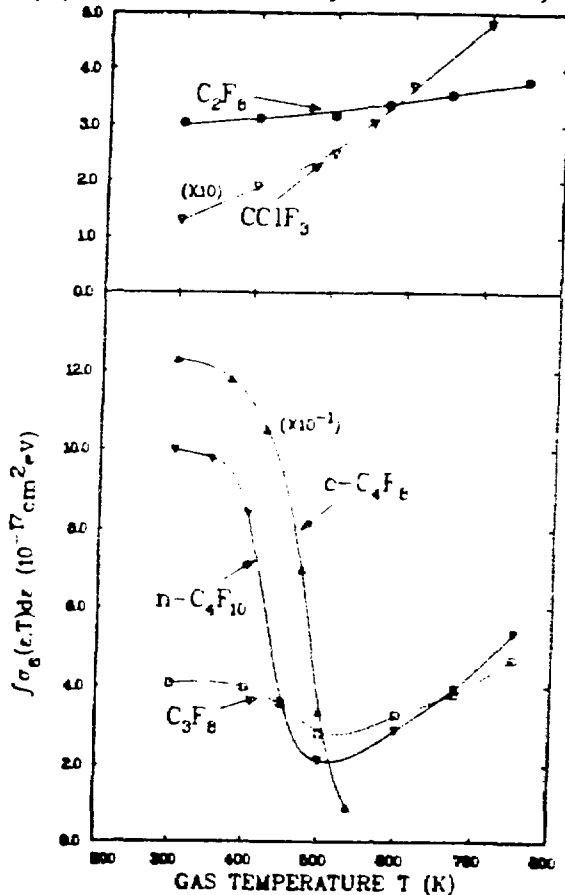(Datskos and Christophorou, 1987a).

Fig. 9. $\int\sigma_a(\epsilon,T)d\epsilon$ versus T for
c-C_4F_8, n-C_4F_8, C_3F_8, C_2F_6, and
CF_3Cl.

Relation of $V_s(T)$ to $k_a(\langle\epsilon\rangle,T)$

While as T increases above room temperature the electron scattering processes change along with electron attachment, it is clear from the present study that the dependence of V_s on T follows the T-dependence of electron attachment. It is also clear that for T ≤ 600K the cross section for nondissociative electron attachment decreases much faster than the cross section for dissociative electron attachment increases, and this is also consistent with the observed changes in $V_s(T)$. To illustrate this further we have plotted in Fig. 10 the ratio R_v vs R_{IA} (see figure caption). By far the largest decrease in R_v occurs for $c\text{-}C_4F_8$ for which electron attachment is nondissociative and decreases greatly with T. For C_3F_8 and $n\text{-}C_4F_{10}$ for which $\int\sigma_a(\epsilon,T)d\epsilon$ first decreases (because of the decrease in nondissociative attachment) and then increases (because of the increase in dissociative attachment) with T, the decrease in R_v is much smaller. Interestingly when (at high T) dissociative attachment causes the R_{IA} to increase with T, the corresponding increase in R_v is smaller than expected indicating changes in the other electron scattering processes and the resultant overlap of $\sigma_a(\epsilon)$ with the electron energy distribution function.

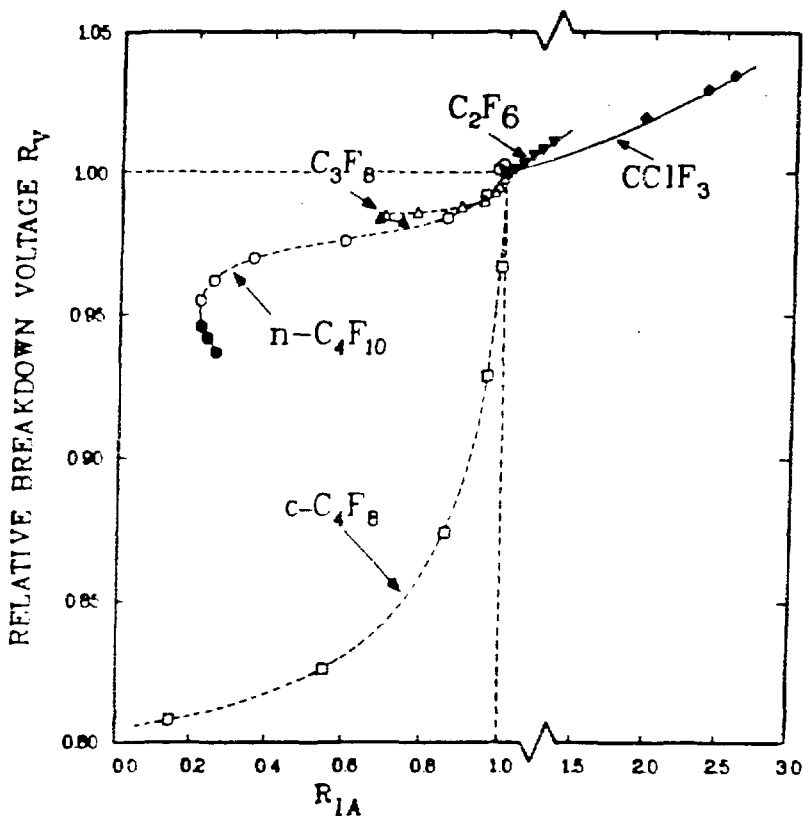Fig. 10. $R_v \equiv [(E/N)_{\ell im}]_T / [(E/N)_{\ell im}]_{Room}$ versus

$R_{IA} \equiv [(\int\sigma_a(\epsilon)d\epsilon)_T / (\int\sigma_a(\epsilon)d\epsilon)_{Room}]$

for $c\text{-}C_4F_8$, $n\text{-}C_4F_{10}$, C_3F_8, C_2F_6, and CF_3Cl.

CONCLUSION

In the temperature range ~295–600K, the $(E/N)_{\text{lim}}$ of electronegative gases increases with T when electron attachment increases with T, a situation applicable to molecules which attach electrons dissociatively. The increases in both $(E/N)_{\text{lim}}$ and attachment are normally small. In the same temperature range, the $(E/N)_{\text{lim}}$ of electronegative gases decreases with T when electron attachment decreases with T, a situation applicable to molecules which attach electrons nondissociatively. In this case the decreases in both $(E/N)_{\text{lim}}$ and electron attachment are large.

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