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COLLISIONAL ELECTRON-DETACHMENT AND ION-CONVERSION PROCESSES IN SF_6

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INTRODUCTION

It has long been hypothesized that collisional electron detachment from negative ions may be the cause of discharge initiation in SF_6-insulated high-voltage equipment. However, uncertainties continue to exist concerning the identities of the significant negative ions, and the magnitudes of the detachment cross sections and corresponding reaction coefficients. Discharge inception studies, which usually assume that SF_6^- is the negative ion of interest, have predicted collisional-detachment cross sections of SF_6^- in SF_6 with thresholds ranging from 1 to 8 eV (Kindersberger, 1986). Collisional-detachment coefficients determined from low-pressure, uniform-field drift-tube experiments (O'Neill and Craggs, 1973; Hansen et al., 1983) lie several orders of magnitude above those calculated from breakdown data (Kindersberger, 1986), while exhibiting an unexplained pressure dependence. Additionally, evidence exists that the destruction of negative ions in SF_6 is dominated by collisional dissociation into ionic fragments (O'Neill and Craggs, 1973; McAfee, Jr. and Edelson, 1963; Compton et al., 1971; McGeehan et al., 1975; Urquijo-Carmona et al., 1986; Nakamura and Kizu, 1987) or by charge-transfer processes rather than by the loss of an electron. However, the exact nature of these ion-conversion processes has not previously been determined.

In this report we summarize results from the first direct measurements of absolute cross sections for electron-detachment and ion-conversion processes involving interactions of SF_6^-, SF_5^-, and F^- with SF_6 (Wang et al., 1989). These cross sections are used to calculate electron-detachment and ion-conversion reaction coefficients as functions of electric field-to-gas density

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ratios (E/N) for the reactions listed in Table 1 (Olthoff et al., 1989). We then discuss the relevance of these results to the interpretation of data from uniform-field drift-tube measurements and measurements of electrical-discharge initiation processes.

CROSS SECTIONS

Details of the experimental method used to measure the cross sections reported here are given elsewhere (Wang et al., 1989; White et al., 1984), and will not be covered here. We shall focus here only on the results obtained for collisions of SF_6^-, SF_5^-, and F^- on the SF_6 target gas, although measurements have also been made using rare gas targets (Wang et al., 1989), namely He, Ne, Ar, Kr, and Xe.

The measured center-of-mass energy dependencies of the collisional electron-detachment cross section, $\sigma_i(\epsilon_{cm})$ for SF_6^-, SF_5^-, and F^- on an SF_6 target are shown in Fig. 1. The thresholds for the "prompt" collisional electron-detachment processes

$$SF_6^- + SF_6 \rightarrow \text{neutral products} + e^-$$

$$SF_5^- + SF_6 \rightarrow \text{neutral products} + e^-,$$

as indicated by the vertical arrow in Fig. 1, are seen to be quite high (approximately 90 eV), while the detachment process for F^-,

$$F^- + SF_6 \rightarrow \text{neutral products} + e^-,$$

has a lower detachment threshold of about 8 eV. At center-of-mass collision energies below the indicated thresholds there is no evidence to suggest non-zero values for the $\sigma_i(\epsilon_{cm})$'s. Similar high values for the collisional electron-detachment thresholds were found for collisions of SF_6^- and SF_5^- ions with rare gas targets (Wang et al., 1989). The implication of these results as shown below is that prompt electron detachment from either SF_6^- or SF_5^- cannot be important for electrical-discharge conditions because, even for the highest E/N values which could conceivably occur in a gas discharge gap, only an insignificant fraction of the negative ions could acquire a kinetic energy of 90 eV or more.

Cross sections for the ion-conversion processes (reactions (4)-(9)) listed in Table 1 are shown in Fig. 2 together with extrapolations down to the thresholds which are used later in the calculation of corresponding rate coefficients. The bases for these extrapolations are also discussed later. The solid symbols indicate cross sections due to collisional-induced-dissociation (CID) processes, and the open symbols indicate cross sections for charge-transfer processes (including charge-transfer decomposition). There is evidence that the charge-transfer process involving SF_6^- on SF_6 is predominately dissociative

Table 1. Collisional processes for which cross sections are presented in the present work

cross section (σ_i)	reaction
σ_1	$SF_6^- + SF_6 \rightarrow e^- + SF_6 + SF_6$
σ_2	$SF_5^- + SF_6 \rightarrow e^- + SF_5 + SF_6$
σ_3	$F^- + SF_6 \rightarrow e^- + F + SF_6$
σ_4	$SF_6^- + SF_6 \rightarrow F^- + SF_5 + SF_6$
σ_5	$SF_5^- + SF_6 \rightarrow F^- + SF_4 + SF_6$
σ_6	$SF_6^- + SF_6 \rightarrow SF_5^- + F + SF_6$
σ_7	$SF_6^- + SF_6 \rightarrow$ charge-transfer products $+ SF_6$
σ_8	$SF_5^- + SF_6 \rightarrow$ charge-transfer products $+ SF_5$
σ_9	$F^- + SF_6 \rightarrow F + SF_6^-$

(Lifshitz et al., 1973; Foster and Beauchamp, 1975), and that charge transfer involving F^- on SF_6 may lead to both SF_6^- and SF_5^- (O'Neill and Craggs, 1973; Lifshitz et al., 1973). It is interesting to note that the ion-conversion processes predominate for ε_{cm} <200eV, i.e., upon collision of an SF_6^- or SF_5^- ion with SF_6, ion conversion is much more likely than prompt electron detachment.

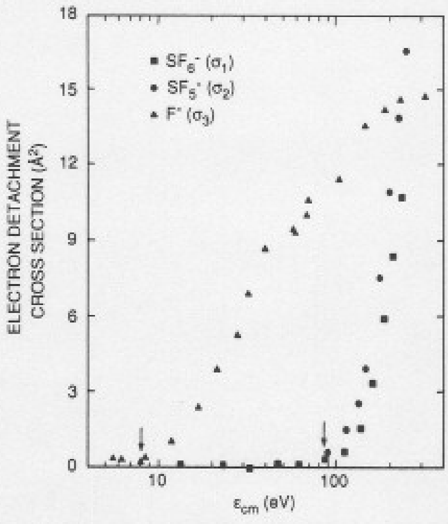

Fig. 1. Collisional electron-detachment cross sections for F^-, SF_5^-, and SF_6^- on SF_6 target gas as a function of center-of-mass energy.

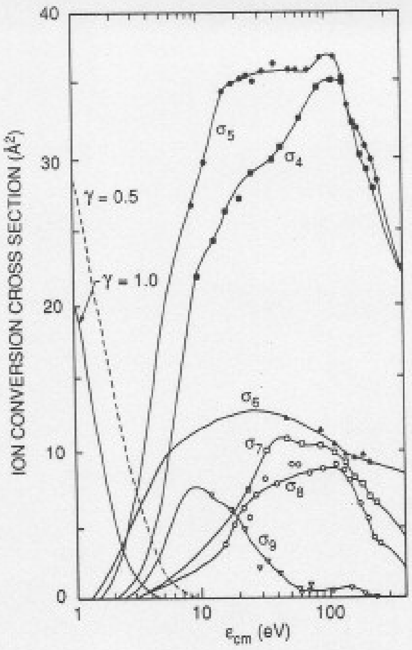

Fig. 2. Measured cross sections for collision-induced ion-conversion processes in SF_6 target gas: (●) F^- from SF_5^-; (■) F^- from SF_6^-; (▲) SF_5^- from SF_6^-; (o) ions due to charge-transfer reactions of SF_5^-; (□) ions due to charge-transfer reactions of SF_6^-; and (∇) ions due to charge-transfer reactions of F^-. The two exponentially-decaying curves on the left side of the figure represent the kinetic-energy distribution of Eq. (5) for $\gamma = 1.0$ and $\gamma = 0.5$ scaled relative to each other.

REACTION RATES AND COEFFICIENTS

Calculations

The analysis of rates for chemical processes in drift tubes or electrical discharges requires expressing inelastic-collision probabilities in terms of rate coefficients rather than cross sections. For a process where the projectiles have a velocity distribution, $f(v)$, the rate coefficient, k, is given by an averaging of the collision cross section over all velocities, namely

$$k = \int_0^\infty \sigma(v) v f(v) dv, \qquad (1)$$

were $\sigma(v)$ is the velocity-dependent cross section for the process and $f(v)$ is subject to the normalization

$$\int_0^\infty f(v) dv = 1. \qquad (2)$$

For measurements where charged particles are accelerated in a gas by an electric field (such as in a drift tube), the reaction coefficient, κ, is defined as the reaction probability per unit length in the direction of the electric field, and is related to the rate coefficient by

$$\frac{\kappa}{N} = \frac{k}{v_d}, \tag{3}$$

where N is the target-gas number density and v_d is the charged particle drift velocity. For the specific case of collisional electron detachment from a negative ion, the reaction coefficient is referred to as the detachment coefficient, δ (i.e. $\kappa/N = \delta/N$ for collisional electron detachment).

Reaction coefficients for detachment and ion-conversion processes involving SF_6^-, SF_5^-, and F^- in SF_6 can be derived from the measured cross sections, $\sigma_i(\varepsilon_{cm})$, presented in Figs. 1 and 2 using

$$\frac{\kappa_i}{N} = \frac{1}{mv_d}\int_o^\infty \sigma_i(\varepsilon_L)f(\varepsilon_L)d\varepsilon_L, \tag{4}$$

where ε_L is the projectile energy in the lab frame, m is the mass of the negative ion, and $f(\varepsilon_L)$ and $\sigma(\varepsilon_L)$ are the ion kinetic-energy distribution and the process cross sections, respectively. The ion drift velocity is assumed to be given by $v_d = \mu E$, where μ is the ion mobility and E is the applied electric-field strength.

It should be noted that the determination of reaction coefficients from collisional cross sections suffers from certain difficulties, the greatest arising from the assumed form of the ion kinetic-energy distribution, $f(\varepsilon_L)$ (Albritton et al., 1977). While determination of ion kinetic-energy distributions has received considerable theoretical (Lin and Bardsley, 1977) and experimental (Khatri, 1984) attention, the theoretical work is hampered by the lack of detailed ion-atom (or molecule) potential-energy surfaces and the experimental work suffers from a lack of reliability (Albritton et al., 1977). Accurate direct measurements of ion-velocity distributions have been demonstrated in recent optical-probing experiments, (Dressler et al., 1988) but to date no experimental data are available for the kinetic-energy distributions of SF_6^-, SF_5^-, or F^- in SF_6.

In general, experimental work has indicated that ions with masses less than or equal to that of the molecules of the gas in which they are moving exhibit kinetic-energy distributions with high-energy tails (Albritton et al., 1977; Moruzzi and Harrison, 1974). Differences in the velocity distributions at high energies in Eq. (4) will obviously have a large effect upon the calculated reaction coefficients derived from cross sections with threshold energies considerably in excess of the average ion kinetic energies.

An example of the large differences in calculated values of reaction coefficients which can occur when different energy distributions are assumed is shown in Fig. 3, where the collisional-detachment coefficient for F^- in $SF_6(\delta_3)$ has been calculated as a function of E/N using the cross section data (σ_3) from Fig. 1 and several different indicated energy distributions. The solid line in Fig. 3 represents detachment coefficients calculated using the kinetic-energy distribution of Kagan and Perel (Kindersberger, 1986; Kagan and Perel, 1954),

$$f(\varepsilon_L) = \frac{\sqrt{6\gamma}}{\pi\, v_d} \exp\left(\frac{-\gamma\varepsilon_L}{\pi\, m v_d^2}\right), \qquad (5)$$

which assumes that charge exchange is the dominant ion-molecule interaction. For the standard Kagan and Perel distribution, $\gamma = 1.0$. However, as will be discussed later, better agreement between ion-conversion reaction coefficients calculated here and those from analysis of drift-tube results is obtained by assuming $\gamma = 0.5$ which introduces a larger high-energy tail in the distribution.

The dashed line in Fig. 3 was obtained using a Maxwellian speed distribution (Kindersberger, 1986) of the form,

$$f(\varepsilon_L) = 3\sqrt{\frac{3m}{\pi}}\, \frac{\varepsilon_L}{\bar{\varepsilon}^{3/2}} \exp\left(\frac{-3\varepsilon_L}{2\bar{\varepsilon}}\right), \qquad (6)$$

where the mean energy of the ion in the lab frame is given by (Wannier, 1951)

$$\bar{\varepsilon} = \frac{3kT}{2} + \frac{m}{2} v_d^2 + \frac{M}{2} v_d^2, \qquad (7)$$

and M is the mass of the collision-gas molecules. This distribution has been used previously when analyzing discharge-inception data (Kindersberger, 1986) and is similar to a strongly anisotropic velocity distribution derived by Skullerud (1973) for ions drifting in a gas composed of molecules of the same mass as the ions under high electric fields.

Figure 3 clearly demonstrates how the use of different ion kinetic-energy distributions in Eq. (4) can produce reaction coefficients which differ by many orders of magnitude. This indicates the need for more accurate ion kinetic-energy distribution measurements.

In addition to the uncertainty associated with the assumed distribution function, another source of uncertainty in deriving reaction coefficients from cross-section data is the choice of experimentally determined values of ion mobilities (μ). Several previous mobility measurements (Brand and Jungblut, 1983; Morrow, 1986; Patterson, 1970; Nakamura, 1988) for SF_6^- and SF_5^- in SF_6 are not in complete agreement.

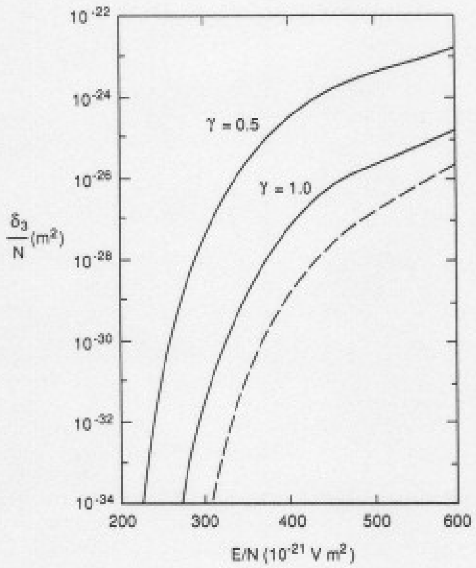

Fig. 3. Calculated collisional electron-detachment coefficients for F^- on SF_6 gas using Eq. (4) and $\sigma_3(\varepsilon_L)$, and assuming different ion kinetic-energy distributions: (——) Kagan and Perel; (- - -) Maxwellian.

However, uncertainties in calculated reaction coefficients using different mobilities are significantly smaller than the uncertainties due to the use of different energy distributions as discussed above. For the remainder of this paper, the mobilities used for SF_6^- and SF_5^- are those reported by Brand and Jungblut (1983) and for F^-, the values of Nakamura (1988).

Detachment Coefficients

As expected, the extremely high apparent thresholds for prompt collisional electron detachment from SF_6^- and SF_5^- yield detachment coefficients from Eq. (4) that are insignificantly small in the E/N range of interest here. Simple estimates of these coefficients using a Kagan and Perel velocity distribution in Eq. (4) indicate that the detachment coefficients for SF_6^- and SF_5^- will be tens of orders of magnitude below the detachment coefficients determined in drift-tube experiments and the detachment coefficients calculated for F^- (Fig. 3). Thus one must conclude that prompt collisional electron-detachment processes for SF_6^- (and SF_5^-) in SF_6 cannot be significant reactions for production of electrons in discharge-inception processes, if, in fact, $\sigma_i(\varepsilon_{cm})$ is zero below the apparent thresholds. It should be noted that this conclusion is independent of the assumed ion kinetic-energy distribution or the ion-mobility data used.

It is clear from Fig. 3, however, that the collisional electron detachment from F^- in SF_6 is a significant process, thus suggesting that previously observed electron-detachment processes due to motion of negative ions in SF_6 are very likely from F^-. This agrees with earlier work (Eccles et al., 1967) which indicated that detachment in SF_6 was predominately from F^-, and also with recent reanalysis of pulsed-electron avalanche experiments (Teich, 1973). In fact, the observed threshold for electron detachment from F^- in SF_6 near 8 eV is consistent with the hypothesized thresholds predicted by some discharge-inception experiments (Kindersberger, 1986).

Other discharge-inception experiments (Van Brunt, 1986) have, however, suggested that negative cluster ions involving H_2O or HF may be responsible for discharge initiation in SF_6. In fact, recent measurements (Sauers et al., 1989) of negative ions produced in negative corona discharges, have indicated the presence of several types of cluster ions of the forms $F^-(HF)_n$, $OH^-(H_2O)_n$, and $SF_6^-(HF)$. Further investigations of the collisional detachment cross sections for these ions are necessary to determine their role in discharge initiation.

The conclusions drawn above depend upon the assumption that $\sigma(\varepsilon_L)$ = 0 at energies below the apparent threshold marked in Fig. 1. If one assumes that $\sigma(\varepsilon_L) = 0.1$ $\mathring{A}^2$ (i.e., the experimental uncertainty) for energies which extend down to the thermodynamic threshold for electron detachment, then detachment coefficients for SF_6^- and SF_5^- are found to be of the same order of magnitude as those determined by drift-tube experiments. However, detachment coefficients derived with such an assumption are not compatible with previously observed pressure dependencies observed in drift-tube experiments (O'Neill and Craggs, 1973; Hansen et al., 1983) as discussed in the next section.

Ion-Conversion Reaction Coefficients

In order to calculate the reaction coefficients for the ion-conversion processes listed in Table 1, it is necessary to extrapolate the measured cross sections down to assumed thresholds at lower energies. The extrapolations used for the subsequent calculations are shown in Fig. 2. These extrapolations were chosen to agree with known thermodynamic thresholds and to minimize the discrepancies with previously determined reaction coefficients as discussed below. The thresholds for production of F^- from SF_6^- and SF_5^- (σ_4 and σ_5) were determined to be 2.0 eV and 1.5 eV, respectively, by using the observed thresholds for F^- production from collisions of SF_6^- and SF_5^- with the rare gas targets (Wang et al., 1989). The cross sections for SF_5^- production (σ_6) and SF_6^- were extrapolated down to the thermodynamic threshold of 1.35 eV. For the charge-transfer reaction involving F^- and SF_6, the cross sections were extrapolated down the thermodynamic threshold of 2.25 eV under the assumption that the primary product is SF_6^-. The other charge-transfer cross sections (σ_7 and σ_8) were both extrapolated down to a threshold near 3 eV which corresponds to the thermodynamic threshold for a symmetric charge transfer between SF_6^- and SF_6 as suggested by Hay (1982). There is a large uncertainty in these last assumed thresholds since the identity of the charge-transfer products in these processes are indistinguishable in the present experiment.

The calculated reaction coefficients for processes 6, 5 and 9 of Table 1 are shown in Figs. 4, 5 and 6 respectively, along with reaction coefficients for the same reactions as determined by previous drift-tube experiments. The solid lines represent the coefficients calculated using the standard Kagan and Perel distribution (i.e. $\gamma = 1$) shown in Eq. (5). Note that these calculated reaction coefficients all fall substantially below those determined previously despite the fact that the extrapolated thresholds for these cross sections were all assumed to be thermodynamic thresholds. Any reasonable change in the assumptions concerning the reaction thresholds or the behavior of the cross sections near threshold would necessarily cause the reaction coefficients to be even smaller, thus implying that the discrepancies cannot be resolved by changing the assumed cross section thresholds or extrapolations.

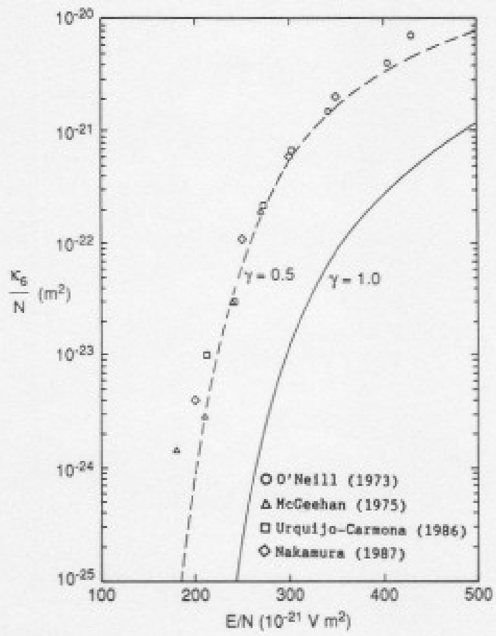

Fig. 4. Calculated reaction coefficients for the reaction $SF_6^- + SF_6 \longrightarrow SF_5^- + F + SF_6$ using measured cross-section data $\sigma_6(\varepsilon_L)$ and a Kagan and Perel energy distribution. The symbols are previously calculated reaction coefficients for the same process derived from uniform-field drift-tube data.

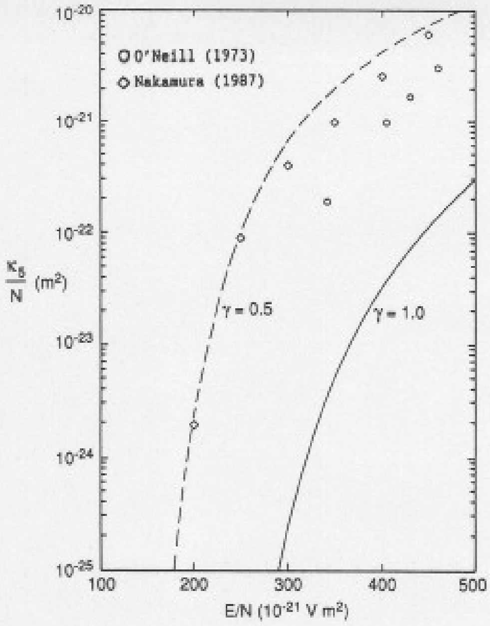

Fig. 5. Calculated reaction coefficients for the reaction $SF_5^- + SF_6^- \longrightarrow F^- + SF_4 + SF_6$ using measured cross-section data $\sigma_5(\varepsilon_L)$ and a Kagan and Perel energy distribution. The symbols are previously calculated reaction coefficients for the same process derived from uniform-field drift-tube data.

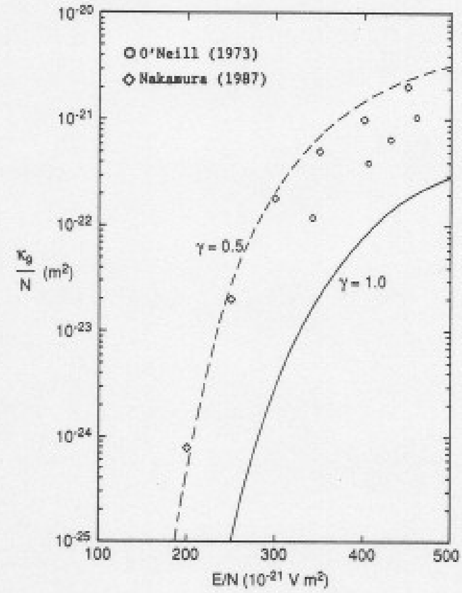

Fig. 6. Calculated reaction coefficients for the reaction $F^- + SF_6 \longrightarrow F + SF_6^-$ using measured cross-section data $\sigma_9(\varepsilon_L)$ and a Kagan and Perel ion kinetic-energy distribution. The symbols are previously calculated reaction coefficients for the same process derived from uniform-field drift-tube data.

Despite the fact that the Kagan and Perel distribution produces the largest coefficients of any of the commonly used ion kinetic-energy distributions, better agreement can be obtained between our calculated coefficients and those from previous experiments if one assumes that the kinetic-energy distribution has a longer high-energy tail, in agreement with the previous discussion of kinetic-energy distributions. The Kagan and Perel distribution in Eq. (5) can be conveniently altered by allowing γ to vary between 0 and 1. The dashed lines in Figs. 4 to 6 represent reaction coefficients calculated with $\gamma = 0.5$, while in Fig. 2 the relative magnitudes of the two distributions ($\gamma = 1$ and $\gamma = 0.5$) are shown for comparison.

Obviously, the curves in Figs. 4-6 with $\gamma = 0.5$ are in better agreement with the previously reported coefficients than are the curves calculated using $\gamma = 1$. This may indicate that previously assumed energy distributions need to be modified (Kindersberger, 1986; Hansen et al., 1983). However, one must note that the reaction coefficients derived from drift-tube data are model-dependent and that only reactions 5, 6 and 9 (Table 1) are assumed in the previous analysis of data from drift tubes. Thus discrepancies may also arise because this commonly used model does not consider the collision-induced dissociation of SF_6^- into $F^- + SF_5$ (reaction 4). This reaction is found here to be significant (see Fig. 2) and its omission may produce errors in the reaction rates derived from drift-tube data.

The calculated reaction coefficients for reaction 4 (and for reactions 7 and 8) are shown in Fig. 7 using Kagan and Perel distributions with γ = 1.0 and 0.5. As stated before, no previously determined coefficients for these processes exist for comparison.

MODEL FOR ELECTRON DETACHMENT FROM ION DRIFT IN SF_6

A different interpretation of the processes which lead to detachment coefficients derived from drift-tube data (O'Neill and Craggs, 1973; Hansen et al., 1983) and their observed pressure dependence can be obtained if one assumes that electron production in a drift tube is not due primarily to prompt electron detachment from SF_6^-, but arises from either detachment from F^- or from collisionally-excited, energetically-unstable $(SF_6^-)^*$ ions as suggested by the previously presented data. A model can then be developed which assumes that under drift-tube conditions, prompt detachment from SF_5^- and SF_6^- is insignificant, and that a steady state condition exists for intermediate products (i.e. $d[SF_5^-]/dt = d[F^-]/dt = d[(SF_6^-)^*]/dt = 0$). If one analyzes the drift-tube data as done previously (O'Neill and Craggs, 1973; Hansen et al., 1983), assuming that all ejected electrons come from SF_6^- ions, then the measured electron-production rate can be written in terms of an "effective" detachment coefficient (δ_{eff}) according to the expression

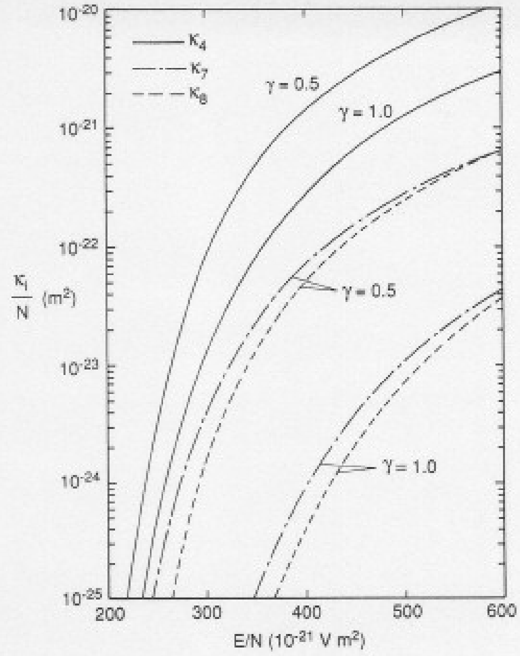

Fig. 7. Calculated reaction coefficients using a Kagan and Perel ion kinetic-energy distribution for the following reactions: (——) $SF_6^- + SF_6 \rightarrow F^- + SF_5 + SF_6$; (— — —) SF_6^- + $SF_6 \rightarrow$ charge-transfer products; and (— · —) $SF_5^- + SF_6 \rightarrow$ charge-transfer products.

$$\frac{d[e]}{dt} = v_d\left(\frac{\delta_{eff}}{N}\right) N[SF_6^-], \tag{8}$$

where [e] is the number of free electrons produced per unit volume which can be detected, v_d refers specifically to the drift velocity of SF_6^- in SF_6, and δ_{eff}/N is determined by analysis of drift-tube data (O'Neill and Craggs, 1973; Hansen et al., 1983). Assuming that the simplified set of processes indicated in Table 2 dominates in a drift tube, an expression for δ_{eff}/N, can be found in terms of the relevant rate coefficients by solving the set of coupled rate equations. The result is

$$k_{eff} = v_d\left(\frac{\delta_{eff}}{N}\right) = k_3\left(\frac{k_6 + k_4}{k_9 + k_3}\right) + k_{12}\left(\frac{k_{10}}{k_{12} + k_{11}N}\right). \tag{9}$$

The effective detachment coefficient given by Eq. (9) is seen to consist of two terms, a pressure independent term which depends upon various ion-conversion and direct-detachment processes involving F^-, and a pressure-dependent term which depends upon the rates for collisional relaxation, excitation and auto-detachment of $(SF_6^-)^*$. This expression is more complex than those previously derived (Kindersberger, 1986; O'Neill and Craggs, 1973;

Table 2. Proposed ion-molecule reactions for drift-tubes containing SF_6

Reaction	Coefficient	Process
$SF_6^- + SF_6 \rightarrow SF_5^- + F + SF_6$	k_6	Dissociative Ion Conversion
$SF_6^- + SF_6 \rightarrow F^- + SF_5 + SF_6$	k_4	Dissociative Ion Conversion
$SF_5^- + SF_6 \rightarrow F^- + SF_4 + SF_6$	k_5	Dissociative Ion Conversion
$F^- + SF_6 \rightarrow F + SF_6^-$	k_9	Charge Transfer
$F^- + SF_6 \rightarrow$ neutrals $+ e^-$	k_3	e^- Detachment
$SF_6^- + SF_6 \rightarrow (SF_6^-)^* + SF_6$	k_{10}	Excitation
$(SF_6^-)^* + SF_6 \rightarrow SF_6^- + SF_6$	k_{11}	De-excitation
$(SF_6^-)^* \rightarrow SF_6 + e^-$	k_{12}	Auto-detachment

Hansen et al., 1983) which assume that direct detachment from SF_6^- was the sole source of electrons.

If $k_{11}N$ is approximately the collision frequency of SF_6^- in SF_6 (e.g., ~ 10^8/sec at 1 kPa) and k_{12} is on the order of the inverse of the excited-state lifetime (τ ~ 10μs to 2 ms) (Odom, et al., 1975), then $k_{11}N >> k_{12}$ and the model predicts an inverse pressure dependence for δ_{eff}/N at low N. This inverse pressure dependence is consistent with previous drift-tube measurements (O'Neill and Craggs, 1973; Hansen et al., 1983). O'Neill and Craggs (1973) also report no detachment from F^- or SF_5^- at low pressures in agreement with the dominance of the second term of Eq. (9) for smaller N. The model proposed here is consistent with the observed (Hansen et al., 1983) variations in δ_{eff}/N with the "age" of the SF_6^- ions if there is a substantial fraction of SF_6 anions which are initially in excited or autodetaching states.

At higher pressures, the first term on the right side of Eq. (9) dominates, giving a δ_{eff}/N that is essentially pressure independent. In this pressure regime, electron production involves mainly process (3) with a threshold of 8 eV. These results are consistent with: 1) the lack of pressure dependence (Kindersberger, 1986; Teich, 1973) for δ_{eff}/N suggested from the analysis of high-pressure electrical-discharge initiation data, and 2) previously discussed results (Eccles et al., 1967) suggesting detachment in SF_6 is predominately from F^-.

Ideally, one would like to calculate the effective detachment coefficients using Eq. (9) to compare with the previously determined drift-tube measurements. However, values for k_{10}, k_{11} and k_{12} are not available, so only the contribution to δ_{eff}/N from the first term of Eq. (9) can be calculated using the reaction coefficients derived above. The solid curve in Fig. 8 shows the contribution from the first term of Eq. (9) using a Kagan and Perel distribution with $\gamma = 1.0$. Note that the

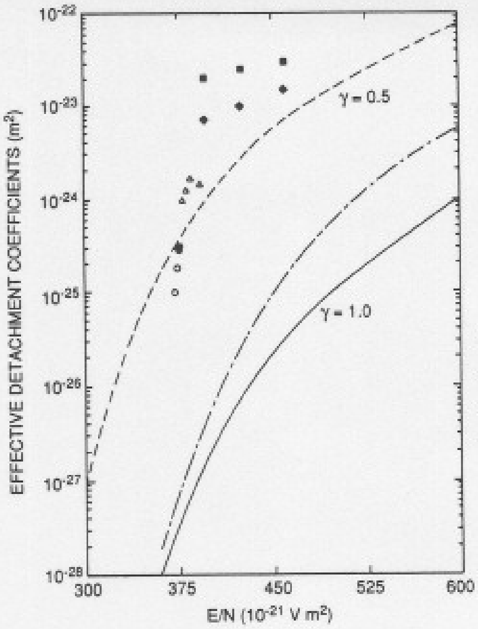

Fig. 8. Effective detachment coefficients determined from drift-tube experiments at different pressures are shown as identified by the symbols in the key. Effective detachment coefficients calculated from discharge-inception data from (Kindersberger, 1986) are also shown (— · —). The contribution to the effective detachment coefficients from the first term of Eq. (9) are shown for $\gamma = 1.0$ (——) and for $\gamma = 0.5$ (- - -).

magnitude of the solid curve is similar to that of the effective detachment coefficient derived from discharge-inception experiments (Kindersberger, 1986) (dot-dashed curve) but is substantially smaller than the coefficients derived from drift-tube experiments (O'Neill and Craggs, 1973; Hansen et al., 1983) (symbols). If one uses the reaction coefficients derived using a Kagan and Perel energy distribution with $\gamma = 0.5$ (dashed curve) then the δ_{eff}/N derived from the first term of Eq. (9) becomes of the same order of magnitude as the coefficients derived from the highest pressure drift-tube experiments. The fact that the dashed curve actually lies above the smallest measured drift-tube values indicates that taking $\gamma = 0.5$ may overestimate the high-energy tail for the kinetic-energy distribution.

CONCLUSION

The measured cross sections for collisional electron detachment and ion conversion of negative ions in SF_6 have been used in a theoretical model which invokes detachment from long-lived, energetically-unstable states of collisionally excited SF_6^- to explain the pressure dependence of previously measured detachment coefficients and the high apparent detachment thresholds implied by analysis of breakdown-probability data for SF_6. The model suggests that measured effective detachment coefficients depend upon many different reaction rates, thus implying that detachment processes in SF_6 are more complex than previously assumed. At high pressures, measured detachment coefficients appear to depend primarily upon the rates for ion-conversion and direct-detachment processes involving F^-, consistent with earlier suggestions. Also, calculation of ion-conversion rates for SF_6^-, SF_5^-, and F^- in SF_6 indicate the need to reexamine both reaction coefficients derived from drift tube experiments and ion kinetic-energy distributions assumed in interpreting the cross section data presented here.

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