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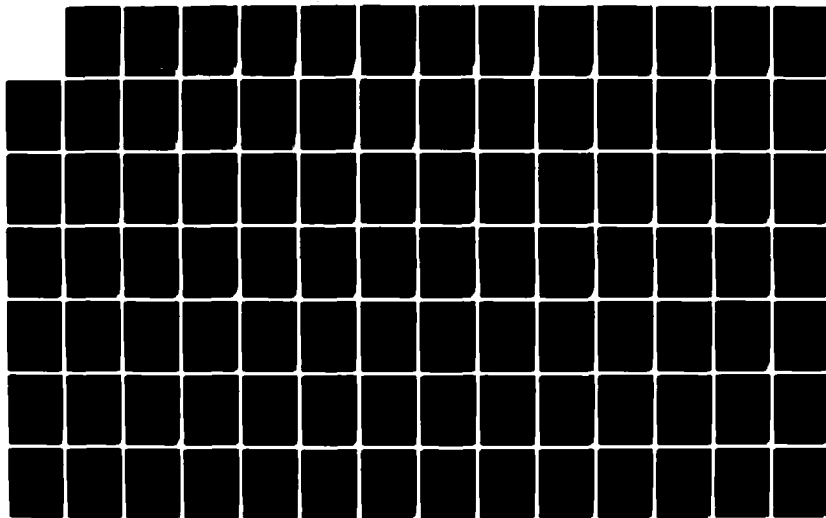
IONIC REACTIONS OF ATMOSPHERIC IMPURIANCE(U) BIRMINGHAM
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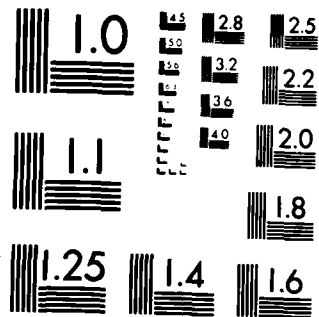
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IONIC REACTIONS OF ATMOSPHERIC IMPORTANCE

BY

DAVID SMITH and NIGEL G. ADAMS

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20. Abstract → A variable-temperature flowing afterglow/Langmuir probe (VT-FALP) apparatus has been used to study several electron-ion dissociative recombination reactions and several electron attachment reactions. Thus the variation with temperature of the respective dissociative recombination coefficients, k_d and electron attachment coefficients, k_a have been determined. The recombination studies have included the species O_2^+ , NO^+ , NH_4^+ , H_3^+ , HCO^+ , N_2H^+ and CH_5^+ , and the attachment studies have included the species CCl_4 , CCl_3F , CCl_2F_2 , $CHCl_3$, Cl_2 , SF_6 , $c-C_7F_{14}$, CH_3Br , CF_3Br , CH_2Br_2 and CH_3I . Some ion molecule reactions have also been studied as a function of temperature and of ion-molecule centre-of-mass energy using a variable-temperature selective ion flow drift tube (VT-SIFDT). ↑		

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PREFACE

This work is part of a larger programme of ionic reaction studies at thermal energies conducted by the authors of this report. The overall programme includes studies of ion-neutral reactions, ion-ion recombination, electron-ion recombination, electron attachment and other plasma reaction processes. The work is largely intended as a contribution to the physics and chemistry of natural plasmas such as the ionosphere and the interstellar medium and of laboratory plasma media such as gas laser systems and etchant plasmas. A great deal of relevant data has been obtained principally by exploiting the versatile Selected Ion Flow Drift Tube (SIFDT) and the flowing Afterglow/Langmuir Probe (FALP) techniques which were developed in our laboratory. Part of the overall programme is also supported by a grant from the Science and Engineering Research Council.

A major contribution to the work described in this report has been made by Dr. Erich Alge.

INTRODUCTION

Our major commitment under the terms of the grant is to study a range of ionic processes which can occur at low temperatures (and low interaction energies) in ionized gases, such as those which occur in the Earth's atmosphere. These processes include ion-ion recombination, electron-ion recombination, electron attachment and ion-neutral reactions. Such studies are possible using the variable-temperature flowing afterglow/Langmuir probe (FALP) and the selected ion flow drift tube (SIFDT) apparatuses which were developed in our laboratory. Prior to the time period covered by this report, we made a detailed study of ion-ion recombination with the FALP, choosing for special study reactions which are considered to be important in stratospheric and tropospheric deionization. This work has been reported in previous scientific reports and in several published research papers. It is also summarised in the review paper included as Appendix 8 to this report.

During the period of this report, the ion-ion recombination studies have continued albeit at a relatively low level of effort since the major effort has been devoted to electron-ion recombination and electron attachment studies as well as to some significant studies of ion-molecule reactions. Thus we have determined the dissociative recombination coefficients as a function of temperature for several molecular ion species, including several known atmospheric and interstellar species. Also we have measured the electron attachment coefficients for several very efficient electron scavenging molecules including SF_6 and some Freons. Some important ion-molecule reactions have been studied also, including one in which vibrational energy is transferred from a neutral molecule to a molecular ion, the first reported observation of this phenomenon at thermal energy. The detailed results of some of these studies have been reported in several recent papers and these are included as Appendices to this report. The following is a brief summary of the results.

II

SUMMARY OF RESULTS

(i) Dissociative Electron-Ion Recombination.

Measurements were made with the VT-FALP of the dissociative recombination coefficients, α , for several species at various temperatures within the temperature range 95 to 600 K. Initially, we measured α for the $O_2^+ + e$ reaction, i.e. $\alpha(O_2^+)$, since the absolute magnitude of $\alpha(O_2^+)$ at 300 K and its variation with temperature are well established. Our data are in excellent agreement with previous data and this we believe establishes the VT-FALP as a technique for accurate α determinations. $\alpha(NO^+)$ was also determined in order to resolve a long-standing discrepancy in previous data regarding the temperature dependence of this coefficient. Additionally $\alpha(NH_4^+)$ was measured in this initial study which is reported in detail in the paper by Alge, Adams and Smith (Appendix 1).

In a recent detailed study, $\alpha(H_3^+)$, $\alpha(HCO^+)$, $\alpha(N_2H^+)$ and $\alpha(CH_5^+)$ have been measured at 95 and 300 K. This study was primarily undertaken as a contribution to interstellar ion chemistry, but the results are also very valuable in the search for an understanding of the fundamentals of dissociative recombination. The most surprising result of this study is that $\alpha(H_3^+)$ is extremely small - we were only able to determine an upper limit to its magnitude - a result which is in conflict with previous experimental data but in accordance with recent theoretical predictions. This study also showed that $\alpha(H_3^+) < \alpha(HCO^+) < \alpha(N_2H^+) < \alpha(CH_5^+)$ at both temperatures and that both $\alpha(HCO^+)$ and $\alpha(N_2H^+)$ varied approximately as T^{-1} whereas $\alpha(CH_5^+)$ varied more slowly with temperature ($\sim T^{-0.3}$). The experimental details and the very interesting results of this study are reported in the paper by Adams, Smith and Alge (Appendix 2). These studies of dissociative recombination are also summarised in Appendix 8.

(ii) Electron Attachment

Using the VT-FALP, we have measured the attachment coefficient, β , for the reactions of electrons with several efficient electron scavenging molecules at several temperatures

within the range 200 to 600 K. The initial study (reported in detail in the paper by Smith, Adams and Alge (Appendix 3)) involved CCl_4 , CCl_3F , CCl_2F_2 , CHCl_3 , Cl_2 and SF_6 . All the reactions except the SF_6 reaction proceeded only via dissociative attachment producing Cl^- ions. For the SF_6 reaction, SF_6^- was the major product ion with SF_5^- becoming increasingly important at the highest temperature. From the variation of β with temperature, activation energies, E_a , were derived for the CCl_2F_2 , CHCl_3 and Cl_2 reactions.

In a more recent study, the β for the reactions of electrons with $\text{c-C}_7\text{F}_{14}$, CH_3Br , CF_3Br , CH_2Br_2 and CH_3I have been determined. The β for all these reactions increased with increasing temperature and the E_a were determined in each case. They ranged from $E_a(\text{CH}_3\text{I}) \approx 25$ meV to $E_a(\text{CH}_3\text{Br}) \approx 300$ meV. All the reactions, except the $\text{c-C}_7\text{F}_{14}$ reaction, proceeded via dissociative attachment generating the corresponding halogen atomic negative ion. The results of this study are reported in detail in the paper by Alge, Adams and Smith (Appendix 4).

(iii) Ion-Molecule Reactions

We have studied a large number of ion-molecule reactions over the temperature range 80 to 600 K using our VT-SIFT and some as a function of ion-molecule centre-of-mass energy, E_{cm} , using our recently-developed VT-SIFDT. These include both binary and ternary reactions. Much of the data is yet to be properly appraised; some have been published in several papers some of which are in press. Included in this report are a recent detailed study of the $\text{N}_2^+ + \text{N}_2 \rightarrow \text{N}_4^+$ association reaction by Smith, Adams and Alge (Appendix 5), the results of a study of some hydrocarbon ion reactions with H_2 by which the heat of formation of C_3H_2^+ ions has been determined (the paper by Smith, Adams and Ferguson (Appendix 6)) and a study of the reactions between $\text{N}_2(\nu=1)$ and $\text{O}_2^+(\nu=0)$ and $\text{NO}^+(\nu=0)$ in which vibrational energy is transferred from the neutral molecules to the molecular ions at thermal energies, the first studies of this kind which have been carried out. This last study is described in the paper by Ferguson, Adams, Smith and Alge (Appendix 7).

III CONCLUSIONS

The studies of electron-ion dissociative recombination and electron attachment summarised in Appendices 1-4 and 8 clearly demonstrate the great value of the VT-FALP for studying these processes at thermal energies. The reactions chosen for study to date were largely selected because of their relevance to atmospheric and interstellar chemistry. Many more such reactions are in need of study, including the dissociative recombination of cluster ions, slow attachment reactions etc. The FALP will continue to be exploited for this purpose. The VT-SIFT technique is now well established as a valuable technique for studying ion-molecule reactions at thermal energies. The inclusion of a drift tube, thus creating the world's first VT-SIFDT, will result in detailed studies of ion-neutral reactions as a function of temperature and ion energy.

APPENDIX 1

MEASUREMENTS OF DISSOCIATIVE RECOMBINATION

COEFFICIENTS OF O_2^+ , NO^+ AND NH_4^+ IN THE

TEMPERATURE RANGE 200-600 K.

J. Phys. B., 16, 1433, 1983

Measurements of the dissociative recombination coefficients of O_2^+ , NO^+ and NH_4^+ in the temperature range 200-600 K

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Abstract. Measurements are presented for α_i , the dissociative recombination coefficient with electrons of O_2^+ , NH_4^+ and NO^+ under truly thermalised conditions with the temperature range 200-600 K, using a flowing afterglow/Langmuir probe apparatus. $\alpha_i(O_2^+)$ is found to vary as $\sim T^{-0.7}$ in close accord with previous pulsed afterglow data for $\alpha_i(O_2^+)$ and $\alpha_e(O_2^+)$ and with values for $\alpha_e(O_2^+)$ inferred from ion trap data. $\alpha_i(NH_4^+)$ is found to vary as $\sim T^{-0.6}$. $\alpha_i(NO^+)$ is found to vary as $\sim T^{-0.9}$ which is reasonably consistent with previous pulsed afterglow data for $\alpha_i(NO^+)$. These data are also compared with values of $\alpha_e(NO^+)$ measured in a pulsed afterglow experiment and those derived from ion trap and merged beam cross section data and from atmospheric observations.

1. Introduction

Dissociative recombination reactions of molecular positive ions with electrons have been studied for many years because they represent an important process of loss of ionisation both in laboratory plasmas such as gaseous lasers (Biondi 1976) and in naturally occurring plasmas such as the ionosphere and the interstellar gas clouds (see the reviews by Smith and Adams 1980, 1981). The primary objective of most studies has been to determine the recombination coefficients, α , for particular positive ion species and the way they vary either with the electron temperature T_e when $T_e > T_+$, T_g , denoted in this paper as α_e , or under thermal equilibrium conditions such that $T_e = T_+ = T_g$ (the electron, ion and gas temperatures respectively), denoted as α_i . Notable amongst the many techniques used for these studies are the pulsed (time-resolved) afterglow technique (Frommhold *et al* 1968, Weller and Biondi 1968) for determining α_i and α_e , and the ion trap technique (Walls and Dunn 1974, Heppner *et al* 1976) and merged-beam technique (Auerbach *et al* 1977, Mull and McGowan 1979) for measuring the variation of the recombination cross section, σ_E , with electron energy.

In this paper we report the results obtained for α_i for the following reactions:



Reactions (1) and (2) are of great significance in the ionosphere but while good

agreement exists between the data obtained with various techniques for reaction (1) that for reaction (2) is still disputed.

We have obtained these data using a new variable-temperature flowing afterglow/Langmuir probe (FALP) apparatus, similar to that previously used to determine positive-ion-negative-ion neutralisation rate coefficients at thermal energies (see the review by Smith and Adams 1983).

2. Experimental

The FALP technique has been described in detail in previous papers (Smith *et al* 1975, Smith and Church 1976, Smith and Adams 1983) and so it is only necessary to outline its general features and to highlight those modifications to the apparatus which were required before the rapid process of dissociative recombination could be studied accurately. The essential elements of the apparatus are illustrated in figure 1(a). A carrier gas, usually helium, is introduced into a stainless-steel flow tube approximately 1 m long and 8 cm in diameter and is constrained to flow down this tube by the action of a Roots pump. Ionisation is created in a microwave discharge upstream in the carrier gas and an afterglow plasma containing He^+ , electrons and He^m is distributed along the length of the flow tube. Typical carrier gas pressures ranged from 0.6 to 1.0 Torr and the electron densities, n_e , established in the afterglow plasma could be varied up to a maximum of about $7 \times 10^{10} \text{ cm}^{-3}$. The absolute electron (and ion) densities and the electron temperature can be measured at any point along the axis

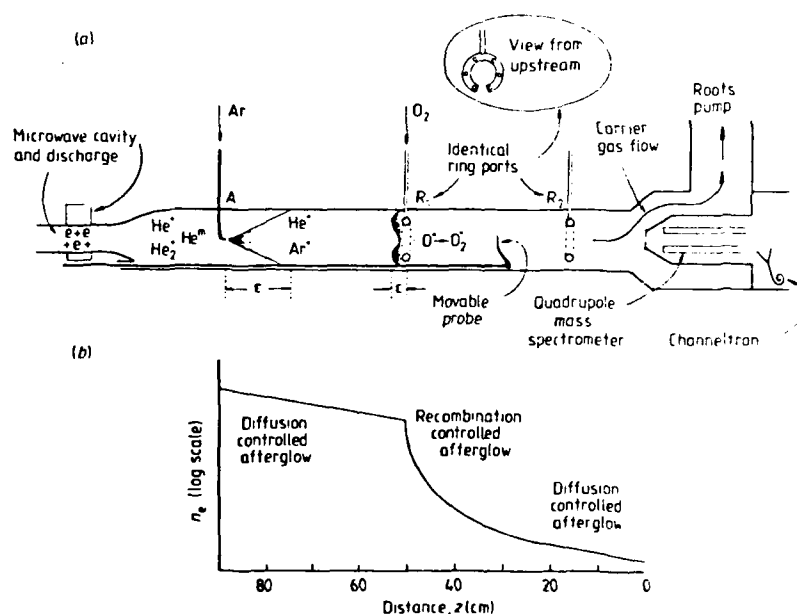


Figure 1. (a) Schematic representation of the FALP experiment, including details of the gas inlet ports, diagnostic instruments, etc. (b) Typical electron density profile along the flow tube during dissociative recombination studies.

of the flow tube using a movable Langmuir probe (see e.g. Smith and Plumb 1972, Smith *et al* 1975).

Argon is introduced through the axial port A (see figure 1(a)) to destroy the He^m thus eliminating a source of ionisation in the afterglow. Also any He_2^+ formed in three-body reactions between He^+ and He will be rapidly converted to Ar^+ . The reactant molecular ions are formed by the addition of a suitable gas via either of the 'ring ports' R_1 or R_2 . These ring ports were designed to minimise the mixing length, ϵ , (often termed the 'end correction' in flow tube experiments) which, for an axial port such as A, is too extensive for dissociative recombination studies (see figure 1(a)). R_1 and R_2 consist of 2 mm diameter stainless-steel tubing in the form of a ring of diameter 3 cm positioned symmetrically about the axis of the flow tube. A series of small holes (diameter 0.5 mm) drilled in the upstream-facing part of the ring direct the effusing reactant gas against the carrier gas flow. This simple procedure reduces ϵ to about 1 to 2 cm depending on the flow rates of the reactant and the carrier gases (for an axial port such as A, $\epsilon \approx 10$ cm). The extent of ϵ can be estimated visually by observing the light emitted from the afterglow following the addition of reactant gas and by inspection of the reciprocal electron density plots (see figure 2(b)). Changes in the ion compositions of the plasmas (both positive and negative ions) were continuously monitored by the downstream quadrupole mass spectrometer/ion detection system.

Prior to the addition of the reactant gas the only loss process for ionisation downstream of port A is due to ambipolar diffusion of He^+ and Ar^+ ions with electrons. This is always the situation between ports A and R_1 and, at the pressures of the experiments, results in a slow exponential decrease in n_e with distance, z , along the flow tube as is illustrated in figure 1(b) (all z distances are referenced to the downstream mass spectrometric sampling orifice). The addition of molecular gas into R_1 initiates a sequence of ion-molecule reactions which generate a terminating molecular ion species. This, at suitably high n_e (and n_+ , the molecular positive ion density), then results in a more rapid decrease of n_e with z due to the onset of recombination (figures 1(b) and 2(a)). Thus the afterglow plasma becomes recombination controlled in this region but further downstream where n_e has decreased to sufficiently small values, the plasma will again become diffusion controlled as illustrated. By measuring n_e as a function of z coupled with a measurement of the plasma flow velocity, v_p , (which is typically 10^4 cm s $^{-1}$ and is measured by pulse modulating the microwave discharge—see Adams *et al* 1975), both diffusion coefficients and recombination coefficients can be determined separately. When both ambipolar diffusion and recombination are occurring simultaneously in the plasma, the appropriate continuity equation for n_e is:

$$v_p \frac{\partial n_e}{\partial z} = D_a \nabla^2 n_e - \alpha_1 n_+ n_e \quad (4)$$

where D_a is the ambipolar diffusion coefficient. To determine α_1 it is desirable to ensure that recombination is the only significant loss process. This can be accomplished by operating at high helium pressure (to diminish diffusive loss) and at high n_e (to enhance recombination loss). Under these conditions the diffusion term in equation (4) can be neglected and the solution to the continuity equation becomes:

$$\frac{1}{n_e(z_1)} - \frac{1}{n_e(z_2)} = \frac{\alpha_1}{v_p} (z_2 - z_1) \quad (5)$$

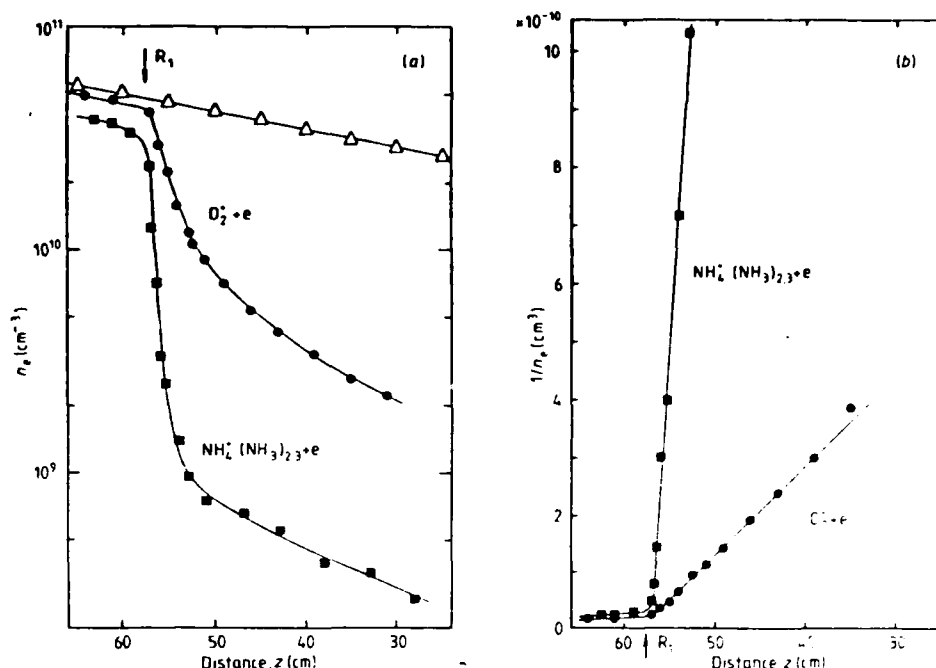


Figure 2. Electron density profiles (a) and the corresponding reciprocal density ($1/n_e$) plots (b) obtained at a helium pressure of 0.6 Torr and a temperature of 295 K. (a) Δ , diffusion controlled afterglow plasma (He^+ , Ar^+ , electrons), i.e. no reactant gas has been added. Upon addition of sufficient reactant gas through port R_1 (see figure 1(a)) the afterglow plasma becomes recombination controlled (full symbols): $\bullet$, plasma containing only O_2^+ ions; $\blacksquare$, plasma containing both $\text{NH}_4^+(\text{NH}_3)_2$ and $\text{NH}_4^+(\text{NH}_3)_3$ ions. (b) The reciprocal electron density plots corresponding to the recombination controlled profiles of (a).

A plot of $1/n_e(z)$ against z then provides a value for α_1 . As examples, plots of n_e against z are given in figure 2(a) for the relatively slowly recombining O_2^+ ions and for the rapidly recombining $\text{NH}_4^+(\text{NH}_3)_{2,3}$ cluster ions. Note the increase in the gradient of n_e immediately downstream of the port R_1 , especially for the cluster ion reaction. This indicates that α_1 for this reaction is larger than that for the O_2^+ reaction. When n_e becomes sufficiently small the plasma will become diffusion controlled again as is best demonstrated by the cluster ion curve in figure 2(a). These data are replotted in figure 2(b) as $1/n_e$ against z and the linearity of these plots is a clear indicator of loss of ionisation by recombination. It should be appreciated that for these plots to be taken as evidence for a recombination controlled plasma they should be linear over at least two factors of two ($\times 4$) and preferably three factors of two ($\times 8$) change in n_e (Gray and Kerr 1962). As can be seen in figure 2(b) these data (as do the data obtained in this study) satisfy this criterion. Note also the very rapid conversion from a diffusion dominated plasma upstream of R_1 to a recombination dominated plasma downstream which indicates a small ϵ (and shows the value of the new port design).

The FALP technique can be used to determine the recombination coefficient for any positive ion which can rapidly be established as the only recombining species in the plasma (as determined using the mass spectrometer). However great care must

be exercised when interpreting mass spectra obtained from a recombining plasma since the recombination process preferentially removes rapidly recombining ions. Thus atomic ions, which do not recombine with electrons at an appreciable rate, may often be dominant components in the downstream region of the plasma even though they are not the most important components of the plasma in the upstream region. To account for this potential problem, port R_2 was specifically included in the apparatus and sited much closer to the mass spectrometer sampling orifice. Thus the reactant gas could be routed between R_1 and R_2 in order to investigate changes in the ion composition of the plasma with z . Also as a routine procedure when determining the identity of the recombining ions, n_e was reduced to values at which dissociative recombination was negligible.

The FALP apparatus can be operated between the temperature limits 80 to 600 K by the use of refrigerant liquids or ohmic heaters. Most of the data reported here were obtained over the range 200 to 600 K, since at lower temperatures ion clustering reactions occurred rapidly (e.g. generating $O_2^+ \cdot O_2$, $NO^+ \cdot NO$ etc). The experiments were conducted under conditions such that $T_e = T_a = T_g = T$ and thus α , was obtained for each reaction studied. The removal of the He^m and the addition of the molecular reactant gas ensured that the electrons were thermalised at the gas temperature. This we have established from previous detailed studies of electron temperature relaxation rates in a FALP apparatus (Dean *et al* 1974) by exploiting the Langmuir probe to determine T_e .

We confidently expect the reactant ions in these experiments to be in their ground electronic and equilibrium vibrational/rotational states at each particular gas temperature (which was measured by calibrated thermocouples immersed in the gas). This we believe to be so because, although the molecular ions on production are almost certainly excited, they will undergo resonance charge or proton transfer with their parent molecules which is known to quench both electronic and vibrational excitation effectively (see Albritton 1979, Lindinger *et al* 1981), as for example:



Rotational relaxation is ensured by the high collision frequency of the molecular ions with the ambient helium atoms.

The absolute values of the measured recombination coefficients are estimated to be subject to an uncertainty of not more than $\pm 15\%$. The main contribution to this error figure arises from the uncertainty in the current collecting area of the probe which is reflected directly in the n_e values ($\leq 10\%$). Smaller contributions are due to inaccuracies in the measured plasma velocity and in the derived best fit slopes of the $1/n_e$ against z plots. Since the uncertainty in the probe area represents a systematic error then the relative values of α_i are subject to an error of not more than $\pm 10\%$.

3. Results

3.1. $O_2^+ + e$

The O_2^+ ions were created by adding O_2 into the afterglow via port R_1 thus initiating the reactions:



The O_2 was added in sufficient concentration ($\sim 5 \times 10^{14}$ molecules/cm³) to ensure that these reactions completely converted the He^+ and Ar^+ into O_2^+ in a distance of about 1 to 2 cm along the flow tube, but insufficient to convert the O_2^+ ions to $O_2^+.O_2$ cluster ions via three-body association (Adams *et al* 1970, Good 1975). Association reactions become increasingly rapid with decreasing temperature and therefore ion clustering is potentially troublesome at low temperatures (see below). $\alpha_i(O_2^+)$ was determined at temperatures of 205, 295, 420, 530 and 590 K from reciprocal density plots of the kind shown in figure 2(b) and the values obtained are presented in the log-log plot in figure 3. Over this temperature range $\alpha_i(O_2^+)$ conforms approximately to a power law of the form:

$$\alpha_i(O_2^+) = 1.95 \times 10^{-7} \left(\frac{300}{T} \right)^{0.7} \text{ cm}^3 \text{ s}^{-1}. \quad (8)$$

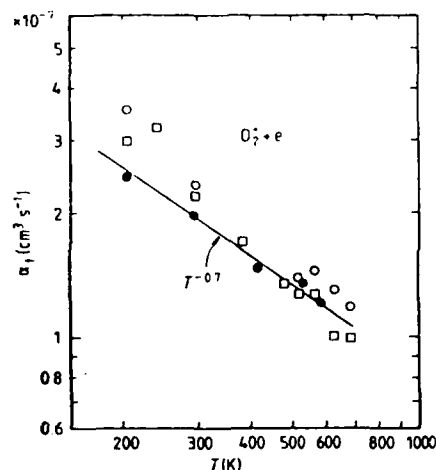


Figure 3. Temperature dependence of the recombination coefficient $\alpha_i(O_2^+)$ (see text). The line is drawn through the present FALP values (●). The various data of Kasner and Biondi (1968) are indicated as: ○, obtained in Ne/ O_2 mixtures; □, obtained in Ne/Kr/ O_2 mixtures.

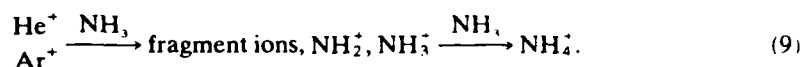
Also included in figure 3 are the data obtained by Kasner and Biondi (1968) using the pulsed afterglow technique and it can be seen that the data from the two experiments are in good agreement above 300 K and indicate essentially the same temperature variation. However, at lower temperatures the pulsed afterglow values are somewhat larger than the present value which may be a manifestation of ion clustering in the higher pressure pulsed afterglow experiment (Biondi and co-workers have shown that cluster ions, including $O_2^+.O_2$, generally have larger recombination coefficients, see e.g. Biondi 1973—see also below). A dependence of order $T_e^{-0.7}$ for $\alpha_e(O_2^+)$ was also obtained in the pulsed afterglow experiment of Mehr and Biondi (1969). Walls and Dunn (1974) using their ion trap technique obtained relative values of $\sigma_E(O_2^+)$ down to electron energies of 0.2 eV. The best fit line to their data indicated an $E^{-1.16}$ variation for σ_E at the lowest energies (which approximates to an α_e variation of $\sim T^{-0.66}$) which is in good agreement with the afterglow results. Data obtained by Mul and McGowan (1979) for $\sigma_E(O_2^+)$ using the merged beam technique agree within

error with the ion trap data but indicate a E^{-1} variation, i.e. a somewhat weaker temperature dependence for $\alpha_e(O_2^+)$ ($\sim T^{-0.5}$). Thus the variation with temperature of both $\alpha_i(O_2^+)$ and $\alpha_e(O_2^+)$ are quite similar, the bulk of the data indicating a common dependence proportional to $T^{-0.7}$ at low temperatures. The $\alpha_e(O_2^+)$ temperature dependence becomes slightly weaker at higher temperatures (Mehr and Biondi 1969, Torr and Torr 1978, Mul and McGowan 1979).

Theoretical descriptions of dissociative recombination distinguish between a 'direct' process and an 'indirect' process (see the review by Bardsley and Biondi 1970). For the direct process, in which the electron is envisaged to be captured directly into a repulsive state of the neutral molecule, α_e (and α_i) is predicted to vary as $T_e^{-0.5}$ at the low temperatures of the present experiment. The indirect process is envisaged to proceed via a vibrationally excited Rydberg level of the neutral molecule from which predissociation occurs and then α_e is predicted to vary as $T_e^{-1.5}$. The combined experimental results for O_2^+ indicate that the direct process is favoured in the low-temperature regime but with some small contribution due to the indirect process.

3.2. $NH_4^+ + e$

The NH_4^+ ions were created by adding ammonia, NH_3 , to the afterglow plasma via port R₁ thus initiating the following reaction sequences:



For these studies, sufficient NH_3 was added to produce the NH_4^+ ions rapidly but insufficient to generate ion clusters of the kind $NH_4^+.(NH_3)_n$. In associated experiments these cluster ions were deliberately produced (see below). $\alpha_i(NH_4^+)$ was determined at temperatures of 295, 415, 460, 540 and 600 K and the values obtained are plotted as a function of temperature in figure 4. Note that $\alpha_i(NH_4^+)$ is typically about an order

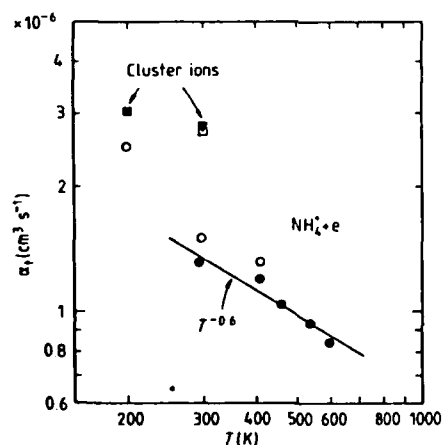


Figure 4. Temperature dependence of the recombination coefficient $\alpha_i(NH_4^+)$ (see text). The line is drawn through the present results ($\bullet$). The data of Huang *et al* (1976) for $\alpha_i(NH_4^+)$ are indicated by $\circ$. Also included are recombination coefficients for cluster ions: $\square$, $NH_4^+.(NH_3)_2$; $\blacksquare$, $NH_4^+.(NH_3)_3$ due to Huang *et al* (1976); ∇ , present results for a mixture of $NH_4^+.(NH_3)_2$ and $NH_4^+.(NH_3)_3$.

of magnitude greater than $\alpha_i(\text{O}_2^+)$. No measurements were made at 200 K in our experiments since at this lower temperature ion clustering prevented the creation of a plasma containing only NH_4^+ and electrons. $\alpha_i(\text{NH}_4^+)$ over this more limited temperature range can approximately be described by the power law:

$$\alpha_i(\text{NH}_4^+) = 1.35 \times 10^{-6} \left(\frac{300}{T} \right)^{0.6} \text{ cm}^3 \text{ s}^{-1}. \quad (10)$$

This $T^{-0.6}$ dependence implies that the direct recombination process is dominant in this reaction. Also included in figure 4 are the pulsed afterglow data of Huang *et al* (1976); note the good agreement between these data and the present data at about 300 and 400 K. However the pulsed afterglow value at about 200 K is somewhat larger than that based on a $T^{-0.6}$ variation; this could be due to insufficient correction to the data to account for the presence in these experiments of the more rapidly recombining cluster ions. In a subsidiary experiment at 300 K we were able to establish an equilibrium concentration ratio of $\text{NH}_4^+(\text{NH}_3)_2$ and $\text{NH}_4^+(\text{NH}_3)_3$ ions in the afterglow by adding excess NH_3 . Recombination proceeded even more rapidly than for NH_4^+ ions and a composite α_i for the recombination of these cluster ions of $2.8 \times 10^{-6} \text{ cm}^3 \text{ s}^{-1}$ was obtained, the largest value obtained to date for any reaction studied in our experiments. This value is in excellent agreement with that obtained by Huang *et al* for $\text{NH}_4^+(\text{NH}_3)_2$ cluster ions at 300 K and very similar to that for $\text{NH}_4^+(\text{NH}_3)_3$ cluster ions at 200 K (see figure 4).

The NH_4^+ reaction has also been studied in the ion trap experiment by DuBois *et al* (1978). To convert the $\sigma_E(\text{NH}_4^+)$ data to α_e values, assumptions had to be made on the form of σ_E at near-thermal energies. The uncertainty in the form of $\sigma_E(\text{NH}_4^+)$ at low energies makes it hazardous to estimate $\alpha_e(\text{NH}_4^+)$ from these data. However based on a $T^{-0.6}$ variation of $\alpha_e(\text{NH}_4^+)$, the absolute magnitudes of the estimated $\alpha_e(\text{NH}_4^+)$ values in the thermal energy range are about a factor 2 smaller than the afterglow values.

3.3. $\text{NO}^+ + e$

The NO^+ ions were created by adding nitric oxide, NO, to the afterglow initiating the reactions:



It is known that the $\text{Ar}^+ + \text{NO}$ reaction generates NO^+ in the metastable a $^3\Sigma^+$ state (Dotan *et al* 1979), but the excess NO present in the plasma ensures that the NO^+ is rapidly quenched to the vibronic ground state via charge exchange with NO (see § 2). Formation of the cluster ions $\text{NO}^+ \cdot \text{NO}$ (which most readily occurs at the lower temperatures) was prevented by limiting the amount of NO introduced into the plasma. Also it was necessary to condense out traces of nitric acid, HNO_3 , from the NO before it was introduced into the plasma, since its presence would result in the loss of electrons in attachment reactions to form negative ions and would therefore distort the dissociative recombination data. It was confirmed mass spectrometrically that attachment was not occurring. $\alpha_i(\text{NO}^+)$ was determined at 205, 295, 465 and 590 K and the values obtained are presented in figure 5. It can be seen that the variation

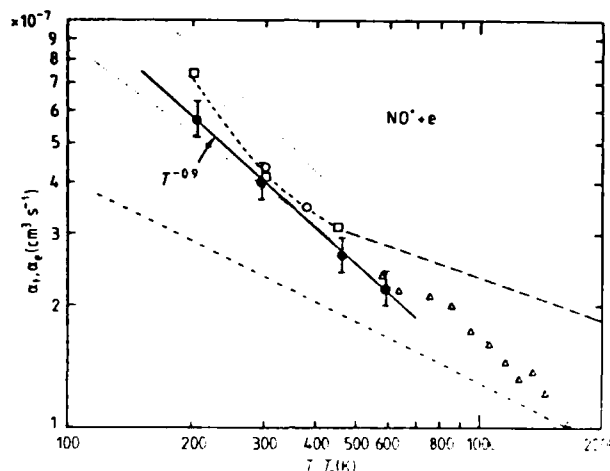


Figure 5. Temperature dependences of $\alpha_i(NO^+)$ and $\alpha_e(NO^+)$. Directly measured rate coefficients. $\alpha_i(NO^+)$: ●, present results, with error bars, joined by full line; □, Weller and Biondi (1968) and ○, Huang *et al* (1975) joined by short dashes. $\alpha_e(NO^+)$: ---, Huang *et al* (1975), measured at $T_e = T_g = 380$ K. Derived rate coefficients, $\alpha_e(NO^+)$: from Walls and Dunn (1974), using $\sigma_E(NO^+)$ data and assuming two different forms of $\sigma_E(NO^+)$ at low energies—see text; - - - - - from Mul and McGowan (1979), using $\sigma_E(NO^+)$ data obtained at low energies at which the energy scale is subject to larger errors; Δ, Torr *et al* (1977), from satellite data.

of $\alpha_i(NO^+)$ over this temperature range can be described by the power law:

$$\alpha_i(NO^+) = 4.0 \times 10^{-7} \left(\frac{300}{T} \right)^{0.9} \text{ cm}^3 \text{ s}^{-1}. \quad (12)$$

Also included in figure 5 are the pulsed afterglow values for $\alpha_i(NO^+)$ measured by Weller and Biondi (1968), and for both $\alpha_i(NO^+)$ and $\alpha_e(NO^+)$ measured by Huang *et al* (1975). These $\alpha_i(NO^+)$ data are in agreement with our data within the error limits of the experiments, except perhaps again for the lowest temperature at which, in the higher pressure pulsed afterglow experiments, effects due to clustering would be most significant. It was confirmed mass spectrometrically that cluster ions were not present in our NO^+ /electron flowing afterglow plasmas. The data of Huang *et al* (1975) indicate that $\alpha_e(NO^+)$ departs from the power law appropriate to $\alpha_i(NO^+)$ to a less rapid variation ($\sim T_e^{-0.37}$) at elevated T_e . It is clear that the value of $\alpha_i(NO^+)$ determined in our experiment at 590 K is significantly smaller than the corresponding value of $\alpha_e(NO^+)$ at $T_e = 590$ K and it is unfortunate that our experiment cannot be operated at higher temperatures to check if this divergence of $\alpha_i(NO^+)$ and $\alpha_e(NO^+)$ is maintained at higher temperatures.

Values of $\alpha_e(NO^+)$ have been derived by Walls and Dunn (1974) from their $\sigma_E(NO^+)$ ion trap data extrapolated on the basis of two different energy variations of σ_E , i.e. according to $\sigma_E \sim E^{-1.5}$, and to $\sigma_E \sim E^{-1.5}$ changing to E^{-1} below 0.01 eV. Mul and McGowan (1979) have also determined $\sigma_E(NO^+)$ using the merged beam technique and have obtained a $\sigma_E \sim E^{-1}$ dependence within the centre-of-mass electron energy range 0.009 to 0.1 eV. Thus they also derived $\alpha_e(NO^+)$ and these values together with the ion trap data are reproduced in figure 5. Since the $\sigma_E(NO^+)$ from the two

experiments are in close accord in the overlapping energy range (≥ 0.05 eV) then the differences in the derived $\alpha_e(\text{NO}^+)$ must be due to the energy dependence for $\sigma_E(\text{NO}^+)$ used at lower energies to calculate $\alpha_e(\text{NO}^+)$ at low temperatures. The form of σ_E at low energies is not readily determined because of the difficulty in accurately defining the centre-of-mass energies below 0.1 eV in ion beam experiments (e.g. see Froelich *et al* 1983). Thus larger inaccuracies are inevitably introduced into calculations of α_e at low temperatures.

As can be seen from figure 5, these derived $\alpha_e(\text{NO}^+)$ values encompass the measured $\alpha_i(\text{NO}^+)$ values but clearly the extremes of $\alpha_e(\text{NO}^+)$ are outside the errors in the present values of $\alpha_i(\text{NO}^+)$. Therefore when α_i values are required it is best to measure them directly, as was accomplished in the afterglow experiments, rather than to infer them from cross section data. Notwithstanding this comment, figure 5 shows that at the highest temperatures, the present afterglow data, the ion trap data and the merged beam data converge towards common values for $\alpha_i(\text{NO}^+)$ and $\alpha_e(\text{NO}^+)$. Also in agreement with these data are the values of $\alpha_e(\text{NO}^+)$ derived by Torr *et al* (1977) from ionospheric observations. Note that the absolute values of $\alpha_i(\text{NO}^+)$ at about 600 K determined in our experiment are in very good agreement with those derived from the ionosphere data. This is to be expected if the ions in the ionosphere are largely in their ground electronic and vibrational states which, although not positively proved, is a reasonable assumption in view of the short lifetime of vibrationally excited NO^+ in the ionosphere (Torr and Torr 1978). Torr *et al* (1977) give a best fit to their data as:

$$\alpha_e(\text{NO}^+) = 4.2 \times 10^{-7} \left(\frac{300}{T_e} \right)^{0.85} \text{ cm}^3 \text{ s}^{-1} \quad (13)$$

which is remarkably similar to our results for $\alpha_i(\text{NO}^+)$.

On balance then it appears that $\alpha_i(\text{NO}^+)$ varies as about $T^{-0.9}$ within the temperature range $200 \text{ K} \leq T \leq 600 \text{ K}$ and also $\alpha_e(\text{NO}^+)$ varies as approximately $T_e^{-0.9}$ for T_e up to 2000 K or so. The reasons why the pulsed afterglow $\alpha_e(\text{NO}^+)$ data are not consistent with this are not obvious but may relate to the uncertainties in determining T_e in these plasmas when it exceeds T_+ and T_g . A $T^{-0.9}$ variation for $\alpha(\text{NO}^+)$ is greater than that for O_2^+ and NH_4^+ and might indicate a greater involvement of the indirect recombination mechanism in this reaction.

4. Conclusions

The accumulated data for $\alpha_i(\text{O}_2^+)$ are in close accord in magnitude and are consistent with a variation proportional to $T^{-0.7}$ within the range $200 \text{ K} \leq T \leq 600 \text{ K}$. Most of the available $\alpha_e(\text{O}_2^+)$ data suggest a similar $T_e^{-0.7}$ variation up to $T_e \approx 5000 \text{ K}$. It is reasonable to expect that $\alpha_i \approx \alpha_e$ at low T (or T_e) ($\leq 1000 \text{ K}$), where vibrational excitation of the molecular ions is minimal, and thus at these temperatures a common variation proportional to $T^{-0.7}$ is appropriate. Departures from this rather simple situation can, however, be expected at higher temperatures where vibrational excitation becomes significant (see e.g. Bardsley 1983). Data for $\alpha_i(\text{NH}_4^+)$ and $\alpha_e(\text{NH}_4^+)$ are sparse. The present $\alpha_i(\text{NH}_4^+)$ data suggests a variation proportional to $T^{-0.6}$ within the range $300 \text{ K} \leq T \leq 600 \text{ K}$ but within error this is indistinguishable from the $T^{-0.5}$ variation theoretically predicted for the direct mechanism of dissociative recombination. The present data for $\alpha_i(\text{NO}^+)$ indicates a variation proportional to $T^{-0.9}$.

in the range $200\text{ K} \leq T \leq 600\text{ K}$ and the $\alpha_e(NO^+)$ derived from ionosphere observations indicate a $T_e^{-0.85}$ variation within the range $600\text{ K} \leq T_e \leq 2500\text{ K}$. The present $\alpha_i(NO^+)$ values and the $\alpha_e(NO^+)$ values derived from the ionospheric data and from the ion trap and merged beam $\sigma_E(NO^+)$ data converge towards common values above 600 K. Significant differences are apparent between the measured $\alpha_i(NO^+)$ and the derived $\alpha_e(NO^+)$ at lower temperatures; these differences are probably due to difficulties in accurately establishing the centre-of-mass electron energies at very low energies (see e.g. the data given in Mul and McGowan 1979 and Froelich *et al* 1983), and the associated uncertainties in determining σ_E at these very low energies. Whilst σ_E values are clearly more fundamental parameters than α_i or α_e values, the latter parameters are of greater practical value in de-ionisation rate calculations in plasmas such as the ionosphere (which is the rational for many of these measurements). An important conclusion to be drawn from the data presented in this paper is that it is preferable to measure α_i and α_e directly when this is practicable. Unfortunately this is not always possible and, even when it is, then the range of temperatures over which such studies can be carried out is rather limited. Then it is necessary to derive α_e from σ_E data. However, as the data of figure 5 illustrate, this procedure has limitations in that the values of α_e derived at low temperatures using this procedure are subject to appreciable errors.

Acknowledgments

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APPENDIX 2

MEASUREMENTS OF DISSOCIATIVE RECOMBINATION

COEFFICIENTS OF H_3^+ , HCO^+ , N_2H^+ AND CH_5^+ AT

95 AND 300K USING THE FALP TECHNIQUE.

J.Chem Phys. 1984. In Press

MEASUREMENTS OF DISSOCIATIVE RECOMBINATION COEFFICIENTS
OF H_3^+ , HCO^+ , N_2H^+ AND CH_5^+ AT 95 AND 300 K
USING THE FALP APPARATUS

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ABSTRACT

Measurements are presented of the dissociative recombination coefficients, α_t , for reactions of electrons with H_3^+ , D_3^+ , HCO^+ , DCO^+ , N_2H^+ , N_2D^+ and CH_5^+ ions at 95 and 300 K. The measurements were made under truly thermalised conditions using a flowing afterglow (FALP) apparatus. Contrary to previous stationary afterglow (SA) studies, $\alpha_t(H_3^+)$ was found to be immeasurably small ($\leq 2 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$) at both temperatures which is consistent with recent theoretical predictions. However some evidence was obtained indicating that vibrationally-excited H_3^+ recombined efficiently, which is also in accordance with the recent theory. At 300 K, $\alpha_t(HCO^+) = 1.1 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ and $\alpha_t(N_2H^+) = 1.7 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ and both were larger by a factor of three at 95 K. $\alpha_t(CH_5^+) = 1.1 \times 10^{-6} \text{ cm}^3 \text{ s}^{-1}$ at 300 K and $1.5 \times 10^{-6} \text{ cm}^3 \text{ s}^{-1}$ at 95 K. The $\alpha_t(HCO^+)$ data are compared with previous SA data and the $\alpha_t(N_2H^+)$ and $\alpha_t(CH_5^+)$ data are discussed in relation to the recombination coefficients $\alpha_e(N_2H^+)$ and $\alpha_e(CH_5^+)$ derived from merged beam (MB) cross section data. Stressed throughout the paper is the need to appreciate the chemical and physical processes which can occur in the afterglow and which may distort α_t determinations. Tentative explanations are given for the differing values of α_t and α_e obtained from FALP, SA and MB experiments.

I. INTRODUCTION

Dissociative recombination is an important loss process for ionization in most laboratory plasmas and also in natural plasmas such as the Earth's ionosphere and interstellar gas clouds (for a discussion of these see Refs. 1-4). The temperatures (T_e (= electron), T_i (= ion), T_g (= gas)) of the component species in these natural plasmas may vary both spatially and temporally and so, for worthwhile modelling of the relative abundances of these species, the temperature dependences of the rate coefficients for the various reaction processes occurring in the plasma are required. These include the temperature dependences of the coefficients for dissociative recombination, α . It is important at the onset to distinguish between the α appropriate to plasmas in which $T_e = T_i = T_g$ which we designate as α_t , and those appropriate to conditions for which $T_e > T_i, T_g$ which we designate as α_e . Much work has been carried out by Biondi and his colleagues⁵⁻¹⁰ to determine both α_t and α_e for many recombination reactions using the stationary afterglow (SA) technique. Dissociative recombination has also been studied in ion trap experiments^{11,12} and merged beam (MB) experiments^{13,14} but in both of these experiments the cross sections for recombination, σ_e , are determined as a function of electron-ion centre-of-mass energy, and then α_e values are derived from these σ_e data.

Most of the SA measurements of α_t have been obtained over the approximate temperature range 200-450 K, and those of α_e at a $T_g \sim 300$ K and up to $T_e \sim 2000$ K. Ion trap and merged beam data are obtained at centre-of-mass energies in excess of about 0.1 eV. The long storage times in the ion trap allow for internal relaxation of

the molecular positive ions but the ions in the MB experiments are in most cases in indeterminate states of internal excitation (both rotational and vibrational¹⁴). The data obtained from these non-thermal experiments are very useful for investigating the fundamental nature of electron-ion interactions; however they cannot be used with confidence to derive α_e values appropriate to low temperatures for use in ion-chemical models of interstellar gas clouds.

Recently we have developed our flowing afterglow/Langmuir probe (FALP) technique to study electron-ion dissociative recombination¹⁵ (having previously used it for extensive studies of ion-ion recombination¹⁶, and quite recently to study electron attachment¹⁷). The FALP technique can be applied to the study of these various reaction processes within the approximate temperature range 80 to 600 K under truly thermalised conditions. In our first studies of dissociative recombination we measured α_t for O_2^+ , NO^+ and NH_4^+ over the temperature range 200 to 600 K¹⁵. Now we have determined α_t at 95 K and 300 K for the important interstellar ions H_3^+ (and D_3^+), N_2H^+ (and N_2D^+), HCO^+ (and DCO^+) and CH_5^+ . The data obtained are presented and discussed in this paper.

II. EXPERIMENTAL

Details of the FALP technique have been given in previous papers^{18,19} and in a recent review¹⁶. The application of the technique to the determination of α_t is described in detail in a very recent paper¹⁵. Briefly, the approach is as follows. An upstream microwave discharge in helium carrier gas (pressure ~ 0.5 to ~ 1.0 Torr) results in the production of an afterglow plasma along the length

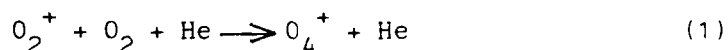
of a flow tube (~ 1 metre long, ~ 8 cm diameter). The upstream region of the afterglow comprises electrons, He^+ and He_2^+ ions and neutral metastable atoms, He^m , in addition to the ground state helium carrier gas atoms. It is then necessary to convert this He^+ , He_2^+ and He^m plasma to one containing only the molecular ion for which the α_t is to be determined. This is achieved by adding a sufficient quantity of an appropriate molecular ion source gas (or vapour) to the afterglow via a downstream inlet port. Details of the ion chemistry involved in the production of each ion species included in these measurements of α_t are given in the next section. The α_t are then derived from measurements of the electron density, n_e , along the axis of the afterglow column (in co-ordinate) using a movable Langmuir probe^{18,20}. When recombination is the dominant loss process for ionization then a plot of n_e^{-1} versus z is linear and α_t is derived from the slope of the line. The reaction time is related to z via the plasma flow velocity, v_p , which is readily determined.²¹ Recombination loss is enhanced and diffusion loss is inhibited by high n_e and high helium pressure. Typical initial values of n_e in these experiments were $(2-4) \times 10^{10} \text{ cm}^{-3}$ (for further details see ref. 15). Measurements were carried out at room temperature and also at 95 K by cooling the flow tube and carrier gas with liquid nitrogen.

III. RESULTS

A Measurement of $\alpha_t(\text{O}_2^+)$ at 95 K and General Discussion of the Ion Chemistry:

Since these studies of α_t were the first we have carried out at very low temperature, we first chose to study $\alpha_t(\text{O}_2^+)$ because

it has been previously studied in detail at higher temperatures using a variety of techniques (including the FALP) and the temperature dependence has been well established between 200 and 600 K as $\alpha_t(O_2^+) \sim T^{-0.7}$ ¹⁵. Measurements at 95 K had to be made very cautiously to avoid the creation of significant concentrations of O_4^+ ions in the afterglow via the three-body association of O_2^+ with O_2 . Such association reactions are promoted by low temperatures and by large number densities of the reactant gas (O_2) and the third body (He). They are potentially a source of serious errors in α_t measurements because the α_t for the dimer (cluster) ions are known to be larger than those for the common diatomic ions⁶. The rate coefficient for the reaction



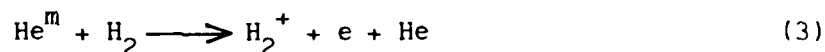
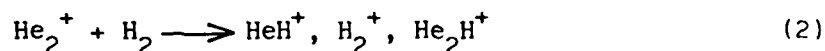
has been measured over a wide temperature range ($k(1) = 2(-29) \text{ cm}^6 \text{ s}^{-1}$ at 95 K²²) and therefore the permissible maximum concentration of O_2 in the afterglow can be determined. Careful use of the downstream mass spectrometer, which is an essential part of the FALP, confirmed for the conditions under which $\alpha_t(O_2^+)$ was determined, that O_4^+ ions were always present in the afterglow but in very small concentrations relative to O_2^+ . Of course, the relative mass spectrometer signals of O_2^+ and O_4^+ at the entrance to the downstream sampling orifice will not necessarily be representative of the relative O_2^+ and O_4^+ number densities upstream in the recombining plasma because of the differential diffusion and recombination rates of these ions. However, the flexibility of the FALP experiment is such that the reaction (recombination) zone can be moved to within a few cms. of the sampling orifice by introducing the O_2 into an inlet port at this

position rather than at the usual position (which is 57 cm from the sampling orifice). Also, the ionization density in the afterglow can be varied and accurately measured over several orders of magnitude (from about 10^{11} cm^{-3} to about 10^7 cm^{-3}). Thus at low n_e , recombination of both O_2^+ and O_4^+ is insignificant and then the ion-molecule chemistry can be investigated and the O_2 flow adjusted to be sure that O_4^+ is not produced in significant concentrations in the afterglow. These kinds of checks were routinely carried out in all of the α_t studies described in this paper.

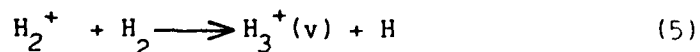
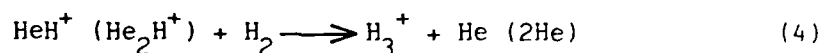
The value of $\alpha_t(\text{O}_2^+)$ obtained at 95 K was $4.8 (-7) \text{ cm}^3 \text{ s}^{-1}$. This is plotted in Fig. 1 together with the previous FALF data obtained at higher temperatures. Clearly the $T^{-0.7}$ power law variation well describes $\alpha_t(\text{O}_2^+)$ over the wider temperature range 95 to 600 K. Actually the 95 K point lies slightly above the line and, although within the estimated errors, it might be the result of the presence of a very small concentration of O_4^+ . The errors on these measurements are quoted in the caption to Table 1.

The determination of α_t for H_3^+ , HCO^+ , N_2H^+ and CH_5^+ involved first the creation of H_3^+ as the dominant ion species in the afterglows, and the determination of $\alpha_t(\text{H}_3^+)$. Then the H_3^+ ions were converted to the other species via proton transfer reactions and their respective α_t determined (see later). The H_3^+ (and D_3^+) were created by adding relatively large concentrations of H_2 (or D_2) to the afterglows. At 300 K, prior to the addition of H_2 , the majority ions in the afterglow were He_2^+ together with smaller concentrations of He^+ and He^m . (The He^m concentration could be readily measured at 300 K by adding excess Ar to the afterglow and then measuring

the increase in n_e using the Langmuir probe¹⁸; however this could not be done at 95 K because of Ar condensation). On adding sufficient H_2 the following reactions occurred:



Reaction (2) is very efficient at 300 K ($k = 5.3 (-10) \text{ cm}^3 \text{ s}^{-1}$)²³ and, as expected, is seen to be so in our experiment at 95 K and 300 K. The rate coefficient for the Penning reaction (3) varies markedly with temperature above 300 K²⁴ (the metastable atoms are mostly 3^3P and not 2^1S). $k(3)$ has been measured to be $3 (-11) \text{ cm}^3 \text{ s}^{-1}$ at 300 K and may fall to about $1 (-13) \text{ cm}^3 \text{ s}^{-1}$ at 95 K.²⁴ This required the presence of substantial concentrations of H_2 in the afterglow at 95 K to ensure that the He^m were totally destroyed (any source of ionization in the afterglow is readily detected using the Langmuir probe). The product ions of reactions (2) and (3) then undergo reactions with H_2 to generate H_3^+ .



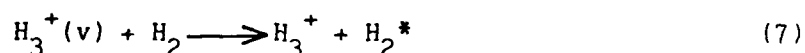
The rate coefficients for both of these reactions are large ($k(4) = 1.5 (-9) \text{ cm}^3 \text{ s}^{-1}$ at 300 K²⁵; $k(5) = 2.1 (-9) \text{ cm}^3 \text{ s}^{-1}$ at 300 K²⁶).

The mass spectrometer was used to confirm that H_3^+ was the dominant ionic species in the afterglow. However a small percentage of He^+ was observed to be present at 300 K. This is because He^+ is relatively

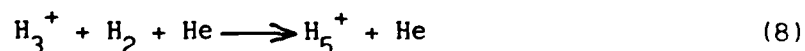
unreactive with H_2 ²⁷ and because the association reaction:



is not sufficiently rapid at 300 K and at a helium pressure of one Torr to convert all the He^+ to He_2^+ ²⁸. However, at 95 K, reaction (6) is more rapid since $k(6)$ is larger²⁹, the number density of He atoms in the afterglow is greater and the plasma flow velocity is smaller (the reaction time is longer) and so the He^+ ions are totally converted to molecular ions. (Indeed, a small signal at mass 12 amu, probably He_3^+ , is observed in the absence of H_2 presumably resulting from the further reaction of He_2^+ with He). So no He^+ is evident in the afterglow at 95 K and therefore on addition of sufficient H_2 , all the He_2^+ and He^m are destroyed and H_3^+ is readily produced. Note that the H_3^+ produced in reaction (5) is initially vibrationally excited^{30,31} but in the presence of H_2 it is de-excited³² via the reaction:



The rate of the de-excitation of $H_3^+(v)$ of course depends on $k(7)$ and the H_2 concentration in the afterglow (further referred to in relation to the $\alpha_t(H_3^+)$ estimates discussed below). At large H_2 concentrations and at 95 K, the association reaction



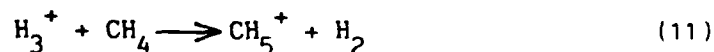
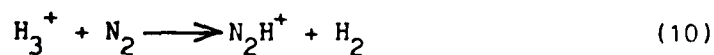
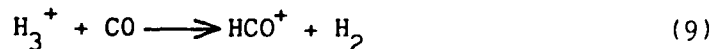
was observed to occur, generating H_5^+ . The H_5^+ was detected by the mass spectrometer in increasing concentration relative to H_3^+ as the

H₂ concentration was increased. In a separate SIFT experiment we measured the rate coefficient of reaction (8) to be $2 (-29) \text{ cm}^6 \text{ s}^{-1}$ at 80 K. This number was useful in interpreting the α_t data for H₃⁺/H₅⁺ plasmas which clearly indicated that α_t (H₅⁺) was much greater than α_t (H₃⁺), as has previously been indicated by SA measurements (see below).

Now that the basic ion-chemistry which leads to the production of H₃⁺ (and H₅⁺) in these afterglows has been discussed, we can proceed to describe the α_t determinations for the various ionic species. It will be very evident that satisfactory interpretation of the surprising data relating to the α_t (H₃⁺) studies relies a great deal on an understanding of the ion chemistry and the physics occurring in these plasmas.

B The n_e versus z data: Determination of α_t for the various reactions:

Having created the H₃⁺ plasma, n_e was measured as a function of z and the data obtained at 300 K are shown as a $\ln n_e$ versus z plot in Fig. 2. Also shown are the data for HCO⁺, N₂H⁺ and CH₅⁺ obtained under identical conditions of temperature, He pressure and H₂ concentration but with smaller admixtures of CO, N₂ and CH₄ as appropriate. This results in the production of the new ions via the proton transfer reactions:



which are rapid at 300 K³³ and also, as expected, at 80 K³⁴.

Upstream of the H₂/reactant gas (e.g. CO) inlet port, the z gradient of n_e , i.e. $\partial n_e / \partial z$ is small since the loss of ionization is due only to the relatively slow process of ambipolar diffusion. However as can be seen in Fig. 2, $\partial n_e / \partial z$ increases downstream of the inlet port, remarkably so for the CH₅⁺ plasma. This increase is due to the onset of dissociative recombination and it is clear from Fig. 2 that the relative α_t are in the order, $\alpha_t(\text{CH}_5^+) > \alpha_t(\text{N}_2\text{H}^+) > \alpha_t(\text{HCO}^+) > \alpha_t(\text{H}_3^+)$. The good linearity of the n_e^{-1} versus z plots over appreciable ranges of n_e , at least for the N₂H⁺ and CH₅⁺ reactions (see Fig. 3), demonstrates the dominance of recombination loss for these reactions. Note also in Fig. 2 that for small z , i.e. well downstream of the inlet port, the semilogarithmic plots become nearly linear which is characteristic of diffusive loss. A further check that recombination is indeed responsible in each afterglow for these increases in $\partial n_e / \partial z$ is made simply by considerably reducing n_e in the afterglow, thus inhibiting recombination loss but without influencing diffusion loss. Under these conditions $\partial n_e / \partial z$ downstream of the inlet port reduced towards that measured upstream of the inlet port.

H₃⁺ and D₃⁺:

The data obtained for D₃⁺ at both 95 K and 300 K were insignificantly different from those for H₃⁺. It is clear from the data in Fig. 2 that $\alpha_t(\text{H}_3^+)$ at 300 K is small, certainly considerably smaller than $\alpha_t(\text{O}_2^+)$ which at the same temperature is $2(-7) \text{ cm}^3 \text{ s}^{-1}$ (the $\alpha_t(\text{O}_2^+)$ data is represented in Fig. 2 by the dashed curve without data points). This was a great surprise in view of previous

SA data⁷ and MB data¹³ which indicated that $\alpha_t(\text{H}_3^+)$ was comparable to $\alpha_t(\text{O}_2^+)$ and that the $\sigma_e(\text{H}_3^+)$ was large. After repeating the FALP experiments several times at 300 K and also at 95 K over a period of many weeks under a wide variety of He pressures and H_2 concentrations we were forced to conclude that $\alpha_t(\text{H}_3^+)$ and $\alpha_t(\text{D}_3^+)$ are indeed very small at both 95 K and 300 K. Recently we have been informed by H.H. Michels³⁵ of his theoretical calculations of $\alpha_t(\text{H}_3^+)$ which indicate an infinitesimal α_t for $\text{H}_3^+(v=0)$ and that α_t only begins to become appreciable when H_3^+ is in the $v=3$ vibrational level (equivalent to about 0.9 eV of vibrational energy!) Clearly, in our experiments we expect that reaction (2) will vibrationally relax the H_3^+ and so the small $\alpha_t(\text{H}_3^+)$ indicated by our experiments is qualitatively consistent with Michels' prediction. However, recombination does occur close to the H_2 inlet port at both 95 and 300 K, albeit only to a small extent, and the question arises as to what the recombination loss is due to if it is not due to $\text{H}_3^+(v=0)$. Several factors may contribute to this small recombination loss including (i) high energy electrons generated in reaction (3) which might effectively excite H_3^+ in the interaction and hence increase $\alpha_t(\text{H}_3^+)$, (ii) vibrationally excited H_3^+ produced in reaction (5), (iii) H_5^+ ions generated in reaction (8) and (iv) impurity ions which have relatively large α_t , e.g. H_3O^+ and N_2H^+ generated from traces of H_2O and N_2 in the H_2 . At 300 K, very small signals of H_3O^+ and N_2H^+ were apparent in the mass spectrum but these represented ion densities which were far too small to be responsible for the observed recombination loss. Also production of H_5^+ at 300 K is far too slow at the concentrations of H_2 in the afterglow to account for the recombination. Electron temperature relaxation in helium at one Torr pressure is very efficient; we estimate that hot electrons from

the Penning process will relax to thermal in about 0.1 ms^{36} . Since recombination is apparent for about 6 cms from the inlet port (see Fig. 2), that is for about 0.5 ms, then 'hot' electrons are not responsible and we are left with vibrationally excited H_3^+ ions as the only possible explanation. It is known that several collisions of $\text{H}_3^+(v)$ with H_2 are necessary to remove the vibrational energy from H_3^+ (reactions (7))^{32,37} and so an equivalent rate coefficient for reaction (7) of $\sim 1 (-10) \text{ cm}^3 \text{ s}^{-1}$ seems reasonable. Combining this rate coefficient with the number density of H_2 in the afterglow ($\sim 10^{14} \text{ cm}^{-3}$) indicates a time constant of $\sim 0.1 \text{ ms}$ for the vibrational relaxation process. Thus $\text{H}_3^+(v)$ could persist for a fraction of a millisecond against reaction (7) and could therefore undergo recombination on a similar timescale to that observed. Thus vibrationally excited H_3^+ could explain the observed recombination loss close to the inlet port.

How can $\alpha_t(\text{H}_3^+)$ be estimated from the n_e versus z data? The above argument implies that the reduction in n_e near to the inlet port is due to recombination of $\text{H}_3^+(v)$ and diffusion of both $\text{H}_3^+(v)$ and H_3^+ . The relative number density of $\text{H}_3^+(v)$ is reducing both via recombination and via collisional relaxation to H_3^+ . This very complicated situation cannot be disentangled but an estimate of an "effective recombination coefficient", α_{eff} , can be obtained assuming a recombination rate law of the form $v_p \frac{dn_e}{dz} = \alpha_{\text{eff}} \cdot n_e \cdot n_{\text{H}_3^+(v)}$. The density of $\text{H}_3^+(v)$ is estimated as the difference between the n_e values ($n_{\text{H}_3^+(v)} + n_{\text{H}_3^+}$) at large z and the values n_e at small z ($= n_{\text{H}_3^+}$) projected back to large z . Thus $\alpha_{\text{eff}} \sim 7(-8) \text{ cm}^3 \text{ s}^{-1}$ and this clearly must exceed $\alpha_t(\text{H}_3^+)$ and be smaller than $\alpha(\text{H}_3^+(v))$. An upper-limit to $\alpha_t(\text{H}_3^+)$ can be estimated by assuming that the decrease in n_e downstream of the recombination zone is due entirely to

recombination of H_3^+ . This indicates $\alpha_t(H_3^+)$ to be $\lesssim 2 \text{ (-8) cm}^3\text{s}^{-1}$. Actually, the $\ln n_e$ versus z plot is almost linear at small z which is indicative of diffusive loss alone and indeed the exponential loss rate is very close to that expected on the basis of the known diffusion coefficient for H_3^+ ions in helium³⁸. This implies that very little recombination of H_3^+ is occurring in the afterglow even at these large n_e and therefore that the upper limit to $\alpha_t(H_3^+)$ is certainly less than $2 \text{ (-8) cm}^3\text{s}^{-1}$. Unfortunately we cannot further quantify this. It seems therefore that Michels' conclusions that $\alpha_t(H_3^+)$ is infinitesimal are vindicated.

At 95 K, and for low concentrations of H_2 , a similar reduction in n_e occurred near to the inlet port which we again attribute to the presence of a small fraction of $H_3^+(v)$ in the afterglow. Thus a small $\alpha_t(H_3^+)$ is indicated at this temperature also ($\lesssim 2 \text{ (-8) cm}^3\text{s}^{-1}$). However, on the addition of larger flows of H_2 , n_e reduced more rapidly with z and this correlated with the appearance of H_5^+ at the mass spectrometer. Clearly H_5^+ was being produced via reaction (8) and recombining at a more rapid rate than H_3^+ which is in qualitative agreement with the previous SA findings.⁷ With the present configuration of the FALP reactant gas flow system we were not able to add sufficient H_2 to convert all the H_3^+ to H_5^+ and so were not able to determine $\alpha_t(H_5^+)$ to a worthwhile accuracy. A crude, approximate analysis of the n_e versus z curve at the maximum H_2 concentration which could be obtained ($7 \times 10^{14} \text{ cm}^{-3}$) together with our measured value of the rate coefficient for reaction (8) indicates only a lower limit for $\alpha_t(H_5^+)$ of $\sim 2 \text{ (-7) cm}^3\text{s}^{-1}$ at 95 K. The SA value⁷ for $\alpha_t(H_5^+)$ at 205 K is $(3.6 \pm 1.0) \text{ (-6) cm}^3\text{s}^{-1}$. The major difference between the FALP and SA values for

$\alpha_t(H_3^+)$ is perplexing. We have no convincing explanation for this except to tentatively suggest that the presence of a small fraction of H_5^+ ions in the SA could have resulted in a larger $\alpha_t(H_3^+)$ because of the much larger $\alpha_t(H_5^+)$ (production of H_5^+ is promoted by the high pressures at which the SA experiments were carried out).

The emission spectra of H_3 and D_3 have been identified by Herzberg³⁹ from hollow cathode discharges in H_2 and D_2 respectively. These were assumed to originate from recombining H_3^+ and D_3^+ . If this were the case then the recombining ions were probably vibrationally excited. However it was noted that the emission intensities from H_3 and D_3 were greatly enhanced when the cathode was cooled with liquid nitrogen and so we suggest that the H_3 and D_3 were most probably produced from the dissociative recombination of H_5^+ and D_5^+ , e.g.

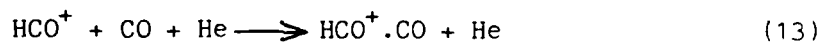


HCO⁺ and DCO⁺:

The addition of relatively small concentrations of CO to the H_3^+ (and D_3^+) afterglows resulted in an immediate enhancement of the n_e gradient. CO addition initiates the fast proton transfer reaction (9) which has a rate coefficient at both 80 K and 300 K of $1.8 (-9) \text{ cm}^3 \text{ s}^{-1}$ ³⁴, and so H_3^+ is rapidly converted to HCO⁺ (similarly for DCO⁺). Clearly $\alpha_t(\text{HCO}^+) > \alpha_t(H_3^+)$ (and indeed $\alpha_t(\text{HCO}^+) > \alpha_{\text{eff}} > \alpha_t(H_3^+)$). A plot of n_e^{-1} versus z for the HCO⁺ data at 300 K is shown in Fig. 3. The range of linearity of this plot is limited because of the relatively small $\alpha_t(\text{HCO}^+)$

of $1.1 (-7) \text{ cm}^3 \text{ s}^{-1}$ and this is reflected in the somewhat greater uncertainty we place on $\alpha_t (\text{HCO}^+)$ at 300 K (see Table I). At 95 K, $\alpha_t (\text{HCO}^+)$ and $\alpha_t (\text{DCO}^+)$ are measured to be $2.9 (-7) \text{ cm}^3 \text{ s}^{-1}$ and $2.6 (-7) \text{ cm}^3 \text{ s}^{-1}$ respectively.

Our $\alpha_t (\text{HCO}^+)$ at 300 K is significantly smaller than the SA value⁸ (see Table I) but not greatly so when the combined errors of both experiments are taken into account. However, our value at 95 K is slightly smaller than the SA value at the higher temperature of 205 K. The larger value derived from the higher pressure SA experiment may be due to the production of small concentrations of the association ion $\text{HCO}^+.\text{CO}$ which presumably will have a larger α_t . This suggestion arises from our observation that for large flows of CO in our experiment, small signals of $\text{HCO}^+.\text{CO}$ were detected by the mass spectrometer. This prompted us to measure with our SIFT the rate coefficient for the reaction:

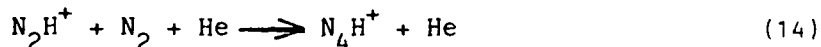


At 80 K, $k(13) = 1.1 (-29) \text{ cm}^6 \text{ s}^{-1}$. Knowing this rate coefficient we were able to estimate the maximum permissible value of the CO concentration in the afterglow for insignificant production of $\text{HCO}^+.\text{CO}$. Safeguards of this kind are very important in this type of work since it is all too easy to fail to detect mass spectrometrically small signals of weakly-bonded ions such as $\text{HCO}^+.\text{CO}$ because these ions are so readily collisionally dissociated in the mass spectrometer sampling system.

Within the limitations of only two data points and assuming a power law dependence, the present data indicate that $\alpha_t(\text{HCO}^+)$ varies approximately as T^{-1} between 95 and 300 K.

N_2H^+ and N_2D^+ :

The addition of small concentrations of N_2 to the H_3^+ (or D_3^+) plasmas again resulted in an obvious enhancement in the n_e gradient (see Fig. 2). This is a result of the production of N_2H^+ (or N_2D^+) via the fast reaction (10). The plot of n_e^{-1} versus z for the N_2H^+ data at 300 K is shown in Fig. 3 and the linearity of the plot is indicative of recombination loss. The value of $\alpha_t(\text{N}_2\text{H}^+)$ thus obtained is $1.7 (-7) \text{ cm}^3 \text{ s}^{-1}$. At 95 K, $\alpha_t(\text{N}_2\text{H}^+)$ and $\alpha_t(\text{N}_2\text{D}^+)$ are measured to be $4.9 (-7) \text{ cm}^3 \text{ s}^{-1}$ and $4.4 (-7) \text{ cm}^3 \text{ s}^{-1}$ respectively. That $\alpha_t(\text{N}_2\text{D}^+)$ is somewhat smaller than $\alpha_t(\text{N}_2\text{H}^+)$ is not significant within error but it is intriguing that $\alpha_t(\text{DCO}^+)$ is also smaller than $\alpha_t(\text{HCO}^+)$ by about the same percentage at the same temperature. Perhaps there is a small isotope effect in these cases. $\alpha_t(\text{N}_2\text{H}^+)$ at 95 K is three times greater than the 300 K value and so a $\sim T^{-1}$ variation for $\alpha_t(\text{N}_2\text{H}^+)$ is also indicated. Again it must be pointed out that large flows of N_2 promoted the association reaction.

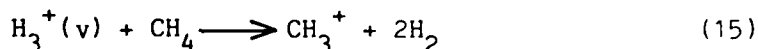


We determined $k(14)$ using the SIFT to be $2.8 (-29) \text{ cm}^3 \text{ s}^{-1}$ at 80 K (i.e. about three times greater than the corresponding $\text{HCO}^+ + \text{CO}$ reaction (13)). In this case the strongly bound N_4H^+ ion is produced. Again, $k(13)$ sets the upper limit to the concentration of N_2 which is permissible in the afterglow.

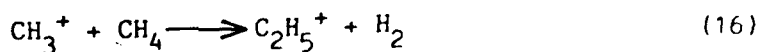
No SA value has been published for $\alpha_t(N_2H^+)$ but electron recombination of N_2H^+ has been studied using the MB technique⁴⁰. A much larger value for $\alpha_e(N_2H^+)$ at 300 K of $7.5 (-7) \text{ cm}^3\text{s}^{-1}$ has been derived from these MB $\sigma_e(N_2H^+)$ data. Whilst it is not too profitable to compare these ion beam data with truly thermal data, a larger value of $\sigma_e(N_2H^+)$ might be expected if vibrationally-excited N_2H^+ has a relatively large σ_e since it is known that N_2H^+ is readily vibrationally excited (from drift tube studies of endoergic proton transfer⁴²) and so it is very likely that $N_2H^+(v)$ is a major component of the ion beam. In the FALP, $N_2H^+(v)$ is rapidly relaxed in proton transfer reactions analogous to reaction (7).

CH₅⁺:

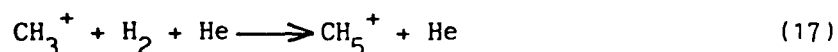
The addition of small concentrations of CH₄ to the H₃⁺ plasma resulted in a rapid increase in the n_e gradient (Fig. 2). The mass spectrometer indicated that CH₅⁺ was the dominant ion (> 95%) but also small signals of CH₃⁺ and C₂H₅⁺ were evident. The CH₅⁺ is formed via the proton transfer reaction (11) and the appearance of CH₃⁺ was a clear indicator of the presence of H₃^{+(v)}, since it is known that the reaction



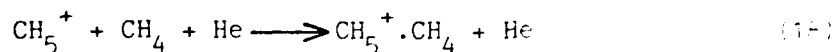
is rapid⁴³. This then is direct evidence for the existence of small concentrations of H₃^{+(v)} which we deduced earlier in relation to the $\alpha_t(H_3^+)$ studies. The C₂H₅⁺ ions are formed via the rapid two-body reaction:



which has a rate coefficient of $1.2 (-9) \text{ cm}^3 \text{ s}^{-1}$ at 300 K^{44} and presumably also at 95 K . CH_3^+ is also converted to CH_5^+ by the three-body association reaction:



which thus enhances the CH_5^+ population in the plasma. Reaction (17) is known to be quite rapid at 80 K^{45} and therefore at 95 K at the pressure conditions ($\sim 1 \text{ Torr}$) of the present experiments. Again, it must be mentioned that association of the ion under study (CH_5^+) with its parent (CH_4) occurs at low temperatures:



The rate coefficient for reaction (18) is $2.5 (-28) \text{ cm}^3 \text{ s}^{-1}$ at 80 K as measured in the SIFT⁴⁶, and so again the concentration of CH_4 in the plasma of the low temperature had to be minimised.

It is worthy of note here that association reactions of HCO^+ and N_2H^+ with H_2 are very slow ($< 5 (-30) \text{ cm}^6 \text{ s}^{-1}$ in He at 80 K) and that association of CH_5^+ with H_2^+ has not been observed even at 80 K in our SIFT. So for the concentrations of H_2 used in these experiments these reactions are unimportant.

The n_e^{-1} versus z data at 300 K are plotted in Fig. 3 and $\alpha_t(\text{CH}_5^+)$ obtained from the slope is $1.1 (-6) \text{ cm}^3 \text{ s}^{-1}$. At 95 K , $\alpha_t(\text{CH}_5^+)$ has increased to $1.5 (-6) \text{ cm}^3 \text{ s}^{-1}$. This relatively small increase in $\alpha_t(\text{CH}_5^+)$ and the correspondingly weak temperature

dependence ($\sim T^{-0.3}$) is typical of α_t which are relatively large such as those for cluster ions^{9,10}. It is perhaps significant that the value for α_e (CH_5^+) at 300 K derived from MB data is rather close to our α_t (CH_5^+) (actually slightly smaller, α_e (CH_5^+) = $7 (-7) \text{ cm}^3 \text{ s}^{-1}$)⁴¹. This unusually good agreement between FALP data and MB predictions may be due to the relatively weak temperature (energy?) dependence of α_t (and α_e) and because any residual excitation in the CH_5^+ ion beam would presumably not greatly influence the σ_e value for this particular ion since, on the basis of the FALP data, σ_e would be expected to be large even for ground state ions.

IV. SUMMARY AND CONCLUSIONS

The very small α_t for ground vibrational state H_3^+ ions (and D_3^+ ions), indicated by these experiments runs contrary to previous experimental results but is consistent with recent theoretical predictions by Michels. Thus H_3^+ is only the second molecular ion which has so far been shown to recombine very slowly, the other well-known case being He_2^+ ⁵. However, recombination of H_3^+ ions does occur when they are vibrationally excited, again in accordance with theoretical predictions. Emission spectra of neutral H_3 and D_3 molecules have been observed from H_2 (and D_2) discharges. This could be due to recombination of $\text{H}_3^+(v)$ but was most likely due to recombination of H_5^+ (and D_5^+). That α_t (H_3^+) is so small is contrary to the usual assumptions made in interstellar ion-chemical models and has major effects on the predictions of these models^{34,47,48}.

The α_t for HCO^+ , N_2H^+ and CH_5^+ have magnitudes as expected on the basis of previous SA data for a variety of ionic species.

The α_t (CH_5^+) is the largest of the three and increases more slowly with decreasing temperature than do α_t (HCO^+) and α_t (N_2H^+). These data illustrate a trend which is gradually emerging, i.e. fast recombination reactions have weaker inverse temperature dependences than slower reactions. Discrepancies between data obtained from collision-dominated thermal experiments such as the SA and the FALP and the non-thermal merged beam data are not unexpected not least because of the different internal states of the recombining ions. The agreement between the SA and FALP results for individual reactions is generally good, except possibly at low temperatures when the SA values are sometimes a little larger. This might be due to the presence of small fractional concentrations of cluster ions in the SA which is operated at higher pressures than the FALP and which promotes the formation of association ions (as does low temperature). The major discrepancy between the α_t (H_3^+) determined in the SA and the FALP is difficult to explain. Clearly, further work and thought are necessary to resolve this perplexing discrepancy.

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TABLE I. Values of the dissociative recombination coefficients, α_t , obtained in the FALP for the ion species indicated at 95 and 300 K. The units are cm^3s^{-1} and, for example 2.9(-7) means $2.9 \times 10^{-7} \text{ cm}^3\text{s}^{-1}$. Also given are the stationary afterglow (SA) data for H_3^+ ¹⁷ and HCO^+ ⁸ at the temperature indicated, and the derived rate coefficients, α_e , from merged beam (MB) data for N_2H^+ ⁴⁰ and CH_5^+ ⁴¹.

The estimated absolute errors for the FALP values of α_t (N_2H^+) and α_t (CH_5^+) are $\pm 15\%$ at 300 K and $\pm 20\%$ at 95 K. For α_t (HCO^+) the errors are somewhat greater at 300 K ($\pm 20\%$) because of the smaller range of n_e from which the α_t was obtained (see Fig. 2) and the correspondingly greater uncertainty in the slope of the reciprocal density plot (see Fig. 3). The total errors in α_t arise largely from the uncertainty in the area of the Langmuir probe ($\sim \pm 10\%$) which reflects directly into the error in n_e and therefore α_t . When this systematic error is allowed for the relative errors in the α_t values are much smaller ($\sim \pm 10\%$).

Ion	FALP data		205 K	Previous data		
	95 K	300 K		300 K	450 K	
H_3^+	$\leq 2(-8)$	$\leq 2(-8)$	2.9(-7)	2.3(-7)	2.0(-7)	SA
D_3^+	$\leq 2(-8)$	$\leq 2(-8)$				
HCO^+	2.9(-7)	1.1(-7)	3.3(-7)	2.0(-7)	—	SA
DCO^+	2.6(-7)	—				
N_2H^+	4.9(-7)	1.7(-7)	} 7.5(-7)(300/Te) ^{0.5}			MB
N_2D^+	4.4(-7)	—				
CH_5^+	1.5(-6)	1.1(-6)	7.0(-7)(300/Te) ^{0.5}			MB

FIGURE CAPTIONS

Fig. 1 FALP measurements of $\alpha_t(O_2^+)$ at several temperatures, T. The solid line describes the power law relationship $\alpha_t(O_2^+) = 2(-7) (300/T)^{0.7}$, which is a good fit to the data points over a temperature range which is unusually wide for dissociative recombination studies. The data points at temperatures of 200 K and above are from our previous FALP study.¹⁵

Fig. 2 Semilogarithmic plots of electron density in the afterglow, n_e , against z , the distance along the afterglow column as measured from the downstream mass spectrometer sampling orifice in the FALP apparatus. R indicates the position of the molecular ion source gas inlet port. The carrier gas was helium at a pressure of 1.2 Torr and the temperature was 300 K. Upstream of R, $\partial n_e / \partial z$ is small since electrons were lost from the afterglow only via ambipolar diffusion. Downstream of R, $\partial n_e / \partial z$ is larger due to the occurrence of dissociative recombination in the H_3^+ , HCO^+ , N_2H^+ and CH_5^+ afterglow plasmas. The magnitudes of the $\partial n_e / \partial z$ for these plasmas indicate that $\alpha_t(CH_5^+) > \alpha_t(N_2H^+) > \alpha_t(HCO^+) > \alpha_t(H_3^+)$. The dashed line without points represents the data for O_2^+ (see text).

Fig. 3 Plots of reciprocal electron density, n_e^{-1} against z from the data given in Fig. 2 for the HCO^+ , N_2H^+ and CH_5^+ afterglow plasmas. The respective α_t are obtained from the slopes of the lines. Thus $\alpha_t(CH_5^+) > \alpha_t(N_2H^+) > \alpha_t(HCO^+)$; the actual values are given in Table I.

Fig.1

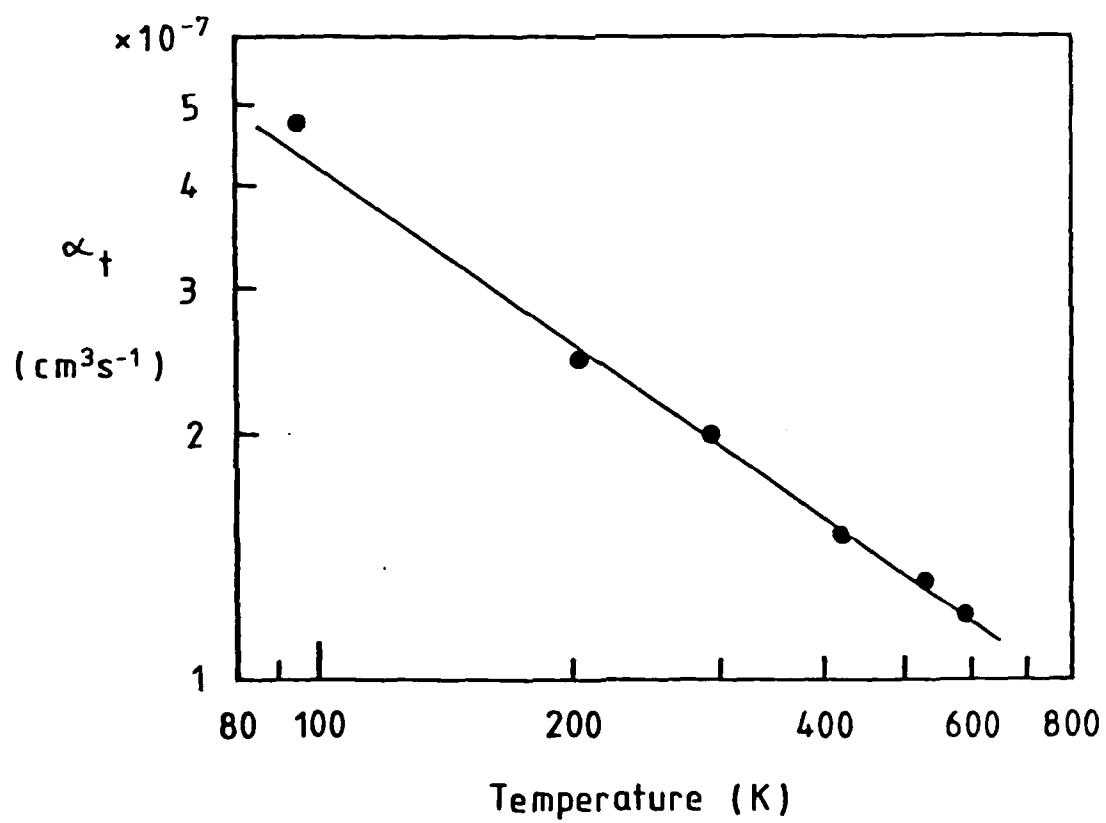


Fig.2

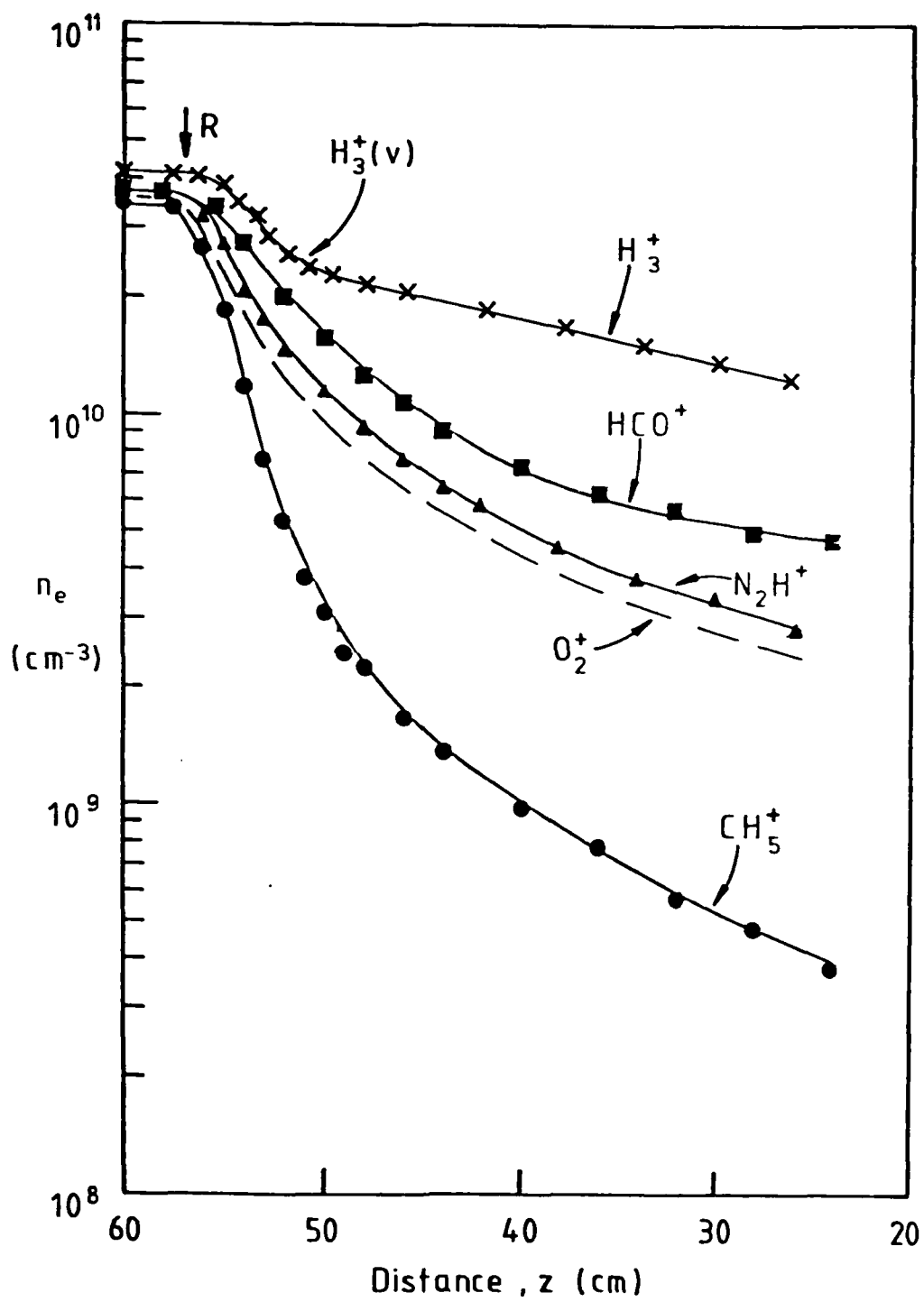
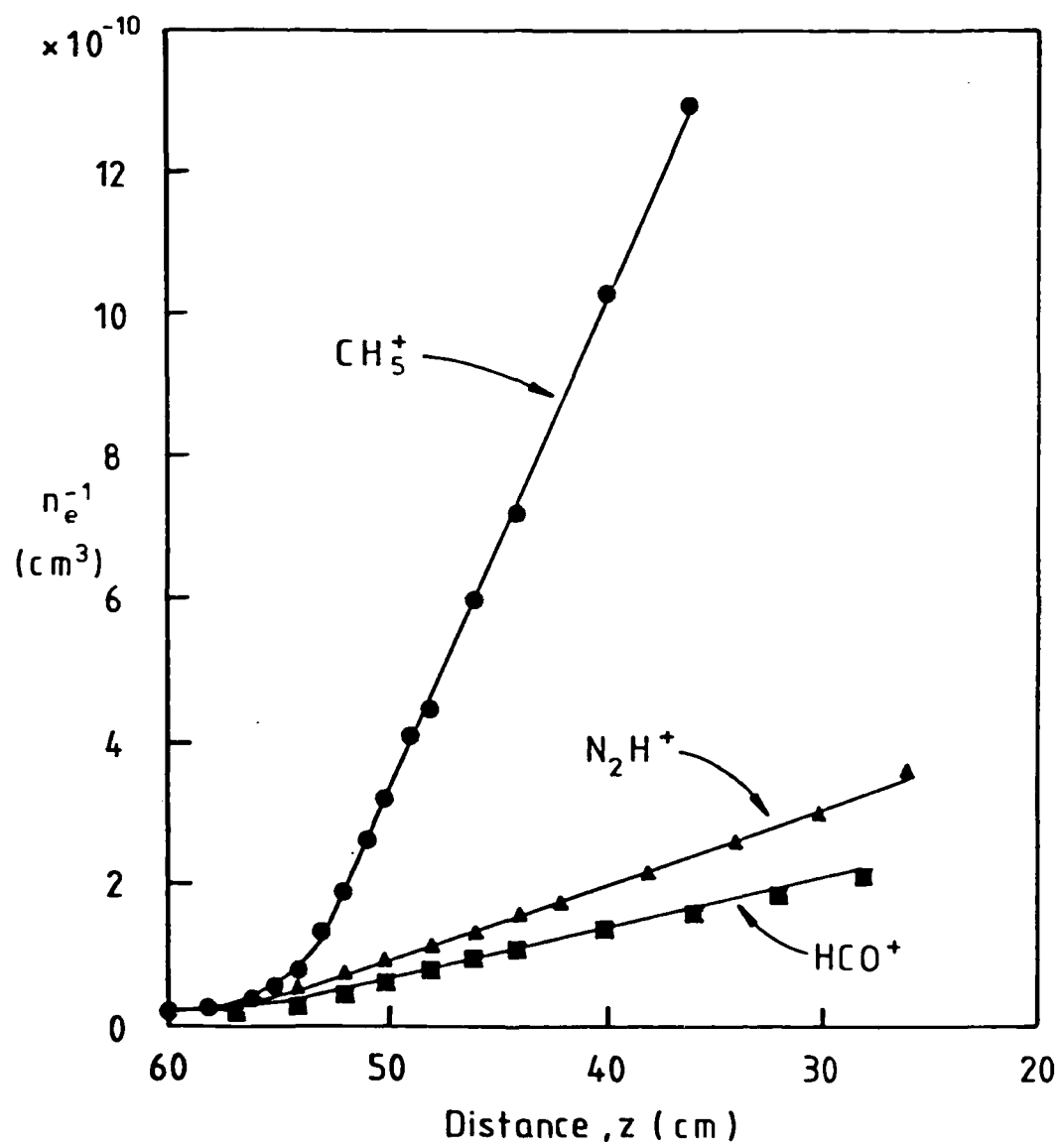


Fig.3



APPENDIX 3

ATTACHMENT COEFFICIENTS FOR THE REACTIONS OF
ELECTRONS WITH CCl_4 , CCl_3F , CCl_2F_2 , CHCl_3 , Cl_2 AND SF_6
DETERMINED BETWEEN 200 AND 600 K USING THE FALP TECHNIQUE.

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Attachment coefficients for the reactions of electrons with CCl_4 , CCl_3F , CCl_2F_2 , CHCl_3 , Cl_2 and SF_6 determined between 200 and 600 K using the FALP technique

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Abstract. The rate coefficients, β , for the attachment reactions of electrons with CCl_4 , CCl_3F , CCl_2F_2 , CHCl_3 , Cl_2 and SF_6 have been measured under truly thermal conditions over the approximate temperature range 200–600 K using a flowing-afterglow/Langmuir probe apparatus. The β values obtained at 300 K are 3.9×10^{-7} , 2.6×10^{-7} , 3.2×10^{-9} , 4.4×10^{-9} , 2.0×10^{-9} and $3.1 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ respectively. From the variation with temperature of β for the CCl_2F_2 , CHCl_3 and Cl_2 dissociative attachment reactions, activation energies, E_a , of 0.15, 0.12 and 0.05 eV respectively were derived. The β for CCl_4 , CCl_3F and SF_6 are close to their theoretical limiting values within the temperature range investigated. While Cl^- was the only product ion observed for the reactions involving chlorine-containing molecules, both SF_6^- and SF_5^- were observed for the SF_6 reaction. The data obtained are compared with previous data and the separate influences of electron temperature and gas temperature are noted.

1. Introduction

Electron attachment studies are of fundamental importance to the understanding of electron-molecule interactions and the mechanism of negative-ion formation (see e.g. Massey 1976) and are of practical value for example in the design of efficient gas lasers (Chantry 1982) and in the choice of insulation suitable for high-voltage devices (Christophorou *et al* 1982). The objective of the work described in this paper was to measure the rate coefficients, β , for the attachment reactions of thermalised electrons with several molecular gases at temperatures in the approximate range 200–600 K using our flowing-afterglow/Langmuir probe (FALP) apparatus. Using the FALP, the rate coefficients for several types of plasma reactions have already been determined under truly thermal conditions, including positive-ion/negative-ion recombination (Smith and Church 1976, Smith and Adams 1983) and electron/ion recombination (Alge *et al* 1983).

Electron attachment has been studied in numerous laboratories using a variety of techniques. Much of the early work (prior to 1976) has been summarised in the books by Massey (1976) and by Christophorou (1971) and many other excellent papers on this topic have been published in the last few years. Some of these papers and the results therein will be referred to in relation to the present work in § 3. The gases chosen for the present study were CCl_4 , CCl_3F , CCl_2F_2 , CHCl_3 , Cl_2 and SF_6 for which previous data indicate the electron attachment rate coefficients, β , to be relatively

large at room temperature. The precise values of β at room temperature and how the β values vary with temperature are not well established and this was a major motivation for this study.

2. Experimental

2.1. Apparatus

The FALP apparatus has been discussed in detail previously in relation to studies of ionic and electronic recombination (Smith and Church 1976, Alge *et al* 1983). A schematic of the apparatus is given in figure 1. In brief, the principle of operation is as follows. Flowing-afterglow plasmas are created in a tube (~ 100 cm long and ~ 8 cm diameter) by a microwave discharge through a fast-flowing carrier gas (helium in the present studies at pressures between 0.5 and 1 Torr). Hence a thermalised afterglow is distributed along the length of the flow tube. By introducing controlled quantities of appropriate gases into the afterglow via one of two 'ring ports' located at different positions along the flow tube (see figure 1(a)), various ionic and electronic reactions can be studied under truly thermalised conditions (Dean *et al* 1974).

The ring ports are shown schematically in figure 1(a). The attaching gas was introduced against the carrier gas flow in order to ensure the rapid dispersion of the electron attaching gases across the diametric plane of the flow tube, thus minimising the mixing distance (ϵ). Temperature variation over the approximation range 80 to

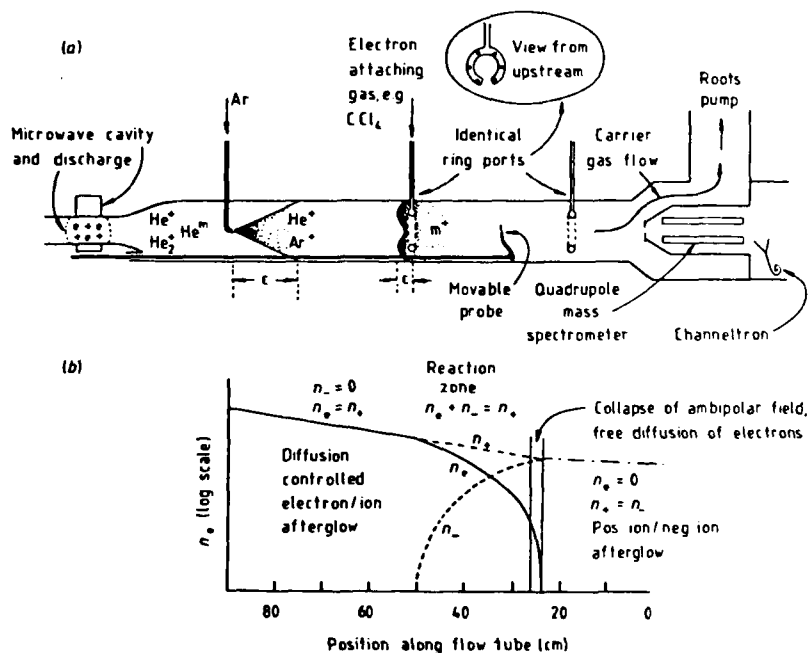


Figure 1. (a) Schematic representation of the FALP experiment including diagnostic instruments, ionisation source, gas inlet ports etc. (b) Typical variations of n_e , n_+ and n_- along the flow tube during electron attachment studies.

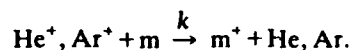
600 K is achieved by heating or cooling the complete flow tube. The essential plasma diagnostic is a small cylindrical Langmuir probe which can be positioned at any point on the axis of the flow tube (the z coordinate). With it, the electron, positive-ion and negative-ion number densities (n_e , n_+ and n_- , respectively) can be determined with a spatial resolution of about 1 mm. The probe technique has been discussed in detail in previous papers (Smith and Goodall 1968, Smith and Plumb 1972). A pinhole orifice/differentially pumped mass spectrometer/detection system is located at the downstream end of the flow tube to determine the positive- and negative-ion composition of the afterglow plasmas. By measuring the axial gradients of n_e , n_+ and n_- as appropriate, and also the plasma flow velocity, v_p , (typically $\sim 10^4 \text{ cm s}^{-1}$, Adams *et al* 1975) the rate coefficients for a wide variety of reactions can be determined.

2.2. Procedure

In the present experiments, appropriate quantities of the electron attaching gases were added into helium afterglow plasmas into which a sufficient amount of argon (equivalent to a pressure of a few millitorr) had been added upstream in order to destroy all $\text{He}(2^1\text{S})$ and $\text{He}(2^3\text{S})$ metastable atoms. When present these metastable atoms react with the electron attaching gas resulting in the production of electrons in the afterglow. n_e was measured with the probe both *upstream* and *downstream* of the attaching gas entry port. In the *upstream* region, the loss of electrons is via ambipolar diffusion predominantly with Ar^+ (and some He^+) and the ambipolar diffusion coefficient for the electrons, D_{ae} , is readily determined from the n_e versus z data. In the *downstream* region, electron attachment occurs in addition to ambipolar diffusion resulting in a greatly increased loss rate of electrons. Analysis of the n_e versus z data provides a value for the electron attachment rate coefficient, β .

In these experiments it is essential to be cognisant of the following important processes which if not properly accounted for may result in erroneous β values.

(a) Molecular positive ions, m^+ , are inevitably generated to some degree due to ion-molecule reactions (rate coefficient k) between the atomic ions Ar^+ and He^+ and the electron attaching gas, m , thus:



Then the relatively rapid process of dissociative recombination of m^+ with electrons (Bardsley and Biondi 1970) can enhance the rate of loss of n_e , unless n_e and/or n_m (the molecular positive ion number density) are sufficiently small that recombination loss is insignificant. Specifically, the loss rate of electrons via dissociative recombination, $\alpha n_e n_m$, must be much less than the loss rate of electrons via attachment, $\beta n_e n_m$, (α is the dissociative recombination coefficient and n_m is the number density of the electron attaching gas, m). If this condition is not satisfied, then the decrease of n_e is influenced by the production rate of m^+ (i.e. $kn_m n_{\text{Ar}^+}$) and when $\alpha n_e n_m > kn_m n_{\text{Ar}^+}$ then the n_e versus z data provide a value for k . The values of k determined in this way are in acceptable agreement with the values determined in associated selected-ion flow tube (SIFT) experiments (see § 3 and table 2). In principle, such problems can be eliminated by performing the experiments at sufficiently low n_e , but unfortunately the probe technique did not allow accurate measurement of n_e much below 10^4 cm^{-3} . Consequently we were unable to accurately measure β values smaller than about $10^{-9} \text{ cm}^3 \text{ s}^{-1}$. Very recently, the probe technique has been refined to allow

measurement of n_e as low as 10^7 cm^{-3} , thus lowering the limiting measurable value of β to about $10^{-10} \text{ cm}^3 \text{ s}^{-1}$.

(b) When studying the most rapid attachment reactions (e.g. the SF_6 and CCl_4 reactions), the number density of the attaching gas, n_m , must necessarily be very small otherwise n_e reduces too rapidly with z (i.e. $\partial n_e / \partial z$ is too large to allow sufficiently accurate n_e versus z measurements to be made). However, n_m must always be appreciably greater than n_e , otherwise the reduction in n_m due to the attachment process results in an axial gradient in n_m . This would greatly complicate the interpretation of the n_e versus z data usually resulting in erroneously small β values. This effect was investigated by measuring ' β ' for different initial values of n_e and from these studies we were able to determine initial values of n_e for which accurate β determinations could be made (i.e. for which β is independent of n_e).

Of the gases used in this study, the CCl_2F_2 and Cl_2 were taken directly from cylinders and passed via a flow measuring system into the afterglow. However, the very large β for the SF_6 , CCl_4 and CCl_3F reactions necessitated that these gases were 'diluted' with helium to facilitate accurate measurements of the flow rates into the afterglow. Since CHCl_3 is a liquid, it was also necessary to use a mixture of its vapour with He. Mixtures typically consisted of 0.1 to 1% of the attaching gases. Experiments were carried out with mixtures of different relative concentrations to check for consistency in preparation and calibration.

2.3. Data analysis

Suitable plasma conditions have been established such that electron loss in the reaction zone was due only to ambipolar diffusion and attachment. The appropriate continuity equation for n_e is then:

$$v_p \frac{\partial n_e}{\partial z} = D_{ae} \nabla^2 n_e - \beta n_e n_m. \quad (1)$$

This equation cannot be solved analytically to give $n_e(z)$ since D_{ae} is a function of n_-/n_e (i.e. $D_{ae} \approx 2D_+(1 + n_-/n_e)$; D_+ is the free diffusion coefficient appropriate to the positive ions present in the plasma). Oskam (1958) and Biondi (1958) have indicated how $n_e(z)$ can be obtained from equation (1) when negative-ion formation is occurring. Their approach is to solve the appropriate continuity equations for $n_+(z)$ and $n_-(z)$ and hence obtain $n_e(z)$ using the quasi-neutrality condition $n_e(z) + n_-(z) = n_+(z)$. Expressions for both $n_+(z)$ and $n_-(z)$ are readily obtained if it is assumed that (i) n_+ reduces by diffusion only, (ii) diffusive loss of n_+ occurs only via the fundamental mode and (iii) there are no volume loss processes for negative ions (i.e. no negative-ion diffusion or recombination). Under these circumstances:

$$n_e(z) = \frac{n_e(0)}{1 - \nu_D/\nu_a} \left[\exp\left(-\frac{\nu_a}{v_p} z\right) - \frac{\nu_D}{\nu_a} \exp\left(-\frac{\nu_D}{v_p} z\right) \right] \quad (2)$$

where $\nu_D = D_{ae}/\Lambda^2$, $\nu_a = n_m\beta$ and Λ is the characteristic diffusion length of the flow tube. As discussed in § 2.2, condition (i) can be satisfied in our experiment by controlling n_e and hence eliminating positive-ion-electron recombination. Condition (ii) is met by taking measurements sufficiently far downstream such that higher-order diffusion modes have decayed (Smith *et al* 1975, Adams *et al* 1975). Condition (iii) is satisfied since even for large ratios of n_-/n_e , the ambipolar space charge field in the plasma

inhibits diffusive loss of negative ions (Oskam 1958), and since it can readily be shown from our previous detailed studies of positive-ion-negative-ion recombination that at small n_+ and n_- ionic recombination loss is negligible. As can be seen from equation (2), the simplest situation from the data analysis viewpoint would be to obtain data under conditions such that $\nu_D \ll \nu_a$ (whence equation (2) reduces to $n_e(z) = n_e(0) \exp(-\nu_a z / v_p)$). In practice this could not usually be achieved (especially at 445 and 590 K) and so the data were analysed according to equation (2) by curve fitting using measured values for the parameters ν_D , n_m and v_p . ν_D was determined in the upstream part of the afterglow or in the absence of the attaching gas (see figures 1 and 2). Equation (2) predicts that the $\ln n_e$ versus z curve (see figure 2) will have an increasing slope with increasing z (that is, as n_-/n_e increases) becoming very steep for $n_-/n_e \gg 1$ when the ambipolar field collapses allowing rapid free diffusion of the remaining electrons to occur (this transition to free diffusion is not described by equation (2)). Thus a rapid transition occurs from an electron-dominated plasma to a negative-ion-dominated plasma devoid of electrons (see figure 1(b)). When this transition can be initiated at sufficiently high n_+ , n_- , then positive-ion-negative-ion recombination can be studied (Smith and Church 1976).

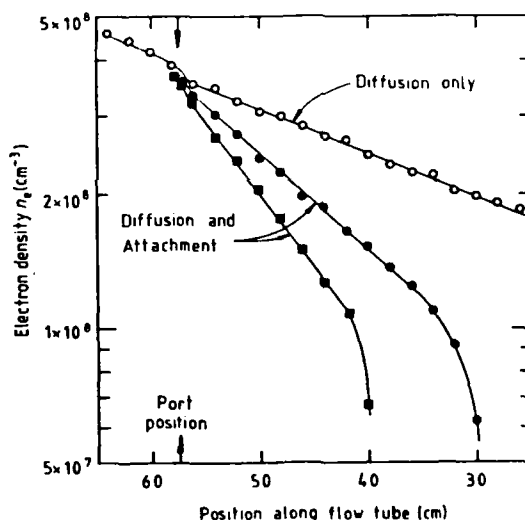


Figure 2. Electron density (n_e) profiles obtained at a helium pressure of 0.6 Torr and a temperature of 205 K. $\circ$, no electron attaching gas is present; n_e decreases due to ambipolar diffusion only. In the presence of CCl_3F electron attachment increases the rate of loss of n_e : $\bullet$, $n(\text{CCl}_3\text{F}) = 9 \times 10^8 \text{ cm}^{-3}$; $\blacksquare$, $n(\text{CCl}_3\text{F}) = 1.6 \times 10^9 \text{ cm}^{-3}$. The transition to an ion-ion plasma is evident at positions of 30 and 40 cm respectively.

3. Results and discussion

3.1. General comments

The summarised values of β obtained from this study are given in table 1 together with some previous values of β determined at 300 K using other techniques. Note that only upper limit values are given for the three slowest reactions at 200 K, these

Table 1. Summary of the electron attachment coefficients, β , obtained in the present study at 205, 300, 455 and 590 K. The total estimated error is $\pm 15\%$ at 205 and 300 K and $\pm 20\%$ at 455 and 590 K. Some values of β obtained at 300 K by other workers using the techniques indicated are also listed.

Electron attachment coefficients β ($\text{cm}^3 \text{s}^{-1}$)						
Molecule	Present results					Previous results, obtained at 300 K using the techniques indicated below
	205 K	300 K	455 K	590 K		
CCl_4	4.1	3.9	3.7	3.5	$\times 10^{-7}$	4.1 ^a , 4.1 ^b , 4.0 ^c , 3.55 ^d , 2.9 ^e , 2.9 ^f , 1.5 ^g , (4.2, 1.6, 4.4, 1.3) ^h
CCl_3F	2.2	2.6	3.6	3.3	$\times 10^{-7}$	1.0 ⁱ , 1.3 ^j , 1.2 ^k , 1.0 ^l , 2.43 ^l , 2.37 ^m
CCl_2F_2	< 1	3.2	16	53	$\times 10^{-9}$	0.7 ⁱ , 5.9 ⁿ , 1.7 ^l , 1.36 ^o , 1.2 ^h , ~ 1 ^p , 0.6 ^q , 0.4 ^r
CHCl_3	< 1	4.4	17	36	$\times 10^{-9}$	(2.6, 2.2) ⁱ , (2.2-2.6) ^h , 4.9 ^s , 3.8 ^t , (3.8, 2.66, 2.3, 2.0) ^h
Cl_2	< 1	2.0	3.3	4.8	$\times 10^{-9}$	0.31 ^v , 1.2 ^l , 3.7 ^l , 0.28 ^z
SF_6	3.1	3.1	4.5	4.0	$\times 10^{-7}$	(3.9, 2.8, 0.54) ^h , 2.6 ^u , 3.1 ^u , (2.7, 2.8) ^u , 2.21 ^w , 2.0 ^x , 2.21 ^x , 2.28 ^u

^a Mothes and Schindler (1971); ECR.

^b Warman and Sauer (1971); microwave.

^c Warman and Sauer (1970); microwave.

^d Davis *et al* (1973); drift-dwell-drift.

^e Blaunstein and Christophorou (1968); swarm.

^f Bouby *et al* (1965); swarm.

^g Lee (1963); swarm.

^h Ayala *et al* (1981b); pulse sampling.

ⁱ Schumacher *et al* (1978); ECR.

^j Wentworth *et al* (1969); pulse sampling.

^k Christophorou and Stockdale (1968); swarm.

^l McCorkle *et al* (1982); swarm.

^m Crompton *et al* (1982) and Crompton and Haddad (1983); Cavalleri technique.

ⁿ Chen and Chantry (1972); beam.

^o Bansal and Fessenden (1973); microwave.

^p Christophorou *et al* (1974); swarm.

^q Buchel'nikova (1959); total ion current.

^r Schultes *et al* (1975); ECR.

^s Christodoulides *et al* (1975); ECR.

^t Sides *et al* (1976); flowing afterglow at 350 K.

^u Mahan and Young (1966); stationary afterglow/microwave.

^v Christophorou *et al* (1971); swarm.

^w Fehsenfeld (1970); flowing afterglow.

^x Davis and Nelson (1970); swarm.

^y Fessenden and Bansal (1970); microwave.

^z Ayala *et al* (1981a); pulse sampling.

being close to the rate coefficients for the ion-molecule reactions of the attaching gases, m , with Ar^+ (the dominant positive ion in the plasma prior to the introduction of the attaching gas). The reason for adopting these limiting values is clear from the discussions given in § 2.2. The rate coefficients for the $\text{Ar}^+ + m$ reactions were accurately determined at 297 K using our selected-ion flow tube (SIFT) apparatus which has been described in detail elsewhere (Smith and Adams 1979). These rate coefficients are listed in table 2 which also includes rate coefficients for several other gases which were originally included in this attachment study but for which the β values were found to be too small to be measured by the present technique. The rate coefficients for all these $\text{Ar}^+ + m$ reactions are essentially equal to their respective ion-molecule collisional limiting values ($\sim 10^{-9} \text{ cm}^3 \text{s}^{-1}$; Su and Bowers 1973), and so they are expected to be sensibly independent of temperature (Ferguson 1972, Adams and Smith 1983).

Sources of error in the determination of β by the FALP technique are as follows. Only relative values of n_e are required for these experiments and these can be determined quite accurately ($\sim 2\%$). (Absolute values of n_e can be determined to about 10%, most of this error being due to uncertainty in the surface area of the

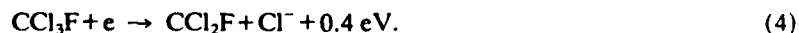
Table 2. Rate coefficients measured at room temperature (297 K) in a SIFT apparatus for the reactions of Ar^+ with the molecules indicated. Also given are the major product ions in order of their importance in the product spectrum.

Reactant molecule	Major product ions	Rate coefficient ($\text{cm}^3 \text{s}^{-1}$)
CCl_4	CCl_3^+ , CCl_2^+	8.1×10^{-10}
CCl_3F	CCl_2F^+ , CCl_3^+	8.7×10^{-10}
CCl_2F_2	CClF_2^+ , CCl_2F^+	1.1×10^{-9}
CClF_3	CF_3^+ , CClF_2^+	8.7×10^{-10}
CF_4	CF_3^+	6.4×10^{-10}
CHCl_3	CCl^+ , CHCl^+	1.4×10^{-9}
CH_2Cl_2	CH_2Cl^+	1.7×10^{-9}
CH_3Cl	CH_3^+ , CH_2Cl^+	2.0×10^{-9}
Cl_2	Cl^+ (80%), Cl_2^+ (20%)	5.6×10^{-10}
SF_6	SF_5^+	9.6×10^{-10}
NF_3	NF_2^+	9.5×10^{-10}

Langmuir probe). The plasma flow velocity, v_p , and the attaching gas number density are both uncertain by about 5%. The temperature in the reaction zone is also subject to a small uncertainty (a maximum of 2% at all temperatures). The largest single source of error relates to the fitting of the n_e versus z curves, examples of which are given in figure 2, including one curve for the pure diffusion case from which ν_D is obtained, and two curves relating to different values of n_m from which the ν_a values and thus the β values are derived. The total estimated error in the β values is $\pm 15\%$ at 205 and 300 K and somewhat larger ($\pm 20\%$) at 455 and 590 K due to the greater importance of diffusive loss relative to attachment loss.

3.2. Comments on the individual reactions

3.2.1. CCl_4 and CCl_3F . Dissociative attachment is so fast that only very small number densities of the reactant gases (n_m) were needed in the afterglow. Indeed, the required n_m were so small that positive-ion reactions did not occur to any extent. This therefore ensured that molecular positive ions were not produced and thus electronic and ionic recombination did not affect the n_e loss rate. In both reactions, only Cl^- ions were observed as products:



The energies released in these reactions and the other reactions discussed in this paper are approximate and are derived from data taken from various papers (Wentworth *et al* 1969, Fehsenfeld 1970, Schultes *et al* 1975, Dispert and Lacmann 1978, Schumacher *et al* 1978). Production of F^- in reaction (4) is about 2 eV endoergic and consequently none was observed in these thermal energy experiments. We speculate that sequential reactions of this kind:



could be occurring but we could not verify this because the product ion in each case

is Cl^- . Although the second reaction stage of (5) can be shown to be exoergic this in itself is no guarantee of an appreciable β value for the reaction.

Table 1 indicates that our $\beta(\text{CCl}_4)$ and $\beta(\text{CCl}_3\text{F})$ values at 300 K are in good agreement with recent values obtained by other workers. A small decrease of $\beta(\text{CCl}_4)$ with temperature has been observed previously (Warman and Sauer 1971) and a slow decrease in $\beta(\text{CCl}_4)$ with increasing temperature is also discernible in the present data. Conversely, $\beta(\text{CCl}_3\text{F})$ slowly but definitely increases from a value about half that for $\beta(\text{CCl}_4)$ at 205 K to a maximum value which, within error, is equal to the value for $\beta(\text{CCl}_4)$ at 455 K. This is consistent with a small activation energy barrier, E_a , in the CCl_3F reaction as indicated by the previous data of Wentworth *et al* (1969). An estimate of the magnitude of $E_a(\text{CCl}_3\text{F})$ can be obtained from the slope of an Arrhenius plot giving $E_a(\text{CCl}_3\text{F}) \approx 0.02 \text{ eV}$ ($\approx 2 \text{ kJ mol}^{-1}$). The nature of activation energy barriers in these attachment reactions has been discussed in several papers (Wentworth *et al* 1967, 1969, Christodoulides *et al* 1975). No activation energy barrier exists in the CCl_4 reaction. The very large value for $\beta(\text{CCl}_4)$ of $3.9 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ at 300 K is close to β_{max} , the theoretical maximum for electron attachment where $\beta_{\text{max}} = 5 \times 10^{-7} (300/T)^{1/2} \text{ cm}^3 \text{ s}^{-1}$. This result is derived from the theoretical maximum cross section for the process which is formulated in terms of the electron de Broglie wavelength (Warman and Sauer 1971). At 455 K, $\beta(\text{CCl}_3\text{F})$ also has apparently reached its upper limit value and thus both it and $\beta(\text{CCl}_4)$ can only decrease at higher temperatures. A more sophisticated theoretical treatment by Klotz (1976) assumes that the interaction is dominated by the polarisation potential and the process is purely s-wave capture. This approach yields a value for $\beta(\text{CCl}_4)$ of $3.29 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ at room temperature. The weak negative temperature variation of $\beta(\text{CCl}_4)$ is presumably a reflection of the weak electron energy dependence predicted by Klotz's approach (West *et al* 1976, Foltz *et al* 1977).

3.2.2. CCl_2F_2 and CHCl_2 . These reactions are similar to each other in that appreciable activation energy barriers exist for both as is manifest by the large increase in the β values with temperature (table 1). Again Cl^- is the only observed product ion in both reactions:



At 205 K these reactions are too slow to allow an accurate determination of β . The previous values at 300 K for both $\beta(\text{CCl}_2\text{F}_2)$ and $\beta(\text{CHCl}_3)$ are quite varied (see table 1) but it is clear that the present values are somewhat larger than the majority. We have no explanation for this. From the present data, values of E_a for both reactions have been obtained from the slopes of the Arrhenius plots shown in figure 3. Thus $E_a(\text{CCl}_2\text{F}_2) \approx 0.15 \text{ eV}$ ($\approx 15 \text{ kJ mol}^{-1}$) and $E_a(\text{CHCl}_3) \approx 0.12 \text{ eV}$ ($\approx 12 \text{ kJ mol}^{-1}$) which are in good agreement in both cases with the previous values derived using different techniques. The previous values in kJ mol^{-1} are: CCl_2F_2 : 19 (electron cyclotron resonance (ECR); Schumacher *et al* 1978), 13 (electron beam; Chen and Chantry 1972), 15 (pulse sampling; Wentworth *et al* 1969); CHCl_3 : 10 (ECR; Schultes *et al* 1975), 9 (microwave; Warman and Sauer 1971), 13 (pulse sampling; Wentworth *et al* 1967). That there is good agreement between the E_a values determined using these different techniques whereas there are significant differences in the absolute values of β implies that systematic errors are involved in one or all the experiments. They

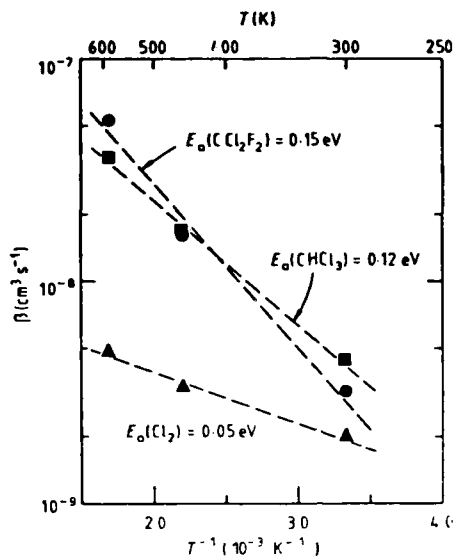


Figure 3. Arrhenius plots for the attachment reactions of electrons with CCl_2F_2 (●), CHCl_3 (■) and Cl_2 (▲). The derived activation energies, E_a , are as indicated.

could, for example, be due to the determination of the partial pressures of the attaching gases. At the highest temperature of the present experiments $\beta(\text{CCl}_2\text{F}_2)$ and $\beta(\text{CHCl}_3)$ are both approaching an order of magnitude smaller than β_{max} . Presumably β_{max} for these reactions would be approached at sufficiently high temperatures such that the E_a do not impede the reactions.

3.2.3. Cl_2 . The present $\beta(\text{Cl}_2)$ values are again represented by an Arrhenius plot in figure 3. A relatively small increase in $\beta(\text{Cl}_2)$ with temperature is indicated leading to a derived activation energy $E_a(\text{Cl}_2) \approx 0.05 \text{ eV}$ ($\approx 5 \text{ kJ mol}^{-1}$). Again it is perhaps significant that this $E_a(\text{Cl}_2)$ is in good agreement with the ECR value of Christodoulides *et al* (1975) (also 5 kJ mol^{-1}) but the magnitudes of the corresponding ECR values of $\beta(\text{Cl}_2)$ are smaller by about a factor of seven. However other ECR data of Schultes *et al* (1975) from the same laboratory indicate a $\beta(\text{Cl}_2)$ at 300 K only a factor of two smaller than the present value. Flowing-afterglow data due to Sides *et al* (1976) indicate that $\beta(\text{Cl}_2) = (3.7 \pm 1.7) \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ at 350 K which is in closer agreement with the present value.

A discussion of the mechanism of this reaction is given by Christodoulides *et al* (1975) where it is concluded that the dissociative attachment reaction at thermal energies proceeds via the intermediate temporary negative ion $\text{Cl}_2^-(^2\Sigma_u^+)$ thus:



Kurepa *et al* (1981) have considered several possible intermediate Cl_2^- states and have calculated $\beta(\text{Cl}_2)$ over a wide range of mean electron energies using their measured cross section data. Their calculated values are quite consistent with the present value obtained at 300 K. Significantly their calculations show little change of $\beta(\text{Cl}_2)$ as a function of the mean electron energy in the thermal energy regime. Thus it appears

that the observed increase of $\beta(\text{Cl}_2)$ with temperature in our experiments is mainly due to the internal excitation of Cl_2 at higher temperatures.

3.2.4. SF_6 . A good deal of effort has been devoted to the determination of the rate coefficients and cross sections for electron attachment to SF_6 . The present and some previous values for $\beta(\text{SF}_6)$ are given in table 1. Most of the previous values of $\beta(\text{SF}_6)$ lie within the range $(2-3) \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ with one set indicating values of $(2.2 \pm 0.2) \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ and another set indicating values of $(2.8 \pm 0.3) \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$. The highest reported value of $3.9 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ was obtained using the pulse sampling technique (Ayala *et al* 1981b, from reanalysis of previous data), although using the same technique under different conditions, values of 2.8 and $0.54 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ were also obtained. The present 300 K value for $\beta(\text{SF}_6)$ of $3.1 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ supports the previous higher values and agrees with the pulsed-afterglow value of Mahan and Young (1966) of $3.1 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ †. Clearly the present measurements cannot be reconciled with the set of measurements close to $2.2 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ which includes the recent value due to Crompton and Haddad (1983). This set also includes the flowing-afterglow value of Fehsenfeld (1970) who also measured $\beta(\text{SF}_6)$ between 293 and 523 K and concluded that, within the scatter of his data, no temperature variation of $\beta(\text{SF}_6)$ could be discerned. However, within the present data there is an indication of a peak in $\beta(\text{SF}_6)$ within the 400–500 K temperature range which is more evident if only the SF_6^- channel is considered (β for SF_6^- production at 590 K is about $3.0 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$, see below). This may be a manifestation of the peak in the attachment cross section for SF_6 production at very low electron energies (McCorkle *et al* 1980).

It is worthy of note that electron transfer from high Rydberg states of atoms to electron-attaching molecules has been demonstrated to be consistent with an 'essentially free' electron model (Dunning and Stebbings 1982). Rate coefficients of about $4 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ have been derived for the process of electron transfer from Xe Rydberg atoms to SF_6 (referring to mean electron energies below 20 meV) by Foltz *et al* (1977) which tends to support the higher values for $\beta(\text{SF}_6)$ derived in the present experiments. The theory of Klots (1976) yields a value for $\beta(\text{SF}_6)$ of $2.64 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ at room temperature. However, it is interesting to note that the ratio of the present experimental values of $\beta(\text{CCl}_4)$ to $\beta(\text{SF}_6)$ at 300 K is identical to the ratio of the room temperature values calculated by Klots (1976).

The SF_6 reaction is unique in the present series of reactions in that both dissociative and non-dissociative attachment occurs:



Fehsenfeld (1970) observed that the fraction of the SF_5^- product increased with increasing temperature according to an Arrhenius-type law, and deduced a value of $E_a = 0.43 \text{ eV}$ ($\approx 43 \text{ kJ mol}^{-1}$) for reaction (9b). Compatible results were obtained in the present experiments, the ratio $\text{SF}_5^-/\text{SF}_6^-$ being about 5×10^{-3} at 300 K, about 7×10^{-2} at 455 K and about 0.25 at 590 K. Again, therefore, it appears that systematic errors are involved in either the present and/or Fehsenfeld's experiments which do not lead to serious differences in derived E_a values (determined from $\text{SF}_5^-/\text{SF}_6^-$ ratios) but do result in significant differences in the absolute values of $\beta(\text{SF}_6)$.

† Fessenden and Bansal (1970) state that this value was incorrectly reported and that the correct value is $2.7 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$.

4. Conclusions

The afterglow plasma is an ideal medium in which to determine electron attachment reaction rate coefficients under truly thermal conditions and over appreciable temperature ranges. In this study we have measured attachment rate coefficients, β , for several gases. For the very fast reactions, for which the β only vary slowly with temperature and which are essentially at their theoretical maximum values (e.g. those for the CCl_4 and CCl_3F reactions), our data are in good agreement with previous data. For the slower reactions (i.e. CHCl_3 , CCl_2F_2 and Cl_2) for which the β vary exponentially with temperature, our β values appear to be somewhat larger than previous values and yet the activation energies derived from our data for these reactions are in good agreement with previous values. Systematic errors in the present or the previous experiments could explain such differences. It appears from the present data that a maximum occurs in $\beta(\text{SF}_6)$ in the 400–500 K range. Since it is known that there is a maximum in the cross section for low-energy electron attachment collisions with SF_6 , we presume that this is a contributing factor to the maximum observed in $\beta(\text{SF}_6)$. Clearly, however, the temperature dependence of the thermal rate coefficients are a convolution of the variations of the cross sections with both electron energy and with the temperature of the attaching gas (the rotational and vibrational states), folded with the Maxwellian distribution of the electron energies in the thermalised plasma. Often an increasing electron energy results in decreasing β (Christophorou *et al* 1971, McCorkle *et al* 1980) whereas an increase in internal excitation of the attaching molecules usually results in an increase in β as activation energy barriers are overcome. The latter phenomenon is manifest by the present data for $\beta(\text{CCl}_2\text{F}_2)$ and $\beta(\text{CHCl}_3)$. Thus it is clear that temperature dependence studies of β can provide fundamental information on electron/molecule interactions and interaction potentials.

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APPENDIX 4

RATE COEFFICIENTS FOR THE ATTACHMENT REACTIONS
OF ELECTRONS WITH $c\text{-C}_7\text{F}_{14}$, CH_3Br , CF_3Br , CH_2Br_2 AND CH_3I
DETERMINED BETWEEN 200 AND 600 K USING THE FALP TECHNIQUE.

J.Phys.B., 1984, In Press

Rate coefficients for the attachment reactions of
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Abstract

The rate coefficients, β , for the attachment reactions of electrons with $\text{c-C}_7\text{F}_{14}$, CH_3Br , CF_3Br , CH_2Br_2 and CH_3I have been determined under truly thermal conditions at temperatures in the range 200 to 600K using the flowing afterglow/Langmuir probe technique. The β values (in units of cm^3s^{-1}) at 300K are 6.8×10^{-8} , 6×10^{-12} , 1.6×10^{-8} , 9.3×10^{-8} , and 1.2×10^{-7} respectively. The β for all of the reactions increase with temperature and approach the theoretical maximum value of β at high temperatures. From Arrhenius plots, activation energies for the reactions have been determined to be 40, 300, 80, 50 and 25 millielectronvolts respectively. All of the reactions, except for that with $\text{c-C}_7\text{F}_{14}$ (for which electron attachment is apparently non-dissociative), proceed by exoergic dissociative attachment producing halogen atomic negative ions. The data are compared with previous data where these are available.

1. Introduction

Electron attachment reactions have been studied for decades using a variety of techniques. Much of the early work has been reviewed in the books by Christophorou (1971) and by Massey (1976), and since their publication many research papers (see later) have reported measurements of attachment rate coefficients, henceforth designated by β in units of cm^3s^{-1} .

However, few studies of the temperature variation of β have been carried out especially under thermalised conditions (i.e. for equal electron and gas temperatures). In a very recent paper (Smith et al 1984), we reported measurements of β at several temperatures within the range 200K to 600K for CCl_4 , CCl_3F , CCl_2F_2 , CHCl_3 , Cl_2 and SF_6 . These attachment reactions were studied in a thermalised flowing afterglow plasma medium using our flowing afterglow/Langmuir probe (FALP) apparatus. The values obtained at 300K were in most cases in reasonable agreement with the previous values (see Smith et al 1984). From the temperature variation of β , we were able to estimate the activation energies, E_a , for some of the attachment reactions and again these are in reasonable agreement with previously reported values.

Subsequently, we improved our Langmuir probe technique and this now allows us to determine β values some two orders-of-magnitude smaller. In this paper, we report our measurements of β at several temperatures for $\text{c-C}_7\text{F}_{14}$, CH_3Br , CF_3Br , CH_2Br_2 and CH_3I . These reactions have not previously been studied as extensively as those for species included in our initial study (except for C_7F_{14}) and consequently the β values—even at 300K—are not so well established. Both absolute values of β and the activation energies for the reactions were obtained in this study.

2. Experimental

A description of the FALP apparatus has been given in previous papers in relation to studies of ionic recombination (Smith and Church 1976, Smith and Adams 1983) and electronic recombination (Alge et al 1983). A full description of its application to the determination of attachment coefficients, including details of data analysis, is given in our recent paper (Smith et al 1984). Briefly, the attaching gas is introduced at a measured flow rate into a flowing afterglow plasma (carrier gas helium), and the change in the axial electron density gradient, $\partial n_e / \partial z$, in the plasma resulting from the loss of electrons to form negative ions is monitored using a Langmuir probe. Prior to the addition of the attaching gas, the only positive ions present in the plasma are He^+ and Ar^+ ions (the latter ions are formed when Ar is added to the plasma to remove metastable helium atoms) and then, $\partial n_e / \partial z$ is due only to ambipolar diffusion. However when the attaching gas is added, then another unwanted electron loss process is possible because ion-molecule reactions can result in the conversion of the non-recombining He^+ and Ar^+ atomic ions to the rapidly recombining molecular ions (derived from the attaching gas). The large dissociative recombination coefficients for molecular ions may therefore contribute to the observed increase in $\partial n_e / \partial z$, thus resulting in erroneous β values. To avoid this potential problem, the experiments are carried out at the smallest values of n_e possible (the recombination loss rate is proportional to $n_e n_m^+$, where n_m^+ is the density of the molecular positive ions, Smith et al 1984). For gases which have large β , this problem does not arise since only very small amounts of attaching gas are added to the plasma and thus there is an insignificant conversion of He^+ and Ar^+ ions to molecular ions.

The lower limit of β which can be measured is determined by the smallest n_e which can be accurately measured. Improvements to our Langmuir probe data acquisition technique have enabled us to measure n_e down to 10^7 cm^{-3} and thus to determine β values as small as $\sim 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ (note that in no way do these improvements in technique diminish the accuracy of our previous measurements of β for other molecules, Smith et al 1984).

The rapidity of many of the attachment reactions included in this study required the introduction of very small flow rates of the attaching gases into the afterglow plasma and this required that the gases were diluted with helium to facilitate accurate measurement of flow rates. For the gases used in this study, the mixtures typically consisted of 1-2% of the attaching gas except for the CH_3Br which had to be introduced as the 'neat' vapour because of the relatively small β for this species. Mixtures of different relative concentrations were used to check for consistency in their preparation.

Measurements were carried out at 205, 300, 452 and 585K (except for CH_3Br which could not be studied at 205K because of its very small β at this temperature). We estimate that the derived values of β are accurate to $\pm 15\%$ at 205 and 300K and $\pm 20\%$ at 452K and 585K (for details see our previous paper, Smith et al 1984).

3. Results and Discussion

3.1 General Comments.

The values of β obtained for $\text{c-C}_7\text{F}_{14}$, CH_3Br , CF_3Br , CH_2Br_2 and CH_3I in this study are given in Table 1 together with some values previously obtained at 300K by other workers. The values of β cover the wide range from $1.8 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ to $6 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ and a variation of β with temperature was apparent for all gases studied. Hence the data are also presented in the form of Arrhenius plots in figure 1 from which activation energies E_a for the attachment reactions can be obtained. These E_a

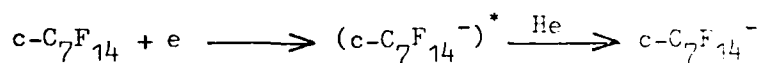
are also given in Table 1 together with previously obtained values. Also included in figure 1 is $\beta_{\max}$ ($\approx 5 \times 10^{-7} (300/T)^{\frac{1}{2}} \text{ cm}^3 \text{ s}^{-1}$), the theoretical maximum value of β which is derived from the theoretical maximum cross section for the attachment process as formulated in terms of the electron de Broglie wavelength (Warman and Sauer 1971). Notice that all of the measured β are significantly smaller than $\beta_{\max}$ over the available temperature range and thus none of the gases used in this study are such efficient electron scavengers at thermal energies as SF_6 and CCl_4 (Smith et al 1984). A more sophisticated theoretical estimate for $\beta_{\max}$ has been given by Klots (1976) which takes into account the polarizability of the attaching molecule. Values of $\beta_{\max}$ so derived are somewhat smaller than those indicated by the simple relationship for $\beta_{\max}$ given above.

Below, we discuss briefly the β and E_a values obtained for each molecular species and compare them with the limited amount of previous data. That the E_a for these reactions are appreciable implies a sensitivity of β on temperature and as such the measured β can be used as an indicator of the experimental conditions (ie. the electron (T_e) and gas (T_g) temperatures, mean electron energy, energy distribution etc.).

Whilst the present FALP values of β were obtained under truly thermalised conditions, this is not the case for many of the other previous values given in Table 1 (which ostensibly relate to 300K), and we suggest that this in some cases, explains the rather large differences in the β values obtained for some reactions. The reasonably good agreement between the E_a determined using the pulse technique of Wentworth et al (1969) and the FALP technique (see Table 1) is a clear indication of the thermalised conditions in both experiments.

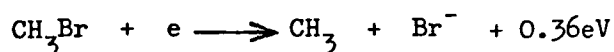
3.2 Comments on the Individual Reactions

3.2.1. $c\text{-C}_7\text{F}_{14}$. This is the cyclic compound perfluoromethylcyclohexane. We deal with this species first since it has been studied more extensively than the others in the present group (see Table 1). It is also unique in the group in that the reaction proceeds via a three-body process in which, first the excited parent negative ion is formed, which then can either autoionize or be stabilised in collision with a helium bath gas atom (Mahan and Young 1966)



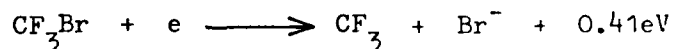
However, we are not able to definitely confirm that $C_7F_{14}^-$ was the only product ion since the large mass of this negative ion ($m/e = 310$ amu) was above the range accessible with our quadrupole mass filter. However we are able to state that no negative ion of $m/e < 300$ amu was a reaction product. The β at 300K for the reaction is several times smaller than β_{max} , increasing towards β_{max} at the higher temperatures. Since the mean time for collisions of $(C_7F_{14})^*$ with helium atoms ($\sim 10^{-7}$ sec) is much shorter than the autoionization lifetime ($\sim 10^{-3}$ sec; Naff et al 1968), then we feel justified in interpreting the increase in β with temperature in terms of an activation energy for the initial electron attachment step. Thus from the linear Arrhenius plot in figure 1, $E_a = 40 \text{ meV}$ ($\equiv 4 \text{ kJ mole}^{-1}$). This is appreciably smaller than the value previously determined by Chen et al (1968), although it is not clear from their paper if the 73 meV given in Table 1 actually refers to an activation energy in the normal (Arrhenius) sense. There is evidence from previous studies for an increasing β with increasing T_e (Davis et al 1973) and for an increasing cross section, σ , for electron attachment with increasing electron energy, E_e , reaching a peak near to $E_e \approx 0.15 \text{ eV}$ (Mothes et al 1972). The earliest values of β at 300K (see Table 1) are grouped near to $8 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ and more recent values are nearer to $5 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$. The present value at 300K is (tantalizingly!) between these at $6.8 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$.

3.2.2. CH_3Br . This reaction, in common with the remaining reactions in the group, proceeds via exoergic dissociative electron attachment:



Br^- was the only observed product ion at each temperature. A remarkable increase in β occurs between 300K and 585K indicating a large E_a for the reaction. Our β at 300K is subject to rather a large uncertainty ($\pm 50\%$) since it is close to threshold for our measurements. This inevitably places an appreciable error on the derived E_a (from figure 1) but nevertheless it is in reasonable agreement with that obtained by Wentworth et al (1969) (see Table 1). Clearly, derived values of β for this reaction will be very sensitively dependent on departures from thermal equilibrium. Significantly, relatively large values were obtained from the non-thermal experiments ($> 10^{-9} \text{cm}^3 \text{s}^{-1}$, see Table 1) which were thought to relate to 300K. However, the data obtained from thermal experiments, including the present value, indicate a 300K value of $\sim 5 \times 10^{-12} \text{cm}^3 \text{s}^{-1}$ i.e. some five orders-of-magnitude smaller than β_{max} . There is experimental evidence for a peak in σ at a small E_e (~ 0.05 to 0.35eV) and a $T_g = 300\text{K}$ (Mothes et al 1972, Stockdale et al 1974). Detailed investigations of the variation of β and σ as a function of T_e , E_e and T_g are necessary to identify the critical parameters which determine the course of this interesting reaction.

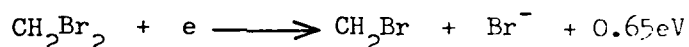
3.2.3. CF_3Br . This reaction proceeds thus:



Again Br^- is the only observed product at each temperature. This reaction also has an appreciable E_a causing β to increase by more than an order-of-magnitude for a temperature increase from 205 to 585K. There are few previous data with which to compare our results. Spence and Schulz (1973) showed that the energy integrated cross section for the reaction did increase with increasing temperature of the CF_3Br molecules.

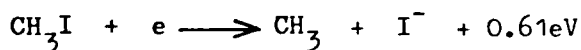
Blaunstein and Christophorou (1968) re-interpreted the early data of Lee (1963) and showed that the mean σ decreases with increasing mean E_e i.e. in the opposite sense to the change of β with temperature. They also derived a value for β at 300K which is in good agreement with the present value (see Table 1). Note the present data show that β quite rapidly approaches $\beta_{\max}$ as the temperature increases.

3.2.4. CH_2Br_2 . This reaction proceeds thus:



The reaction exhibits a small activation energy (see Table 1). The E_a derived from our data (from the three highest temperature points) is within error in agreement with that due to Wentworth et al (1966). The 205K point does not lie on the linear plot indicating that an Arrhenius plot is not appropriate over the complete temperature range. At the highest temperature, β has increased to within a factor of two of $\beta_{\max}$. Spence and Schulz (1973) showed that the energy integrated cross section for this reaction did not noticeably change with increasing temperature of the CH_2Br_2 molecules and Blaunstein and Christophorou (1968), again from a re-interpretation of Lee's data, showed that the decrease in the mean σ with increasing E_e was much less rapid than for CF_3Br which is qualitatively consistent with the relative rates of change of β with temperature for the two species. However the derived value of β for CH_2Br_2 from Lee's data, is a factor of about three smaller than the present value and thus well outside the error limits of our measurements.

3.2.5. CH_3I . This reaction also proceeds by exoergic dissociative attachment



in this case I^- being the only observed product ion over the accessible temperature range. However, in this reaction, although our data indicates

an increasing β between 200 and 452K, the value at 585K is smaller than at 452K (the relative error in β is less than the $\pm 20\%$ appropriate to each absolute value). Of course, β must begin to decrease at some temperature; the observed decrease is only mildly surprising since β at the peak is within about a factor of two of $\beta_{\max}$. The Arrhenius plot for the three lowest temperature data points indicates a small E_a which is in good agreement with that obtained by Wentworth et al (1969). The β derived by Blaunstein and Christophorou (1968) from Lee's data, ostensibly referring to 300K, is several times smaller than the present value. The cross sections for this reaction have been investigated by Spence and Schulz (1973) and by Stockdale et al (1974).

4. Conclusions

The rate coefficients, β , for each of the attachment reactions included in this study are controlled by the presence of an activation energy barrier as is manifest by the increasing β values with increasing temperature. In the case of dissociative attachment, this is generally understood to occur as a result of the internal excitation of the reactant molecules - either thermally in collisions with the helium carrier gas atoms or via electron collisional excitation - to a state which is crossed by a repulsive atomic negative ion/neutral radical potential curve (e.g. see Wentworth et al 1969). The $\text{c-C}_7\text{F}_{14}$ reaction occurs via a three-body process in which an excited parent negative ion is formed and is stabilized in a collision with a helium atom. Nevertheless, the β for this reaction also increases with temperature in a similar manner to the other (dissociative) attachment reactions.

Where other truly thermal values of β are available, these and the derived E_a values are in good agreement with the present FALP data. However discrepancies are evident between the thermal data and those

obtained using non-thermal techniques, highlighting the differences between electron temperature, molecule temperature and electron energy in influencing the rate of electron attachment. Detailed studies of specific attachment reactions are required at several fixed molecule temperatures for varying electron energies in order to better understand the detailed mechanisms of this type of reaction.

Acknowledgment

We are grateful to the United States Air Force for providing a research grant in support of this work. We are also indebted to Dr John F. Paulson for many stimulating discussions.

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Wentworth W.E. George R. and Keith H. 1969. J. Chem. Phys. 51 1791.

Table Caption

Table 1. Electron attachment coefficients, β , and activation energies, E_a , obtained in the present FALP study at 205, 300, 452 and 585K. The total estimated absolute errors in β are $\pm 15\%$ at 205 and 300K and $\pm 20\%$ at 452 and 585K (except for the very small β for CH_3Br at 300K for which it is $\pm 50\%$). The E_a values are considered to be accurate to within $\pm 20\%$. Some values of β at 300K and some E_a values obtained by other workers using the techniques indicated are also given.

Figure Caption

Figure 1. Arrhenius plots for the attachment reactions of electrons with the molecules indicated. The activation energies, E_a , derived from these plots are given in Table 1. The dashed line represents $\beta_{\text{max}} = 5 \times 10^{-7} (300/T)^{\frac{1}{2}} \text{ cm}^3 \text{ s}^{-1}$ (see text).

Table 1

Molecule	Electron attachment coefficient β ($\text{cm}^3 \text{s}^{-1}$)					Activation energy (meV)	
	205K	300K	452K	585K	Previous values at 300K	this work	previous results
$\text{c-C}_7\text{F}_{14}$	0.45	0.68	1.3	1.6	0.82^a , 0.98^b , 0.798^c , 0.52^d , 0.40^e , 0.56^f	40	73^c
CF_3Br	0.53	1.6	4.9	7.7	1.36^g	80	
CH_2Br_2	0.81	0.93	1.6	2.2	0.32^g	50	52^k
CH_3Br	-	0.06	2.3	25	33^g , 10^h , 0.07^i , 0.04^{nj} , 0.036^d	300	247^k
CH_3I	0.85	1.2	1.8	1.1	0.25^g	25	26^k

a Asundi and Craggs (1964); total ion current

b Mahan and Young (1966); microwave

c Chen et al (1968); pulse sampling

d Mothes et al (1972); ECR

e Davis et al (1973); drift-dwell-drift

f Christodoulides and Christophorou (1979); swarm

g Blaunstein and Christophorou (1968);
from analysis of data due to Lee (1963)

h Christodoulides and Christophorou (1971)
at electron energy 0.05eV; swarm

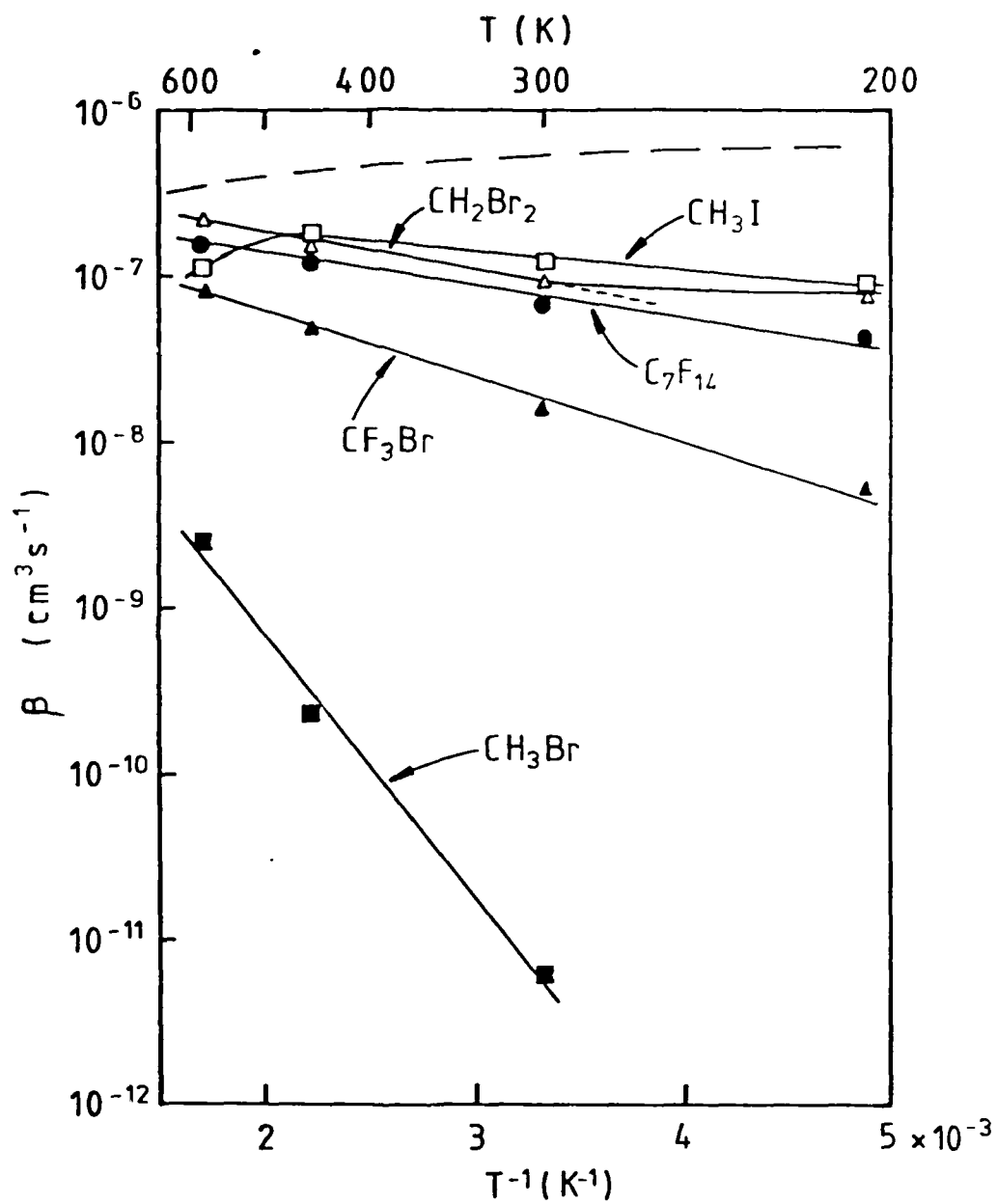
i Bansal and Fessenden (1972); microwave

j Bansal and Fessenden (1972);

from analysis of data due to Wentworth
et al (1969)

k Wentworth et al (1969); pulse sampling

Figure 1



APPENDIX 5

FURTHER STUDIES OF THE $N_2^+ + N_2 \rightarrow N_4^+$ ASSOCIATION REACTION.

Chem. Phys.Lett., 105, 317, 1984

FURTHER STUDIES OF THE $N_2^+ + N_2 \rightarrow N_4^+$ ASSOCIATION REACTION

D. SMITH, N.G. ADAMS and E. ALGE

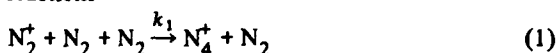
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Received 9 December 1983; in final form 3 January 1984

Data are presented which strongly suggest that stabilisation of the excited intermediate $(N_4^+)^*$ complex in the reaction (1) $N_2^+ + 2N_2$ (rate coefficient k_1) occurs via N_2 switching whereas for (2) $N_2^+ + N_2 + He$ (rate coefficient k_2) it occurs via superelastic He collisions. This explains the differing temperature variations of k_1 and k_2 previously obtained for these reactions. Drift tube data are also presented which show how k_1 varies with N_2^+/N_2 centre-of-mass energy as compared with thermal energy.

1. Introduction

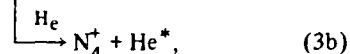
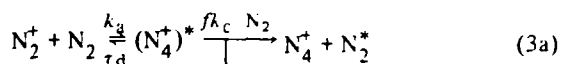
The rate coefficients k_1 and k_2 for the association reactions



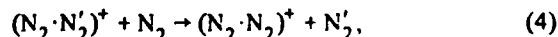
and



have been measured in several experiments and have become "test reactions" for most experiments in which three-body (ternary) association reactions are studied [1-6]. The experimental values of k_1 and k_2 have also been used as tests of theoretical models which describe association reactions [7-10]. The earliest measurements of k_1 and k_2 were made over relatively small temperature ranges and then, as is usual, the values were fitted to a power law of the form $k \propto T^{-m}$. Large variations of the exponent m were apparent between the various experiments, ranging from about 1.5 to 4 for both reactions [11-13]. However, most recent studies are in much closer accord, both in the magnitudes of k_1 and k_2 and in the respective m values for the two reactions. Thus m is indicated to be 1.7 ± 0.2 for reaction (1) and 2.3 ± 0.2 for reaction (2) over the approximate temperature range 100-500 K for both reactions [11-13]. The interesting question is why the k and m values are different for these two reactions. The reactions are envisaged to proceed thus:



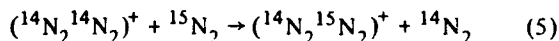
where k_a is the rate coefficient for the formation of the excited intermediate complex, $(N_4^+)^*$, τ_d is its lifetime against unimolecular decomposition, f is the collision stabilisation efficiency and k_c is the collisional rate coefficient for N_4^+/N_2 or N_4^+/He collisions as appropriate. In recent theories, m is equated to $(l/2 + \delta)$, where l is the number of rotational degrees of freedom in the separated ion/molecule reactants which combine to form $(N_4^+)^*$, and δ is included as a parameter which accounts for the temperature variation of the collisional stabilisation rate coefficient, $f k_c$, in reactions (3a) and (3b). Obviously, the binary process of $(N_4^+)^*$ formation is not directly dependent on the nature of the third body (i.e. the bath gases N_2 or He in which the reaction is occurring), and these theories predict that the rate coefficient for this stage of the reaction should vary as T^{-2} . The observed deviation from this T^{-2} dependence can therefore be attributed at least in part to the temperature variation of the collisional stabilisation step which apparently varies as $T^{+(0.3 \pm 0.2)}$ for reaction (1) and $T^{-(0.3 \pm 0.2)}$ for reaction (2). But why are these temperature dependences different? In a recent paper [13], we suggested that the stabilisation step in (3a) proceeds via switching of N_2 molecules:



whereas the stabilisation step in (3b) involves only superelastic collisions between the $(N_4^+)^*$ and He atoms. In this letter, we present experimental evidence from drift tube studies which gives some support to these suggestions.

2. Experimental

Very recently we have included a drift tube in our variable-temperature selected ion flow tube [14] (thus converting it to a selected ion flow drift tube, VT-SIFDT) and with it ion-molecule reactions can now be studied as a function of the reactant ion/reactant molecule centre-of-mass kinetic energy, KE_{cm} , at any carrier gas temperature within the range 80–600 K. The measurements described in this letter are the first to be obtained using this VT-SIFDT. Reaction (2) and the switching reaction



have been studied for several values of KE_{cm} at fixed gas temperatures. KE_{cm} is varied, as is usual in drift tubes, by varying the parameter E/N , where E is the electric field strength established in the carrier gas of number density N [15]. KE_{cm} values are determined using the well-known Wannier expression [16] in conjunction with the ion drift velocities (or ionic mobilities) which are routinely determined in the VT-SIFDT using conventional techniques [17,18].

Reaction (2) was studied by injecting $^{14}N_2^+$ ions into helium carrier gas at 80 K and then adding $^{14}N_2$ at a position downstream of the ion injection point in the usual manner [19]. Since k_2 decreases with increasing KE_{cm} , measurements were made at the lowest accessible carrier gas temperature to permit accurate measurements of k_2 to be made at appreciable KE_{cm} . In order to establish that this was an unsaturated three-body reaction under our experimental conditions, measurements were made as a function of pressure for selected values of KE_{cm} . The data, as exemplified by fig. 1, established that we were indeed studying truly unsaturated three-body kinetics.

Reaction (5) was studied by injecting $(^{14}N_2\ ^{14}N_2)^+$ ions into helium carrier gas at 300 K and reacting them with $^{15}N_2$. The higher carrier gas temperature was chosen for these measurements because higher values of E/N (and hence KE_{cm}) can be attained at this higher

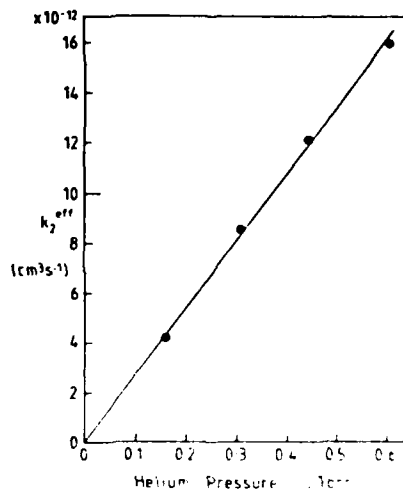


Fig. 1. Variation with helium pressure of the effective two-body rate coefficient, k_2^{eff} , for the reaction $N_2^+ + N_2 + He$ at a KE_{cm} of 15 meV and a gas temperature of 80 K. This reaction clearly exhibits unsaturated three-body kinetics under these conditions.

temperature [17]. Measurements were made at $E/N = 0$ and at three finite values of E/N .

3. Results and discussion

The rate coefficients, k_5 , obtained for reaction (5) are given in table 1 where it can be seen that for zero E/N no measurable reaction is observed ($k_5 < 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ at 300 K). However, as E/N is increased, k_5 becomes quite large, reaching about 30% of the collisional limiting value $k_c (= 6.7 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1})$ at the highest E/N achievable in the experiment. Significantly, at the highest value of E/N and in the absence of $^{15}N_2$ reactant gas, partial collisional break up of the $^{14}N_4^+$ in the drift field becomes apparent. Clearly, therefore, collisional excitation of the N_4^+ must be occurring in the drift tube. We believe it is this which facilitates the exchange of the N_2 molecules in the $(N_4^+)^*/N_2$ collisions thus promoting reaction (5) at high E/N . The data of table 1 suggest that further internal excitation of the N_4^+ will take k_5 to its upper-limit value which simple statistics of $^{14}N_2/^{15}N_2$ exchange in reaction (5) indicate to be $\frac{2}{3}k_c$ (i.e. $4.4 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$). It seems certain, therefore, that N_2 exchange will be facile for the

Table 1

Rate coefficients for the reaction $^{14}\text{N}_4^+ + ^{15}\text{N}_2 \rightarrow ^{14}\text{N}_2 ^{15}\text{N}_2^+ + ^{14}\text{N}_2$ for the values of E/N indicated, as determined in the VT-SIFT at a helium carrier gas pressure of 0.4 Torr and a temperature of 300 K. The KE_{cm} are the centre-of-mass kinetic energies of the N_4^+/N_2 interaction. The units of E/N are townsend (Td) and $1 \text{ Td} = 10^{-17} \text{ V cm}^2$. The collisional rate coefficient for this reaction is $6.7 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$

E/N (Td)	KE_{cm} (eV)	Rate coefficient ($\text{cm}^3 \text{ s}^{-1}$)
0	0.039	$< 10^{-12}$
36.1	0.21	4.0×10^{-11}
48.5	0.31	9.7×10^{-11}
67.9	0.46	1.8×10^{-10}

highly excited $(\text{N}_4^+)^*$ complexes formed in the association reaction (1) and that these complexes are indeed stabilised with near unit efficiency ($f \approx 1$) by this process.

Previous measurements have clearly shown that the magnitude of k_1 is several times greater than k_2 [13]

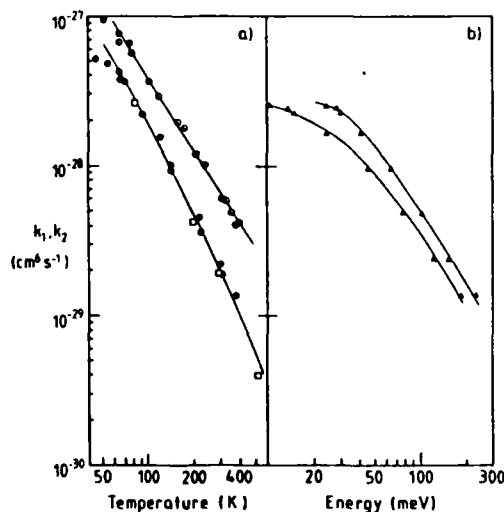


Fig. 2. Log-log plots of (a) k_1 (○) and k_2 (●, ▲) as a function of temperature as obtained by ○ Böhlinger and Arnold [11], ● Adams and Smith [6] and ● Böhlinger et al. [13]. Detailed discussion of these temperature data are given by Böhlinger et al. [13]. (b) k_2 as a function of KE_{cm} (▲) and total energy, (▲) at a gas temperature of 80 K. The absolute error on each data point is estimated to be $\pm 25\%$ except at the highest E/N where the error is $\pm 30\%$. Relative errors are $\pm 10\%$.

(these previous data are reproduced in fig. 2 to facilitate the present discussion), indicating that the efficiency of stabilisation of $(\text{N}_4^+)^*$ is several times smaller for superelastic He collisions than for the switching collisions with N_2 . The latter very efficient process is also expected to be sensibly independent of temperature in common with most rapid ion-molecule reactions [20–22]. This would mean that $\delta \approx 0$ for reaction (1) independent of temperature and therefore that k_1 should vary as T^{-2} (i.e. as $T^{-1/2}$). That the measured variation is $T^{-(1.7 \pm 0.2)}$ (i.e. perhaps as slow as $T^{-1.5}$) might be indicating that the rotational modes in the reactants are not fully active in prolonging the lifetimes, τ_d , of the $(\text{N}_4^+)^*$ excited complexes.

A further implication of this analysis is that the efficiency of the helium atom stabilisation process is definitely temperature dependent and that the δ value appropriate to the temperature range studied lies between 0.2 and 1.0 (obtained by considering the limits of m for reactions (1) and (2)). In fact, it can be argued that for reaction (2), δ itself should be temperature dependent, since at low temperatures as f increases towards its maximum value of 1, and thus becomes independent of temperature, then δ will reduce to zero (at 80 K, $f \approx 0.7$ and at 500 K, $f \approx 0.2$ as derived by comparison of k_1 with k_2 at 80 and 500 K taking into account the collisional rate coefficients for the $\text{N}_4^+ + \text{N}_2$ and $\text{N}_4^+ + \text{He}$ collisions; see fig. 2a). However, if δ increases with temperature, T , then the plot of $\ln k_2$ against $\ln T$ will not be linear. Some curvature of this plot (fig. 2a) is discernible, although previously this has been ignored in order to derive a mean value of m [13]. Significantly, for reaction (1) the $\ln k_1$ against $\ln T$ plot is more linear, suggesting a constant value of m over the available temperature range and is another indicator that $\delta \approx 0$ and $f \approx 1$ over the whole temperature range, as suggested above for this reaction.

Further information can be obtained about reaction (2) from the drift tube data of k_2 as a function of KE_{cm} which is presented in fig. 2b. Clearly an increasing KE_{cm} results in a reducing k_2 as expected if the addition of energy to the reactants in any form is equivalent to an increase in the "effective temperature", T_{eff} , of the reactants. When determining T_{eff} it is more appropriate to consider the total energy in the interaction, E_T , which includes all available sources of energy. The E_T is composed of KE_{cm} for the N_2^+/N_2 collision together with the rotational energies of the N_2^+ ion and

the neutral N_2 molecule. The rotational energy of the N_2 is that appropriate to a temperature of 80 K and that for N_2^+ is assumed to be the equilibrium rotational energy attained by the N_2^+ in collisions with the helium buffer gas (obtained from KE_{cm} for the N_2^+/He collisions [23]). Vibrational excitation of the N_2^+ is considered to be negligible in the N_2^+/He collisions at the KE_{cm} accessible in these experiments. k_2 is plotted as a function of E_T in fig. 2b in order to facilitate comparison with the k_2 versus T curve shown in fig. 2a. In order to more readily compare these curves, E_T has been equated to $\frac{7}{2}kT_{eff}$, by assuming that the energy E_T is distributed amongst the kinetic and rotational modes discussed above. Another "effective temperature", T_{eff}' can be obtained for each E_T by using the measured k_2 versus T plot to relate E_T to temperature. When this is done it is apparent that T_{eff}' is appreciably larger than T_{eff}'' at all values of E_T (e.g. $T_{eff}' \approx 2 T_{eff}''$ at the highest E_T). This implies that E_T , which is largely KE_{cm} at the higher E_T , is not as effectively utilized in reducing τ_d (and hence k_2) as is truly thermal energy. It is also possible that the f factor does not decrease as rapidly with E_T as it does with T . However, detailed modeling of the k_2 against E_T curve will not be warranted until a proper description of the interaction can be formulated and until it has been established that all sources of available energy have been properly included in E_T . Certainly this curve must contain information about τ_d and f .

The separate variation of τ_d with E_T can presumably be obtained by studying the variation of k_1 with KE_{cm} (since it is expected for this N_2 stabilized reaction that $f \approx 1$ and hence it is independent of E_T). Some such data are available from previous drift tube studies [11, 24]; however they are not sufficiently accurate for any positive conclusions to be drawn. Unfortunately, sufficiently accurate measurements of k_1 cannot be made in the VT-SIFDT when the buffer gas is also the reactant gas, as is the case in this reaction. It would also be profitable to determine k_1 and k_2 as a function of E_T at different T in order to more fully establish the relative importance of internal and kinetic energy on the rate coefficients for these three-body association reactions.

4. Summary

The data presented here strongly support our ear-

lier suggestion that in the association reactions (1) and (2), stabilisation of the $(N_4^+)^*$ excited intermediate complexes is via rapid temperature-independent N_2 switching in reaction (1) (i.e. $f \approx 1$ and $\delta \approx 0$) whereas for reaction (2) stabilisation occurs via He superelastic collisions which become increasingly efficient with decreasing temperature (i.e. f increases as T decreases). Thus for reaction (2), δ is a function of temperature and this we believe is responsible for the small, but significant, departure from power law behaviour in the $\ln k_2$ against $\ln T$ plot.

The dependence of k_2 on E_T suggests either that E_T (mostly KE_{cm}) is less effective than truly thermal temperature in reducing k_2 or that the stabilisation efficiency, f , varies more slowly with KE_{cm} than with temperature. A separate study of the dependence of k_1 on E_T in which f is invariant (since $f \approx 1$) is required to determine the relative importance of these two processes. A proper theoretical study of the rate coefficients for association reactions which can be determined in drift tube experiments is urgently needed.

Acknowledgement

We are grateful to Mr. P. Beasley for his excellent contribution in constructing the drift tube.

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APPENDIX 6

THE HEAT OF FORMATION OF $C_3H_2^+$

Int.J.Mass Spectrom Ion Processes., 1984, In Press

The Heat of Formation of $C_3H_2^+$

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Abstract

Reaction rate coefficients have been measured in a variable temperature selected ion flow drift tube (SIFDT) for the reaction $C_3H^+ + H_2 \rightarrow C_3H_2^+ + H$, which is found to be 1 kcalmol⁻¹ endothermic. This implies a substantially lower value for $\Delta H_f(C_3H_2^+)$ (329 ± 5 kcalmol⁻¹) than has previously been reported (~ 357 kcalmol⁻¹). The $C_3H_2^+$ ion reacts with H_2 at elevated ion kinetic energy to produce $C_3H_3^+$ with ~ 4 kcalmol⁻¹ endothermicity. This implies that the $C_3H_2^+$ ion reacts to form the linear propargyl ion, $CH_2C \equiv CH^+$, $\Delta H_f = 281$ kcalmol⁻¹, and not the more stable cyclic $C_3H_3^+$ ion, $\Delta H_f = 257$ kcalmol⁻¹. This would seem to be strong evidence that the $C_3H_2^+$ ion is linear and not cyclic. The reaction $C_2H_2^+ + H_2 \rightarrow C_2H_3^+ + H$ is found to be 1.6 kcalmol⁻¹ endothermic which implies $\Delta H_f(C_2H_3^+) = 267 \pm 1$ kcalmol⁻¹, in excellent agreement with more recent determinations that are slightly lower than older values.

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Introduction

Recently a series of hydrocarbon ion reactions with H_2 were studied in connection with problems of molecular synthesis in interstellar molecular clouds¹. These data provided some interesting new thermochemical information and they have therefore been extended with that specific objective in mind. The observation of fast ion-molecule reactions is a clear indication that the reaction is exothermic. Slower, but observable, reactions can be at most only slightly endothermic. In the case of slightly endothermic reactions, the temperature dependence of the reaction rate coefficient can be used to determine the endothermicity rather precisely. This of course is a fortuitous circumstance from a thermochemical point of view. In the present case, the binary reaction of C_3H^+ with H_2 was observed to produce $C_3H_2^+$. This reaction is $\sim 25 \text{ kcal mol}^{-1}$ endothermic using literature values of $\Delta H_f(C_3H^+)$ and $\Delta H_f(C_3H_2^+)$, implying a large error in one of these values. The present investigation was carried out to address this problem. Additionally, the less controversial reaction $C_2H_2^+ + H_2 \rightarrow C_2H_3^+ + H$ was studied and a value for $\Delta H_f(C_2H_3^+)$ was derived.

Experimental

The Birmingham selected ion flow tube (SIFT) experiment has been extensively used to study ion-molecule reactions and has been described in the literature^{2,3}. Recently, a drift tube has been included in this SIFT thus converting it to a variable temperature selected ion flow drift tube (VT-SIFDT). The $C_2H_2^+$ ions were generated in an electron impact ion source containing C_2H_4 and injected into helium buffer gas. The C_3H^+ ions were generated in this source from propyne (methyl acetylene). The reactant neutral H_2 was added to

the helium carrier gas downstream from the reactant ion entry port, and the primary ion count rates were measured as a function of H₂ flow rate by a downstream mass spectrometer detection system. Rate coefficients were obtained in the usual manner.

Results

The reaction



was in competition with a fast three-body association reaction,



At 80K, with no applied electric field, E, on the drift tube (i.e. at zero E/N, N = helium number density), only the three-body reaction was detected. When an electric field was applied, the binary reaction (1) also occurred. At 300K, with the He pressure $\approx$ 0.4 Torr, the binary channel represented about 14% of the reaction, k_2 was $1.3 \times 10^{-27} \text{ cm}^6 \text{ s}^{-1}$. At 530K, the binary channel accounted for 80% of the reaction. This data leads to an endothermicity of 1.6 kcal mol⁻¹. Since $\Delta H_f(\text{C}_2\text{H}_2^+)$ is very well known⁴ to be 317 kcal mol⁻¹, from ionization potential and spectroscopic measurements (Rydberg series limits) for acetylene, this leads to a value of 267 ± 1 kcal mol⁻¹ for $\Delta H_f(\text{C}_2\text{H}_3^+)$. This is slightly lower than the tabulated value 269 kcal mol⁻¹ and in excellent agreement with a recent value of 266 kcal mol⁻¹ of Bohme, et al.⁵.

The reaction



also competed with a fast three-body association,



At 80K, only reaction (4) is observed at zero E/N, but reaction (3) appears when a weak electric field is applied. At 300K reaction (3) is a minor channel and $k_4 = 2.6 \times 10^{-27} \text{ cm}^6 \text{ s}^{-1}$. At 550K, the binary channel accounts for over half the reaction. From these data an endothermicity of $\sim 1 \text{ kcal mol}^{-1}$ is inferred. This in turn implies that $\Delta H_f(\text{C}_3\text{H}^+) - \Delta H_f(\text{C}_3\text{H}_2^+) = \Delta H_f(\text{H}) - 1 = 51 \text{ kcal mol}^{-1}$. However, the literature values for these heats of formation, listed in Table I, give an average value $\Delta H_f(\text{C}_3\text{H}^+) - \Delta H_f(\text{C}_3\text{H}_2^+)$ of 29 kcal mol^{-1} with values ranging from 24 kcal mol^{-1} for allene to 30 kcal mol^{-1} for cyclopropene sources of both ions (from the NBS group⁶). This of course is a very large discrepancy although A.C. Parr (private communication) has informed us that the value of $\Delta H_f(\text{C}_3\text{H}_2^+)$ could be lower than the values reported in the NBS studies. Because of this and since the value $\Delta H_f(\text{C}_3\text{H}^+)$ is supported by theoretical calculations⁷ as well as a recent C_3 proton affinity determination⁸, we assume the error lies in the value of $\Delta H_f(\text{C}_3\text{H}_2^+)$ and accordingly deduce that the value of $\Delta H_f(\text{C}_3\text{H}_2^+) = 332 \text{ kcal mol}^{-1}$, with the same uncertainty as applies to $\Delta H_f(\text{C}_3\text{H}^+)$ which seems to be about 5 kcal mol^{-1} . This uncertainty is large compared to the uncertainty in the endothermicity of reaction (3).

The stable form of C_3H^+ is the linear $\text{HC}\equiv\text{C}-\text{C}^+$ ion which lies $52.7 \text{ kcal mol}^{-1}$ below an excited non-linear form⁷. In view of the fact that the results of the present studies of reactions (3) and (4) are the same for C_3H^+ ions produced by electron impact on propyne and via the reaction of C_3^+ with H_2 , then it seems unlikely that the ions generated in the electron impact ion source are excited. The C_3H^+ ions were also produced from propyne in the NBS measurements⁶ and it seems equally unlikely that these ions were excited.

In addition to rationalizing the occurrence of reaction (3), the lower value for $\Delta H_f(C_3H_2^+)$ also rationalizes another observation by Herbst et al.¹, namely the failure of the reaction



to occur, $k_5 < 5 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$ at 298K, in spite of the large exothermicity of the reaction. This is an exceptional circumstance, since a large number of exothermic ion reactions with H_2 occur very rapidly by H atom abstraction, essentially a reaction per collision. This includes⁹ the ions Ar^+ , Ar_2^+ , CH^+ , CH_2^+ , CHN^+ , CO^+ , CO_2^+ , C_2^+ , C_2H^+ , NH^+ , O^+ , OH^+ , H_2O^+ , N^+ , and N_2^+ . Exceptions to fast exothermic H atom abstraction from H_2 are rare if any. Presumably the problem here is essentially a steric one, the most stable form of $C_3H_3^+$ is the cyclic ring structure. Apparently the $C_3H_2^+$ ion does not abstract an H atom from H_2 and close the ring, even though this is exothermic. This does not seem too surprising if $C_3H_2^+$ is linear. However a linear form of $C_3H_3^+$ lies 24 kcal mol⁻¹ above the stable ring form⁴ (A theoretical value¹⁰ for the energy difference between the ring and linear configurations of $C_3H_3^+$ is 34 kcal mol⁻¹). If $\Delta H_f(C_3H_2^+)$ were as high as 357 kcal mol⁻¹, reaction (5) to produce linear $C_3H_3^+$ would be exothermic by 24 kcal mol⁻¹ and so it would be difficult to explain the lack of reactivity since the geometrical constraint would not apply. With the present value $\Delta H_f(C_3H_2^+) = 332 \text{ kcal mol}^{-1}$, reaction (5) to form linear $C_3H_3^+$ is 1 kcal mol⁻¹ endothermic. Reaction (5) was also studied in the presence of a drift field. Only modest values of E/N were required to drive the reaction and an endothermicity of ~ 4 kcal mol⁻¹ was deduced. Accordingly we recommend a value of

$\Delta H_f(C_3H_2^+)$ of 329 ± 5 kcal mol⁻¹. Since the 4 kcal mol⁻¹ endothermicity of reaction (5) corresponds to the endothermicity to produce the linear propargyl ion, $CH_2C \equiv CH^+$ ($\Delta H_f = 281$ kcal mol⁻¹) this strongly implies that a linear $C_3H_2^+$ ion reacts with H_2 to form a linear $C_3H_3^+$ ion at threshold. There is little doubt that the most stable form of $C_3H_2^+$ is linear.

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IONIC REACTIONS OF ATMOSPHERIC IMPORTANCE (U) BIRMINGHAM
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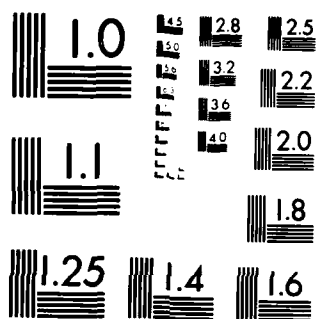
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TABLE I

Ion Heats of Formation

Ion ΔH_f^0 (kcal mol⁻¹)

	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)
$C_2H_2^+$	317							
$C_2H_3^+$	269	266						267±1
$C_3H_3^+$ (cyclic)	257							
$C_3H_3^+$ (linear)	281	propargyl $H_2C-C \equiv CH^+$						
C_3H^+			381	387	390	383±5	383±8	
$C_3H_2^+$			354	357	360			329±5

a) Ref 4

b) Ref 5

c) Ref 6 A.P. from allene

d) Ref 6 A.P. from propyne

e) Ref 6 A.P. from cyclopropene

f) Ref 7 Theory

g) Ref 8 Proton Affinity of C_3

h) Present results

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APPENDIX 7

RATE COEFFICIENTS AT 300 K FOR THE VIBRATIONAL ENERGY
TRANSFER REACTIONS OF N_2 ($\nu=1$) WITH $O_2^+(\nu=0)$ AND $NO^+(\nu=0)$.

J.Chem.Phys., 80, 6095, 1984

Rate coefficients at 300 K for the vibrational energy transfer reactions from $N_2(v=1)$ to $O_2^+(v=0)$ and $NO^+(v=0)$

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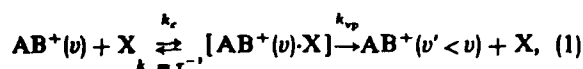
(Received 10 February 1984; accepted 16 March 1984)

Rate coefficients for the reactions $N_2(v=1) + O_2^+(v=0) \rightarrow N_2(v=0) + O_2^+(v=1)$ and $N_2(v=1) + NO^+(v=0) \rightarrow N_2(v=0) + NO^+(v=1)$ have been measured in a SIFT/flowing afterglow system at 300 K, the first measurements of thermal energy vibrational transfer from neutrals to ions. The values are $k = 1 \times 10^{-12}$ and $< 10^{-13} \text{ cm}^3 \text{ s}^{-1}$, respectively. These values are consistent with an intermediate complex vibrational predissociation model which has been successful in rationalizing earlier ion vibrational relaxations by neutral collisions. The NO^+ result establishes that the efficient quenching of $NO^+(v=1)$ by N_2 is not a resonant $V \rightarrow V$ process as was previously assumed.

I. INTRODUCTION

Recently, measurements of the rate coefficients k_q for the vibrational quenching of $O_2^+(v)$ ions¹ and $NO^+(v)$ ions² by a variety of neutral molecules have been carried out in flow drift tubes. The values of k_q are generally relatively large, decrease with increasing center-of-mass translational energy of the reactant ion-neutral pair in the drift tube and show a marked correlation with the ion-neutral electrostatic bond energy. These results clearly indicate that the vibrational relaxation is controlled by the long range attractive forces. Neutral-neutral vibrational relaxation is also controlled by the long range attractive potential in those (less common) cases where a large interaction potential exists which is comparable to typical ion-neutral interaction potentials of several tenths of an eV or greater.

The ion vibrational relaxation is described rather well by an intermediate complex model^{3,4} in which vibrational predissociation of the complex competes with normal unimolecular decomposition back to reactants. Schematically this model can be represented as



where k_c , k_u , and k_{vp} are the rate coefficients for the formation of the complex, for its unimolecular decomposition back to the reactants ($= \tau^{-1}$), and for the vibrational predissociation, respectively. Vibrational predissociation occurs when the vibrational energy in the AB^+ bond is transferred to the $AB^+ \cdots X$ bond, causing the complex to dissociate. Vibrational predissociation has been recently well studied in the case of weakly bound neutral van der Waals molecules.⁵ For example, the weakly bound $He-I_2(v)$ molecule has a value of $k_{vp} = 4.5 \times 10^9 \text{ s}^{-1}$ when the I_2 is excited to the $v=12$ level.⁶ The $[AB^+(v) \cdot X]$ complexes are unbound, they do have significant lifetimes however, due to rotational excitation of reactants^{7,8} and motion on the potential surface.

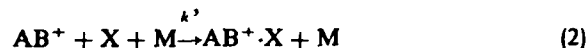
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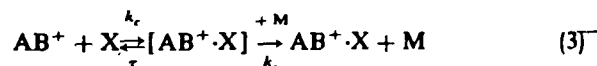
Remarkably, the values of k_{vp} for most of the vibrational quenching reactions for which they have been determined³ (~ 10) are in the range 10^9 – 10^{10} s^{-1} and insensitive to the nature of the intermediate complex. The rate coefficient for vibrational quenching by the mechanism of (1) is given by

$$k_q = \frac{k_c \cdot k_{vp}}{k_u + k_{vp}}$$

which reduces to $k_c k_{vp}/k_u = k_c k_{vp} \tau$ for $k_u \gg k_{vp}$ and to k_c for $k_u \ll k_{vp}$. Values of the product $k_c \tau$ can be obtained from studies of the three-body association,



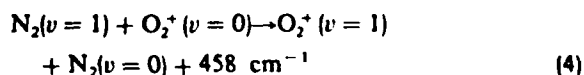
by the conventional mechanism



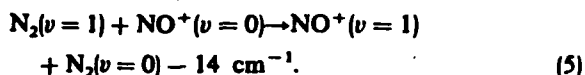
from which the three-body rate coefficient $k^3 = k_c k_s \tau$, where k_s , the stabilization rate coefficient is generally assumed to be equal to the Langevin collision rate coefficient, $k_L = 2\pi e\sqrt{\alpha/\mu}$. Thus k_{vp} can be determined as $k_{vp} = k_q k_s / k^3$ for those cases in which both k_q and k^3 have been experimentally determined (and for which $k_u > k_{vp}$).

Since k_{vp} is so insensitive to the particular O_2^+ and NO^+ complexes involved it is reasonable to expect that the vibrational predissociation of the complex will be quite comparable if the reactant neutral is vibrationally excited rather than the ion (so long as they have comparable frequencies). It was the purpose of this investigation to examine this conjecture. In addition, as we shall see, one may discriminate between possible competitive quenching channels by examining the reverse of one such channel and considering detailed balance.

The reactions studied in the present investigation were



and



To our knowledge these are the first measurements of vibrational transfer from a neutral to an ion at thermal energy.

II. EXPERIMENTAL

The experiments were carried out in a new variable temperature flow tube apparatus which has a Y shaped section upstream of a conventional flow tube. On one arm of the Y is a SIFT type ion injection system and on the other arm is a glass tube which allows a microwave discharge to be established in a carrier gas. Thus the apparatus can be used as a conventional SIFT⁹ or as a flowing afterglow apparatus.¹⁰ It has recently been used successfully as a flowing afterglow-Langmuir probe (FALP) apparatus to study ion-ion recombination,¹⁰ electron-ion recombination,¹¹ and electron attachment.¹² In the present experiment both arms of the Y section were used simultaneously in the following manner. Ground state ions were produced in a high pressure electron impact ion source associated with the SIFT arm of the Y and injected into a helium carrier gas flow. Multiple collisions of the ions with neutrals in the ion source removed any vibrational and electronic excitation of the ions produced by electron impact. This was verified by the vibrational ion monitor gas method to be described below.

A controlled flow of N_2 was added to the He flow in the other arm of the Y section and vibrationally excited by the external microwave discharge cavity in a familiar procedure.¹³ The extent of N_2 vibrational excitation was determined by means of the reaction



for which the rate coefficient is a very steep function of the N_2 vibrational temperature.¹³ The rate coefficient k_6 increases from $1.2 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ at $T_v = 300 \text{ K}$ to $6 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ at $T_v = 6000 \text{ K}$. With O_2 in the ion source it was a simple matter to selectively inject O^+ ions rather than O_2^+ ions and thus utilize reaction (6) to determine T_v .

Vibrational excitation of $\text{O}_2^+(\nu=0)$ by reaction (4) was detected using Xe as a monitor gas. The charge transfer of $\text{O}_2^+(\nu=0)$ with Xe is endothermic and slow, $k = 6.4 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ at 300 K ,¹ whereas the charge transfer of $\text{O}_2^+(\nu>0)$ is exothermic and rapid,¹ $k = 6.2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, close to the Langevin value, $k_L = 9.3 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$. The Xe was added to the flow tube at either of two positions (57 or 22 cm from the sampling orifice of the conventional downstream ion detection system of the SIFT/flowing afterglow apparatus). The experiment thus involved the determination of the O_2^+ and Xe^+ signals at the downstream detector with and without discharging the N_2 [i.e., in both the presence and absence of $\text{N}_2(\nu>0)$]. These ion signals were used to determine the rate coefficient for reaction (4) in the usual manner.⁹

In the case of NO^+ , CH_3I was used as a monitor gas.² This is a more ideal monitor gas for $\text{NO}^+(\nu>0)$ than is Xe for $\text{O}_2^+(\nu>0)$ since CH_3I charge transfers rapidly to $\text{NO}^+(\nu>0)$ but not detectably to $\text{NO}^+(\nu=0)$.^{2,4}

III. RESULTS

A. $\text{N}_2(\nu) + \text{O}_2^+$ [reaction (4)]

When the N_2 was vibrationally excited by the microwave discharge, the O_2^+ count rate decreased and the Xe^+ count rate increased, indicating that reaction (4) was occurring, i.e., vibrational energy was being transferred from $\text{N}_2(\nu)$ to O_2^+ in accordance with expectation. Quite small O_2^+ count rates were available due to the high O_2 pressure and low potentials used in the ion source to avoid excitation of the injected O_2^+ ions. However these count rates were adequate for a determination of the reaction rate coefficient which was done as follows. An O_2^+ count rate of 640 cps (integrated over 20 s) reduced to 470 cps when the N_2 was discharged and the Xe^+ signal increased from ~ 230 to 380 cps. The Xe^+ signal is less certain than the O_2^+ signal because of the many Xe isotopes and because of mass discrimination so that correction factors have been applied. Considering these uncertainties the Xe^+ increase (~ 150) adequately balanced the O_2^+ decrease (170). The reaction length was 57 cm. The Xe density was $3 \times 10^{12} \text{ cm}^{-3}$ which gives an e -folding length for the $\text{O}_2^+(\nu>0) + \text{Xe}$ reaction of $\sim 4 \text{ cm}$ so that this did not significantly reduce the 57 cm reaction length for the vibrational transfer reaction. The total N_2 density in the flow tube was $2.6 \times 10^{14} \text{ cm}^{-3}$ and the N_2 vibrational temperature was determined to be $T_v \sim 1500 \text{ K}$ from the enhancement in the rate of the $\text{O}^+ + \text{N}_2$ reaction (6) when the discharge was struck. This corresponds to $\sim 15\%$ vibrational excitation of the N_2 , i.e., $[\text{N}_2(\nu>0)] = 3.8 \times 10^{13} \text{ cm}^{-3}$, which would be essentially all in the $\nu=1$ level. The ion flow velocity was $7.7 \times 10^3 \text{ cm s}^{-1}$ giving a reaction time of 7.5 ms. Therefore the rate coefficient for reaction (4) was determined to be $k_4 = \ln(640/470)/(3.8 \times 10^{13} \times 7.5 \times 10^{-3}) \approx 1.1 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$. When all of the possible sources of error are considered, k_4 may be uncertain to as much as a factor of 2 or 3.

A second experiment was carried out in which the Xe was introduced 22 cm from the orifice (rather than 57 cm). The changes in count rates were smaller and less certain in this case, with a poorer O_2^+ loss-Xe⁺ gain balance (factor 2). The analysis of this data gave $k_4 = 9.7 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$, which is very close to the value obtained in the first experiment so that we take as the mean value $k_4 = 1 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ with an accuracy of a factor of 2.

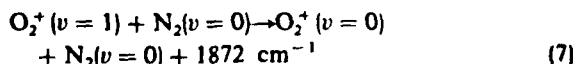
B. $\text{N}_2(\nu) + \text{NO}^+$ [reaction (5)]

In the case of $\text{N}_2(\nu) + \text{NO}^+$ [reaction (5)] we observed no reaction from which it can be concluded that $k_5 < 1 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$. Since CH_3I is an ideal monitor for $\text{NO}^+(\nu>0)$, having no detectable reaction with $\text{NO}^+(\nu=0)$, this experiment was considerably more sensitive than the O_2^+ experiment. Also the value of T_v ($\sim 2000 \text{ K}$) was somewhat higher in this experiment.

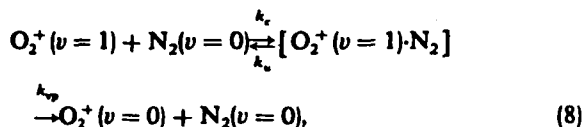
IV. DISCUSSION

A. $\text{N}_2(\nu) + \text{O}_2^+$

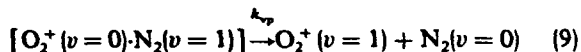
The reaction



has a rate coefficient $k_7 = 1.9 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$. Using the intermediate complex vibrational predissociation model,^{3,4}



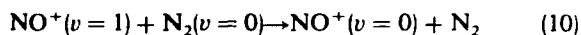
k_{vp} was found³ to be $1.4 \times 10^9 \text{ s}^{-1}$ and $k_{-1} = 6 \times 10^{11} \text{ s}^{-1}$, from the experimentally known value of k^3 for $\text{O}_2^+ + \text{N}_2 + \text{M} \rightarrow \text{O}_2^+ \cdot \text{N}_2 + \text{M}$. The value of k_{vp} for



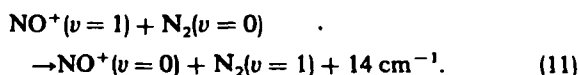
from the present measurements is $\sim 0.7 \times 10^9 \text{ s}^{-1}$ (within $\sim$ factor 2). The vibrational predissociation channel to produce $\text{O}_2^+(v=0) + \text{N}_2(v=0)$ may also occur in the reaction between $\text{N}_2(v=1)$ and $\text{O}_2^+(v=0)$ so that we do not have a comparison between the total k_{vp} 's for the two cases in which the vibrational quantum is in the ion and in the neutral. It is at least clear that a substantial fraction, and perhaps most, of the $\text{N}_2(v=1)$ quenching by $\text{O}_2^+(v=0)$ leads to $\text{O}_2^+(v=1)$, since the total $\text{N}_2(v=1)$ quenching by $\text{O}_2^+(v=0)$ is not likely to exceed significantly the $\text{O}_2^+(v=1)$ quenching by $\text{N}_2(v=0)$.

B. $\text{N}_2(v) + \text{NO}^+$ [reaction (5)]

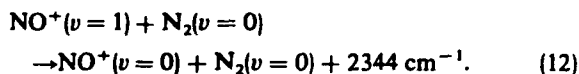
The negative result for this reaction was entirely unexpected. The reaction



has a rate coefficient,² $k_{10} = 7 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$. This is larger than k_7 and appears to be anomalous because in all the other six cases of common quenchers for $\text{O}_2^+(v=1)$ and $\text{NO}^+(v=1)$, the O_2^+ quenching rate coefficient is larger,³ which is attributed to the higher NO^+ vibrational frequency (2344 cm^{-1}) compared to that for O_2^+ (1872 cm^{-1}). This anomaly was suggested² as being due to a resonant $V \rightarrow V$ transfer,



However $k_{11} \sim k_5$ from detailed balance (since $14 \text{ cm}^{-1} \ll kT = 200 \text{ cm}^{-1}$). It therefore follows that $k_{11} < 1 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$. Thus reaction (10) appears to be



The detailed balance argument implicitly assumes that rotational energy factors do not play a large role. This seems plausible since reaction (11) is so nearly thermoneutral that large rotational excitation of the $\text{NO}^+(v=0)$ or $\text{N}_2(v=1)$ products cannot occur. It thus seems unlikely that a substantial deviation from the Boltzmann distribution applicable to reaction (5) could be produced in reaction (11). Considering the width of a Boltzmann distribution ($\sim 200 \text{ cm}^{-1}$) compared to the 14 cm^{-1} exothermicity it seems quite unlikely that the microscopic rates could be sufficiently sensitive to the slight rotational energy variations that are energetically possible to lead to approximately a two order of magnitude

difference in rate coefficients between reactions (5) and (11). The anomalously large value of k_{10} ($> k_7$) remains unexplained however.

It is clear that reaction (12) will dominate reaction (11) in the vibrational predissociation process from essentially phase space arguments. The $[\text{NO}^+(v=1) \cdot \text{N}_2(v=0)]$ complex has only a 14 cm^{-1} energy band to vibrationally dissociate into $\text{NO}^+(v=0) + \text{N}_2(v=1)$, compared to a 2344 cm^{-1} band for $\text{NO}^+(v=0) + \text{N}_2(v=0)$ and this is a prohibitively small amount of accessible phase space. One might expect crudely that $k_{11}/k_{12} \sim 14 \text{ cm}^{-1}/2344 \text{ cm}^{-1} \sim 6 \times 10^{-3}$.

From a dynamical point of view, the process of $[\text{NO}^+(v=1) \cdot \text{N}_2(v=0)]$ complex formation, a prerequisite to vibrational predissociation, involves N_2 and NO^+ rotational excitation. A single rotational excitation of only the N_2 ($\Delta J = 2$) by the anisotropic $\text{NO}^+ \cdot \text{N}_2$ potential would transfer substantially more ($\sim 70 \text{ cm}^{-1}$) than 14 cm^{-1} energy from relative translational motion into internal energy of the complex. Thus separation of the complex into $\text{NO}^+(v=0) + \text{N}_2(v=1)$ is endothermic in the r -($\text{NO}^+ \cdot \text{N}_2$) separation coordinate, whereas most of the 2344 cm^{-1} energy band for vibrational predissociation into $\text{NO}^+(v=0) + \text{N}_2(v=0)$ is still accessible. This model implies that the N_2 and/or NO^+ products of reaction (12) are rotationally excited. This may eventually be subject to experimental test.

The $\text{N}_2(v=1) + \text{O}_2^+(v=0) \rightarrow \text{N}_2(v=0) + \text{O}_2^+(v=1)$ reaction has a 458 cm^{-1} energy band available so that such severe phase space or dynamical constraints do not apply. It would be very interesting from a mechanistic view point to know just what the competition between $\text{O}_2^+(v=1) + \text{N}_2(v=0)$ and $\text{O}_2^+(v=0) + \text{N}_2(v=0)$ is, but of course our experiment can only detect vibrationally excited ions.

V. CONCLUSION

The rate coefficient for $\text{N}_2(v=1)$ quenching by $\text{O}_2^+(v=0)$ to produce $\text{O}_2^+(v=1) + 458 \text{ cm}^{-1}$ kinetic energy has a rate coefficient $\sim 1/2$ the rate coefficient for $\text{O}_2^+(v=1)$ quenching by $\text{N}_2(v=0)$ to produce $\text{O}_2^+(v=0) + \text{N}_2(v=0) + 1872 \text{ cm}^{-1}$ kinetic energy. This result is qualitatively consistent with a model in which vibrational predissociation occurs on a $\sim 10^{-9} \text{ s}$ time scale in the $[\text{O}_2^+ \cdot \text{N}_2]$ complex when either the O_2^+ or the N_2 is vibrationally excited.

Vibrationally excited N_2 was found not to react with $\text{NO}^+(v=0)$ to produce $\text{NO}^+(v=1)$. This proves that the fast quenching of $\text{NO}^+(v=1)$ by N_2 is not a resonant ($\Delta E = 14 \text{ cm}^{-1}$) $V \rightarrow V$ transfer as previously assumed but rather a vibrational predissociation into ground vibrational state NO^+ and N_2 (probably rotationally excited). This is consistent with simple phase space and dynamical model expectations. Presumably vibrationally excited $\text{N}_2(v=1)$ would be quenched by NO^+ ions to produce $\text{N}_2(v=0)$ and kinetic energy with a rate constant $\sim 7 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ but this experiment is not currently feasible.

ACKNOWLEDGMENT

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APPENDIX 8

STUDIES OF PLASMA REACTION PROCESSES USING A FLOWING AFTERGLOW/LANGMUIR PROBE APPARATUS.

In "Swarms of Ions and Electrons in Gases"
Eds. W. Lindinger, T. D. Mark and F. Howorka,
Springer-Verlag, Wien, 1984, pp 284-306.

STUDIES OF PLASMA REACTION PROCESSES USING A FLOWING AFTERGLOW/
LANGMUIR PROBE APPARATUS

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1. Introduction

The thermalised afterglow plasma, in association with appropriate diagnostic techniques, is a suitable medium for investigating a wide variety of ionic processes under well-defined conditions. The pioneering work of S.C.Brown and M.A.Biondi and their co-workers using the pulsed (stationary) afterglow/microwave cavity diagnostic technique has provided a wealth of data, notably that relating to electron-ion dissociative recombination. Pulsed afterglows have also been used successfully by H.J.Oskam, D.Smith and W.C.Linberger and their colleagues to study a wide variety of processes. Brief summaries of these studies, including descriptions of the experimental techniques, are given in the book by McDaniel and Mason [1]. Later the flowing afterglow was conceived, developed and exploited by E.E.Ferguson, F.C.Fehsenfeld and A.L.Schmeltekopf at Boulder to study ion-molecule reactions at thermal energies. The flowing afterglow has subsequently been exploited to great effect by the Boulder group and by several other groups, and this work has laid the foundations for an understanding of ion-molecule reactions at thermal energies. The flowing afterglow technique has been discussed in detail by Ferguson et al. [2], and it has been compared and contrasted with the more recently developed Selected Ion Flow Tube (SIFT) technique by Smith and Adams [3].

The standard diagnostic used in most flowing afterglow apparatuses is a downstream mass spectrometer; indeed, this is the only diagnostic required for ion-molecule reaction studies. For the study of most other plasma reaction processes, it is necessary to be able to determine the charged particle number densities within the body of the plasma, that is along the afterglow plasma column. This is the unique feature of the Flowing After-

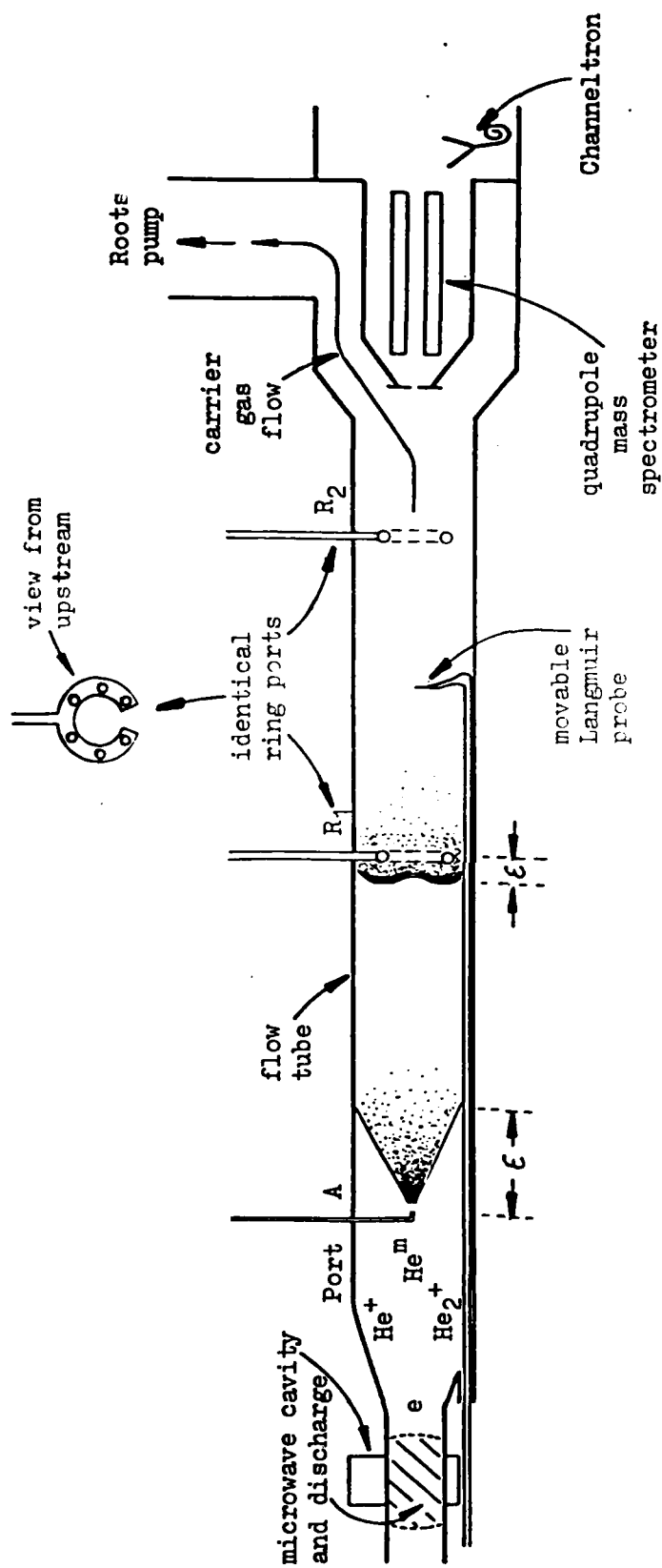


Fig.1 Schematic representation of the Flowing Afterglow/Langmuir Probe (FALP) experiment indicating the flow tube, the microwave discharge, the density distribution of ion source and/or reactant gases entering the axial inlet port A and the ring ports R_1 and R_2 , the Langmuir probe and the quadrupole mass spectrometer and Channeltron detector. The "end corrections" for each type of port are labelled as ϵ . The flow tube is surrounded by a vacuum vessel to facilitate its temperature variation but this has been omitted for clarity.

glow/Langmuir Probe (FALP) apparatus in which a cylindrical Langmuir probe is used to determine electron temperature (T_e), electron density (n_e), positive ion density (n_+) and negative ion density (n_-) along the axis of the afterglow column with a spatial resolution of about one millimetre. A brief description of the FALP technique is given in the next section. To date, it has been exploited to study ambipolar diffusion, electron temperature relaxation, electron-ion dissociative recombination, electron attachment and ion-ion recombination, in many cases over appreciable temperature ranges. The results from these studies will be summarised in this paper.

2. The FALP Technique

In essence, a flowing afterglow consists of a flow tube along which a carrier gas (usually pure helium) is constrained to flow by the action of a large Roots-type pump, and in which ionization is created in the upstream region by a gas discharge or some other ion source. An afterglow plasma is thus distributed along the flow tube and, under favourable conditions, the charged particle energies will be relaxed in the afterglow to those appropriate to the carrier gas temperature. Distance along the flow tube and the residence (or reaction) time of the individual ionized or neutral species in the plasma are coupled via their respective flow velocities which can readily be determined if the flow dynamics are understood (a detailed appraisal is given in the paper by Adams et al. [4]). The various reaction processes can then be studied by adjusting n_e , n_- and n_+ to suitable values (appropriate to the particular process to be studied, e.g. recombination, attachment, etc.) and by adding controlled amounts of appropriate reactant gases into the thermalised afterglow plasma via one or more inlet ports situated at fixed positions along the flow tube. (In some conventional flowing afterglow apparatuses, a single inlet port is used which can be moved along the flow tube axis [5]). Different reactant gases are often added simultaneously via separate inlet ports in order to generate suitable plasma media or, for example, to remove helium metastable atoms from the afterglow (specific examples are given in the following sections). A major objective is to create afterglow plasmas in which the loss of a particular charged species occurs solely by the process which it is desired to study.

The original FALP apparatus [6], like the original flowing afterglow [2], was constructed from Pyrex glass but a change to stainless steel was inevitable with the desire to study processes over a wide temperature range. A schematic of the latest FALP is shown in Figure 1. The stainless steel flow tube is approximately one metre long and eight centimetres in diameter. The ionization source is a microwave discharge through the carrier gas at

pressures of the order of one Torr. In helium carrier gas, the maximum n_e in the upstream region of the afterglow is about 10^{11} cm^{-3} as determined with the Langmuir probe (discussed below). The axial inlet ports (such as port A in Fig.1), which are used in most flowing afterglow experiments, have large mixing lengths (or end corrections, $\ell \sim 10 \text{ cm}$). In contrast, the ring ports, R_1 and R_2 , have a small ℓ which is essential for the study of fast processes such as electron-ion recombination and electron attachment. With these ring ports the reactant gas is introduced into the afterglow against the flow of carrier gas (a contraflow technique) and this reduces ℓ to about 1 or 2 cm [7]. A differentially-pumped mass spectrometer is located at the downstream end of the flow tube so that the positive and negative ion species in the plasmas can be identified.

The Langmuir probe technique has been used for decades to study steady state discharge plasmas (see, for example, the book by Swift and Schwar [8]) but, prior to the work in our laboratory, it had not been satisfactorily applied to the study of decaying (afterglow) plasmas. Our probe technique was first developed for use in pulsed (stationary) afterglows [9] and subsequently we combined it with the flowing afterglow to create the FALF apparatus [6]. The details of the probe technique are given in several papers [6, 9-11] and only an outline is necessary here. A small cylindrical wire (the probe) is swept in potential, relative to the local plasma potential and a current/voltage characteristic is recorded and analysed to provide values for T_e, n_e, n_+ and n_- as appropriate. In fact, it is the gradients of these parameters along the axis (defined here as the z coordinate) of the flowing plasma which provides values for attachment and recombination coefficients etc. under truly thermalised conditions. The complete flow tube is enclosed in a vacuum vessel which facilitates the temperature variation of the flow tube over the range 80-600 K and minimises temperature gradients. The Langmuir probe data also provide values for the mass ratios m_+/m_e in positive ion/electron plasmas and m_+/m_- in positive ion/negative ion plasmas (or mean values of these ratios in plasmas containing more than one species of positive or negative ion [14, 15]). This is a valuable supplement to the mass spectrometric data.

3. Ambipolar Diffusion and Electron Temperature Relaxation Studies

Ambipolar diffusion is always a finite loss process for ions and electrons in flowing afterglow plasmas. Sufficiently far away from the disturbed upstream region of the afterglow, fundamental mode diffusive loss prevails and n_e and n_+ in an electron-ion plasma decrease exponentially with z . Thus it is a straightforward matter to determine $\partial n_e / \partial z$ and hence to derive values for the ambipolar diffusion coefficients, D_a , for plasmas of various ionic compositions

[6]. Theory predicts [16] that, at a given temperature, $D_a p = \text{const.}$ (where p is the gas pressure), a prediction amply supported by experiment [1]. Since D_a is inversely proportional to p then, when ambipolar diffusion needs to be inhibited, i.e. when studying other reaction processes, the FALP must be operated at suitably high pressure. Of course, ambipolar diffusive loss also occurs in ion-ion plasmas (but at a slower rate than in electron-ion plasmas, since $D_- \ll D_e$ (D_- and D_e are the free diffusion coefficients of negative ions and electrons respectively)). In plasmas in which electrons and negative ions co-exist, the situation is more complicated with respect to diffusion (see Section 5).

In the region near to the discharge, which generates the flowing afterglow, T_e is much greater than T_+ or T_g (the ion and gas temperatures respectively) and there the diffusive loss is most rapid (since $D_a = D_+(1 + T_e/T_+)$ [1]). The 'hot' electrons which exist in this region are 'cooled' in collisions with positive ions and carrier gas atoms during their passage down the tube. It is important to estimate this rate of cooling, dT_e/dt , so that it can be ascertained where downstream thermalisation has been reached (i.e. where $T_e = T_+ = T_g$). The Langmuir probe can be used to determine T_e and hence dT_e/dt (knowing the plasma flow velocity which can also be readily determined, again using the probe [4]). Such T_e relaxation has been studied in both stationary afterglows [17] and in the FALP [18,19]. The rate of electron temperature relaxation is described by:

$$\frac{dT_e}{dt} = - \frac{1}{\tau} (T_e - T_{+,g}) \quad (T_+ \sim T_g \text{ in these plasmas}) \quad (1)$$

The time constant, τ , describes the net effect due to electron-ion ($\tau_{e,+}$) and electron-neutral ($\tau_{e,n}$) collisions such that $\tau^{-1} = \tau_{e,+}^{-1} + \tau_{e,n}^{-1}$. The small fractional ionization in these afterglow plasmas ($\sim 10^{-6}$) ensures that electron-neutral collisions control the rate of T_e relaxation. This is especially so when the neutral gas is molecular since electron cooling can occur via excitation of rotational and vibrational states of the molecules.

τ_{en} has been determined in inert gas stationary afterglows and thus cross sections for momentum transfer in electron-inert gas atom collisions have been deduced [17]. Using the FALP, the fractions of energy transferred in electron collisions with the molecular gases N_2 and O_2 have been determined as a function of T_e from τ_{en} measurements [18,19]. Such measurements can also provide other fundamental data such as quadrupole moments.

It should be noted that T_e relaxation is inhibited when helium metastable atoms are present in an afterglow due to heating of the electrons in super-

elastic collisions with these excited atoms. To avoid this undesirable situation, a small amount of argon can be added to the upstream region of the afterglow to quench the metastable atoms (via Penning reactions [6]). The addition of argon also reactively removes any He_2^+ ions which are produced in the three-body association of He^+ with He [20]. This does of course mean that, in addition to He^+ ions, Ar^+ ions will be present in the afterglow, however this does not result in severe complications in practice when studying other processes.

The quantity of data so far obtained which relates to T_e relaxation is relatively small, but it very well illustrates the potential of the FALP for such studies.

4. Electron-Ion Dissociative Recombination Studies

Dissociative recombination reactions of molecular positive ions with electrons have been studied for many years because they are an important loss process of ionization both in laboratory plasmas such as gas lasers [21] and in naturally occurring plasmas such as the ionosphere and interstellar gas clouds (for further discussion of these subjects see the reviews by Smith and Adams [22,23]). The primary objective of most studies has been to determine the recombination coefficients, α , for particular positive ion species and how these coefficients vary (i) with T under truly thermal equilibrium conditions such that $T_e = T_+ = T_g$ when α_t is obtained, and (ii) with T_e for $T_e > T_+, T_g$ when α_e is obtained. Notable amongst the many techniques used to determine α_t and α_e is the stationary afterglow [24,25]. The variation of the dissociative recombination cross section with electron energy, σ_E , has been studied using ion traps [26,27] and merged beams [28]. Very recently, the FALP technique has been used for studies of α_t [7].

As previously mentioned, it is crucial in plasma experiments such as the FALP to establish conditions such that the process under investigation is the dominant loss process. In the FALP for dissociative recombination studies this is achieved in the following manner. The active species upstream in the afterglow plasma are electrons, He^+ and He_2^+ ions and He metastable atoms, He^m . Argon is introduced upstream (via port A, Fig.1) to destroy He_2^+ and He^m . The plasma then contains only electrons and atomic ions (He^+ and Ar^+). Recombination of atomic ions with electrons in these plasmas is negligibly slow and so ambipolar diffusion followed by wall recombination is the only loss process for ionization. A molecular reactant gas is then added to this diffusing plasma via one of the ring ports (R_1, R_2) in sufficient quantity to convert the atomic ions to appropriate molecular positive ions (e.g. O_2 and NH_3 to produce O_2^+ and NH_4^+ etc.). Knowledge of the vast

literature on ion-molecule reactions and careful use of the downstream mass spectrometer are essential in creating the desired positive ion species as the only ionic species in the plasma. At low temperatures and high pressures a potential problem is the creation of ion clusters (e.g. $O_2^+.O_2, NH_4^+.NH_3$, etc.) and then careful use of the mass spectrometer is especially important.

When the desired plasma conditions have been established, the electron density, n_e , is determined along the flow tube axis using the Langmuir probe and an obvious increase in $\partial n_e / \partial z$ is observed downstream of the molecular gas inlet port (see Fig.2a as an example). Under conditions of large n_e and sufficiently high helium pressure, recombination loss dominates diffusion loss and then we have :

$$\frac{1}{n_e(z_1)} - \frac{1}{n_e(z_2)} = \alpha_t \frac{(z_2 - z_1)}{v_p} \quad (2)$$

where $n_e(z_1)$, $n_e(z_2)$ are the values of n_e at positions z_1 and z_2 , and v_p is the plasma flow velocity. Hence α_t can readily be obtained from a plot of $1/n_e$ versus z . Typical plots are shown in Fig.2b to illustrate the quality of the data obtained. Experiments can be carried out within the temperature range 80-600 K, although the low temperature limit is higher than 80 K when it is necessary to use ion source gases which are condensible (e.g. H_2O, NH_3 etc.).

The measurement of $\alpha_t(O_2^+)$ has become a 'test' for recombination studies, since its value has been very well established using a variety of techniques. It has been measured in the FALP using O_2 as the reactant gas at 95, 205, 295, 420, 530 and 590 K and the data are shown in the log-log plot in Fig.3. The linearity of the graph is good and the power law: $\alpha_t(O_2^+) = 1.95 \times 10^{-7} (300/T)^{0.7} \text{ cm}^3 \text{ s}^{-1}$ closely describes $\alpha_t(O_2^+)$ over the complete temperature range. Good agreement is found with the values obtained previously at 300 K using a variety of techniques (see e.g. Ref.26) and with pulsed stationary afterglow data obtained above 300 K [29]. The small discrepancy at low temperatures between the present values and the pulsed afterglow data [29] at low temperatures is thought to be due to the presence of cluster ions in the higher pressure stationary afterglow experiment. The results are also in good agreement with pulsed afterglow data for $\alpha_e(O_2^+)$ [30] and with results for $\alpha_e(O_2^+)$ derived from cross sections measured with the ion trap technique [26]. All these experiments essentially indicate a common $T^{-0.7}$ dependence of $\alpha_t(O_2^+)$ and $\alpha_e(O_2^+)$. A somewhat weaker $T^{-0.5}$ temperature dependence was derived from cross section measurements made using the merged beam technique [31].

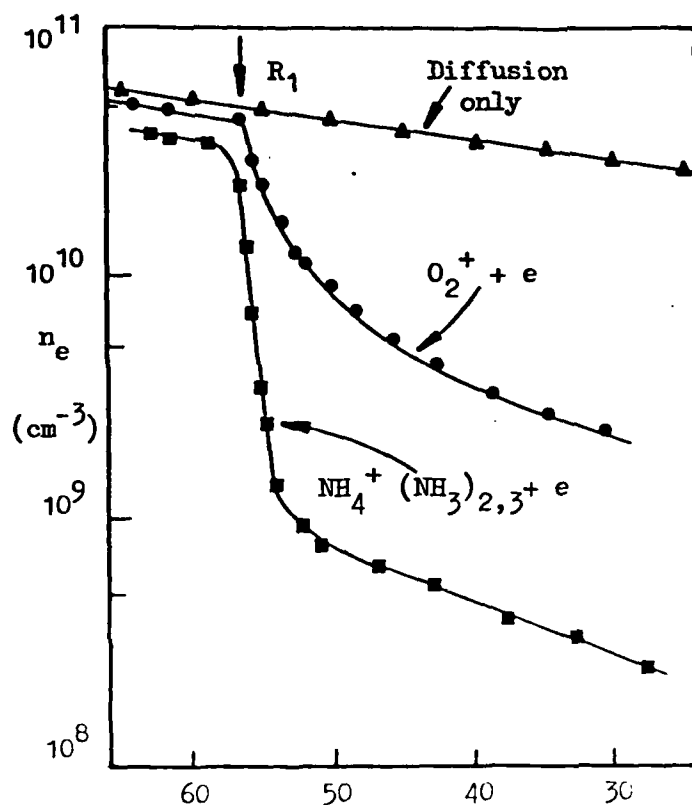


Fig.2(a) n_e versus z data (z is measured from the mass spectrometer sampling orifice) obtained using the FALP at a helium pressure of 0.6 Torr and a temperature of 300 K for:
 ▲, diffusion controlled plasma (He^+ , Ar^+ , electrons) with the addition of Ar through port A (see Fig.1) to destroy He^m and He_2^+ but without the addition of ion source gases:
 • with addition of O_2 via port R_1 (see Fig.1) which results in an increased loss rate of electrons due dissociative recombination of O_2^+ ions: ■ with addition of NH_3 ; the rapid decrease of n_e is due to dissociative recombination of NH_4^+ (NH_3)_{2,3} ions.

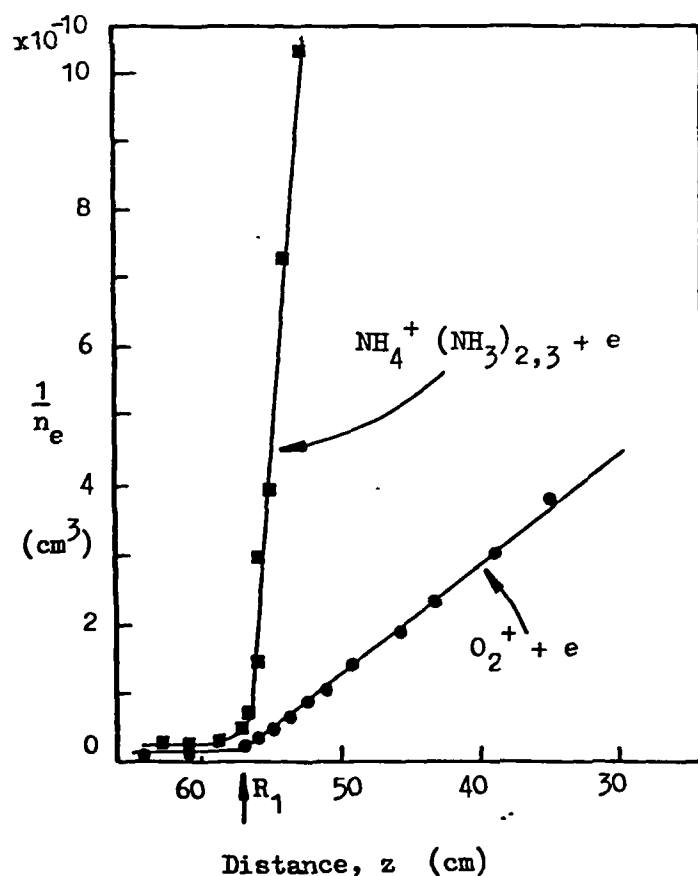


Fig.2(b) $1/n_e$ versus z plots of the data for O_2^+ and NH_4^+ (NH_3)_{2,3} shown in (a). The slopes of these plots provide values for the recombination coefficients, α_t . The very different slopes indicate that $\alpha_t(\text{NH}_4^+(\text{NH}_3)_{2,3})$ is much larger than $\alpha_t(\text{O}_2^+)$ at 300 K. Note that these plots are linear over a factor of more than 20 which is quite sufficient to define the α_t accurately. At small z (and low n_e) upcurving of these plots occurs (not shown) as ambipolar diffusion rather than dissociative recombination becomes the dominant loss process for ionization.

An important point to make, which is relevant to all the dissociative recombination reactions we have studied to date, is that the molecular ions, for which α_t have been measured, are confidently expected to be in their ground electronic and equilibrium vibrational/rotational states. This is so because the ions, although on production may well be internally excited, will undergo resonant charge or proton transfer with their parent molecules (which are present in the afterglow). Such reactions are known to quench both electronic and vibrational excitation very efficiently [32,33]. Rotational relaxation is ensured by the high collision frequency of the molecular ions with the ambient carrier gas atoms.

The temperature dependence of $\alpha(\text{NO}^+)$ has been in dispute for several years. The dispute centred around the difference between the stationary afterglow data of Biondi and co-workers [25,34] and the ion trap data of Walls and Dunn [26]. The stationary afterglow data indicate that α_t (for $200 < T < 450\text{K}$) has a markedly different temperature dependence than α_e (for $500 < T_e < 2000\text{K}$), whereas no indication of such a deviation was noticeable in the α_e derived from σ_E data obtained in the ion trap experiment. Thus, FALP studies of α_t were undertaken in an attempt to clarify this situation.

NO^+ ions are generated in the FALP by introducing NO (from which HNO_3 impurities had been removed to avoid negative ion production) into the He^+/Ar^+ afterglow. $\alpha_t(\text{NO}^+)$, which was measured at 205, 295, 465 and 590 K, is very well described by the power law $\alpha_t(\text{NO}^+) = 4.0 \times 10^{-7} (300/T)^{0.9} \text{cm}^3 \text{s}^{-1}$, see Fig.3. This is in good agreement with the pulsed afterglow data for $\alpha_t(\text{NO}^+)$ and with the $\alpha_e(\text{NO}^+)$ ion trap data. Results obtained from satellite measurements in the ionosphere [35] indicate that $\alpha_e(\text{NO}^+) \sim T_e^{-0.85}$ and are in remarkable agreement in magnitude with the FALP data at the temperature common to both data sets. However, the $\alpha_e(\text{NO}^+)$ stationary afterglow results cannot be reconciled with the FALP data for $\alpha_t(\text{NO}^+)$. It does seem that on balance, a common $T^{-0.9}$ dependence for $\alpha_t(\text{NO}^+)$ and $\alpha_e(\text{NO}^+)$ is appropriate below about 10^3K . Values of $\alpha_e(\text{NO}^+)$ derived from merged beam data [31] are not reconcilable with the other data referred to above. A more detailed discussion of all these data is given by Alge et al.[7].

$\alpha_t(\text{NH}_4^+)$ was measured at 295, 415, 460, 540 and 600K in the FALP. The NH_4^+ ions were generated by adding small amounts of NH_3 to the afterglows (large NH_3 flows initiated ion clustering, see below). The data obtained (see Fig.3) are reasonably well described by the power law $\alpha_t(\text{NH}_4^+) = 1.35 \times 10^{-6} (300/T)^{0.6} \text{cm}^3 \text{s}^{-1}$. This is in good agreement with stationary afterglow data in the overlapping temperature range [36], although not in good agreement with ion

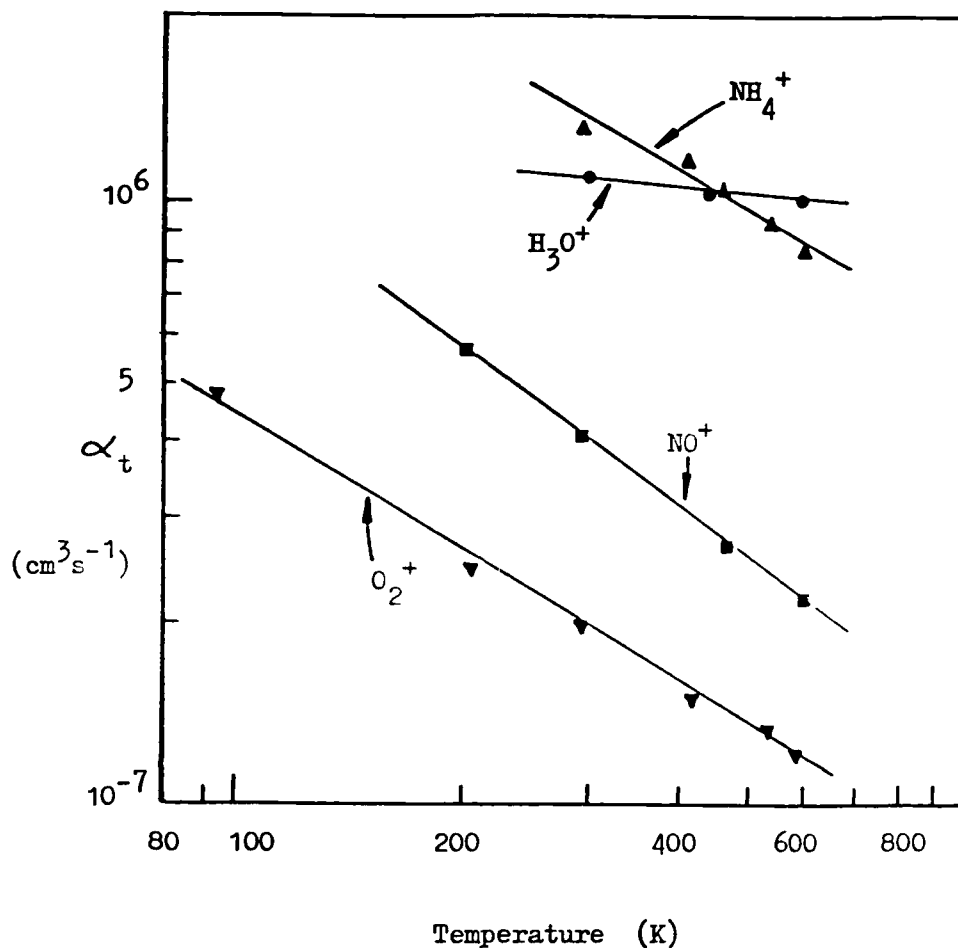


Fig.3 Electron-ion dissociative recombination coefficients, α_t (i.e. for $T_e = T_+ = T_g$), for O_2^+ , NO^+ , NH_4^+ and H_3O^+ determined at several temperatures using the FALP technique. These data indicate that $\alpha_t(\text{O}_2^+) \sim T^{-0.7}$, $\alpha_t(\text{NO}^+) \sim T^{-0.9}$, $\alpha_t(\text{NH}_4^+) \sim T^{-0.5}$ and that $\alpha_t(\text{H}_3\text{O}^+)$ does not vary significantly with temperature over the available range.

trap data (see Ref. 7). By adding excess NH_3 to the afterglow at 300 K, on equilibrium ratio of $\text{NH}_4^+(\text{NH}_3)_2$ and $\text{NH}_4^+(\text{NH}_3)_3$ cluster ions could be established. A composite α_t of $2.8 \times 10^{-6} \text{ cm}^3 \text{ s}^{-1}$ was obtained for these ions which is in excellent agreement with the stationary afterglow value for $\text{NH}_4^+(\text{NH}_3)_2$ cluster ions at 300 K [36].

$\alpha_t(\text{H}_3\text{O}^+)$ was measured at 295, 450 and 600 K and, somewhat surprisingly, no significant variation was observed with temperature, a constant value of $1.0 \times 10^{-6} \text{ cm}^3 \text{ s}^{-1}$ being obtained. An identical value was obtained in a stationary afterglow experiment at 540 K [37]. Recent values for $\alpha_e(\text{H}_3\text{O}^+)$ derived from merged beam data [38] are significantly smaller than the FALP values and also show a marked 'temperature' (energy) dependence. A similar marked 'temperature' dependence for $\alpha_e(\text{H}_3\text{O}^+)$ was also indicated by ion trap data [27]. Collectively, the data may be indicating that $\alpha_t(\text{H}_3\text{O}^+)$ and $\alpha_e(\text{H}_3\text{O}^+)$ have different T and T_e dependences.

The most recent FALP studies of dissociative recombination have been directed towards the measurement of α_t at suitably low temperatures for ions which are known (or expected) to exist in interstellar gas clouds [23, 39, 40]. Thus the α_t for electron recombination of the ions HCO^+ , DCO^+ , H_2E^+ , H_2D^+ , CH_3^+ , H_3^+ and D_3^+ have been determined at a temperature of 95 K [41]. At this temperature, it was not possible to use argon to destroy helium metastables in the afterglow; rather, an excess of the gases from which the ions were generated (ion source gases) was introduced to rapidly destroy the metastables. The very slow Penning reactions of He^m with most gases expected at low temperatures [42] required that relatively large amounts of ion source gases were needed, especially in the case of H_2 and D_2 . The major ion in the helium afterglow at 95 K, prior to addition of the ion source gases, was He_2^+ which is known to react rapidly with most gases, including H_2 [43]. Thus, to study $\alpha_t(\text{H}_3^+)$, H_2 was added in excess and Penning reactions and ion molecule reactions established H_3^+ as the major ionic species. At excessively high H_2 pressures, the three-body association reaction $\text{H}_3^+ + \text{H}_2 + \text{He} \rightarrow \text{H}_5^+ + \text{He}$ led to appreciable concentrations of H_5^+ in the afterglow. Whilst the data for $\alpha_t(\text{H}_3^+)$ are as yet preliminary, the startling indication is that $\alpha_t(\text{H}_3^+)$ at 95 K is very small ($< 10^{-7} \text{ cm}^3 \text{ s}^{-1}$) contrary to expectations and to pulsed afterglow data [44, 45]. If confirmed, this will have a profound effect on current thinking on interstellar chemistry and physics! Similar experiments indicate that $\alpha_t(\text{D}_3^+)$ is also very small. However, $\alpha_t(\text{H}_5^+)$ and $\alpha_t(\text{D}_5^+)$ are much larger ($\sim 10^{-6} \text{ cm}^3 \text{ s}^{-1}$ at 95 K) in keeping with previous data [44, 45] and with general expectations for polyatomic ions [46].

$\alpha_t(\text{HCO}^+)$ and $\alpha_t(\text{N}_2\text{H}^+)$ and their deuterated analogues were determined by adding small amounts of CO and N_2 respectively into the H_3^+ (or D_3^+) afterglows whence rapid proton transfer reactions occurred generating HCO^+ and N_2H^+ respectively as the only ion species in the afterglow plasmas. Rapid recombination was immediately observed with the introduction of the CO or N_2 indicating that $\alpha_t(\text{HCO}^+)$ and $\alpha_t(\text{N}_2\text{H}^+)$ are much greater than $\alpha_t(\text{H}_3^+)$ (and similarly for the deuterated ions). The actual values obtained at 95 K are $\alpha_t(\text{HCO}^+) = 2.9 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$, $\alpha_t(\text{N}_2\text{H}^+) = 4.9 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$. $\alpha_t(\text{DCO}^+)$ and $\alpha_t(\text{N}_2\text{D}^+)$ were insignificantly different from the values for their hydrogenated analogues. $\alpha_t(\text{HCO}^+)$ has been measured at 200 and 300 K by other workers [47]; these low temperature FALP data are not inconsistent with expectations from these earlier data. Addition of CH_4 to the H_3^+ afterglow rapidly generated CH_5^+ ions and hence $\alpha_t(\text{CH}_5^+)$ was readily determined to be $1.5 \times 10^{-6} \text{ cm}^3 \text{ s}^{-1}$ at 95 K, which is quite typical of α_t for polyatomic ions previously measured, albeit at higher temperatures.

These FALP data are the first data obtained for α_t at such low temperatures. Much more still remains to be done. The FALP technique also offers the possibility of determining the products of dissociative recombination - a very worthwhile pursuit for the future.

5. Electron Attachment Studies

Electron attachment reactions have been studied for decades using a variety of techniques. Much of the early work has been reviewed in the books by Christophorou [48] and by Massey [49]. Since the publication of these books, many research papers have reported measurements of attachment coefficients (designated here as β in units of $\text{cm}^3 \text{ s}^{-1}$; see the review by Christophorou et al. [50] and the papers by Smith et al. [51] and Alge et al. [52] for comprehensive references). Negative ion formation in electron-molecule interactions can occur via a two-body process in which fragmentation (dissociation) of the molecule occurs e.g.



or via a three-body interaction generating the negative ion of the parent molecule e.g.



Reaction such as (4) usually occur at appreciable rates only at relatively high pressures, although there are exceptions to this (e.g. SF_6 attachment). Some two-body reactions such as (3) are exoergic (in which case they are loosely called thermal attachment reactions), although this does not mean that they are necessarily rapid at thermal energies because often activation energy

Table 1. Electron attachment coefficients, $\beta(300\text{ K})$, determined using the FALP at 300 K.

Molecule	CCl_4	SF_6^*	CCl_3F	CH_3I	C_6F_6^*	CH_2Br_2
$\beta(300\text{K})$	3.9(-7)	3.1(-7)	2.6(-7)	1.2(-7)	1.1(-7)	9.3(-8)
Product Ion	Cl^-	SF_6^-	Cl^-	I^-	C_6F_6^-	Br^-
E_a (meV)	-	-	~ 20	-	-	~ 48

Molecule	C_7F_{14}	CF_3Br	CHCl_3	CCl_2F_2	Cl_2	CH_3Br
$\beta(300\text{ K})$	8.1(-8)	1.6(-8)	4.4(-9)	3.2(-9)	2.0(-9)	6(-12)
Product Ion	$\text{C}_7\text{F}_{14}^-$	Br^-	Cl^-	Cl^-	Cl^-	Br^-
E_a (meV)	42	86	120	150	50	307

The measurements were made in helium carrier gas at a pressure of 0.6 Torr. The units of β are cm^3s^{-1} and, for example, $3.9(-7) = 3.9 \times 10^{-7}$. Reactions with the molecules marked with an asterisk are presumably saturated three-body attachment reactions since the parent ions are the observed products and so the β are the equivalent two-body attachment coefficients. All of the other reactions proceed via dissociative attachment giving the product ions indicated. The β values for several of the reactions increase with increasing temperature (see Fig.4) and then the activation energies, E_a (given in milli-electronvolts (meV)) have also been obtained.

barriers exist (see below). Endoergic (non-thermal) two-body attachment reactions are those which have threshold energies for dissociative electron attachment such as the $e + O_2 \rightarrow O^- + O$ reaction.

The variable-temperature FALP is very suitable for the study of thermal attachment reactions, that is for the determination of β coefficients and how they vary with temperature under truly thermal conditions. The product negative ions are also readily identified in the experiments. The principle of the method is straightforward; controlled amounts of the attaching gas are introduced into the thermalised He^+/Ar^+ afterglow (see previous section) and the density gradient of electrons ($\partial n_e / \partial z$) is monitored in the usual manner. Two practical points which must be recognised if accurate values of β are to be obtained are the following. Firstly, n_e must be sufficiently small so that any molecular positive ions formed in reactions of He^+ or Ar^+ with the attaching gas cannot recombine with electrons at a significant rate (and therefore contribute to $\partial n_e / \partial z$). Secondly, n_e must be much smaller than n_m , the number density of attaching molecules in the afterglow, so that n_m is invariant with z (i.e. $\partial n_m / \partial z = 0$), otherwise data interpretation would be prohibitively difficult. These constraints place a practical lower limit of $\sim 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ on the value of β which can be accurately measured. When these potential difficulties are avoided, the loss of electrons is only via ambipolar diffusion and attachment, and then :

$$v_p \frac{\partial n_e}{\partial z} = D_a \nabla^2 n_e - \beta n_e n_m \quad (5)$$

This equation cannot be solved analytically to give $n_e(z)$ because D_a is a function of n_-/n_e . However, Oskam [53] and Biondi [54] have shown how $n_e(z)$ can be obtained when negative ion formation is occurring. Thus :

$$n_e(z) = \frac{n_e(0)}{1 - v_D/v_a} \left[\exp \left(- \frac{v_a z}{v_p} \right) - \frac{v_D}{v_a} \exp \left(- \frac{v_D z}{v_p} \right) \right] \quad (6)$$

where $v_D = D_{ae}/\Lambda^2$ (D_{ae} is the diffusion coefficient in the absence of negative ions, Λ is the characteristic diffusion length of the flow tube), $v_a = \beta n_m$, v_p is the plasma flow velocity and $n_e(0)$ is the electron density at the position of entry of the attaching gas into the plasma. When $v_D \ll v_a$, equation (6) reduces to a single exponential solution and the derivation of β from the $n_e(z)$ data is easy. In practice, however, this condition cannot be realised and so $n_e(z)$ is first determined in the absence of attaching gas to derive v_D , $n_e(z)$ then determined for given values of n_m and then v_a (and hence β) is obtained by computer fitting $n_e(z)$ according to equation (6).

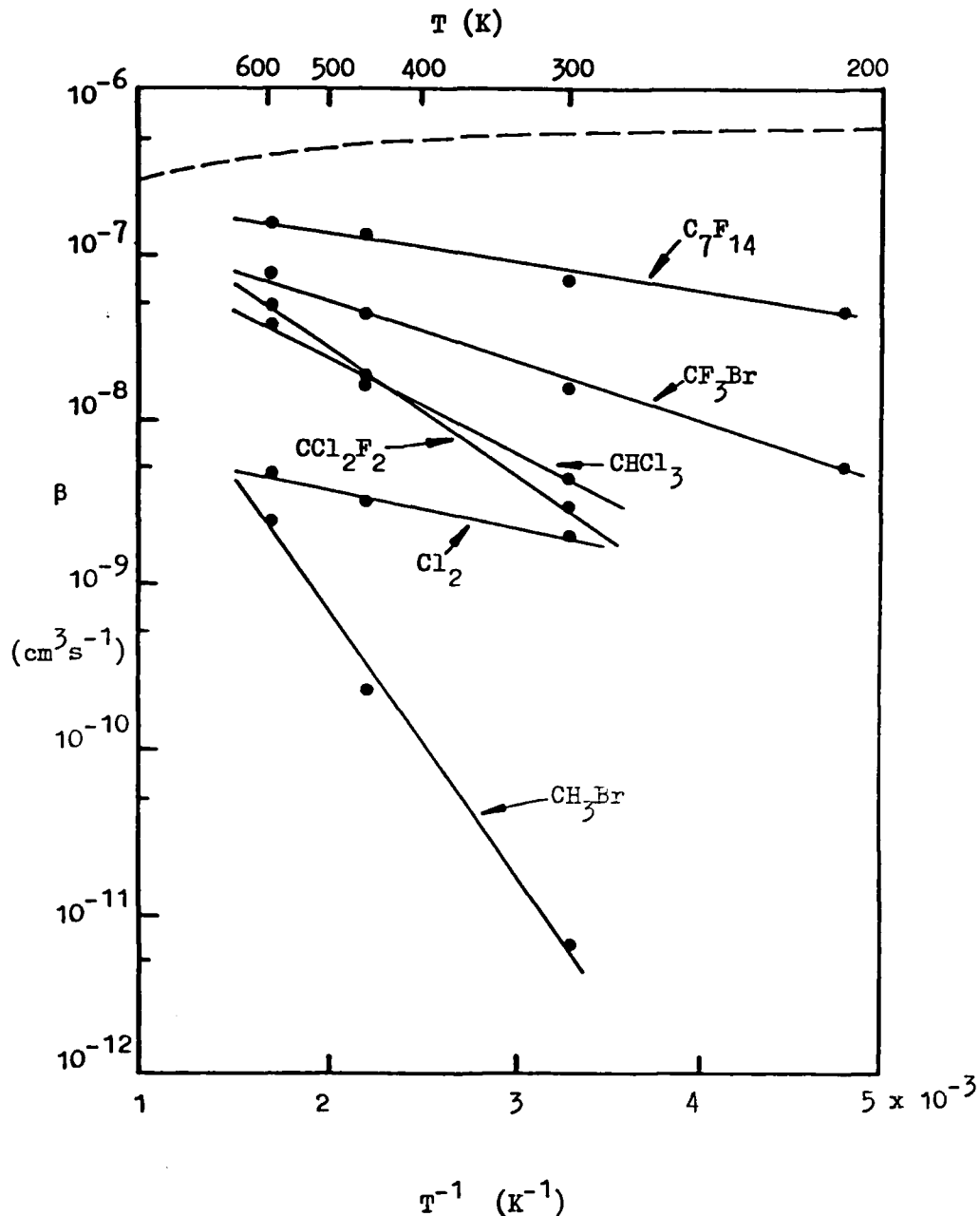
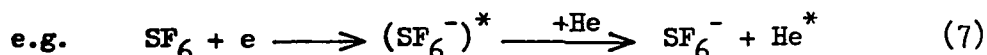


Fig.4 Arrhenius plots ($\ln \beta$ versus $1/T$) derived from FALP data for the attachment reactions of electrons with C_7F_{14} , CF_3Br , CHCl_3 , CCl_2F_2 , Cl_2 and CH_3Br . The slopes of the lines provide values for the activation energies, E_a , for the reactions and these values are given in Table 1. The dashed line describes $\beta_{\text{max}} = 5 \times 10^{-7} (300/T)^2 \text{ cm}^3 \text{s}^{-1}$ which (following Warman and Sauer [55]) gives the approximate upper limit values of β for any reaction (a more sophisticated treatment has been given by Klots [56], see text).

The twelve molecular gases included to date in FALP studies of electron attachment are given in Table 1 together with the measured β values at 300 K arranged in order of their magnitudes. They range from the very large $\beta(\text{CCl}_4) = 3.9 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ to that for $\beta(\text{CH}_3\text{Br})$ which is some five orders-of-magnitude smaller. The measured $\beta(\text{CCl}_4)$ is near to the theoretical maximum for electron attachment which is given by Warman and Sauer [55] as $\beta_{\text{max}} \sim 5 \times 10^{-7} (300/T)^{1/2} \text{ cm}^3 \text{ s}^{-1}$, a result obtained from a consideration of the electron de Broglie wavelength. A more sophisticated theoretical treatment by Klotz [56] yields a value for $\beta(\text{CCl}_4)$ of $3.29 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ at room temperature. $\beta(\text{CCl}_4)$ exhibits a weak inverse temperature dependence within the range 200 to 600 K (the temperature range over which most of these FALP attachment studies were carried out). However, the β values for the reactions involving several of the other molecular gases increased markedly with increasing temperature. This is attributed to energy barriers in these reactions and the associated activation energies, E_a , have been estimated from the slopes of the Arrhenius plots shown in Fig. 4. The E_a values range from about 20 meV for the CCl_3F reaction to 307 meV for the CH_3Br reaction (see Table 1). The manifestation of the large value for $E_a(\text{CH}_3\text{Br})$ is the rapid increase in $\beta(\text{CH}_3\text{Br})$ with increasing temperature. The origin of activation energy barriers in these attachment reactions has been discussed by Wentworth et al. [57] and Christodoulides et al. [58].

To date, all except three of the reactions included in the FALP studies proceed via dissociative attachment with the production of atomic negative ions (see Table 1). The three exceptions are the SF_6 , C_6F_6 and C_7F_{14} , reactions in which the parent negative ions SF_6^- , C_6F_6^- and $\text{C}_7\text{F}_{14}^-$ respectively are the products. Presumably, therefore, these are three-body reactions involving first the binary attachment of an electron to the molecule followed by a collision of the excited negative ion with a helium carrier gas atom:



Actually, above 300 K, SF_5^- becomes an increasingly important product of the SF_6 reaction. Detailed studies of Fehsenfeld [59] have shown that $E_a = 0.43 \text{ eV}$ for SF_5^- production.

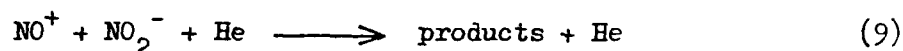
The values of β derived from these studies are considered to accurate to $\pm 15\%$ within the range 200 to 400 K and $\pm 20\%$ at the higher temperatures (up to 600 K). Further details of the result of these studies are given elsewhere [51, 52] together with comparisons of these FALP data with corresponding β and E_a values obtained from other studies. Very rarely have reliable β and E_a values been obtained previously in the same experiment. This is the great advantage of the FALP.

6. Ion-Ion Recombination Studies

Ion-Ion (or ionic) recombination describes reactions in which a positive ion and a negative ion neutralize each other. This can occur (i) in a two-body collision (binary mutual neutralization) such as



which is usually considered to involve only electron transfer at a pseudo-crossing of potential curves [60] or (ii) in an interaction in which, prior to neutralization, collisions occur between the reactant ions and neutral third bodies (i.e. the bath gas atoms or molecules in which the reaction is occurring) resulting in the dissipation of energy as the ions accelerate in their mutual Coulombic field. This process is usually referred to as three-body ionic recombination [61,62] and is written as, for example,



This process (9) is less well defined than mutual neutralization and can involve ion-ion coalescence and chemical bond disruption and formation. A further process known as collision-enhanced mutual neutralization, which combines the essential features of (i) and (ii), has also been identified [63].

The FALP is essentially a low pressure experiment (in relation to ionic recombination) and so the most detailed FALP studies have been of the two-body process. The major motivation for such studies has been to provide critical data for tropospheric and stratospheric ion chemical models and to this end most of the initial FALP work was directed towards ionic recombination reactions involving atmospheric ions. Prior to the FALP work, no reliable data at thermal energies were available relating to this important class of ionic interactions, although data were available at higher energies from merged beam studies [60].

For FALP studies of ionic recombination it is necessary to create afterglow plasmas devoid of electrons and only containing the desired species of positive and negative ions. Then either $n_+(z)$ or $n_-(z)$ (or preferably both) are measured from which the ionic recombination coefficients, α_i , are determined in the same way as the electronic recombination coefficients, α_e , are determined (see equation (2) et seq.) i.e. from reciprocal n_- (or n_+) versus z/v_p plots. Sample plots for two reactions having very different α_i are shown in Fig.5. It is also essential (as in the electronic recombination studies) to ensure that n_+ and n_- are sufficiently large that ionic recombination dominates over ambipolar diffusion in the ion-ion plasmas. These ion-ion plasmas are created by adding sufficient quantities of appropriate electron attaching gases to the thermalised afterglows.

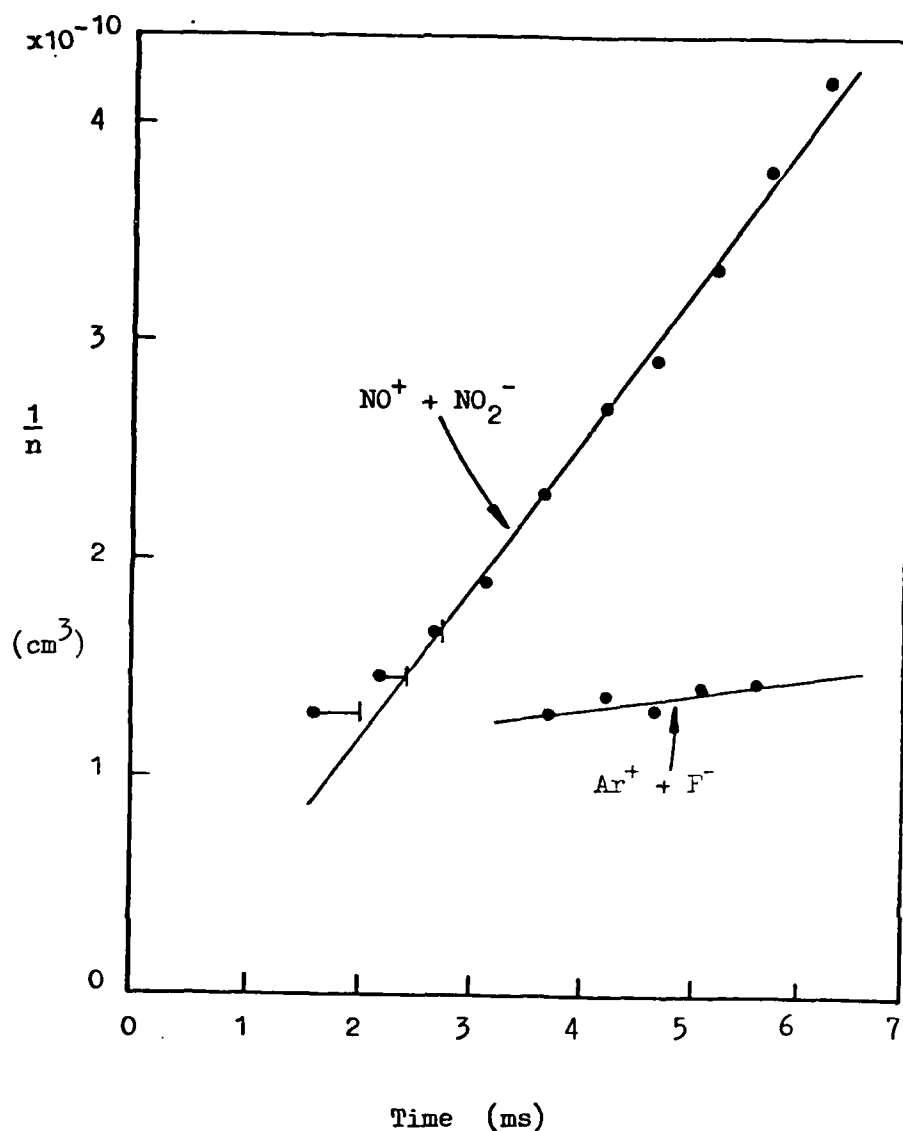


Fig. 5 Reciprocal ion density versus time ($= z/v_p$) plots obtained at 300 K using the FALP technique for $\text{NO}^+ + \text{NO}_2^-$ and $\text{Ar}^+ + \text{F}^-$ ion-ion plasmas. The data were obtained in argon carrier gas (rather than the usual helium carrier gas) in order to minimise loss of ions by ambipolar diffusion. The steeper slopes of the line relating to the molecular ion plasma results from ion-ion recombination and provides a value for the recombination coefficient, α_i for this reaction. This contrasts with the line of shallower slope for the atomic ion plasma from which only an upper limit to α_i for the $\text{Ar}^+ + \text{F}^-$ reaction can be obtained since the loss of ions is predominantly via ambipolar diffusion (see text and Table 2).

Familiarity with ion-molecule reactions and electron attachment reactions is invaluable in creating such plasmas, but also the mass spectrometer is essential to identify the positive and negative ions present in the plasmas. In order to determine n_+ or n_- from Langmuir probe data, it is necessary to know m_+ and m_- (the ionic masses as, of course, it is necessary to know m_e for n_e determinations). The essential details of these aspects of the technique are given in an early paper [64] and in a recent review [65].

Many ionic recombination reactions have been studied involving positive and negative ions of varying complexity, including reactions involving 'simple' molecular ions (e.g. NO^+ , O_2^+ , NO_2^- , NO_3^-) [66-69] 'cluster' ions (e.g. $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$, $\text{NO}_3^-(\text{HNO}_3)_m$) [68,70-72] and atomic ions (e.g. Ar^+ , Cl^-) [69]. Much attention has been given to reaction (8). The α_i for this reaction was first measured at 300 K [66] and then as a function of temperature which showed that it varied as $T^{-\frac{1}{2}}$ [71] in accordance with theoretical predictions [73]. Emission spectroscopy was then used to establish that the energy released in the reaction was largely converted into electronic excitation of the product NO [74].

A few representative α_i for reactions involving both 'simple' and 'cluster' ions are given in Table 2 where it can be seen that there is remarkably little variation of α_i with the complexity of the reaction molecular ions (see the recent review [65] for a detailed list) ranging only from $(3-10) \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ at 300 K. The most recent measurements of α_i have been for the relatively simple reactions $\text{O}_2^+ + \text{Cl}^-$ and $\text{NO}^+ + \text{Cl}^-$ (unpublished data). For these reactions, the α_i are the smallest measured to date for any reaction involving molecular ions. The magnitudes of α_i for reactions involving only atomic ions are, in general, much smaller because of the sparsity of available energy levels in the neutral atomic products into which the majority of the reaction energy must be deposited [75]. Indeed, the binary α_i expected for most of these reactions are too small to be measured using the FALP and, to date, only upper limits to α_i for several such reactions have been determined (see Fig.5 and the examples in Table 2).

The large majority of the ionic recombination reactions studied in the FALP have been carried out in helium carrier gas at pressures below one Torr. That the α_i are independent of pressure in this régime identifies the recombination as a two-body process. Two reactions (i.e. $\text{NO}^+ + \text{NO}_2^- \longrightarrow$ products and $\text{SF}_3^+ + \text{SF}_5^- \longrightarrow$ products) have been studied in helium up to pressures of eight Torr and the α_i are observed to increase with pressure more rapidly than expected on the basis of much higher pressure data [65,76]. This has been interpreted as a manifestation of the phenomenon of collision-

Table 2. Some examples of two-body ion-ion recombination coefficients, α_i , determined using the FALP at 300 K.

	Reaction	$\alpha_i \times 10^8 \text{ cm}^3 \text{ s}^{-1}$	$\bar{\sigma}_i \times 10^{12} \text{ cm}^2$
(a)	$\text{NO}^+ + \text{NO}_2^-$	6.4	1.1
	$\text{SF}_5^+ + \text{SF}_6^-$	3.9	1.3
	$\text{Cl}_2^+ + \text{Cl}^-$	5.0	1.0
	$\text{O}_2^+ + \text{CO}_3^-$	9.5	1.7
(b)	$\text{H}_3\text{O}^+(\text{H}_2\text{O})_3 + \text{NO}_3^-$	5.5	1.3
	$\text{NH}_4^+(\text{NH}_3)_2 + \text{Cl}^-$	7.9	1.4
	$\text{H}_3\text{O}^+(\text{H}_2\text{O})_3 + \text{NO}_3^- \cdot \text{HNO}_3$	5.7	1.5
(c)	$\text{Ar}^+ + \text{F}^-$	< 0.2	< 0.04
	$\text{Xe}^+ + \text{Cl}^-$	< 0.5	< 0.07

(a) one (or both) of the reactant ions is a 'simple' molecular ion, (b) one (or both) of the reactant ions is a 'cluster' ion, (c) both reactant ions are atomic. Comprehensive lists of α_i , values are given in Refs. 65 and 69. Note the very large mean thermal cross sections, $\bar{\sigma}_i$, for these reactions which have been determined by dividing α_i by the mean relative velocity between the reactants at 300 K. Note, also, the relative insensitivity of α_i (and especially $\bar{\sigma}_i$) to the complexity of the reactant molecular ions, and the relating small values of α_i and $\bar{\sigma}_i$ when both reactant ions are atomic.

enhanced binary recombination referred to earlier in this section, although much more work is required to substantiate this.

7. Summary

The exploitation of the variable temperature FALP apparatus is only just beginning. Data acquisition using a microcomputer is now fast and accurate and optical viewports have been included at several positions along the flow tube. Thus unique opportunities exist to study in detail electronic and ionic recombination, electron attachment, Penning processes etc. over a wide temperature range, including the determination of the rate coefficients for these processes and - via radiation emission studies - the states of excitation of the product ions or neutrals of some of these reactions. Also, a SIFT-type ion injector has now been added to the FALP thus providing the opportunity to inject mass-analysed ion beams into afterglow plasmas. If this can be achieved, it will enormously expand the range of ionic reaction which can be studied and will result in a further growth in the understanding of thermal energy reaction processes.

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