MEASUREMENTS OF THE DISSOCIATIVE RECOMBINATION COEFFICIENTS FOR SEVERAL POLYATOMIC ION SPECIES AT 300 K

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The dissociative recombination coefficients, α , have been measured at 300 K for several polyatomic positive ion species using a flowing afterglow/Langmuir probe (FALP) apparatus. The α range from 1.1×10^{-7} cm³ s⁻¹ for H₂F⁺ to 2.2×10^{-6} cm³ s⁻¹ for the clustered species H⁺(CH₃OH)₃. Several of the ionic species included in this study are considered to be involved in the synthesis of interstellar molecules.

1. Introduction

Electron-positive ion dissociative recombination is an important loss process in gaseous plasmas in which significant fractions of the ions are molecular. The dissociative recombination coefficients, α , for the reactions of a number of diatomic, triatomic and polyatomic species with electrons have been determined using a variety of techniques, including the collision-dominated stationary afterglow technique [1] and the merged (ion-electron) beam technique [2]. The flowing afterglow/Langmuir probe (FALP) technique, developed in our laboratory, is well suited to the determination of α over the temperature range 90-600 K (the actual range being limited by condensation or decomposition of vapours used to create the ions) for any positive ion species which can be created as the dominant ion in the flowing afterglow plasma. The well-known chemical versatility of the flowing afterglow, which has been demonstrated principally by numerous studies of ion-molecule reactions [3], has provided the opportunity to determine the α for many ionic species, including NO⁺ and O_2^+ [4], and a few simple interstellar ion species, including HCO⁺, N₂H⁺ and CH₅⁺ [5,6]. During the latter measurement programme, we also observed that, contrary to previously published work, H_3^+ ions do not rapidly dissociatively recombine with electrons. Indeed, the H_3^+ recombination coefficient, $\alpha(H_3^+)$, was too small to be measured in the FALP

The F.), was too small to be measured in the FALP previous 2614/88/\$ 03.50 © Elsevier Science Publishers B.V.

[5]. This observation has considerable significance to interstellar chemistry because of the central role which H_3^+ ions play in that chemistry [7–9]. From a practical viewpoint, this observation is also important in that it provides the opportunity to study α for a wide range of ionic species in the FALP by the following method. It is simple to create H_3^+ / electron afterglow plasmas since these do not decay significantly by recombination. Because protons are readily transferred from H_3^+ to most molecular species (a consequence of the small proton affinity, PA, of H_2), then the addition of a sufficient concentration of a molecular species, X, to a H_3^+ /electron afterglow will create a plasma consisting of XH⁺ ions and electrons following the reaction

$$\mathbf{H}_{3}^{+} + \mathbf{X} \rightarrow \mathbf{X}\mathbf{H}^{+} + \mathbf{H}_{2} \,. \tag{1}$$

Such reactions are always rapid when PA(X) exceeds $PA(H_2)$, as is the case for many molecular species, X. Thus, we have exploited this process in the present study to determine the α for a number of molecular ions using the FALP. Several of the molecular ions included in this study are considered to be involved in interstellar molecular synthesis.

2. Experimental

The FALP technique has been described in detail previously [4,10,11]. It has been used successfully

to determine ion-ion recombination coefficients [12] and electron attachment coefficients [11,13] as well as electron-ion recombination coefficients [4,5]. For the last mentioned studies, a microwave discharge is created upstream in flowing helium carrier gas at a pressure of about 1 Torr. The afterglow formed downstream contains metastable helium atoms. He^m. and He_2^+ ions (formed by the ternary association of He⁺ ions with He atoms). The addition of sufficient argon downstream of the discharge (but upstream of the reaction zone where recombination is to be observed) destroys both the He^m and He₂⁺, thus producing Ar^+ ions. The addition of H_2 to the Ar⁺/electron afterglow plasma rapidly converts the Ar^+ to ArH^+ , which then reacts rapidly with H_2 thus forming a non-recombining H₃⁺/electron afterglow plasma. In this plasma, loss of electrons occurs only via the slow process of ambipolar diffusion as is readily demonstrated by measuring the reduction in the electron density, $n_e(z)$, with distance z, along the axis of the flow tube using a movable Langmuir probe, which is the primary diagnostic tool in the FALP. The addition of a gas or vapour, X, results (according to eq. (1)) in the rapid creation of a recombining plasma consisting of XH⁺ ions and electrons. This is manifest by an increase in the gradient in $n_{c}(z)$ immediately downstream of the inlet port through which X is introduced (i.e. in the reaction zone). This port is located 57.5 cm from the sampling point of the downstream quadrupole mass filter which is used to identify the ion types present in the plasma. It is then a simple matter to analyse the $n_{\rm e}(z)$ data to determine α for the XH⁺ ions in the afterglow plasma. Since diffusive loss can be ignored,

$$v_{\rm p} \,\partial n_{\rm e}/\partial z = -\alpha n_{\rm e}(z) \,n_+(z) \,, \tag{2}$$

where the XH⁺ number density, $n_+(z) = n_e(z)$ in the quasi-neutral plasma, and v_p is the plasma flow velocity which is readily determined as described in a previous paper and is typically $10^4 \text{ cm}^3 \text{ s}^{-1}$ [14]. The continuity equation (2) is readily integrated and indicates that a plot of $n_e^{-1}(z)$ against z should be linear with a slope equal to α/v_p . All the α reported below were obtained using this analytical approach at a helium carrier gas temperature of 300 K.

3. Results

A wide variety of molecules, X, were chosen for this study, these varying in complexity from HF to C₂H₅OH. Thus, the α for the corresponding protonated molecules XH^+ , i.e. H_2F^+ , $C_2H_5OH_2^+$, etc. were determined at 300 K. Fortunately, the rate coefficients and product ions for the reactions of H_3^+ with the majority of the molecular species X included in this work (table 1) had been studied previously [15] and these data were a helpful guide in understanding the chemistry involved in the production of the recombining FALP plasmas. For the H_3^+ reactions which had not been studied previously (i.e. for X = HF, CH_3C_2H , CH_3SH , C_2H_5OH and CH_3NH_2), we measured the rate coefficients at 300 K in a parallel selected ion flow tube (SIFT) study. All five reactions proceeded rapidly, the rate coefficients, k(X), being close to the respective collisional rate coefficients.

The terminating ions of most of these primary $H_3^+ + X$ reactions (and any subsequent secondary reactions of the primary product ions with X) are the protonated ions XH^+ (except for the reaction involving CH_3C_2H which results in a mixture of $C_3H_5^+$ and $C_6H_5^+$; see table 1). For some X, the proton-transfer reaction with H_3^+ is sufficiently exothermic (i.e. $PA(X) \gg PA(H_2)$) that dissociative proton transfer and other chemistry occur, e.g.

Table 1

Dissociative recombination coefficients measured at 300 K using the FALP $% \left({{\rm{T}}_{\rm{ALP}}} \right)$

Recombining ion	Recombination coefficient, α (cm ³ s ⁻¹)	Source gas, X
H ₂ F ⁺	1.1(-7)	HF
HCO ₂ ⁺	3.4(-7)	CO_2
$C_3H_5^+/C_6H_5^+ \approx 1/1$	3.5(-7)	CH ₃ C ₂ H
H ₂ CN ⁺	3.5(-7)	HCN
H ₃ S ⁺	3.7(-7)	H_2S
HN ₂ O ⁺	4.2(-7)	N ₂ O
C₄H³	6.2(-7)	C ₂ H ₂
C₂H₅⁺	7.4(-7)	C ₂ H ₆
CH ₃ SH ⁺	7.7(-7)	CH ₃ SH
HCS ₂ ⁺	9.1(-7)	CS,
CH ₃ NH ⁺	1.4(-6)	CH ₃ NH,
$H^{+}(CH_{3}OH)_{1,2,3}$	$8.8(-7) \rightarrow 2.2(-6)$	CH ₃ OH
$H^+(C_2H_5OH)_{1,2,3}$	$1.1(-6) \rightarrow 1.9(-6)$	C ₂ H ₅ OH

$$H_3^+ + CH_3NH_2 \rightarrow CH_3NH_3^+ + H_2,$$

→ $CH_3NH_2^+ + H_2 + H,$
→ $CH_2NH_2^+ + H_2 + H_2.$ (3)

However an excess of CH_3NH_2 ensures that secondary reactions occur, generating $CH_3NH_3^+$ as the terminating ion in the plasma. Also the H_3^+ reaction with C_2H_6 proceeds thus,

$$H_3^+ + C_2 H_2 \rightarrow C_2 H_5^+ + 2H_2$$
 (4)

and, since the rate coefficient for the subsequent reaction of the product ion $C_2H_5^+$ with C_2H_6 is small, the $\alpha(C_2H_5^+)$ could be determined. On addition of C_2H_2 to the H_3^+ plasma, rapid primary and secondary reactions led to $C_4H_3^+$:

$$H_3^+ + C_2 H_2 \rightarrow C_2 H_3^+ + H_2$$
 (5)

$$C_2H_3^+ + C_2H_2 \rightarrow C_4H_3^+ + H_2$$
, (6)

allowing $\alpha(C_4H_3^+)$ to be obtained but not $\alpha(C_2H_3^+)$.

The α which have been determined in this study are given in table 1 and the gases or vapours, X, from which the ions were generated are indicated. To our knowledge, the α for these recombination reactions have not been determined previously and so comparisons cannot be made. The measured α are considered to be accurate to $\pm 25\%$. For the mixture $C_3H_5^+/C_6H_5^+$ ions (in approximately equal concentrations) a "mean α " is all that could be obtained. However, if the α values for C₃H⁺₅ and C₆H⁺₅ had been greatly different from each other then this would have been apparent as a curvature of the plots of n_{ϵ}^{-1} against z (referred to in section 2). Mean α are also given in table 1 for the protonated clusters of CH₃OH and C₂H₅OH. The smallest value of α in each case refers to the protonated ("core") ions $CH_3OH_2^+$ and $C_2H_3OH_2^+$. As the flow rates (number densities) of the CH₃OH and C₂H₅OH were increased in the plasma afterglow, clustering of the parent molecules to the "core" ions occurred (as indicated by the mass spectrometer) and the derived α increased as a result by a factor of two to three. The largest value of α in each case indicates the *lower limits* to the α for the cluster ions H⁺(CH₃OH)₃ and $H^+(C_2H_3OH)_3$. Increases in α by similar factors have been observed previously for the clustering of

 H_2O ligands to H_3O^+ [16] and NH₃ ligands to NH₄⁺ [17].

The α in table 1 are arranged vertically in order of increasing magnitude so that it can be seen that there is a general trend towards an increasing magnitude of α with increasing complexity (atomicity) of the recombining ion, as previous work has also indicated [18]. However, this is by no means a "golden rule" and each recombining system should be considered independently (note, for example, that $\alpha(CH_5^+)=1.1\times10^{-6}$ cm³ s⁻¹ at 300 K [5,6], which exceeds $\alpha(CH_3OH_2^+)$, see table 1). These are unique recombination data which will find applications in calculations of deionization rates for laboratory plasmas and especially for dense interstellar cloud chemistry.

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