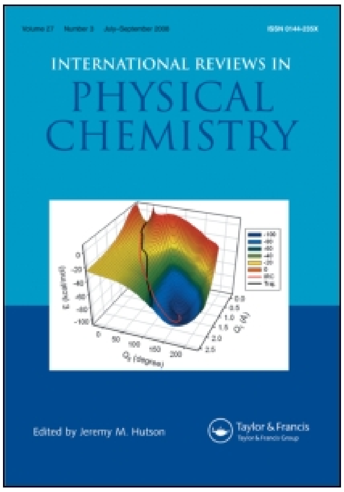

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The recombination of electrons with complex molecular ions

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The last few years have seen a number of measurements performed of recombination rates for electrons with (mostly hydrocarbon) polyatomic ions. This review sets out to summarize the work to date and to provide some analysis of trends seen amongst these measurements. A discussion is given of cluster ion recombination which is inherently different from that for covalently bonded molecules. Finally an update of recent investigations of product branching ratios is given with particular reference to merged-beam and afterglow studies of the dissociative recombination of H_3O^+.

1. Introduction

In an ionized medium, the constituent ions can undergo charge-changing collisions with neutral atoms and molecules but the ultimate decay of the charge is governed by collisions in which positive ions capture free electrons, electrons bonded into negative ions or electrons on the surfaces of solid structures. The general classification of this type of process is *recombination*. In this article, we shall restrict ourselves to a discussion of the former process and in particular to the case where the recombining ion is molecular in form. With molecular ions, it is possible for the neutral molecule, formed by electron capture, to disperse the excess energy that has been previously injected into the system to produce the ion, in the form of fragment kinetic energy, generated when the recombined neutral molecule breaks apart or dissociates. This is known as *dissociative recombination*. This reaction was first postulated by Bates [1, 2] to explain the rapid decay of the night-time E region of the ionosphere and the mechanism for this reaction was investigated experimentally in a series of pioneering studies performed by Biondi and co-workers in the early 1950s and 1960s [3]. The process that Bates first envisaged involved the capture of the electron by the molecular ion into an excited neutral state that lies above the ion state, in the vicinity of its equilibrium position, and that this state would subsequently undergo dissociation, its potential energy falling below that of the molecular ion and being transferred to the kinetic energy of the products. This is referred to as the *direct mechanism* for dissociative recombination.

This simple picture was subsequently modified by the suggestion by Bardsley [4] and Chen and Mittleman [5] that electron capture could also occur to form a vibrationally excited Rydberg state that would likewise lie above the ion potential curve, subsequently decaying by pre-dissociation via some suitable intersecting neutral state. This is referred to as the *indirect mechanism* for dissociative recombination. A number of workers [6–9] have investigated the interference that can occur between these two processes, leading to resonances in the cross-section for dissociative recombination for the case of diatomic molecules. An extension of the direct mechanism, to include the effects of subsequent interactions by lower-lying Rydberg states has been suggested by O'Malley [10] in what has become known as the *full direct mechanism* [11]. It is now well established that the indirect process can have a

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considerable influence on the recombination of diatomic molecular ions. What is less well understood is exactly what role indirect electron capture to form Rydberg states plays in the recombination of polyatomic molecular ions. Since these types of molecule have many different vibrational modes, it has been suggested [12–14] that this will lead to very large recombination rates. A considerable amount of confusion has arisen concerning this since indeed very large rates (as high as 10^{-5} cm^3 s^{-1}) have been found for some cluster ion species [15, 16] and this has been interpreted as being due to the range of states available for the electron capture process. More recently, Bates [17] has re-examined this hypothesis and has rejected it, arguing that the necessity to violate the Born–Oppenheimer approximation, involved in the indirect mechanism, will limit the number of available capture transitions so that the recombination rate for polyatomic molecules will not become excessive. The so-called $\Delta v = +1$ propensity rule, first proposed by Berry [18], was invoked by Bates to support this statement. In a separate analysis, Bates [19, 20] has sought to explain the large observed recombination rates for cluster ions as being the result of the large electron capture width involved in such processes caused by the shallowness of the gradient of the crossing states, through which the electron capture and subsequent dissociation proceeds. This so-called *super-dissociative recombination* [20] is not limited to complex species, however, being responsible for the large recombination rates observed for rare-gas molecular ions.

2. Applications

Polyatomic ions, and in particular hydrocarbon ions, are formed in a number of media and their recombination dynamics are very important to the physical and chemical state of these media. Perhaps one of the most studied applications of polyatomic molecular ion chemistry has been the astrochemistry of interstellar clouds [21] where more than 100 molecular species have been identified using spectroscopic astronomical techniques [22]. Some of these molecules are quite complex, having as many as 14 atoms. Perhaps just as tantalizing is the possibility that a long unidentified series of features in the infrared and visible spectrum of the interstellar medium, the so-called *diffuse interstellar bands*, may be attributable to the presence of *polycyclic aromatic hydrocarbon* ions [23, 24]. This raises the question of even more complex chemistry that must be evaluated and modelled to determine whether the existence of such species is feasible and viable in the cold, low-density but strongly irradiated environment of deep space.

Hydrocarbon ions have been identified as an important component of the ionospheres of some of the moons of the giant planets including Titan and Triton. The chemistry of these atmospheres has been modelled [25–27] and the need for information concerning the rate coefficients for aliphatic hydrocarbon molecular ions has been indicated.

On a terrestrial level, a wide range of hydrocarbon and polycyclic aromatic hydrocarbon molecular ions have been identified in flames [28, 29] and have been implicated (although not without debate) in the formation of soot precursors [30].

Electron–ion recombination has been recognized to play a key role in the conversion of electrical energy into chemical energy in the ignition of gasoline in the spark ignition engine [31] and much information is needed to further our understanding the chemistry of this surprisingly sparsely researched phenomenon. Such information may even improve our ability to monitor and diagnose spark ignition engine performance [32].

3. Experimental techniques

Our knowledge of the recombination of complex ions is derived almost entirely from experimental investigations. It is worthwhile therefore to review briefly the methods by which these species may be studied. These methods essentially fall into two categories involving merged beams and afterglow techniques. In the former, mass-analysed beams of the ions to be studied are produced in an ion source, accelerated to a high energy (high velocity) and then made to interact with a beam of electrons (of equal or nearly equal velocity) [33]. The advantage of this type of experiment is that one deals with only one ion which is well identified at least with respect to mass. In past experiments, the internal energies of the ions have often been less well defined although by using high-pressure ion sources [34], ion traps [35–57] and, most recently, storage ring technologies [38] it is possible to produce beams in which the ions have vibrationally cooled, either radiatively [39, 40] or collisionally [41]. One can determine exactly the interaction energy between the electrons and the ions, knowing the primary beam velocities and their intersection angle and this interaction energy can be smoothly varied over a very wide range (from millielectron volts to tens of electron volts). Since one detects the products directly, one can apply techniques which allow the identity [42–45] and internal energy [46] of the products to be determined. The main drawbacks to this type of approach for the study of complex ions in the past was that, as implemented in various laboratories, the complexity of the ions was limited by the ability to work with rather light particles. This was determined by the available accelerators [47] and by the design of the ion optics used to inject ions into storage rings [48] although recently, for example, C_{60}^+ has been successfully stored at the Astrid storage ring at Aarhus in Denmark [38, 49].

The second class of experiments that has been directed towards this field involve the method of afterglows. The original implementation of this was the stationary afterglow (SA) technique which has been described in detail in the review by Bardsley and Biondi [3]. In these experiments, an afterglow is created in a vacuum vessel containing the gas to be studied, by absorption of a microwave pulse or by photoionization. The subsequent decay of the electron density in the chamber, following the termination of the excitation pulse, is then monitored using microwave absorption techniques and, from this decay rate, the recombination rate of the ions in the plasma can be determined. Mass spectrometric sampling of the ions in the afterglow is essential to identify the actual species undergoing recombination. Although responsible for much of our early knowledge of dissociative recombination, this technique presents a number of technical difficulties [50] and has largely been superseded by methods in which flowing afterglows are used. In the flowing-afterglow langmuir probe (FALP) technique [51, 52], the ion to be studied is created by reactions between rare-gas buffer ions and a suitable precursor gas. The initial ions (and the associated free electrons) are created usually by means of a microwave discharge formed at one end of a tube through which the buffer gas is made to flow, under the action of powerful pumps. The electron density in the afterglow, downstream of the discharge region, can then be measured as a function of the distance along the flow (and therefore as a function of time) using a moveable Langmuir probe. By monitoring the rate of decay of the electron density, the total recombination coefficient of the ions in the afterglow, can be determined. Provided that the afterglow is dominated by one ion, its individual recombination rate can therefore be obtained. The FALP–mass spectrometry (MS) technique [53] is a variation on the FALP method and employs a moveable mass spectrometer, in combination with a moveable Langmuir probe to measure the decrease in both the electron and the ion densities along the flow tube. This technique is much more specific and can be used in plasmas where there are a mixture of ions, provided that they are terminal ions, that is ions that are destroyed by recombination and not by ion–molecule reaction with another species.

In a number of experiments, detection of the products has been accomplished by means of optical spectroscopy, enabling branching ratios for different dissociation channels [54] and the internal energy of the recombination products [55–57] to be measured. The technical details concerning these various experimental methods are explained in detail in the publications cited in this section.

4. Previous reviews of dissociative recombination

A large number of reviews have been written on the subject of dissociative recombination and rather than going over ground that has already been extensively covered, the reader is directed towards these publications. Early work on this subject has been described by Bardsley and Biondi [3], Oskam [58] and Eletskii and Smirnov [59] these reviews dealing mainly with results obtained for atmospheric and rare-gas ions, studied by stationary afterglow and shock tube methods. The developments of the merged-beam and flowing afterglow techniques, are covered in reviews by Mitchell and McGowan [60], McGowan and Mitchell [61], Mitchell [62] and Smith and Adams [51]. The state of the art experimentally, as of 1990, was described by Mitchell [63] in an article that heralded the need to address the problem of the recombination of more complex species and in particular for the need for the measurement of branching ratios for final-state dissociation channels. This article is complemented by the reviews of Smirnov [64] and of Biondi [12] who specifically addressed the subject of cluster ion recombination.

Theoretical aspects of dissociative recombination, prior to 1990 have been the subject of reviews by Bardsley [65] and by O'Malley [66] who discussed the basic theory of the subject. Guberman [67, 68] has discussed the calculation of the potential energy curves; the basis for a clear understanding of the dynamics of the electron capture and subsequent dissociation process, and in 1986 Giusti-Suzor [69] reviewed the multichannel quantum defect theory which has proved to be a very powerful tool for taking account of the participation of the neutral Rydberg manifold in the capture process.

In more recent years a number of important reviews have appeared. In an article, published in 1994, Bates [70] has surveyed the recent theoretical and experimental developments in the field of dissociative recombination. This is of course a topic not only which he pioneered but also to which he devoted much of his efforts and to which he made major contributions, in the last years of his life. The early 1990s also saw major advances in our understanding of the problem of identifying final products of the dissociation process with the coupling of spectroscopic techniques to flowing afterglow apparatuses. This work has been reviewed extensively by Adams [71]. One of the most dramatic developments in the field of dissociative recombination research has been the application of ion storage ring technology to the measurement, not only of recombination cross-sections but also of product branching ratios and energy distributions between the various dissociation fragments. A number of reviews of this subject have appeared, notably those of Larsson [38, 72]. New developments have also occurred in theory with the development of a semiclassical theory by Flannery [73] and of the tunnelling mode theories, which do not require there to be a crossing of potential energy curves for recombination to proceed. These have been reviewed by Guberman [74] and Bates [70]. General reviews of electron–ion recombination have been given by Flannery [75] and in the book by McDaniel *et al.* [76].

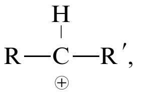
In addition to these specific articles, the interested reader is also directed to the proceedings of the three international symposia that have been held so far on the topic of dissociative recombination [77–79]. These books contain many articles covering theory, experiment and applications.

5. Total rate coefficients

Table 1 lists some 33 molecular ion species that could be classified as complex, having between four and 25 atoms. It should be stated that these ions were identified mass spectrometrically and so, in most cases, the exact structure of the molecules must be a matter for some speculation. The molecules $C_6H_6^+$, $C_7H_5^+$, $C_6H_5{-}CH_3^+$ and possibly $C_3H_3^+$ are believed to be cyclic in form [82, 85] while $C_{10}H_8^+$ and $C_{14}H_{10}^+$ are believed to be polycyclic. Lehfaoui *et al.* [86] have recently examined the ions formed from a series of straight-chain alkanes from methane to octane and the ions derived from these molecules are believed to contain saturated bonds although they could be isomerized into branched form. Molecules such as ethylene and acetylene containing unsaturated bonds have been studied by these workers but the ions derived are not directly related to the parents (e.g. $C_4H_9^+$ in the case of ethylene) and so are not believed to be necessarily representative of unsaturated species. It would seem that such species react rapidly in the afterglow environment being destroyed via ion–molecule reactions rather than by electron recombination.

Given the fact that the ions listed in the table are terminal ions under the afterglow conditions in which they were created, it must be said that their subsequent loss from a plasma environment (neglecting wall effects) is dominated by recombination. This raises an interesting question for the reactivity of molecular ions (at least with respect to ion–molecular reactions other than charge exchange and proton transfer [88]) seems to decrease with increasing size. In flames, however, ions with molecular weight in excess of 1000 are found [29].

One thing that is evident from the rates listed in table 1 is that there seems to be little correlation between the number of atoms in the molecule and the rate coefficient. This is particularly evident for the case of the protonated ions $C_2H_5^+$ to $C_8H_{17}^+$ derived from alkanes which all display essentially the same rate coefficient (between 6×10^{-7} and 8×10^{-7} cm^3 s^{-1}). These ions can be represented as follows:



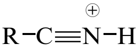
$$\mathrm{R{-}\overset{\displaystyle H}{\underset{\oplus}{C}}{-}R'},$$

where R and R′ are alkyl groups (except for the case of $C_2H_5^+$ where R′ is H). Given the similarity of their recombination rates, it would seem reasonable to surmise that the capture process for these ions takes place at a privileged site and that this will be the same site for each species. In such molecules, the electrons are typically very immobile, being strongly associated with the carbon atoms. Thus one could make the hypothesis that the recombination occurs through the neutralization of the protonated site, it being fixed for each species. Presumably this would release a hydrogen atom or cause the severing off of a CH_3 radical which would carry away the recombination energy. Such dissociations involved the rupture of a single bond which should be relatively easy and so the absolute rate coefficients are rather large.

Table 1. Recombination rates coefficients for complex ions, sorted by ascending rate.

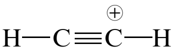
Molecular formula	Recombination rate (10^{-7} cm^3 s^{-1})	Technique used	Reference
$C_2H_2^+$	2·70	Merged beam	[80]
HSO_2^+	2·70	FALP	[81]
$C_{10}H_8^+$	3·00	FALP–MS	[82]
CH_3CNH^+	3·30	FALP	[81]
HCO_2^+	3·40	FALP	[83]
$C_3H_5^+/C_6H_5^+$	3·50	FALP	[83]
$HCNH^+$	3·5	FALP	[83]
H_3S^+	3·70 (5·20)	FALP	[83]
CH_3CHOH^+	3·90	FALP	[81]
HN_2O^+	4·20	FALP	[83]
$C_2H_3^+$	4·50	Merged beam	[80]
$C_2H_5CNH^+$	4·70	FALP	[81]
$C_7H_{15}^+$	5·50	FALP–MS	[82]
$C_{15}H_9^+$	5·50	FALP–MS	[84]
$C_2H_5^+$	6·00 (7·4)	FALP–MS (FALP)	[82, 83]
$C_4H_3^+$	6·20	FALP	[83]
C_6H_5–CH_3^+	6·50	FALP–MS	[85]
$C_3H_3^+$	7·00	FALP–MS	[82]
$C_7H_5^+$	7·00	FALP–MS	[82]
CH_5^+	7·00 (11·00, 14·0)	FALP–MS (FALP)	[52, 86, 87
$C_5H_{11}^+$	7·20	FALP–MS	[86]
$C_{14}H_{10}^+$	7·5	FALP–MS	[84]
$C_6H_{13}^+$	7·60	FALP–MS	[86]
$CH_3SH_2^+$	7·70	FALP	[83]
$C_8H_{17}^+$	8·2	FALP–MS	[86]
$C_3H_7^+$	8·30	FALP–MS	[86]
$C_4H_9^+$	8·30	FALP–MS	[86]
$C_5H_3^+$	9·00	FALP–MS	[82]
HCS_2^+	9·10	FALP	[83]
$C_6H_6^+$	10·0	FALP–MS	[82]
H_3O^+	10·0	SA	[15]
$CH_3NH_3^+$	14·0	FALP	[83]
NH_4^+	15·0	SA, (ion trap)	[16, 35]

From table 1, we see that the benzene ion $C_6H_6^+$, the toluene ion C_6H_5–CH_3^+ and the phenanthrene ion $C_{14}H_{10}^+$ also display rather large rates (10×10^{-7}, $6{\cdot}5\times10^{-7}$ and $7{\cdot}5\times10^{-7}$ cm^3 s^{-1} respectively). In these three cyclic cases, the electrons are quite mobile and so, as the electron approaches, it will easily be presented with a site for recombination. On the other hand, the rates for the molecules

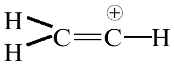

$$R{-}C{\equiv}\overset{\oplus}{N}{-}H$$

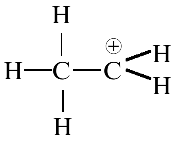
(where R is H, CH_3 or C_2H_5) are rather small ($3{\cdot}5\times10^{-7}$, $3{\cdot}3\times10^{-7}$ and $4{\cdot}7\times10^{-7}$ cm^3 s^{-1}) compared with the rates for $CH_3NH_3^+$ or NH_4^+. In these molecules, the positive charge on the molecule (but also the electron density) is strongly concentrated around the C≡N bond. Electron mobility is greatly reduced in such species and so they might again be expected to present a specific privileged recombination site. Breaking of the triple bond will be unlikely [89], and so the recombination should proceed through the throwing off of a hydrogen atom or the CH_3 or C_2H_5 radical.

Another example of the role of electron mobility can be seen by comparing the rates for the ions



$H-C\equiv\overset{\oplus}{C}-H$





which from table 1 are seen to have values of $2{\cdot}7 \times 10^{-7}$, $4{\cdot}5 \times 10^{-7}$ and $6{\cdot}0$ $(7{\cdot}4) \times 10^{-7}$ $cm^3\ s^{-1}$ respectively. As we go from a triply bonded species, to a double bond and then to a single bond, the electron density around the C atom decreases, making the approach of an incoming electron easier and facilitating capture, thus resulting in the larger observed recombination rates.

The role of electron mobility in determining the electron capture efficiency of complex species was first proposed by Bates [90] who used this concept to explain the increase in the recombination rate with cluster size, as observed for water clusters. This is discussed in the next section.

A final point to notice is that the absolute magnitude for these rate coefficients is not actually very large compared with those found for cluster ion species (see table 2 later), and even for heavy rare-gas molecular ions (see table 3 later). This is very important to highlight for the experience of discovering such large rates has led a number of us in the field to imagine that complex species will recombine with very high rates [91] which will increase with increasing complexity and clearly this is false.

It should be pointed out, however, that in the studies carried out using afterglow techniques, one is inevitably constrained to examine ions that are reasonably stable in the plasma, that is ions which are not destroyed either rapidly by ion–molecule reactions or by recombination. Thus one cannot say that the results listed in table 1 are in themselves exhaustive and that there are no complex molecular ions that would display very high recombination rates were they not to meet their demise via a competitive process. This is an interesting question from a fundamental standpoint although it may not necessarily be of prime importance in evaluating the chemistry and physical properties of practical ionized environments. If a molecular structure, which would in isolation recombine rapidly, becomes reactively metamorphized into a structure that recombines less rapidly, then its existence will be masked. Thus the FALP–MS technique, for example, is an invaluable tool for evaluating the effects of recombination of ions that would exist in the interstellar medium or a planetary environment but it is somewhat limited for evaluating the fundamental physics behind the recombination process except in simple cases with terminal ions. In this regard, the beams method, where a single ion can be extracted from a source and independently reacted with single electrons is inherently better suited to such a surgical investigation. The subsequent utilization of the knowledge thus gained must rely more heavily, however, on the accuracy of the chemical model used for the description of the chemical synthesis in an ionized environment containing a mixture of parent species.

6. Cluster ion recombination

A number of experimental investigations of the recombination of cluster ions have been made and the results of these investigations are given in table 2. As can be seen from the table, these species typically display very high recombination rates compared to normal, polyatomic species.

Table 2. Recombination rate coefficients for cluster ions.

Formula	Rate coefficient (10^{-7} cm s^{-1})	Technique	Reference
H_5^+	18·0	SA	[92]
$N_2.N_2^+$	14·0 (26·0)	SA	[93, 94]
$CO.CO^+$	13·0	SA	[95]
$(CO_2).CO^+$	19·0	SA	[95]
$O_2.O_2^+$	42·0	SA	[96]
$NO.NO^+$	17·0	SA	[97]
$(H_2O)_1.H_3O^+$	25·0	SA	[15]
$(H_2O)_2.H_3O^+$	30·0	SA	[15]
$(H_2O)_3.H_3O^+$	36·0	SA	[15]
$(H_2O)_4.H_3O^+$	36·0	SA	[15]
$(H_2O)_5.H_3O^+$	50·0	SA	[15]
$(H_2O)_6.H_3O^+$	$>$ 100·0	SA	[15]
$(NH_3)_1.NH_4^+$	28·0	SA	[16]
$(NH_3)_2.NH_4^+$	27·0	SA	[16]
$(NH_3)_3.NH_4^+$	30·0	SA	[16]
$(NH_3)_4.NH_4^+$	30·0	SA	[16]
$(CH_3OH)_1.H^+$	(8·80	FALP	[69]
$(CH_3OH)_2.H^+$	↓	FALP	[69]
$(CH_3OH)_3.H^+$	22·0)	FALP	[69]
$(C_2H_5OH)_1.H^+$	(11·0	FALP	[69]
$(C_2H_5OH)_2.H^+$	↓	FALP	[69]
$(C_2H_5OH)_3.H^+$	16·0)	FALP	[69]
$(CH_3CO)_2H^+$	14·0	FALP	[68]
$O_2.Na^+$	50·0	SA	[98]
$CO_2.Na^+$	50·0	SA	[98]

Bates [90, 99] has investigated the reasons for these large recombination rates and has shown that cluster ions can be separated into two families. The first type of clusters are dimers such as $N_2.N_2^+$, $O_2.O_2^+$, etc. These molecules are bound by electron delocalization (exchange) forces and have rather low dissociation energies. Their dissociative recombination results in the production of molecules in highly excited Rydberg states so that there are many final channels available. In addition, the gradients of the dissociating states will be very low, ensuring a large overlap between the wavefunctions of the ion and neutral states. These two facts lead to large probabilities for recombination which Bates [20] has described using the term *super-dissociative recombination* and it is interesting to note that such behaviour is not limited only to dimer ions but also shows up in rare-gas molecular ions, whose rates are listed in table 3.

Experiments by Shui and Biondi [100, 101] showed that many of the products of rare-gas recombination are highly excited although recent studies by Ramos *et al.* [102] have indicated that ground-state atoms also play a major role for Ne_2^+ and Ar_2^+. It is interesting to note that super-dissociative recombination can occur even for H_2^+ recombination [103]. Measurements of highly excited products that can only be formed in this case from the recombination of H_2^+ ions in sparsely populated, high vibrational states ($v > 15$) have indicated that the cross-sections for individual levels have to be very large (greater than 1×10^{-13} cm^2) in order to give rise to the observed numbers of excited products. Again the reason for this is the high density of suitable crossing states and the shallow gradients of such states.

Table 3. Recombination rate coefficients for rare-gas molecules.

Molecule	Rate coefficient (10^{-7} cm s^{-1})	Technique	Reference
He_2^+	0·001–0·1	SA	[104]
Ne_2^+	1·75	SA	[105]
Ar_2^+	9·1	SA	[106]
Kr_2^+	16·0	SA	[100]
Xe_2^+	23·0	SA	[101]

The second family of ions that demonstrate very large recombination rates are the cluster ions such as $H_3O^+.(H_2O)_n$, $NH_4^+.(NH_3)_n$, etc., which are bound by proton bridges. For example, $(H_3O^+).H_2O$ can be represented as $(H_2O).H^+.(OH_2)$. These species are different from the dimer ions in that they have deep potential wells and, since there is not sufficient energy to allow for the production of products in excited electronic states, this means that only a single state is available to drive the recombination. The reason that such species exhibit large recombination rates is that the reaction proceeds via electron capture by the proton which, being neutralized, releases the attached molecules which carry off the recombination energy. This neutralization involves a single-electron transition as opposed to the double-electron transition normally required for dissociative recombination and, since single-electron transitions are much more probable than double-electron transitions, this explains the large observed rates.

From this model of Bates for the proton bridge clusters, one would imagine that the process would be very site specific and so one would not expect to find much variation in the recombination rate with increasing cluster size, as seen for example in the case of the protonated alkanes. In fact, as seen in table 2 this is what is found for the ammonia clusters. Water clusters on the other hand are observed to have rate coefficients which increase with increasing size and in fact Bottcher's [13] model for cluster recombination predicted this behaviour. Bates explains this variation by pointing out that the ionization potential for O is very similar to that for H, so that electrons in this molecule should be very mobile. Thus, when the electron approaches such a cluster ion, it will always be presented with a suitable ion site to recombine with and, the larger the cluster, the larger the area presented. It is not clear, however, from this model how the rate is expected to vary beyond the first layer of solvent H_2O molecules surrounding the central positive charge.

The very large recombination rates, characteristic of such cluster ions, must have important consequences for the electron density of ionized environments. One such consequence has been examined by Jones *et al.* [107] who suggested that water cluster ion recombination is responsible for the rapid neutralization of certain types of meteor trails in the high atmosphere. A meteoroid, if it contains some frozen water ice, must spray out water vapour as it undergoes violent heating upon entering the atmosphere. The debris from the meteoroid becomes photoionized by radiation emanating from the shock heated fragments, forming a short ionized wake, referred to as a head echo which is visible by radar. Since this trail is seen to be very short, this signifies that the ionization is rapidly neutralized. Water cluster ions, with their enormous recombination rates, provide a suitable means of effecting such rapid neutralization. Thus this model can explain the observed behaviour of these meteor trails and in doing so gives us some information concerning the structure and composition of the meteoroids.

7. Branching ratio measurements

The identification of the final products of the recombination of complex ions has been well reviewed by Adams [71] and it would be a duplication of effort to discuss prior work in this area in this report. Instead, we shall confine our discussion to some recent work that illustrates the importance of this aspect of recombination.

Two recent measurements have been reported of the branching ratios for the recombination of H_3O^+:

$$\begin{aligned} H_3O^+ + e &\rightarrow H_2O + H && 6{\cdot}4\ \mathrm{eV}\ (N_1),\\ &\rightarrow OH + H_2 && 5{\cdot}7\ \mathrm{eV}\ (N_2),\\ &\rightarrow OH + H + H && 1{\cdot}3\ \mathrm{eV}\ (N_3),\\ &\rightarrow O + H_2 + H && 1{\cdot}4\ \mathrm{eV}\ (N_4), \end{aligned}$$

where the energies indicated are for the production of ground state products and N_i is the fraction of the total reaction appearing in that particular channel. This reaction has important astrophysical implications. Water as an interstellar molecule plays a key role in the cooling of molecular clouds. Such cooling leads to gravitational collapse and star formation. Channel 1 shown above is believed to be the primary source for H_2O and so the fraction N_1 is a critical value, needed for astrochemical models. The branching fractions have recently been determined in measurements, using a gridded detector technique at the ASTRID storage ring [108] and values of $N_1 = 0{\cdot}33 \pm 0{\cdot}08$, $N_2 = 0{\cdot}18 \pm 0{\cdot}07$, $N_3 = 0{\cdot}48 \pm 0{\cdot}08$ and $N_4 = 0{\cdot}01 \pm 0{\cdot}04$ have been found. Thus we see that this experiment indicates that dissociative recombination does result in the production of water.

Unfortunately, dissociative recombination, being a very complex process, is often the subject of controversy and a recent afterglow measurement of the branching fractions by Williams *et al.* [109] has yielded values of $N_1 = 0{\cdot}05$, $N_2 = 0{\cdot}36$, $N_3 = 0{\cdot}29$ and $N_4 = 0{\cdot}30$, in contradiction to the storage ring results. This suggests that, in the afterglow, the water molecules are mostly dissociated *en route* to the asymptotic limit for that channel. No doubt this will be the subject of more investigation.

8. Conclusions

This brief overview of the subject of complex ion recombination highlights the fact that at least the basic reaction rates can perhaps be understood from a knowledge of bonding in organic chemistry. Many more examples will have to be examined, however, to put this hypothesis on a firm footing. The determination of final product yields is still in its infancy and this needs much more attention. The storage ring technique is emerging as a powerful tool in this endeavour but experience in this field has taught us that the use of more than one technique is essential in order to gain a balanced perspective of the reaction process. Thus afterglow techniques still have much to contribute in this aspect of recombination research. What is clear is that molecular–ion recombination remains a fertile area of research that has much to offer the prospective investigator and has many secrets still to be uncovered.

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