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CHEMICAL PHYSICS LETTERS

Chemical Physics Letters 274 (1997) 473–477

Electron-temperature dependence of the recombination of $\text{NH}_4^+(\text{NH}_3)_n$ ions with electrons

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Received 12 May 1997; in final form 30 May 1997



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Publication information: Chemical Physics Letters (ISSN 0009-2614). For 1997, volumes 264–280 are scheduled for publication. Subscription prices are available upon request from the publisher. Subscriptions are accepted on a prepaid basis only and are entered on a calendar year basis. Issues are sent by surface mail except to the following countries where Air delivery via SAL is ensured: Argentina, Australia, Brazil, Canada, Hong Kong, India, Israel, Japan, Malaysia, Mexico, New Zealand, Pakistan, PR China, Singapore, South Africa, South Korea, Taiwan, Thailand, USA. For all other countries airmail rates are available upon request. Claims for missing issues must be made within six months of our publication (mailing) date.

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0009-2614/1997/\$17.00

US mailing notice – Chemical Physics Letters (ISSN 0009-2614) is published weekly by Elsevier Science B.V., Molenwerf 1, P.O. Box 211, 1000 AE Amsterdam. Annual subscription price in the USA US\$ 7818.00, including air speed delivery, valid in North, Central and South America only. Periodicals postage paid at Jamaica, NY 11431. USA POSTMASTERS: Send address changes to Chemical Physics Letters, Publications Expediting, Inc., 200 Meacham Avenue, Elmont, NY 11003. Airfreight and mailing in the USA by Publication Expediting.

Printed in The Netherlands

Published weekly

Library of Congress Catalog Card Number 68–26532

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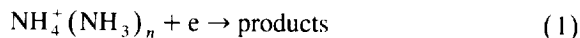
Received 12 May 1997; in final form 30 May 1997

Abstract

The two-body recombination of $\text{NH}_4^+(\text{NH}_3)_{2,3}$ cluster-ions with electrons has been studied in an afterglow experiment in which the electron temperature T_e was elevated by radio-frequency heating from 300 K up to 900 K. The recombination coefficients for the $n = 2$ and $n = 3$ cluster ions were found to be equal, $\alpha_2^{(2)} = \alpha_3^{(2)} = (4.8 \pm 0.5) \times 10^{-6} \text{ cm}^3/\text{s}$, and to vary with electron temperature as $T_e^{-0.65}$ rather than to be nearly temperature-independent as had been inferred from measurements in microwave-heated plasmas. © 1997 Published by Elsevier Science B.V.

1. Introduction

Plasma-afterglow experiments [1–4] have consistently shown that the two-body gas-phase recombination of ammonia cluster ions with electrons



is an extremely rapid process compared to that of simple diatomic ions [5]. Experiments in pure ammonia vapor [1–3] at pressures above 1 Torr have shown that the recombination coefficient increases with ammonia concentration $[n]$ approximately linearly, i.e.

$$\alpha = \alpha^{(2)} + \alpha^{(3)}[n]. \quad (2)$$

Here, $\alpha^{(2)}$ and $\alpha^{(3)}$ denote the two- and three-body coefficient, respectively. The values of $\alpha^{(2)}$ obtained by extrapolating such data to $[n] = 0$ are *effective* recombination coefficients for a mixture of clusters, i.e.

$$\alpha^{(2)} = \sum \alpha_n^{(2)} f_n \text{ with } \sum f_n = 1, \quad (3)$$

where f_n denotes the fractional abundance, and $\alpha_n^{(2)}$ denotes the recombination coefficient of the n th cluster, respectively. The experiments described in this article deal exclusively with the low-pressure, two-body recombination process, in particular its dependence on electron temperature and its dependence on cluster size. We will review the measurements in high-pressure ammonia only to the extent that they have a bearing on these questions.

In an early experiment, Maier and Fessenden [1] measured the conductivity decay in gaseous ammonia subsequent to irradiation by a pulse of high-energy electrons. They observed a positive pressure dependence of the apparent recombination rate but they believed that this increase was due to a gradual shift to larger clusters as the ammonia pressure was raised. Their low-pressure (1 Torr of NH_3) value of $\alpha_2 \sim 4.6 \times 10^{-6} \text{ cm}^3/\text{s}$ is quite close to later, presumably more accurate results.

A more detailed study was performed in a series of measurements by Warman et al. [2] and

Sennhauser et al. [3]. Their experiments also made use of conductivity measurements during the afterglow of electron-beam-excited ammonia vapor. From a linear fit of their data to Eq. (2), Warman et al. obtained $\alpha^{(2)} = 5.6 \times 10^{-6} \text{ cm}^3/\text{s}$ and $\alpha^{(3)} = 6.9 \times 10^{-24} \text{ cm}^6/\text{s}$. Again, no mass analysis of the plasma ions was performed, but the authors concluded from thermochemical data on cluster equilibria [6] that the $n = 4$ cluster would remain the most abundant species over the entire range of ammonia pressures from 1–100 Torr. Warman et al. explained the pressure dependence by a mechanism in which the recombining electron transfers energy to a neighboring neutral ammonia molecule. Later, Monte Carlo simulations of the recombination in dense gases were done by Morgan and Bardsley [7] which support such a model.

Sennhauser et al. [3] also measured the gas-temperature dependence of the three-body recombination coefficient in ambient ammonia and found that it varied as $T_{\text{gas}}^{-2.5}$ in the range $243 \text{ K} < T_{\text{gas}} < 371 \text{ K}$. An extrapolation of their data to $[n](\text{NH}_3) = 0$ was found to be compatible with the surprising observation of Huang et al. [4] that the two-body coefficient $\alpha^{(2)}$ showed essentially no variation with temperature. However, the Sennhauser et al. results are not a strong corroboration of the Huang et al. work since their extrapolated values had an uncertainty of about 20%. Over the narrow range of temperatures from 243 to 371 K, a $T_e^{-1/2}$ dependence of $\alpha^{(2)}$, which is typical for two-body recombination, would have changed $\alpha^{(2)}$ by only 25%.

To summarize: the afterglow measurements in pure ammonia yielded a two-body coefficient that most likely refers to the $n = 4$ cluster. No firm conclusions can be drawn from those measurements as to the variation of $\alpha^{(2)}$ with cluster size or with temperature.

We now discuss the results obtained by Huang et al. [4]. Their goal was to measure the two-body recombination coefficients for mass-identified ammonia cluster ions as a function of *electron temperature*. Their measurements were carried out in microwave generated helium afterglow plasmas with only minute additions of ammonia. By varying the *gas temperature* from 200 to 410 K the distribution of cluster sizes could be adjusted from $n = 0$ to $n = 4$. The authors used a microwave field to elevate the *electron temperature*, but this method (see be-

low) may not have worked as the authors had expected.

The experiments by Huang et al. gave two results, namely that (1) the two-body recombination coefficients were nearly independent of electron temperature and that (2) they varied very little with cluster size after addition of the first ammonia molecule. The first finding was found to be surprising because all available experimental evidence and theory indicated that two-body recombination coefficients fall off with temperature as approximately $T_e^{-1/2}$. There is no firm theoretical argument indicating that recombination rates should necessarily increase with the cluster size, but experiments on water clusters [8] suggest that this might be a general feature.

We believe that the experiments by Huang et al. were subject to complications that were not fully understood at the time. The authors thought that microwave heating of electrons would be as effective in gas mixtures containing molecular additives as it is in pure rare gases. However, as has been discussed by Dulaney et al. [9], Johnsen [5] and Penetrante and Bardsley [10], there are reasons to suspect that the degree of microwave heating of an electron gas is strongly reduced when molecular gases, especially polar gases such as water or ammonia vapor, are added to a predominantly rare-gas plasma. The reduction in heating efficiency results from the transfer of electron kinetic energy to vibrational and rotational degrees of freedom of the molecular additives. A similar lack of temperature variation was once believed to exist in the case of water cluster ions, but later measurements [8] have shown that the actual electron temperatures were far lower than the experimentalists had calculated.

We have remeasured the electron-temperature dependence using a different experimental method. Our results show that the recombination coefficient for the $n = 2$ cluster varies with electron temperature as $T_e^{-0.65}$ and that the same is probably true for the $n = 3$ cluster.

2. Experimental method

Our experiment employs radio-frequency ($f = 14.7 \text{ MHz}$) conductivity measurements and mass-spectrometric observations of ions during the after-

glow phase of a photoionized helium plasma (pressures from 250–300 Torr) with small additions of ammonia (less than 20 mTorr). The apparatus and experimental methods have been described in detail in earlier publications [8,11], and the procedures were essentially identical to those used in the study of water cluster ions [8]. As in the earlier work, a weakly ionized plasma (electron density $\sim 1 \times 10^9 \text{ cm}^{-3}$) is created by a short UV flash (less than 1 μs in duration) from a spark gap that is fired up to 20 times per second.

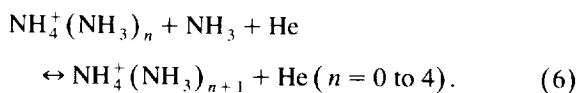
To produce ammonia cluster ions, a small amount of a 200:1 He:NH₃ mixture was added to the chamber filled with 250–300 Torr of pure helium. Photoionization of ammonia



initially produces NH₃⁺ ions which are rapidly ($k = 1.7 \times 10^{-9} \text{ cm}^3/\text{s}$) converted to NH₄⁺ ions by proton transfer



Subsequently, cluster ions are formed in a sequence of three-body reactions



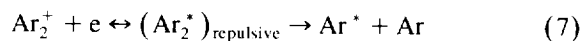
The relative abundances of the clusters can be adjusted by varying the ammonia concentration and, in principle, they can be calculated from the known equilibrium constants [12,13] of reaction (6). We attempted to add known and reproducible amounts of ammonia, but in practice this was found to be difficult. Hence, we simply used the mass spectrometer to measure the relative abundances. The mass spectrometer was also used to learn how fast the cluster equilibria were approached. Under typical conditions, the formation of $n = 2$ and $n = 3$ clusters occurred in a time of about 30 μs . The abundance of the $n = 4$ cluster was always negligible ($< 1\%$), as might have been expected, since the equilibrium constant between the third and fourth cluster is quite small ($\sim 1.2 \times 10^{-17} \text{ cm}^{-3}$) [12]. Relying on mass spectrometric abundances can lead to erroneous results due to poorly known mass discrimination effects. Fortunately, this problem did not really arise in this work, since, as we will show later, the recom-

binations coefficients appear to be independent of cluster size.

Although the usual precautions, such as passing the helium buffer gas through a liquid-nitrogen-cooled Zeolite trap were taken to reduce gaseous impurities, some impurity ions were present, e.g. N₂⁺, O₂⁺, H₃O⁺, NO⁺, and two unidentified species at 76 u and 92 u. Their total abundance during the afterglow time of interest was $< 3\%$ of that of the ammonia cluster ions. Measurements were terminated whenever the mass spectrum showed evidence of excessive impurities.

The hyperbolic decay of the plasma conductivity during the afterglow directly yields the recombination coefficient, since diffusion of ions and electrons is negligible at high pressures. Typically, deviations from the hyperbolic decay law became noticeable only in the late afterglow when more than 80–90% of the ions had recombined. Measurements at elevated electron temperatures follow the same procedure, except that the radio-frequency voltage is made sufficiently high to heat the electrons. It is important to note that the actual electron temperature in this method can be inferred from the value of conductivity at the onset of recombination. However, as an additional check we calculated the electron energy distribution function from the theory of Margenau [14]. The distribution functions are slightly non-maxwellian. Needed averages, such as mean energies, collision frequencies, and the plasma conductivity were obtained by numerical methods. We repeated the calculations that have been described earlier [8] and we carried out further experimental tests of the relation between the plasma conductivity and the applied electric field. As was found before, the measured and calculated quantities agreed very well.

As an additional test of our experimental procedures, we remeasured the electron temperature dependence of the dissociative recombination of Ar₂⁺ ions with electrons



and compared our results to those of microwave afterglow measurements [15,16]. Since the microwave data were obtained in pure argon they were not affected by electron cooling due to molecular additives. Using the present technique, we obtained

$\alpha(\text{Ar}_2^+) = (9.3 \pm 0.9) \times 10^{-7} \text{ cm}^3/\text{s}$ at 300 K with a temperature dependence of $T_e^{-0.6}$ from 300 K to 900 K, in good agreement with $\alpha(\text{Ar}_2^+) = (8.5 \pm 0.8) \times 10^{-7} (300/T_e)^{0.67} \text{ cm}^3/\text{s}$ and $\alpha(\text{Ar}_2^+) = (9.1 \pm 0.9) \times 10^{-7} (300/T_e)^{0.61} \text{ cm}^3/\text{s}$ that were obtained in microwave afterglows [15,16]. The good agreement indicates that our experimental methods are reliable and accurate.

3. Measurements and results

Fig. 1 shows the measured recombination coefficient at 300 K (no electron heating) as a function of a fractional abundance f_3 of the $n = 3$ clusters. It is evident that the effective recombination coefficient shows no measurable dependence on f_3 , which means that $\alpha_2^{(2)}$ and $\alpha_3^{(2)}$ have a common value of $(4.8 \pm 0.5) \times 10^{-6} \text{ cm}^3/\text{s}$.

Fig. 2 shows an example of measured recombination coefficients for the $n = 2$ cluster, f_3 being less than 0.03, as a function of electron temperature from 300–900 K. We have plotted those data together with those for the Ar_2^+ ion to show that the recombination rates differ considerably in magnitude, but that their temperature dependencies are very similar. The curves drawn through the data are results of convoluting a model recombination cross section, varying with electron energy as $\epsilon^{-1.15}$, with the computed Margenau electron energy distribution.

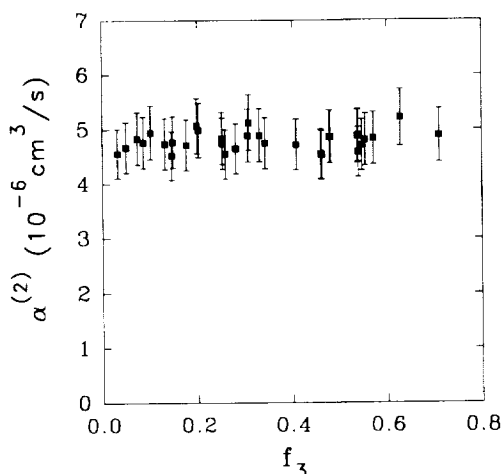


Fig. 1. Variation of $\alpha^{(2)}$ for the $n = 2$ and $n = 3$ cluster ions as a function of f_3 at $T_e = 300 \text{ K}$.

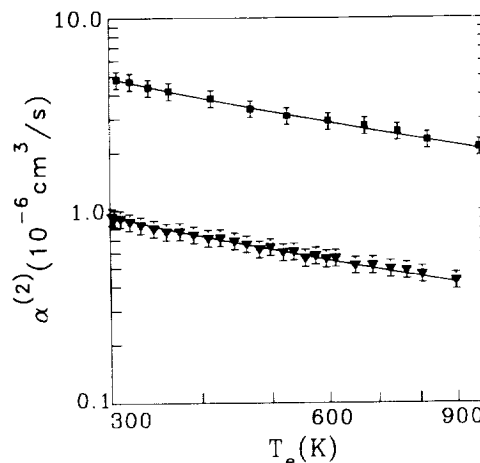


Fig. 2. Calculated (solid lines) and measured recombination coefficients for Ar_2^+ ions (triangles) and for $n = 2$ ammonia cluster ions (squares) as a function of the electron temperature T_e . Calculated values were normalized to experimental data at $T_e = 300 \text{ K}$.

Clearly, the model cross section reproduces the measured data quite well. If we had plotted the fit obtained for a Maxwellian energy distribution function it would be almost indistinguishable from that for the Margenau distribution. Since the model calculations produce a good fit to the experimental data, it is justified to convert the cross sections to a temperature-dependent rate coefficient. A cross section varying as ϵ^{-x} implies that $\alpha^{(2)}$ varies as $T_e^{-(2x-1)/2}$ and we obtain

$$\alpha_2^{(2)} = (4.8 \pm 0.5) \times 10^{-6} (300/T_e)^{(0.65 \pm 0.06)} \text{ cm}^3/\text{s}. \quad (8)$$

The results are based on a larger set of data than those shown in Fig. 2. No systematic measurements were carried out in which both f_3 and T_e were varied, but one set of electron-heated data was taken in which the abundance of the $n = 3$ cluster was as high as $f_3 = 0.25$. The temperature dependence of $\alpha_3^{(2)}$ was very much the same as that for the $n = 2$ cluster, indicating that probably $\alpha_3^{(2)}$ also varies as $T_e^{-0.65}$.

4. Discussion of results

Our data show that the recombination rate coefficient for $n = 2$ and most likely that for $n = 3$ ammo-

nia cluster ions varies with electron temperature as $T_e^{-0.65}$. This finding is very much what was expected, since most ions exhibit a very similar (slightly faster than $T_e^{-0.5}$) behavior. A similar power law was reported by Alge et al. [17] for unclustered ammonia ions, namely $\alpha_0^{(2)} = 1.35 \times 10^{-6} (300/T_e)^{0.6} \text{ cm}^3/\text{s}$ over the narrower temperature range $300 \text{ K} < T_e < 600 \text{ K}$. The apparent lack of a temperature dependence that was deduced from microwave afterglow experiments [4] almost certainly resulted from an erroneous interpretation of the original data. The same situation existed in the case of water cluster ions and the problem there was traced [8] to the presence of H_2O .

Our 300 K values of $\alpha_2^{(2)}$ and $\alpha_3^{(2)}$ are very close to the zero-pressure limit of measurements in high-pressure ammonia but they are considerably higher than those obtained in microwave afterglows [4] [$\alpha_2^{(2)}(300\text{K}) = (2.7 \pm 0.2) \times 10^{-6} \text{ cm}^3/\text{s}$, $\alpha_3^{(2)}(200\text{K}) = (3 \pm 1) \times 10^{-6} \text{ cm}^3/\text{s}$] and in flowing afterglows [17] [$\alpha^{(2)}(300\text{K}) = 2.8 \times 10^{-6} \text{ cm}^3/\text{s}$]. The discrepancy is unexpectedly large considering that the agreement is quite good for Ar_2^+ ions. Perhaps, the microwave plasmas contained an unrecognized fraction of slowly recombining unclustered ions. It is also conceivable that the electron temperature was higher than 300 K as a result of coupling between the electron gas and vibrationally excited molecules that were left from the discharge phase of the experiment. The latter comment does not explain the lower values measured in a flow tube [17], but here the ion composition was inferred from mass spectrometric measurements at the downstream end of the tube, rather than in the region where recombination takes place. Possibly the recombination region contained more unclustered, slowly recombining ions than were detected by the mass spectrometer, but the situation is not quite clear.

In many ways, the recombination of ammonia cluster ions is quite similar to that of water cluster ions. Both are exceedingly rapid, but there is one significant difference: adding one more water molecule to an $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ cluster appears to en-

hance the recombination [8], while adding one more ammonia molecule to the $n = 2$ ammonia cluster has no measurable effect. Bates once proposed [18] that the near-equality of the ionization potentials of H and O makes the charges in hydronium clusters very mobile, so that the ‘‘proton bond moves to be as close as possible to the incident electron’’, but that this would not be the case in ammonia clusters. To our knowledge, this qualitative conjecture has not been put on a more rigorous basis.

Acknowledgements

This work was supported, in part, by NASA under Grant No. NAGW-1764.

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