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Thermal electron detachment of the molecular anion of azulene at elevated pressures by ion mobility spectrometry

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Abstract

Rate constants, k_{TED}, and their temperature and pressure dependence for the thermal electron detachment (TED) reaction of the molecular anion of azulene ($Az^- \rightarrow Az + e$) have been determined by ion mobility spectrometry (IMS). By this method, Az^- ions are periodically introduced to a drift tube containing nitrogen gas at pressures ranging from 300 to 1100 Torr and temperatures ranging from 75 to 175 °C. During the time required for an Az^- ion packet to drift to a Faraday detection plate, either a portion (at lower temperatures) or essentially all (at higher temperatures) of the Az^- ions undergo TED. From the TED-modified IMS waveforms thereby produced, the magnitudes of k_{TED} values have been deduced and compared with previous measurements of k_{TED} for Az^- made in buffer gases of much lower and higher pressures. The present results support a trend noted in the prior studies that the rate of TED by Az^- is decreased by large increases in pressure to the near-atmospheric pressure range. A potential explanation of this unexpected effect of a buffer gas that is normally considered to be chemically inert is that a weak chemical interaction exists between the Az^- ion and the nitrogen buffer gas molecules and this provides increased stability to the Az^- ion under conditions of very high pressure and thereby increases the activation barrier of the TED reaction. (Int J Mass Spectrom 179/180 (1998) 117–127) © 1998 Elsevier Science B.V.

Keywords: Ion mobility spectrometry; Thermal electron detachment; Azulene

1. Introduction

An important and somewhat neglected aspect of gas phase ion chemistry concerns the reactions of ions under conditions of very high buffer gas pressure [1]. In all but a relatively small number of studies, buffer gas pressures have not exceeded a few Torr. In order to reach higher buffer gas pressures, several different experimental approaches have been investigated. Noninstrumental approaches have been developed by Cacace and co-workers in which the neutral products generated in gas phase ionic reactions were collected and identified by conventional methods of organic analysis [2–4]. Instrumental approaches have involved the in situ measurement of reactant and/or product ions by atmospheric pressure mass spectrometry [5–9], by the emission of optical radiation [10–13], by electron photodetachment from negative ions [14], and by ion mobility spectrometry [15–19]. In recent years, research in our laboratory and at the University of Birmingham, UK [20,21], has shown that the ion mobility spectrometry (IMS) approach can be used to obtain accurate rate and equilibrium

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Dedicated to Professor Fulvio Cacace in recognition of his outstanding contributions for many decades to gas-phase ion chemistry and physics.

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constants for a variety of negative ion–molecule and electron–molecule interactions at atmospheric pressure. In the present study, we describe the use of IMS for the determination of thermal electron detachment (TED) rate constants for the molecular anion of azulene (Az^-) over a pressure range of 300–1100 Torr and a temperature range of 82–174 °C.

In describing the TED process, it is convenient to first describe the reverse process known as resonance electron capture (REC) indicated by Eq. (1).

$$e + M \xrightarrow{k_{REC}} M^- \tag{1}$$

In Eq. (1), a thermal-energy molecular anion, M^-, is formed by the direct attachment of a thermal-energy electron followed by stabilization of an initially formed excited species (M^{-*}) by collisions with a buffer gas. With use of sufficiently high buffer gas pressures, the rate of Eq. (1) is expected to be independent of buffer gas pressure and will depend only on the concentrations of electrons and M. Phenomenologic second-order rate constants for the REC reactions of numerous compounds have been determined under these conditions [22–24]. Once formed, the thermal-energy anions, M^-, can undergo TED, as represented by Eq. (2).

$$M^- \xrightarrow{k_{TED}} M + e \tag{2}$$

In the TED process, M^- loses its extra electron because of thermal activation provided by the buffer gas medium and is expected to do so in the high pressure limit with a phenomenologic first-order rate constant that is also independent of the buffer gas pressure. Knowledge of both k_{REC} and k_{TED} for a given compound is expected to provide important information concerning the dynamics and thermal chemistry of the electron–molecule interactions of a given compound. From these rate constants, the equilibrium constant for electron attachment/detachment ($K = k_{REC}/k_{TED}$) could be experimentally obtained and compared with K values obtained from statistical mechanics, along with electron affinity and entropy data that have been compiled for numerous compounds [25]. Comparison of these two sets of independent determinations of K for a variety of compounds provides a test of the consistency of all the data, equations, and assumptions concerning the electron–molecule interactions for each compound of interest [26,27].

Unfortunately, very few measurements of TED rate constants have been reported in the literature to date. These have been for O_2^- [28–30], NO^- [31–33], $C_6F_6^-$ [34,35], $C_4F_6^-$ [36], cyclo-$C_4F_8^-$ [27], and $C_{10}H_8^- = Az^-$ [26,37]. Because the present investigation focuses on the TED reaction of the molecular anion of azulene, the prior studies of this negative ion are of particular interest here. Grimsrud et al. [26] developed a method based on pulsed high pressure mass spectrometry (PHPMS) in which the simultaneous presence of the electron-scavenger, perfluoromethylcyclohexane (C_7F_{14}), allowed the direct observation of TED by Az^- over the range of buffer gas (methane) pressures of 2–5 Torr. In that study, it was found that k_{TED} and the temperature dependence of k_{TED} for Az^- is given by Eq. (3),

$$k_{TED} = 1.14 \times 10^{11}\ (s^{-1}) \times \exp\,[-15.7\ (\text{kcal/mol})/RT] \tag{3}$$

where R is the gas constant and T is temperature in kelvin. This result was shown to be in reasonably good agreement with predictions of k_{TED} obtained from prior determinations of k_{REC} and from electron affinity/entropy data for azulene, through the expected relationship, $k_{TED} = k_{REC}/K$. Grimsrud et al. [26] also observed in that study that k_{TED} for Az^- was constant over the pressure range 2–5 Torr, suggesting that this process is operating within its high pressure limit of kinetic behavior in the low Torr range.

A second study of TED by Az^- was reported by Mock and Grimsrud [37] in which an entirely different experimental approach and a much greater buffer gas pressure were used. Their method was based on the photodetachment-modulated electron capture detector (PDM-ECD) and used a buffer gas of 10% methane in argon at a total pressure of 2.0 atm (1520 Torr). By that method, the rate of Az^- loss by TED was measured relative to that caused by a competing ion–ion recombination reaction. The k_{TED} values thereby obtained were in agreement with those obtained by PHPMS, in that a strong, positive temperature dependence was observed for k_{TED} over the temperature range 130–190 °C. However, the absolute magnitude of the TED rate constants observed by the PDM-ECD method were consistently much lower (about one third as great) than those observed by the PHPMS method. Only a portion of the rate constant differences could be explained in terms of the estimated uncertainties of the two methods. Therefore, the lower k_{TED} values obtained by the PDM-ECD method were thought to be most probably due to either an unknown source of systematic error in the PDM-ECD method or to a real effect of the unusually high buffer gas pressure used in the PDM-ECD study. If a depression of k_{TED} is actually caused by the use of very elevated buffer gas pressures, that effect would be a novel one that might provide new insight into the effects of elevated buffer gas pressures on gas phase ionic reactions. Therefore, a specific point of interest in the present investigation was to further explore the effect of elevated pressures on k_{TED} for Az^- by a third, independent, method.

2. Experimental

The IMS instrument used here has been described in detail in several other publications [15–19] and includes all of the modifications recently described [18,19] that have enabled the pressure and temperature of the IMS to be varied from 300 to 1100 Torr and from 20 to 200 °C, respectively. The only instrumental change made here was that a gas handling plant that had previously been used for the addition of chemicals to the drift gas was not needed for the present experiments and was removed. Only purified buffer gas (usually nitrogen) was passed through the drift tube in the present experiments. Specific operational conditions of the IMS used for the present study are listed in Table 1.

Table 1
Conditions of the ion mobility spectrometer

Drift gas/flow rate	N_2/700 cm^3 min^{-1}
Source gas/flow rate	N_2/25 cm^3 min^{-1}
Temperature	82–174 °C
Pressure	300–1100 Torr
Drift field strength	40–200 V cm^{-1}
Drift tube length	23.5 cm
Bradbury-Nielson gate pulse width	0.5 ms
Sweeps per IMS spectrum	1000–5000

In the present study, a low concentration of Az was continuously delivered to the ion source by insertion of a swedgelock T and short glass vial containing azulene crystals (Aldrich Chemical, Milwaukee, WI) into the source gas supply line leading to the ion source. The vial was wrapped with a heater tape and warmed to a temperature of about 80 °C in order to enhance the sublimation of azulene. Although there was no need to know the exact concentration of Az in the ion source, care was taken to use the minimum amount required to obtain a measurable signal by the IMS. This precaution was taken to ensure that no significant amount of Az passed into the drift region of the IMS where electron attachment to Az might have complicated the nature of the IMS waveforms observed. In the ion source, Az^- ions were continuously produced by the REC mechanism shown by Eq. (1) and were also being continuously lost by TED [Eq. (2)]. Small packets of the source-produced electrons and Az^- ions were then allowed to enter the drift region of the IMS by momentarily (0.5 ms) opening a Bradbury-Nielson ion gate. The drift tube contains a counterflowing current of nitrogen gas that prevents the penetration of source gas into the drift region. In the drift tube, all ions and electrons are transported to a Faraday detection plate at rates determined by their respective mobilities and the applied electric field. The efficiency of ion collection at the Faraday plate is thought to be the same and near unity for all ions that enter the drift region. This is because the diameter of the Faraday plate (3 cm) is much greater than that of the ion cloud, which is about 1.0 cm as it enters the drift region and increases by only about 50% through radial diffusion as the ion cloud is transported to the Faraday plate [15]. Because the mobility of electrons is several orders of magnitude greater than that of all negative ions, the occurrence of a thermal detachment event by Az^- anywhere along the drift tube is expected to result in the near-instantaneous arrival of that detached electron at the Faraday plate. The efficiency of electron collection at the Faraday plate is also predicted to be near unity, based on the known mobilities and diffusion coefficients of electrons in nitrogen buffer gas [38] under the present experimental conditions. The accumulation of these events for the entire Az^- packet thereby produces a reaction-modified IMS waveform from which a k_{TED} value can be deduced at each selected temperature.

Measurements of ion arrival at the Faraday plate were also made by an associated mass spectrometer that continuously samples a small amount of drift gas that flows through a 50-μm aperture located at the center of the Faraday plate [15]. In this way, a "single ion" mobility spectrum for any selected ion of interest could be simultaneously obtained whenever desired along with the "total ion" mobility spectrum provided by the Faraday plate. Mass spectrometric measurements of this type were used here only to verify the identity of the negative ions responsible for observed IMS peaks and were not used for determinations of TED rate constants.

An experimental difficulty was presented here by electron capture reactions to trace-level impurities within the ion source. In spite of our best efforts to remove all impurities, the creation of unwanted ions of this type appears to be unavoidable whenever the free electron concentration within the ion source is significant. The major ion formed by these unwanted processes was the Cl^- ion. This problem is amplified in the present study under conditions of relatively high temperatures where the fast TED reaction of Az^- ensures that additional electrons will be made available for attachment to trace-level impurities even if those electrons were initially attached to Az molecules. Because the electron attachment reactions to these impurities were clearly irreversible processes (as evidenced by the normal IMS peak shapes that these ions produced), the relative abundance of these unwanted negative ions can become significant with use of high temperatures even though the concentrations of the impurities are undoubtedly many orders of magnitude below that of azulene. Fortunately, these uninteresting ions are readily recognized by the associated mass spectrometer and their contributions to the observed waveforms are easily accounted for.

3. Waveform predictions and methods of analysis

The waveforms expected here when packets of Az^- negative ions are introduced to the IMS drift tube are shown in Fig. 1, where three different values of k_{TED} have been assumed. In Fig. 1(A), a relatively low value of $k_{TED} = 10\ s^{-1}$ has been selected, corresponding to a temperature of 68 °C by Eq. (3). Based on the known reduced mobility of Az^- of 1.94 $cm^2\ V^{-1}\ s^{-1}$ [39], this ion is expected to have a drift time of about 65 ms under the experimental conditions listed for Fig. 1(A) and about 52% of the Az^- ions are expected to survive transport to the Faraday plate. About 48% of the Az^- ions are expected to undergo TED during the Az^- drift period, and this is expected to cause the apparent baseline between

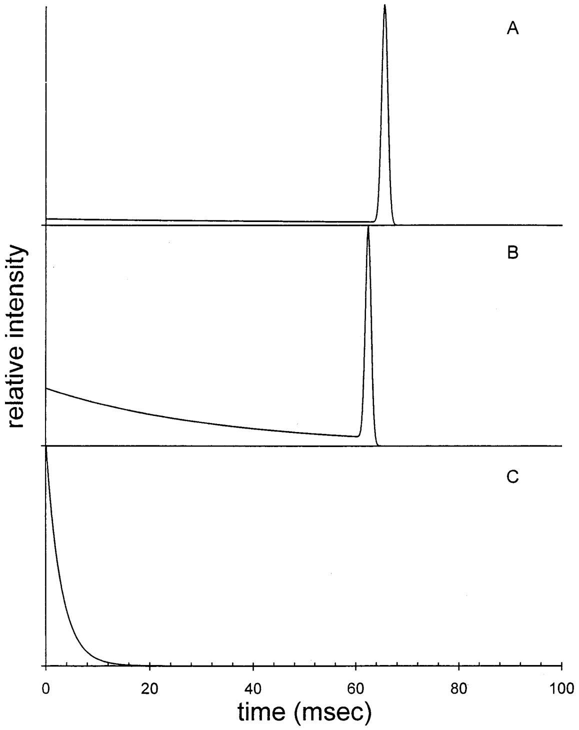

Fig. 1. Predictions of TED-modified IMS waveforms for the molecular anion of azulene under the following set of assumed conditions: (A) $k_{TED} = 10\ s^{-1}$ corresponding to $T = 68$ °C by Eq. (3), (B) $k_{TED} = 30\ s^{-1}$ corresponding to $T = 85$ °C, and (C) $k_{TED} = 350\ s^{-1}$ corresponding to $T = 130$ °C; reduced mobility of $Az^- = 1.94\ cm^2\ V^{-1}\ s^{-1}$ [39]; drift tube electric field = 144 V cm^{-1}; drift tube length = 23.5 cm; and pressure = 740 Torr.

$t = 0$ and 65 ms to be elevated somewhat relative to the true baseline observed after the arrival of the Az^- ion packet. Under this low temperature condition, the elevated portion of the baseline is expected to be relatively flat because the population of Az^- that is producing this electron current is reduced by only a factor of about 2 by the TED reaction as the Az^- packet passes along the entire length of the drift tube.

In Fig. 1(B), a value of $k_{\mathrm{TED}} = 30\ \mathrm{s}^{-1}$ has been assumed, corresponding to a temperature of 85 °C by Eq. (3). Under this condition, only about 15% of the Az^- ions are expected to survive transport to the Faraday plate, and 85% are expected to undergo TED within the drift tube. It is also noted in Fig. 1(B) that the electron current recorded at the Faraday plate between $t = 0$ and 63 ms is now expected to decrease much more significantly with increased drift time. This is because the population of Az^- is now being decreased by a factor of about 7 by TED as the ion packet passes through the entire length of the drift tube. In Fig. 1(C), a value of $k_{\mathrm{TED}} = 350\ \mathrm{s}^{-1}$ has been assumed, corresponding to a temperature of 130 °C by Eq. (3). Under this condition, no detectable amount of Az^- is expected to survive transport to the Faraday plate. The only signal observed should be due to the thermally detached electrons that are produced as the Az^- packet passes through the initial portions of the drift tube.

From waveforms such as those simulated in Fig. 1, it is expected that rate constants, k_{TED}, can be determined at any temperature where some measurable evidence of TED by Az^- is indicated in the reaction-modified waveforms. At all temperatures, the decay of the elevated baseline observed between 0 and t_d for Az^- is expected to be given by Eq. (4),

$$\ln I = -k_{\mathrm{TED}}\, t + \ln I_0 \tag{4}$$

where I is the instantaneous electron current measured at the Faraday plate, t is the drift time, and I_0 is the initial electron current. A plot of ln I versus t is thereby expected to provide a straight line of slope equal to $-k_{\mathrm{TED}}$. This is expected to provide a means of determining k_{TED} under conditions of relatively high temperature where the magnitude of the slope will be large and much greater than its uncertainty of measurement. Under conditions of low-to-moderate temperatures, where a significant Az^- ion peak is observed, k_{TED} can also be obtained from Eq. (5),

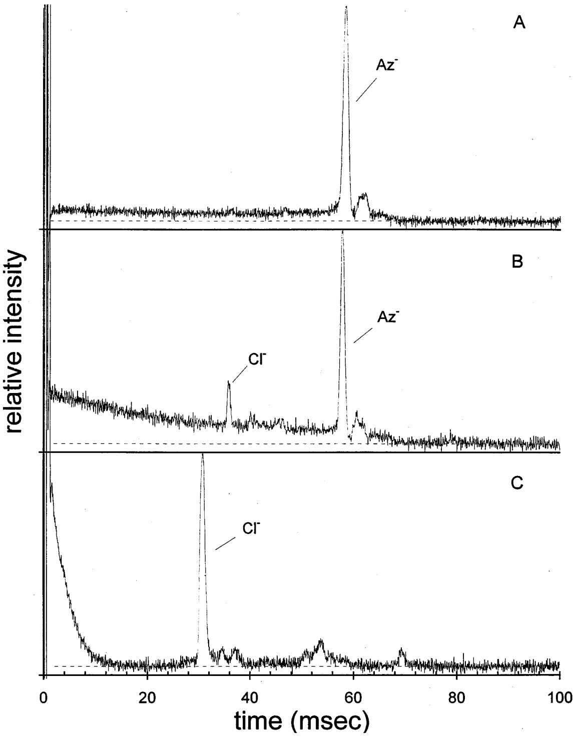

Fig. 2. Selected examples of TED-modified IMS waveforms observed under the following experimental conditions: (A) $T = 102$ °C, (B) $T = 114$ °C, and (C) $T = 154$ °C; drift tube field = 144 V cm^{-1}; pressure = 740 Torr.

$$k_{\mathrm{TED}} = \ln\,(A_{\mathrm{az}}/A_e)/t_d \tag{5}$$

where A_{az} and A_e are the integrated portions of the IMS waveform corresponding to the arrival of Az^- and detached electrons, respectively, at the Faraday plate and t_d is the drift time of Az^-.

4. Results

In Fig. 2, three typical IMS waveforms are shown that were observed at relatively low (A), moderate (B), and high (C) IMS temperatures. For the sake of convenience, the IMS temperatures chosen for illustration in Fig. 2 are three that happened to produce waveforms similar to the predicted ones provided in Fig. 1. In each of the IMS waveforms, an initial intense pulse is observed during the first millisecond of drift time that is due to the passage of sampled electrons through the drift tube. The intensity of this signal was of no interest and was not measured. After this electron pulse, an IMS waveform is then defined by the electron current associated with TED of Az^- and with the arrival of Az^- and other impurity-based ions (see discussion of these in Sec. 2) at the Faraday plate. All of the ion identities (Cl^- and Az^-) indicated in Fig. 2 were made by single-ion, mass-selected IMS waveforms that were simultaneously obtained by the associated mass spectrometer. The Cl^- ion was observed at all but the lowest temperatures used and is due to electron attachment by trace-level impurities in the ion source. Although the masses of the additional and unassigned IMS peaks also observed in Fig. 2 were measured by the mass spectrometer, their chemical identities are not known. Because distinct IMS peaks were observed for the Cl^- ion and all of the unknown ions, it is clear that all these extraneous ions were formed in the ion source and not in the drift tube. Therefore, the IMS waveforms of interest could be obtained simply by subtracting the unwanted peaks from the observed waveforms. In Fig. 2(B) and (C), it is seen that the relative intensities of the impurity-based ions are greatly increased as the temperature is increased. This is expected because of the increased TED of Az^- that will be occurring within the ion source with the use of higher temperatures. This decreases the steady-state concentration of Az^- in the ion source and increases the steady-state concentrations of electrons and the impurity-based negative ions that are being formed by the irreversible attachment of the electrons to the impurities. For each IMS waveform in Fig. 2, the zero-level baseline is indicated by a dashed line that was determined by the baseline observed at very long drift times, between 80 and 100 ms.

It is noted in Fig. 2(A) that the observed baseline between $t = 1$ ms and t_R for Az^- is elevated relative to the zero-level baseline. This is an expected effect of TED by Az^- that was illustrated by the predictions shown in Fig. 1(A). It is also noted, however, that a temperature of 102 °C was required in Fig. 2(A) to produce this waveform, whereas a temperature of only 68 °C was predicted to produce the waveform shown in Fig. 1(A). When an IMS temperature of 68 °C was used, there was no detectable elevation of the baseline between $t = 1$ ms and t_R for Az^-. This is the first of many indications to follow that the rate of TED by Az^- is significantly lower under the present conditions of the IMS experiment than is predicted by Eq. (3).

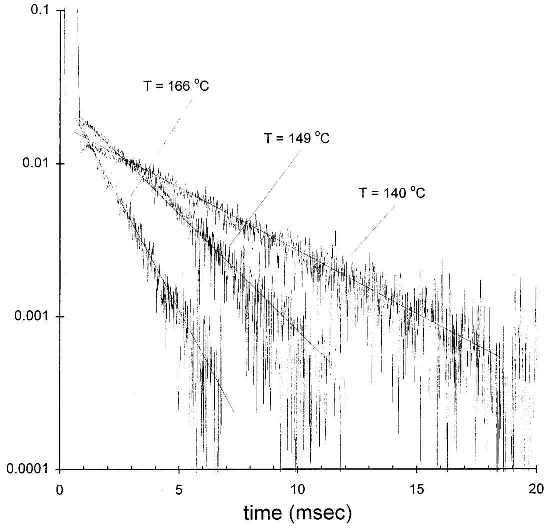

Fig. 3. Initial portions of TED-modified waveforms observed at three different temperatures and plotted in the form of Eq. (4).

The effects on the IMS waveforms of increased TED by Az^- ions at successively higher IMS temperatures are shown in Fig. 2(B) and (C) and are in good qualitative agreement with the predicted effects of increased temperature shown in Fig. 1(B) and (C). It is again noted, however, that the temperatures required to achieve the TED-modified waveforms in Fig. 2(B) and (C) are significantly greater than those used for the predictions in Fig. 1(B) and (C).

Another test of the experimental method is provided in Fig. 3 where the initial portion of the IMS waveforms observed at three different temperatures are plotted in the form of Eq. (4). As indicated in these examples, straight lines were invariably obtained, and from the slopes of these plots, k_{TED} values were

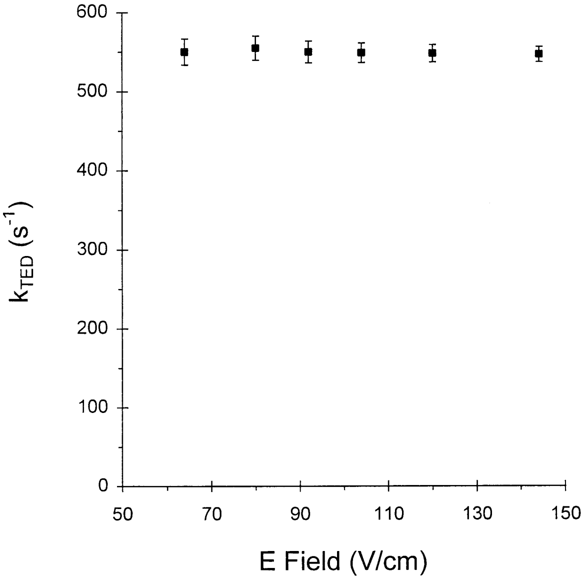

Fig. 4. TED rate constants for Az^- determined by the IMS method using six different electric field strengths within the drift tube. P = 740 Torr. T = 158 °C.

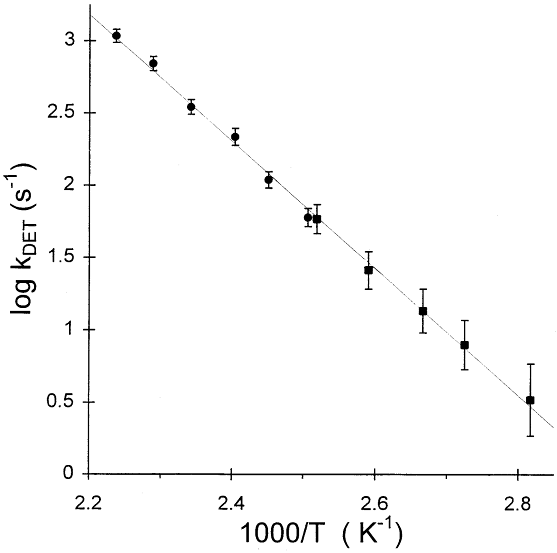

Fig. 5. Arrhenius plots of k_{TED} values determined by IMS in nitrogen buffer gas at a pressure of 740 Torr. Determinations made by the initial slope method [Eq. (4)] are indicated by the solid circles. Those by the relative areas method [Eq. (5)] are indicated by the solid squares. The error bars shown were determined from the estimated uncertainties of the slopes or areas observed at each temperature.

determined over the temperature range 125–175 °C. At temperatures >175 °C, the amount of Az^- entering the drift tube was insufficient for reliable measurement of the TED-modulated waveform. At temperatures lower than 125 °C, the slopes were not of sufficient magnitude as to allow accurate determination of k_{TED} by this method. Another test of the method is provided in Fig. 4 where k_{TED} was determined at a constant temperature of 158 °C by using a range of electric field strengths within the drift region. It is seen that the rate of TED by Az^- is not affected by the drift field. This is consistent with the expectation [15] that the amount of internal energy imparted to the Az^- ions by the electric field is insignificant relative to the thermal energy of Az^-.

In Fig. 5 the rate constants determined here have been plotted in the Arrhenius form. The k_{TED} values determined over the high temperature range of measurements (125–175 °C) by the initial slopes method [Eq. (4)] are indicated by the solid dots. The solid squares indicate the values of k_{TED} determined over a lower temperature range of measurements (80–125 °C) by the alternate method [Eq. (5)] involving the integrated areas of the electron and Az^- ion currents within a given IMS waveform (note that the estimated uncertainties of the k_{TED} values determined in this way are larger than those determined by the initial slope method and become particularly large at the lowest temperatures used). The excellent agreement between the two k_{TED} values determined by the two methods at the near-common temperature of about 125 °C provides support for the validity of both of the IMS methods described here. In addition, it is reassuring that the slopes of the Arrhenius plots formed by these two data sets are in good agreement.

All the IMS measurements described above were also performed using nitrogen buffer gas pressures of 300 and 1100 Torr. The IMS waveforms thereby obtained differed from those shown in Fig. 2 only in that the observed drift time-scale was shifted by a magnitude inversely proportional to the change in buffer gas pressure. The k_{TED} values thereby obtained are shown in Fig. 6, again in the Arrhenius form, along with the values obtained at 740 Torr. By

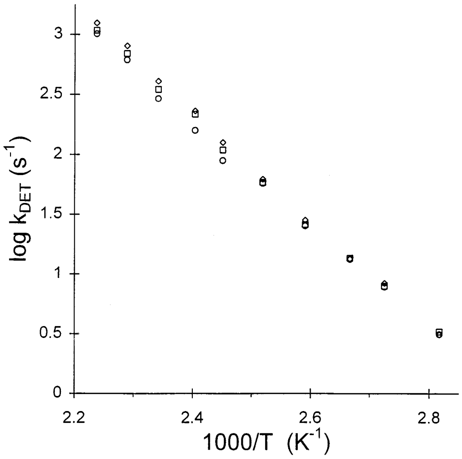

Fig. 6. Arrhenius plots of k_{TED} values determined by IMS in nitrogen buffer gas at pressures of 300 (diamonds), 740 (squares), and 1100 (circles) Torr.

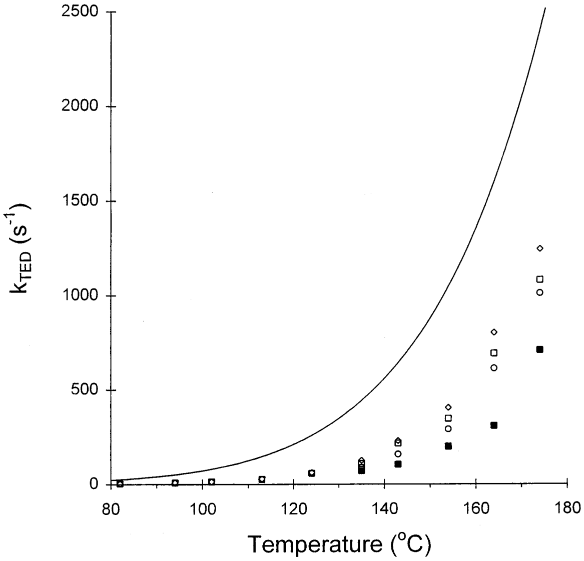

Fig. 7. k_{TED} values determined by IMS in nitrogen buffer gas at pressures of 300 (diamonds), 740 (squares), and 1100 (circles) Torr as a function of temperature. The curved line shown represents the k_{TED} values previously determined [see Eq. (3)] by the PHPMS method using methane buffer gas at 4 Torr [26]. The solid squares are k_{TED} values previously determined [37] by the PDM-ECD method using argon–10% methane buffer gas at a pressure of 2.0 atm (1520 Torr).

inspection of the error bars provided previously in Fig. 5, it is seen that a small, but detectable, effect of these pressure changes on k_{TED} was noted in the high temperature range. The Arrhenius activation and pre-exponential factors obtained from these three plots are listed in Table 1.

In Fig. 7 all the present k_{TED} determinations have been plotted in the form of k_{TED} versus temperature, along with the values previously reported for the PHPMS method [26] using methane buffer gas at pressures less than 4 Torr (solid line) and those reported for the PDM-ECD method [37] using nitrogen buffer gas at a pressure of 2.0 atm. The present set of measurements are seen to lie between those obtained at much lower and somewhat greater buffer gas pressures. In addition, within the present set of measurements an apparent depression of k_{TED} is observed as the pressure in increased over the range of 300 (open diamonds) to 740 (open squares) to 1100 (open circles) Torr.

5. Discussion

The present IMS measurements support the suggestion made in the prior study by the PDM-ECD that unusually high buffer gas pressures significantly retard the TED reaction of Az^-. If an increase in k_{TED} had been noted with an increase in buffer gas pressure, that effect might have been explainable in terms of the classic Lindemann model [40] for first-order reactions in the gas phase in which the rate constant increases with increased pressure until the “high pressure limit” of collisional activation by the buffer gas is reached. However, a decrease in the rate constant of a first-order process with increased pressure, such as that which has been observed here, is more difficult to explain. In addressing this question two possibilities have been considered.

As the pressure of the buffer gas is increased, the diffusion coefficients of molecules, ions, and electrons will be proportionately decreased. At some point of increased pressure, the rate of a gas phase reaction could become affected by and then limited by the decreased diffusion rates [1]. This effect of diffusion has been shown to begin to retard the rate constants of ion–ion recombination reactions in air as the total pressure is raised to a level of about 1.0 atm [41]. This effect of diffusion might not be expected to be of significance in the present study, however, because the diffusion coefficients for electrons are expected to be at least three orders of magnitude greater that those of ions and molecules [38]. This difference might be expected to cause a proportional increase in the pressure at which a diffusion effect would be detectable for a reaction involving an electron as one of the reactants or products. This expectation is additionally supported by another study of the effects of diffusion on the rate of the recombination reaction between iodine atoms [42]. For this reaction, no effect of diffusion on the reaction rate was noted under those conditions where the ratio of the diffusion coefficients (in units of $cm^2\ s^{-1}$) for iodine atoms and the rate coefficient for collisions between iodine atoms (about $1 \times 10^{-10}\ cm^3\ s^{-1}$) was made greater than about $10^7\ cm^{-1}$. In applying this result to the chemical system under investigation here, the ratio of the following two parameters is of interest. The diffusion coefficient of electrons in nitrogen buffer gas at pressures near 1 atm will be about 300 $cm^2\ s^{-1}$ [38]. The collision rate constant of electrons with simple molecules is thought to be about $3 \times 10^{-7}\ cm^3\ s^{-1}$ [43]. Therefore, the ratio of these two factors (about $1 \times 10^9\ cm^{-1}$) suggests that the buffer gas pressures used here are approximately two orders of magnitude lower than the pressure that would be required for the onset of a diffusion effect. For these reasons, we do not believe that the rate-retarding effects of increased pressure observed here can be assigned to decreased diffusion rates.

The present results might be more readily explained in terms of a chemical effect of the buffer gas on the ions suspended in the buffer gas. In studies of gas phase ion chemistry, it is generally assumed that the buffer gas serves only as a chemically inert physical medium in which the neutral and ionic reactants are suspended and maintained at thermal energy by frequent collisions. With use of very high buffer gas pressures, however, it is appropriate to consider the possibility that weak chemical interactions between ions and buffer gas molecules might cause significant alterations in the potential energy surface and rate constants of the reaction. The energetics of only a few of these weak interactions have been measurable by the conventional methods of gas phase ion chemistry that typically operate in the low Torr pressure range. For example, the weak clustering interactions, $Na^+(N_2)_{n-1} + N_2 \rightleftharpoons Na^+(N_2)_n$, where $n = 1$ and 2, are sufficiently strong to have been measured by Perry et al. [44] using the flowing afterglow method. For these reactions, they reported $\Delta H_1^0 = -8.0$ kcal/mol, $\Delta H_2^0 = -5.3$ kcal/mol, $\Delta S_1^0 = -18.6$ cal/K mol, and $\Delta S_2^0 = -18$ cal/K mol. These thermochemical values suggest that the clustering of Na^+ by nitrogen can be significant and even dominant if elevated pressures of nitrogen buffer gas are used. For example, in nitrogen buffer gas of 1.0 atm pressure and 100 °C, equilibrium abundances of Na^+, $Na^+(N_2)_1$, and $Na^+(N_2)_2$ of 17%, 72%, and 11%, respectively, are expected. Only at much lower nitrogen pressures would an insignificant amount of Na^+ clustering occur (at 1 Torr and 100 °C, 99.5% of the Na^+ ions will be unclustered).

Table 2
Arrhenius activation and preexponential factors for TED by Az^-, $k_{TED} = A\ \exp(-E_a/RT)$

Method	P (Torr)	A (s^{-1})	E_a (kcal/mol)
PHPMS[a]	4	1.14×10^{11}	15.7 ± 1.0
IMS[b]	300	3.4×10^{13}	21.3 ± 2.0
IMS[b]	740	2.1×10^{13}	21.0 ± 2.0
IMS[b]	1100	1.3×10^{14}	22.7 ± 2.0

[a] From Grimsrud et al. [26].
[b] From the Arrhenius plots shown in Fig. 6.
Key: A, pre-exponential factor; E_a, activation energy; IMS, ion mobility spectrometry; P, pressure; PHPMS, pulsed high pressure mass spectrometry; RT, product of gas constant and temperature (K); TED, thermal electron detachment.

If a chemical interaction of this type is operative between nitrogen buffer gas molecules and Az^- negative ions, a depression of the TED rate constant for Az^- in a buffer of unusually high pressure might be explained by making the following alteration of the TED process:

$$Az^-(N_2)_n \rightarrow Az + nN_2 + e \qquad (6)$$

It is noted that the Arrhenius factors listed in Table 2 indicated that E_a increases from 15.7 ± 1.0 to 21.0 ±

2.0 kcal/mol upon a change in buffer gas from methane at 4.0 Torr pressure to nitrogen at 1.0 atm pressure. In terms of Eq. (6), this increase in E_a of about 5 ± 2 kcal/mol might be viewed as reflecting the stabilizing influence of the buffer gas on the reactant ion relative to the transition state for this reaction under conditions of very high pressure. It is also noted in Table 1 that the Arrhenius preexponential factor is significantly increased (by about 2 orders of magnitude) by this buffer gas change. This might also be viewed to be qualitatively consistent with Eq. (6) in that the partial dissociation of the clustered entity, $Az^-(N_2)_n$, in the reaction transition state would provide an entropic driving force, not present in the normal TED reaction shown by Eq. (1).

The presence or absence of a suspected cluster ion might normally be verifiable by the mass spectrometer associated with the IMS apparatus [16] and, in fact, cluster ions of the type, $Az^-(N_2)_n$, were typically observed in the present study with relative intensities on the order of a few percent. However, extensive cooling is also expected to occur within the free-jet expansion of gas that accompanies aperture-sampling of an atmospheric pressure gas and this is also expected to lead to clustering between ions and major buffer gas components [45]. In addition, collisional dissociation of weakly bound cluster ions is expected to occur within the first vacuum region of the mass spectrometer. For these reasons, the relative intensities of cluster ions, $Az^-(N_2)_n$, that were observed here by the associated mass spectrometer were not considered to contain any useful information concerning the relative abundance of these ions in the drift gas.

An obvious extension of the present work would be to repeat the experiments described here using different buffer gases and we have, in fact, made preliminary efforts in this direction. Unfortunately, these efforts have not been successful, to date, with either helium or argon buffer gases because electrical discharges within the IMS have invariably occurred when either of these have been tested. At this point, we have been able to perform several experiments using methane buffer gas, however, and in these, somewhat greater (about 50% at 100 °C) rate constants for TED by Az^- have been consistently observed. If the depression of TED rate constants observed in nitrogen buffer gas is due to a chemical interaction between Az^- and the buffer gas molecules, our preliminary experiments with methane buffer gas suggests that this interaction is weaker in methane than in nitrogen. Because no literature exists (to our knowledge) concerning the interactions of methane with gas phase ions, perhaps it can be assumed that interactions of ions with methane are weaker than those with nitrogen. In that case, the greater k_{TED} values that we observe using methane buffer gas would provide additional support to the validity of the altered TED mechanism expressed by Eq. (6).

6. Conclusions

We have shown here that the IMS method for studying gas phase ionic reactions at unusually high buffer gas pressures can be successfully applied to TED reactions. Rate constants determined here for TED by the molecular anion of azulene support a suggestion previously made that k_{TED} for this process decreases when the buffer gas pressure is increased into the atmospheric pressure range. This effect of pressure is the opposite of that expected by the conventional Lindemann model for the pressure dependence of gas phase first-order processes. The most plausible explanation appears to be that k_{TED} of Az^- is being depressed with use of high buffer gas pressures by a chemical interaction between the Az^- ion and the nitrogen buffer gas molecules. By this interaction, it appears that the potential energy of the reactant ion is lowered and the activation energy of the reaction is increased. It would seem likely that the effect of pressure identified here for the TED reaction of Az^- might also be operative for other ion–molecule reaction systems for which unusually high buffer gas pressures are used.

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