International Journal of Mass Spectrometry 195/196 (2000) 481–489

Effect of buffer gas alterations on the thermal electron attachment and detachment reactions of azulene by pulsed high pressure mass spectrometry

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Received 10 June 1999; accepted 15 July 1999

Abstract

A principal motivation for the present study is to determine the ion source conditions required for achievement of the high pressure limit (HPL) of kinetic behavior for the resonance electron capture (REC) reaction of azulene (Az), $Az + e \rightarrow Az^-$. This goal is accomplished here by measuring rate constants for the reverse process, thermal electron detachment by molecular anions of azulene, $Az^- \rightarrow Az + e$, by pulsed high pressure mass spectrometry by using a variety of buffer gases, methane, argon, nitrogen, and helium, over a range of pressures, from 1 to 6 Torr, over a range of temperatures, from 150 to 200 °C. From these measurements, it is shown that the ion source conditions commonly used in electron capture mass spectrometry for the trace analysis of REC-active molecules would not be sufficient for achievement of the HPL of the REC reaction of azulene and, therefore, would likely result in significantly reduced sensitivity to this compound. The problem highlighted here for the case of azulene is undoubtedly shared by many other REC-active compounds. The resolution of this problem is expected to require accommodation of several relevant factors shown here to be important in the case of azulene, including the choice of buffer gas, pressure, and ion source temperature. (Int J Mass Spectrom 195/196 (2000) 481–489) © 2000 Elsevier Science B.V.

Keywords: Electron capture; Electron attachment; Thermal electron detachment; Azulene

1. Introduction

An important consequence of the introduction of chemical ionization mass spectrometry [1,2] for chemical analysis in 1966 was the recognition which steadily followed [3–7] that negative ions, as well as positive ions, can be readily produced within high pressure ion sources by the attachment of near-thermal-energy electrons to specific compounds. Subsequently, methods that are based on the production of molecular anions in high pressure ion sources by electron capture (EC) reactions have proven to be particularly useful in the environmental [8–11] and biomedical [12–15] sciences, where exceedingly high levels of sensitivity and chemical specificity are required in order to detect trace levels of target substances in complex samples. The high chemical specificity of electron capture mass spectrometry (ECMS) arises from the fact that only a minority of compounds react with thermal-energy electrons

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Dedicated to Bob Squires for his many seminal contributions to mass spectrometry and ion chemistry.

PII S1387-3806(99)00142-6

[16,17]. In order to undergo an EC reaction, the parent molecule must have a positive electron affinity and, upon initial electron attachment, form a molecular anion that either dissociates immediately or is sufficiently long-lived to be stabilized by collisions with buffer gas molecules [17]. The high sensitivity of ECMS is attributed to the fact that the rate constants of EC reactions can be very large, often exceeding the rate constants of fast ion–molecule reactions by more than two orders of magnitude [17,18]. In the detection and analysis of substances by ECMS, it is often preferred that the compound of interest undergo EC predominantly by resonance electron capture (REC), rather than by dissociative electron capture processes, because REC reactions lead to intact molecular anions which are directly indicative of the parent compound of interest [17].

The elementary steps involved in REC reactions are shown in

$$e + M \underset{k_2}{\overset{k_1}{\rightleftharpoons}} M^{-*} \underset{k_4[B]}{\overset{k_3[B]}{\rightleftharpoons}} M^- \tag{1}$$

By this mechanism, a short-lived excited molecular radical anion, M^{-*}, is first formed by the attachment of a thermal-energy electron to M with second-order rate constant k_1. The M^{-*} species contains significant excess internal energy equal to the electron affinity of M and will undergo autodetachment with first-order rate constant, k_2, if it is not first stabilized by collisions with the buffer gas, B, with second-order rate constant, k_3, to form a thermal-energy molecular radical anion, M^-. Finally, the product, M^-, can also be collisionally reactivated back to the intermediate state, M^{-*}, with second-order rate constant, k_4. This reverse process is expected to be important, however, only for compounds with relatively weak electron affinities of less than about 20 kcal mol^{-1} [17].

In reaction (1), it is clear that if thermal-energy M^- ions are to be efficiently produced by REC reactions, the buffer gas pressure must be sufficiently high so that collisional quenching of the M^{-*} species occurs rapidly relative to autodetachment (that is $k_3[B] \gg k_2$). This condition is called the high pressure limit (HPL) of kinetic behavior for the REC process where (assuming k_4 is of negligible magnitude) the overall observed rate constant, k_{REC}, is expected [17] to equal the initial attachment rate constant, k_1. Unfortunately, k_2 values have been measured for only a few REC-active compounds and these measurements have been made primarily at room temperature. Therefore, the buffer gas conditions needed to meet the HPL for most compounds is generally not known.

Johnson et al. [19] have provided some measurements of autodetachment lifetimes for the molecular anions, M^{-*}, of a set of substituted nitrobenzenes formed at room temperature, and from these measurements some speculation concerning the HPL for substituted nitrobenzenes can be provided. The measurements by Johnson et al. indicated that k_2 values for the molecular anions of substituted nitrobenzenes varied by approximately an order of magnitude with a maximum value of about 1×10^5 s^{-1} for the molecular anion of *p*-fluoronitrobenzene. In assessing the minimum buffer gas pressure of methane required to reach the HPL for REC by *p*-fluoronitrobenzene, it is also necessary to know the efficiency, ϕ_B, of the buffer gas collisions for removing energy from the M^{-*} species, since $k_3 = \phi_B k_{col}$ ($k_{col} \approx 1.0 \times 10^{-9}$ cm^3 s^{-1} is the calculated collision constant [20] for this ion in CH_4). Since ϕ_B for the excited molecular anion of *p*-fluoronitrobenzene is not known, only a rough estimate can be obtained from previous investigations of the collisional relaxation of other vibrationally excited ions in a variety of buffer gases [21–23]. From these studies, a rough estimate of ϕ_B for this case might lie somewhere between 0.01 and 0.1. This, in turn, sets our estimate for k_3 somewhere between 1×10^{-11} and 1×10^{-10} cm^3 s^{-1}. Assuming a methane buffer gas pressure of 1.0 Torr and an ion source temperature of 150 °C (where $[B] \approx 2.3 \times 10^{16}$ molecules cm^{-3}), $k_3[B]$ is then expected to fall between 2×10^5 and 2×10^6 s^{-1}, which is about 2–20 times greater than $k_2 = 1 \times 10^5$ s^{-1}. From these considerations, it appears that the REC reaction of *p*-fluoronitrobenzene would be just barely onto its HPL of kinetic behavior under these buffer gas conditions provided that the k_2 used here is valid at a temperature of 150 °C. If k_2 for *p*-fluoronitrobenzene is substantially greater at 150 °C than at room temperature, the HPL might then not be obtained for this compound in 1 Torr methane buffer gas at 150 °C. In addition, many other classes of compounds that readily undergo REC might be expected to have k_2 values that are significantly larger than those of substituted nitrobenzenes due to differences in relevant molecular parameters such as electron affinity and the number of vibrational modes of freedom. Therefore, it cannot be assumed at this point that the HPL of REC processes, in general, are achieved for REC-active compounds over the 0.1-to-1.0 Torr buffer gas conditions commonly used for ECMS. For those REC-active compounds for which the HPL is not attained under standard ECMS conditions, the observed magnitude of k_{REC} will be reduced relative to that of k_1 in accordance with the expression, $k_{REC} = k_1k_3[B]/(k_2 + k_3[B])$ [17]. If $k_2 \gg k_3[B]$ under a given condition, $k_{REC} = k_1k_3[B]/k_2$ will become exceedingly small relative to k_1.

In the present study, additional insight into the dynamics of a REC process is provided by an investigation of the thermal electron detachment (TED) reaction of the molecular anion of azulene (Az^-), $C_{10}H_8^-$, under a variety of buffer gas conditions by pulsed e-beam high pressure mass spectrometry (PHPMS). Although several studies of the TED reaction of azulene have previously appeared in the literature [24–26], the present study adds additional detail to these by including the effects of buffer gas and temperature changes over the pressure range, 1–6 Torr. The detailed steps in the TED reaction of Az^- are indicated in

$$Az^- \underset{k_3[B]}{\overset{k_4[B]}{\rightleftharpoons}} Az^{-*} \xrightarrow{k_2} Az + e \qquad (2)$$

Inspection of reactions (1) and (2) indicates that the overall TED process is, in fact, the reverse of the overall REC process and that the rate constant assigned to the individual steps in Sequences (1) and (2) are the same. Although azulene is known to capture thermal electrons rapidly [27], it is also known to have an electron affinity, about 17 kcal/mol [24,28], of only moderate magnitude. Therefore, TED by Az^- can be readily observed with use of moderately high ion source temperatures. The electron attachment step (k_1) has not been included in reaction (2) because this step will be intentionally prevented in the present study by the inclusion of an electron scavenger (CF_2Cl_2) in the buffer gas. From the set of TED measurements provided here, the buffer gas conditions under which the HPL might be expected to be reached for the REC reaction of azulene will be deduced.

2. Experimental

The pulsed e-beam high pressure mass spectrometer used here has been previously described in detail [29–31]. In addition, a study of the TED reaction of Az^- using a very similar PHPMS technique has also been previously reported [24]. The significant difference between the present and former study of TED for Az^- by PHPMS is that the present study focuses much more intensely on the effect of buffer gas changes on k_{TED} for Az^-. In the present experiment, a mixture of gases with suitable composition flows into a thermostated ion source of 5.5 cm^3 volume at various rates selected to produce total ion source pressures between 1 and 6 Torr. In the present study, this gas mixture exits the ion source only by passage through the electron beam entrance and ion exit slits (both 25×1000 μm). Gas mixtures were prepared in an associated gas-handling plant and consisted of relatively small quantities of azulene and CF_2Cl_2 added to much larger amounts of either methane, nitrogen, argon, or helium gas. Although it has been previously shown [29,30] that concentration enrichment of the heavier components of a gaseous mixture will occur in an ion source of the present design (due to mass-dependent molecular flow through its narrow slits), this factor is not important in the present study because accurate knowledge of the component concentrations will not be required. Nevertheless, the appropriate correction for this enrichment effect [29,30] has been applied to all ion source concentrations reported here.

A short (30 μs) pulse of 3000 V electrons produces positive ions and electrons within the ion source. At

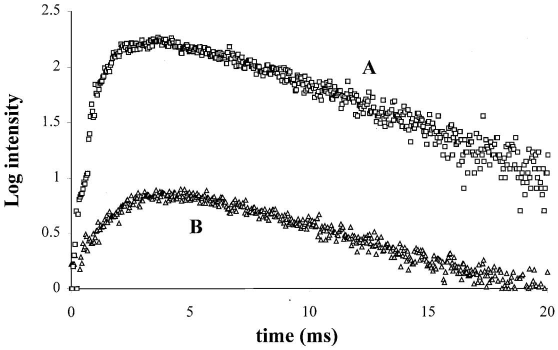

Fig. 1. A typical PHPMS result obtained with use of a relatively low ion source temperature. The buffer gas is methane at a pressure of 3.0 Torr and temperature of 50 °C. The partial pressures of azulene and CF_2Cl_2 are 0.18 and 12 mTorr, respectively. Data points A indicate the observed time dependence of the Cl^- ion and data points B indicate the observed time dependence of the Az^- ion.

the total pressures used here, thermalization of the secondary electrons occurs quickly and these electrons are then rapidly captured by azulene and CF_2Cl_2 to produce Az^- and Cl^- ions, respectively. The number density of ions is sufficiently low so that the dominant loss of the total negative ion population is by first-order diffusion to the walls [32]. The diffusional wall current thereby established is measured by an associated quadrupole mass spectrometer that monitors either the Az^- or Cl^- ions as a function of time after the e-beam pulse as the ions diffuse to all points on the ion source walls. A multichannel scaler accumulates the results of many such experiments that are repeated at a frequency of about 10 Hz for a duration of about 1.0 min.

3. Results and discussion

Fig. 1 displays the results typically obtained with use of a relatively low ion source temperature (50 °C). In this example, the ion source contains about 0.1 mTorr azulene and about 6 mTorr CF_2Cl_2. The buffer gas is methane set to a total pressure of 3.0 Torr. Under these conditions, the only reactions of importance are DEC by CF_2Cl_2 to form the Cl^- fragment ion and REC by azulene to form the Az^- molecular ion. After about 5 ms, all of the secondary electrons have been captured and a first-order diffusional mode [32] for the transport of all ions to the ion source walls is established. When the relative concentrations of CF_2Cl_2 and azulene were altered at this source temperature, the only effect observed was that the relative intensities of the two ions initially produced by the two electron capture reactions were changed in proportion to the altered concentration ratios of CF_2Cl_2 and azulene. The slopes of the observed log intensity versus time plots for each ion were not altered by these changes, however. In addition, if either CF_2Cl_2 or azulene, alone, was added to the ion source along with buffer gas at a relatively low temperature, the time dependence of the resulting Cl^- or Az^- ion signal took the same form and displayed the same decay rate as shown in Fig. 1. These results indicate that the only means of loss for either of these ions at low ion source temperatures is their simple diffusion to the walls of the ion source and that Cl^- ions do not react with azulene molecules and that Az^- ions do not react with CF_2Cl_2 molecules, as expected [33]. From experiments such as the one shown in Fig. 1, a first-order rate constant for diffusional loss of Az^-, ν_{dif} (CH_4, 3 Torr, 50 °C), is obtained [24] under these conditions from the relationship, $\nu_{\mathrm{dif}} = 2.303 \times$ slope (where slope $= \Delta\log$ intensity$/\Delta t$ over the period of the first-order diffusional mode between $t = 5$ and 18 ms). The magnitude of ν_{dif} for Az^- at higher ion source temperatures and other ion source pressures is then deduced from $\nu_{\mathrm{dif}}(CH_4$, 3 Torr, 50 °C) from the expected [24] relationship, $\nu_{\mathrm{dif}}(CH_4, X$ Torr, Y °C$) = \nu_{\mathrm{dif}}(CH_4$, 3 Torr, 50 °C$)(3/X)[(Y + 273)/323]^2$. Analogous measurements and this equation were also used for determining ν_{dif} for Az^- in all other experiments performed at higher temperatures in nitrogen, argon, and helium buffer gases.

In Fig. 2 a set of results obtained under conditions of moderately high ion source temperature (180 °C) and methane buffer gas at 6.0 Torr pressure is shown. For all experiments A–E, the ion source contains 0.1 mTorr azulene and the time dependence of the Az^- signal, only, is shown (whereas a Cl^- ion of much greater intensity is also observed when CF_2Cl_2 is present, the time dependence of this ion is not

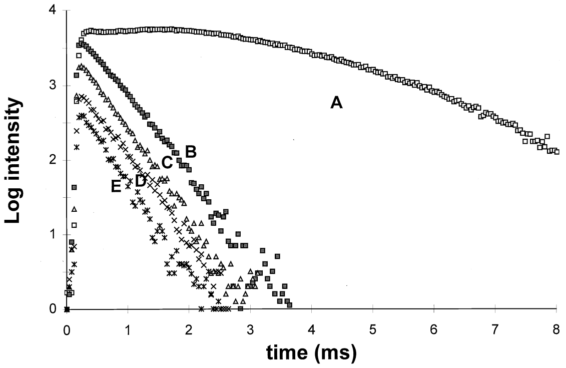

Fig. 2. Time dependencies of the Az^- ion observed with use of a moderately high ion source temperature for five different experiments using five different partial pressures of CF_2Cl_2. The buffer gas is methane at a pressure of 6.0 Torr and temperature of 180 °C. In all cases, the partial pressure of azulene was 0.1 mTorr. The partial pressures of CF_2Cl_2 are (A) 0.0, (B) 5, (C) 10, (D) 16, and (E) 29 mTorr.

required for subsequent determinations of k_{TED} for Az^- and, therefore, has not been included in Fig. 2). In experiment A of Fig. 2, no CF_2Cl_2 was added to the ion source and, therefore, only Az^- was made by the initial capture of the secondary electrons. At this temperature it is noted that a simple first-order diffusional loss rate of Az^- was not observed as it was in Fig. 1 with use of a lower ion source temperature. This is because the TED reaction of Az^- is much faster at 180 °C and this maintains a relatively large concentration of electrons within the ion source throughout the course of the measurement. These electrons either undergo another REC reaction with Az or diffuse to the walls of the ion source. The simultaneous presence of electrons with negative ions in the source gas introduces a complexity [24,32] to the diffusional process which results in the nonlinear relationship observed between log intensity and time. Because of these complications, no meaningful information has been extracted here from experiments performed under condition A.

In experiment B of Fig. 2, it is seen that the addition of 5.0 mTorr CF_2Cl_2 to the ion source causes a dramatic change in the time dependence of the Az^- signal. It is then noted that the slope, Δlog intensity/Δt, is much greater and is constant throughout most of the experiment. This change has been caused by the rapid scavenging of electrons by CF_2Cl_2, which eliminates the diffusional loss complexities referred to above that are operative when electrons as well as negative ions are present in significant abundance [24,32]. In addition, the presence of CF_2Cl_2 prevents the reattachment of electrons to azulene during the period of diffusional loss. As a result, the v_{Az-} values obtained from experiment B of Fig. 2 by the relationship, $v_{Az-} = 2.303 \times$ slope, can be expressed [24] by

$$v_{Az-} = k_{TED} + v_{dif} \tag{3}$$

In experiments C, D, and E in Fig. 2, progressively greater amounts of the electron scavenger, CF_2Cl_2, were added to the buffer gas. Although this decreases the amount of Az^- initially produced by the capture of the original secondary electrons, it is seen that v_{Az-} is not significantly changed by these large increases in the concentration of CF_2Cl_2. This indicates that electron reattachment to azulene has been effectively prevented in all experiments B–E in Fig. 2 and again indicates that, as expected [33], Az^- does not undergo a bimolecular reaction with CF_2Cl_2.

As described previously, measurements of v_{dif} and v_{Az-} were obtained in methane, nitrogen, argon, and helium buffer gases over a pressure range from 1 to 6 Torr, a temperature range from 150 to 200 °C, with 10–20 mTorr CF_2Cl_2 present in the ion source. By Eq. (3), determinations of k_{TED} were then obtained under each of these conditions. The values of k_{TED} obtained at an ion source temperature of 190 °C, for example, are shown in Fig. 3. From these measurements, it is clear that k_{TED} is distinctly dependent on the choice of buffer gas and on the magnitude of the buffer gas pressure.

In order to better understand the variations of k_{TED} shown in Fig. 3, it is useful to develop a more detailed model of the processes represented in reaction (2). The rate constant, k_3, can be set equal to the rate constant, k_{col}, for collisions of the M^{-*} species with the buffer gas molecules, B, times the efficiency, ϕ_B, for stabilization of M^{-*} by each collision ($k_3 = \phi_B k_{col}$). If K is defined to be the equilibrium constant for the first step in reaction (2) (that is, $K = k_4/k_3$),

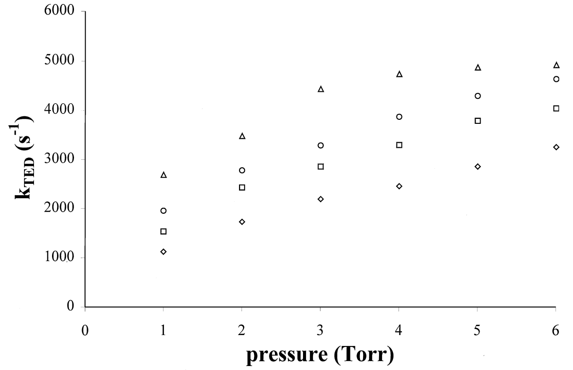

Fig. 3. Rate constants observed for the TED reaction of Az$^-$ as a function of ion source pressure at a temperature of 190 °C. The buffer gases used are methane (triangle), nitrogen (circle), argon (square), and helium (diamond).

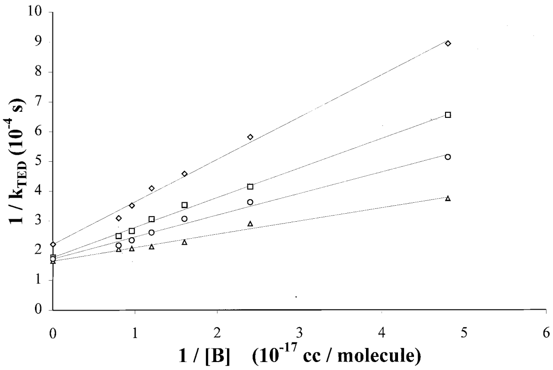

Fig. 4. Rate constants for TED by Az$^-$ at 190 °C plotted in the form of Eq. (5). The buffer gases used are methane (triangle), nitrogen (circle), argon (square), and helium (diamond).

then $k_4 = K\phi_B k_{col}$. By application of the steady-state approximation to the species, M^{-}*, in reaction (2), the following general expression for k_{TED} is then obtained:

$$k_{TED} = \frac{k_2 K \phi_B k_{col}[B]}{\phi_B k_{col}[B] + k_2} \tag{4}$$

The HPL for Eq. (4) would be obtained when $\phi_B k_{col}[B] \gg k_2$. Under this condition Eq. (4) would be simplified to the form, $k_{TED}(HPL) = k_2 K$, for which no change in k_{TED} would be expected with changes in either identity of the buffer gas or the ion source pressure. Since such changes are, in fact, evident in Fig. 3, the TED reaction of Az$^-$ has clearly not reached its HPL of kinetic behavior under most of the buffer gas conditions represented in Fig. 4.

In order to determine the magnitudes of some of the individual constants included in Eq. (4), it is useful to rearrange Eq. (4) into the following form:

$$\frac{1}{k_{TED}} = \frac{1}{Kk_2} + \frac{1}{\phi_B k_{col} K[B]} \tag{5}$$

Equation (5) predicts that a plot of $1/k_{TED}$ versus 1/[B] should produce a straight line for a set of measurements made with a specific buffer gas at a specific temperature and that the intercepts and slopes of these plots should be equal to $(Kk_2)^{-1}$ and $(\phi_B k_{col} K)^{-1}$, respectively. In Fig. 4 the experimental results shown in Fig. 3 have been replotted in the form of Eq. (5) and it is seen that straight lines are then obtained. The results obtained at all other temperatures also produced linear plots of this type and their intercepts and slopes are listed in Table 1. From these intercepts and slopes, it would be possible to determine the magnitudes of k_2 and ϕ_B under each ion source condition if the magnitudes of k_{col} and K were both known. Although values for k_{col} can be reliably

Table 1
Magnitudes of slopes, intercepts, and k_2/ϕ_B deduced from plots of $1/k_{TED}$ vs. 1/[B]

	150 °C	170 °C	190 °C	200 °C
CH_4 buffer gas				
Intercept (s)	1.3×10^{-3}	5.1×10^{-4}	1.6×10^{-4}	1.2×10^{-4}
Slope (s cm^{-3})	1.1×10^{13}	7.3×10^{12}	3.3×10^{12}	3.1×10^{12}
k_2/ϕ_B (s^{-1})	8.3×10^{6}	1.5×10^{7}	2.0×10^{7}	2.5×10^{7}
Ar buffer gas				
Intercept (s)	1.4×10^{-3}	4.9×10^{-4}	1.8×10^{-4}	1.3×10^{-4}
Slope (s cm^{-3})	2.7×10^{13}	1.7×10^{13}	9.6×10^{12}	8.1×10^{12}
k_2/ϕ_B (s^{-1})	1.1×10^{7}	1.9×10^{7}	2.9×10^{7}	3.4×10^{7}
N_2 buffer gas				
Intercept (s)	1.3×10^{-3}	5.0×10^{-4}	1.7×10^{-4}	1.2×10^{-4}
Slope (s cm^{-3})	2.0×10^{13}	1.2×10^{13}	7.3×10^{12}	5.1×10^{12}
k_2/ϕ_B (s^{-1})	9.9×10^{6}	1.5×10^{7}	2.7×10^{7}	2.7×10^{7}
He buffer gas				
Intercept (s)	1.3×10^{-3}	4.5×10^{-4}	2.2×10^{-4}	1.3×10^{-4}
Slope (s cm^{-3})	3.8×10^{13}	2.7×10^{13}	1.4×10^{13}	9.1×10^{12}
k_2/ϕ_B (s^{-1})	1.6×10^{7}	3.3×10^{7}	3.6×10^{7}	3.7×10^{7}

calculated [20] by means of the Langevin equation (for buffer gases CH_4, N_2, Ar, and He, k_{col} is predicted to be 1.01×10^{-9}, 0.64×10^{-9}, 0.54×10^{-9}, and 0.54×10^{-9} $cm^3\ s^{-1}$, respectively, at all temperatures), the magnitudes of K at each temperature cannot be reliably obtained by independent means. It is therefore useful to also consider the slope-to-intercept ratio of each of these plots where K cancels out and is expected to equal the quantity, $k_2/\phi_B k_{col}$. Since k_{col} is known, the ratio, k_2/ϕ_B, is thereby obtained from these measurements and this quantity is also indicated in Table 1 for each ion source condition.

In assessing the data shown in Table 1, the observed intercepts are expected to be equal to the quantity, $(Kk_2)^{-1}$, and should not vary significantly with changes in the identity of the buffer gas at a given ion source temperature. This expectation is seen to be reasonably well met. On the other hand, the observed slopes are expected to be equal to the quantity, $(\phi_B k_{col} K)^{-1}$, and are expected to vary somewhat with changes in the identity of the buffer gas due to their differences in ϕ_B and k_{col}. This expectation is also met and, since the k_{col} values are known, the ratio of observed slopes at a given temperature (where K will be a constant value) provides a means of determining the ratio of the ϕ_B values for the four different buffer gases. Since the collision efficiency for methane is consistently observed to be the greatest among the buffer gases used here, it is useful to also define the term relative collision efficiency, $\phi'_B = \phi_B/\phi_{CH_4}$. By assessing the observed slopes in this manner, the ϕ'_B values for each buffer gas were obtained at each of the four temperatures and have been plotted in Fig. 5. The average ϕ'_B values in nitrogen, argon, and helium at all temperatures were found to be about 0.85, 0.75, and 0.55, respectively. The degree of variation noted in these measurements of ϕ'_B from one temperature to another is thought to result merely from uncertainties associated with the measurements and not from real effects of temperature change.

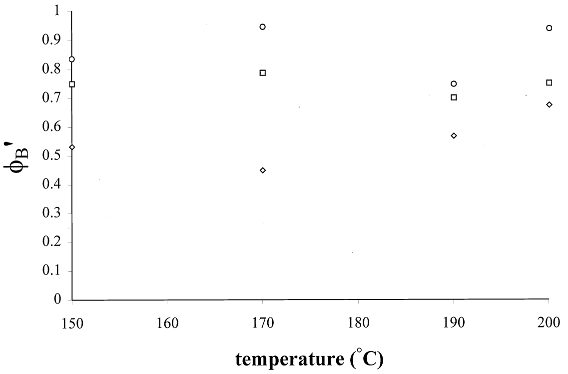

Fig. 5. Relative collisional quenching efficiencies, $\phi'_B = \phi_B/\phi_{CH_4}$, observed for nitrogen (circle), argon (square), and helium (diamond) at four different ion source temperatures.

The k_{TED} measurements that were previously presented in Fig. 3 can now be presented in the alternative manner shown in Fig. 6 where the k_{TED} values observed in all buffer gases at 190 °C have been plotted as a function of the combined quantity, $k_{col}\phi'_B[B]$. When plotted in this form, the expected differences in quenching rates of the different buffer gases are accounted for and a relatively continuous curve is then observed. From this curve, it is apparent that the HPL for the TED reaction of Az^- is being reached only under the conditions shown where the collective term, $k_{col}\phi'_B[B]$, is relatively large. In addition, these data suggest that the HPL is reached in methane buffer gas only if the ion source pressure is set at 3 Torr or greater. In Fig. 7 the same type of plot is shown for all measurements of k_{TED} made at all four temperatures. Inspection of the curves shown

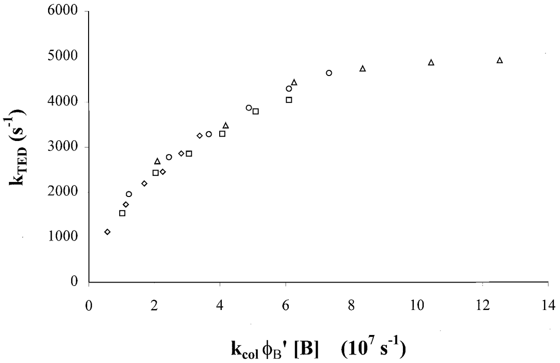

Fig. 6. Rate constants for TED by Az^- at 190 °C as a function of the collective term, $k_{col}\phi'_B[B]$, using buffer gases methane (triangle), nitrogen (circle), argon (square), and helium (diamond).

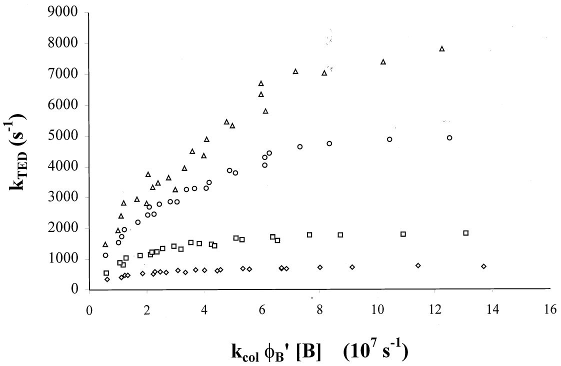

Fig. 7. Rate constants for TED by Az$^-$ observed at 150 (diamond), 170 (square), 190 (circle), and 200 °C (triangle) in all four buffer gases as a function of the collective term, $k_{col}\phi'_B$[B].

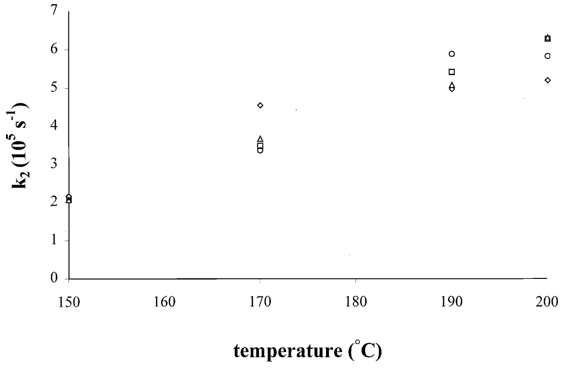

Fig. 8. Estimates of the autodetachment rate constant, k_2, for the Az$^-$* species as a function of ion source temperature in buffer gases methane (triangle), nitrogen (circle), argon (square), and helium (diamond).

indicates that the point at which the HPL for the TED reaction of Az$^-$ is reached also varies significantly with ion source temperature. At 150 °C, the HPL appears to be reached at a magnitude of $k_{col}\phi'_B$[B] that is approximately 1/4 as great as that required to reach the HPL at 200 °C.

In order to deduce the magnitudes of k_2 values from the measurements of k_2/ϕ_B listed in Table 1, it would be necessary to know the magnitudes of ϕ_B for each buffer gas at each temperature and this information is not available. Therefore, in the interest of obtaining rough estimates of the k_2 values operative here, it will be momentarily assumed that the efficiency of methane for collisional stabilization of the Az$^-$* species of interest is the same as that reported by Ahmed and Dunbar [23] for the collisional stabilization of photoexited bromobenzene positive ions, for which they found $\phi_{CH_4} = 0.025$. If it is assumed that this ϕ_{CH_4} value can be applied at all temperatures used here, the corresponding ϕ_B values for the other three buffer gases at each temperature are then also set by the relationship, $\phi_B = 0.025\phi'_B$, and the ϕ'_B values indicated in Fig. 5. The k_2 values thereby obtained from all measurements of k_2/ϕ_B indicated in Table 1 are shown in Fig. 8. From Fig. 8, the lifetime ($1/k_2$) of the Az$^-$ species against autodetachment is suggested to decrease continuously with increased temperature from about 5 μs at 150 °C to about 2 μs at 200 °C. There appears to be at least an approximate level of agreement, therefore, between the present measurements and our interpretations of them with a previous report by Chaney et al. [27], who observed a lifetime of about 7 μs against autodetachment for Az$^-$* formed by its REC reaction with near thermal electrons at room temperature.

4. Conclusions

It has been shown here that the HPL for the TED reaction of Az$^-$ is not reached in methane buffer gas unless the ion source pressure is elevated to levels of about 1 Torr at an ion source temperature of 150 °C and to levels of about 4 Torr at an ion source temperature of 200 °C. Because the individual steps associated with REC reactions are the same as those associated with TED reactions, it is reasonable to assume that the buffer gas pressures required for attaining the HPL for REC reactions will be the same as those required for the corresponding TED reactions. Therefore, the present study provides evidence for an important point of concern in the application of ECMS for the sensitive detection of REC-active compounds. In common applications of the ECMS technique, methane buffer gas is typically used and is set at some pressure between about 0.1 and 1 Torr. Due to limitations of the pumping systems commonly associated with ECMS instruments, the lower value of about 0.1 Torr is most often selected. In addition, the ion source temperature is typically greater than 150 °C and is commonly in excess of 200 °C. The selection of lower ion source temperatures is difficult with routine ECMS instruments because of the close proximity of an e-beam filament. Therefore, the present results suggest that the HPL for the REC reaction of azulene would not be reached in an attempt to detect azulene using standard ECMS instrumentation. In fact, the sensitivity achieved in such an analysis would fall far short of that which could potentially be achieved using some other specialized ECMS instrument designed specifically to ensure that the HPL for this reaction was reached. For example, with use of an ECMS ion source condition of 0.1 Torr methane buffer gas and 200 °C, the present measurements indicate that only about 8% of the initially formed Az^{-*} ions would be stabilized by collisions with the buffer gas, resulting in a corresponding loss of sensitivity. It seems likely that the problem suggested to exist here for the case of azulene will also be operative for many other REC-active compounds.

Acknowledgement

This work was supported by a grant from the Chemistry Division of the National Science Foundation (grant no. CHE-9816643).

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