A Simple Method for Estimating Effective Ion Source Residence Time

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A method is presented that uses the well-understood O_2/Ar ion-molecule reaction system to determine the effective ion source residence time of a chemical ionization source. The process consists of: (1) defining the kinetic system in terms of reactions, reaction rates, and ionization cross sections; (2) solving the differential equations that describe the time evolution of the kinetic system, and (3) comparing the calculated results to experimentally measured relative ion intensities. These steps are repeated for a variety of O_2/Ar sample ratios and inlet pressures. The method leads to a simple relationship between inlet pressure and effective ion source residence time, independent of the O_2/Ar sample ratio. (*J Am Soc Mass Spectrom* 1993, 4, 787-791)

For over twenty years, chemical ionization (CI) has been used to elucidate information about the structure and identity of organic compounds [1]. CI mass spectra are generally quite different from electron ionization (EI) spectra, and are often more informative. In CI mass spectrometry, the ionization of the "unknown" material is produced by reactions with an ionized reagent gas. The spectra produced are characteristic of the particular reagent gas used. Typical reagent gases include deuterium oxide, methane, ammonia, and nitric oxide [2]. The extent of CI depends on the amount of time that the sample and reagent gases spend in the ionization source. This residence time, t_r , while of experimental interest, is often an unknown quantity and is dependent on the pressure inside the ionization source (P_{so}). This article presents a simple method for estimating an effective ion source residence time as a function of inlet pressure (P_{in}). The effective ion source residence time, $\hat{t}_r$, is defined as the apparent time available for source ions to undergo reactions if P_{so} is taken to be equal to P_{in} . Because P_{in} and P_{so} can be very different from one another, t_r and $\hat{t}_r$ can also differ considerably. However, under the usual pseudo-first-order conditions of a CI source, knowing $\hat{t}_r$ and P_{in} is sufficient to predict the extent of the ion-molecule reactions in the source.

Methods

Instrumentation

Shown in Figure 1 is the ion source used in this study. Ions are produced initially by EI of the inlet gas.

Ionizing electrons are produced from a hot Re filament located externally to the ion source with total emission current regulated. The ionizing energy (E_e) was taken to be the nominal voltage between the filament and the source, and E_e for this investigation was kept constant at 80 eV. Ions exiting the source are accelerated to 5 keV, magnetically mass resolved, and detected by a channeltron electron multiplier. Various O_2/Ar mixtures were used in this study, and P_{in} ranged from 0.32–1.60 torr, as measured by a capacitance manometer. All experiments were done at 300 K.

Ion-Molecule Reaction System

The O_2^+ internal state distribution produced by EI with $E_e = 80$ eV initially consists of ions in the $X^2\Pi_g$, $a^4\Pi_u$, $A^2\Pi_g$, $b^4\Sigma_g^-$, and dissociative $B^2\Sigma_g^-$ states [3–8]. The lifetimes of the $A^2\Pi_g$ and $b^4\Sigma_g^-$ states are sufficiently short [3, 4] as to assume the O_2^+ ions participating in the ion-molecule reactions consist of only $X^2\Pi_g$ and metastable $a^4\Pi_u$ state ions (O_2^+ and O_2^{+*} , respectively). While it is possible that a variety of excited Ar^+ states are produced in the initial ionization step, none of these excited states should live long enough to be considered in the reaction system, as the doublet and quartet terms are well connected by observed intersystem combinations [9, 10]. Additionally, O^+ ions will also be present in the source in both ground ($^4S_{3/2}$, O^+) and excited ($^2D_{3/2}$ and $^2P_{1/2}$, O^{+*}) states. O^+ and O^{+*} reactions with Ar are sufficiently slow as to be neglected [11]. Thus, there are five relevant ion-molecule reactions for the O_2/Ar kinetic system [11–13]:

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Figure 1. Diagram of the chemical ionization source used in this investigation.

Because [neutrals] $\gg$ [ions] under the present experimental conditions, the time evolution of the kinetic system is well described by the coupled first-order linear differential equations:

$$\frac{d[\text{O}_2^+]}{dt} = k_2'[\text{Ar}^+] + k_3'[\text{O}_2^{+*}] + k_4'[\text{O}^+] + k_5'[\text{O}^{+*}] \quad (6)$$

$$\frac{d[\text{O}_2^{+*}]}{dt} = -k_1'[\text{O}_2^{+*}] - k_3'[\text{O}_2^{+*}] \quad (7)$$

$$\frac{d[\text{Ar}^+]}{dt} = k_1'[\text{O}_2^{+*}] - k_2'[\text{Ar}^+] \quad (8)$$

$$\frac{d[\text{O}^+]}{dt} = -k_4'[\text{O}^+] \quad (9)$$

$$\frac{d[\text{O}^{+*}]}{dt} = -k_5'[\text{O}^{+*}] \quad (10)$$

where $k_1' = k_1[\text{Ar}]$, $k_2' = k_2[\text{O}_2]$, $k_3' = k_3[\text{O}_2]$, $k_4' = k_4[\text{O}_2]$, and $k_5' = k_5[\text{O}_2]$. Integration of eqs 6-10 leads to:

$$\begin{aligned} [\text{O}_2^+] &= [\text{O}_2^+]_0 - [\text{Ar}^+]_0(e^{-k_2't} - 1) \\ &\quad - [\text{O}^+]_0(e^{-k_4't} - 1) - [\text{O}^{+*}]_0(e^{-k_5't} - 1) \\ &\quad + [\text{O}_2^{+*}]_0 \left(\frac{k_1'e^{-k_2't}}{\{k_2' - k_1' - k_3'\}} \right. \\ &\quad \left. - \frac{(k_1'k_2' + k_3'(k_2' - k_1' - k_3'))e^{-(k_1'+k_3')t}}{\{k_1' + k_3'\}(k_2' - k_1' - k_3')} + 1 \right) \end{aligned} \quad (11)$$

$$[\text{O}_2^{+*}] = [\text{O}_2^{+*}]_0 e^{-(k_1' + k_3')t} \quad (12)$$

$$[\text{Ar}^+] = \frac{[\text{O}_2^{+*}]_0 k_1' \{e^{-(k_1' + k_3')t} - e^{-k_2't}\}}{\{k_2' - k_1' - k_3'\}A} + [\text{Ar}^+]_0 e^{-k_2't} \quad (13)$$

$$[\text{O}^+] = [\text{O}^+]_0 e^{-k_4't} \quad (14)$$

$$[\text{O}^{+*}] = [\text{O}^{+*}]_0 e^{-k_5't} \quad (15)$$

In eqs 11-15, $[]_0$ are the initial ion concentrations given by:

$$[\text{O}_2^+]_0 = S(1 - \alpha)\sigma_{\text{O}_2}[\text{O}_2] \quad (16)$$

$$[\text{O}_2^{+*}]_0 = S\alpha\sigma_{\text{O}_2}[\text{O}_2] \quad (17)$$

$$[\text{Ar}^+]_0 = S\sigma_{\text{Ar}}[\text{Ar}] \quad (18)$$

$$[\text{O}^+]_0 = S(1 - \beta)\sigma_{\text{O}}[\text{O}_2] \quad (19)$$

$$[\text{O}^{+*}]_0 = S\beta\sigma_{\text{O}}[\text{O}_2] \quad (20)$$

where σ is the 80 eV cross section for ionization ($1.57 \times 10^{-16} \text{ cm}^2$, $2.5 \times 10^{-16} \text{ cm}^2$, and $0.8 \times 10^{-16} \text{ cm}^2$ for O_2 , Ar , and O from O_2 , respectively [14-16]), α is the fraction of O_2^+ ions initially produced in the excited state at 80 eV ($\alpha = 0.33$ [17]), β is the fraction of O^+ ions initially produced in the excited states at 80 eV ($\beta = 0.30$ [17]), and $S = [\text{total ions}]_0 / (\sigma_{\text{O}_2}[\text{O}_2] + \sigma_{\text{O}}[\text{O}_2] + \sigma_{\text{Ar}}[\text{Ar}])$. In general, determination of S is difficult, and cannot be done readily for our ion source. However, if ion ratios are compared instead of individual ion intensities, the results are independent of S .

Ion loss due to diffusion to the walls of the source can be a complex problem in an ion-molecule reaction scheme. However, the choice of the O_2/Ar system simplifies this consideration. Because Ar^+ and O_2^+ ions have nearly identical mobilities in Ar [18], the $[\text{Ar}^+]/[\text{O}_2^+]$ ratio is largely unaffected by the diffusion of Ar^+ and O_2^+ to the walls. The reaction rate of O^{+*} with O_2 is sufficiently fast (approximately 80% of the Langevin collision rate), so that under present source conditions, diffusional wall loss of O^{+*} can be ignored. Alternatively, the reaction of O^+ with O_2 is sufficiently slow so that it does not react significantly in the time scale of interest. Thus, diffusion effects can be neglected in the system.

The Relationship of P_{so} and P_{in}

The residence time is dependent upon the concentration of all species in the source ($[i]_{\text{so}}$), which is related to the inlet pressure through:

$$[i]_{\text{so}} = \frac{P_{\text{so}}}{k_B T} = \frac{\gamma_i(P, T)P_{\text{in}}}{k_B T} = \gamma_i(P, T)[i]_{\text{in}} \quad (21)$$

where $P_{i,so}$ is the partial pressure of species i inside the source, $P_{i,in}$ is the partial pressure of species i as measured at the inlet, k_B is Boltzmann's constant, T is the absolute temperature, and $\gamma_i(P, T)$ is the proportionality function between $P_{i,so}$ and $P_{i,in}$. Insight into γ_i can be obtained by modeling flow into the source with Poiseuille's formula for flow through a tube and flow out of the source by Graham's law of effusion. In such a model, the rate of change in the number of molecules of species i in the source ($dN_{i,so}/dt$) is given by [19]:

$$\frac{dN_{i,so}}{dt} = \frac{\pi r^4 P_{i,in} (1 - \gamma_i^2)}{k_B T l 6 \eta} - \frac{\gamma_i P_{i,in} A}{\sqrt{2 \pi m_i k_B T}} \quad (22)$$

where r is the radius of the inlet gas tube, l is the length of the inlet gas tube, η is the viscosity of the inlet gas, m_i is the mass of the species i , and A is the area of the escape apertures on the source. Under steady-state conditions, $dN_{i,so}/dt = 0$ so that eq 22 can be solved for γ_i giving:

$$\gamma_i = \frac{1}{2} \left[\frac{-P_i}{P_{i,in}} \pm \left(\frac{P_i^2}{P_{i,in}^2} + 4 \right)^{1/2} \right] \quad (23)$$

where only the positive combination is physically meaningful and P_i is given by:

$$P_i = \frac{16 A l \eta}{\pi r^4} \left(\frac{k_B T}{2 \pi m_i} \right)^{1/2} \quad (24)$$

which is independent of pressure at low pressures. In the limit of high and low $P_{i,in}$, γ_i can be approximated by:

$$\gamma_i \approx 1 - \frac{P_i}{2 P_{i,in}} \quad (P_{i,in} \gg P_i) \quad (25a)$$

$$\gamma_i \approx \frac{P_{i,in}}{P_i} \quad (P_{i,in} \ll P_i) \quad (25b)$$

From eq 24 and the parameters of the ion source, $P_{Ar} \approx 27$ torr and $P_{O_2} \approx 26$ torr are calculated, indicating that the present experiments were performed under the low pressure conditions ($P_{i,in} < 2$ torr) where eq 25b is valid, and that the gas-flow characteristics of the source can be reasonably approximated by a single γ . It is important to note that under the pseudo-first-order kinetic conditions of the ion source, this single γ is also the proportionality constant between t_r and $\bar{t}_r$ (i.e., $\bar{t}_r = \gamma t_r$). Thus, in the low pressure limit, it is expected that $\bar{t}_r$ will vary with the square of P_{in} because γ is proportional to P_{in} and t_r is proportional to P_{so} [18] which is taken to be P_{in} in the determination of $\bar{t}_r$.

Figure 2. Variation of the calculated $[Ar^+]/[O_2^+]_{tot}$ ratio as a function of time for three different initial Ar/O_2 compositions and five different inlet pressures.

Results

The ratio of argon ion concentration to total oxygen ion concentration:

$$\frac{[Ar^+]}{[O_2^+]_{tot}} = \frac{[Ar^+]}{[O_2^{+*}] + [O_2^+]} \quad (26)$$

was calculated as a function of time, total pressure, and O_2/Ar composition using eqs 11-15. The results of these calculations are shown in Figure 2a-e. Since O_2^+ is the ultimate product in this ion-molecule kinetic system, $[Ar^+]/[O_2^+]_{tot}$ will approach zero at long times. By comparing the experimentally measured Ar^+/O_2^+ intensity ratio with the calculated ion concentration ratios, $\bar{t}_r$ for a particular inlet pressure and O_2/Ar composition were determined (Figure 3a). As anticipated, $\bar{t}_r$ is a quadratic function of pressure with a plot of $\bar{t}_r/P_{in}$ vs P_{in} being linear (Figure 3b), and because O_2 and Ar have similar polarizabilities [21], $\bar{t}_r$ is largely unaffected by the O_2/Ar composition.

Discussion

In principle, the kinetic scheme could be simplified by operating at $E_e \leq 16$ eV, which would eliminate the need to consider excited ionic states. However, at such

Figure 3. (a) Effective ion source residence time as a function of inlet pressure for three different initial Ar/O_2 compositions; (b) the ratio of effective ion source residence time to inlet pressure as a function of inlet pressure.

low E_e , σ_{O_2} and σ_{Ar} are strong functions of E_e [14-16], causing the relative initial ion concentrations to depend on the details of the (unknown) E_e distribution. Thus, it was determined to be advantageous to operate at 80 eV and consider the kinetics in detail.

It would be useful to have this type of analysis for a variety of commonly used gases; however, this can be impractical. The analysis requires detailed knowledge of the electronic states of all species in the ion source, as well as the kinetics of the system, generally including diffusion to the walls of the source. Such information is not readily available for more complicated systems, and thus it is more useful to scale the results of the O_2/Ar characterization for other gases. Under conditions in which the composition of the source gas is dominated by a single component, the ion source residence time appropriate for an alternate major source gas ($\bar{t}'_r$) can be estimated by scaling $\bar{t}_r$ to account for changes in the rate of ions reaching the source exit and changes in γ . Ion mobility (κ) is given by the Langevin mobility equation in the polarization limit [18] as:

$$\kappa = \frac{0.5105}{(\rho(D-1))^{1/2}} \left(\frac{M+m}{m} \right)^{1/2} \quad (27)$$

where M is the mass of the bath gas, m is the mass of the ion, ρ is the density of the bath gas, D is the dielectric constant of the bath gas, and the constant is dimensionless. In the low pressure limit, viscosity of the source gas [19] is given by:

$$\eta = \frac{2}{3\pi d_i^2} \left(\frac{m_i k_B T}{\pi} \right)^{1/2} \quad (28)$$

where d_i and m_i are the collisional diameter and mass of the major source gas component, respectively. Substituting eq 28 into eq 24 leads to:

$$P_i = \frac{16\sqrt{2} Ak_B T l}{3\pi^3 r^4 d_i^2} \quad (29)$$

indicating that d_i is the only species-dependent parameter upon which P_i depends. Therefore, within the polarization limit, the appropriate scaling in the low pressure limit is $\bar{t}'_r = (\bar{t}_r \kappa d_i^2) / (\kappa' d_i'^2)$. In the high pressure limit, $\gamma \approx 1$ (eq 25a) and the scaling is given by $\bar{t}'_r = \bar{t}_r \kappa / \kappa'$.

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