Mechanism and Product Energy Disposal in the Reaction of $Ar^+({}^2P_{3/2})$ with $CS_2(\tilde{X}{}^1\Sigma_a^+)$

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The reaction of Ar⁺ with CS₂ is investigated at thermal and near thermal energies by using both tandem ion cyclotron resonance (ICR) spectroscopy and kinetic energy ICR. At thermal energies the absolute rate constant is measured to be 2.9×10^{-10} cm^3/s , and the ionic product branching ratio to be 97% S⁺ and 3% CS₂⁺. Kinetic energy studies revealed the CS₂⁺ product is 90% formed in the $\tilde{A}^2\Pi$ state with a near Franck-Condon vibrational state distribution and 10% in the $\bar{X}^2\Pi$ state. The S^+ product is formed exclusively in the ground $S^+(^4S)$ state with the maximum kinetic energy allowed by energy and momentum conservation. The implication is the originating Ar^+/CS_2 charge transfer takes place via a long-range electron jump since no momentum transfer occurs (in contrast to the formation of $CS_2^+(\tilde{A}^2\Pi)$, where substantial momentum transfer occurs). These data strongly suggest the S⁺(⁴S) product arises from nascent $CS_2^+(\tilde{B}^2\Sigma_u^+)$ that is rapidly predissociated by the $4\Sigma^$ state that leads to $S^{+(4S)}/CS(X^{1}\Sigma^{+})$ products. The crossing of the two states must occur very near the recombination energy of Ar⁺ (~15.7 eV). This interpretation is consistent with known $CS_2^+(\tilde{B}^2\Sigma_u^+)$ radiative lifetimes and theoretical spin-orbit induced couplings between similar states in CO₂⁺. The data and interpretations are compared to those in the literature where available.

Introduction

One of the challenges facing those studying reaction chemical dynamics is the determination of product state distributions. This is an especially formidable task when one chooses to study thermal energy ion-molecule reactions. Nonetheless, substantial progress is being made. Emission from electronically excited products of reactions occurring in flow tubes has been observed for many years.¹ More recently emission from vibrationally excited products of thermal ion-molecule reactions has been detected for favorable cases.² A more widely useful technique, laser-induced fluorescence (LIF) probing of product states has also been recently developed³ and applied to a number of simple systems⁴ with spectacular success. Of particular importance is the ability in recent experiments⁴ to probe both vibrational and rotational product state distributions in the absence of collisions while retaining relatively low collision energies ($\sim 0.5 \text{ eV}$ in the laboratory).

While these spectroscopic measurements are extremely powerful, they do have shortcomings. In the emission studies, for example, one is not sure how important the emitting states are relative to the dark states in the overall product distribution. LIF can only be conveniently applied to a limited range of product molecules, and often information on excitation in neutral fragments is lost. Consequently, it is useful to have available a technique, while intrinsically of low resolution, that can be applied to most simple thermal energy ion-neutral molecule reactions.

ICR kinetic energy spectroscopy⁵ is such a technique and will be utilized here. This experiment measures product kinetic energies for simple excergic ion-molecule reactions. Energy conservation arguments allow determination of product electronic-state distributions and semiquantitative vibrational-state distributions in favorable cases. When this technique is used in conjunction with a tandem ICR⁶ that measures absolute rate constants, branching ratios, and their dependence on kinetic energy, significant insight into the details of the reaction mechanism are obtained.

In this paper we are concerned with the reaction of $Ar^{+}(^{2}P_{3/2})$ with $CS_2(\tilde{X}^1\Sigma_g^+)$, as shown in eq 1a-d. The energetics for the

$$Ar^{+}({}^{2}P_{3/2}) + CS_{2}(\bar{X}{}^{1}\Sigma_{g}^{+})$$

$$\rightarrow CS_{2}^{+}(\bar{X}{}^{2}\Pi_{g}) + Ar({}^{1}S) \qquad \Delta E = 5.6 \text{ eV}$$
(1a)

 \rightarrow CS₂⁺($\tilde{A}^2\Pi_u$) + Ar(¹S) $\Delta E = 3.1 \text{ eV}$ (1b)

$$\rightarrow CS_2^+(\tilde{B}^2\Sigma_u^+) + Ar(^1S) \qquad \Delta E = 1.2 \text{ eV}$$
(1c)

$$\rightarrow S^{+}(^{4}S) + CS(X^{1}\Sigma^{+}) + Ar(^{1}S) \qquad \Delta E \sim 1.0 \text{ eV} \qquad (1d)$$

reaction are schematically given in Figure 1. There are four excergic product channels. Emission from the $\tilde{A}^2 \Pi_{\mu}$ state of CS₂⁺ has been observed in flow tube studies,^{7,8} but no emission was observed from the $\tilde{B}^2\Sigma_u^+$ state. The S⁺/CS₂⁺ branching ratio has recently been reported⁹ along with measurements of the total rate constant.^{8,9}

The objective of this paper is to apply tandem and kinetic energy ICR techniques to reaction 1 and investigate the mechanism of this interesting reaction. The tandem ICR will be used to measure accurate absolute rate constants and branching ratios and their dependence on translational energy. The kinetic energy ICR will be used to measure the branching ratio of the CS_2^+ product into the three energy-allowed electronic states and to provide evidence of the mechanism of formation of the S⁺ product.

Experimental Section

Results are presented in this paper from two very different ion cyclotron resonance spectrometers. The experimental procedure used for both instruments has been presented in detail previously¹⁰ and will only be very briefly summarized here.

Kinetic Energy ICR. The kinetic energy ICR used in these studies has been described in detail in the literature.^{11,12} It was patterned after the instrument first reported by Mauclaire et al.⁵ Ions are formed by an electron beam pulse, stored, allowed to react, and finally detected by using total ion current methods. Specific ions can be cyclotron ejected at any point in the sequence either to eliminate complicating reactions or as a means of determining ion relative abundances. The central feature of the instrument is its ability to measure the fraction of a specific product ion trapped as a function of the trap well depth. For the geometry of ICR cell that we employ, the fraction, f, of ions of translational

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Figure 1. Schematic potential energy diagram for CS₂⁺. The bottom of each well and the dissociation asymptotes are drawn to scale in energy. The recombination energy of Ar⁺(²P_{3/2}) is shown as the dashed line. Only those surfaces believed relevant to the Ar⁺(²P_{3/2})/CS₂($\tilde{X}^{1}\Sigma_{g}^{+}$) system are shown.

energy E_t that are trapped by a trapping voltage V_T applied to the cell is

$$f = 1; \quad V_{\rm T} \ge E_t \tag{2a}$$

$$f = (V_{\rm T}/E_{\rm t})^{1/2}; V_{\rm T} < E_{\rm t}$$
 (2b)

For a reaction in which the products have only a single value of E_t , a plot of f versus $V_T^{1/2}$ is constant at f = 1 until $V_T = E_t$, at which point a break occurs and f linearly decreases to zero as $V_T^{1/2}$ goes to zero. In real systems, of course, a distribution of translational energies would result due to the vibration/rotation distribution in the products. Consequently, instead of a sharp break, curvature will occur. Finally, if the products are formed in several electronic states, separated by a significant amount of energy, several breaks will occur, with each break corresponding to a specific electronic state. Extrapolation to the f axis of the linear portion following each break gives the fraction of products formed in that electronic state.

In principle the experimental f versus $V_T^{1/2}$ curves can be deconvoluted, and approximate product vibrational state distributions obtained. In practice it is more useful to computer synthesize f versus $V_T^{1/2}$ curves by using trial vibrational distributions and comparing with experiment.¹⁰ Such comparisons are often useful when comparing our results to spectroscopic data or when approximate product vibrational state distributions are desired.

Tandem ICR. The UCSB tandem ICR used in these studies was patterned after the original design of Smith and Futrell⁶ and has been described in detail in the literature.^{13,14} An important and unique feature of the UCSB instrument is that both the source and detector regions are composed of ICR cells. A second unique feature is the inclusion of a miniature Wien velocity filter immediately following the entrance slit to the detector ICR. This filter greatly reduces the probability that high-energy ions are injected into the detector ICR.



Figure 2. A plot of $(Ar^+)/(Ar^+)_0$ versus p_{CS_2} (in Torr), with a Ne buffer gas pressure of 1.5×10^{-3} Torr for reaction of Ar^+ with CS_2 . The ratio $(Ar^+)/(Ar^+)_0$ is the measured power absorption signal ratio for the Ar^+ ion. The reactant Ar^+ ions are formed in the source ICR by using 70-eV electron impact and injected into the detector ICR. Data from two separate experiments are shown. The solid line is the dependence expected for a total rate constant of 2.9×10^{-10} cm³/s.

Ar⁺ ions are made in the source ICR cell by 70-eV electron impact. They are extracted, accelerated, mass selected, decelerated, and injected into the differentially pumped detector ICR cell for reaction with CS₂. The exact kinetic energy of the Ar⁺ ions injected into the detector ICR cell is not known. However, previous titration experiments¹³ indicate that this energy is between 0.5 and 1.0 eV in the laboratory frame.

If the kinetic energy dependence of the reaction is desired, then the Ar^+ ions can be cyclotron heated upon entrance to the detector ICR. The average kinetic energy of the Ar^+ ion is given by

$$\bar{E}_t = \bar{E}_{to} + \bar{E}_{ICR} \tag{3}$$

where \bar{E}_{to} is the average injection energy and \bar{E}_{ICR} is the average cyclotron excitation energy, determined by using well-known techniques.¹⁵ The useful range of \bar{E}_{ICR} is generally $0 \le \bar{E}_{ICR} \le 3 \text{ eV}$.

If thermal energy rate constants and branching ratios are desired, then a buffer gas can be added in excess to the detector ICR cell. In the work described in this paper Ne was used. Use of a buffer gas requires that the general form of the power absorption equations be used to analyze the data.^{13,16} In a typical experiment the CS₂ pressure would be 1×10^{-5} Torr and the Ne pressure 2 $\times 10^{-3}$ Torr. Under these conditions the Ar⁺ ions are completely thermalized before reaction occurs.

Results

A plot of the power absorption intensities of $(Ar^+)/(Ar^+)_0$ versus CS₂ partial pressure is given in Figure 2 at Ne buffer gas pressure of 1.5×10^{-3} Torr. $(Ar^+)_0$ is the Ar⁺ power absorption signal due to Ar⁺ ions injected into the detector ICR without CS₂ added. The presence of Ne buffer gas requires a full power absorption analysis to be accomplished.¹⁶ The solid line is the predicted curve for a total rate constant of 2.9×10^{-10} cm³/s. Clearly the fit is excellent.

It is apparent from Figure 2 that a single rate constant fits the data. Consequently either $Ar^{+}(^{2}P_{1/2})$ and $Ar^{+}(^{2}P_{3/2})$ react with the same rate constant or $Ar^{+}(^{2}P_{1/2})$ is not present in significant concentrations. Deactivation of $Ar^{+}(^{2}P_{1/2})$ to $Ar^{+}(^{2}P_{3/2})$ could occur in the source ICR due to collisions with either electrons or Ar atoms or in the detector ICR due to the thermalizing collisions with Ne buffer gas.

At low pressure, without Ne buffer gas, a rate constant between 2×10^{-10} and 3×10^{-10} cm³/s is obtained. In this instance linear plots of ln $[(Ar^+)/(Ar^+)_0]$ versus P_{CS_2} are observed, indicating

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Figure 3. A plot of the fraction of product ions versus Ar^+ kinetic energy in the center of mass. The thermal energy point was obtained as described in the text. The average energy of Ar^+ ion injected into the detector ICR was taken to be 0.5 eV (cm) for reasons discussed in the text.

a single reaction rate constant. Thus either $Ar^{+}({}^{2}P_{1/2})$ is not in the beam injected into the detector ICR, or it reacts with a rate identical with that of $Ar^{+}({}^{2}P_{3/2})$. The fact that the low-pressure rate constant is somewhat smaller than the thermal rate constant could reflect the fact these ions have ~0.5-eV laboratory kinetic energy. On the other hand the absolute uncertainties of the rate constants are of the order $\pm 20\%$, and hence the two values could simply be due to experimental uncertainty. Both measurements are in good agreement with rate constants of 3.4×10^{-10} and 2.6×10^{-10} cm³/s recently measured by using flow tube techniques.^{8,9}

Measurement of the branching ratio for reaction 4 is given in $A_{2}^{+} + CS \rightarrow S^{+} + CS + A_{2}$ (4c)

$$Ar^{+} + CS_{2} \rightarrow S^{+} + CS + Ar$$
 (4a)

$$\rightarrow CS^+ + S + Ar \tag{4b}$$

$$\rightarrow CS_2^+ + Ar \tag{4c}$$

Figure 3. At thermal energies only the S⁺ and CS₂⁺ product ions are observed with the fraction of S⁺ ions $f_{S^+} = 0.97$ and $f_{CS_2^+} =$ 0.03, with a probable error of ±5%. (These values are to be compared with flow tube values of $f_{S^+} = 0$ and $f_{CS_2^+} = 1.00$ by Upshulte et al.⁸ and $f_{S^+} = 0.88$ and $f_{CS_2^+} = 0.12$ by Shul et al.⁹) Consequently nearly all charge-transfer reactions are dissociative. Great care had to be taken in determining this branching fraction as S⁺ undergoes a very rapid secondary charge-transfer reactions with CS₂ to form CS₂⁺. Our thermal energy branching ratio was obtained by using a Ne buffer gas pressure of 2×10^{-3} Torr and variable amounts of CS₂ gas (between 1×10^{-6} and 1×10^{-5} Torr). The true branching fraction was obtained from a plot of the branching fraction versus p_{CS_2} extrapolated to zero CS₂ pressure.

In the absence of buffer gas the Ar⁺ ions are injected with about 0.5-eV laboratory translational energy. This energy was gradually increased by cyclotron heating the injected Ar⁺ ions. As shown in Figure 3 this energy has the effect of decreasing the amount of S⁺ product formed and increasing the amount of CS⁺ product formed. This is not an unreasonable result since the CS⁺(²Σ⁺)/S(³P) channel is slightly endoergic relative to the recombination energy of Ar⁺(²P_{3/2}). Perhaps more surprising is the fact that the fraction of CS₂⁺ increases with kinetic energy to approximately 18% of the total products. Since this ion is nearly totally predissociated at thermal collision energies, this result signals at least a partial change in reaction mechanism as kinetic energy increases. Either the neutral Ar fragment takes off more of the available energy in translational energy, or the initial CS₂⁺ state formed emits light at a rate more competitive with dissociation.

The results from the kinetic energy ICR are given in Figures 4 and 5. In Figure 4 a plot of the percent CS_2^+ product trapped versus $V_T^{1/2}$ is given (percent trapped = 100*f*). The CS_2^+ ion



Figure 4. Plot of the percentage CS_2^+ ions trapped versus the square root of the trapping voltage for the reaction of $Ar^+(^2P_{3/2})$ with CS_2 to yield CS_2^+ product ions. Note that this channel comprises only 3% of the total products. The data are plotted as filled circles. The solid line is drawn simply to lead the eye. The threshold energies for the \bar{X} , \bar{A} , and \bar{B} electronic states are shown. The extrapolation of the small break occurring near the $\bar{X}^2\Pi_g$ threshold is extrapolated to the vertical axis by the dashed line, indicating $10 \pm 5\%$ of the CS_2^+ product ions are formed in the $\bar{X}^2\Pi_g$ state.



Figure 5. Plot of the percentage of S⁺ ions trapped versus the square root of the trapping voltage for the reaction of $Ar^{+}(^{2}P_{3/2})$ with CS₂ to form S⁺. Note that it is the major channel for this reaction (97%). The data are plotted as filled circles. The solid line is used merely to lead the eye. The point labeled S⁺(⁴S) maximum E_{t} is where a break would occur if all of the available energy were channeled into S⁺(⁴S)/CS(X¹Σ⁺) translational energy.

comprises only 3% of the products at thermal energy. Hence these are very difficult experiments to perform. Great care was taken to make sure the data were reproducible. The dominant S^+ ion was continuously ejected to eliminate complications due to secondary formation of CS_2^+ .

The data show a major break near $E_t = 1.0$ eV. On the graph arrows indicate where breaks should occur if the CS₂⁺ ion is formed in ($\tilde{X}^2\Pi_g$, v = 0), ($\tilde{A}^2\Pi_u$, v = 0), and ($\tilde{B}^2\Sigma_u^+$, v = 0). The fact that the break corresponds very closely to the prediction for $\tilde{A}^2\Pi_u$ is very strong evidence that most of the *surviving* (i.e., nondissociated) CS₂⁺ ions are formed in this state.

There is no break at or above the threshold for formation of $(\tilde{B}^2\Sigma_u^+)$ CS₂⁺ ions. Consequently either no ions are formed in this state, or all CS₂⁺ ions formed in the $\tilde{B}^2\Sigma_u^+$ state are predissociated.

A small break occurs near the onset of the $X^2 \Pi_g$ state. These experiments were repeated many times to ensure this break actually existed. Extrapolation of the straight-line portion following the break to the vertical axis indicates 10% of the *surviving* CS_2^+ ions are originally formed in $\tilde{X}^2 \Pi_g$ and, by difference, 90% of the surviving CS_2^+ ions in $\tilde{A}^2 \Pi_u$.

Nothing can be said about the vibrational distribution in the $\tilde{X}^2 \Pi_g$ state because the break is so shallow. The $\tilde{A}^2 \Pi_u$ state break is fairly well rounded, however, indicating a fairly broad distribution of vibrational states. This point will be addressed further in the Discussion.

The results for the dominant S⁺ channel are given in Figure 5. The only break occurs near $E_t = 0.71$ eV. The break coincides with the maximum amount of kinetic energy that can possibly be channeled into S⁺ laboratory translational energy, assuming the argon atom carries off no translational energy and momentum and energy are conserved.¹⁷ The break is somewhat rounded, indicating either a small amount of rotational excitation in the $CS(X^{1}\Sigma^{+})$ molecule, or some translation excitation of the Ar atom in the initial charge-transfer step, or both. This is a very unusual and unexpected result and indicates the dynamics for the dissociative charge-transfer reaction are very specific.

Discussion

Endoh et al.⁷ were the first to observe emission from the $CS_2^+(A^2\Pi_u)$ state in a flow tube. They observed that transitions originating from $v'_1 = 0$ in the $\tilde{A}^2\Pi_u$ state carried 90% of the emitting oscillator strength and $v'_1 = 1$ carried 10%. No $\tilde{B}^2\Sigma_u^+ \rightarrow \tilde{X}^2\Pi_g$ emission was observed. By plotting the emission intensity versus År pressure, they deduced that the $CS_2^+(\tilde{A}^2\Pi_u)$ ions were formed by reaction 5. They obtained what they termed nascent

$$Ar_{2}^{+} + CS_{2} \longrightarrow CS_{2}^{+} (\widetilde{X}^{2} \Pi_{u}) + 2Ar$$

$$(5)$$

$$CS_{2}^{+} (\widetilde{X}^{2} \Pi_{u}) + h\nu$$

vibrational-state branching ratios by plotting the fractional vibrational-state populations versus Ar pressure in the range 0.65-5 Torr and extrapolating to zero. They concluded that the charge-transfer reaction 5 resulted in a strongly non-Franck-Condon distribution in $CS_2^+(\tilde{A}^2\Pi_u)$.

Emission from $CS_2^+(\tilde{A}^2\Pi_u)$ formed in a discharge flow tube containing Ar has also been studied by Upshulte et al.⁸ They compared \tilde{A} -state emission intensities with Ar⁺ and Ar₂⁺ ion intensities as various flow parameters were varied (Ar pressure, flow velocity, discharge voltage) and concluded that reaction 6

$$Ar^{+} + CS_{2} \rightarrow CS_{2}^{+}(A^{2}\Pi_{u}) + Ar$$
$$CS_{2}^{+}(\tilde{A}^{2}\Pi_{u}) \rightarrow CS_{2}^{+}(\tilde{X}^{2}\Pi_{g}) + h\nu$$
(6)

and not reaction 5 was the source of the emission. A vibrational distribution in the $\tilde{A}^2 \Pi_u$ state similar to that observed by Endoh et al. was found. Upshulte et al. were not able to explain where the relatively large amount of available energy went (the difference between the recombination energy of Ar^+ and the (0,0,0) state of $CS_2^+(A^2\Pi_u)$ is about 3 eV). They speculated that perhaps CS_2^+ was originally formed in very high vibrational levels and vibrational relaxation occurred before emission.

Substantial insight into the mechanism of this reaction can be obtained from the data in Figure 4. First, it is clear that the Ar neutral atom and CS_2^+ ion carry off the bulk of the excess energy as relative translation. Consequently, for that fraction of Ar^+/CS_2 ions formed in either $CS_2^+(\tilde{A}^2\Pi_u)$ or $CS_2^+(\tilde{X}^2\Pi_g)$, intimate collisions are required to facilitate the large amount of momentum transfer that occurs. Secondly, it is absolutely clear that $CS_2^+(\tilde{A}^2\Pi_u)$ is not formed in very high vibrational levels of the $\tilde{A}^2\Pi_u$ state that are subsequently vibrationally deactivated. It is interesting, however, to compare the experimentally observed trapping curve of CS_2^+ with that predicted by using Franck-Condon factors.^{19,21} This comparison is given in Figure 6. It



Figure 6. Filled circles are the data plotted in Figure 4 for the reaction of $Ar^+(^2P_{3/2})$ with CS_2 to give CS_2^+ . The symbols (I) reproduce the curve that would occur if the CS_2^+ product ions were formed with a Franck-Condon distribution. The solid line is the curve predicted by the emission data of Endoh et al.⁷

is apparent from the figure that a nearly exact match is obtained. This result strongly suggests that the nascent vibrational distribution in $\tilde{A}^2 \Pi_u CS_2^+$ is Franck-Condon. A trapping curve that reflects the vibrational distribution of Endoh is given as the solid line. Clearly this curve does not fit the data well.

Apparently the reason the Franck–Condon distribution was not observed in the flow tube studies is collisional deactivation. The emission lifetime of $CS_2^+(\tilde{A}^2\Pi_u)$ is ~4.1 μ s and relatively independent of vibrational state.²⁰ This lifetime implies that at 1 Torr a typical $CS_2^+(\tilde{A}^2\Pi_u)$ ion undergoes approximately 135 collisions before emitting a photon. Consequently, vibrational deactivation may well be occurring. It is still possible that Ar_2^+ is the source of the $CS_2^+(\tilde{A}^2\Pi_u)$ emission (reaction 5) and that this reaction preferentially populates low vibrational states of $\tilde{A}^2\Pi_u$. The experiments of Upshulte et al.⁸ strongly suggest this is not the case, however.

One interesting point is that the vibrational distribution of nascent $CS_2^+(\tilde{A}^2\Pi_u)$ appears to be Franck–Condon, but an intimate collision between Ar^+/CS_2 is required to explain the momentum conservation. Apparently the electron transfer is nonadiabatic and rapid relative to nuclear motion even though an intimate encounter occurs. Historically it has been thought¹⁸ that reactions dominated by Franck–Condon factors were associated with long-range electron-jump mechanisms, but clearly the Ar^+/CS_2 system is an exception to that rule.

The majority of the reaction does not produce $CS_2^+(\tilde{A}^2\Pi_u)$. Rather 97% of the collisions at thermal energy form $S^+(^4S)/CS(X^1\Sigma^+)$ products. The data in Figure 5 indicate that the $S^+(^4S)$ ion is formed with the maximum translational energy consistent with energy and momentum conservation. Consequently, the argon neutral product cannot carry off significant translational energy nor can the $CS(X^1\Sigma^+)$ fragment be vibrationally excited. This is a very unusual result and suggestive of very specific reaction dynamics. One possible mechanism is

$$\begin{aligned} \operatorname{Ar}^{+(^{2}\mathrm{P}_{3/2})} + \operatorname{CS}_{2}(\tilde{X}^{1}\Sigma^{+}) &\rightarrow [\operatorname{CS}_{2}^{+}(\tilde{B}^{2}\Sigma_{u}^{+})]^{*} + \operatorname{Ar} \\ \bar{E}_{t}(\operatorname{Ar}-\operatorname{CS}_{2}^{+}) &\simeq 0 \\ \bar{E}_{vib}[\operatorname{CS}_{2}^{+}(\tilde{B}^{2}\Sigma_{u}^{+})]^{*} &\simeq 1.0 \text{ eV} \\ [\operatorname{CS}_{2}^{+}(\tilde{B}^{2}\Sigma_{u}^{+})]^{*} &\rightarrow \operatorname{S}^{+}(^{4}\mathrm{S}) + \operatorname{CS}(X^{1}\Sigma^{+}) \\ \bar{E}_{t}(\mathrm{S}^{+}) &\simeq 0.71 \text{ eV} \\ \bar{E}_{t}(\operatorname{CS}) &\simeq 0.42 \text{ eV} \\ \bar{E}_{vib}(\operatorname{CS}) &\simeq 0.0 \text{ eV} \end{aligned}$$

The first step requires a "resonant" electron-transfer process without momentum transfer and thus must occur at long range.

^{(17) (}a) The break actually occurs at a slightly larger energy than allowed by energy and momentum conservation, assuming $Ar^+(^2P_{3/2})$ reactant ions and literature values for the heats of formation of the various sulfur-containing species (see ref 17b). Hence, in the trapped ICR cell the $Ar^+(^2P_{1/2})$ ion could be contributing (adding 0.18 eV to the available energy). In addition, the heat of formation of the CS molecule is still not very well-known. If this number decreases by only a few tenths of an electronvolt, the data would be in compliance with the conservation laws. (b) Eland, J. H. D.; Berkowitz, J. J. Chem. Phys. 1979, 70, 5151, and references therein. (18) Bowers, M. T.; Ellemen, D. D. Chem. Phys. Lett. 1972, 16, 486.

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While such processes are not unknown, they seem to be favored when the ionization step $(CS_2(\tilde{X}) \rightarrow CS_2^+(\tilde{B}))$ has a large Franck-Condon factor.¹⁸ The Franck-Condon factor for ionization of CS₂ at the recombination energy of Ar⁺ (15.7 eV) is small.^{18,19}

The second step requires electronic predissociation via a repulsive state on a short time scale relative to emission from the B state ($\sim 3 \times 10^{-7}$ s).²⁰ This certainly could occur via the $^{4}\Sigma^{-}$ state that is repulsive and is the only state that correlates to S⁺(⁴S) and CS X($^{1}\Sigma^{+}$). The intersection of the lowest vibrational asymptote of the $^{4}\Sigma^{-}$ state and the $\tilde{B}^{2}\Sigma_{u}^{+}$ state must occur very close to the recombination energy of Ar⁺($^{2}P_{3/2}$), i.e., near 15.76 eV. (A similar conclusion was made by Shul et al.⁹ for completely different reasons.)

The crossing from the $\bar{B}^2 \Sigma_u^+$ state to the ${}^{4}\Sigma^-$ state is a twoelectron process. Praet et al.²² have investigated a similar transition in the dissociation of CO₂⁺ and concluded the spin-orbit coupling is small. For CO₂⁺ they calculated the crossing has a rate constant of ~4 × 10⁷ s⁻¹, or the CO₂⁺ ion would have a dissociative lifetime of 2.5 × 10⁻⁸ s. The spin-orbit coupling in CS₂⁺ is expected to be somewhat larger than in CO₂⁺, leading to a somewhat larger rate constant and smaller lifetime. Consequently, dissociation should be rapid relative to emission, which would explain why no B² Σ_u^+ emission was observed.⁷

From the above analysis the following nascent branching ratio can be obtained:

 $Ar^{+}({}^{2}P_{3/2}) + CS_{2}(\tilde{X}{}^{1}\Sigma^{+}) \rightarrow Ar({}^{1}S) + CS_{2}{}^{+}(\tilde{X}{}^{2}\Pi_{g})$ 0.3%

 $\rightarrow \operatorname{Ar}({}^{1}\mathrm{S}) + \operatorname{CS}_{2}^{+}(\tilde{\mathrm{A}}{}^{2}\Pi_{\mathrm{u}}) \qquad 2.7\%$

$$\rightarrow \operatorname{Ar}({}^{1}\mathrm{S}) + \operatorname{CS}_{2}^{+}(\tilde{B}^{2}\Sigma_{u}^{+}) \qquad 97.0\%$$

 $CS_2^+(\tilde{B}^2\Sigma_u^+) \rightarrow S^+(^4S) + CS(X^1\Sigma^+)$

The B state products are formed without significant momentum transfer while the \tilde{A} and \tilde{X} state products result from an intimate Ar^+/CS_2 collision. The S⁺(⁴S) product is formed with the maximum allowed value of kinetic energy, indicating the repulsive ${}^{4}\Sigma^{-}$ state that correlates to this product intersects and predissociates the $\tilde{B}^2 \Sigma_u^+$ state very near the recombination energy of $Ar^+({}^2P_{3/2})$, i.e., near 15.7 eV. As the Ar⁺ kinetic energy increases, the fraction of S^+ decreases, the fraction of CS_2^+ significantly increases, and CS⁺ becomes a substantial product. One possible explanation is the probability of intimate collisions increases as the kinetic energy of the Ar^+/CS_2 reactants increases. Consequently, more \tilde{A} and \tilde{X} state CS_2^+ may be initially formed. The \tilde{A} state will presumably radiate to the $\mathbf{\tilde{X}}$ state, while the nascent $\mathbf{\tilde{X}}$ state directly formed in the charge-transfer reaction will vibrationally predissociate to form $CS^+(X^2\Sigma^+)/S(^3P)$, as suggested by the correlation diagram in Figure 1. Of course, other surfaces correlating to $CS^+(X^2\Sigma^+)$ could be responsible for the appearance of this ion, but the significant abundance at energies very near its thermochemical threshold suggests the $\bar{X}^2 \Pi_g$ state is probably the primary CS₂⁺ state involved.

This interpretation is at complete variance with that suggested by Shul et al.⁹ They suggest that the thermal energy chargetransfer reaction initially forms highly vibrationally excited $\tilde{A}^2 \Pi_{\mu}$ CS_2^+ , which is predissociated by a repulsive state (presumably the ${}^{4}\Sigma^{-}$ state) to form S⁺. This is a highly unlikely circumstance because it would require formation of a strongly bimodal A-state vibrational population: those that are predissociated with high vibrational excitation and those that emit with essentially no vibrational excitation. The very highly vibrationally excited A states that lead to S⁺(⁴S) via predissociation would have to be formed via a long-range electron jump because the kinetic energy results indicate the Ar atom leaves without momentum transfer occurring. The Franck-Condon factors are extremely small for these high vibrational states, and it is unlikely that the distortion that occurs at long range in the collision would be sufficient to compensate.²³ In addition, we have shown the nondissociative $CS_2^+(A^2\Pi_2)$ products are formed with a Franck-Condon distribution, and there appears to be no physically plausible mechanism for forming a second distribution of $CS_2^+(A^2\Pi_u)$ molecules in a narrow range of very large vibrational states. On the other hand, the Franck-Condon factors for the low vibrational levels of the B state at 15.7 eV are small, but not extremely so, and the distortion in the $B^2\Sigma_u^+$ potential surface by the interacting argon ion/atom could be sufficient to allow efficient "long-range" electron transfer. The absolute rate constant is, in fact, only 20-30% of the collision rate constant,²⁴ which may well be due to the poor match in the Franck-Condon factors.

Our interpretation above is also in direct conflict with deductions of Shul et al.⁹ from data on the kinetic energy dependence of the S^+/CS_2^+ branching ratio in the reaction of Ar⁺ with CS₂. They correlate observed variations in this branching ratio with successive curve crossings of the dissociative $^{4}\Sigma^{-}$ state with the $\tilde{A}^{2}\Pi_{\mu},\,\tilde{B}^{2}\Sigma_{g}{}^{+},\,$ and $\tilde{C}^2 \Sigma_g^+$ states, respectively. Our data indicate the \tilde{A} state is only a minor product at thermal energies and the B state is almost certainly initially the dominant state formed in the charge-transfer reaction at this energy. Hence, their deduction that the A state is exclusively formed at thermal energies, the \tilde{B} state at $\sim 0.1 \text{ eV}$ Ar^+/CS_2 center of mass kinetic energy, and the \tilde{C} state at ~0.3 eV Ar^+/CS_2 center of mass kinetic energy appears not to be correct, and other explanations must be found for the change in product distribution with kinetic energy. Perhaps their interpretation was founded, in part, on the incorrect correlation diagram they used, and this fact may have led to what now appears to be an incorrect interpretation of their data.

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