Absolute Fluorescence Yields from Electron-Irradiated Gases. 3. XeCl* and XeI*

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The absolute total fluorescence yield for the XeCl* (B,C) $^2\Sigma_{1/2}^+ \rightarrow {}^2\Sigma_{1/2}^+$ transition has been determined from pulse electron-irradiated Xe/$CFCl_3$ gas mixtures. Since no experimental resolution of the two formation pathways was achieved, individual, unquenched limiting yields for the excited state, Xe* + $CFCl_3 \rightarrow$ XeCl* + $\cdot CHCl_2$, G_o* = 2.4 ± 0.6, and ionic recombination, $Xe_2^+ + Cl^- + Xe \rightarrow$ XeCl* + 2Xe, $G_o^+ = 3.2 \pm 0.5$, reactions have been calculated by modeling the dependence of the total fluorescent yield on xenon and halide gas pressure. Analogous experiments were also conducted for the formation of the XeI* exciplex from the irradiation of Xe/CF_3I gas mixtures. Individual values for the two component formation processes were again calculated from total gas yields, giving G_o* = 0.31 ± 0.08 and $G_o^+ = 4.5 \pm 0.6$. These yields are compared to the predictions of current theoretical models, and the effects of alternate recombination pathways are discussed.

Introduction

One of the most important quests of experimental radiation chemistry is to determine the identity and yields of the ionized species, secondary electrons, and excited neutral atoms/molecules or free radical fragments generated within irradiated systems. Although general characterization of these species in gases has been achieved by over a century of investigations, only a few measurements of absolute yields of excited states in irradiated gases have been reported.[1,2] These have mainly focused on emission from excited nitrogen and air[3,4] and from atmospheric nuclear weapons[5] testing, as well as upper atmosphere studies.[6] However, the development of powerful gas-phase, e-beam-pumped exciplex lasers over the past 20 years has stimulated further investigations in this field, with reported determinations of the total and component process yields in some rare gas systems.[7]

In several recent experimental investigations[8,9] absolute fluorescence yields of pulse electron-irradiated rare gas/halogen source gas mixtures (R/AX) for the RX* (B,C) states of XeBr* (Xe/CF_3Br),[8] KrF* (Kr/SF_6),[9] and XeF* (Xe/SF_6)[9] have been measured. By modeling of the established[10−17] general mechanism for the formation of these exciplexes,

$$R \rightsquigarrow R^*, R^+, e^-_{(s)} \quad \text{production of initial species} \quad (1)$$

$$e^-_{(s)} + R \rightarrow e^-_{(th)} \quad \text{hot secondary electron thermalization} \quad (2)$$

$$e^-_{(th)} + AX \rightarrow X^- + A \quad \text{thermal electron capture} \quad (3)$$

$$R^* + AX \rightarrow RX^* + A \quad \text{rare gas excited-state reaction} \quad (4)$$

$$R^+ + 2R \rightarrow R_2^+ + R \quad \text{cation dimerization} \quad (5)$$

$$R_2^+ + X^- + R \rightarrow RX^* + 2R \quad \text{three-body ionic recombination} \quad (6)$$

$$RX^* \rightarrow R + X + h\nu \quad \text{exciplex emission} \quad (7)$$

the two formation channels, the energy-transfer (harpooning) reaction of rare gas electronically excited states with the halide gas, reaction 4, and the three-body ionic recombination, reaction 6, have been characterized and their individual fluorescence yields determined for these three species.

The XeF* exciplex had significantly lower fluorescence yields for both formation processes compared to the other two exciplexes. Moreover, despite the KrF* and XeBr* limiting excited-state yields being equal, the ionic recombination value was much larger for XeBr*.[8] This was attributed to the presence of other recombination products,[9] for example, from trimer exciplex formation reactions,

$$R_2^+ + X^- + R \rightarrow R_2X^* + \text{products} \quad (8)$$

being enhanced by the molecular SF_6^- anion being involved in the KrF* recombination.

The purpose of this study was to further investigate this proposed effect by measuring the atomic halide ion recombination fluorescence yields in the production of the analogous XeCl* (Xe/$CFCl_3$) and XeI* (Xe/CF_3I) exciplexes.

Experimental Section

The established pulse radiolysis facilities in the Department of Chemistry at the University of Melbourne were used for this study.[14,18] The experimental conditions were similar to those reported previously, and thus, only a brief description will be given here.

The gas samples were irradiated by a Field Emission Corporation Febetron 706 electron pulser. The integrated exciplex emission yields were generated by terminating the photomultiplier output into large capacitors (*nF*) in parallel with a 1 MΩ resistor.

The absolute sensitivity of the optical system was calibrated using a Scientech 38-0101 calorimeter and an Oriel 150 W xenon lamp. Based on the fixed geometry of the light-detecting system, the fraction of photons emitted by the source that was detected could be readily calculated. The energy deposited in the gas mixtures was determined from the dose determined to oxygen, calculated by conventional ozone dosimetry;[19] corrections to other gases were made using tabulated molar stopping powers.[20]

The gases used in this study were Matheson research grade (99.999%) xenon and oxygen, Matheson pure grade (99.9%) SF_6 and $CFCl_3$, and Bristol Organics Limited (>99.9%) CF_3I. All gases were subjected to several freeze−pump−thaw cycles prior to use.

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All emission yields were calculated from a series of stepwise integrated measurements at 2 nm intervals across the exciplex emission spectrum. At least seven measurements were done at each wavelength. A linear relationship between photon yield and absorbed dose per pulse was found for all gas mixtures studied, thus demonstrating that the yield was independent of the absorbed dose rate.

The exciplex emission curves showed contributions from X-rays, background Xe_2*, and fluorescence formed by the energy-transfer and ionic recombination pathways.[14,17] The interfering intensity from X-rays and Xe_2* was subtracted from the exciplex integrated measurements before the summation across the spectrum was performed. This was done by determining the relative background intensity at each wavelength, from a separate irradiation of only xenon, and then converting these to absolute values by normalizing them to the fluorescence intensity observed from the irradiated xenon/halide gas mixture at a wavelength just outside the exciplex spectrum. The wavelengths used for this normalization for XeCl* and XeI* were 316 and 262 nm, respectively.

All measurements were performed at room temperature.

Results and Discussion

Xe/$CFCl_3$ Measurements. The emission spectrum for the XeCl* $^2\Sigma_{1/2}^+ \rightarrow {}^2\Sigma_{1/2}^+$ transition, obtained from the pulsed electron beam irradiation of Xe/$CFCl_3$ gas mixtures, covered the range 294−314 nm with a maximum at 308 nm.[18,21]

The relative contributions of the energy-transfer and ionic recombination processes could not be temporally resolved in this system. It has been shown previously[15] that the energy-transfer process could be isolated by lowering the incident pulse energy and intensity to extremely low values and also by using very low xenon pressures. This slowed the ionic recombination reaction to such an extent that at short times (<200 ns) the fluorescence from this process was negligible. Although rate constants for the excited-state reactions were obtained by this method,[15] the integration of the fluorescence under these conditions, to obtain the relative yields of the two formation processes, was not reproducible. Therefore, the relative contributions of the two formation pathways were *calculated* by the following procedure.

The choice of $CFCl_3$ as the halide gas was deliberate, since this molecule is known to dissociatively capture thermal electrons[22] to produce Cl^- with a rate constant of $(1.54 \pm 0.09) \times 10^{14}$ dm^3 mol^{-1} s^{-1}.[23] This large rate constant ensured complete formation of Cl^-, eliminating any problem with competition from the reaction

$$Xe_2^+ + e^- \rightarrow Xe^* + Xe \quad k = 8.4 \times 10^{14}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}\ ^{24} \tag{9}$$

as seen previously for the Xe/CF_3Br system.[8] Also, its ionization potential (11.77 eV)[25] is less than that of Xe^+ (12.130 eV)[26] and thus the charge-transfer reaction

$$Xe^+ + CFCl_3 \rightarrow Xe + (CFCl_3)^+ \tag{10}$$

will occur in competition with the exciplex formation reactions

$$Xe^+ + 2Xe \rightarrow Xe_2^+ + Xe \tag{5}$$

$$Xe_2^+ + Cl^- + Xe \rightarrow XeCl^* + 2Xe \tag{11}$$

At high $CFCl_3$ pressures, the charge-transfer reaction dominates, and thus, the observed exciplex fluorescence is *only* formed by the energy-transfer pathway. An analysis[27] of the above competition shows that a plot of the inverse of the total yield of XeCl*, G_T^{-1}, against total $CFCl_3$ pressure will give a limiting straight line at high $CFCl_3$ pressure, corresponding to the exciplex formation by only the energy-transfer process.

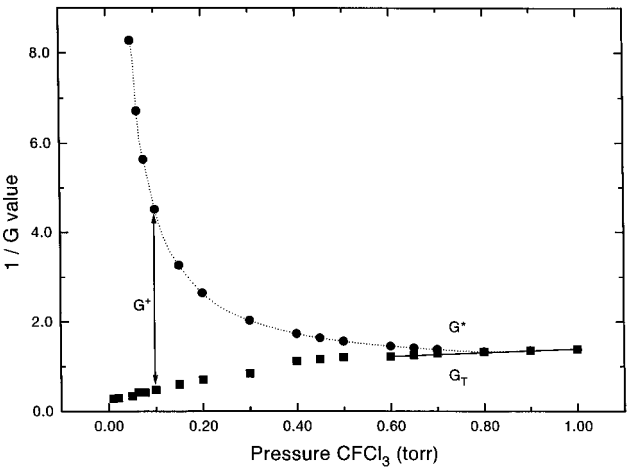

Figure 1. $CFCl_3$ pressure dependence of the calculated excited-state fluorescence yield G^* (●) contribution to the measured XeCl* total yield G_T (■) values at a constant xenon pressure of 80 Torr. The difference between these two curves at 0.10 Torr $CFCl_3$ is due to the yield from ionic recombination reactions, G^+. The limiting straight line observed for $CFCl_3$ pressures above 0.60 Torr gives the region where XeCl* fluorescence is formed only by the excited-state reaction pathway.

For a constant xenon pressure of 80 Torr, the total exciplex yields as a function of $CFCl_3$ pressure, over the range 0.01−1.00 Torr, were measured. The inverse plot of these yields (Figure 1) shows a limiting linear slope at $CFCl_3$ pressures above 0.60 Torr. At lower pressures, the deviation from this linearity has been demonstrated[15] to be due to the ionic recombination-formed fluorescence being significant.

The production of exciplex fluorescence by only the energy-transfer process (corresponding to the higher $CFCl_3$ gas pressures) has been shown previously[14−17] to be accurately modeled by the general mechanism:

$$Xe^* + CFCl_3 \rightarrow XeCl^* \qquad k_{12} = 1.4 \times 10^{11}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}\ ^{15} \tag{12}$$

$$Xe^* + Xe \rightarrow \text{products} \qquad k_{13} = 5.5 \times 10^{8}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}\ ^{15} \tag{13}$$

$$Xe^* \rightarrow Xe + h\nu \qquad k_{14} = 2.1 \times 10^{6}\ \mathrm{s^{-1}}\ ^{15} \tag{14}$$

$$XeCl^* + CFCl_3 \rightarrow \text{products} \qquad k_{15} = 2.8 \times 10^{11}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}\ ^{28,29} \tag{15}$$

$$XeCl^* + Xe \rightarrow \text{products} \qquad k_{16} = 3.0 \times 10^{9}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}\ ^{30} \tag{16}$$

$$XeCl^* + 2Xe \rightarrow \text{products} \qquad k_{17} = 4.7 \times 10^{11}\ \mathrm{dm^6\ mol^{-2}\ s^{-1}}\ ^{30} \tag{17}$$

$$XeCl^* \rightarrow Xe + Cl + h\nu \qquad k_{18} = 4.0 \times 10^{7}\ \mathrm{s^{-1}}\ ^{30} \tag{18}$$

The pulsed electron irradiation of xenon produces a wide range of electronically excited states, and these are collectively denoted by Xe*. The rate constants for reactions 12−14 under these experimental conditions have previously been measured.[15]

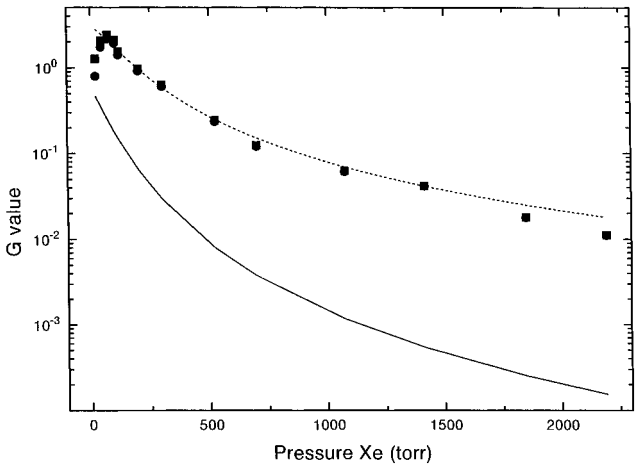

Figure 2. Xenon pressure dependence of the experimental G_T (■) and calculated G^* (−) and G^+ (●) yields at a constant $CFCl_3$ pressure of 0.10 Torr. Dashed line corresponds to the calculated ionic recombination yield pressure dependence using eq 20 and values given in the text.

Owing to the relatively high xenon pressures used in these experiments, collisional coupling of the XeCl* (B,C) states was assumed to be maintained,[31] and therefore, the effective radiative lifetime of this coupled state is ca. 25 ns[30] (corresponding to a rate constant of $k_{18} = 4.0 \times 10^7$ s^{-1}). The two- and three-body rate constants for xenon quenching of XeCl* (B,C) have been directly measured as $(3.0 \pm 1.2) \times 10^9$ dm^3 mol^{-1} s^{-1} and $(4.7 \pm 1.4) \times 10^{11}$ dm^6 mol^{-2} s^{-1}, respectively.[30] Since no literature value could be found for $CFCl_3$ quenching of XeCl*, this rate constant was assumed to be equal to the value for CCl_4,[28,29] as previously.[15]

For this reaction scheme, the excited-state yield of fluorescence is given by[14]

$$G^* = G_o^*\left[\frac{R_{12}}{R_{12}+R_{13}+R_{14}}\right]\left[\frac{R_{18}}{R_{15}+R_{16}+R_{17}+R_{18}}\right] \quad (19)$$

where G_o^* is the maximum possible yield of excited-state XeCl* production and R_i is the reaction rate for the ith reaction in the scheme.

Assuming that at 0.80 Torr $CFCl_3$ only the excited-state formation of XeCl* occurs, then eq 19 can be used to calculate the unquenched, limiting excited-state formed yield as $G_o^* = 2.4$. A sensitivity analysis of the rate constants used in this equation, and their relative errors, shows that this calculated value is only accurate to ±25%. This yield is much larger than previously determined for XeBr* (0.68 ± 0.10),[8] KrF* (0.70 ± 0.10),[9] and XeF* (<0.05).[9]

From this limiting value, the $CFCl_3$ pressure dependence of the excited-state fluorescence yield can be calculated, and these values are also shown in Figure 1. The difference between the two sets of values, as indicated at 0.10 Torr, is the yield due to the ionic recombination pathway, G^+. For $CFCl_3$ pressures less than 0.30 Torr, ionic recombination is seen to be the dominant formation mode.

The calculated xenon pressure dependence of G^*, at a constant $CFCl_3$ pressure of 0.10 Torr, is shown in Figure 2, in comparison with the experimentally determined G_T values. The difference between these two yields is again attributed to the ionic recombination contribution, with this seen to be essentially the only formation process at xenon pressures over 100 Torr. Above this pressure the ionic yield constantly decreases, and this is believed to be due only to the quenching reactions of XeCl*.[15] This decrease can therefore be modeled by the equation

$$G^+ = G_o^+\left[\frac{R_{18}}{R_{15}+R_{16}+R_{17}+R_{18}}\right] \quad (20)$$

By fitting these calculated G^+ values to eq 20 at xenon pressures above 100 Torr, a value of $G_o^+ = 3.15$ is obtained. This value is believed to be accurate to ±15%. The calculated G^+ dependence on xenon pressure is also given in Figure 2 and is seen to be in very good agreement with the experimental data.

The limiting XeCl* ionic recombination yield is in very good agreement with the value obtained for XeBr* ($G_o^+ = 3.40 \pm 0.18$) and thus supports our premise[9] that for recombining atomic anions, the formation of the exciplex RX* (B,C) state dominates. The XeCl* value is still lower than the theoretical value of 4.5, based on the W value of xenon of 22.1 eV/ion-pair;[20] the experimental measurement gives the photon yield per ion pair as 0.70 ± 0.10.

The total yield of ions and excited states in an irradiated gas may be estimated from an equation proposed by Platzman[33]

$$\frac{W}{I} = \frac{E_i}{I} + \left(\frac{n_{ex}}{n_i}\right)\frac{E_{ex}}{I} + \frac{E_{se}}{I} = 1.82 \quad (21)$$

where W is the mean energy deposition required to produce an ion pair (22.1 eV),[20] I is the xenon ionization potential (12.130 eV),[26] E_i is the mean ionization energy (1.15I),[34] E_{ex} is the mean excitation energy (0.8I),[34] E_{se} is the mean subexcitation energy (0.33I),[34] and (n_{ex}/n_i) is the ratio of excited states to ions produced.

For xenon this results in $(n_{ex}/n_i) = 0.43$, this value being in very good agreement with a previously reported calculation of 0.45.[7]

Based on the theoretical ion yield of 4.5 and this calculated ratio, an excited-state yield of $G_o^* = 1.95$ would be anticipated. The measured value of 2.4 ± 0.6 is within error of this calculated value, indicating that every excited-state reaction leads to the production of the fluorescent XeCl* (B,C) state (allowing for all quenching reactions). The photon yield per excited state is calculated to be 1.2 ± 0.3.

The experimental photon yields determined in this study also allow a calculation of the upper conversion efficiency expected for the $^2\Sigma_{1/2}^+ \rightarrow {}^2\Sigma_{1/2}^+$ XeCl* lasing from irradiated Xe/$CFCl_3$ gas mixtures. Assuming no deactivation by collisional processes or photoabsorption by the medium, the maximum output power possible (per 100 eV input energy) is given by

$$(G_o^* + G_o^+)h\nu \quad (22)$$

where $h\nu$ is the mean energy of fluorescent radiation (assumed to be 4.03 eV corresponding to a wavelength of 308 nm). Substituting the appropriate values (with G_o^* at its quantitative value of 1.95) into this equation gives the maximum efficiency in converting input energy into XeCl* luminescence as approximately 21%, in good agreement with the analogous XeBr* (Xe/CF_3Br) value of 18%.[8]

At lower xenon pressures, a rise in the experimental G_T and calculated G^+ values with increasing xenon pressure is observed. This rise cannot be explained in terms of our model. Since there is a sufficiently high $CFCl_3$ concentration to ensure complete capture of the thermalized electrons, this effect must be due to changes in the nature of the ionic recombination process itself. As proposed previously,[9] this increasing yield is believed to be due to competition between the three-body ionic recombination reaction giving XeCl* (B,C) and other reactions that do not, such as the two-body, mutual neutralization

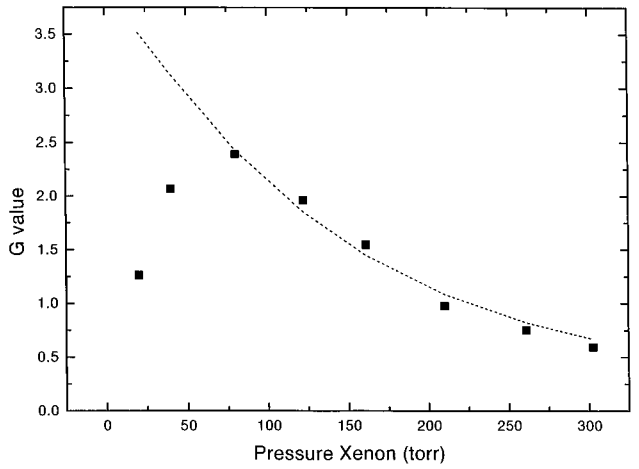

Figure 3. Xenon pressure dependence of the experimental G_T yields at a constant $CFCl_3$ pressure of 0.50 Torr. Dashed line is the calculated ionic recombination yield pressure dependence based on the model presented in the text.

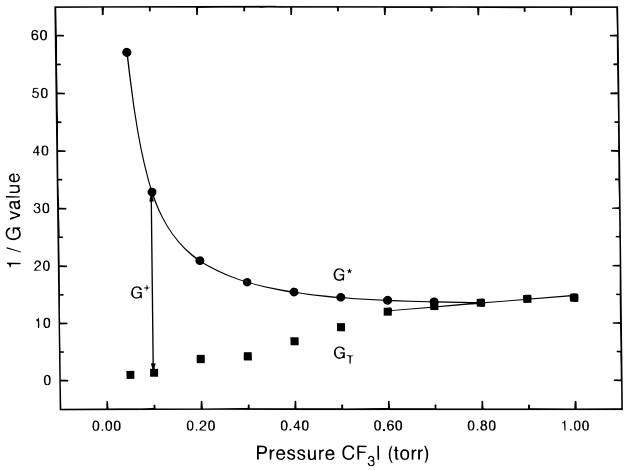

Figure 4. CF_3I pressure dependence of the calculated excited-state fluorescence yield G^* (●) contribution to the measured XeI* total yield G_T (■) values at a constant xenon pressure of 80 Torr. The difference between these two curves at 0.10 Torr CF_3I is due to the yield from ionic recombination reactions, G^+. The limiting straight line observed for CF_3I pressures above 0.60 Torr gives the region where XeI* fluorescence is formed only by the excited-state reaction pathway.

reaction[35]

$$Xe_2^+ + Cl^- \rightarrow 2Xe + Cl^* \qquad (23)$$

As the xenon pressure is increased, the efficiency of the termolecular process would increase, giving a rise in the exciplex fluorescence yield.

When an attempt was made to model the experimental yield data with the inclusion of mutual neutralization reactions, no meaningful convergence was obtained. This is believed to be due to the additional complication that the mutual neutralization recombination is greatly enhanced by the presence of an ambient gas.[35] This has been shown to be due to the collisional conversion of the free ion pair into a bound pair that allows the avoided crossing required for two-body recombination to be traversed many times. Unfortunately, it was beyond the scope of this study to perform a detailed calculation of this process.

A further test of the results of this analysis for XeCl* was made by using total fluorescence yield data measured for 0.50 Torr $CFCl_3$. Although the xenon pressure range studied was not as extensive as for the 0.10 Torr experiments, the data (see Figure 3) above 100 Torr were successfully modeled using the limiting yield value and rate constants derived from the 0.10 Torr $CFCl_3$ data.

Xe/CF_3I Measurements. The analogous XeI* system, from irradiated Xe/CF_3I gas mixtures, was also investigated in this study. The emission spectrum for the $^2\Sigma_{1/2}^+ \rightarrow {}^2\Sigma_{1/2}^+$ transition covers the range 239−260 nm with a peak at 251 nm.[21,27]

No temporal separation of the energy-transfer and ionic recombination pathways could be achieved for this system. Since the thermal electron capture by CF_3I to produce I^- is again fast,[23] $k = (1.16 \pm 0.07) \times 10^{14}$ dm^3 mol^{-1} s^{-1}, and the ionization potential of CF_3I (10.4 eV)[36] is lower than that of Xe^+ (12.130 eV),[26] the excited-state yield component in this system was again calculated, as for XeCl*.

The inverse plot of the total yield dependence on CF_3I pressure, at a total xenon pressure of 80 Torr, is shown in Figure 4. A limiting, high-pressure, linear region is again seen, indicating that charge transfer dominates for CF_3I pressures above 0.60 Torr. At this CF_3I pressure, the production of the XeI* fluorescence by only excited-state reaction can be modeled by the standard mechanism using the following rate constants:

$$Xe^* + CF_3I \rightarrow XeI^* \qquad k_{24} = 2.4 \times 10^{11} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}\ ^{10} \qquad (24)$$

$$Xe^* + Xe \rightarrow \text{products} \qquad k_{25} = 5.5 \times 10^{8} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}\ ^{10} \qquad (25)$$

$$Xe^* \rightarrow h\nu \qquad k_{26} = 2.1 \times 10^{6} \text{ s}^{-1}\ ^{10} \qquad (26)$$

$$XeI^* + CF_3I \rightarrow \text{products} \qquad k_{27} = 5.0 \times 10^{11} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}\ ^{20} \qquad (27)$$

$$XeI^* + Xe \rightarrow \text{products} \qquad k_{28} = 2.0 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \qquad (28)$$

$$XeI^* + 2Xe \rightarrow \text{products} \qquad k_{29} = 2.9 \times 10^{12} \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1} \qquad (29)$$

$$XeI^* \rightarrow h\nu \qquad k_{30} = 8.3 \times 10^{7} \text{ s}^{-1}\ ^{28} \qquad (30)$$

The rate constants for Xe* reaction, eqs 24−26, have previously been measured under the experimental conditions of this study.[17] The rate constant for XeI* quenching by CF_3I has been determined as $k_{27} = (5.0 \pm 1.0) \times 10^{11}$ dm^3 mol^{-1} s^{-1}.[27] The collisional mixing of the B and C states of XeI* has been shown to be pressure dependent,[37] with essentially only the B state present for bulk pressures above 25 Torr. The lifetime of this state has been calculated as 12 ns,[38] corresponding to a rate constant of $k_{30} = 8.3 \times 10^7$ s^{-1}. No value for either the two- or three-body xenon-quenching rate constants for XeI* could be found.

The three-body xenon-quenching rate constant was derived from a reported measurement of the ratio $k_{29}/k_{30} = 35\,200$.[17] From the XeI* calculated lifetime of 12 ns,[38] a value of $k_{29} = 2.9 \times 10^{12}$ dm^6 mol^{-2} s^{-1} is obtained.

The unknown k_{28} rate constant was determined from the XeI* yield dependence on xenon pressure (Figure 5). Assuming that at xenon pressures above 400 Torr the excited-state yield is negligible, then eq 20 can be used to simultaneously fit the

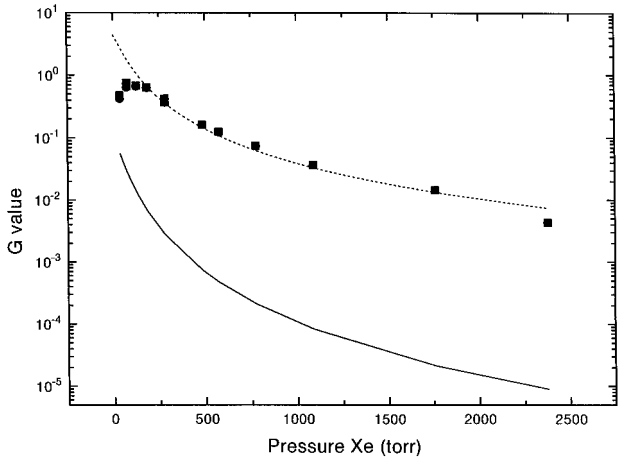

Figure 5. Xenon pressure dependence of the experimental G_T (■) and calculated G^* (−) and G^+ (●) yields at a constant CF_3I pressure of 0.10 Torr. Dashed line corresponds to the calculated ionic recombination yield pressure dependence using eq 20 and XeI* values given in the text.

values of k_{29} and $G_o{}^+$, using the rate constants for XeI* as listed in eqs 24−30. Convergence values of $k_{28} = (2.0 \pm 0.4) \times 10^{10}$ dm^3 mol^{-1} s^{-1} and $G_o{}^+ = 4.5 \pm 0.6$ were obtained. The calculated ionic recombination yield dependence on xenon pressure is also given in Figure 5. It can be seen that except at very low xenon pressures the excited-state yield contribution is negligible, justifying our initial assumption.

Using this fitted value of k_{28} the limiting excited state formation yield was then calculated. Assuming that at 0.70 Torr CF_3I all the exciplex fluorescence was formed by excited-state reaction, then eq 19 was used to calculate $G_o* = 0.31$, again using XeI* values. Given the errors associated with the component rate constants, it is believed that this value is accurate to ±25%. The calculated CF_3I pressure dependence of G^* is also shown in Figure 4, and it is seen that the ionic recombination-formed fluorescence, G^+, is the dominant pathway for CF_3I pressures less than 0.4 Torr.

There have been two reported values for the lifetime of XeI*, the calculated lifetime of 12 ns[38] and an experimental determination of 77 ± 13 ns.[27] However, when this entire analysis was repeated using the longer lifetime, no meaningful values for k_{28} or $G_o{}^+$ were obtained from the fitting procedure.

The value for $G_o{}^+$ determined in this study is in excellent agreement with the theoretical value of 4.5 calculated from the xenon W value. Although there is a relatively large error associated with this derived value, corresponding to a photon yield per ion pair of 1.00 ± 0.13, this result again supports our proposal that atomic anion recombination favors the formation of the exciplex (B,C) states.[9] Based on the Platzman theoretical calculation, a G_o* value of 1.95 would again be expected. The low experimental value of $G_o* = 0.31$ (photon yield per excited state of 0.16 ± 0.04) suggests that alternative reaction pathways dominate in this gas system. The experimental excited state yield is somewhat lower than the value obtained previously for XeBr* (0.68 ± 0.10).[8]

These experimental limiting yields can again be substituted into eq 22 to give the upper conversion efficiency limit expected for XeI* luminescence. For an energy of 4.94 eV (corresponding to a wavelength of 251 nm) a value of 24% is obtained. This system has the highest conversion efficiency of all the exciplex systems investigated to date.[8,9]

It was again observed that at low xenon pressures, G_T and G^+ increased with increasing pressure. This is again attributed to competition between the exciplex producing three-body ionic recombination with mutual neutralization type reactions giving other products. The much higher xenon pressure of the maximum fluorescence yield seen in Figure 5, as compared to previous exciplex determinations,[8,9] again corroborates the finding that these reactions dominate to a much greater extent for this exciplex at these low xenon pressures.

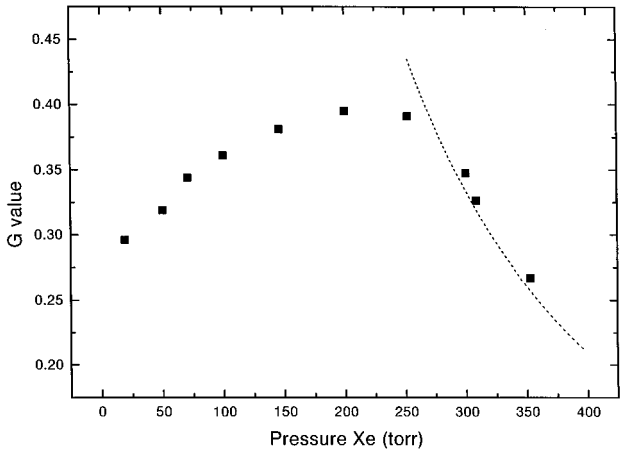

Figure 6. Xenon pressure dependence of the experimental G_T yields at a constant CF_3I pressure of 0.50 Torr. Dashed line is the calculated ionic recombination yield pressure dependence based on the model presented in the text.

TABLE 1: Summary of the Limiting, Unquenched Fluorescence Yields for the Neutral Excited State, G_o*, and Ionic Recombination, $G_o{}^+$, Reactions for the Electron-Irradiated Rare Gas/Halide Gas Mixtures Studied to Date

gas system	exciplex	G_o*	$G_o{}^+$	D_{A-X}[a] eV
Xe/CF_3I	XeI*	0.31 ± 0.08	4.5 ± 0.6	2.32
Xe/CF_3Br	XeBr*	0.68 ± 0.10	3.4 ± 0.2	3.06
Xe/CCl_3F	XeCl*	2.4 ± 0.6	3.2 ± 0.5	3.16
Xe/SF_6	XeF*		0.26 ± 0.02	2.96
Kr/SF_6	KrF*	0.70 ± 0.10	1.70 ± 0.10	2.96

[a] From ref 39.

In this study, XeI* yield data were also obtained using 0.50 Torr CF_3I, and these results are shown in Figure 6. The maximum fluorescence yield for this higher halide gas pressure is again observed at a much higher xenon pressure (∼200 Torr) than seen for the equivalent $CFCl_3$ data (∼100 Torr in Figure 3). At the higher xenon pressures, these XeI* yields are seen to be well modeled by the values obtained from the 0.10 Torr CF_3I data, thus supporting these calculated values.

The limiting, unquenched fluorescence yields for both the neutral, excited-state reaction and the ionic recombination process for all the exciplex gas systems investigated by us are summarized in Table 1, along with the corresponding bond dissociation energies for the different halide source gases used.[39] The trends observed in these yields can be qualitatively supported by examination of the energetics of these reactions.

The measured yield of $G_o{}^+ = 4.5$ for the ionic recombination process in irradiated Xe/CF_3I implies that, within error, every ion pair formed recombines to give the fluorescent (B,C) XeI* exciplex. The analogous yields for XeBr* and XeCl* are only slightly lower, about 75% of this theoretical value. Given the accepted errors in measuring fundamental emission yields, it is doubtful whether these differences have any mechanistic significance. One possible explanation, however, could lie in the rate coefficients for the ionic recombination process in these three systems.[15,17] It was shown[17] that for only the XeI* exciplex, the measured rate constants were much larger than predicted by either the universal three-body recombination theory[35] or even the Langevin−Harper[40,41] diffusion-controlled theory at xenon pressures greater than 1000 Torr. This was

attributed to the ionic recombination process being extremely efficient for this system; the initial encounter complex is formed at very large distances with a binding energy very much less than thermal, and the collisional reopening of this orbit was extremely inefficient. At this time it was proposed that the long-range three-body encounter complex would then quantitatively convert to the two-body fluorescent exciplex, this assumption being confirmed in this study.

The excited state yields for these three exciplexes range over an order of magnitude, with only the value for XeCl* in agreement with the quantitative theoretical prediction.[33] Although a range of xenon excited states are produced in the initial irradiation pulse, given the relatively high gas pressures and long time scales involved in these yield determinations, it can be assumed that only the longer-lived xenon metastable states, the 1s and 2p levels with energy ranges 8.31−9.56 and 9.58−11.14 eV, respectively,[42] would be involved in exciplex formation reactions.

For XeI*, the excited-state yield is only 16% of its expected value, which implies that another reaction channel dominates. We believe that this additional process is the production of the electronically excited iodine atom by the reaction

$$Xe^* + CF_3I \rightarrow I^* + {}^{\cdot}CF_3 + Xe \qquad (31)$$

The lowest excited state of the iodine atom has an energy of 0.9 eV.[43] However, the second lowest excited level is 6.95 eV. The addition of this latter value to the energy necessary for the appropriate bond dissociation in CF_3I (2.32 eV;[39] see Table 1) requires the minimum energy of the initial xenon electronically excited state to be 9.27 eV. This means that the higher 1s, as well as all the 2p, levels could participate in this dissociative reaction, thereby markedly decreasing the yield of the XeI* formed.

A similar alternative pathway may be present in the Xe/CF_3Br system. For XeBr* formation the greater C−Br bond strength of 3.06 eV[39] and the higher second energy level for the excited state of Br* (8.31 eV[44]) would mean that only the upper 2p levels of the excited xenon atoms would be able to produce this electronically excited halide atom. Since the population of these high excited states is lower, the amount of reaction proceeding by this pathway would be less, giving a concomitant increase in the yield of exciplex production, as observed. In the Xe/CCl_3F system, the stronger C−Cl bond (3.16 eV[39]) and the higher energy level of Cl* (9.23 eV[44]) mean that the excited state of xenon is required to have an energy of 12.39 eV, which is greater than the ionization potential of this atom. Thus, the exit channel via Cl* is energetically impossible, and hence, the exciplex production is the only feasible channel, giving the quantitative yield experimentally observed.

The two systems that incorporated SF_6 as the halide source gas have both excited-state reaction and ionic recombination limiting yields that are much lower than the other three systems, suggesting that alternate pathways are the most abundant in these two systems. This is attributed to the greater dissipation potential of the $SF_5^{\bullet}$ product radical, where energy can be absorbed by further S−F bond breakage or by additional excitation of this radical or smaller fragments. The lack of an excited-state reaction pathway for XeF* production for this halide gas source implies that almost all the energy of reaction is channeled into these alternative pathways, thus leaving insufficient energy to form this fluorescent exciplex. The relatively small excited-state yield for KrF* is similar to the yield measured for XeBr*[8] and likewise suggests that only the highest electronically excited krypton atoms have sufficient energy to form this exciplex. This is in agreement with a previous kinetic study of the Kr/SF_6 system,[12] which showed that the very high KrF* formation rate constant of $(1.2 \pm 0.2) \times 10^{12}$ dm^3 mol^{-1} s^{-1} was in good agreement with the observed quenching rate constants of the krypton 2p levels, $(8.9 \pm 1.0) \times 10^{11}$ dm^3 mol^{-1} s^{-1}, but was much larger than the 1s values of $(2.0 \pm 0.2) \times 10^{11}$ dm^3 mol^{-1} s^{-1}.

Summary

Total emission yields for the XeCl* (B,C) and XeI* (B,C) $^2\Sigma_{1/2}^+ \rightarrow {}^2\Sigma_{1/2}^+$ transition have been measured from irradiated Xe/$CFCl_3$ and Xe/CF_3I gas mixtures. The yields for the individual excited-state and ionic recombination pathways have been calculated by determining the limiting excited-state yields, G_o*, under conditions where charge transfer from Xe^+ ensures that no ionic recombination occurs. Values of $G_o^* = 2.4 \pm 0.6$ and 0.31 ± 0.08 were obtained for XeCl* and XeI*, respectively. By application of the known general mechanism of exciplex formation, the limiting ionic recombination yields were derived as $G_o^+ = 3.2 \pm 0.5$ (XeCl*) and 4.5 ± 0.6 (XeI*). These latter values further support the theory that the recombination involving atomic halide anions favors the formation of these particular exciplex states. A qualitative understanding of the trends in these limiting yields for these exciplex systems is obtained by examining the energetics of the reactions involved.

The ionic recombination process was the major formation pathway of these two exciplexes under most of the conditions of this study. At lower xenon pressures, the observed increase in the total and ionic yields with increasing xenon pressures was attributed to the three-body ionic recombination channel becoming dominant over competing, mutual neutralization type reactions that do not produce the fluorescent exciplex. The importance of these mutual neutralization reactions was seen to be far greater for XeI*.

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