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Daimay Lin, Y. C. Yu, and D. W. Setser

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Rate constants and branching fractions for xenon halide formation from $Xe({}^{3}P_{2})$ and $Xe({}^{3}P_{1})$ reactions

Daimay Lin, Y. C. Yu,^{a)} and D. W. Setser

Chemistry Department, Kansas State University, Manhattan, Kansas 66506

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The rate constants for XeF(B,C), XeCl(B,C), and XeI(B,C) formation from reactions of Xe(${}^{3}P_{1}$) and Xe(${}^{3}P_{2}$) with NF₃, N₂F₄, NF₂, CCl₄, and CF₃I have been measured relative to XeCl(B,C) formation from the reactions with Cl₂. The XeCl(B,C) formation rate constants from Cl₂ are assumed to equal the total Xe(${}^{3}P_{2}$) and Xe(${}^{3}P_{1}$) quenching rate constants. The dependence of the XeX* formation rate constants upon reagent for Xe(${}^{3}P_{1}$) and Xe(${}^{3}P_{2}$) are similar with the polyatomic reagents having considerably smaller XeX* product formation rate constants than does Cl₂. The previous claim from this laboratory that the XeF(B,C) formation rate constant from NF₃ was approximately equal to the total quenching rate constant is revised downward in this work.

In a series of papers from this laboratory¹⁻⁴ the rate constants k_{XeX}^{RX} and branching fractions Γ_{XeX}^{RX} for XeX(B,C) formation from reaction of Xe(³P₂) with halogen containing molecules were reported. These measurements, which were done in a flowing-afterglow apparatus (Pyrex glass) at 300 K with Ar carrier gas, were based upon a comparison of the XeX(B,C) emission intensities from reactions (1) to the XeCl(B,C) emission intensity from reaction (2). For the same [Xe(³P₂)] and for low [RX] such that the

$$Xe({}^{3}P_{2}) + RX \xrightarrow{k_{XeX}} XeX(B,C) + R; X = halogen atom, (1)$$

$$Xe({}^{3}P_{2}) + Cl_{2} \xrightarrow{k_{XeCl}^{Cl}} XeCl(B,C) + Cl$$
(2)

differential rate law holds, $k_{XeX}^{RX} = k_{XeCI}^{Cl_2} (I_{XeX}^{RX} / I_{XeCI}^{Cl_2})$ $([Cl_2]/[RX])$; the intensities are the integrated XeX(B) and XeX(C) emission intensities. The comparison of intensities assumes that radiative decay determines the loss of XeX(B,C), which is valid at 1 Torr of Ar and the low [RX]. The branching fraction $\Gamma_{\text{XeX}}^{\text{RX}}$ is given by $k_{\text{XeX}}^{\text{RX}}/k_Q^{\text{RX}}$, where k_{O}^{RX} is the total quenching rate constant.⁵ The first report¹ dealing with RF molecules was the most difficult of the series¹⁻⁴ because of the extended XeF(C-A) spectrum and because of the problems in quantitative measurements of [RF]. Recent experiments in our laboratory, as well as communication with other laboratories, have indicated that our previous claim for $\Gamma_{XeF}^{NF_3} \sim 1$ was too high. Therefore, we have remeasured the emission intensities from NF₃ and some other reagents for reaction (1), extended the measurements to include the Xe(${}^{3}P_{1}$) reactions, and studied Xe(${}^{3}P_{2}$) + NF₂. The k_{0}^{RX} values reported earlier⁵ were used to compute Γ^{RX}_{XeX}.

The emission intensities from the $Xe({}^{3}P_{2})$ atom reactions were measured in a flowing-afterglow reactor using dilute Xe in Ar carrier gas.¹⁻⁴ The detection system composed of a 0.3 m monochromator, RCA C31034 PM tube, and SSR photon counter was calibrated with standard lamps prior to the current measurements. The spectra were recorded via computer, corrected for detector response and background, and integrated. The reagent gases were purified by distillation and stored as dilute mixtures in argon before being metered to the reaction zone. The NF₂ was obtained by heating (200 °C) the N_2F_4 flow prior to injection into the reactor. The dissociation of N₂F₄ was ensured by observing the disappearance of the ArF(C-A) emission (260 nm) from $Ar({}^{3}P_{0,2}) + N_{2}F_{4}$ as the line was heated. ^{6(a)} Some XeF(B-X) and XeF(C-A) spectra from $Xe({}^{3}P_{2})$ atom reactions are shown in Fig. 1(b) to illustrate the width of the spectral range needed for integration. The differences betweeen the spectra should be noted, especially the low vibrational distribution displayed by the XeF(B) spectra from NF₂, which implies reaction via a $Xe^+NF_2^-$ bound intermediate. In spite of the low XeF(B,C) vibrational excitation, the Xe(${}^{3}P_{2}$) + NF₂ reaction gave significant amounts of XeF(D) and NF($b^{-1}\Sigma^{+}$). Although the observed NF(b-X) intensity is only ~ 0.1 of that from XeF(B,C), the rate constant for NF(b) formation is significant, since most of the [NF(b)] flows out of the observation zone without decay because of its 20 ms radiative lifetime.⁶

Plots of I_{XeX}^{RX} vs [RX] and $I_{XeC1}^{Cl_2}$ vs [Cl₂] were made [see Fig. 1(a)] to find the [RX] range for which the differential rate law holds. Measurements of the integrated XeX(B-X.C-A) intensity ratios were carried out using [RX] and $[Cl_2]$ in this range. The differential rate law was then used to calculate the XeX* formation rate constants relative to $k_{XeCl}^{Cl_2}$; measurements were done for three different sets of [RX] and [Cl₂] for each experiment. At least two independent experiments, i.e., separately prepared [RX] reagent mixtures were done for each reagent, except for CCl₄. The results are summarized in Table I. Since two intensity measurements are being compared, each with \pm 10% uncertainty, the reproducibility of the $k_{\text{XeX}}^{\text{RX}}$ is of the order of $\pm 20\%$. Four separate experiments were done with CF₃I, a molecule with no gas handling difficulties, and indeed the statistical uncertainty was \pm 30%. In addition to making the intensity plots for low reagent flows (i.e., the first order regime), experiments were done for high [RX] corresponding to complete conversion of $Xe({}^{3}P_{2})$ to products. This method works well for measuring product branching fractions for stable products such as H and O atoms, as shown by Golde.^{7,8} If the volume observed by the monochromator was masked, con-

^{a)} Present address: Chemistry Department, National Sun Yat-Sen University, Kaohsiung, Taiwan 800, Republic of China.



FIG. 1. (a) Plots of the peak intensity of XeX(B-X) emission vs [RX] for the reaction of Xe(${}^{3}P_{2}$) with Cl₂, CF₃I, and NF₃; at higher concentrations these plots cease to be linear. (b) Comparison of emission spectra from Xe(${}^{3}P_{2}$) with NF₃, N₂F₄, and NF₂ at ~1.5 Torr (Ar) pressure. The broad envelopes from 240–370 and from 370–570 nm are the XeF(B-X) and XeF(C-A) transitions, respectively. The sharp bands at 250 and 530 nm in the NF₂ spectrum are XeF(D-X) and NF(B-X) transitions, respectively. The sharp features around 400–500 nm are scattered Xe atomic lines from the discharge used to generate Xe(${}^{3}P_{2}$) atoms.

stant emission signals were obtainable for a suitable range of high reagent concentration⁹ and the relative intensities were roughly proportional to the relative Γ_{XeX}^{RX} values ($\Gamma_{XeCI}^{Cl_2}$ = 1.0 was used as a reference). The Γ_{XeX}^{RX} from high [RX] experiments are only approximate; but they are included in Table I.

The $Xe({}^{3}P_{1})$ experiments were done by the resonance sensitization method in which a Xe/RX mixture was slowly flowed through a cell that was attached via an O-ring seal to a microwave powered Xe resonance lamp.^{10,11} The Xe resonance emission from the lamp passed to the reaction cell via a sapphire window. The XeX(B,C) spectra from a given reagent are nearly identical to that from the analogous $Xe({}^{3}P_{2})$ reaction.^{4,10} The same approach as for $Xe({}^{3}P_{2})$ was used to measure the relative k_{XeX}^{RX} for the Xe(³P₁) reactions, i.e., the I_{XeX}^{RX} was compared to a reference reaction for constant $[Xe, {}^{3}P_{1}]$. The XeX(B,C) intensity measurements were more difficult for $Xe({}^{3}P_{1})$ because of the need to control the very low [Xe] in the sensitization cell and because of greater materials problems associated with the stainless cell. To maintain constant $[Xe({}^{3}P_{1})]$, we used pre-prepared mixtures of Xe/ RX/Ar and Xe/CCl₄/Ar containing exactly the same partial pressure of Xe. Spectra were collected pairwise at the same [Xe] for three different total pressures ranging from 0.3-0.9 Torr with [Xe] and [RX] ranging from 7.5-22.5 and

TABLE I. XeX^{\bullet} formation rate constants and branching fractions from Xe(³P₂) and Xe(³P₁) reactions.^{\bullet}

Reagent	Product	$k_{\rm XeX} (10^{-11} {\rm cm}^3 { m molecule}^{-1} { m s}^{-1})$	$\Gamma_{\rm XeX}^{\rm RX}$
Cl ₂	XeCl*	72.0	1.0
		72.0	1.0
CF ₃ I	XeI*	12.9 ^c	0.25(0.38) ^b
		7.9	
CCl₄	XeCl*	17.3 ^d	0.24 ^d (0.13) ^b
		9.4	
NF ₃ ⁸	XeF*	2.4°	0.27°(1.1) ^b
		6.5	. ,
N.F.	XeF*	16.6 ^e	0.50° (0.50) ^b
NF.	XeF*	1.1 ^f	f

See Ref. 1 for assignment for Γ_{Xec1}^{Cl} ; the result could be uncertain by $\pm 20\%$. If there are two entries, the first entry is for $Xe({}^{3}P_{2})$ and the second is for $Xe({}^{3}P_{1})$; both measurements were made relative to the Cl₂ reaction.

^b Previous results from Refs. 1-3; the new results are favored.

^c Average of four separate experiments; the high [CF₃I] comparison with high [Cl₂] gave $\Gamma_{\text{Xel}}^{\text{CF}} = 0.28$.

^d Based upon one experiment.

- ^eBased upon three separate experiments; the high [NF₃] and [N₂F₄] comparisons with high [Cl₂] gave $\Gamma_{XeF}^{NeF} \approx 0.2$ and $\Gamma_{XeF}^{NeF} \approx 0.25$.
- ^fBased upon two separate experiments, $\Gamma_{Xe_{1}}^{Ne_{1}}$ is not given because $k_{Q}^{NF_{1}}$ is unknown. Qualitative inspection of the flame geometry for a given [NF₂] suggest $k_{Q}^{NF_{1}} \approx k_{Q}^{NF_{1}}$ and $\Gamma_{Xe_{1}}^{NF_{2}} < 0.1$. A similar value is implied by the high [NF₂] experiments.

⁸ The previous Γ_{KF}^{NF} value (Ref. 1) also probably is too large, see Ref. 13.

17-62 mTorr, respectively. Two separate mixtures were used for each of the reagents $Cl_2/NF_3/CCl_4/CF_3I$ that were studied. Problems were encountered for Cl₂/NF₃ pairwise comparison because NF₃ displaced Cl₂ from the stainlesssteel cell walls. For this reason the pairwise intensity comparisons were done relative to CCl₄ and then the CCl₄ reaction was compared to the Cl₂ reaction. Since $k_Q^{Cl_2}$ for Xe(³P₁) is not known, we assumed that $\Gamma_{XeCl}^{Cl_2} = 1$ and $k_{XeCl}^{Cl_2} = 72 \times 10^{-11} \text{ cm}^3$ molecule⁻¹ s⁻¹ by analogy to the Xe(³P₂) reaction, and these assumptions were used to obtain the $k_{\text{XeX}}^{\text{RX}}$ values for the Xe(³P₁) reactions in Table I. Based upon our understanding⁴ of the interaction of Xe(6s) states with halogens, similar $k_{XeX}^{X_2}$ and $\Gamma_{XeX}^{X_2}$ for Xe(³P₂) and Xe(³P₁) are expected. We do not report Γ_{XeX}^{RX} for $Xe({}^{3}P_{1})$ reactions because the $k_{Q}(Xe, {}^{3}P_{1})$ values are not known. However, the $Xe({}^{3}P_{1})$ rate constants are expected to be equal to or larger^{5,12} than for $Xe({}^{3}P_{2})$ and the reader can construct upper limit estimates to $\Gamma_{XeX}^{RX}(Xe, {}^{3}P_{1})$ by using the same k_{O} values as for $Xe({}^{3}P_{2})$. If this is done, the $Xe({}^{3}P_{1})$ branching fractions for CCl_4 and CF_3I are somewhat smaller than for $Xe({}^{3}P_2)$ reactions; but that for NF_3 is about 2.5 times larger.

Our former measurements^{1,2} provided a survey of donors for RgX formation; we had estimated uncertainties of the branching fractions of ~20% for cases with $\Gamma_{XeX}^{RX} > 0.1$ and $\approx 50\%$ for $\Gamma_{XeX}^{RX} < 0.1$. In the early experiments one or two pairwise intensity comparisons were made rather than constructing first order intensity vs [RX] plots. With benefit of hindsight, the estimated errors^{1,2} probably should be increased by a factor of 2.¹³ The general trends identified earlier are correct⁴; but, this work shows that the individual branching factors may be more uncertain than formerly thought. New product branching factor data, including ionization, by $Ar({}^{3}P_{0,2})$ reactions will be summarized in a separate paper.¹⁴

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