

METASTABLE RARE GAS ATOM QUENCHING REACTIONS: PRODUCT STATE DISTRIBUTIONS

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The excitation energies of the lowest excited state (3P_2) of the $(np^{n+1}s)$ manifold are 11.5, 9.9 and 8.3 eV for Ar, Kr and Xe, respectively. Since these are metastable states, they can be conveniently studied by the flowing afterglow technique. Observation of the decay of the metastable concentration in the presence of known concentrations of added reagents gives the total quenching rate constants. The emission spectra from the quenching reaction identifies the product states and comparison of the relative emission intensities from a given reaction to that of a reference reaction provides the rate constants for individual product channels that lead to luminescence. The reference reactions for Ar(3P_2) are ArCl* and ArF* formation reaction with Cl₂ and F₂ and Kr($5p^5$)* formation from reaction with Kr. Formation of the chloride and fluoride excimers from reaction with Cl₂ and F₂ are the reference reactions for Kr(3P_2) and Xe(3P_2). These reference reactions are satisfactory for comparison of product emissions that are in the visible, ultraviolet or vacuum ultraviolet regions.

Using the techniques mentioned above, product distributions from reactions of metastable atoms with some simple halogen containing molecules, a few diatomic molecules and some atoms have been identified. A summary is given in Table 1. The branching fractions in Table 1 may add to less than unity indicating that some channels have not been identified or to slightly more than unity indicating experimental error. The k_0 values labeled as approximate were obtained from the correlation of the cross sections with the C_6 coefficient rather than being directly measured. In addition to the results in Table 1, work that is in progress on the Kr(3P_2) + Hg, Xe, CO and N₂ reactions will be reported. From Table 1 several generalizations can be made: (i) the branching fraction for rare gas halide formation declines with increasing complexity of the reagent, (ii) for the same reagent the branching fraction for rare gas halide formation normally declines in the Xe*, Kr*, Ar* series, (iii) with the exception of CN containing compounds (not shown in Table 1) quenching by the halogen containing compounds rarely leads to significant emission other than that of the rare gas halide. The excitation of the halogen atomic emission arises from predissociation of the rare gas halide excimer and can be included with that reaction channel. For some of the examples, molecular beam studies provide the dependence of the cross-section for a given product channel upon collision energy. In general the cross sections for reagents with small rate constants for quenching (such as N₂) have a positive dependence upon collision energy and those with a large rate constant have a negative dependence. The main point of including the H, O, and Cl examples in Table 1 is to illustrate that the rate constants can be large for exit channels that are below the entrance channel energy (1.3, 0.5 and 2.5 eV, respectively, for H, O and Cl).

Table 1. Product Channel Distributions.

Metastable Atom	Reagent	$k_Q (10^{-11} \text{ cm}^3 \text{ sec}^{-1})$	Product Branching Fraction
Ar(3P_2)	F ₂	75	ArF(0.53)
Kr(3P_2)	F ₂	72	KrF(1.0)
Xe(3P_2)	F ₂	75	XeF(1.0)
Ar(3P_2)	NF ₃	14	ArF(0.30)
Kr(3P_2)	NF ₃	12	KrF(0.57)
Xe(3P_2)	NF ₃	9	XeF(1.1)
Ar(3P_2)	OF ₂	57	ArF(0.62)
Kr(3P_2)	OF ₂	53	KrF(1.0)
Xe(3P_2)	OF ₂	57	XeF(0.92)
Ar(3P_2)	CF ₃ OF	43	ArF(0.15)
Kr(3P_2)	CF ₃ OF	42	KrF(0.58)
Xe(3P_2)	CF ₃ OF	47	XeF(0.40)
Ar(3P_2)	Cl ₂	71	ArCl(0.35), Cl [*] (0.13), Cl ₂ [*] (0.03)
Kr(3P_2)	Cl ₂	73	KrCl(0.90), Cl ₂ [*] (0.10)
Xe(3P_2)	Cl ₂	72	XeCl(1.0)
Ar(3P_2)	ClF	74	ArCl(0.51), Cl [*] (4s)(0.12), ArF(0.04)
Kr(3P_2)	ClF	68	KrCl(0.59), KrF(0.17)
Xe(3P_2)	ClF	60	XeCl(0.80), XeF(0.20)
Ar(3P_2)	CCl ₄	100	ArCl(0.03)
Kr(3P_2)	CCl ₄	69	KrCl(0.06)
Xe(3P_2)	CCl ₄	63	XeCl(0.13)
Ar(3P_2)	PCl ₃	53	ArCl(0.09), PCl [*] (0.01)
Kr(3P_2)	PCl ₃	~50	KrCl(~0.05)
Xe(3P_2)	PCl ₃	~49	XeCl(~0.10)
Ar(3P_2)	S ₂ Cl ₂	54	ArCl(0.15), S ₂ [*] (0.04), Cl [*] (0.08)
Kr(3P_2)	S ₂ Cl ₂	48	KrCl(0.45)
Xe(3P_2)	S ₂ Cl ₂	49	XeCl(0.35)
Ar(3P_2)	Br ₂	65	Br [*] (1.0)
Kr(3P_2)	Br ₂	63	KrBr(0.65), Br [*] (0.45)
Xe(3P_2)	Br ₂	60	XeBr(0.99), Br ₂ [*] (0.01)
Xe(3P_2)	CF ₃ Br	42	XeBr(0.14)
Kr(3P_2)	CF ₃ Br	50	KrBr(0.08)
Xe(3P_2)	CH ₂ Br ₂	~60	XeBr(~0.02)
Xe(3P_2)	CH ₃ Br	~45	XeBr(~0.02)
Xe(3P_2)	CF ₃ I	52	XeI(0.27)
Ar(3P_2)	Kr	0.6	Kr(5p[3/2] ₂)(0.90), Kr(5p[3/2] ₁)(0.10)
Ar(3P_2)	Xe	18	Xe(7d, 5f, 8p, 9s, 5d') (0.58; 0.23; 0.09; 0.04; 0.06)
Ar(3P_2)	H	25	H(n=2)(1.0)
Ar(3P_2)	O	4.1	O(3p)(1.0), O(3s)(?)
Ar(3P_2)	Cl	25	Cl(4s)(0.85); Cl(4p)(0.15)
Ar(3P_2)	N ₂ ^a	3.3	N ₂ (C)(0.60), N ₂ (B)(0.5)

a. Recent work (M. Touzeau and D. Pagnon, Chem. Phys. Lett., 53, 355 (1978) indicates N₂(C):N₂(B) = 4:1.

Computer simulation of the low-pressure bound-free spectra from XeCl*, XeF* and KrF* have been done. By matching the spacings and depths of the oscillations of the spectra, it is possible to assign a vibrational distribution of the initially formed molecules. Simulations have been done for the (III, 1/2 - I, 1/2) and (II, 3/2 - I, 3/2) transitions. A fairly extensive study has been done for Xe(³P₂) reacting with a series of chlorine containing molecules and some of the results are given in Table 2. All reactions give both the III,1/2 and II,3/2 states but the ratio does depend upon the reagent. Only the PCl₃ reaction favored XeCl(II,3/2) more than XeCl(III,1/2). The PCl₃ reaction also was the only case for which the vibrational energy disposal was different for the two electronic states. This probably is a consequence of the involvement of two different PCl₃⁻ states in the formation of the XeCl(III) and XeCl(II) products. The $\langle f_v \rangle$ values exhibit a wide range, 0.75 to 0.10. For Cl₂, ClF and SCl₂ the actual vibrational distribution consists of two components $\sim 1/4$ flat + $\sim 3/4$ linear surprisal with a large $-\lambda_v$. The intermediate cases such as CCl₄ and CCl₃F have linear surprisal type distributions with $-\lambda_v = \sim 7$. The vibrational distributions for PCl₃ were triangular in shape and those for COCl₂ and CCl₂F₂ were exponentially declining functions.

Reaction of the metastable atoms with the halogen containing reagents proceeds by the ionic-covalent curve-crossing mechanism. Formation of the rare gas halide product molecule occurs when the collision successfully traverses the complete ionic potential. Branching fractions for rare gas halide excimer formation of less than unity are a consequence of strong couplings between the ionic potential and excited states of the reagent molecule. The data in Tables 1 and 2 provide the basis for a discussion of models for these reactions. The role of the ionic potential curves in the quenching reactions of H, O and Cl also will be mentioned.

Table 2. Vibrational and Electronic Distributions from Xe(³P₂) + RCl

Reagent	$\langle E \rangle$, kcal	XeCl(III)/XeCl(II)	$\langle f_v(\text{XeCl, III}) \rangle$	$\langle f_v(\text{XeCl, II}) \rangle$
Cl ₂	43	1.3	0.77	0.73
ClF	39		0.71	
SCl ₂	55	1.0	0.69	
CCl ₄	31	1.3	0.67	0.67
CCl ₃ F	27	1.1	0.57	
PCl ₃	24 ^a	0.4	0.47	0.64
COCl ₂	24	1.0	0.20	0.25
CCl ₂ F ₂	27	1.2	0.10	

a. Based upon $D^\circ(\text{PCl}_2\text{-Cl}) = 76 \text{ kcal mole}^{-1}$, which is an upper limit.