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The Role of XeF as an Intermediate in the
Photochemical Synthesis of XeF₂ in Flash-
Photolysed Xe/Ar/F₂ Mixtures[†]

by

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D. The Role of XeF as an Intermediate in the Photochemical Synthesis of XeF₂ in Flash-Photolysed Xe/Ar/F₂ Mixtures

1. Introduction

One of the first syntheses of rare gas compounds reported in the early 1960's was a photochemical preparation of xenon difluoride:¹ an Xe/F₂ mixture in a pyrex bulb was placed in the sun for a day, resulting in the formation of colorless crystals of XeF₂ of high purity. In a study of the photochemical mechanism of this unusual synthesis, Weeks and Matheson² flash-photolysed Xe/F₂ mixtures and obtained indirect photographic spectral evidence for a diatomic photochemical intermediate which they guessed might be XeF. More recently, there have been some steady state photochemical studies of the quantum yield of XeF₂ formation³ which propose XeF as an intermediate.

It has been shown by Bischel et al.⁴ that gain can be achieved on the C-A transition of XeF at 460 nm by flash-photodissociating XeF₂. Since ground state XeF is a product of both this pumping mechanism and of the more common e-beam or discharge-pumped XeF excimer lasers, it is important to establish the chemical fate of this weakly bound diatomic free radical. This paper presents preliminary results of an investigation of the photochemistry of flash-photolysed Xe/Ar/F₂ mixtures using kinetic absorption spectroscopy with photoelectric detection. We show that there are rapid bimolecular reactions which destroy XeF and produce XeF₂.

2. Experimental

The photolysis apparatus was similar to that used in our previous photographic studies of the absorption spectrum of XeF.^{5,6} The quartz photolysis cell (2.2 cm i.d. x 50 cm long) was baked for 12 hours at 2×10^{-5} Torr before filling with Xe and F₂, and no etching of the quartz was noted. The F₂ delivery system was monel with the exception of a manometer with fluorocarbon oil for measuring F₂ pressures. The F₂ used was supplied by Argonne National Laboratories from their high-purity F₂ source, and the Xe and Ar were research grade (Air Products).

The photolysis lamp was 50 cm long and dissipated 350 Joules per flash (3.5 kv charging voltage, 60 μ F capacitor). An oscilloscope trace of the flash duration is shown in Fig. 1; more careful photoelectric measurements of the flash show that the ultraviolet atomic lines of the source peak in intensity 30 μ sec from flash initiation, while the underlying black-body continuum from the flash lamp plasma peaks at 55 μ sec, with the whole trace showing a full-width at one-third maximum intensity of 80 μ sec. An aluminum ellipsoidal reflector (Alzak aluminum architectural decorator sheet) surrounded cell and flash lamp. Since $\epsilon_{\text{max}} = 6.0 \text{ liter mole}^{-1} \text{ cm}^{-1}$ at 2800 Å for F₂, the gas mixture is optically thin in the transverse direction for the fluorine pressures used (50-60 Torr).

By varying the delay of the Garton flash source with respect to the photolysis flash we were able to study photographically the build-up and decay of XeF concentration during the photolysis flash by observing transient absorption in both the B-X and D-X transitions. Fig. 1 shows the results of one such study, in which XeF(D-X) absorption was

monitored in 50 Torr F_2 and 300 Torr Xe. Although quantitative kinetic information from such studies is not easy to get because the chemical composition of the photolysed mixture changes slightly with the number of flashes, Fig. 1 does show that for time delays comparable to the flash duration (~ 300 μ sec) the XeF ground state concentration has decayed substantially. We show below that this fast decay results from rapid bimolecular processes which destroy XeF and produce XeF_2 .

In order to obtain more complete kinetic data at one absorption wavelength, we assembled the kinetic absorption spectroscopy apparatus shown in Fig. 2. The 50 ohm input impedance of the fast amplifier was shunted with a 0.01 μ F capacitor to provide some low-pass filtering of the multiplier output. The probe light intensity was adjusted so that the multiplier operated at $\sim 10^{-2}$ ma anode current and 500 v. Under these conditions, the signal from the xenon lamp with no sample cell or photolysis flash was constant to $\pm 3\%$ over a period of two msec, indicating minimal flickering of the xenon arc, and showed a signal-to-noise ratio of about 100:1. Both electrical transients and stray light from the photolysis flash were serious problems, but a combination of filters between flash lamp and cell, apertures, and electrical shielding reduced unwanted interference from these sources to at most $\pm 5\%$ of the unabsorbed signal I_0 , all during the first 50 μ sec. Because this transient (mostly stray light and thus wavelength dependent) was quite reproducible, it was recorded during each experiment with the Biomation 8100 and then subtracted from the desired signal recorded on a subsequent flash.

Transient absorptions were recorded at a number of wavelengths (Table I) for a series of two- and three-component gas mixtures (Table

II), with argon playing the role of a third body. Each mixture was photolysed an average of 40 times over a two-day period. For many mixtures a white solid had deposited in the cell by the time the photolysis had been completed.

3. Results

The time-dependence of the XeF concentration in the one photographic study was determined from measured film optical density for a number of bands in both the B-X and D-X transition. Some of the photographic data from which these time dependencies were determined are those shown in Fig. 1. These data show XeF concentrations peaking 10-20 μ sec after the photolysis flash maximum, and decaying by an order of magnitude in 80-100 μ sec. A comparison of temporal behavior for absorption bands originating in $v'' = 0$ and $v'' = 1$ of the ground state of XeF shows that, even at the shortest delay time recorded (~ 10 μ sec), XeF(X) appears to be fully vibrationally relaxed. This is not surprising, given the rapid rate of the reactions which form and redissociate XeF under the conditions of this experiment (vide infra).

The kinetics of this fast XeF decay was studied photoelectrically by following transient absorption due to single vibrational bands of both the B-X and D-X transitions. Several other wavelengths were monitored to check for the possibility of other absorbing species. (Table I). Data from a typical experiment are shown in Fig. 3, where the contents of the Biomation 8100 memory are shown for xenon lamp plus photolysis flash with no absorption and with transient absorption at several wavelengths.

We have estimated the absolute XeF concentration from our photoelectric absorption data using the relationship

$$\int_{\text{band}} k_{\lambda} d\left(\frac{1}{\lambda}\right) = \frac{8\pi^3}{3hc} \frac{N_{v''}}{\lambda_{v'v''}^2} q_{v'v''} |D_e|^2, \quad (1)$$

where the absorption coefficient k_{λ} is defined by $I(\lambda)/I_0(\lambda) = \exp(k_{\lambda}l)$ where l is the pathlength; $N_{v''}$ is the number density of XeF(X) in level v'' ; $\lambda_{v'v''}$ is the wavelength of the band head; $q_{v'v''}$ is the Franck-Condon factor and D_e the electronic transition moment evaluated at the r-centroid for the (v', v'') band. For a monochromator of band width $\delta\lambda$, broad enough to incorporate the entire rotational structure of the (v', v'') band, it can easily be shown that

$$\begin{aligned} \int_{\text{band}} k_{\lambda} d\left(\frac{1}{\lambda}\right) &= \frac{2.303}{\lambda_{v'v''}^2} \int d\lambda \text{ O.D. } (\lambda) \\ &= \frac{2.303}{\lambda_{v'v''}^2} \delta\lambda \overline{\text{OD}} \end{aligned} \quad (2)$$

where O.D. (λ) is the observed optical density at some wavelength in the band, $\delta\lambda$ is the bandwidth in wavelength, and $\overline{\text{OD}}$ is the "band-averaged optical density." Equating $\overline{\text{OD}}$ to the measured optical density ($\equiv \log_{10} \frac{I_0}{I}$) will be accurate only in the weak absorption limit, a reasonable approximation in our case (typically $0.1 < \overline{\text{OD}} < 0.4$ and no observable rotational structure in high resolution spectrographs of the bands employed). Combination of Eqs. (1) and (2) permits the determination of $N_{v''}$, which, under the assumption of vibrational equilibration of XeF at 300 K, yields the ground state XeF concentration:

$$\begin{aligned} (\text{XeF}) &= N_{v''} Q_{\text{vib}} \exp[+E_{v''}/kT] \\ &= 1.70 N_{v''} \end{aligned} \quad (3)$$

where Q_{vib} is the vibrational partition function. Using the values of $q_{v',v''}$ and D_e for the (7,0) band of XeF(B-X) given in Table I, we estimate that typical XeF concentrations at the peak of the photolysis flash are $1-2 \times 10^{14} \text{ cm}^{-3}$.

Fig. 3 and Table I also show another important result of the photoelectric measurements: the build-up to steady state of another species besides XeF . Whereas the optical density at 321 nm (XeF(B-X)) decays to zero after the photolysis flash, the $\overline{\text{O.D.}}$ at 253 nm (XeF(D-X)) does not. Furthermore, at 235 nm where ground state XeF does not absorb, there is a steady increase in $\overline{\text{O.D.}}$, levelling off 600-700 μsec after the flash. We have identified this new species as XeF_2 on the basis of the following evidence:

(a) Averaging the results of six experiments, the ratio of the absorbances at 253 nm and 235 nm in the steady-state limit is within 10% (with a standard deviation of 0.30) of the ratio of XeF_2 absorption cross-sections reported by Pysh, Jortner, and Rice.⁷

(b) After 10-20 flashes of a given mixture, solid XeF_2 was observed as an aerosol which eventually settled out on the walls of the photolysis cell.

(c) The concentration of XeF_2 calculated from the measured steady-state absorbances at 253 and 230 nm is from 5 to $10 \times 10^{15} \text{ cm}^{-3}$, which corresponds to the formation of 0.16 - 0.32 Torr XeF_2 per flash. In our apparatus the probability of photodissociating XeF_2 itself is negligible because cellulose acetate filters between flashlamp and cell absorb strongly in the region of the XeF_2 absorption at 240 nm. Since the vapor pressure of XeF_2 at 300°K is 3.8 Torr, our observation of achieving saturation pressures after 10-20 flashes (i.e., a production

rate of 0.19-0.38 Torr XeF₂ per flash) seems quite reasonable.

In an attempt to better characterize the photochemical kinetics of Xe/Ar/F₂ mixtures, the transient recorder traces were further analysed by plotting the XeF absorption data at 323.0 nm both as $1/\overline{O.D.}$ vs. time and $\log \overline{O.D.}$ vs. time for gas mixtures 2 through 8 of Table II. While neither mode of plotting gave linear fits over the entire range, for mixtures 2, 3, 7 and 8 the pseudo-first-order fit ($\log \overline{O.D.}$ vs. t) was superior, while for mixtures 5 and 6 the second-order fit ($1/\overline{O.D.}$ vs. t) was slightly better. Mixture 4 showed strong non-linearities for both modes of plotting. Although the kinetic analysis given below suggests that the XeF decay should be second-order rather than first-order, we choose to summarize the results as pseudo-first-order decay constants k'_{XeF} , where

$$-\frac{d \ln(\text{XeF})}{dt} = k'_{\text{XeF}} \quad (4)$$

Table III presents the rate constants determined in this manner.

The transient absorption of XeF₂ in these mixtures resembled that shown in Fig. 3, although both the rate of build-up of XeF₂ and the steady-state concentration achieved depended on the gas mixture.

We summarize rate data for the approach of the XeF₂ absorbance to its final steady-state value with another pseudo-first-order relationship:

$$-\frac{d}{dt} [\ln[\text{XeF}_2(\infty) - \text{XeF}_2(t)]] = k'_{\text{XeF}_2} \quad (5)$$

This characteristic build-up rate and the steady-state concentrations achieved are also given in Table III.

For each experiment in which pseudo-first-order rate constants were determined, the (XeF) density was calculated from Eqs. (2) and (3) at the mid-point t_m of the time interval of the fit. These densities are also given in Table III.

Discussion

We postulate the following reaction mechanism for the photochemical synthesis of XeF₂:

(a) Flash photodissociation of fluorine:

We have not yet done the actinometry to determine the ultraviolet photon flux from the flashlamp contributing to J_6 , but we know that the time dependence of the flash is well modelled by the relationship $J(t) = P[\exp(-qt) - \exp(-2qt)]$ with $q = 2.4 \times 10^4 \text{ sec}^{-1}$.

(b) Formation and collisional dissociation of XeF:

We have recently⁸ calculated the equilibrium constant at 300K for this reaction and have reviewed what is known about the forward and reverse rate constants. Using these rates it can easily be shown that for the gas mixtures in Table II the equilibrium in (7) is established within less than 1 μsec . It is convenient then in the present analysis to express the fluorine atom density in terms of the density of XeF:

$$(F) = \frac{(XeF)}{(Xe) K_{eq}} \quad (7a)$$

For $K_{eq} = 2.20 \times 10^{-21} \text{ cm}^3$ and for a xenon pressure in torr, this yields

$$(F) = (XeF) \frac{1.413 \times 10^4}{P_{Xe}} \quad (7b)$$

At the highest xenon pressure we use, less than 6% of the atomic fluorine produced by the flash is tied up as XeF.

(c) reactions which make XeF_2 :

Neither rate constant has been measured.

(d) reactions which reconstitute F_2 :

The only reaction for which rate constants are available is (10). Fluorine atoms recombine two orders of magnitude more slowly than other halogens⁹: the rate constant $k_{10} = 8.0 \times 10^{-35} \text{ cm}^6 \text{ sec}^{-1}$ for $M = Ar$.¹⁰

From the measured XeF densities of Table III and Eq. 7b we can calculate F atom densities ($\sim 10^{15} \text{ cm}^{-3}$) in the time range over which rate constants of Table III were determined. We find that the pseudo-first-order rate constant for F atom recombination, defined by $-\frac{d \ln(F)}{dt} \equiv k(F)(M)$, is at most 10 sec^{-1} , several orders of magnitude less than the measured XeF decay rates. We conclude that even though (XeF) and (F) are in equilibrium during and after the flash, termolecular recombination of F atoms does not contribute to the measured disappearance of XeF. The

decay rate for (XeF) may then be written

$$\begin{aligned} -\frac{d\ln(\text{XeF})}{dt} &= (k_8 + k_{13})(\text{XeF}) + k_{11}(\text{F}) + (k_9 + k_{12})(\text{F})(\text{M}) \\ &= (\text{XeF})\left[k_8 + k_{13} + \frac{k_{11}}{K_{\text{eq}}(\text{Xe})} + (k_9 + k_{12}) \frac{(\text{M})}{K_{\text{eq}}(\text{Xe})}\right] \end{aligned} \quad (14)$$

where Eq. (7a) has been used.

This result shows that the decay of XeF should be second-order, a conclusion at variance with some of our observations (vide supra). We are not sure why first-order kinetics provide a better fit to the time dependence. In order to interpret our results, however, we can calculate a "pseudo-second-order" rate constant k''_{XeF} from the data of Table III by writing

$$-\frac{d\ln(\text{XeF})}{dt} = k''_{\text{XeF}} (\text{XeF}). \quad (15)$$

This rate constant is also tabulated in Table III, and represents the most direct comparison we have with the predicted decay rate in Eq. 14.

The first thing to notice is that the values of k''_{XeF} are reasonable for a bimolecular reaction rate. If the only process forming XeF_2 is the two-body reaction of XeF and if all other processes besides (13) which make F_2 are ignored, then $k''_{\text{XeF}} = k_8 + k_{13}$ and the calculated reaction cross-section is $\sim 51 \text{ \AA}^2$. Steps (8) and (13) are examples of a highly unusual process - the reaction of two van-der-Waals molecules to form a stable molecular species. From the measured¹¹ dissociation energy of ground state XeF ($D_e = 1175 \text{ cm}^{-1} = 3.4 \text{ kcal}$) and the heat of formation of the F atom we determine that

$$\Delta H_{\text{F}_{298}}^{\circ} [\text{XeF(g)}] = +15.5 \text{ kcal} \quad (16)$$

While there is still some controversy over the heat of formation of the gaseous xenon polyfluorides,¹² the JANAF value of ΔH_f^0 (XeF₂(g)) = -26 kcal makes reaction (8) highly exothermic (-57 kcal), and reaction (13) somewhat less so (-31 kcal). The disposition of this excess energy in the reaction products is an interesting subject for further study.

As an aside, we point out some interesting implications of (16). Although the average Xe-F bond energy in XeF₂ is ~ 32 kcal, the 3.4 kcal bond energy of XeF implies that the energy required to remove the first F from XeF₂ is ~ 61 kcal. It also implies that reactions (9), (11) and (12) are also quite exothermic.

The data of Table III show no clear trend in the variation of k_{XeF}'' with third body. The results of mixtures 5 through 8 imply that three-body processes with M = Ar may not be too important. The results of the two-component mixture studies (2 through 4) are more puzzling, since Eq. (14) implies a decrease of k_{XeF}'' with increasing xenon pressure if reactions (9) and (12) are ignored - a decrease which is not observed. Further study of the kinetics of these processes will be needed before rate constants can be given.

Since the steady-state photochemical quantum yield of XeF₂ in Xe/Ar/F₂ mixtures depends upon the relative rates of processes (8) and (9) to those of (10) through (13), no definitive mechanism for XeF₂ formation involving an intermediate XeF can be given at this time. It is interesting to note, however, that the pseudo-first-order rate constant k_{XeF_2}' used to characterize the build-up of XeF₂ is at least comparable to the rate of decay of XeF as measured by k_{XeF}' , implying that the XeF₂ quantum yield is not small.

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Table I. Wavelengths and Absorption Strength Data for Photoelectric Monitoring of Transients in Photolysed Xe/F₂ Mixtures

Wavelength (nm)	Molecule and Transition	Absorption Strength
323.0	XeF(B-X), (7,0) band ^(a)	$q_{7,0} = 0.057$ (b); $D_e = 2.70$ Debye ^(b)
285	no absorption	
253.5	XeF(D-X), (4,0) band ^(a)	$q_{4,0} = 0.108$ (b); $D_e = 2.30$ Debye ^(b)
	XeF ₂	$\epsilon = 30 \text{ l mol}^{-1} \text{ cm}^{-1}$ (c)
235	XeF ₂	$\epsilon = 75 \text{ l mol}^{-1} \text{ cm}^{-1}$ (c)

Notes:

(a) See Reference 5.

(b) from A. L. Smith, L. Messing, and B. Gelernt, "R-Variation of Electronic Transition Moments from Vibrationally Crowded Spectra: the B-X and D-X Transitions of Xenon Fluoride," J. Chem. Phys., in press.

(c) Reference 7.

Table II. Gas Mixtures Photolysed in XeF
Formation and Decay Study

Mixture Number	Pressures (Torr)			Comments
	P _{F₂}	P _{Xe}	P _{Ar}	
1	50	300	-	photographic
2	50	200	-	photoelectric
3	52	400	-	photoelectric
4	63	840	-	photoelectric
5	51	200	450	photoelectric
6	52	200	800	photoelectric
7	52	200	1500	photoelectric
8	52	100	760	photoelectric

Table III. Pseudo-First-Order Rate Constants for Transients in Flash-Photolysed Xe/Ar/F₂ Mixtures

Gas Mixture (a)	Time Range (b) (μsec)	XeF			XeF ₂	
		k' _{XeF} (c) (sec ⁻¹)	(XeF) _{tm} (d) (cm ⁻³)	k'' _{XeF} (e)	k' _{XeF₂} (f) (sec ⁻¹)	(XeF ₂ (∞)) (f) (cm ⁻³)
2	300-900	2.2(3)	1.9(13)	1.1(-10)	1.9(3)	5.2(15)
3	250-450	7.1(3)	5.4(13)	1.3(-10)	-	7.6(15)
4	100-200	2.5(4)	5.2(13)	4.8(-10)	-	1.0(16)
5	150-500	4.1(3)	2.9(13)	1.4(-10)	8.3(3)	8.9(15)
6	250-650	2.8(3)	1.9(13)	1.5(-10)	1.9(4)	7.4(15)
7	300-1000	3.2(3)	1.7(13)	1.9(-10)	1.2(4)	8.5(15)
8	400-1200	2.5(3)	9.1(12)	2.7(-10)	1.1(4)	8.6(15)

Footnotes:

(a) See Table II

(b) The range of delay times from flash initiation over which the pseudo-first-order fit was made

(c) See Eq. (4)

(d) xenon fluoride concentration at the midpoint of the time range

(e) See Eq. (15)

(f) See Eq. (5)

SPEC
FLASH

FLASH PHOTOLYSIS

KINETICS OF XeF

D-X ABSORPTION

DELAY TIME

2600

2500

2400

τ (μ SEC)

0

30

100

150

300

SPEC FLASH ONLY

Hg 2537

SCHEMATIC DIAGRAM ILLUSTRATING PRINCIPLES OF FLASH PHOTOLYSIS AND KINETIC SPECTROSCOPY

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Stochastic Simulation of Chemical and Photochemical
Kinetics on Minicomputers*

by

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E. Stochastic Simulation of Chemical and Photochemical Kinetics on Minicomputers

1. Introduction

The traditional procedure for formulating and solving kinetic problems in spatially homogeneous chemical systems in which a number of molecular species are reacting with each other involves the following steps:

- (a) Specify a reaction mechanism, which may contain both reversible and irreversible elementary chemical reactions.
- (b) Assign rate constants and/or equilibrium constants for all reactions in the mechanism.
- (c) Write down a set of ordinary differential equations, one per species, embodying the reaction mechanism.
- (d) Specify the initial concentrations of all species and any other boundary conditions or constraints [i.e., time - dependent source terms].
- (e) Solve the set of coupled differential equations for the time dependence of the concentration of all species.

The mathematical approach implied in steps (c) through (e) of this algorithm is often referred to as the deterministic approach to chemical kinetics. While numerical methods for integrating these deterministic equations are well known,¹ implementing these methods on small computer systems is not easy, particularly when both the number of elementary reaction steps and the number of molecular species are large. In addition, many problems in chemical kinetics exhibit "stiff" systems of equations,² in which both concentrations and their time derivatives vary over many orders of magnitude for the species of interest.

Over the past several years D. T. Gillespie, in a series of papers, has presented an alternate formulation of chemical kinetics from

the stochastic or probabilistic point of view.³⁻⁵ While others before him have developed theories of stochastic chemical kinetics, Gillespie's contribution has been to provide a sound statistical mechanical basis for stochastic kinetics and to present a very simple FORTRAN algorithm for the stochastic simulation of a homogeneous, multi-component reacting chemical system.

It is the purpose of this paper to point out that Gillespie's algorithm can easily be implemented on minicomputers in BASIC, FORTRAN, and PASCAL to solve non-trivial problems in chemical and photochemical kinetics.

2. The Stochastic Simulation Algorithm

While Gillespie's papers clearly present the algorithm for simulating the kinetic behavior of a multicomponent system using stochastic methods, a brief summary is in order here. Consider a system in which NS different chemical species i ($i=1, NS$) of number density n_i participate in a total NR different chemical reactions μ ($\mu=1, NR$). Choose a small volume V of this system such that $X_i \equiv n_i V$, the population numbers of reacting species i , is small (typically less than 10^8). Assign deterministic rate constants k_μ to each reaction, classifying each as unimolecular, bimolecular, or termolecular. Using these rate constants, the average probability that a given reaction μ will occur in volume V during time dt is for unimolecular reactions ($S_i \rightarrow \text{products}$),

$$a_\mu dt = X_i k_\mu; \quad (1)$$

for bimolecular reactions ($S_i + S_j \rightarrow \text{products}$),

$$a_\mu dt = V^{-1} X_i X_j k_\mu; \quad (2)$$

for termolecular reactions ($S_i + S_j + S_k \rightarrow \text{products}$),

$$a_\mu dt = V^{-2} X_i X_j X_k k_\mu, \quad (3)$$

where k_μ is the usual deterministic rate constant. At time t the probability that the next reaction in volume V will be of type μ and will occur in the time interval $(t + \tau, t + \tau + d\tau)$ is termed the reaction probability density function, and is given by

$$P(\tau, \mu) = a_\mu \exp\left[-\sum_{\mu=1}^{NR} a_\mu \tau\right] \quad (4)$$

The first step in the actual simulation algorithm is to specify the starting time, the initial population numbers $X_i(0)$, and the rate constants k_μ . The Monte Carlo method is then used to generate a random pair (τ, μ) according to the reaction probability density function. The time is then advanced by τ and the species numbers are changed to reflect the occurrence of one reaction of type μ . For example, if the reaction is

then the changes in species numbers are

$$S_1 := S_1 - 1$$

$$S_2 := S_2 - 1$$

$$S_3 := S_3 + 2$$

Here the PASCAL symbol $:=$ is used to mean "becomes", or "is replaced by".

The system evolves in time by successive generation of random pairs, enough iterations being taken in order to cover the time span of interest. Output can be provided at any stage of the simulation to follow the time-dependence of any species.

3. A PASCAL Implementation: Photochemical Kinetics of Xenon/Fluorine Mixtures

We first became interested in studying the kinetics of multi-component systems through some laboratory investigations we are presently

doing of the photochemistry of the xenon polyfluorides.⁶ Using kinetic spectroscopy, we have flash-photolyzed mixtures of xenon and fluorine and detected the free radical XeF as an intermediate in the photochemical formation of xenon difluoride. One of the first reaction mechanisms we postulated for the reactions occurring in our flash photolysis cell is the following:

We have coded the stochastic simulation for this mechanism in FORTRAN, BASIC, and PASCAL. To illustrate the Monte Carlo algorithm, as well as to give the reader an opportunity to judge if PASCAL programs really are self-documenting (as is claimed by PASCAL-ophiles), we present our PASCAL code for this problem in Appendix 1. This code was written by Davis.

The kinetics of this mechanism are slightly non-standard in that a time-dependent photodissociation rate constant is used for the first step, in order to simulate the flash-lamp intensity. In addition, we assume that the xenon is present in the mixture in such excess that its concentration is unchanged; thus, atomic xenon is not included as one

of the species followed in the simulation. The composite random-number generator used in the procedure GETRANDOMNUMBER was proposed by Marsaglia and Bray.⁷

This program was compiled and run on a PDP11/10 with 32k bytes of memory, using the OMSI PASCAL-I compiler. Because of the well-known transportability of PASCAL, we expect that this program will run on any micro-computer which supports PASCAL, and would be interested in communicating with others who may wish to try this approach on their PASCAL system.

To show the type of data obtained in such simulations, Fig. 1 presents the time dependence of the transient species of interest in the photolysis of xenon/fluorine mixtures. It can be seen that the concentration of fluorine atoms shows statistical fluctuations, as might be expected in a discrete simulation with a finite number of molecules.

From our experience in simulating photochemical kinetics in these mixtures, we can see several features of the stochastic approach which affect its suitability for implementing on micro- and minicomputers:

- 1) Memory requirements for array storage are minimal, since arrays are one-dimensional, with size equal either to NS or NR. There are no matrix operations, unlike numerical approaches for integrating systems of coupled equations.² Thus, simulations with large numbers of species and/or reactants are quite feasible.

- 2) Execution time is large, making overnight runs on a "captive", single-user system sometimes necessary. The simulation of Fig. 1 contained 15033 elementary reaction steps and ran in 24.5 minutes, for an average rate of 10.2 steps per second.

By comparison, a more elaborate version of the same photochemical simulation coded in BASIC by Gustin (see below) executed at a rate

of 7.75 steps/sec, about 3/4th as fast as the PASCAL version. A FORTRAN IV version of this problem, coded by Bew for the IBM 370/168, executed at a rate of 1564 steps/CPU sec, over a factor of 100 faster than the BASIC and PASCAL versions for the PDP 11/10. Since the PASCAL program in Appendix 1 is an almost literal translation of the original FORTRAN algorithm of Gillespie (except for I/O), it has not been optimized for speed or revised to utilize the flexibility of PASCAL's data structures. Most of the time is spent in I/O; only $\sim 2\%$ of the execution time per cycle is in the random number generator. The main point we wish to make is that the algorithm is simple, and the program can easily be changed to solve other kinetic problems, as the next section shows.

As an illustration of the size of kinetic problem easily handled by the stochastic simulation algorithm, we present in Table I an extended mechanism for the kinetics of flash-photolysed Xe/Ar/F₂ mixtures. The BASIC program implementing this reaction mechanism, called XEFSIM and coded by Gustin, has a number of useful features:

- 1) It is internally well documented and well structured. At the beginning is a description of the role of each variable, flag, array, and function used. At the end is a table of input data, consisting of the initial partial pressures of all species, the temperature, the scale of the simulation (vide infra), the order and the deterministic rate constant for each reaction. Structured programming methods are evident in the body of the program.

- 2) It is highly interactive. Parameters governing the execution of a given simulation (such as the number of elementary reaction steps between outputs and the format of the output) are set at execution time on a video display terminal with error checking at each step. The output of the simulation can be routed either to the terminal or to disk.

3) A form of signal-averaging is provided. Suppose that species population numbers are outputted after every NC reaction steps. Let the population number of species i after k reactions since the last print-out be X_{ik} and the corresponding time be t_k ($k = 1, NC$). A mean population number over the print-out interval is then

$$\bar{X}_i(\bar{t}) = (NC)^{-1} \sum_{k=1}^{NC} X_{ik}(t_k)$$

where $\bar{t} = (t_{NC} - t_1)/2$.

4) An estimate of the execution time of the simulation is given before starting. This estimate is calculated from a non-linear least-squares fit of data gathered for similar simulations of varying size and complexity.

5) At the end of the simulation the frequency of occurrence of each of the NR reactions is provided. We have found this occurrence frequency distribution to be very helpful in determining which reactions are dominant in the mechanism at any given time, and which pairs of forward and reverse reactions may be assumed to be in equilibrium.

4. Other Kinetic Problems

We have also treated the following kinetic problems using stochastic simulation:

a) Consecutive unimolecular reactions: $X \rightarrow A \rightarrow B$. Since this classical problem is exactly soluble in the deterministic formulation, its stochastic implementation provides a check on the validity of the stochastic method. Bew wrote the program. He found that the statistical fluctuations from the deterministic concentrations depend upon the initial "seeding" of the random number generator, and that thus fluctuations can be reduced by "ensemble averaging": doing a number of runs of identical simulations differing only in the seeding. The ensemble-averaged time-

dependence of the intermediate a) shows the expected form, and agrees with the exact result to within the expected statistical uncertainty.

b) Oscillating chemical reactions (the Lotka mechanism).⁵ This is a particularly interesting system to study because the chemistry has its own built-in "clock" - the period of oscillation in the concentration of the species X and Y. Studying this system helped to clarify considerably the concept of the scale of the simulation. In a deterministic formulation of this problem one deals entirely with intensive variables - concentrations and their time derivatives - and the units of the rate parameters reflect the choice of concentration units. On the other hand, stochastic simulation is finite in size, since one is modelling elementary reactions among a finite number of molecules. There is therefore one additional, extensive parameter which must be specified in a stochastic simulation: we call it the scale. For example, one could define the scale as the initial population number of the most abundant specie, and express all other populations as fractions of that extensive variable. Our stochastic results show that the chemical period of oscillation in X and Y concentrations is independent of the scale, as it should be, but that the execution time of the simulation per chemical period is proportional to scale. Since the percentage fluctuations of the concentrations about their deterministic value are inversely proportional to the square root of the scale, there is a trade-off in running stochastic simulations which is quite similar to that faced in signal averaging any experimental data. A simulation performed in a reasonable execution time may provide data that are too "noisy" to be useful, but to double the S/N ratio one must scale the simulation up by a factor of 4, thus increasing execution time by that

factor.

c) Carbon Transport in the Global Carbon Biogeochemical Cycle

An important area of geochemistry is the dynamics of transport of elements such as carbon, nitrogen, and sulfur between various parts of the atmosphere, the hydrosphere (primarily oceans), the lithosphere (rocks and soil), and the biosphere (both marine and land-born). It is common practice to treat this dynamical problem in terms of a box diffusion model,⁸ in which reservoirs containing known amounts of the element are connected by first-order transfer rates.

Our method of numerically treating box models is to apply the stochastic method used by Gillespie³⁻⁵ to simulate coupled chemical reactions. Our justification for using stochastic simulation arises from the use that geochemical box modellers have made of the principles of chemical kinetics in their explanations of first and second order exchanges between boxes. Although modellers use chemical and physical exchange concepts in their determination of the exchange rates between the boxes, the models themselves deal only with the contents of the boxes and the exchange rates between them. If exchange processes can be represented accurately with a statistically based description, then there should be no cause to deny the suitability of the stochastic approach.

We have applied Gillespie's techniques to the modelling of the global carbon geochemical cycle. To accomplish this, an independent model was fashioned after the example of Machta.⁹ The biospheric portion of Machta's model has been eliminated, as Machta had used a modification of first order transfer to describe the interchanges of the troposphere and mixed layer of the ocean with the biosphere.

Machta's model (see Fig. 2) consists of four well mixed boxes with six first order exchanges among them. A seventh process, an injection into the troposphere, is used to represent the anthropogenic insertion of CO_2 from the combustion of fossil fuels. In the standard approach to first order transfer, the rate of transfer (the flux between boxes) is equal to the product of the quantity of substance within a box (N) and the first order rate constant (λ). Thus, in Fig. 2 there are six transfer probabilities of the form " $N\lambda$." The chemical kinetic equivalent is the reaction probability $X_i K_{ij}$ of Eq. (1).

The model used in this paper was written in WATFIV and run first on an IBM 370/168 computer and later on the PDP 11/10E. Smoothing of the output of the model was performed on a Digital Equipment Corporation PDP-8 computer by a least squares fit program developed by Dr. A. L. Torres of Drexel University. The program, written in BASIC, fits the data to a polynomial of any order up to ten.

The results of the first run of the model are shown in Fig. 3. The points are fitted to a fourth order polynomial curve. It was noted that the carbon content of the atmosphere decreased noticeably over the fifty year interval of the computer run. Thus, the model is out of equilibrium: the rate of carbon transfer from the mixed layer of the ocean to the deep ocean was more than twice the return rate. These and other observations have led to the conclusion that Machta did not model the global carbon cycle as such, but only perturbations of the carbon cycle. The basic cycle is assumed to be in equilibrium, and was brought into equilibrium in our study by lowering the first order transfer coefficient for the flux from the mixed layer of the ocean to the deep ocean. The scale of the simulation was decreased by a factor of ten, thus decreasing

the execution time by the same factor. The resulting computer outputs are shown in Fig. 4. The data for the first run with a balanced system (Run 4) had scatter about the best curve fit that was over three times the scatter for the run in Fig. 3, consistent with the stochastic character of the calculations.

Ensemble averaging of several repeats of Run 4 (with different seeding of the random number generator) was adopted to reduce the data scatter. The average values of the five runs of the balanced model are also shown in Fig. 4. The averaged fifty-one data points were then fit to a series of polynomial curves. The best curve fit is drawn for these data in Fig. 4, and a comparison of the scatter of the data in the various sets of runs (determined numerically by computing the standard deviation of the data points from the curve fits) is shown in Table 2. The least scatter was evident in Run 1, with a three-fold increase for Run 4. The standard deviation for the five averaged computer runs was considerably less than for Run 4 alone, but noticeably greater than for Run 1.

The model was then run to examine its response to a short-term injection of carbon into the troposphere. Carbon was injected at a rate of $25 \times 10^{16} \text{ g yr}^{-1}$ for a period of two years, an amount of carbon expected to produce a significant perturbation in the atmospheric carbon level. Five computer runs were made and averaged according to the previously explained technique. These results are shown in Fig. 5. The data are fit to a fifth order curve, and the standard deviation of the data with respect to the curve is 3.39. In the model run the amount of carbon in the atmosphere declined from an initial value of $94 \times 10^{16} \text{ g}$ of carbon at $T = \text{two years}$.

Finally, the first five years of the pulse were examined in greater detail. The scale was increased by a factor of twenty, and five computer runs were made, each with a different random number. The average time per step for these runs was 5.50×10^{-4} , compared with a value of 1.74×10^{-3} for the best previous run (Run 1). The effects of the increase in scale and of the averaging process can be seen in Fig. 6. The standard deviation of the data from the curve is 1.03, and much of this difference is due to the inability of the curve to properly match the sharp peak at $T = \text{two years}$.

The FORTRAN IV version of this stochastic simulation runs on a PDP 11/10 at a rate of 40 steps per second, significantly faster than either the BASIC or PASCAL simulations mentioned above.

5. Conclusion

We see several interesting advantages to the stochastic formulation of chemical kinetics. First, the stress on reaction probabilities provides a useful alternate view of the kinetics of chemical reactions, one which may be taught along with the usual deterministic view. Second, carrying out a stochastic simulation of a complex reaction mechanism is a straightforward application of simple programming concepts, and involves no calculus whatsoever. The fact that Gillespie's algorithm is easily implemented in BASIC and PASCAL suggests that stochastic simulations can easily be run on personal computers, making a practical method of kinetic modelling available without the need to resort to sophisticated software packages only executable on large main frames.

On the other hand there are some limitations to the method, as Gillespie himself has pointed out.⁵ Because of the discrete nature of the simulation, problems involving species whose concentrations and re-

action rates vary over many orders of magnitude are not well handled. In order to develop enough statistical precision for minor components, one must employ large execution times. But running a stochastic simulation is much like doing an experiment in the laboratory, in that the S/N ratio of the observations may be varied by changing the measurement time. Often an exact (i.e., deterministic) answer is not required, particularly if trends and orders of magnitudes are the desired results. We feel that stochastic simulation of the kinetics of complex reaction mechanisms should become a technique in the repertoire of the experimental chemist.

Table 1.

The Initial Output of a BASIC Program for the Stochastic Simulation of
the Photochemical Kinetics of Xenon/Fluorine/Argon Mixtures

OLD"XEFSIM.BAS"

READY

RUN

XEFSIM 18-DEC-79 BASIC V01B-02

STOCHASTIC SIMULATION FOR THE PHOTOLYSIS OF XE-AR-F2

AUTHOR	:KENNETH M. GUSTIN	LA SALLE COLLEGE	PHILA., PA
REF.	:DR. ALLAN L. SMITH	DREXEL UNIV.	PHILA., PA

REACTION PATHWAY

DETERMINISTIC RATE CONSTANT

1)	F2 + LIGHT	----> F + F	
	190 (EXP(- 19804 *T)-EXP(-2* 19804 *T))		
2)	F + XE + AR	----> XEF + AR	2.20000E-33
3)	XEF + AR	----> F + XE + AR	9.10000E-13
4)	F + F + AR	----> F2 + AR	8.00000E-35
5)	F + XEF	----> XE + F2	2.00000E-11
6)	F + XEF + AR	----> XEF2 + AR	1.00000E-32
7)	XEF + XEF	----> XEF2 + XE	1.00000E-10
8)	XEF + XEF	----> F2 + XE + XE	1.00000E-10
9)	XEF + XEF2	----> XEF3 + XE	1.00000E-12
10)	F + XEF2	----> XEF + F2	1.00000E-12
11)	XEF3 + XEF	----> XEF2 + XEF2	1.00000E-12
12)	F + F + XE	----> F + XEF	8.00000E-35
13)	F + XE + XE	----> XE + XEF	2.20000E-33
14)	F + F2 + XE	----> XEF + F2	2.20000E-33
15)	XEF + F2	----> XE + F + F2	9.10000E-13
5)	XEF + XE	----> XE + XE + F	9.10000E-13
17)	F2 + LIGHT + XE + XE	----> XEF + XEF	
	4.59341E-12 (EXP(- 19804 *T)-EXP(-2* 19804 *T))		

AN EQUILIBRIUM CONSTRAINT HAS BEEN PLACED ON REACTIONS 13,14,15, AND 16.

Model Run	Total Steps	Total Time (years)	Average Time Per Step (years)	Standard Deviation of Model Output from Best Curve Fit
1	28,724	50	1.74×10^{-3}	1.93 (4th order curve)
4	6,563	100	1.52×10^{-2}	6.57 (4th order curve)
4	6,563	100	1.52×10^{-2}	
7	6,801	100	1.52×10^{-2}	
8	6,879	100	1.45×10^{-2}	
9	6,978	100	1.43×10^{-2}	2.67 for the average of the five runs fit to a 4th order curve
10	6,598	100	1.52×10^{-2}	

Table 2. The effect of variation in scale on the relative "smoothness" of the output from the model. The scale for runs 4, 7, 8, 9, and 10 is approximately one-tenth of the scale of Run 1. Run 1 has the model parameters set according to Machta, and the other runs have the mixed layer and the deep ocean transfer rates balanced.

Stochastic Simulation of Photolysis of Xe-F₂ Mixture

Figure 2. Atmospheric carbon content from the first run of the model. Parameters for the run were obtained from Machta (1972), p. 125.

Figure 2. Machta's (1972) model of the global carbon cycle (without the biosphere). The quantity, λ , denotes the fraction of the CO_2 in one reservoir being transferred to an adjacent reservoir according to the sense of the arrow.

Atmospheric Carbon
($\times 10^{-16} \text{ g}$)

Figure 5. A detailed look at the first 5 years of the perturbation shown in Figure 4. The reaction times for this run are approximately 1/20 of those in Figure 4. This best fit curve (5th order) is unable to properly document the sharp change in slope at the end of the 2 year injection period.

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Appendix I
Stochastic Simulation of Photochemical Kinetics of
Xenon-Fluorine Mixtures; a PASCAL Version

For those unaccustomed to reading PASCAL programs: this program consists of a variable declaration part, a procedure and function declaration part, and a statement part. The overall structure of the program is best seen from the end of the program.

```
PROGRAM SIMULATION(KINETC,OUTPUT);
```

```
VAR    C,A:ARRAY[1..6] OF REAL;  
        S:ARRAY[1..5] OF REAL;  
        SA:ARRAY[1..128] OF CHAR;  
        R:ARRAY[1..2] OF REAL;  
        NR:ARRAY[1..128] OF REAL;
```

```
    TIME,F,F2,XEF,XEF2,TPRINT,TPRINTX:REAL;  
    SUM,TX,TI,T,T2,TINT,P,Q,A0,R2A0:REAL;  
    MK,ML,MM:REAL;  
    L,M,K:REAL;
```

```
    N,NS,I,J:INTEGER;  
    MAXCYC,KOUNT,MU:INTEGER;  
    LEN:INTEGER;  
    RANDOMSEED:INTEGER;  
    KINETC:TEXT;
```

```
PROCEDURE GETINITIALDATA;  
BEGIN
```

```
    READLN(KINETC,T,T2,TINT,N,NS,P,Q);
```

```
    FOR I:=1 TO NS DO  
        READ(KINETC,SA[I]);  
    READLN(KINETC);
```

```
    FOR MU:=1 TO N DO  
        READ(KINETC,C[MU]);  
    READLN(KINETC);
```

```
    FOR I:=1 TO NS DO  
        READ(KINETC,SC[I]);  
    READLN(KINETC);
```

```
    READLN(KINETC,MK,ML,MM,K,L,M);
```

```
(* PUT ODD INTEGERS INTO NR VEXTOR *)
```

```
    J:=-1;
```

```
    FOR I:=1 TO 128 DO
```



```
      BEGIN
        J:=J+2;
        NREIJ:=J
      END (* NEXT I *);

    (* ASSIGN NUMBER OF MOLECULES *)
    F:=S[1];
    F2:=S[2];
    XEF:=S[3];
    XEF2:=S[4];

    TPRINT:=T;
    MAXCYC:=0;
    KOUNT:=0
  END (* GET INITIAL DATA *);
```

```
PROCEDURE PRINTINPUTDATA;  
BEGIN
```

```
  WRITELN('T= ',T:7);  
  WRITELN('T2= ',T2:7);  
  WRITELN('TINT=',TINT:7);  
  WRITELN('N= ',N:7);  
  WRITELN('P= ',P:7:4);  
  WRITELN('Q= ',Q:7:4);  
  WRITELN;
```

```
  FOR I:=1 TO 6 DO
```

```
    WRITELN('C(',I:1,')=',C[I]:7:4);
```

```
  WRITELN('F= ',F:7);  
  WRITELN('F2= ',F2:7);  
  WRITELN('XEF= ',XEF:7);  
  WRITELN('XEF2=',XEF2:7);  
  WRITELN('K= ',K:7);  
  WRITELN('L= ',L:7);  
  WRITELN('M= ',M:7);  
  WRITELN('MK= ',MK:7);  
  WRITELN('ML= ',ML:7);  
  WRITELN('MM= ',MM:7);  
  WRITELN;WRITELN;WRITELN
```

```
END (* PRINT INPUT DATA *);
```

```
FUNCTION RANDOM(VAR SEED:INTEGER):REAL;  
BEGIN
```

```
  RANDOM:=SEED/32500;
```

```
  SEED:=(13500*SEED+6800) MOD 32500
```

```
END (* RANDOM FUNCTION *);
```

```
PROCEDURE RANDOMNUMBER;  
BEGIN
```

```
  R[1]:=ABS(RANDOM(RANDOMSEED));
```

```
  R[2]:=ABS(RANDOM(RANDOMSEED));
```

```
END (* RANDOM NUMBER *);
```



```
PROCEDURE FINDLIGHTINTENSITY;  
BEGIN  
  TI:=P*(EXP(-Q*T)-EXP(-2*Q*T));  
  CC1]:=TI  
END (* FIND LIGHT INTENSITY *);
```

```
PROCEDURE SUMREACTIONTYPES;  
BEGIN  
  AC1]:=CC1]*F2;  
  AC2]:=CC2]*F;  
  AC3]:=CC3]*F*(F-1)/2.0;  
  AC4]:=CC4]*XEF*(XEF-1)/2.0;  
  AC5]:=CC5]*XEF*F;  
  AC6]:=CC6]*XEF*F;  
  
  A0:=0;  
  FOR I:=1 TO N DO  
    A0:=A0+ACI]  
  END (* SUM REACTION TYPES *);
```

```
PROCEDURE PRINTPOPULATIONS;  
BEGIN  
  IF RC1] < 0.001 THEN RC1]:=0.5;  
  T:=T+LN(1.0/RC1])/A0;  
  
  IF T > TPRINT THEN  
    BEGIN  
      TPRINTX:=TPRINT*1.E6;  
      TX:=T*1.E6;  
  
      WRITELN(TPRINTX:7,TX:7,KOUNT:8,F:10,F2:10,XEF:10,XEF2:10);  
      MAXCYC:=MAXCYC+KOUNT;  
      KOUNT:=0;  
      TPRINT:=TPRINT+TINT  
    END (* WHILE T<TPRINT *)  
  END (* PRINT POPULATIONS *);
```

```
PROCEDURE USERANDOMNUMBER;  
BEGIN
```

```
  R2A0:=R[2]*A0;  
  KOUNT:=KOUNT+1;  
  SUM:=0;
```

```
  WHILE SUM < R2A0 DO  
  BEGIN
```

```
    FOR MU:=1 TO N DO  
      SUM:=SUM+ACMU;
```

```
    END (* WHILE SUM<R2A0 *)  
  END (* USE RANDOM NUMBERS *);
```

```
PROCEDURE CHOOSEREACTIONTYPE;  
BEGIN
```

```
  CASE MU OF
```

```
    1:BEGIN
```

```
      F2:=F2-1;  
      F:=F+2
```

```
    END;
```

```
    2:BEGIN
```

```
      F:=F-1;  
      XEF:=XEF+1
```

```
    END;
```

```
    3:BEGIN
```

```
      F:=F-2;  
      F2:=F2+1
```

```
    END;
```

```
    4:BEGIN
```

```
      XEF:=XEF-2;  
      XEF2:=XEF2+1
```

```
    END;
```

```
    5:BEGIN
```

```
      XEF:=XEF-1;  
      F:=F-1;  
      XEF2:=XEF2+1
```

```
    END;
```

```
    6:BEGIN
```

```
      XEF:=XEF-1;  
      F:=F-1;  
      F2:=F2+1
```

```
    END;
```

```
  END (* CASE *)
```

```
END (* CHOOSE REACTION TYPES *);
```

```
BEGIN (* SIMULATION *)
  RESET(KINETC,'DX1:KINETC','DAT',LEN);
  GETINITIALDATA;
  PRINTINPUTDATA;
  REPEAT
    RANDOMNUMBER;
    FINDLIGHTINTENSITY;
    SUMREACTIONTYPES;
    PRINTPOPULATIONS;
    USERANDOMNUMBER;
    CHOOSEREACTIONTYPE;
    TIME:=T
  UNTIL TIME > T2;

  WRITELN;WRITELN;WRITELN;
  WRITELN('TOTAL CYCLES=',MAXCYC:6)
END (* SIMULATION *).
```

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