

Photochemical studies of atomic species (F, Br, O) in solution¹

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Abstract

The reactions of fluorine, bromine and oxygen atoms in solution have been examined using nanosecond laser flash photolysis techniques. In each system it was necessary to identify a suitable precursor (XeF₂ for fluorine, vicinal dibromides for bromine, and pyridine-*N*-oxide for oxygen) and a convenient probe species having a readily observable absorption band in the UV–vis region. The kinetics of the debromination of β-bromoalkyl radicals have been examined for silicon-substituted radicals.

Keywords: Laser flash photolysis; Fluorine; Bromine; Oxygen

1. Introduction

Few absolute rate constants are available for atomic species in solution. The exceptions are hydrogen and chlorine atoms; for the latter several absolute rate constants have been reported [1–3], while for hydrogen many values are available from studies involving the radiolysis of water [4]. For the subject elements of this article, little was known about oxygen [5] and bromine [6,7] and no values were available for fluorine atoms.

In this account we summarize our studies on the dynamics of selected reactions of atoms in solution. Laser flash photolysis techniques have proven extremely useful in the study of these reaction intermediates. We emphasize the importance of characterizing suitable precursors and probes that greatly facilitate the study of atomic species in solution. Our research on this field has been the subject of several recent publications [8–13].

2. Finding an appropriate precursor and probe species

The atomic species which are the subject of this report are “invisible” in the spectral region (near UV and visible)

normally available in laser flash photolysis experiments. In this context, we note that the precursors normally available frequently have strong absorptions in the UV region, which tends to mask some spectral regions, which as a result are not available for monitoring the time evolution of transient absorption changes. Further, the selection of a precursor must give proper consideration to the availability of a laser pulse in the wavelength region where the precursor photodecomposes efficiently. The following sections discuss our selections of precursors and probes for each atomic species.

2.1. Atomic fluorine

We had anticipated that fluorine atoms would present a very challenging problem. We were pleasantly surprised by the discovery that xenon difluoride, a commercially available product, readily decomposed at 248 or 266 nm to yield fluorine atoms and XeF, according to reaction (1) [10]. Xenon difluoride requires some protection from humidity, but other than that, its handling is straightforward under normal laboratory conditions.



The solvent of choice in this system is Freon-113 (CF₂Cl–CFCl₂) which is sufficiently inert to allow fluorine atom studies. Fluorine atoms form a complex with many chlorine-containing halocarbons. In the case of Freon-113 fluorine forms a loose complex with a strong absorption band at 320 nm. The spectrum of this intermediate is shown in Fig. 1.

¹ This article is based on the Porter Medal Lecture presented by JCS at the 1995 International Conference of Photochemistry, at Imperial College, London, UK. Closely related reports have been submitted and will appear in the conference proceedings of the 9th Latin American Physical Organic Chemistry Conference, held in Florianopolis, Brazil, April 1995, and the 3rd Conference on Organic Photochemistry held at El Escorial, Spain, September 1995.

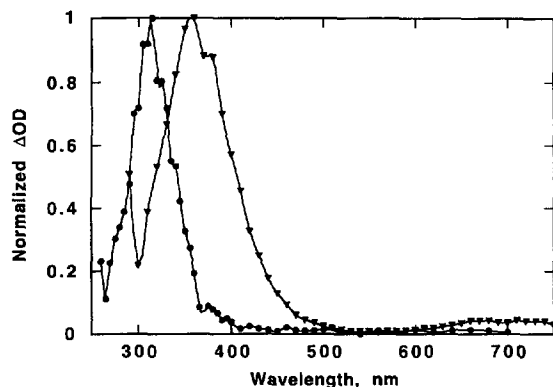


Fig. 1. Transient spectra of the complex between fluorine atoms and Freon-113 (●), and of Br_2^- (▼).

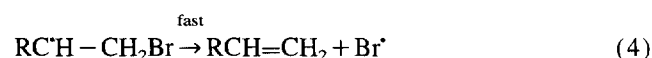
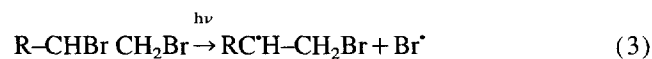
The strong transient absorption from the fluorine complex of Fig. 1 provides an adequate probe allowing the study of the dynamics of fluorine atom reaction [10]. At the same time, the fact that this complex is quite loose, means that the rate constants obtained (vide infra) reflect predominantly the reactivity of atomic fluorine, rather than that of the complex of reaction (2).

The other product of reaction (1), XeF , is relatively long-lived and weakly absorbing and does not interfere in the time scale of these experiments. XeF can be readily detected in solvents where the fluorine atom is removed rapidly by chemical reaction. Interestingly, XeF may be a more selective fluorinating agent than fluorine itself.

Interestingly, XeF_4 , a frequent impurity in XeF_2 , is photosensitive at 308 nm, leading also to fluorine atoms. Thus, the commercial samples can also be used to produce F^* at this laser wavelength.

2.2. Bromine atoms

Our work on bromine atoms was triggered by our interest in the development of efficient photoacid generators for photoresist applications [13–16], particularly in connection with applications in amplified negative resists (ANR). Vicinal dibromides which undergo photoinduced decomposition according to reactions (3) and (4) proved to be excellent precursors for bromine atoms [8,9].



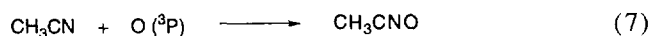
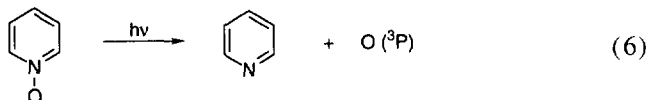
Reaction (4) is generally sufficiently fast ($> 5 \times 10^7 \text{ s}^{-1}$), that in the time scale of our experiments, vicinal dibromides behave as an “instantaneous” source of two bromine atoms. While bromine atoms are not readily detectable under our conditions, they react rapidly ($k_5 = 1.6 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) [8,9] with bromide ions to yield Br_2^- which has a strong absorption band at 370 nm. Thus, reaction (5) can be used as a “probe” in order to visualize bromine atoms. The spec-

trum of Br_2^- has been included in Fig. 1. In a later section we discuss one example where we have been able to study the kinetics of a debromination reaction similar to that of reaction (4) (vide infra).

2.3. Atomic oxygen, $\text{O}(^3\text{P})$

Finding an adequate source of oxygen atoms for solution studies proved difficult. Pyridine-oxides are known to be photolabile [17]; the precursor selected, pyridine-*N*-oxide, produces oxygen atoms by 308 nm photolysis with only modest ($\sim 5\%$) quantum yield. In addition, radiationless deactivation and intramolecular rearrangements also take place. While these rearrangements have not been characterized in detail, they occur essentially instantaneously in the nanosecond time scale and do not interfere in the study of $\text{O}(^3\text{P})$ reactions.

Interestingly, $\text{O}(^3\text{P})$ reacts with acetonitrile at a convenient (vide infra) rate to yield acetonitrile-*N*-oxide, CH_3CNO , which has a weak absorption at $\sim 330 \text{ nm}$. In acetonitrile as solvent this absorption grows-in with a lifetime of 530 ns which we attribute to reaction (7). CH_3CNO has a lifetime of $\sim 60 \mu\text{s}$ under our experimental conditions.



3. Determination of rate constants for atomic reactions in solution

The approach employed was slightly different for each of the three species under study. In the case of fluorine atoms, the signal from the complex $\text{F} \leftarrow (\text{CCl}_2\text{F}-\text{CClF}_2)$ was treated as a direct measure of the fluorine atom concentration. Under these conditions a plot of the pseudo-first order rate constant for the decay (k_{obs}) as a function of quencher concentration yields the rate constant for reaction, k_q , from the slope, i.e.

$$k_{\text{obs}} = k_o + k_q[Q] \quad (8)$$

where k_o is the rate constant for decay in the absence of quencher. Table 1 gives rate constants for fluorine atom reactions.

Fluorine atoms are highly reactive intermediates, showing very low selectivity. The strong H-F bond ($136.4 \text{ kcal mol}^{-1}$) is largely responsible for this behavior. Some of the rate constants in Table 1 are well above the rates for diffusional processes ($1-2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) that can be calculated using Debye's approximation [18]. This approximation assumes reactants of comparable size, as well as large reactants in a solvent consisting of small molecules, all conditions that do not apply to small atoms in solution. While diffusional coefficients for fluorine atoms in solution are not available in

Table 1
Absolute rate constants for some reactions of fluorine atoms in Freon-113 at room temperature [10]

Substrate	k ($10^9 \text{ M}^{-1} \text{ s}^{-1}$)
Acetonitrile	27
Acetonitrile- d_3	16
Chloroform	1.8
Chloroform- d	0.96
Oxygen	5.6
Hydrogen	5.8
Water	40
Water- d_2	40
Methane	7.0
n-Pentane	57
Cyclohexane	73
Tetrachloroethylene	100
Hexafluorobenzene	71

Errors in the rate constants estimated as 10–15%.

the literature, diffusional data are available for neon, a good model for fluorine (and oxygen, see below). Analysis of these data [19,20] indicates that the rate constants obtained are within the diffusional limits expected for small atomic species in solution.

The modest isotope effects observed (see entries for chloroform and acetonitrile in Table 1) are in line with the high reactivity of fluorine atoms.

In the case of atomic oxygen, quenching rate constants can be derived from an analysis of the influence of quenchers on the pseudo-first order rate constants (k_{obs}) for the growth of the CH_3CNO signal. Eq. (8) also applies in this case. The rate constant for reaction with $(\text{EtO})_3\text{P}$ was measured as $3.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ employing this technique. In spite of its simplicity, the method is far from ideal in the case of oxygen atoms, since the signals involved are very weak (usually $\Delta\text{OD} < 0.01$) and the rates quite fast. For most systems, a Stern–Volmer type of approach proved most convenient. In this method the yield of CH_3CNO (based on its transient absorption) is determined as a function of quencher concentration. The relevant kinetic parameters are related according to

$$\frac{\phi_o}{\phi} = 1 + k_q \tau [Q] \quad (9)$$

where ϕ and ϕ_o are the yields in the presence and absence of quencher, and t the (growth) lifetime in the absence of quencher ($\tau = k_o^{-1}$). For $(\text{EtO})_3\text{P}$ the value obtained was $3.8 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, in good agreement with that measured employing Eq. (8) (vide supra). Table 2 shows the rate constants obtained for $\text{O}(^3\text{P})$ in solution [11].

While highly reactive, $\text{O}(^3\text{P})$ is considerably less reactive than fluorine atoms or $\text{HO}\cdot$ [4], and substantially more selective than these intermediates. Just as in the case of fluorine, some rate constants (e.g. see Cl^- and Br^-) are remarkably fast. The same explanation also applies; i.e. Debye's approximation is not adequate for small atomic species in solution,

for which substantially higher diffusional limits should be anticipated.

Isotope effects for oxygen atom reactions are significant for those processes expected to involve hydrogen transfer (e.g. see cyclohexane in Table 2), but not in systems involving addition reactions, such as acetonitrile and benzene.

In the case of bromine atoms the method of reactions (3)–(4) is a convenient source, but is limited to reactants that are reasonably transparent in the UV region, since vicinal dibromides require photolysis in the 250 nm region. Convenient laser wavelengths are available at 248 and 266 nm. When these wavelengths are not suitable, α -bromoacetophenone can be used as a convenient atom precursor at 308 nm [21]. The pseudo-first order rate constant for the formation of $\text{Br}_2^{\text{Y}\cdot-}$ in the presence of variable bromide concentrations is given by Eq. (10).

$$k_{\text{obs}} = k_o + k_{\text{bromide}}[\text{Br}^-] \quad (10)$$

Analysis of the experimental data in acetonitrile according to Eq. (10) leads to $k_{\text{bromide}} = 1.6 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. The rate constants for reactants that do not yield a readily detectable signal can be readily obtained using the probe technique by studying the influence of the substrate on the growth kinetics for the probe signal, in this case the complex $\text{Br}_2^{\text{Y}\cdot-}$. The growth kinetics for $\text{Br}_2^{\text{Y}\cdot-}$ are given by

$$k_{\text{obs}} = k_o + k_{\text{bromide}}[\text{Br}^-] + k_x[\text{X}] \quad (11)$$

or, at fixed bromide concentration, where the term $\{k_o + k_{\text{bromide}}[\text{Br}^-]\}$ can be taken as a constant, k'_o :

$$k_{\text{obs}} = k'_o + k_x[\text{X}] \quad (12)$$

Table 3 shows rate constants for bromine atoms in acetonitrile obtained employing these techniques.

Clearly bromine atoms are very selective intermediates in comparison with other atomic species such as the highly reactive F, O or Cl. There appears to be a clear preference for substrates where polar interactions are possible; for example, rate constants for alcohols are considerably higher than for cyclohexane, although bond energies are comparable.

Table 2
Rate constants for some reactions of oxygen atoms [$\text{O}(^3\text{P})$] in acetonitrile at room temperature [11]

Substrate	k ($10^9 \text{ M}^{-1} \text{ s}^{-1}$)	Substrate	k ($10^9 \text{ M}^{-1} \text{ s}^{-1}$)
Br^- (as Bu_4N^+)	200	Benzene	0.30
Cl^- (as Bu_4N^+)	58	Benzene- d_6	0.38
Oxygen	4.1	Pyridine	0.11
Triethylphosphite	38	Pyridine- d_5	0.10
Tetrachloroethylene	0.093	Cyclohexane	0.34
Cyclopentene	16	Cyclohexane- d_{12}	0.057
1-Octene	8.7	Cyclopentane	0.38
1-Octyne	7.9	n-Pentane	0.25
Chloroform	0.0019	Methane	~0.016
Chloroform- d	0.00035	Vitamin C	14
Dichloromethane	0.0020	Acetonitrile	~0.0001

All values ± 15 –20%.

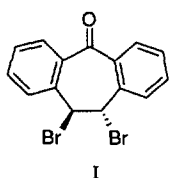
Table 3

Rate constants for reactions of photogenerated bromine atoms in acetonitrile at room temperature

Substrate	k_r ($M^{-1} s^{-1}$)	Reference
Bromide (Br^-)	1.6×10^{10}	[8,9]
Methanol	9.3×10^5	[9]
Ethanol	1.6×10^7	[9]
2-Propanol	4.2×10^7	[9]
Benzhydrol	4.1×10^9	[24]
p-Cresol	3.0×10^{10}	[9]
Dioxane	1.2×10^6	[9]
Diethyl ether	1.7×10^7	[9]
Triethylamine	2.9×10^{10}	[9]
Piperidine	2.2×10^{10}	[13]
Morpholine	2.7×10^{10}	[13]
Ethylmorpholine	4.2×10^{10}	[13]
Ethylpiperidine	3.2×10^{10}	[13]
N,N-diethylaniline	4.5×10^{10}	[13]
Methylimidazol	3.7×10^{10}	[13]
Quinuclidine	3.0×10^{10}	[13]
Di-n-propyl sulfide	2.2×10^{10}	[13]
Cyclohexane	$< 1.0 \times 10^5$	[9]

4. Fragmentation of β -bromoalkyl radicals

As indicated earlier, simple vicinal dibromoalkenes, such as those derived from 1,2-dibromoethane or 1,2-dibromodecane undergo rapid photoinduced loss of two bromine atoms, usually with a quantum yield (for bromine atom formation) of ~ 2.0 and in time scales of the order of 10^{-7} s [8,9]. Similarly, 10,11-dibromodibenzosuberone (**I**) also loses two bromine atoms efficiently [22]. In contrast, 1,2-dibromoethyl arenes frequently lose only one bromine atom to yield a resonance stabilized radical that has no tendency to cleave in the short time scales usually studied with laser techniques [23].



While the β -cleavage leading to loss of bromine in reaction (4) and related systems proved too fast for nanosecond techniques, we reasoned that the reaction could be slowed down if β -cleavage involved a "somewhat" stabilized radical. Such stabilization would have to be "modest" enough, not to totally prevent radical fragmentation as in the case of 1,2-dibromoethyl arenes [23]. Laser flash photolysis of tetra(1,2-dibromoethyl) silane in the presence of 6 mM tetrabutylammonium bromide in acetonitrile at 23 °C led to a laser photolysis trace consisting of a rapid "jump", followed by a resolved growth with a lifetime of ~ 43 ns [12]. This contrasts with the case of CH_2BrCH_2Br , where the "growth" observed in the presence of comparable bromide concentrations is essentially instantaneous, or rather, controlled by the

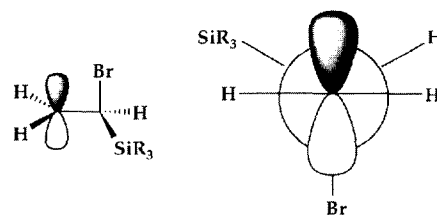
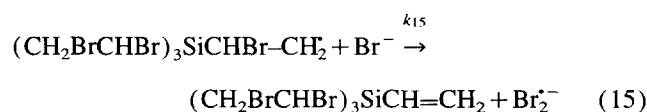
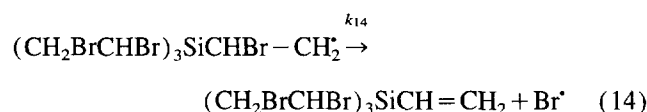
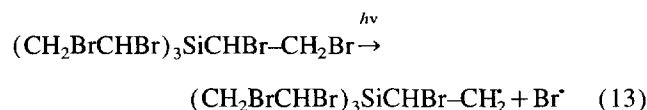


Fig. 2. Structure and Newman diagram for silicon-substituted β -bromoalkyl radicals. Only one of the heavy groups (Br or SiR_3) can eclipse the radical center at any given time.

laser pulse duration. We believe that in this system the radical can gain some degree of β -stabilization from both the second bromine atom and the silicon substituent, although, as shown in Fig. 2 both substituents cannot fully eclipse the radical center at the same time.

Our studies in the case of tetra(1,2-dibromoethyl)silane lead to the $(CH_2BrCHBr)_3SiCHBrCH_2\cdot$ radical that undergoes rapid debromination ($t \sim 58$ ns in acetonitrile at 23 °C) to yield vinyl-tri(1,2-dibromoethyl)silane (see reactions (13)–(15)) [12]. This radical also appears to be insensitive to the presence of oxygen suggesting that bromine, or conceivably silicon, bridging plays an important role. Debromination of this radical (presumed to have the radical site at the β -position) also occurs in an unprecedented assisted mode via its reaction with bromide ion (see reaction (15)). This new reaction occurs with a rate constant of $9.0 \times 10^8 M^{-1} s^{-1}$.



In summary, this account provides an overview of recent work in our laboratory aimed at understanding the reactivity of atoms, some of the structurally simplest reaction intermediates. Laser flash photolysis techniques are a valuable tool in the study of atomic species; the fact that these tend to show no useful absorptions for monitoring purposes can be overcome by characterization of suitable precursors and probe reactions for each system.

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