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EFFECT OF O_2 ON MOLECULAR IODINE PRODUCTION FOLLOWING FLASH PHOTODISSOCIATION OF CF_3I

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Summary

The temporal production of molecular iodine following the gas phase flash photodissociation of CF_3I (CO_2 inert diluent gas) has been studied. In the absence of O_2 there is an induction period of about 200 μs determined by quenching of $I(^2P_{1/2})$ atoms, followed by three-body recombination of ground state $I(^2P_{3/2})$ atoms. Addition of small amounts of O_2 greatly enhances the rate of I_2 production, such that at $P(O_2) \geqslant 0.2$ Torr I_2 formation occurs during the photolyzing flash. These results are discussed in terms of formation of a strong intermediate exciplex ($K \geqslant 10^4$ dm^3 mol^{-1}) between $I(^2P_{1/2})$ and O_2 as precursor to I_2 formation.

1. Introduction

The optically pumped atomic iodine laser, operating on the magnetic dipole allowed transition $^2P_{1/2} \rightarrow {}^2P_{3/2}$ and oscillating at 1315 nm, was the first laser to utilize photodissociation as a mode of excitation [1]. The long natural lifetime of $I(^2P_{1/2})$ resulting from the electric dipole forbidden character of the radiative decay, the superior beam distortion and power-dissipating characteristics of gas relative to solid state lasers, the potential for nearly full extraction of the stored energy and the exceedingly high gain and potential for high power density operation make this laser a good prospect for repetitively pulsed laser plasma and fusion research. Pulse powers of 1 TW have recently been reported [2].

The photodissociation and stimulated emission steps

$$RI \xrightarrow[(220 - 330 \text{ nm})]{h\nu} R + xI^* + (1-x)I \qquad (1)$$

$$I^* \xrightarrow{h\nu} I + h\nu_{1315\,\text{nm}} \qquad (2)$$

where RI is an alkyl or perfluoroalkyl iodide molecule, $I^* = I(^2P_{1/2})$ and $I = I(^2P_{3/2})$, are well established in the literature [1]. In many cases the fraction

x of excited atoms produced in reaction (1) is very high, *e.g.* 0.92 for CH_3I, 0.91 for CF_3I and greater than 0.99 for n-C_3F_7I [3], leading to a very high degree of population inversion and high gain stimulated emission. Premature termination of laser oscillation is now generally accepted [4] to occur from a high temperature rise and pyrolytic build-up of I_2 which is an extremely efficient quencher of I^* atoms.

It has also been suggested [5] that population inversion and hence potential stimulated emission in the iodine atom system may be possible through energy transfer from $O_2(^1\Delta_g)$:

$$I + O_2(^1\Delta_g) \rightarrow I^* + O_2(^3\Sigma_g^-) \qquad (3)$$

Continuous (c.w.) laser action has now been accomplished by generating $O_2(^1\Delta_g)$ chemically from the reaction of chlorine with H_2O_2 [6], and population inversion has been observed when $O_2(^1\Delta_g)$ is produced by reaction between chlorine fluorosulfate and H_2O_2 [7]; ground state iodine atoms are produced by the "energy-pooling" process [8]

$$2O_2(^1\Delta_g) \rightarrow O_2(^3\Sigma_g) + O_2(^1\Sigma_g^+) \qquad (4)$$

$$O_2(^1\Sigma_g^+) + I_2 \rightarrow 2I + O_2(^2\Sigma_g^-) \qquad (5)$$

Energy transfer between $O_2(^1\Sigma_g^+)$ and I_2 leading to excited I_2 (but not necessarily dissociation) is extremely efficient, occurring at every collision [9].

Reaction (3) is exothermic by only 3.3 kJ, and therefore nearly resonant with the reverse I^* quenching reaction. Possibly because of this molecular oxygen is also a very efficient quencher of $I(^2P_{1/2})$ atoms, although the O_2 quenching mechanism is not clear [10]. At sufficiently high concentrations of $O_2(^1\Delta_g)$, and hence $O_2(^1\Sigma_g^+)$ by energy pooling, I_2 is kept almost completely dissociated by reaction (5). We report here temporal studies on the formation of I_2 following production of I^* by the flash photolysis of CF_3I in the presence of O_2 with no (initially) $O_2(^1\Delta_g)$ or $O_2(^1\Sigma_g^+)$, but under conditions of flash energy and "inert" third-body pressures such that pyrolytic production of I_2 was insignificant.

The reaction of CF_3 radicals with O_2 in low intensity (continuous) photolyses has been studied in several laboratories. Francis and Hazeldine [11] obtained CF_2O, CO_2 and SiF_4 as the only detected products in the photolysis of CF_3I–O_2 mixtures. They proposed a reaction scheme involving CF_3 + O_2 additives:

$$CF_3 + O_2 \rightarrow CF_3O_2 \qquad (6)$$

$$2CF_3O_2 \rightarrow 2CF_3O + O_2 \qquad (7)$$

$$CF_3O \xrightarrow[\text{wall}]{SiO_2} CF_2O + SiF_4 + CO_2 \qquad (8)$$

Similarly, CF_3O_2 formation by the addition reaction (6) has been suggested in the photochemical fluorination of fluoroform in the presence of O_2 [12]. Other products identified were $CF_3O_2CF_3$ and $CF_3O_3CF_3$, with the latter undergoing partial conversion to CF_2O in the IR spectrophotometer detection cell. However, Heicklen [13] proposed direct formation of CF_2O by an exchange reaction

$$CF_3 + O_2 \rightarrow CF_2O + FO \qquad (9)$$

Presumably F_2 and O_2 are then formed by

$$2FO \rightarrow F_2 + O_2 \qquad (10)$$

although F_2 was not found as a reaction product.

2. Experimental

The flash spectrophotometric apparatus has been described elsewhere [14]. A xenon–oxygen (approximately 80:1 mixture) flash lamp was discharged at 900 J (12.5 μF, 12 kV) and its light filtered through 10 mm of a UV filter solution (200 g dm^{-3} $CoCl_2 \cdot 6H_2O$ and 100 g dm^{-3} $NiCl_2 \cdot 6H_2O$ in 1 M HCl, upper wavelength cut-off approximately 380 nm). The continuous analyzing beam from a 450 W Osram xenon arc was split after passing through the cell: time-resolved generation of I_2 following flash photodissociation of CF_3I was monitored at 498 nm ($\epsilon(I_2, 498) = 585$ dm^3 mol^{-1} cm^{-1}) with the Zeiss MM12 monochromator bandwidth maintained at about 1 nm; simultaneously, the flash profile was monitored at 360 nm with a Bausch and Lomb grating monoghromator.

All gases were introduced into a vacuum transfer system through a phosphorous pentoxide drying column. Oxygen (Matheson Research Grade minimum purity 99.99%) was used without further purification. CO_2 (from dry ice), CF_3I (PCR Incorporated), SF_6 (Matheson, Instrument Purity minimum purity 99.99%), xenon (Airco Research Grade, minimum purity 99.99%) and propane (Matheson, Instrument Purity, minimum purity 99.5%) were outgassed by several freeze–pump–thaw cycles prior to being condensed into the cylindrical quartz photolysis cell (100 mm light path, 25 mm internal diameter). The total amount of I_2 produced after each flash or series of flashes was measured spectrophotometrically at 498 nm on a Beckman DU Spectrophotometer.

The initial flashing of each I_2-free cell was carried out at room temperature. Molecular iodine accumulates by irreversible processes as detailed in Section 3, and following flashes on the same cell maintained at room temperature led to some transitory I_2 dissociation that masked I_2 photogeneration. (This dissociation probably occurs by energy transfer since direct photodissociation was prevented by the 380 nm cut-off filter; that no direct I_2 photodissociation occurred was confirmed by flashing a cell containing only CO_2 and I_2.) Accordingly, subsequent flashes were carried out after the condensable contents of the cell had first been frozen into a side-arm at −196 °C and then maintained at −39 °C with a benzyl chloride slush bath (vapor pressure of I_2 at −39 °C, 4.5×10^{-4} Torr). Under these conditions, results on cells in which I_2 had been produced previously were consistent with initial-flash temporal I_2 production results.

3. Results and discussion

3.1. *Photolysis of CF_3I in the absence of O_2*

Figure 1 is a typical oscillogram monitored at 498 nm showing temporal behavior of I_2 production following UV flash photodissociation of CF_3I in the presence of about 400 Torr CO_2; comparable oscillograms were obtained with xenon or SF_6 as the inert diluent gas. It is seen that generation of I_2 is preceded by an induction period of approximately 200 μs. This induction period decreases with increasing pressure of CF_3I, ranging from 190 μs at 24 Torr CF_3I to 425 μs at 4 Torr CF_3I.

A similar delay in I_2 production occurs in the iodine photodissociation laser [15] where accumulation of I_2 is attributed primarily to thermal decomposition of the active medium in the laser; the induction period is the time needed to reach a pyrolysis threshold temperature (about 1000 K). Pyrolysis of CF_3I clearly cannot be the source of I_2 in the non-laser flash results reported here, however. Under the flash conditions typically used (total flash energy of the order of 1 kJ with non-collimated light output distributed roughly uniformly over the UV and visible spectral regions), the temperature rise within the photolysis cell was limited to less than 1 °C per flash by the gas pressure (greater than 0.5 atm).

In the absence of CF_3I pyrolysis, three-body atom recombination is the major source of I_2. Photodissociation of CF_3I leads to over 90% I^* atoms [3]; these excited atoms do not combine themselves and they combine with

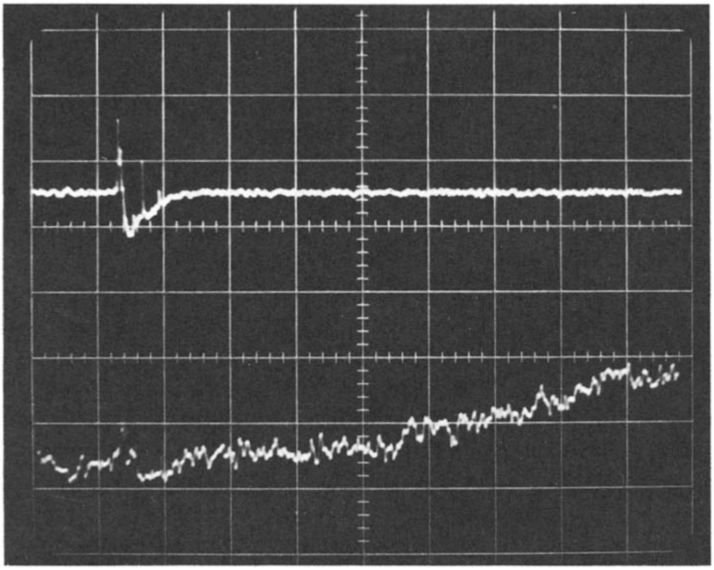

Fig. 1. I_2 formation following flash photodissociation of CF_3I in CO_2: upper trace, scattered light from cell (monitored at 360 nm) showing time of flash initiation; lower trace, absorption at 498 nm. Sweep time, 50 μs per major division; vertical sensitivity, 4.9×10^{14} I_2 molecules cm^{-3} per major division; $P(CF_3I)$ = 16 Torr; $P(CO_2)$ = 400 Torr.

ground state I atoms two orders of magnitude slower than recombination of two ground state atoms [16]. The induction period in I_2 production in the absence of O_2 thus results from time-delayed deactivation of I*:

$$I^* + M \xrightarrow{k_{Q,M}} I + M \tag{11}$$

Trifluoromethyl radicals are very efficient quenchers of I*: $k_{Q,CF_3} = 2.9 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} [17]. However, the high pressure second order recombination $2CF_3 \rightarrow C_2F_6$ is at least four times as fast as the deactivation $CF_3 + I^* \rightarrow CF_3 + I$ [17, 18] so that under the conditions of the work reported here it is assumed that no quenching by CF_3 occurs. (It should be noted that if appreciable deactivation by CF_3 did occur during the short lifetime of the CF_3 radicals in the system, then I_2 production would have occurred by recombination at a much shorter time than actually observed, as for example in Fig. 1). Conversely, CO_2 and CF_3I are weak quenchers of I*: $k_{Q,M} = 1.3 \times 10^{-16}$ and 3.5×10^{-16} cm^3 molecule^{-1} s^{-1} for CO_2 [19] and CF_3I [20] respectively. The results are qualitatively consistent, however, with the following mechanism utilizing the extremely efficient quenching by I_2 ($k_{Q,I_2} = 3.6 \times 10^{\ 11}$ cm^3 molecule ^{1} s ^{1} [21]):

$$I^* + CO_2 \xrightarrow{k_{Q,CO_2}} I + CO_2 \tag{12}$$

$$I^* + I_2 \xrightarrow{k_{Q,I_2}} I + I_2 \tag{13}$$

$$2I + M \xrightarrow{k_{R,M}} I_2 + M \tag{14}$$

The third-order recombination rate constants $k_{R,M}$ for CO_2, CF_3I and I_2 are 5.0×10^{-32} (this work, in agreement with earlier results [22]), 3.1×10^{-31} [23] and 3.0×10^{-30} [24] cm^6 molecule^{-2} s^{-1}. In all of the work reported, $P(CO_2)/P(I_2) > 6000$ and $P(CO_2)/P(CF_3I) > 15$, so that CO_2 is the predominant third body in reaction (14). We have simulated this mechanism on an EAI TR-10 analog computer using k_{Q,I_2} as an adjustable parameter, assuming M = CO_2 only and that the concentration of I* at the time of maximum flash intensity is $[I^*]_0 = 0.91 (2 \times [I_2]_\infty)$, where $[I_2]_\infty$ is the total amount of I_2 produced for one flash. Results for the flash oscillogram in Fig. 1 are shown in Fig. 2, giving a best fit value for k_{Q,I_2} of 7.4×10^{-11} cm^3 molecule^{-1} s^{-1}. Computer simulations for CF_3I pressures of 8 Torr and 24 Torr give best fit values of 4.0×10^{-11} and 2.5×10^{-11} cm^3 molecule^{-1} s^{-1} for k_{Q,I_2}. In view of the major assumptions involved in the simulations, these best fit values are in satisfactory ageement with the literature value given above and support mechanism (12) - (14) as the major source of the induction period preceding I_2 production.

Propane is an efficient quencher of I*: $k_{Q,C_3H_8} = 1.6 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} [25]. Addition of about 3 Torr propane to the reaction mixture of Fig. 1 greatly reduces the induction period but has negligible effect on the subsequent rate of I_2 production, as seen in Fig. 3. Inclusion of

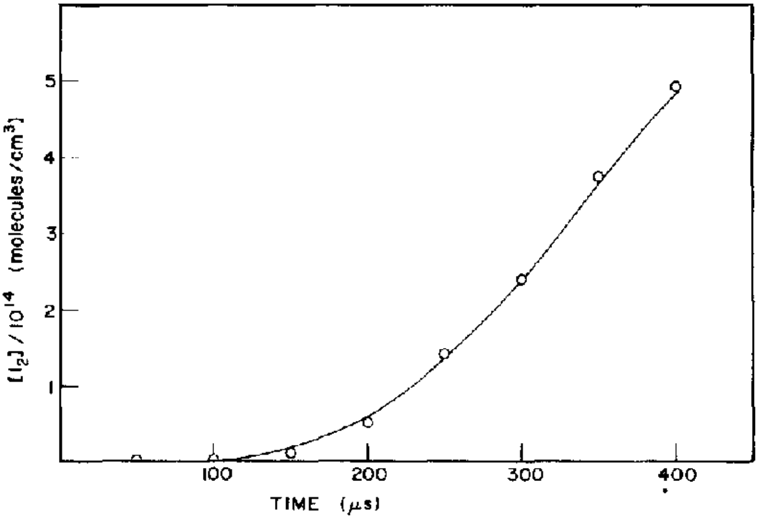

Fig. 2. Computer simulation (solid curve) of experimental (○) formation of I_2 following flash photodissociation of CF_3I in CO_2: $P(CF_3I)$ = 16 Torr; $P(CO_2)$ = 400 Torr.

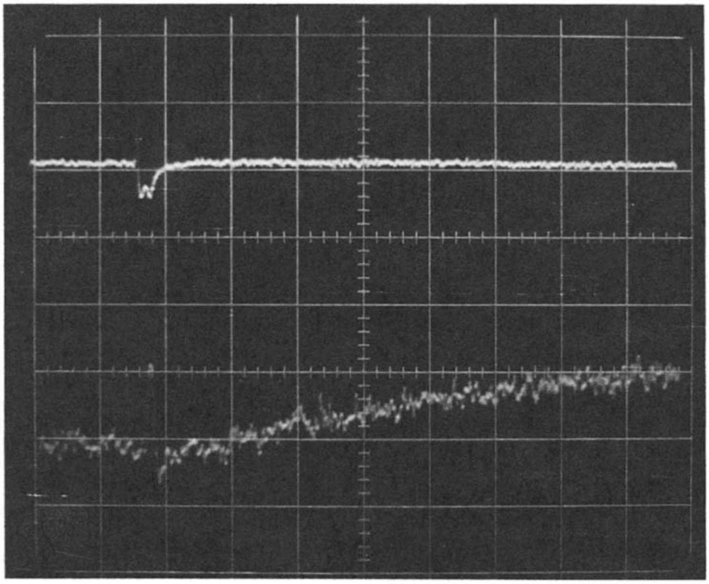

Fig. 3. I_2 formation following flash photodissociation of CF_3I in CO_2 with C_3H_8 quencher upper trace, scattered light at 360 nm; lower trace, absorption at 498 nm. Sweep time, 100 μs per major division; vertical sensitivity, 4.9×10^{14} I_2 molecules cm^{-3} per major division; $P(CF_3I)$ = 16 Torr; $P(CO_2)$ = 400 Torr; $P(C_3H_8)$ = 3 Torr.

$$I^* + C_3H_8 \xrightarrow{k_{Q,C_3H_8}} I + C_3H_8 \tag{15}$$

in the computer simulation gives a best fit value for k_{Q,C_3H_8} of 5.6×10^{-13} cm^3 molecule^{-1} s^{-1}. Substitution of propane (400 Torr) for CO_2 completely eliminates the induction period and leads immediately following the flash to the expected third order recombination (Fig. 4).

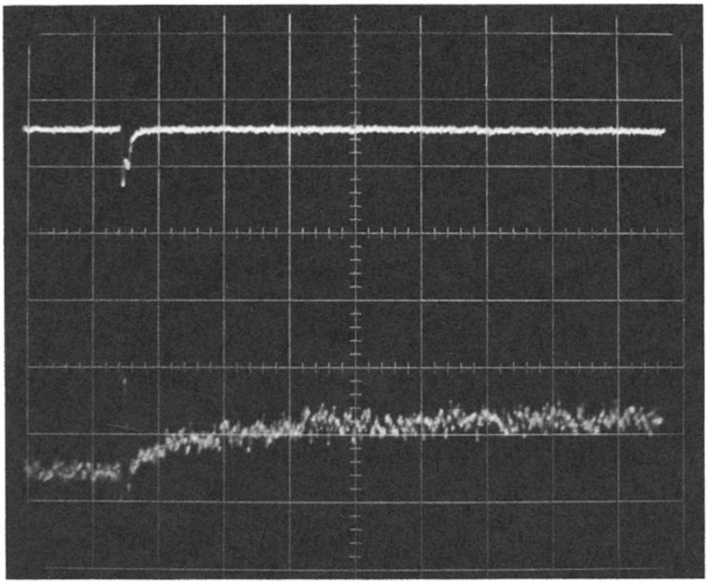

Fig. 4. I_2 formation following flash photodissociation of CF_3I in C_3H_8: upper trace, scattered light at 360 nm; lower trace, absorption at 498 nm. Sweep time, 500 μs per major division; vertical sensitivity, 4.9×10^{14} I_2 molecule cm^{-3} per major division; $P(CF_3I)$ = 16 Torr; $P(C_3H_8)$ = 400 Torr.

3.2. *Photolysis of CF_3I in the presence of O_2*

Molecular oxygen is an extremely efficient quencher of I* (k_{Q,O_2} = 2.5×10^{-11} cm^3 molecule^{-1} s^{-1} [26]) but is a poor third body in ground state I atom recombination, being only about half as effective as CO_2 [27]. Addition of about 2 Torr O_2 to the system represented in Fig. 1 should be as effective as 400 Torr propane in quenching I*; on this basis I_2 production following flash photodissociation of CF_3I in the presence of O_2 might be expected to follow that of Fig. 4. The results, however, are quite different, as shown by the oscillogram in Fig. 5. Although the induction period has been eliminated (less than 10 μs) by addition of 2 Torr O_2 to CF_3I (16 Torr) and CO_2 (400 Torr), the rate of I_2 production is rapid and essentially that of the activating flash intensity, *i.e.* about 7×10^{19} I_2 molecules cm^{-3} s^{-1}. This behavior is followed at all higher pressures of O_2 and to O_2 pressures less than 0.2 Torr. At $P(O_2) \approx 0.03$ Torr, the rate of I_2 production is less than that of the light intensity: initial rate = $R_0(I_2) \approx 4 \times 10^{18}$ molecules cm^{-3} s^{-1}. Similarly, at $P(O_2)$ = 1 Torr, $P(CF_3I)$ = 4 Torr, the rate of I_2 production is slightly less than the flash intensity profile.

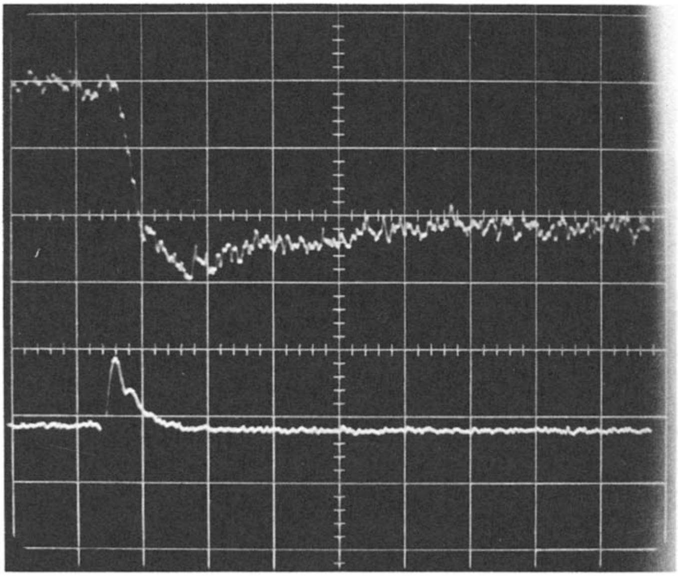

Fig. 5. I_2 formation following flash photodissociation of CF_3I in CO_2 with O_2 quencher: upper trace, scattered light at 360 nm; lower trace, absorption at 498 nm. Sweep time, 50 μs per major division; vertical sensitivity, 4.9×10^{14} I_2 molecules cm^{-3} per major division; $P(CF_3I)$ = 16 Torr; $P(CO_2)$ = 400 Torr; $P(O_2)$ = 2 Torr.

At $P(O_2) \geqslant 1$ Torr, the molecular iodine concentration reaches a maximum value at about 60 μs after flash initiation followed by a first order disappearance ($k_1 \approx 10^4$ s^{-1}) that is independent of CF_3I or O_2 pressure. The results are summarized in Table 1. It is seen that both the maximum I_2 concentration and the equilibrium concentration reached several hundred microseconds after the flash are roughly independent of O_2 pressure, but do increase with increasing CF_3I pressure (and hence increased light absorption). The fall-off in a linear dependence at the highest (23 Torr) CF_3I pressure is due in part to high, and hence non-linear, absorption by CF_3I (decadic ϵ = 155 dm^3 $mole^{-1}$ cm^{-1} at 270 nm).

This rapid I_2 production cannot be due solely to three-body atom recombination of ground state atoms. Assuming that all of the I^* atoms are quenched in a time short compared with the flash duration and that the initial iodine atom concentration is twice that of $[I_2]_{max}$, then the initial rate of I_2 production by ground state recombination at $P(CO_2) \approx 400$ Torr would be about 2.5×10^{18} molecules cm^{-3} s^{-1}, or approximately 30 times slower than actually observed.

Enhanced I atom recombination in a large excess of O_2 has been observed when the flash radiation extends as low as 200 nm [28]. This results from generation of more effective third bodies such as O_3 and singlet $O_2(^1\Delta_g)$:

$$2I + O_3 \rightarrow I_2 + O_3 \tag{16}$$

TABLE 1

Molecular iodine production following room temperature flash photolysis of CF_3I in the presence of O_2

Diluent gas (~400 Torr)	$P(O_2)$ (Torr)	$[I_2]_{max} \times 10^{-14}$ (molecules cm^{-3})	$[I_2]_\infty \times 10^{-14}$ (molecules cm^{-3})
$P(CF_3I) \approx$ 10 Torr			
CO_2	0.03		6
CO_2	0.2		8
CO_2	1	9	7
Xe	1	10	6
SF_6	1	8	6
CO_2	2	7	4
CO_2	2	9	6
CO_2	5	10	7
CO_2	8	12	9
$P(CF_3I) \approx$ 16 Torr			
CO_2	1	13	10
C_3H_8	1	16	9
CO_2	2	14	10
CO_2	4	14	10
CO_2	6	17	13
CO_2	9	17	13

Diluent gas (~400 Torr)	$P(CF_3I)$ (Torr)	$[I_2]_{max} \times 10^{-14}$ (molecules cm^{-3})	$[I_2]_\infty \times 10^{-14}$ (molecules cm^{-3})
$P(O_2) \approx$ 1 Torr			
CO_2	4	4	2
Xe	4	4	2
CO_2	8	9	7
Xe	8	10	6
SF_6	8	8	6
CO_2	16	13	10
SF_6	15	16	9
CO_2	23	16	11

$$2I + O_2(^1\Delta_g) \rightarrow I_2 + O_2(^1\Delta_g) \qquad (17)$$

or by inclusion of the rapid bimolecular step

$$2IO \rightarrow I_2 + O_2 \qquad (18)$$

The O_3, $O_2(^1\Delta_g)$ and IO species result from photodissociation of O_2 in the Herzberg region near 200 nm; Antrim *et al.* [28] obtained no kinetic evidence for IO formation from I or I* atoms reacting with ground state $(^3\Sigma_g^-)$ O_2 even though energetically favorable for I* atoms (and possibly I + I* atoms, depending on IO bond energy). (It should also be noted that in fact IO disappears by first order kinetics with $t_{1/2} \approx 85$ μs [29], rather than by the second order combination required by reaction (18); this IO lifetime is too long to account for the rapid I_2 generation reported here.) Since the UV filter solution used in the work reported here limited radiation to $\lambda >$ 235 nm and since inclusion of reactions (16) and (17) would require unreasonably large ground state I atom recombination rate constants (more than 5000 times that for $O_2(^3\Sigma_g^-)$ as a third body), we rule out formation of O_3, $O_2(^1\Delta_g)$ and IO as significant intermediate contributors to I_2 formation.

Although I* atoms in general recombine much slower than I atoms [16], a possible mechanism for the rapid build-up of I_2 in the presence of O_2 is the formation of a strong intermediate complex (exciplex) between I* and ground state O_2:

$$O_2(^3\Sigma_g^-) + I^* \rightleftarrows (O_2 \cdot I)^* \tag{19}$$

followed by

$$2(O_2 \cdot I)^* \rightarrow I_2 + 2O_2 \tag{20}$$

or

$$(O_2 \cdot I)^* + I \rightarrow I_2 + O_2 \tag{21}$$

A similar exciplex between I_2 and O_2 has been proposed in the laser-induced photodecomposition of CHI_3 in the presence of trace amounts of I_2 and O_2 [30].

Stability of $(O_2 \cdot I)^*$ may be enhanced by the near-resonant energies of I* and $O_2(^1\Delta_g)$. However, although near resonance enhances quenching of I* [31] and $Br(^2P_{1/2})$ [32] atoms, it does not appear to be a major factor in O_2 quenching of triplet states [33]. More reasonable perhaps is a high level of charge transfer complexation resulting from the large electron affinity of the I* atom, which is greater than that of ground state I atoms by the excitation energy (0.94 eV).

We may estimate a lower limit for the strength of $(O_2 \cdot I)^*$ if $R_0(I_2) \geqslant 7 \times 10^{19}$ molecules cm^{-3} s^{-1} (*i.e.* that of the photolysis flash). Assuming that reaction (19) is in equilibrium (K_{19}), that reaction (20) occurs at every encounter and that $[I^*]_0 = 0.91\ (2 \times [I_2]_{max})$, then it follows from simple collision frequency for $P(O_2) = 1$ Torr, $P(CF_3I) = 8$ Torr ($[I_2]_{max} \approx 10^{15}$ molecules cm^{-3}, Table 1) that $K_{19} \geqslant 10^4$ dm^3 mol^{-1}. This is very large in general compared with that for ground state I atom charge transfer complexes which in many cases may be solely contact interactions [34] although stability constants in excess of 10^6 dm^3 mol^{-1} at 400 K have been obtained for complexes between I and NO or NO_2 [35].

3.3. *Reactions following flash-initiated I_2 production*

Undoubtedly other undetected transient species such as CF_3 and CF_3O_2 may contribute to the overall mechanism, as evidenced (Fig. 5) by the relatively slow first order disappearance of approximately 30% of the I_2 following the photolyzing flash. The rate constant for the reaction of trifluoromethyl radicals with iodine

$$CF_3 + I_2 \rightarrow CF_3I + I \tag{22}$$

is at least nine times smaller than that for two-body CF_3 recombination [36], so that an unreasonably large CF_3 concentration is required in order for reaction (22) to contribute substantially to I_2 disappearance. This is also shown directly in other work in this laboratory, to be reported later, in which CF_3I or CF_3COCF_3 is flash photolyzed with UV light in the presence of I_2; although I_2 is dissociated within the lifetime of the flash with a quantum yield suggesting very efficient collision energy transfer leading to I_2 dissociation in addition to reaction (22), there is no induction period in the reappearance of I_2 as would be required if reaction (22) is important several hundred microseconds after the flash.

Trifluoromethyl radicals react with O_2 to form CF_3O_2 radicals. Very little is known of the reactions of CF_3O_2, but undoubtedly they will react to some extent with I_2 in addition to leading to fluorinated and oxygenated products such as CF_2O. If F_2 is an intermediate, such as by reaction (10), then I_2 may be decomposed by the bimolecular reaction [36, 37]

$$F_2 + I_2 \rightarrow I_2F + F \tag{23}$$

Unidentified solid products were produced in all O_2- containing reaction mixtures, as shown by light scattering of the continuous analyzing beam immediately following the photolyzing flash. This cloudiness disappeared when the reaction mixture was frozen out with liquid nitrogen and then maintained at -39 °C, or after 24 h at room temperature for cells with $P(O_2)$ less than 2 Torr. Mass spectral analyses suggested products considerably larger than CF_2O but yields were too small and variable for characterization.

Acknowledgments

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