

PHOTOPHYSICS OF $\text{CF}_2(\tilde{\text{A}}^1\text{B}_1(0,6,0))$ EXCITED BY A KrF LASER AT 248 nm**I: QUENCHING OF $\text{CF}_2(\tilde{\text{A}})$ BY ITS COMMON PRECURSORS**

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Summary

Rate constants at room temperature were measured for the quenching of electronically excited $\text{CF}_2(\tilde{\text{A}}(0,6,0))$ by its most common precursors in the gas phase. The $\text{CF}_2(\tilde{\text{X}})$ was produced by the photolysis of the precursor CF_2Br_2 in an unfocused KrF laser beam and of the precursors C_2F_4 , CF_2Cl_2 and CF_2HCl in a focused KrF laser beam. $\text{CF}_2(\tilde{\text{X}})$ was excited to the $\tilde{\text{A}}^1\text{B}_1$ state using the same beam, and the fluorescence of the $\tilde{\text{A}}$ state was used to monitor its decay. The values of the bimolecular quenching rate constants for CF_2Br_2 , C_2F_4 , CF_2Cl_2 , CF_2HCl and CF_4 are $24 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $4.7 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $2.0 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $1.5 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $0.2 \times 10^{13} \text{ cm}^2 \text{ mol}^{-1} \text{ s}^{-1}$ respectively.

1. Introduction

Difluoromethylene appears in two interesting photolytic systems: (i) CF_2 radicals are produced in the stratosphere by the photodissociation of chlorofluorocarbons by sunlight and is therefore an interesting species with respect to atmospheric photochemistry [1]; (ii) CF_2 radicals are produced in the IR multiphoton dissociation of halomethanes such as CF_2Cl_2 , CF_2HCl and CF_2Br_2 and several products observed in these systems are due to CF_2 reactions [2]. In these systems the presence and effect of CF_2 in its electronically excited $\tilde{\text{A}}^1\text{B}_1$ state cannot be excluded. In order to study the dynamics of $\text{CF}_2(\tilde{\text{A}})$ it is first necessary to know the quenching rates of $\text{CF}_2(\tilde{\text{A}})$ by its precursors. To our knowledge little is known about these quenching rates. Wampler *et al.* [3] have estimated the rate of the removal of $\text{CF}_2(\tilde{\text{A}})$ by CF_2Br_2 . In this study we investigated the quenching rates of $\text{CF}_2(\tilde{\text{A}})$ by its most common precursors CF_4 , CF_2HCl , CF_2Cl_2 , C_2F_4 and CF_2Br_2 which were used in further experiments to produce CF_2 radicals either by UV or IR laser photolysis or by microwave discharge.

2. Experimental details

The radiation source was a KrF excimer laser constructed in our laboratory which operated at 248 nm. The maximum energy per pulse was 100 mJ, but for most experiments the power was reduced to avoid formation of polymers. The pulse duration was 17 ns (full width at half-maximum). The gas was irradiated inside a Teflon cell at room temperature. The diameter of the cell was 50 mm and its height was 80 mm. Four Suprasil-I windows enabled the gas to be irradiated in the cell and the fluorescence to be observed at right angles to the laser beam. Laser radiation could be focused onto the centre of the cell using a concave mirror ($f = 150$ mm). The cell was part of a vacuum line operated at pressures from 0.05 to 160 mbar which were measured using MKS 220 Baratron pressure heads. An MKS 254 flow controller permitted constant overall and partial pressures to be maintained in the gas flow. Thus no photoproducts could accumulate in the cell during the experiments. The gas was at room temperature during all experiments. Heating of the samples by the absorption of laser radiation was ignored.

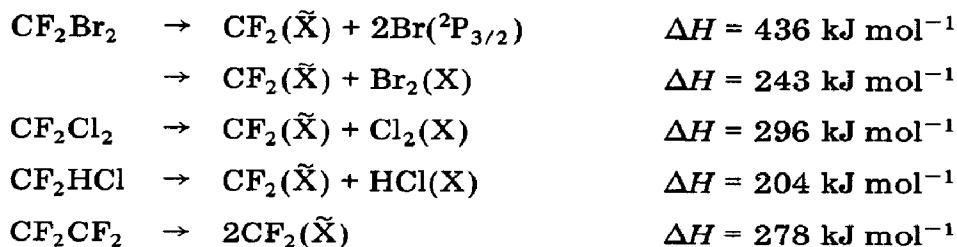
The emission was dispersed using a Jobin-Yvon THR monochromator which was normally set to 257.5 nm with a resolution of 0.2 nm. The fluorescence was recorded with a high time resolution using an RCA 4831 photomultiplier connected to a Tektronix R 7912 transient digitizer and evaluated using a DEC PDP 11/04 minicomputer coupled to the digitizer. All the observed lifetimes represent single-exponential decays [4].

CF₂Br₂ (purity, 97%) obtained from Merck, C₂F₄ (purity, 99.5% (stabilized)) obtained from PCR-Ventron, and CF₂Cl₂ (purity, 98.5%), CF₂HCl (purity, 98.5%) and CF₄ (purity, 99.7%) obtained from Messer Griesheim were used without further purification. CF₂Br₂ was degassed before use.

3. Results and discussion

In all experiments CF₂(\tilde{X}) was generated by the photodissociation of a precursor and was then excited to the CF₂(\tilde{A} (0,6,0)) state using the same pulse. Only the (0,6,0) vibronic level of the first excited singlet \tilde{A} is excited in this process. Further methods of synthesizing CF₂ are discussed in ref. 4.

The KrF laser photon (248.4 nm \equiv 481.3 kJ mol⁻¹) contains sufficient energy to dissociate the following precursors to form the CF₂(\tilde{X} ¹A₁ ($\nu = 0$)) ground state and various other products:



The photodissociation of CF_4 at 248 nm requires at least two photons:



These values were calculated using the data given in the literature [5].

CF_2Br_2 absorbs strongly at the laser wavelength ($\epsilon \approx 10^5 \text{ cm}^2 \text{ mol}^{-1}$ [6]). Care had to be taken that only a small number of the molecules in the cell absorbed a laser photon. Otherwise dissociation products would contribute significantly to the quenching and no exact determination of the concentration of CF_2Br_2 would be possible. In the unfocused laser beam less than 0.01% of the CF_2Br_2 molecules absorb a photon when the energy per pulse is reduced to 10 mJ.

C_2F_4 , CF_2HCl and CF_2Cl_2 absorb very weakly at 248 nm. The absorption coefficient of the methane derivatives is known to be less than $1 \text{ cm}^2 \text{ mol}^{-1}$ [7]. No literature data are available for C_2F_4 but we did not observe significant absorption of the KrF laser radiation up to atmospheric pressures of C_2F_4 . Only after focusing the laser beam onto samples of C_2F_4 , CF_2HCl or CF_2Cl_2 could fluorescence from $\text{CF}_2(\tilde{\text{A}})$ be detected. The concentration of CF_2 near the focus was estimated to be about 10^7 mol cm^{-3} . No fluorescence at all could be seen when CF_4 was irradiated. A small amount of CF_2Br_2 was added which yielded CF_2 . Thus allowance had to be made for quenching of $\text{CF}_2(\tilde{\text{A}})$ by CF_2Br_2 itself.

In order to determine the quenching rates of the different gases the time behaviour of the emission $\text{CF}_2(\tilde{\text{A}}^1\text{B}_1(0,6,0)) \rightarrow \text{CF}_2(\tilde{\text{X}}^1\text{A}_1(0,2,0))$ was observed at 257.5 nm. The resolution of the monochromator and the pressure interval were chosen such that rotational deactivation and population of other states could be avoided [4].

Figure 1 depicts fluorescence decay rates as a function of quencher pressures. We found linear Stern-Volmer relationships for all the quenchers discussed here and derived the following rates from the slopes of the plots:

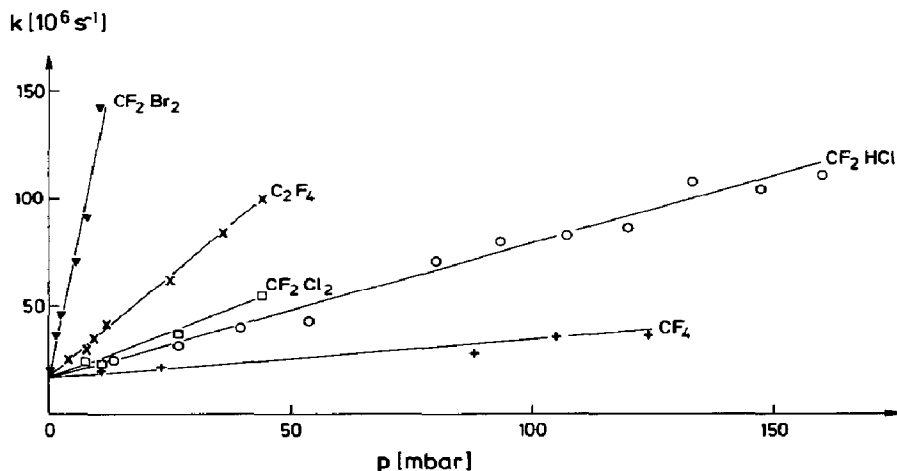


Fig. 1. Stern-Volmer plots of the deactivation of $\text{CF}_2(\tilde{\text{A}})$ by various precursors of CF_2 : \blacktriangledown , CF_2Br_2 ; \square , CF_2Cl_2 ; \circ , CF_2HCl ; \times , C_2F_4 ; $+$, CF_4 .

$$\begin{aligned}
 k(\text{CF}_2\text{Br}_2) &= (2.4 \pm 0.6) \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \\
 &0.07 \text{ mbar} \leq p(\text{CF}_2\text{Br}_2) \leq 10.7 \text{ mbar} \\
 k(\text{CF}_2\text{CF}_2) &= (4.7 \pm 0.3) \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \\
 &2.3 \text{ mbar} \leq p(\text{CF}_2\text{CF}_2) \leq 44 \text{ mbar} \\
 k(\text{CF}_2\text{Cl}_2) &= (2.0 \pm 0.2) \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \\
 &2.3 \text{ mbar} \leq p(\text{CF}_2\text{Cl}_2) \leq 44 \text{ mbar} \\
 k(\text{CF}_2\text{HCl}) &= (1.5 \pm 0.2) \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \\
 &10.0 \text{ mbar} \leq p(\text{CF}_2\text{HCl}) \leq 160 \text{ mbar} \\
 k(\text{CF}_4) &= (2.0 \pm 0.9) \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \\
 &2.6 \text{ mbar} \leq p(\text{CF}_4) \leq 123 \text{ mbar}
 \end{aligned}$$

These rates represent the sum of electronic and vibrational quenching. For the fast quenchers the vibrational deactivation can be neglected with respect to the electronic deactivation whereas for CF_4 the vibrational deactivation of the removal of the initial $\tilde{\text{A}}(0,6,0)$ state may be significant. The deactivation channels and the collision-free lifetime τ_0 which is evaluated from the intercept of Fig. 1 to be 55 ns will be discussed in detail elsewhere.

The quenching rate constants change by two orders of magnitude from CF_4 to CF_2Br_2 as a quenching gas. The quenching cross section for $\text{CF}_2\text{Br}_2 + \text{CF}_2(\tilde{\text{A}})$ is close to the gas kinetic collision cross section. This rate is in agreement with the estimate of $k = 1.5 \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ given by Wampler *et al.* [3]. The large quenching cross section of CF_2Br_2 could be due to electronic energy transfer since CF_2Br_2 absorbs in the same wavelength range in which $\text{CF}_2(\tilde{\text{A}})$ emits strongly. This overlap is a precondition for electronic energy transfer. The same argument, however, does not explain the high quenching rate for CF_2Cl_2 compared with other quenchers, *e.g.* CF_4 , since both molecules have no electronic states with lower excitation energies than the singlet of CF_2 .

Quenching rate constants for $\text{CF}_2(\tilde{\text{A}})$ are to our knowledge not available in the literature, but we can compare our results with the quenching rate constants of other electronic excited molecules. Such a comparison can yield information on the deactivation mechanism. If for instance the quenching rates and their dependence on the collision partners are similar for two different electronic excited molecules we can assume that the quenching mechanisms are the same. Comparable data are only available for UF_6^* . The molecules CF_4 , CF_2HCl , CF_2Cl_2 and CF_2Br_2 studied in this work were used to quench UF_6 excited at 393 nm [6, 8, 9]. The rates were indeed close to those reported here. Moreover a comparison of $\text{CF}_2(\tilde{\text{A}})$ with UF_6^* is justified because both molecules are perfluorinated and thus should have a pronounced inhomogeneous internal charge distribution. A comparison of the rates for the two molecules is given in Table 1.

The quenching of UF_6^* was attributed to chemical processes which ruptured the U—F bond [10]. In our system we would have to postulate the rupture of a C—F bond which appears to be very unlikely. A more general concept for quenching processes which can be applied to our results and to

TABLE 1

Comparison of the rates of quenching $\text{CF}_2(\tilde{\text{A}})$ and UF_6^* with fluorinated methanes

	Quenching rate ($\times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)		Ionization potential (eV)
	$\text{CF}_2(\tilde{\text{A}})$	UF_6^* [3]	
CF_4	0.2	0.2	16.18 [6]
CF_2HCl	1.5	6.9	12.6 [8]
CF_2Cl_2	2.0	6.4	12.3 [8]
CF_2Br_2	24	32	11.18 [9]

the UF_6 data postulates the formation of a complex between the quencher and excited molecule which is stabilized by differential charges. Quenching by such complexes is characterized by a correlation of the ionization potential and the rate for different quenchers. Table 1 shows that such a correlation can indeed be found. The values for the first ionization potentials given in Table 1 refer to orbitals localized at the substituents bromine, chlorine and fluorine [8, 9]. The bond linking the complex together may thus be formed by a lone electron pair of the quencher. In the case of the CF_2 we find two free valences at the carbon atom, and one of them can be employed for the complex. In contrast UF_6 is a saturated molecule, but its high electron affinity (4.9 eV [11]) tends to stabilize the complex as discussed here.

Whether chemical quenching or physical quenching or both occurs depends only on which decay channels are active for the complex. In our system (CF_2 plus methanes), we can postulate a complex which is an isomer of a halogenated ethane and which has an energy equivalent to that required to excite $\text{CF}_2(\tilde{\text{X}})$ to $\text{CF}_2(\tilde{\text{A}})$. Chemically activated ethanes can either split off HCl (in the case of $\text{CF}_2 + \text{CHClF}_2$) and form an ethylene derivative, break down into two methyl radicals or be stabilized by collisions. These processes are well known in the decomposition of the ground electronic state of vibrationally excited haloethane molecules [12].

In contrast with the perfluorinated methane CF_4 , the perfluorinated ethylene C_2F_4 quenches $\text{CF}_2(\tilde{\text{A}})$ at a high rate. As will be discussed in ref. 4, $\text{CF}_2(\tilde{\text{A}})$ appears to insert into π systems and to form a propane derivative even better than ground state $\text{CF}_2(\tilde{\text{X}})$ does. Although no direct evidence that this process leads to chemical quenching has been reported to date it is very likely that at least a partial chemical reaction occurs.

4. Conclusion

Apart from our general interest in quenching kinetics, we measured the data presented here because they are relevant to two types of experiments. In the study of photoreactions of $\text{CF}_2(\tilde{\text{A}})$ the rapid deactivation of CF_2 by

most of its precursors has to be taken into account. If the intention is to study the ground state reactions of $\text{CF}_2(\tilde{\text{X}})$ it is very important to prevent the formation of $\text{CF}_2(\tilde{\text{A}})$ or to scavenge it because of its reactivity. A convenient source for $\text{CF}_2(\tilde{\text{X}})$, e.g. in flash photolysis experiments or IR photolysis, is C_2F_4 because it only dissociates to CF_2 , it rapidly quenches $\text{CF}_2(\tilde{\text{A}})$ and it forms C_3F_6 as the only product.

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