PHOTOCHEMICAL REACTION OF MOLECULAR IODINE WITH FLUORINATED HYDROCARBONS

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(Received May 13, 1983; in revised form July 16, 1983)

Summary

Molecular iodine excited by the ArF laser at 193 nm splits C—F, C—H and C—C bonds in a direct non-pyrolytic reaction with a quantum yield of about 2%. The radicals thus formed then combine with I_2 to yield organic iodides.

1. Introduction

One of the more trivial possibilities offered to photochemistry by exciplex lasers is that they make new wavelengths available. One of these is the ArF laser wavelength (193 nm) which is at the borderline of near UV and vacuum UV. We have investigated the chemical reactions of CF_3H, C_2F_5H, iso-C_3F_7H, CF_4 and C_2F_6 with I_2 excited at this wavelength by analysing the organic iodides formed as end products.

The upper state D $^1\Sigma_u^+$ of the transition [1, 2] is coupled by rapid collisional relaxation [3 - 5] to the nearby state D$'$ $^3\Pi_{2g}$ [1, 2], which is the upper state of the I_2 laser emitting at 342 nm [6, 7]. Both states are non-dissociative or possibly slightly predissociative [3]. Therefore the excitation leaves the molecules with an internal energy of 620 kJ mol^{-1} (6.45 eV) or, after vibrational deactivation, with 490 kJ mol^{-1} (D state) or 485 kJ mol^{-1} (D$'$ state). In contrast with the relatively inert iodine atoms and the slightly more reactive I_2 B $^3\Pi_{0u}^+$ (produced by excitation in the visible region), such very energetic molecules must be highly reactive. In fact they can even split C—F bonds, as we have found in this work. The reactions of several hydrocarbons and halogenated hydrocarbons with I_2 excited at 193 and 185 nm to form organic iodides has already been studied by two groups [8 - 10]. To investigate the synthetic potential of this reaction, we chose highly fluorinated

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hydrocarbons as starting materials because the expected iodides do not absorb at 193 nm.

2. Experimental details

In the experiment a cell containing iodine and the fluorinated hydro-carbon was irradiated and the end products were analysed. A commercial multigas exciplex laser (Lumonics TE 262) was used. When operated as an ArF laser, the pulse width is about 17 ns. The cell was irradiated with 2000 pulses at a rate of 1 pulse s^{-1} in each experiment. In order not to hit the cell wall, the beam was limited by an iris to a diameter of 1.5 cm at the entrance window. The average energy density was 46 mJ cm^{-2} (intensity, 2.7 MW cm^{-2}) just behind the entrance window, except in the experiment in which the intensity was varied. This variation was performed by changing the discharge voltage of the laser. Energies were measured using a calibrated pyroelectric joulemeter (Gen Tec).

We used an all-quartz cell of inner diameter 1.8 cm and length 11 cm. With ArF radiation at an energy density of 14 mJ cm^{-2} we found a trans-mission of the I_2 in the absence of foreign gas of 26%, corresponding to an absorption cross section σ of 1.2×10^{-17} cm^2 in agreement with the spectro-scopic value [9, 11]. At 56 mJ cm^{-2} (3.4 MW cm^{-2}) σ had apparently dropped to 5×10^{-18} cm^2. This can be understood on the basis of bleaching with a saturation intensity $hf/\sigma\tau_{rad}$ of 5 MW cm^{-2}. Because of this bleaching effect and also because of possible pressure broadening effects the absorbed energy, which was measured independently in each experiment, was used to determine the quantum yields. The cell was also used to measure the UV absorption spectra of the product organic iodides. Since all the monoiodides have broad maxima of almost equal wavelength (265 - 275 nm) and cross section (6×10^{-19} cm^2), their total yield is easy to determine in this way. CF_2I_2 appears to have a peak at 303 nm [9]. Its yield was determined from the ratio of absorbances at 303 and 265 nm without taking into account the ratio of the cross sections (which is probably between 2 and 5). The ratios of the monoiodides formed were qualitatively determined from their molecular ion peaks in the mass spectra. A quantitative calibration of these peaks was not attempted because some of the iodides produced were difficult to prepare by alternative methods.

After the addition of a few milligrams of iodine crystals (Merck), the cell was evacuated. The iodine was then sublimed to non-irradiated parts of the cell wall. The experiments were performed at a temperature of 23 - 25 °C, at which the vapour pressure of I_2 is 0.43 mbar. CF_3H, C_2F_5H (Peninsular Chemresearch), CF_4 and C_2F_6 (Matheson) were used without further purifi-cation. 2H-heptafluoropropane was prepared by the hydrolysis of iso-C_3F_7I (Riedel–de Haen) by KOH in acetone [12]. The sample used contained 1% acetone according to the UV spectrum.
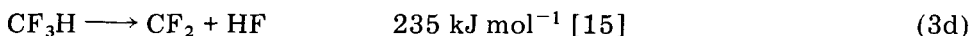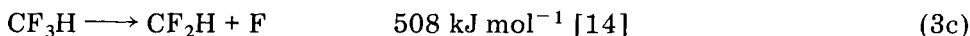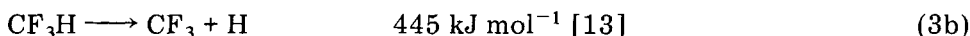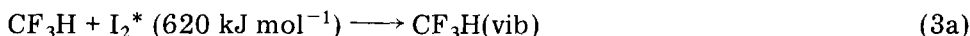
3. Results and discussion

When I_2 was irradiated in the presence of CF_3H we observed CF_3I and roughly stoichiometric amounts of HI. The presence of a small amount of C_2F_6, the dimer of CF_3, suggested a radical formation mechanism:

$$CF_3H + I_2^* \longrightarrow CF_3 + HI + I \tag{1}$$

$$CF_3 + I_2 \longrightarrow CF_3I + I \tag{2}$$
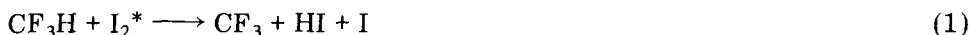
Glasgow and Willard [9] excluded such a mechanism for methane because of their failure to suppress the reaction by scavenging CH_3 with O_2. However, this failure may have been due to chain reactions. Accordingly, they also observed the ethyl radical when a mixture of C_2H_6 and I_2 was irradiated in a matrix. The concerted four-centre mechanism suggested by them appears less probable to us.

Below 300 mbar of CF_3H we also observed the typical pyrolysis product CF_4, which was identified by its IR spectrum, together with three other iodides CF_2HI, CF_2I_2 and C_2F_5I. These side products raise the question of whether there is a direct reaction of the electronically excited state similar to reaction (1) or whether there is only pyrolytic fragmentation with the fragments then forming the iodides in subsequent reactions:

$$CF_3H + I_2^* \ (620 \ \text{kJ mol}^{-1}) \longrightarrow CF_3H(\text{vib}) \tag{3a}$$

$$CF_3H \longrightarrow CF_3 + H \qquad 445 \ \text{kJ mol}^{-1} \ [13] \tag{3b}$$

$$CF_3H \longrightarrow CF_2H + F \qquad 508 \ \text{kJ mol}^{-1} \ [14] \tag{3c}$$

$$CF_3H \longrightarrow CF_2 + HF \qquad 235 \ \text{kJ mol}^{-1} \ [15] \tag{3d}$$

An answer to this question can be found by attempting to deactivate the CF_3H within its expected fragmentation lifetime. Therefore we increased the CF_3H pressure to 2 bar. CF_4 and C_2F_5I disappeared and the yield of CF_2I_2 was substantially reduced, but the yield of CF_2HI increased (Fig. 1). Since CF_3H is a small molecule, its lifetime after transfer of the full energy in reaction (3a) may be too short to allow deactivation before fragmentation. Therefore we investigated two larger molecules, C_2F_5H and iso-C_3F_7H (Fig. 1). However, no increase in the yield of most of the iodides was apparent even at the highest pressures. Therefore non-pyrolytic direct bimolecular reactions of the type

$$RH + I_2^* \longrightarrow R + HI + I \tag{4}$$

$$R'F + I_2^* \longrightarrow R' + IF + I \tag{5}$$

$$R''CF_3 + I_2^* \longrightarrow R'' + CF_3I + I \tag{6}$$

must be assumed to explain their formation. The radicals formed in these reactions will subsequently combine with I_2, as in reaction (2), to form the observed iodides. The yields of the iodides $R''I$ were not determined because they could not unambiguously be separated in the mass spectrum from the
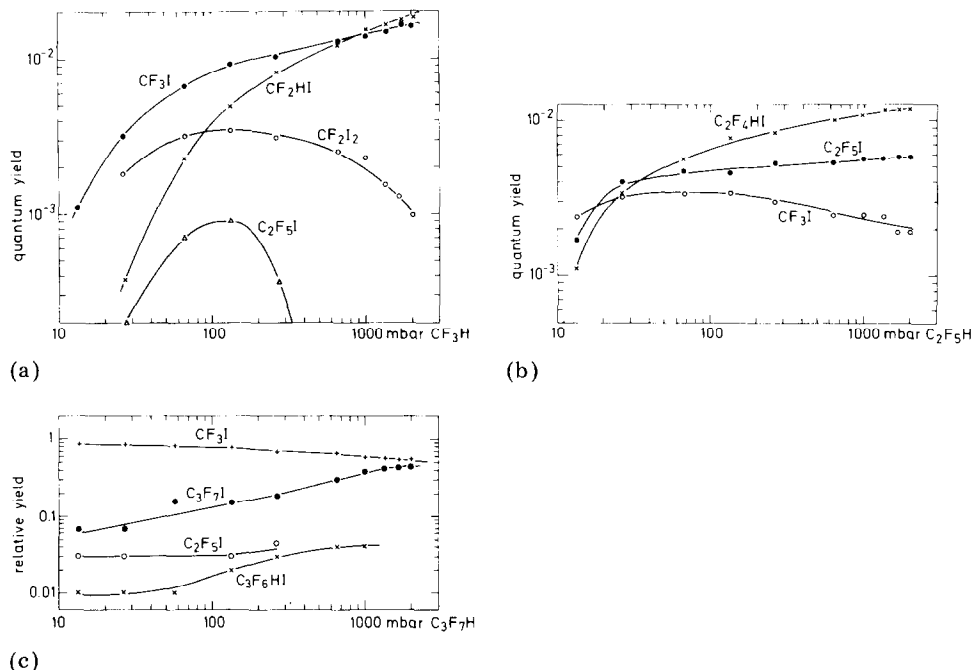
(a)

(b)

(c)

Fig. 1. Quantum yields of iodides as functions of the reactant pressure. The sum of the monoiodide quantum yields is obtained from the UV absorbance A at 267 nm. The yield ratios were determined from the ratios of the molecular peaks in the mass spectra. The diiodide yield was taken to be $A(303 \text{ nm})/A(265 \text{ nm})$ multiplied by the monoiodide yield. Only relative yields are given in (c) because CH_3I formed from the acetone impurity in C_3F_7H interfered with the determination of A.

$R''CF_2I \equiv R'I$ fragment of equal mass. The isomeric compositions of C_2F_4HI and C_3F_6HI were not determined.

We also investigated the possibility that the C—F bond splitting may have arisen from secondary photolysis of the intermediate radicals. Like CH_3 [16], CF_3 [17] absorbs weakly around 200 nm. However, the intensity dependence described below (Fig. 2) was the wrong way around: the quantum yield of CF_2HI produced by C—F bond splitting decreased with increasing intensity.

To establish further the C—F and C—C bond splitting reactions (5) and (6), we looked for iodides formed from C_2F_6. In fact CF_3I and C_2F_5I form with quantum yields of 1.3% and 0.7% respectively, independent of pressure from 70 to 2000 mbar. CF_4 also forms the iodide CF_3I. This reaction has been reported [9] to occur with a quantum yield of 2×10^{-3} at 185 nm. At 193 nm we found a quantum yield of only 10^{-3} between 100 and 400 mbar and an even smaller yield at 20 mbar. This latter yield was too small to establish the pressure dependence.

Callear and Metcalfe [4] have reported that the formation of IO from $O_2 + I_2$ occurs only from the D state of I_2 and not from the D' state. Donovan and coworkers [8] have presented evidence that the D and D' states both
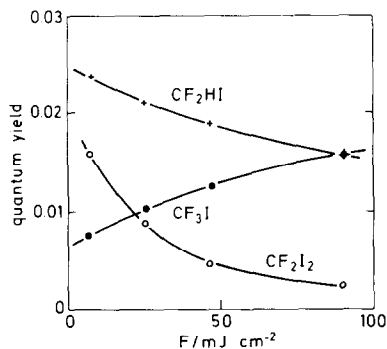
Fig. 2. Quantum yields as functions of the laser energy density F.

react with methane and chloromethane. These are probably also the states relevant to our reactions. However, to check whether all the iodides are produced by iodine pumped by one photon only, we studied the intensity dependence of the reaction with CF_3H (Fig. 2). The quantum yield of CF_2I_2 is almost inversely proportional to the incident energy density, i.e. the absolute quantity formed per pulse is a constant. Secondary photochemical (or thermal) decomposition probably prevents it from rising to a higher level. The total quantum yield of the two monoiodides remained constant, but the ratio of their yields changed substantially. Higher intensity favours CF_3I and militates against CF_2HI. The ratio was changed by a factor of 2 at an energy density of 40 mJ cm^{-2}. This is close to the saturation energy (50 mJ cm^{-2}) of the ground state absorption and is also fairly near 10 mJ cm^{-2} which is the corresponding value for the transition to the ionization continuum calculated from the estimated σ value of 10^{-16} cm^2 [2]. Two states of different energies appear to be involved: the lower state produces more CF_2HI and the upper state produces more CF_3I. Their relative population is altered by an absorption process with a cross section not less than 10^{-17} cm^2, but the sum of their populations does not depend on intensity. We find it difficult to understand why $I_2^+ + e^-$ should prefer to split the C—H bond. Instead, we assume that the two states are closely related and differ only in (perhaps vibrational) energy. High energy will be less probable at low intensity and also at high pressure, the latter being a relaxation effect. It should be noted that high pressure favours CF_2HI, as does low intensity. If this view is correct, the differences in the reactivities can be readily understood in terms of activation energies.

Since higher pressure means a lower average energy of I_2^*, the channel most enhanced by high pressure probably corresponds to the lowest activation energy. Thus according to Figs. 1(a) and 1(b) the smallest activation energy is associated with splitting of the C—F bond by I_2^*, followed by splitting of the C—H bond and then the C—C bond. The C—H bond in C_2F_5H [18] is weaker by 15 kJ mol^{-1} than that in CF_3H [13], and in iso-C_3F_7H it will be even weaker. Therefore it is reasonable that C_3F_7I and C_3F_6HI are preferred to CF_3I with increasing C_3F_7H pressure (Fig. 1(c)). Further evi-

dence for the important role of bond energies is provided by the inefficient reaction of CF_4: breaking its C—F bond requires 538 kJ mol^{-1} [15] compared with 530 kJ mol^{-1} for C_2F_6 [19].

A quantitative analysis of the pressure dependence of the individual yields is not appropriate because little is known about the interrelation between the two states. However, analysis of the sum $[I_2^*]$ of their populations and the sum of the iodide quantum yields is straightforward. If $[I_2^*]$ is assumed to be stationary, we have

$$0 = \frac{d[I_2^*]}{dt} = \sigma I([I_2] - [I_2^*]) - k_f[I_2^*] - (k_d + k_r)M[I_2^*] \tag{7}$$

where the first term is the pumping rate at intensity I (it will not be used explicitly in the following), k_f is the fluorescence (plus predissociation) rate, k_d and k_r are the deactivation and reaction rate constants respectively and M is the concentration of the reactant molecules such as CF_3H. Dividing eqn. (7) by the reaction rate $k_rM[I_2^*]$ yields the inverse of the quantum yield:

$$\varphi^{-1} = \frac{\sigma I([I_2] - [I_2^*])}{k_rM[I_2^*]} = \frac{k_f}{k_rM} + \frac{k_d}{k_r} + 1 \tag{8}$$

Figure 3 shows that φ^{-1} is in fact a linear function of M^{-1}. The relative reaction and deactivation rate constants found from the slopes and intercepts are shown in Table 1.

If the fluorescence lifetime of the directly pumped D state (15 ns [20]) or the D$'$ state (also 15 ns [21]) which is closely coupled to the D state by
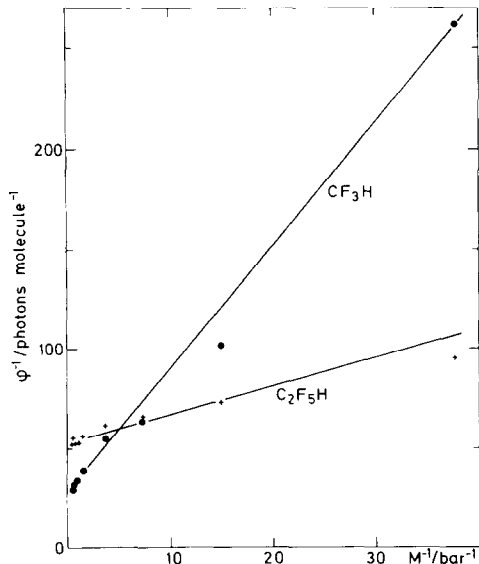

Fig. 3. Inverse total quantum yield φ^{-1} of iodides as functions of reciprocal reactant pressure M^{-1}.

TABLE 1

Molecule	k_r/k_f ($\times 10^{-20}$ cm^3 molecule^{-1})	k_d/k_f ($\times 10^{-20}$ cm^3 molecule^{-1})
CF$_3$H	0.68	29
C$_2$F$_5$H	2.9	150

collisions is used for k_f^{-1}, k_d for the deactivation by C$_2$F$_5$H is 10^{-10} cm^3 s^{-1} molecule^{-1}, *i.e.* a probability of once in every four collisions. Such fast quenching is responsible for the low quantum yield of the reaction. However, the buffer gases used in the optically pumped iodine laser [6] (see also refs. 2 - 5) do not deactivate the D and D$'$ states so rapidly. For example, we obtain from ref. 5, Fig. 3, k_d(N$_2$) = 1.7×10^{-12} cm^3 s^{-1} molecule^{-1} and k_d(SF$_6$) = 1.3×10^{-12} cm^3 s^{-1} molecule^{-1} for the deactivation of the D$'$ level, and CF$_4$ appears to quench at a similar rate. This can be concluded from ref. 3 in which the rate of deactivation of D$'$ was apparently negligible compared with the conversion of D to D$'$. Unfortunately the small reaction quantum yield of CF$_4$ prevented a determination of its pressure dependence and hence its deactivation constant. However, in view of the large difference between C$_2$F$_5$H and CF$_3$H, a deactivation constant of the order of 10^{-12} cm^3 s^{-1} molecule^{-1} would be compatible with our other data. Therefore we feel confident that one of the reacting states is the D or the D$'$ state of I$_2$, or a state intermediate between them. Evidence that intermediate states are involved was reported in ref. 8.

4. Conclusion

Our result that I$_2$ excited at 193 nm can split C—H, C—C and C—F bonds shows that this molecule is an outstanding example of how strongly photochemistry can depend on the exciting wavelengths. For comparison iodine atoms generated by the irradiation of I$_2$ between 500 and 350 nm react only with relatively active double bonds, whereas I$_2$ excited below its dissociation threshold (*i.e.* above 500 nm) also adds to inactive multiple bonds, *e.g.* to acetylene [22]. A reaction with methane, ascribed to a highly excited iodine atom, has also been stimulated by 147 nm radiation [23]. The splitting of C—F bonds is not so surprising if we recall the substantial electron affinity of the fluorocarbons and the low ionization energy of the highly excited I$_2$. Thus a transition state with partial charge transfer could form. It is conceivable that such a state preferentially transfers a fluorine atom. Although the reaction has a reasonable efficiency (one reaction every 200 collisions with C$_2$F$_5$H), the total quantum yield is small (about 2%) because of the fast competing deactivation. Furthermore, since more than one iodide is usually produced, the reaction will not be useful for synthesis except in special cases. Such a case may be the preparation of CF$_2$HI, which

is difficult to prepare by alternative methods. At low intensity (Fig. 2) and high CF_3H pressure it is formed with only small quantities of side products.

Acknowledgments

References

1 J. Tellinghuisen, *Chem. Phys. Lett.*, *29* (1974) 359; *49* (1977) 485.
2 M. Martin, C. Fotakis and R. J. Donovan, *Nuovo Cimento B*, *63* (1981) 300.
3 A. B. Callear and M. P. Metcalfe, *Chem. Phys. Lett.*, *43* (1976) 197.
4 A. B. Callear and M. P. Metcalfe, *Chem. Phys.*, *20* (1977) 233.
5 Yu. Yu. Stoilov, *Sov. J. Quantum Electron.*, *8* (1978) 223.
6 M. J. Shaw, C. B. Edwards, F. O'Neill, C. Fotakis and R. J. Donovan, *Appl. Phys. Lett.*, *37* (1980) 346.
7 J. J. Ewing and C. A. Brau, *Appl. Phys. Lett.*, *27* (1975) 557.
  R. S. Bradford, E. R. Ault and M. L. Bhaumik, *Appl. Phys. Lett.*, *27* (1975) 546.
  A. K. Hoffman and G. C. Tisone, *Chem. Phys. Lett.*, *39* (1976) 353.
8 B. V. O'Grady, L. Lain, R. J. Donovan and M. C. Gower, *Chem. Phys. Lett.*, *91* (1982) 491.
  R. J. Donovan, B. V. O'Grady, L. Lain and C. Fotakis, *J. Chem. Phys.*, *76* (1983) 3727.
9 L. C. Glasgow and J. E. Willard, *J. Phys. Chem.*, *77* (1973) 1585.
10 T. A. Gover and J. E. Willard, *J. Am. Chem. Soc.*, *82* (1960) 3816.
   G. M. Harris and J. E. Willard, *J. Am. Chem. Soc.*, *76* (1954) 4678.
11 J. A. Myer and J. A. R. Samson, *J. Chem. Phys.*, *52* (1970) 716.
12 R. D. Chambers, W. K. R. Musgrave and J. Savory, *J. Chem. Soc.*, (1961) 3779.
13 J. C. Amphlett and E. Whittle, *Trans. Faraday Soc.*, *64* (1968) 2130.
14 A. J. Ferrer-Correia and K. R. Jennings, *Int. J. Mass Spectrom. Ion Phys.*, *11* (1973) 111.
15 D. R. Stull and H. Prophet (eds.), JANAF thermochemical tables, 2nd edn., *NBS Natl. Stand. Ref. Data Ser. 37*, 1971 (National Bureau of Standards, U.S. Department of Commerce).
16 G. Herzberg, *Molecular Spectra and Molecular Structure*, Vol. 3, Van Nostrand, New York, 1966.
17 K. Glänzer, M. Maier and J. Troe, *J. Phys. Chem.*, *84* (1980) 1683.
18 B. S. Evans and E. Whittle, *Int. J. Chem. Kinet.*, *13* (1981) 59.
19 E.-C. Wu and A. S. Rogers, *J. Am. Chem. Soc.*, *98* (1976) 6112.
20 A. B. Callear, P. Erman and J. Kurepa, *Chem. Phys. Lett.*, *44* (1976) 599.
21 M. Diegelmann, *Thesis*, University of Munich, 1980.
22 V. S. Kushawaha, *Chem. Phys. Lett.*, *72* (1980) 451; *J. Am. Chem. Soc.*, *102* (1980) 256.
23 P. John, G. J. Kennedy and B. G. Gowenlock, *J. Chem. Soc., Chem. Commun.*, (1973) 683.