433

YIELDS AND QUENCHING OF I($5^2P_{1/2}$) FOLLOWING PHOTODISSOCIATION OF C_6H_5I AND C_6F_5I

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Summary

The yields of electronically excited iodine atoms I($5^2P_{1/2}$) following the UV photodissociation of C_6H_5I and C_6F_5I have been studied using time-resolved atomic absorption spectrophotometry. The yields are shown to be low and spin–orbit relaxation by both molecules is rapid ($k(C_6H_5I) = (5.2 \pm 0.4) \times 10^{-13}$, $k(C_6F_5I) = (2.1 \pm 0.2) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}). The suitability of C_6H_5I and C_6F_5I as photochemical laser materials is discussed.

1. Introduction

The first photochemical laser [1], reported in 1964, was based on the UV photodissociation of CF_3I. Since then a wide range of alkyl and perfluoroalkyl iodides have been shown to give rise to laser action [2 - 4] (1.315 μm) following photodissociation. These studies have stimulated considerable interest in the photodissociation dynamics of organic iodides, and they have probably been studied in more detail than any other single class of molecules. Among the most detailed studies are those of Riley and Wilson [5] using photofragment spectroscopy and Dzvonik *et al.* [6] who examined the anisotropy in the angular distribution of the photofragments. A review of this area has recently been given by Simons [7].

The aryl iodides, unlike the alkyl iodides, exhibit more than one region of continuous absorption in the UV ($\lambda > 200$ nm). Dzvonik *et al.* [6] have studied photodissociation in the first continuum ($\lambda_{max} \approx 254$ nm) and have obtained information on the orientation of the electronic transition moment and the lifetime of the photodissociating state. However, no direct information on the partitioning of electronic energy in the iodine atom fragment could be derived. The second continuum ($\lambda_{max} \approx 226$ nm) is of much greater intensity (about 20 times greater than that of the first) and is generally assigned to an n → π^* transition. The third continuum ($\lambda_{max} \approx 207$ nm) is weaker by a factor of 2 compared with the second continuum and is not

expected to be of any significance in the present work (the output from our flash lamp falls rapidly in this region). No information on the photochemistry of the aryl iodides in the second and third continua exists; however, as fluorescence is not observed photodissociation is the most likely result of excitation in these regions.

The higher extinction coefficient of the aryl iodides compared with the alkyl iodides offers some advantages for their use in photochemical laser systems, principally because the laser could be operated at lower pressure where quenching of the excited state would be less important. However, the yield of $I(5^2P_{1/2})$ is clearly of prime importance and the present work was undertaken to establish this. Data for quenching of $I(5^2P_{1/2})$ by C_6H_5I and C_6F_5I are also reported.

2. Experimental

The experimental arrangement employed for time-resolved atomic absorption spectrophotometry has been described previously [8, 9]. C_6H_5I (BDH, laboratory reagent grade) and C_6F_5I (Imperial Smelting) were thoroughly degassed before use. Their purity was checked using mass spectrometry and infrared analysis. No significant level of impurity was observed. Reagent pressures were measured using an MKS Baratron pressure gauge (type 221; range $0.1 - 10^3$ N m^{-2}). Absorption spectra for C_6H_5I and C_6F_5I were recorded using a Perkin–Elmer 137 UV spectrophotometer.

3. Results

Photolysis of C_6H_5I and C_6F_5I gave rise to readily observable concentrations of $I(5^2P_{1/2})$, and quenching data were obtained by monitoring the decay of the excited atom in absorption ($\lambda = 206.2$ nm) as a function of time following photolysis of the parent molecule. Both iodides were mixed with excess N_2 to maintain isothermal conditions; typical conditions were $P(RI) = 13.3$ N m^{-2}, $P(N_2) = 2.3$ kN m^{-2}. The decays were found to be first order in every case, plots of $\ln[I(5^2P_{1/2})]$ against time being linear, allowing absolute rate data to be obtained from relative concentration measurements. First order rate coefficients, determined over a range of iodide pressures, were plotted against the partial pressure of the iodide to yield second order quenching constants [9]. These data were corrected for the small departure from the Beer–Lambert relation, as described previously (γ was taken as equal to 0.82) [9]. The quenching data for C_6H_5I and C_6F_5I, together with data reported previously [3, 10, 11] for C_6H_6, C_6D_6, CF_3I and CH_3I, are presented in Table 1.

The yields of $I(5^2P_{1/2})$ from C_6H_5I and C_6F_5I were compared with that from CH_3I (for which the yield $[I(5^2P_{1/2})]/([I(5^2P_{1/2})] + [I(5^2P_{3/2})])$) has been measured previously [12] as 0.92 ± 0.02). Yields of $I(5^2P_{1/2})$ were com-

TABLE 1

Quenching data for $I(5^2P_{1/2})$

Quenching molecule	Rate constant k (cm^3 molecule^{-1} s^{-1})	Reference
C_6H_5I	$(5.2 \pm 0.4) \times 10^{-13}$	This work
C_6F_5I	$(2.1 \pm 0.2) \times 10^{-13}$	This work
C_6H_6	$(4.6 \pm 0.7) \times 10^{-13}$	10
C_6D_6	$(9.9 \pm 1.0) \times 10^{-15}$	10
CH_3I	$(2.6 \pm 0.6) \times 10^{-13}$	3
CF_3I	$<3.5 \times 10^{-16}$	11

pared over a range of pressures such that the samples were optically thin to the radiation from the flash lamp (*i.e.* the percentage absorption was low (not more than 10%) and thus uniform across the reaction vessel).

The observed concentrations of $I(5^2P_{1/2})$ from C_6H_5I and C_6F_5I were found to be greater (by factors of 2.6 and 1.3 respectively) than that from CH_3I when the same pressure of each iodide was photolysed. However, these observed concentrations must be corrected for the difference in integrated absorption by the three iodides. For equal pressures of the iodides, under optically thin conditions, the degree of photolysis is proportional to the integrated absorption. The corrected yields of $I(5^2P_{1/2})$ from C_6H_5I and C_6F_5I were found to be 0.25 and 0.1 respectively.

The absorption spectrum for C_6H_5I determined in the course of this work was compared with earlier work [6] and was found to agree quantitatively where the results overlapped ($\lambda \geqslant 230$ nm). C_6F_5I was found to be a stronger absorber than C_6H_5I but the overall features and the positions of the absorption continua were similar.

4. Discussion

4.1. Removal mechanism for $I(5^2P_{1/2})$

Abstraction of an iodine atom from C_6H_5I by $I(5^2P_{1/2})$ to yield I_2 can be ruled out on thermochemical grounds. The C_6H_5—I bond strength has been reported [13] as 266.3 ± 4.8 kJ mol^{-1}, which would make the abstraction channel endothermic by 22.6 kJ mol^{-1}. The C—I bond strength in C_6F_5I is even greater [14], 277 kJ mol^{-1}, and abstraction can again be ruled out.

We have recently shown [10] that quenching of $I(5^2P_{1/2})$ by C_6H_6 proceeds with a rate constant $k = (4.6 \pm 0.7) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}, which is very close to that for C_6H_5I determined here (see Table 1). The quenching mechanism in the case of C_6H_6 was thought to involve the formation of a charge transfer complex (direct spectroscopic evidence for a charge transfer complex between $I(5^2P_{3/2})$ and C_6H_6 has been presented), and

we might expect a similar type of complex to be formed with C_6H_5I also. We propose therefore that quenching of $I(5^2P_{1/2})$ by C_6H_6 and C_6H_5I proceeds by a similar mechanism, a detailed discussion of which is given in ref. 10.

Quenching of $I(5^2P_{1/2})$ by C_6F_5I is remarkably efficient when compared with perfluoro-alkyliodides (see Table 1). While the ionization potential of C_6F_5I is similar to that of C_6H_5I, and the formation of a charge transfer complex is similarly favourable, we would not expect quenching to be nearly so efficient. Quenching of $I(5^2P_{1/2})$ by C_6D_6 is very much less efficient than C_6H_6 $(k(C_6H_6)/k(C_6D_6) \approx 50)$ despite having a closely similar ionization potential [10]. It has been suggested that this difference in quenching efficiency is due to the larger number of vibrational quanta that must be excited in C_6D_6, compared with C_6H_6, in the E → V transfer process. We should therefore expect C_6F_5I to be even less efficient than C_6D_6 on this basis (the highest frequency mode in C_6F_5I is about 1500 cm^{-1} compared with about 2300 cm^{-1} for C_6D_6). The high efficiency for quenching by C_6F_5I is not readily explicable at the present time. The presence of an efficient quenching impurity was considered, but no evidence could be found from the mass spectral and infrared analyses. The sample we used was clear and colourless and the presence of molecular iodine can be ruled out.

4.2. Yield of $I(5^2P_{1/2})$

The present results clearly show that, while the observed concentrations of $I(5^2P_{1/2})$ following the broad band UV photolysis of C_6H_5I and C_6F_5I are high, population inversions are not produced. It is possible, however, that population inversions could be produced by photolysis over a limited wavelength range and we therefore give brief consideration to excitation in the first and second continua.

The photodissociation of C_6H_5I in the first continuum (λ_{max} = 254 nm) has been studied in detail by Dzvonik et al. [6]. They have shown that the transition moment lies along the C—I bond and that the lifetime in the excited state, about 5×10^{-13} s, is an order of magnitude larger than that for CH_3I. A factor of 2 only would be expected on the basis of increased mass and it was suggested therefore that a predissociative mechanism is involved. It was proposed that initial excitation occurred to a $\pi*$ orbital on the aromatic ring, followed by predissociation onto a repulsive $(\pi - \sigma*)$ surface induced by the large spin—orbit coupling on the iodine atom. The final dissociative $\sigma*$ state may be considered as analogous to that in CH_3I and should therefore lead to the formation of $I(5^2P_{1/2})$ with a population inversion. The present results are consistent with this proposal, provided that a sizable fraction of the observed $I(5^2P_{1/2})$ results from photolysis in the first continuum. Further work using cut-off filters will, however, be required to establish this. Photolysis of C_6F_5I in the first continuum is expected to be entirely analogous to that of C_6H_5I.

Photolysis of C_6H_5I and C_6F_5I in their second continua ($\lambda_{max} \approx$ 230 nm) must lead predominantly to ground state atoms. The excited state involved in this transition is thought to result from the interaction between

the dπ orbital in iodine and the π orbital of the benzene ring. Clearly this excited state must be predissociated to yield mainly ground state atoms and the predissociating state (or states) must cross the σ^* state discussed above. Branching at this crossing, with a low probability, may be responsible for the low yield of $I(5^2P_{1/2})$.

4.3. Photochemical laser applications

Considering all the information available on the photodissociation of C_6H_5I in the long wavelength continuum ($\lambda_{max} = 254$ nm), it seems likely that a population inversion could be produced provided that the output from the flash lamp was restricted to λ greater than 245 nm by using a suitable filter. However, the yield of $I(5^2P_{1/2})$ is not the only consideration. For the construction of an efficient photochemical laser system the rate of quenching of the excited state by the parent molecule is also of considerable significance. We have previously shown that the output characteristics of the CH_3I and CD_3I photochemical laser systems are markedly different [3], owing mainly to the large difference in quenching efficiency between the two molecules. Furthermore, the preferred use of the highly efficient perfluoro-alkyliodides as laser materials stems mainly from their low quenching efficiency.

To some extent the problems associated with quenching can be overcome by increasing the rate of photochemical pumping; however, conventional high energy flash photolysis techniques have now effectively reached a limit with capacitor and plasma characteristics determining the pump rate. The use of Q-switched lasers improves the pump rate significantly but lowers the overall efficiency of the system and greatly increases the costs.

C_6H_5I and C_6F_5I would thus appear to be of little value for use as photochemical laser materials because of both their low yields of excited iodine atoms (following broad band photolysis) and their high quenching efficiencies.

Acknowledgments

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