Short Communication

Photodissociation of ICN

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Several detailed studies of the energy partitioning in the photodissociation of polyatomic molecules have recently been made and are of relevance in establishing the nature of continuous electronic spectra of such molecules, as well as being of fundamental importance to photochemistry and hot radical chemistry. The molecular dynamics of the photodissociation of cyanogen iodide have been examined by a number of workers[1-7], and relatively detailed information now exists concerning the energy distribution in the primary fragments following absorption of radiation over a range of wavelengths. Jakovleva[2] demonstrated that the CN radical was formed in the $B^2\Sigma^+$ state when ICN was photolyzed in the second region of continuous absorption ($\tilde{a} \leftarrow \tilde{X}$), and Okabe *et al.*[3] have recently extended these observations and thereby determined the bond strengths and heats of formation of a number of cyanogen compounds. Norrish *et al.*[4] have shown that the CN radicals formed by photodissociation in the longest wavelength continuum, ICN ($\tilde{A} \leftarrow X$) are predominantly in the zero vibrational level of the ground electronic state and that secondary absorption by the CN radical ($B^2\Sigma^+ \leftrightarrow X^2\Sigma^+$) was responsible for the vibrational excitation observed under flash photolysis conditions. Wilson[5], has given a preliminary report on the use of "translational spectroscopy" to examine the primary photochemical process and confirms the results of Norrish *et al.*[4]. Wilson *et al.*[6], have further presented a detailed theoretical model using classical mechanics for the photodissociation of ICN and more recently, Shapiro and Levine[7] have given a quantum mechanical treatment; these studies indicate that very little of the recoil energy ($\sim 4\%$) will appear in rotation. However, despite the detailed information relating to the energetic state of the CN radical, little comment has been made on the spin orbit state of the iodine atom. The higher of the spin orbit multiplets ($5^2P_{1/2}$) possesses 0.93 eV of electronic energy relative to the "ground state" ($5^2P_{3/2}$) and thus the translational energy possessed by the CN radical will depend on the electronic state of the iodine atom. This could clearly be of importance in classical photochemical studies where the effects of translational energy and "hot" radical reactions may be conveniently studied. Furthermore, the electronic state of the iodine atom is of

intrinsic interest as a number of atomic photodissociation lasers, based on light amplification from the forbidden transition between the spin orbit multiplets of the halogen atoms, have now been reported[8]. This communication reports the direct observation of the electronic state of the iodine atom formed by photodissociation of the ICN in the $(\tilde{A} \leftarrow \tilde{X})$ system and indicates that this molecule may provide a source of translationally hot CN radicals with kinetic energies in the range 0.8–2.3 eV (the lower limit is only approximate, being governed by the rapidly decreasing extinction coefficient towards longer wavelengths).

The apparatus was similar to that described previously[9] and employed a 1 m vacuum ultra-violet spectrograph, which permitted observations in the region of 250–120 nm. The reaction vessel was 30 cm in length (18 mm i.d.) and constructed of Vitreosil quality quartz. The flash lamp was constructed of the same material and dissipated *ca.* 800 J, with a flash duration (τ_e) of 30 μsec. Photolysis was thus restricted to $\lambda \gtrsim 200$ nm. The ICN was prepared by addition of excess KCN solution $(2M)$ to a continuously stirred suspension (saturated solution) of powdered I_2 in distilled water (both reagents were A. R. grade). The precipitated ICN was extracted with diethyl ether, the extract dried over anhydrous calcium sulphate, filtered and the ether removed under vacuum. The ICN was degassed by trap-to-trap sublimation under vacuum. The vacuum ultra-violet spectrum of the ICN prepared in this manner was identical to that reported by King and Richardson[10] and the absence of any new features established the purity of the sample (in particular the absence of I_2 for which an upper limit of 0.5% could be established).

The isothermal flash photolysis of ICN was investigated over a range of partial pressures $P_{ICN} = 41$–4 N m^{-2} in the presence of spectroscopically pure argon (B.O.C.) as diluent gas $(P_{Ar} = 40$ kN m$^{-2})$. Typically 10% photolysis was achieved by the flash (800 J) and a strong spectrum of atomic iodine could be observed for several milliseconds, being replaced at longer times by a strong spectrum of I_2 (Fig. 1). Iodine atoms were formed predominantly in the lower of the spin orbit states $(5^2P_{1/2})$ associated with the ground electronic configuration; however, for the highest pressures of ICN employed, a weak spectrum of the $(5^2P_{1/2})$ atom could be observed (179.9 nm); the decay of the $^2P_{1/2}$ state was relatively slow $(\tau_e \simeq 1$–2 msec) and by monitoring the decay in the presence of different partial pressures of ICN, the efficiency for spin orbit relaxation was determined as $(8.2 \pm 1.0) \times 10^{-14}$ cm^3 molecule^{-1} sec^{-1} in agreement with the approximate value given previously by Hathorn and Husain[11]. Using our value for the efficiency of spin orbit relaxation, the relative concentration of $I(5^2P_{1/2})$ at zero time could be calculated and thus by comparing the intensities of the atomic lines at 179.9 nm and 183.0 nm and using the line strengths calculated by Lawrence[12], an upper limit for the yield of $I(5^2P_{1/2})$ atoms was established as $\leqslant 5\%$. This value is quoted as an upper limit as $I(5^2P_{1/2})$ may result from a small extent of photolysis in the $(\tilde{a} \leftarrow \tilde{X})$ system which commences at 210 nm.

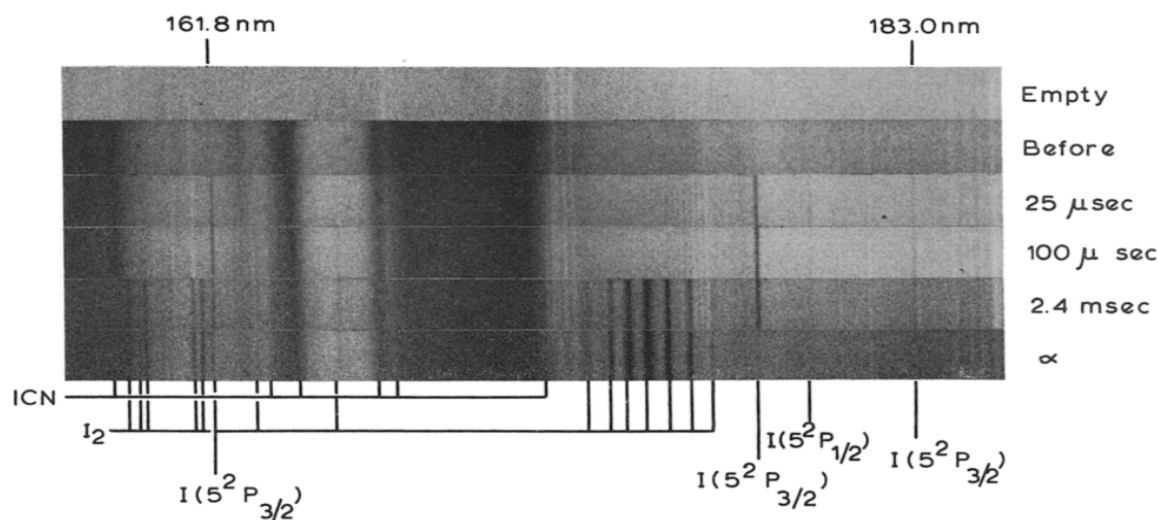The ultra-violet and vacuum ultra-violet spectrum of ICN has been reported

Fig. 1. The formation and decay of atomic iodine in the photolysis of ICN (P_{ICN} = 41 N m^{-2}, P_{Ar} = 40 kN m^{-2}; E = 800 J).

and discussed by King and Richardson[10], who assigned the $(\tilde{A} \leftarrow \tilde{X})$ continuum to a transition involving the promotion of an electron from the $n\,p\pi$ molecular orbital to the $n\,p\sigma^*$ orbital (both mainly localized on the halogen atom). The latter orbital is C–I anti-bonding and the absence of structure under high resolution indicates that the potential surface is repulsive. The theoretical treatment by Wilson et al.[6] using classical mechanics and the quantum mechanical treatment of Shapiro et al.[7], both make the assumption that only one upper electronic state is involved. However, it is well known that the first region of continuous absorption for HI and the alkyl iodides involves two states[13], one correlating with $I(5^2P_{3/2})$ and the other with $I(5^2P_{1/2})$. Furthermore there does not appear to be a reliable method for predicting the extent to which each state contributes to the continuum at a given wavelength and it is therefore necessary to determine this experimentally. The present results demonstrate that the "single state" assumption made in the theoretical treatments is, in fact, valid for ICN.

In conjunction with all the previous evidence, the present results indicate that CN radicals may be formed with a narrow range of kinetic energies by photolysis of ICN using monochromatic radiation. The energy available to the recoiling photofragments is expected to go predominantly (86%) into translation[4,6], with the CN radical taking over 80% of this. Thus it may be possible to form translationally 'hot' CN radicals with energies in the range 0.8–2.3 eV. A small uncertainty ($\pm 7\%$) in this energy due to the small fraction of energy which may appear as vibration and rotation of CN, is unlikely to be of importance in experimental investigations. We are currently extending the present work to examine the chemical behaviour of translationally hot CN radicals.

G. Hancock and K. R. Wilson have recently informed us that their latest work on the photofragment spectrum of ICN indicates that the CN radical receives relatively little translational energy. They suggest that the CN radical may be formed in the $A^2\pi$ state, contrary to the assignment made by King and Richardson[10].

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