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Chemical Reactions of Excited Iodine Atoms

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Summary Measurements of the methyl iodide quantum yield from the photolysis of I_2–CH_4 mixtures at 147·0 nm suggest that $I(^4P_{5/2})$ atoms are important intermediates in this system.

The advent of sophisticated spectroscopic techniques has resulted in the extensive tabulation of rate data for the collisional deactivation of electronically excited atoms.[1] Studies of the higher spin–orbit multiplet of the ground state np^5 electronic configuration of halogen atoms have been of particular importance.

Electronically excited $I(^2P_{1/2})$ atoms possess 90·8 kJ of energy above the lower multiplet and hence the rates of chemical reaction are enhanced and in certain cases are comparable to the competing spin-orbit relaxation process. Callear and Wilson[2] have employed this fact to study hydrogen atom abstraction from a series of alkanes by $I(^2P_{1/2})$ produced from the photolysis of I_2 in the B–X continuum. Chemical analysis of the corresponding alkyl iodide allowed relative rate data for chemical reaction and collisional deactivation to be determined. The results were in general agreement with data derived from direct spectroscopic observation of the $I(^2P_{1/2})$ atom. Accurate rate data were not obtained for the simplest reaction [equation (1)]

$$I(^2P_{1/2}) + CH_4 \rightarrow HI + CH_3 \qquad (1)$$

since the endothermicity of the reaction prevents effective competition with the corresponding collisional deactivation process.

In the present work methyl iodide has been identified by gas chromatography as the sole gaseous product arising from the photolysis of methane–iodine mixtures at 147·0 nm. No dark reaction was observed under the same experimental conditions. Similarly no dark reaction occurred in mixtures containing small amounts of methyl iodide. Methane was not photolysed at this wavelength, in agreement with the published value of the extinction coefficients in the vacuum ultraviolet. A quartz window attached to the LiF window of the resonance lamp reduced the methyl iodide yield to $< 5\%$ of the standard experiments.

Our analytical data show that the methyl iodide quantum yield for the photolysis of 46·55 kN m^{-2} of CH_4 and 0·035 kN m^{-2} of I_2 was 0·31 ± 0·04 at 330·0 K. The light output of the xenon resonance lamp was determined to be $2{\cdot}5 \pm 0{\cdot}2 \times 10^{14}$ q s^{-1} by CO_2 actinometry.

An estimate of the activation energy (55 kJ mol^{-1}) for H abstraction by $I(^2P_{1/2})$ from methane, combined with the equivalent collisional relaxation rate data, indicates that the relative rate of the quenching to abstraction reaction is 5×10^6 at 303 K.

Purely on energetic considerations, a prerequisite for the observation of H atom abstraction from methane would be the formation of an excited $I(6s^4P_J)$ atom. Reaction (2) is energetically possible. Population of the higher $I(^4P_J)$

$$I_2(X'\Sigma_g^+) + h\nu(147{\cdot}0\ \text{nm}) \rightarrow I(5p^5, {}^2P_{1/2}) + I(6s, {}^4P_{5/2}) \qquad (2)$$

multiplet states is energetically barred, even if vibrational excitation of the ground state I_2 is considered. In view of the direct evidence of Bemand and Clyne[3] that $Br(5s, {}^4P_{5/2})$ and $Br(5s, {}^4P_{3/2})$ are produced during the photolysis of Br_2 at 121·6 nm and 123·6 nm it seems reasonable to suppose that the formation of methyl iodide in the present study occurs *via* the reactions of the $I(^4P_{5/2})$ state.

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