# Reactions of Excited Atomic Iodine $(5^2P_{\frac{1}{2}})$

Part 4.--Reaction with n-Butane and Methane

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The kinetics of the photochemical formation of butyl iodides in mixtures of  $n-C_4H_{10}$  and  $I_2$ , in the range 303 to 373 K, were shown to be consistent with H atom abstraction by  $I(5^2P_{\frac{1}{2}})$ . Rate coefficients were determined relative to deactivation of  $I(5^2P_{\frac{1}{2}})$  by molecular iodine, and the activation energy for secondary H atom abstraction was reported to be  $23.2(\pm 1.25)$  kJ/mol. The activation energy for H atom abstraction from CH<sub>4</sub> was recorded as  $\geq 55$  kJ/mol. For the interpretation of rate measurements in the range 303 to 373 K, the temperature variation of the extinction coefficients of  $I_2$  vapour was examined.

In parts 1 and 2<sup>1, 2</sup> it was established that the production of alkyl iodides, on irradiation of iodine with visible light in the presence of  $C_2H_6$ , and  $C_3H_8$ , is due to H atom abstraction by excited atoms,  $I(5^2P_{\frac{1}{2}})$ . The kinetics of product formation were similar on both sides of the 4985 Å convergence limit of the B-X system which is the energy threshold for direct photochemical formation of  $I(5^2P_{\frac{1}{2}})$ .<sup>3</sup> It was proposed that release of  $I(5^2P_{\frac{1}{2}})$  from bound vibrational levels of  $I_2B^3\Pi_{uo^+}$  occurs by uptake of energy in collisions. Direct spectroscopic observation of excited atoms following flash photolysis of  $I_2$  at wavelengths greater than 4985 Å conclusively demonstrated the occurrence of some such process.<sup>4</sup> Further support for endothermic production of  $I(5^2P_{\frac{1}{2}})$  has been reported by Steinfeld *et al.*<sup>5</sup>

Described here is an extension of the earlier studies to mixtures of iodine with  $n-C_4H_{10}$  and  $CH_4$ . Fettis and Knox<sup>6</sup> have shown that the activation energy for H atom abstraction by halogen atoms from hydrocarbons is, to a good approximation, a unique function of the internal energy change. Accordingly the activation energies for secondary H atom abstraction from  $n-C_4H_{10}$  or  $C_3H_8$  by  $I(5^2P_4)$  would be expected to be of similar magnitude (~21 kJ/mol) whilst the activation energy for H atom abstraction from  $CH_4$  is expected to be considerably larger (~63 kJ/mol). Reaction between iodine and  $CH_4$ , induced by visible light, is known to be much slower than with  $C_3H_8$  at ambient temperature.<sup>7, 8</sup> It has been suggested <sup>2</sup> that H atom abstraction by  $I(5^2P_4)$  might occur in part via a transition to the lower  $I(5^2P_{\frac{1}{2}})$ —RH potential hypersurface, the effect of which on the rates should be largest at high reaction endothermicities.

A prerequisite for the determination of the activation energies in this system is a knowledge of the change of the extinction of iodine vapour with temperature. The variation between 420 and 1320 K was investigated by Sulzer and Wieland<sup>9</sup> and our experiments were designed to examine the validity of their equation in the 300-400 K range.

#### EXPERIMENTAL

The apparatus employed for the photochemical experiments was as described in Part 1.<sup>1</sup> In system A a cylindrical reaction cell was irradiated with a parallel beam of light for use

with interference (narrow band) or neutral density filters. Other experiments were performed in systems B and C (duplicate sets) in which light from a 1000 W quartz-iodine-lamp was filtered through  $CuSO_4$  solution and a broad band gelatin filter (Ilford 502) to limit photolysis to the iodine continuum below 4985 Å.

After photochemical reaction, a preliminary separation of the reaction products from the excess  $C_4H_{10}$  or  $CH_4$  was achieved with a low temperature distillation. The alkyl iodides were analyzed by gas chromatography, on columns packed with 60/80 mesh firebrick containing 10 % w/w of squalane. The unit of calibration was a quantity of vapour in a fixed volume in equilibrium with the alkyl iodides at 195 K.

The extinction of iodine vapour at various temperatures was measured by passing a parallel beam of light from a tungsten ribbon lamp through a cylindrical cell onto the slit of a Hilger constant deviation spectrograph. Transmitted light was detected with an R.C.A. photomultiplier and millivoltmeter. The slit aperture was adjusted so that the detector received light over a 25 Å band width. Iodine crystals were thermostatted at 293 K in a wide bore side-arm, other gases being added to pressure broaden the absorption above 5000 Å. The uncertainty in the photomultiplier readings due to noise and drift was  $\pm 0.4$  %; the corresponding errors in individual values of  $(I_0 - I)/I_0$  ( $I_0$  = incident and I = transmitted intensity) varied between  $\pm 3$  % at 5100 Å and  $\pm 30$  % at 4400 Å. Temperatures were controlled to  $\pm 0.2$  K.

Phillips research grade  $n-C_4H_{10}$  (99.99 %) was thoroughly degassed. Matheson CH<sub>4</sub> (99.99 %) was stored over reduced copper at 500 K to remove traces of O<sub>2</sub>.

#### RESULTS

## EXTINCTION OF IODINE VAPOUR BETWEEN 4400 AND 5600Å

In the banded region of the B—X system the absorption increases with added gas pressure because of line broadening.<sup>10, 11</sup> The effect tends to saturate with added gas/iodine ratios in excess of  $30.^{12}$  Therefore at least 100 Torr\* of a hydrocarbon or He was added to 0.20 Torr of I<sub>2</sub> for all the extinction coefficient measurements to realise conditions similar to those in the photochemical experiments. However the absorption recorded at 333 K with 100 Torr of added He was about 20 % less than with propane as the broadening gas, both above and below the 4985 Å convergence limit. The difference was attributed to a pronounced thermal diffusion effect in the experiments with He, due to the heavy I<sub>2</sub> diffusing preferentially to the cooler side-arm (293 K); the iodine extinction measured with the absorption cell at 300 K was independent of the nature of the pressure broadening gas; with the cell at 333 K the intensity of the continuum below 4985 Å with 100 Torr of added C<sub>3</sub>H<sub>8</sub> was indistinguishable from that without added gas. Further investigation of the effect of thermal diffusion showed it to be insignificant for the reaction mixtures employed in all the photolysis experiments.

At constant pressure, the total light absorption decreased with increasing temperature due to the corresponding drop in iodine concentration. Simultaneously the maximum extinction coefficient decreased from  $710(\pm 5)$  l. mol<sup>-1</sup> cm<sup>-1</sup> at 293 K (~5170 Å) to  $650(\pm 10)$  l. mol<sup>-1</sup> cm<sup>-1</sup> at 373 K (~5200 Å). The measurements were not sufficiently precise to describe quantitatively the broadening of the absorption with increasing temperature, but were adequate to test the Sulzer and Wieland relation below 400 K.

The maximum value of the extinction coefficient reported by Rabinovitch and Wood <sup>10</sup> (~295 K) is 830 l. mol<sup>-1</sup> s<sup>-1</sup>, which differs from the present observations. In their research there is uncertainty about the vapour pressure employed. Iodine was distilled into the cell at " about 19°C", but the pressure recorded was 0.157 Torr,

\* 1 Torr  $\equiv$  133.3 Nm<sup>-2</sup>

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which is not appropriate to 292 K (v.p.  $\sim 0.187$  Torr <sup>13, 14</sup>). Multiplied by 0.157/ 0.187, the extinction coefficients of Rabinovitch and Wood agree well with those presented here. A disparity with the measurements of Rabinovitch and Wood was also noted by Marshall and Davidson <sup>15</sup> and the three sets of data are compared in table 1.

Table 1.—" Room temperature " extinction coefficients of iodine vapour between 5600 and 4600 Å

λ (Å)	Rabinowitch and Wood <sup>9</sup> (reported)	Rabinowitch and Wood (corrected)	Marshall and Davidson 14	this work (303 K)
4600	200	170		215(±20)
4700	300	250		315(±20)
4800	440	370		420(±20)
4900	620	520	478	545(±20)
4980	750	630	580	$640(\pm 20)$
5000	770	645	—	660(±20)
5100	820	690	700	705(±20)
5200	830	700	751	710(±20)
5300	810	680		655(±20)
5400	740	620		645(±20)
5500	650	545		555(±20)
5600	540	450	<b>49</b> 0	440(±20)

Sulzer and Wieland <sup>9</sup> demonstrated an excellent fit between their measurements and a relationship of the form  $\varepsilon_T = k B(T, \lambda)$ , where  $B(T, \lambda)$  is a Gaussian with temperature dependent height and half-width. Our measurements of the continuous absorption at 303, 333 and 373 K were consistent with this function after a small (+4 %) adjustment to their value of k, as shown for example in fig. 1. The adjustment of k does not significantly impair the fit to their own results at higher temperatures. The computed extinction-coefficients at 303 and 373 K are depicted in fig. 2.



FIG. 1.—Percent absorption by 0.20 Torr I<sub>2</sub> vapour at 333 K. (150 mm path length.) Points are experimental results; the curve was computed from the semi-empirical expression of Sulzer and Wieland.<sup>9</sup>  $\bullet$ , I<sub>2</sub>+added C<sub>3</sub>H<sub>8</sub>;  $\bigcirc$ , I<sub>2</sub> alone.

Relative light absorptions  $(I_a)$  in reaction system A at 303, 333 and 373 K were calculated by graphical integration.

$$I_a \propto \int_{\lambda} I_0(\lambda) F(\lambda) (1 - \exp\left[-\varepsilon c l\right]) d\lambda.$$

 $F(\lambda)$  is the filter transmission and  $I_0(\lambda)$  the energy-wavelength distribution of the quartz-iodine-lamp-source for a black body temperature of 3000 (±100) K, measured by optical pyrometry. Coincidentally, with the Ilford 502 filter the relative total absorptions per unit concentration were found to be independent of temperature (~0.1 %). The decrease in extinction above 4700 Å with increasing temperature is almost exactly offset by the increase below 4700 Å.



FIG. 2.—Computed wavelength dependence of extinction coefficient of the I<sub>2</sub> absorption, at 303 K (solid curve) and 373 K (dashed curve)

#### REACTION OF $I(5^2P_{\frac{1}{2}})$ WITH n-BUTANE

The products formed in irradiated  $I_2/n-C_4H_{10}$  mixtures were identified by gas chromatography as 2- and 1-butyl iodides, with the former predominating to the extent of ~30:1. The product yields were proportional to the exposure duration at 303 and 373 K. The yields were shown to be accurately proportional to the first power of the light intensity by irradiation through neutral filters.

To demonstrate that excited rather than ground state atoms are responsible for reaction, the rate of butyl iodide formation was compared in experiments with interference filters transmitting at  $5020(\pm 15)$  Å and  $5330(\pm 35)$  Å. The quantum yield of 2-butyl iodide formation was a factor of 7 smaller at 5330 Å whereas the total yields of the free atoms are very nearly the same at both wavelengths.<sup>16</sup> This observation was consistent with the reported wavelength dependence of the quantum yield for collisional release of excited atoms.<sup>1</sup>

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The evidence detailed above indicates that the reaction mechanism is analogous to that established for irradiated mixtures of  $I_2$  and  $C_3H_8$ , viz.

$$I_2 + hv \rightarrow I^* + I$$

$$I^* + RH \rightarrow R + HI$$
(2)

$$R + I_2 \rightarrow RI + I \tag{3}$$

$$\mathbf{I}^* + \mathbf{I}_2 \to \mathbf{I} + \mathbf{I}_2 \tag{4}$$

$$\mathbf{I}^* + \mathbf{R}\mathbf{H} \to \mathbf{I} + \mathbf{R}\mathbf{H} \tag{5}$$

$$\mathbf{I} + \mathbf{I} + \mathbf{M} \to \mathbf{I}_2 + \mathbf{M}. \tag{6}$$

Therefore the butyl iodide quantum yield,  $\Phi_{RI}$ , is given by

$$[\Phi_{\rm RI}]^{-1} = (k_4[\rm I_2] + k_5[\rm RH])/\beta k_2[\rm RH]$$

since  $k_2 \ll k_5$ .  $\beta$  is the quantum yield for I(5<sup>2</sup>P<sub>4</sub>) formation.

The quantum yields for production of butyl iodides were measured by comparison with the rate of propyl iodide formation in 100 Torr of  $C_3H_8$  and 0.20 Torr of  $I_2$  at 333 K, for which the absolute quantum yield was determined by Callear and Wilson to be  $1.51(\pm 0.20) \times 10^{-4}$ . Whence the quantum yield of 2-butyl iodide formation in 50 Torr of  $n-C_4H_{10}$  and 0.20 Torr of  $I_2$  was recorded as  $0.795(\pm 0.05) \times 10^{-4}$  at 303 K and  $3.00(\pm 0.15) \times 10^{-4}$  at 373 K. The quoted error limits do not include the uncertainty in the absolute quantum yield for propyl iodide formation.



Fig. 3.—Variation of the reciprocal quantum yield of 2-butyl iodide formation with the reciprocal n-butane pressure for photolysis of 0.201 Torr of  $I_2$  in the continuum.  $\bigcirc = 303$  K;  $\bigcirc = 333$  K;  $\bigcirc = 373$  K.

In fig. 3 reciprocal quantum yields for 2-butyl iodide formation at 303 and 373 K are plotted against reciprocal n-C<sub>4</sub>H<sub>10</sub> pressure. The points shown are the mean of about three individual measurements with a particular temperature and pressure. A few measurements were also made at 333 K. The slopes and intercepts of fig. 3 yield relative rate coefficients for relaxation and reaction of  $I(5^2P_1)$  which are compared in table 2 with those previously determined for C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub>. In fig. 3, the

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line drawn through the 333 K results corresponds to Arrhenius parameters derived from the 303 and 373 K data. The original results have been corrected for the variation of the iodine extinction with temperature and adjusted to  $\beta = 0.5$  instead of  $\beta = 1$  which was assumed previously. (Oldman *et al.*<sup>17</sup> have shown that part of the iodine continuum below 4985 Å arises from a transition to a 1*u* state, correlating with two  $I(5^2P_{\frac{3}{2}})$  atoms. Callear and Wilson's absolute quantum yield measurement was conducted with light of wavelength 4830 Å and it now appears that the true yield of  $I(5^2P_{\frac{1}{2}})$  is close to 0.5 at this wavelength. The *A* factors will require correction when the precise quantum yield is known. The activation energies are independent of the quantum yield.)

TABLE	2.—Rate	COEFFICIENTS	FOR	REACTION	AND	RELAXATION	OF	$I(5^2 P_{\frac{1}{2}})$	RELATIVE	TO
COLLISIONAL DEACTIVATION BY $l_2$										

hydrocarbon	process	303 K	333 K	363 K	373 K
CH₄	reaction				
	relaxation	$\sim 2 \times 10^{-3}$			$\sim 3 \times 10^{-3}$
C <sub>2</sub> H <sub>6</sub>	reaction		$5.28 \times 10^{-8}$	$13.8 \times 10^{-8}$	
	relaxation		$1.73 \times 10^{-3}$	$2.6 \times 10^{-3}$	
C <sub>3</sub> H <sub>8</sub>	reaction	$0.66 \times 10^{-6}$	$1.59 \times 10^{-6}$	$3.14 \times 10^{-6}$	
	relaxation	$2.4 \times 10^{-3}$	$3.23 \times 10^{-3}$	$4.39 \times 10^{-3}$	
$n-C_4H_{10}$	reaction	$1.18(\pm 0.6) \times 10^{-6}$			$6.6(\pm 0.3) \times 10^{-6}$
	relaxation	$3.4(\pm 0.5) \times 10^{-3}$			$7.0(\pm 0.7) \times 10^{-3}$

Since relaxation of  $I(5^2P_{\frac{1}{2}})$  by molecular iodine is very efficient, the activation energy of the process may be taken to be zero. The activation energy, *E*, for secondary H atom abstraction from n-C<sub>4</sub>H<sub>10</sub> by  $I(5^2P_{\frac{1}{2}})$  is therefore determined by the slopes of the fig. 4 plots :

$$\frac{\text{slope at 303 K}}{\text{slope at 373 K}} = \exp\left[\frac{E}{R}\left(\frac{1}{303} - \frac{1}{373}\right)\right]$$

whence  $E = 23.2(\pm 1.25)$  kJ/mol. The A factor (rate coefficient =  $A \exp(-E/RT)$ ) was evaluated by taking the absolute rate coefficient for deactivation of  $I(5^2P_{\pm})$  by  $C_3H_8$  to be  $5.7 \times 10^{-14}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 303 K, as reported by Donovan and Husain.<sup>18, 19</sup> The data of Callear and Wilson<sup>2</sup> then yield  $k_4 = 2.64 \times 10^{-11}$  cm<sup>-3</sup> molecule<sup>-1</sup> s<sup>-1</sup> which is taken to be temperature invariant. Rate parameters for secondary H abstraction from n-C<sub>4</sub>H<sub>10</sub> are compared with the corrected data of Callear and Wilson in table 3.

Table 3.—Rate parameters for H atom abstraction from hydrocarbons by  $I(5^2P_{\frac{1}{2}})$  and rate coefficients for relaxation at 300 K

	rate parameters	for abstraction	relaxation rate coefficients (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )(300 K)		
hydrocarbon	A factors (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	activation energies (kJ/mol)	Callear et al	Donovan and Husain <sup>18, 19</sup>	
CH <sub>4</sub>	_	≥ 55	$\sim 5 \times 10^{-14}$	6×10 <sup>-14</sup>	
$C_2H_6$	$1.39 \times 10^{-13}$	32.2(±1.25)	$3.3 \times 10^{-14}$		
$C_3H_8$	$2.0 \times 10^{-13}$	23.8(±1.25)	$[5.7 \times 10^{-14}]$	$5.7 \times 10^{-14}$	
$n-C_4H_{10}$ (secondary)	$2.77 \times 10^{-13}$	23.2(±1.25)	$8.3 \times 10^{-14}$	_	
$n-C_4H_{10}$ (primary)	$\sim 0.75 \times 10^{-13}$	29.0(±1.5)			

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In fig. 4, the 1-butyl iodide yields, from a variety of experiments, are plotted against the 2-butyl iodide yields at 303 and 373 K. The difference in the slopes of the lines corresponds to an activation energy difference of  $5.5(\pm 0.85)$  kJ/mol, for abstraction of primary and secondary H atoms.



FIG. 4.—Relative yields of 1- and 2-butyl iodides, at 303 K and 373 K (arbitrary units).

## REACTION OF $I(5^2P_4)$ WITH $CH_4$

With the Ilford 502 filter in reaction system C, methyl iodide could not be detected after irradiation of  $CH_4/I_2$  mixtures for 12 h at 433 K, the highest temperature attainable with the equipment. With the filter removed, traces of  $CH_3I$  were detected but the yields were too small for quantitative measurements. The photochemical yield was estimated to be roughly  $10^{-10}$  mol/h with " white light " irradiation at 433 K, decreasing by about 4 fold at 393 K. These observations suggested that the quantum yield for formation of  $CH_3I$  in 100 Torr of  $CH_4+0.20$  Torr of  $I_2$  is  $\sim 3 \times 10^{-4}$  at 433 K. From the generalized mechanism above, this can be identified with

$$k_{2,CH_4}[CH_4](k_{5,CH_4}[CH_4]+k_4[I_2])^{-1}$$
.

To evaluate  $k_{5,CH_4}$ , the efficiency of CH<sub>4</sub> to inhibit the formation of i-C<sub>3</sub>H<sub>7</sub>I formation in the C<sub>3</sub>H<sub>8</sub>/I<sub>2</sub> reaction was investigated, to yield  $k_{5,CH_4}/k_4 = 3 \times 10^{-3}$  at 373 K and  $= 2 \times 10^{-3}$  at 303 K. Hence  $k_{2,CH_4}/k_4$  was deduced to be of the order of  $2 \times 10^{-9}$  at 433 K. An activation energy of  $55(\pm 4.2)$  kJ/mol for CH<sub>3</sub>I formation was estimated by assuming the same A factor as that for abstraction from C<sub>2</sub>H<sub>6</sub>. However, since the mechanism of reaction in CH<sub>4</sub> could not be established, e.g., by conducting experiments with the interference filters, 55 kJ/mol should be considered to be an approximate lower limit for the activation energy for H atom abstraction from CH<sub>4</sub> by I(5<sup>2</sup>P<sub>4</sub>).

#### DISCUSSION

The experiments with  $CH_4$  were undertaken to test the possibility that reaction with  $I(5^2P_4)$  could occur via a crossing to the lower  $I(5^2P_4)$ — $CH_4$  potential hypersurface. Unfortunately the experimental activation energy could not be measured sufficiently accurately to permit any conclusion to be reached. The Fettis-Knox relation predicts an activation energy of 63 kJ/mol for the adiabatic reaction, and 55 kJ/mol for the non-adiabatic reaction. A schematic illustration of the potential surfaces was given by Callear and Wilson.<sup>2</sup> It can only be concluded that the magnitudes of the activation energies for alkyl iodide formation are consistent with what would be expected for reactions of  $I(5^2P_1)$ , and these results therefore provide further evidence for the general validity of the reaction mechanism.

In the final part of this series we discuss the mechanism of " collisional release ". We have discovered that the wavelength quantum-yield function for formation of excited atoms at wavelengths >4985 Å is indistinguishable if the diluent gas is either He or Xe. Although the rate of the collisional process is slower in He than in Xe,<sup>5</sup> the net yield of excited atoms is the same. These results rule out the possibility that the endothermic formation of excited atoms is explicable solely in terms of the atommolecule complex theory. On the contrary the form of the release function appears to be consistent with the Hornig-Palmer<sup>20</sup> model in which energy from all the rotations of the system, as well as from relative translation, contributes very efficiently to bond rupture.

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