# PRIMARY AND SECONDARY PROCESSES IN THE PHOTOLYSIS OF GeH$_3$I

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## Summary

Time-resolved atomic absorption spectrophotometry and flash spectroscopy in the vacuum ultra-violet have been employed to investigate primary and secondary processes in the photolysis ($\lambda > 200$ nm) of GeH$_3$I. The initial yield of I($5^2P_{1/2}$) and I($5^2P_{3/2}$) atoms has been measured ($[I(5^2P_{1/2}]_0/[I(5^2P_{3/2})]_0 \cong 1.3$) and the subsequent reactions of these two states to yield HI have been investigated. Formation of HI by reaction of I($5^2P_{3/2}$) atoms with GeH$_3$I implies a limit to the bond dissociation energy $D$ (H–GeH$_2$I) $\lesssim 298$ kJ/mol. The rate constant for removal of I($5^2P_{1/2}$) by GeH$_3$I has been determined as $k_2 = (6.9 \pm 1.0) \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$: failure to observe laser emission at 1.315 $\mu$m, in this work, is ascribed to the large value for $k_2$.

## Introduction

In the past few years considerable effort has been directed towards an understanding of primary and subsequent processes in the photolysis of alkyl and related iodides, inspired partly by interest in the iodine atom photodissociation laser. Progress has been made towards a detailed description of the photofragmentation at various wavelengths, particularly for methyl iodide [1], and initial relative populations of ground state I($5^2P_{3/2}$) and electronically excited I($5^2P_{1/2}$) atoms, produced in broad-band photolysis of a number of iodides have been measured [2]. Electronic to vibration–rotation energy transfer from I($5^2P_{1/2}$) atoms to a range of molecules has also been investigated [3].

The photolyses of other Group IV iodides have not previously been studied and may provide interesting comparisons with CH$_3$I both in the manner in which the absorption spectrum and photofragmentation change as the central atom is altered, and in the possibilities which may appear of competition between inelastic and chemically reactive channels in collisions of I($5^2P_{1/2}$) atoms with the parent molecule. We describe here an investigation of some aspects of the photochemistry of GeH$_3$I employing three complemen-

tary techniques: kinetic absorption spectrophotometry to monitor the decay of excited iodine atoms, time-resolved spectroscopy in the vacuum ultra-violet and a photodissociation laser apparatus, all employing flash photolysis at $\lambda > 200$ nm.

## Experimental

### Kinetic absorption spectrophotometry

This apparatus has previously been described in detail [4]. $I(5\,^2P_{1/2})$ atoms were monitored by attenuation of the resonance line at 206.2 nm, produced by a microwave discharge in molecular iodine. Decay curves were stored in a fast analogue to digital converter (DL 905) and recorded with an $X-Y$ plotter for subsequent analysis. $GeH_3I$ was photolyzed under isothermal conditions at a flash energy of 45 J. The pressure of iodide employed was between 3 and 6 $N/m^2$, diluted with pure $N_2$, which is a relatively inefficient quencher of excited I atoms, to a total pressure of 2.8 $kN/m^2$. Mixtures were prepared in blackened bulbs and experiments conducted in the dark to minimize decomposition of $GeH_3I$ prior to photolysis.

### Vacuum ultra-violet kinetic spectroscopy

A Vitreosil quartz reaction vessel, length 20 cm, with LiF or $MgF_2$ end windows, was mounted at the entrance slit of a Hilger E766 1 m vacuum spectrograph. Parallel to this within an aluminium reflector was a flashlamp filled with Kr (1.33 $kN/m^2$) typically dissipating $\sim$845 J (10 $\mu$F capacitor charged to 13 kV, giving a flash of $\sim$4 $\mu$s FWHM). The spectroscopic source was a quartz capillary flashlamp filled with Kr (2.67 $kN/m^2$) dissipating 147 J (1.5 $\mu$F capacitor changed to 14 kV, flash duration $\sim$2.5 $\mu$s FWHM). Spectra were recorded on Ilford HP4 film sensitized with sodium salicylate (0.5 $M$ in methanol). Optical density traces were obtained with a Joyce—Loebl recording microdensitometer.

### Chemical laser system

This comprised a quartz reaction vessel, active length 15 cm, with de-mountable sapphire Brewster angle windows, parallel to two Kr-filled flash-lamps in an aluminium reflector. The optical cavity was defined by two totally reflecting gold-coated mirrors. The lamps were fired simultaneously, in parallel, so that the substantial time-varying magnetic fields associated with the two lamps cancel along the axis of the reaction vessel: the effect of the field generated by a single flashlamp is to reduce the gain of the laser in a complex manner by Zeeman splitting of the zero-field hyperfine sublevels and magnetic field induced mixing between states [5]. Chemical laser emission at 1.315 $\mu$m reflected from one of the Brewster windows was detected with an InSb detector (Mullard ORP-10) operated at room temperature, the output being displayed on a storage oscilloscope (Tektronix 549).
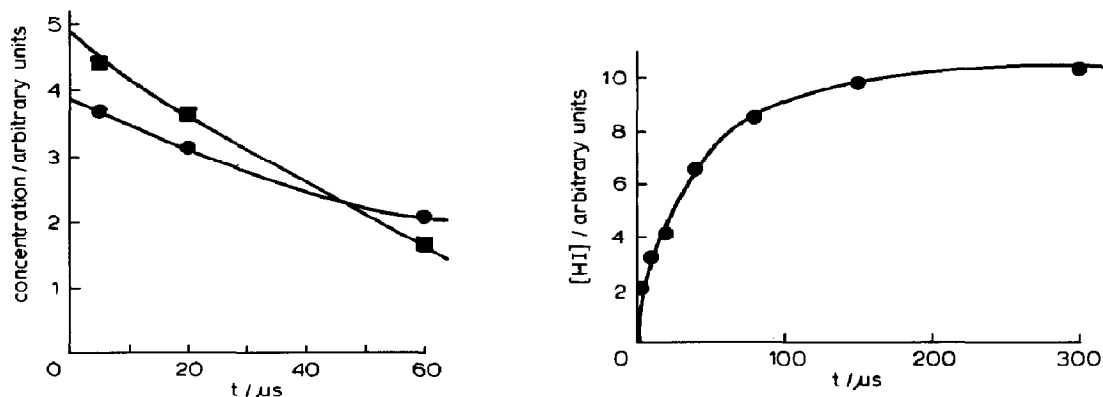
Fig. 1. Concentrations of iodine atoms following photolysis of $GeH_3I$. $P_{GeH_3I}$ = 8 N/m$^2$, $P_{Ar}$ = 10.9 kN/m$^2$; flash energy = 845 J; ■, $I(5^2P_{1/2})$; ●, $I(5^2P_{3/2})$.

Fig. 2. Formation of HI following photolysis of $GeH_3I$. $P_{GeH_3I}$ = 1.33 N/m$^2$, $P_{Ar}$ = 667 N/m$^2$; flash energy = 845 J.

## Results and Discussion

*Time resolved spectrographic investigation*

Photolysis of $GeH_3I$ ($\lambda$ > 200 nm) resulted in production of both ground and excited state iodine atoms, $I(5^2P_{3/2})$ and $I(5^2P_{1/2})$, whose initial relative yield was determined by plate photometry using the transitions at 178.3 nm ($5p^46s\ ^2P_{3/2} \leftarrow 5p^5\ ^2P_{3/2}$) and 179.9 nm ($5p^46s\ ^2P_{1/2} \leftarrow 5p^5\ ^2P_{1/2}$). The continuous absorption by the parent molecule overlies these lines quite strongly under the conditions required to produce sufficient concentrations of atoms for plate photometry, but by using 8 N/m$^2$ of $GeH_3I$ and recording multiple exposures (12 exposures at each time delay with a fresh sample for each exposure) the points on Fig. 1 were obtained. Line heights have been converted to relative concentrations using the Einstein $A$ coefficients calculated by Lawrence [6] assuming equal pressure broadening for the two lines. Thus the initial relative populations are $[I(5^2P_{1/2})]_0/[I(5^2P_{3/2})]_0$ = 1.3 ± 0.1, corresponding to population inversion by a factor of 2.6.

HI was formed in these experiments and detected by the intense Rydberg transitions at 160.47 nm and 176.21 nm. By photolyzing identical mixtures of $GeH_3I$ in Ar with varying flash energies, and monitoring [HI] at a fixed delay of 200 $\mu$s, it was verified that absorption by HI followed the Beer–Lambert law. The kinetic behaviour (Fig. 2) indicates that HI is the product of a secondary reaction, rather than a primary product of photolysis.

Possible sources of HI are: (i) H abstraction by $I(5^2P_{3/2})$ or $I(5^2P_{1/2})$ atoms, if the $GeH_2I$–H bond dissociation energy is sufficiently low:

$$I(5^2P_{3/2}) + GeH_3I \rightarrow GeH_2I + HI \tag{1}$$

$$I(5^2P_{1/2}) + GeH_3I \rightarrow GeH_2I + HI \tag{2}$$

(ii) a sequence involving H atoms:

$$GeH_3I + h\nu \rightarrow GeH_2I + H \tag{3}$$

$$H + GeH_3I \rightarrow GeH_3 + HI \tag{4}$$

Behaviour analogous to reactions (3) and (4) has been observed in the short wavelength photolysis (140 nm < $\lambda$ < 170 nm) of $CH_3I$ [7].

While a contribution from reactions (3) and (4) is not necessarily excluded, a number of observations suggest that H abstraction by both $I(5^2P_{1/2})$ and $I(5^2P_{3/2})$ is occurring: (i) as far as the present results allow a comparison to be made, the growth of [HI] appears to mirror the decay of [I]$_{total}$; (ii) disappearance of $I(5^2P_{3/2})$ is very fast and cannot be explained by atomic recombination: if it is assumed that all the I atoms are removed in collisions with $GeH_3I$, the data in Fig. 1 yield the approximate rate constants $k_1 \cong 5 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, $k_{1*} \cong 9 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. The figure for ground state atoms may conceal the effect of feeding from the excited state; (iii) further evidence that ground state iodine atoms can abstract H from $GeH_3I$ may be adduced in the observation that in photolysis in the presence of a large excess of $H_2$ ($P_{GeH_3I}$ = 1.33 N/m$^2$, $P_{H_2}$ = 13.3 kN/m$^2$), conditions such that 99.5% of $I(5^2P_{1/2})$ atoms were quenched to $I(5^2P_{3/2})$ before reacting further [8], HI formation was very similar to that observed in the presence of Ar, an inefficient quencher.

Following photolysis of $GeH_3I$ at 200 nm to give $I(5^2P_{3/2}) \sim 400$ kJ/mol excess energy is available. Under the conditions of the present experiments, however, excess translational energy is essentially thermalized in less than 1 $\mu$s, so that it may be concluded that the $GeH_2I$–H bond dissociation energy $D_{298}$ ($GeH_2I$–H) = $\Delta H^\circ_{f,298}$ ($GeH_2I$) + $\Delta H^\circ_{f,298}$ (H) — $\Delta H^\circ_{f,298}$ ($GeH_3I$) $\lesssim$ 298 kJ/mol. No previous determination appears to have been made. This value may be compared with the limit $D(GeH_3$–H$) \lesssim 326$ kJ/mol obtained by Setser and coworkers [9] from observation of the highest (v,J) level of HF populated in the reaction of F atoms with $GeH_4$. A lower value in the iodine-substituted molecule is to be expected. We note that no $I_2$ was detected in these experiments, indicating that any removal of I atoms by reactions (5) and (6) is negligible:

$$I(5^2P_{3/2}) + GeH_3I \rightarrow I_2 + GeH_3 \tag{5}$$

$$I(5^2P_{1/2}) + GeH_3I \rightarrow I_2 + GeH_3 \tag{6}$$

*Kinetic spectrophotometry*

The present data do not permit an evaluation of the extent of deactivation of $I(5^2P_{1/2})$ to $I(5^2P_{3/2})$ by $GeH_3I$ and hence a determination of $k_2$. The *overall* rate constant for removal of $I(5^2P_{1/2})$ atoms by $GeH_3I$ was determined by atomic absorption spectrophotometry (Table 1 and Fig. 3). Rate constants previously determined [10] for $CH_3I$ and $CD_3I$ are included in Table 1 for comparison. Because of polymerization of products of $GeH_3I$ photolysis in the reaction vessel, leading to a reduction in signal, only a limited number of experiments were performed. It was verified that the measured rate for

**TABLE 1**

Rate constants ($k$/cm$^3$ molecule$^{-1}$ s$^{-1}$, at 298 K)
for removal of electronically excited iodine atoms,
I($5\,^2P_{1/2}$), by GeH$_3$I, CH$_3$I and CD$_3$I.

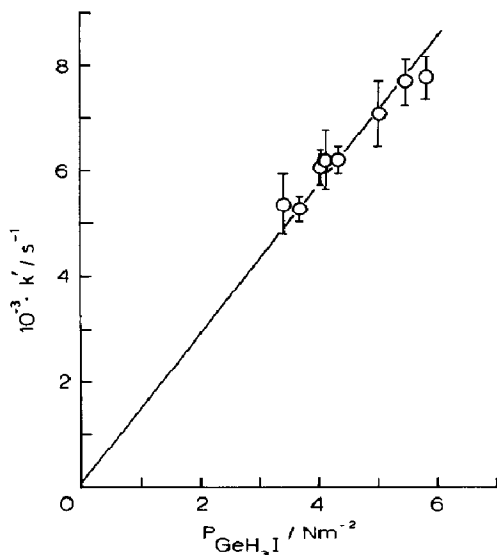| Molecule | $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ |
|----------|-------------------------------------|
| GeH$_3$I | $(6.9 \pm 1.0) \times 10^{-12}$ |
| CH$_3$I | $(2.6 \pm 0.6) \times 10^{-13}$ |
| CD$_3$I | $(4.6 \pm 0.8) \times 10^{-15}$ |



Fig. 3. Plot of first order rate coefficients $k'$ for decay of I($5\,^2P_{1/2}$) vs. pressure of GeH$_3$I.
$P_{\text{total(with N}_2)} = 2.8$ kN/m$^2$, flash energy = 45 J.

identical mixtures remained constant for flash energies in the range 10 - 125 J,
indicating that there is no complication by radical—radical processes. Flashing
the same mixture repetitively had no effect on the rate of removal of excited
atoms, showing that there was no significant build-up of products which have
substantially different rate constants for removal of I($5\,^2P_{1/2}$), such as I$_2$. As
expected in view of the discussion in the previous section, the rate constant
is larger than would normally be associated with purely energy-transfer col-
lisions of I($5\,^2P_{1/2}$) atoms. A determination of the relative contributions of
energy transfer and chemical reaction would be of great interest, but experi-
mentally very difficult to obtain.

*Photochemical laser investigation*

The population inversion observed for the lowest spin-orbit states of
the iodine atom, following photolysis of GeH$_3$I, suggests that under appro-
priate conditions laser action (1.315 $\mu$m) should occur. We have previously

investigated $CH_3I$ and $CD_3I$ photochemical laser systems [11] and could therefore optimize conditions for laser action with our experimental arrangement. However, no laser emission could be observed from $GeH_3I$ even under conditions where $CH_3I$ gave a large output of stimulated emission. Thus although a sizeable population inversion occurs for $GeH_3I$, rapid removal of the excited atoms appears to prevent the system reaching threshold. We may compare this with $CH_3I$, where rather restrictive conditions for lasing have been observed [11]. The difference in laser output between $CH_3I$ and $CD_3I$ has been ascribed to the difference in quenching rate constants for the two molecules, and in a computer simulation of the $CH_3I$ laser, output was found to be critically dependent on the value of the rate constant for quenching of $I(5\,^2P_{1/2})$ by the parent molecule. Laser action with $GeH_3I$ might be achieved if the photochemical pumping rate were increased (*i.e.* the flash lamp duration reduced), thus allowing threshold to be reached on a time scale which is short by comparison with the relaxation time for $I(5\,^2P_{1/2})$.

## Acknowledgements

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