# DETERMINATION OF PHOTODECOMPOSITION QUANTUM YIELDS

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## Summary

Expressions were developed to calculate the overall quantum yields of reactions from absorbance measurements made at different times in systems where the reactant is the only light-absorbing species. These expressions are applied to the determination of $\Phi$ for the photolysis of pure $CH_3I$ both in the absence and the presence of $O_2$. The strong influence that the presence of $O_2$ exerts on $\Phi$ is shown. This behaviour is attributed to the relative abundance of translationally excited $CH_3 \cdot$.

## 1. Introduction

Several methods for the determination of quantum yields have been reported in the literature. The quantum yield is one of the most important parameters utilized in the description of a photoreaction. It is the only kinetic parameter associated with a photoreaction that can be directly measured in the steady state and its importance is emphasized by the information it can supply about the different paths by which an electronically excited molecule can dispose of its energy. Recently, expressions have been developed to calculate the quantum yields of reaction in solution in systems where the reaction products compete with the starting material for absorption of the incident light [1].

In this paper we develop a simple method for the determination of the overall quantum yield $\Phi$ from absorbance measurements made at different times in systems where the reactant is the only light-absorbing species. Many of the difficulties associated with such determinations [2 - 5] are avoided in this method. The equations derived are applied to the determination of $\Phi$ for the photolysis of pure $CH_3I$ in both the absence and the presence of $O_2$.

## 2. Theory

The mechanism by which a molecule undergoes photodecomposition as a result of energization by light absorption can be expressed as

$$S \underset{\Sigma k_s}{\overset{h\nu}{\rightleftarrows}} S^* \xrightarrow{\Sigma k_r} \text{products} \tag{1}$$
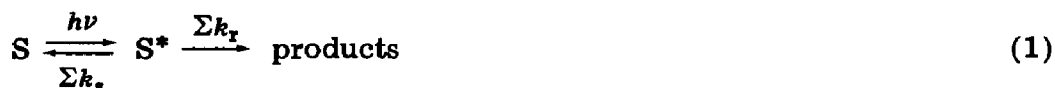
where $\Sigma k_r$ and $\Sigma k_s$ account for the different paths leading to the decomposition and stabilization respectively of the species S. Assuming a steady state for the species $S^*$, we can write

$$[S^*] = \frac{\int B_{nr}[S]\rho(\nu_{nr})\,d\nu}{\Sigma k_r + \Sigma k_s}\phi \tag{2}$$

where $B_{nr}$ is Einstein's coefficient for the transition between the $|n\rangle$ and the $|r\rangle$ states of S, $\rho(\nu_{nr})$ is the photon density of frequencies near $\nu_{nr}$ and $\phi$ is the primary quantum yield.

The rate of disappearance of the species S, according to eqn. (2), is given by

$$\frac{d[S]}{dt} = -\int B_{nr}[S]\rho(\nu_{nr})\,d\nu\left(\frac{\Sigma k_r}{\Sigma k_s + \Sigma k_r}\phi\right) \tag{3}$$

The integral on the right-hand side of eqn. (3) represents the number of photons absorbed by S per unit volume and unit time, *i.e.* the absorbed light intensity $\bar{I}_{abs}$ per unit volume. The term in parentheses represents the number of molecules of the species S which undergo photodecomposition when a photon is absorbed, *i.e.* the overall quantum yield $\Phi$. Therefore, provided that the reactant is the only light-absorbing species present, eqn. (3) can be rewritten in the well-known form

$$\frac{d[S]}{dt} = -\bar{I}_{abs}\Phi \tag{4}$$

If the Lambert–Beer law is assumed, the absorbed light intensity is given by

$$\bar{I}_{abs} = \bar{I}_0[1 - \int F(\nu)\exp\{-\epsilon(\nu)[S]l\}\,d\nu] \tag{5}$$

where $F(\nu)$ represents the lamp excitation spectrum, normalized and corrected for the monochromator and detector response and referred to the total intensity, which must be determined by actinometry, and $l$ is the optical path length. Substitution of $\bar{I}_{abs}$ from eqn. (5) into eqn. (4) and further integration yields

$$\int_{A_t}^{A_o} \{1 - f(A^m)\}^{-1}\,dA = \bar{I}_0\epsilon^m l\Phi t \tag{6}$$

where $f(A^m)$ is given by

$$f(A^m) = \int F(\nu)\exp\left\{-\frac{\epsilon^i(\nu)A^m}{\epsilon^m(\nu)}\right\}\,d\nu \tag{7}$$

and the superscripts i and m denote excitation and measurement respectively.

For monochromatic excitation, eqn. (7) becomes

$$f(A^m) = \exp\left(- \frac{\epsilon^i A^m}{\epsilon^m}\right) \tag{8}$$

Substitution of eqn. (8) into eqn. (6) yields

$$A^m_0 - A^m_t + \frac{\epsilon^m}{\epsilon^i} \ln\left\{\frac{1 - f(A^m_0)}{1 - f(A^m_t)}\right\} = \bar{I}_0 \epsilon^m l \Phi t \tag{9}$$

where $A^m_0$ and $A^m_t$ are the absorbances of the substrate at the measurement frequency at times zero and $t$ respectively. Equation (9) can be rewritten

$$A^m_t + \frac{\epsilon^m}{\epsilon^i} \ln\{1 - f(A^m_t)\} = A^m_0 + \frac{\epsilon^m}{\epsilon^i} \ln\{1 - f(A^m_0)\} - \bar{I}_0 \epsilon^m l \Phi t \tag{10}$$

and it is obvious that a plot of the left-hand side of this equation against the irradiation time will yield a straight line, from the slope of which $\Phi$ can be calculated. Equation (10) is particularly useful when the measurement of $A^m_0$ presents some degree of difficulty. In addition, for $A^m_0 < 0.1$ this equation can be simplified to

$$\ln A^m_t = \ln A^m_0 - \Phi \bar{I}_0 l \epsilon^m t \tag{11}$$

with an error of less than 5%.

Finally, if it is necessary to account for the spectral distribution of the excitation lamp, eqn. (6) can be solved numerically by standard integration methods. However, if the spectral distribution of the excitation lamp is composed of a set of very narrow bands, eqn. (6) can be simplified to

$$\int_{A_t}^{A_0} \left[1 - \Sigma W_j \exp\left\{- \frac{\epsilon^i(\nu) A^m}{\epsilon^m(\nu)}\right\}\right]^{-1} dA = \bar{I}_0 \epsilon^m l \Phi t \tag{12}$$

where $W_j$ is the percentage of the total area corresponding to the band centred at the excitation frequency $\nu_j$. Alternatively, eqn. (10) can be utilized with an excitation coefficient corresponding to the average excitation frequency $\langle \nu \rangle$ defined by

$$\langle \nu \rangle = \Sigma W_j \nu_j \tag{13}$$

## 3. Photodecomposition quantum yields of $CH_3 I$ under various conditions

A potassium ferrioxalate actinometer [6] was used in this work. Possible lamp decay or instability was taken into account by alternating the actinometer cell with the photolysis cell every 5 min.

Irradiation experiments were performed with a 550 W medium pressure mercury lamp (Hanovia, 679A36) coupled to a high intensity monochromator (Bausch and Lomb); the bandpass of the system was 9.6 nm. A photolysis cell 1.8 cm in diameter with quartz windows was used. Path lengths of 1 and 5 cm were available. The band spectrum of the Bausch and

Lomb monochromator at 253.7 nm was analysed using a 0.5 m Jarrell–Ash monochromator. Figure 1 shows the electronic absorption spectra of $CH_3I$ and the irradiating light.

Plots of the left-hand side of eqn. (10) against the irradiation time for the photolysis of $CH_3I$ in the absence and the presence of $O_2$ are shown in Figs. 2 and 3 respectively. An average excitation coefficient of 334 $M^{-1}$ $cm^{-1}$ was assumed. The overall quantum yields were calculated from the slopes of the lines obtained. Table 1 shows these results together with those obtained from eqn. (12) for several experiments under different conditions. The agreement is good, and hence the utilization of eqn. (10) to obtain a first-order approximation of $\Phi$ is justified.

The strong influence that the presence of $O_2$ exerts on $\Phi$ is evident. Also, the values of $\Phi$ for the cases when the ratio $CH_3I/O_2$ and the initial

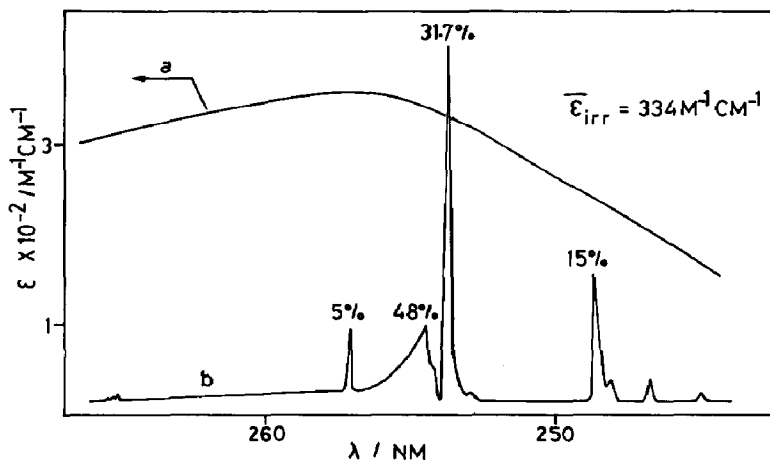

Fig. 1. Electronic absorption spectra of (a) $CH_3I$ and (b) the irradiating light. The percentages of the total area corresponding to the bands centred at the excitation frequencies are shown.
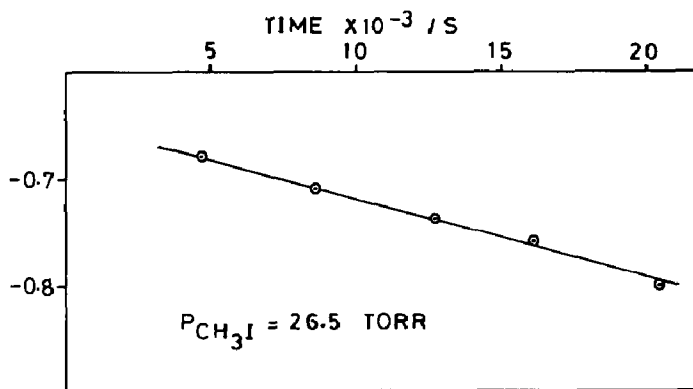


Fig. 2. Plot of the left-hand side of eqn. (10) against the irradiation time: ⊙, experimental values obtained with an optical path length of 1 cm.
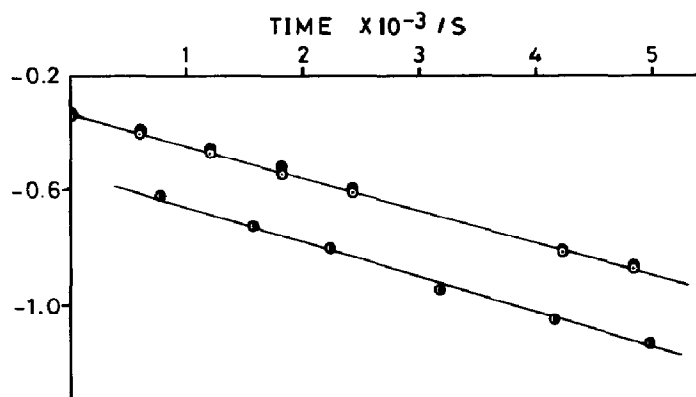
Fig. 3. Plot of the left-hand side of eqn. (10) against the irradiation time: ⊙, $P_{CH_3I}$ = 30 Torr, $P_{O_2}$ = 500 Torr (optical path length, 1 cm); ●, $P_{CH_3I}$ = 6 Torr, $P_{O_2}$ = 100 Torr (optical path length, 5 cm); ◑, $P_{CH_3I}$ = 28 Torr, $P_{O_2}$ = 650 Torr (optical path length, 1 cm).
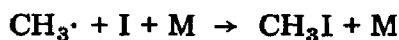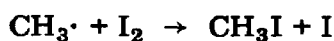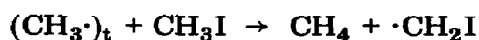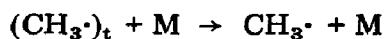
TABLE 1

Photodecomposition quantum yields of $CH_3I$ under various experimental conditions

| Pressure (Torr) | | Quantum yield [a] | | |
|---|---|---|---|---|
| $CH_3I$ | $O_2$ | I | II | III |
| 26.5 | — | $(5.19 \pm 0.05) \times 10^{-2}$ | $(5.01 \pm 0.05) \times 10^{-2}$ | $(5.4 \pm 0.1) \times 10^{-2}$ |
| 28.0 | 650 | $0.90 \pm 0.01$ | $0.87 \pm 0.01$ | $0.94 \pm 0.03$ |
| 30.0 | 500 | $0.89 \pm 0.01$ | $0.86 \pm 0.01$ | $0.93 \pm 0.01$ |
| 6.0 | 100[b] | $0.86 \pm 0.01$ | $0.83 \pm 0.01$ | $0.92 \pm 0.01$ |

[a] I, calculated using eqn. (12); II, calculated using eqn. (12) with a single band centred at 254 nm; III, calculated using eqn. (10) with $\bar{\epsilon}_i$ = 334 $M^{-1}$ $cm^{-1}$.
[b] 5 cm optical path; the other experiments were carried out with a 1 cm optical path length.

absorbance of the photolysis mixture are identical are not equal. According to the mechanism of $CH_3I$ photolysis proposed by Costela et al. [7], if $\lambda$ is greater than 220 nm $CH_3\cdot$ is translationally excited $((CH_3\cdot)_t)$. The rate of deactivation is a factor of 12 faster [8] for M ≡ $CH_3I$ than for M ≡ $O_2$. The participation of $(CH_3\cdot)_t$ and $CH_3\cdot$ in the mechanism of photolysis is as follows:

$$(CH_3\cdot)_t + M \rightarrow CH_3\cdot + M$$

$$(CH_3\cdot)_t + CH_3I \rightarrow CH_4 + \cdot CH_2I$$

$$CH_3\cdot + I_2 \rightarrow CH_3I + I$$

$$CH_3\cdot + I + M \rightarrow CH_3I + M$$

$$CH_3\cdot + I^* + M \rightarrow CH_3I + M$$

Therefore the increase in $\Phi$ in the presence of $O_2$ can be attributed to the relative abundance of $(CH_3{\cdot})_t$.

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