

THE TREATMENT OF SERIOUS DEPLETION EFFECTS IN PHOTOCHEMICAL SYSTEMS

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(Received January 18, 1974; in revised form March 20, 1974)

Summary

An analytical formula has been derived to enable the accurate estimation of the degree of light absorption in photochemical systems under conditions where the Beer—Lambert law can be shown to be inapplicable owing to depletion of the absorber. A computer program has been developed which also allows for depletion effects and in addition can be applied under conditions in which the extinction coefficient varies rapidly with wavelength. The regions in which these methods of calculation should be used are given in terms of simple practical criteria. Some applications of these methods to flash photolytic systems, together with the appropriate actinometry, are discussed briefly. Evidence is presented that the intensity of the flash lamp used was sensibly constant over the emitted wavelength range.

Introduction

A common description of the variation of the decomposition yield with substrate pressure in gas phase flash photolytic investigations is "the increase in decomposition yield is due to increased light absorption". To the author's knowledge, no attempts have been made to quantify the amount of light absorption under flash photolytic conditions except where the conditions are pertinent to Beer—Lambert law behaviour. The present paper describes the development of a simple analytical expression which overcomes this problem and has been shown to predict results which are consistent with experimental observations under conditions where the Beer—Lambert law is inapplicable owing to depletion of the absorber [1]. In circumstances where the extinction coefficient varies rapidly with wavelength the analytical expression is liable to be in serious error and consequently a computer program has also been developed to deal with these conditions. The analytical expression itself is sufficient for calculating the absorption in monochromatic photolysis ex-

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periments appertaining to high optical density conditions where the Beer-Lambert law is also known to be inapplicable.

The normal form of the Beer-Lambert law may be expressed as:

$$\frac{I_t}{I_0} = \frac{n_t}{n_0} = \exp(-\epsilon cL)$$

where I_t/I_0 is the ratio of the transmitted to the incident light intensities; n_t/n_0 is the ratio of transmitted to incident quanta; ϵ is the extinction coefficient; c is the constant uniform concentration; and L is the path length.

The derivation of this familiar result assumes that the active absorbing molecules relax in a sufficiently efficient manner such that the concentration is not sensibly altered. This condition will obviously not be satisfied when the molecules decompose to non-absorbing fragments subsequent to the absorption of a photon.

Derivation of analytical expression

Before examining the consequences due to depletion with time of the number of molecules present it is convenient to consider the effects of non-uniform concentration in the path length.

In general we have for unit cross-sectional area for the number of quanta absorbed in the path length increment, l to $l + dl$

$$dn = -\epsilon n(l) c(l) dl \quad (1)$$

$n(l)$ and $c(l)$ being respectively the incident photon density and concentration at the position l in appropriate units.

$$\therefore \frac{dn}{n} = -\epsilon c(l) dl \quad (2)$$

and hence

$$\int_{n_0}^{n_T} \frac{dn}{n} = -\epsilon \int_0^L c(l) dl \quad (3)$$

where n_0 and n_T are respectively the incident and transmitted photon densities.

On completing the integration we obtain:

$$\ln\left(\frac{n_T}{n_0}\right) = -\epsilon M \quad (4)$$

where M is the total number of moles in the path length and ϵ is now the molar extinction coefficient. But this result is, of course, no different to the usual result for constant concentration and demonstrates that variation of concentration in the path length is of no significance.

Now let the number of moles, per unit area, in the cell path at time t be:

$$M(t) = \bar{c}(t)l \quad (5)$$

where $\bar{c}(t)$ is the average concentration at time t . Then the change in the number of moles in the time interval t to $t + dt$ due to absorbing photons is:

$$dM(t) = -[n_0(t) - n_T(t)] dt = -n_0(t) \left[1 - \frac{n_T(t)}{n_0(t)} \right] dt \quad (6)$$

n_0 and n_T now being expressed in Einsteins per unit area per unit time. As we have shown in eqn. (4) for the case of non-uniform concentration we can still write:

$$\frac{n_0(t)}{n_T(t)} = \exp[-\epsilon M(t)] \quad (7)$$

and substitution in eqn. (6) gives:

$$dM(t) = -n_0(t) \{ 1 - \exp[-\epsilon M(t)] \} dt \quad (8)$$

As the incident intensity, $n_0(t)$, is considered to be a function of time the result will be adequate to deal with cases in which the incident "light" or "flash" has a "time profile".

Integrating eqn. (8) over the period, t , for which light is supplied gives:

$$\int_{M(0)}^{M(t)} \frac{dM}{1 - \exp(-\epsilon M)} = - \int_0^t n_0(t) dt = -n_Q \quad (9)$$

$M(0)$ being the initial number of moles and n_Q the total Einsteins supplied in the time t .

Completing the integration and rearranging the result appropriately gives for the fractional amount of moles remaining after time t :

$$\frac{M(t)}{M(0)} = \frac{1}{\epsilon M(0)} \left\{ \ln[(\exp[\epsilon M(0)] - 1) \exp(-\epsilon n_Q) + 1] \right\} \quad (10)$$

Unfortunately it is not possible to modify the above treatment to take account of the variation of extinction coefficient with wavelength except for very special cases which are not of practical interest (see next section).

If the total Einsteins supplied in a time t , is expressed in terms of the number of moles initially present, *i.e.*

$$n_Q = \alpha(t) M(0) \quad (11)$$

then eqn. (10) can be more suitably expressed as:

$$\frac{M(t)}{M(0)} = \frac{1}{\epsilon M(0)} \left\{ \ln[(\exp[\epsilon M(0)] - 1) \exp[-\alpha(t) \epsilon M(0)] + 1] \right\} \quad (12)$$

It is interesting to compare this expression with the analogous expression which ensues if depletion is ignored, *i.e.* Beer-Lambert law holds.

After simple manipulation one obtains:

$$\frac{M(t)}{M(0)} = 1 - \alpha (1 - \exp[-\epsilon M(0)]) \quad (13)$$

For high absorbing powers, $\epsilon M(0) \gg 1$, and values of α somewhat less than unity both eqns. (12) and (13) approximate to:

$$\frac{M(t)}{M(0)} \simeq 1 - \alpha^* \quad (14)$$

For low absorbing powers, $\epsilon M(0) \ll 1$, both expressions approximate to:

$$\frac{M(t)}{M(0)} \simeq 1 - \alpha \epsilon M(0) \quad (15)$$

In Table 1 numerical values for the fractional amount remaining calculated from expression (12) and the Beer-Lambert law are compared.

If negative values given by the Beer-Lambert law are taken to represent zero then it is quickly obvious that deviations are significant only in the range of $\alpha \epsilon M(0)$, around unity together with a sufficiently large supply of quanta. Within this range the deviations can be large.

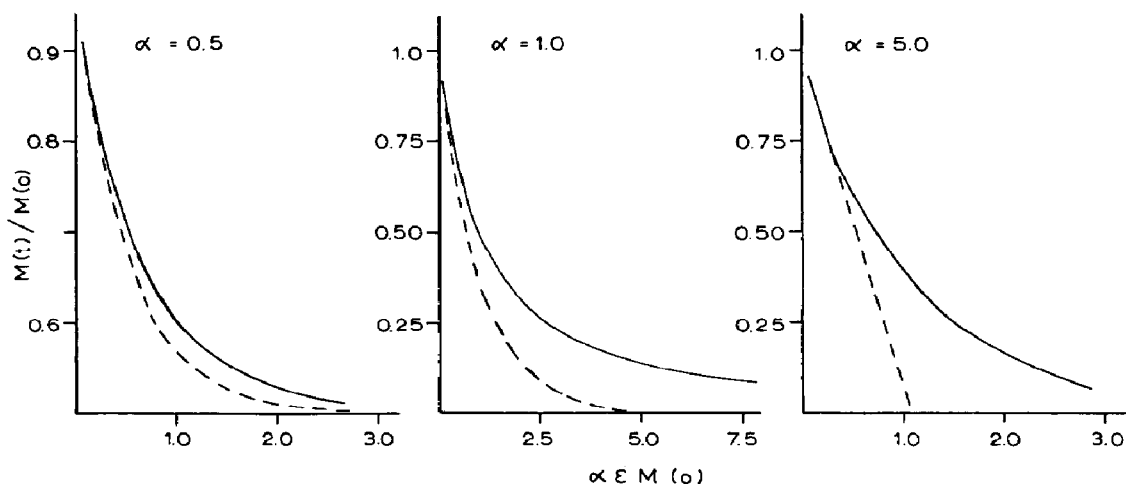


Fig. 1. Deviations from Beer-Lambert law for various values of α : ---- Beer-Lambert values; —, expression(12) values. Terms defined in the text.

Figure 1 shows graphically the extent of the deviations for a range of values for the quanta supplied. A closer examination of the numerical results suggests that the expression derived in this work should be utilized when the conditions employed satisfy the following criteria:

$$0.2 < \alpha \epsilon M(0) < 10 \quad \text{and} \quad \alpha > 0.25$$

*If α is greater than one then Beer's law gives a negative answer.

TABLE 1

Comparison of values of $M(t)/M(0)$ predicted by expression (12) and Beer-Lambert law values*

$\epsilon M(0)$	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	1	10^1	10^2
10^{-2}								
10^{-1}	Beer-Lambert obeyed					<u>0.938</u>		
						0.937		
1					<u>0.909</u>	<u>0.490</u>	$\frac{5.9 \times 10^{-2}}{4.5 \times 10^{-5}}$	$\frac{1.38 \times 10^{-2}}{0}$
					0.905	0.368		
10^1				<u>0.905</u>	<u>0.380</u>	$\frac{7.8 \times 10^{-5}}{4.8 \times 10^{-2}}$		
				0.900		0		
10^2			<u>0.905</u>	<u>0.369</u>	$\frac{4.8 \times 10^{-5}}{5.0 \times 10^{-3}}$			
			0.900		0			
10^3		<u>0.905</u>	<u>0.368</u>	$\frac{4.6 \times 10^{-5}}{5.0 \times 10^{-5}}$				
		0.900		0				
10^4	<u>0.905</u>	<u>0.368</u>	$\frac{4.5 \times 10^{-5}}{5.0 \times 10^{-5}}$					
	0.900		0					
							Negative values by Beer-Lambert law assigned zero values	
10^5	<u>0.368</u>	$\frac{4.5 \times 10^{-5}}{5.0 \times 10^{-6}}$						
	5.0×10^{-6}							

*Upper underlined values calculated using expression (12).

Development of the computer program*

The basic principle used in the numerical integration procedure is that the Beer-Lambert law will yield valid results describing the amount of light absorption, provided that the depletion of the molecules in the light path is properly accounted for. The total quanta per flash, n_Q , are divided into a series of m equal time increments so that the incident quanta, $(n_Q)_i$, for each increment i , are:

$$(n_Q)_i = \frac{n_Q}{m} \quad (16)$$

Each incremental pulse of quanta is passed through the absorbing medium

*Copies of the computer program may be obtained from Mr. R. Whitehead.

and the number of quanta absorbed is determined. The number of molecules remaining in the cell, M_i , is subsequently corrected for the number of molecules depleted before the next pulse of quanta is permitted to traverse the cell path.

During the development of this computer program a number of situations were examined in order to ensure that the program was functioning correctly. Equation (4) predicts that M_i is independent of any variations of the concentration within the light path, hence identical values of M_i should be obtained when the cell is considered to be divided into several increments or a single increment; the data in Table 2 verify this point.

TABLE 2

Effect of cell path increments at a single time increment

α	$\epsilon M(0)$	Fraction remaining		
		Number of cell increments		
		1	5	10
184.6	3.02×10^{-3}	0.447	0.447	0.447
0.9844	5.69×10^{-1}	0.576	0.576	0.576
0.554	1.015	0.650	0.650	0.650

The program allows for the depletion of molecules in time by using a series of incremental values of the total quanta. Table 3 shows that the values predicted by the computer program approach the values of expression (12) asymptotically as the number of time increments is increased and hence depletion is properly accounted for. The results for one time increment, *i.e.* Beer-Lambert law condition, considerably overestimate the amount of light absorption. Equation (12) shows, for a given absorbing power, that the num-

TABLE 3

Effect of time increments

α	$\epsilon M(0)$	Fraction remaining			
		Eqn. (12)	Number of time increments		
			1	10	20
184.6	3.02×10^{-3}	0.573	0.447	0.561	0.567
0.9844	5.69×10^{-1}	0.638	0.576	0.632	0.636
0.554	1.015	0.684	0.650	0.681	0.684

ber of residual molecules depends only on α , the measure of the total number of quanta supplied and hence is independent of the shape of the quanta

pulse. The values in Table 4 from the program, which correspond respectively to a square wave pulse and a "flash-profiled" pulse of incident quanta [1], show the necessary agreement.

TABLE 4

Effect of various flash profiles

α	$\epsilon M(0)$	Fraction remaining		
		Eqn. (12)	Square wave	Flash profiled
184.6	3.02×10^{-3}	0.573	0.570	0.567
0.9844	5.69×10^{-1}	0.638	0.638	0.636
0.544	1.015	0.684	0.684	0.684

When large variations of the extinction coefficient with wavelength occur then expression (12) can only be applied utilizing an average extinction coefficient. In order to assess the error this entails the computer program was designed appropriately. Comparisons were obtained between the two methods for a variety of extinction coefficient profiles. Typical results are shown in Table 5.

Good agreement is obtained between the analytical expression and the computer program when the extinction coefficient profile is "flat" or fairly symmetrical and the average value of ϵ in each section does not vary by more than a factor of about 4 (profiles 1, 2 and 3). The analytical equation is, however, in serious error in the cases of "spiked" profiles (profile 5) or a rapidly decreasing continuous profile (profile 4). The discrepancy between the two methods becomes very serious for the latter cases at very high values of the extinction coefficient. It should be noted that both the analytical expression and the computer program can be used to determine the change in absorption with distance from the light source. Such knowledge is important when sampling photoinitiated fast reactions, *i.e.*, flash photolysis-mass spectrometry experiments [2, 3].

Application to flash photolysis studies

The flash photolytic decomposition of several methyl radical generators has recently been studied in this laboratory [1]. The total quanta emitted by the flash photolysis lamps used were determined by uranyl oxalate actinometry [4] under conditions identical to subsequent experimental investigations. The quanta were considered to be absorbed in the wavelength range 200 (short wavelength cut-off of Vitreosil quartz [5]) - 490 nm (long wavelength absorption limit of uranyl oxalate [4]). The assumption was then made that the intensity of emitted light per unit wavelength was solely determined by the optical characteristics of Vitreosil quartz in this wavelength range, *i.e.* it

TABLE 5

Effects due to variable extinction coefficients

α	$\epsilon M(0)$	Fraction remaining					
		Eqn. (12)	Computer program				
			Profile				
			1	2	3	4	5
184.6	3.02×10^{-3}	0.573	0.567	0.567	0.567	0.567	0.568
0.9844	5.69×10^{-1}	0.638	0.636	0.650	0.656	0.651	0.703
0.544	1.015	0.684	0.684	0.703	0.710	0.712	0.766
0.9844*	11.4	0.069	0.064	0.087	0.087	0.162	0.159
0.544*	7.2	0.446	0.446	0.446	0.446	0.457	0.455
<i>Profile</i>	2.303ϵ						
1	500; 500; 500; 500						
2	250; 750; 750; 250						
3	250; 1000; 500; 250						
4	1000; 500; 350; 150						
5	250; 1500; 150; 100						
1*	10,000; 10,000; 10,000; 10,000						
2*	5000; 15,000; 15,000; 5000						
3*	5000; 20,000; 10,000; 5000						
4*	30,000; 5000; 3000; 2000						
5*	2500; 30,000; 5000; 2500						

should be approximately constant. The described methods could then be used to estimate the number of quanta absorbed in the various systems under investigation. The value of the incident quanta required for the calculations was obtained from the expression:

$$\text{number of incident quanta} = \frac{\Delta\lambda (\text{substrate})}{\Delta\lambda (\text{actinometer})} \times \text{actinometry value}$$

where $\Delta\lambda$ (substrate) is the width of the ultra-violet absorption band of the substrate, in nm, and $\Delta\lambda$ (actinometer) is the width of the absorption band of the actinometer, *i.e.* 290 nm for uranyl oxalate. A few typical results will now be discussed.

Tetramethyllead and dimethylmercury absorb light in the 200 - 280 nm region of the u.v. spectrum [7, 8]. In the presence of large amounts of inert gas, *i.e.* isothermal conditions, the quantum yield for the decomposition of these substrates was obtained by division of the experimentally observed decomposition yield by the calculated number of quanta absorbed. For both substrates a value of unity for the quantum yield was obtained in agreement with monochromatic results of 1.1 for tetramethyllead [7] and unity for dimethylmercury [9] at 256 nm.

Similar calculations on the flash photolysis of azomethane in Pyrex, absorption region 280 - 410 nm [10] indicated a quantum yield of unity for

the decomposition in agreement with the static photolysis results at 366 nm [11 - 13]. For acetone, the absorption region is 200 - 336 nm [10] and a quantum yield of 0.3 was obtained for initial pressures of acetone in excess of 40 Torr in agreement with an average value of 0.3 for the total absorption band obtained by Norrish *et al.* [14]. The flash photolysis of azomethane in Vitreosil vessels involves absorption of light mainly in the region 200 - 212 nm [10]. For initial pressures of azomethane below 5 Torr the decomposition quantum yield was unity.

The consistent agreement of the results obtained in our investigations with the quantum yield data of other authors, for a variety of absorptions regions, is good evidence that the flash lamps emitted light of constant intensity per unit wavelength and also for the effectiveness of the methods for calculating the amount of light absorbed.

Fornstedt and Lindquist [15] also concluded that their flash lamp emitted light of constant intensity over a wide wavelength range. The latter authors utilized a series of different actinometers appertaining to various parts of the spectrum. This conclusion, which we have reached by indirect methods, assumes considerable importance when it is remembered that there is no available direct data concerning the variation of the emitted intensity with wavelengths for any flash photolysis lamp. Indeed Christie and Porter [6] attempted such direct measurements but were unsuccessful.

Acknowledgements

One of us (D.R.A.C.) is indebted to the Science Research Council for an S.R.C. award during the period of this investigation.

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