The Application of Intermittent Illumination to the Bleaching of Dye. I. A General Consideration of the Method

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It is well-known that intermittent illumination (the sector method) has been successfully applied to kinetic studies of polymerization, but it has not yet been introduced in the photobleaching reaction of dye solutions. It is certain, however, that this method would also afford valuable information about the behavior of the intermediate produced by the irradiation of the dye solution. For example, if a certain intermediate with a lifetime of τ absorbs light, there is a possibility that the reaction is accelerated by an intermittent illumination with a frequency comparable with $1/\tau$, as compared with the case in which it is illuminated by a light with a lower frequency. There will be many other cases in which such specific effects may be anticipated. We undertook such experiments by employing the strobolight as a light source. This consists of successive flashes, the duration of which is several microseconds and the frequency of which can be changed within a certain region. Furthermore, one flash can emit a considerable amount of light. It is expected that such a light source has, in some cases, certain advantages over an intermittent light source by means of a sector.

The object of the present paper is to discuss the basic points necessary for such a quantitative application. For example, two factors, the intensity and the frequency of the flash, when varied over a wide range, may have some specific effects on the reaction which may be attributed to the method itself; therefore, it is necessary to consider them beforehand. For example, when the intensity of the flash is increased beyond a certain limit, the quantity of the reaction will become independent of the intensity. The present paper will first discuss four subjects which are closely connected with the experimental results to be presented later.

The Establishment of the Steady State.—When a certain intermediate with a rather long life, τ, is generated by an illumination, its concentration will rise with a successive flash. It is desirable to know the number of flashes which are necessary to get the maximum concentration of the intermediate (X) and the value of the latter when the net reaction does not take place. These findings will be helpful in considering the situation in which the eventual reaction proceeds.

The Effect of ν on the Quantity of Reaction at Various Flash Intensities when $\nu \ll 1/\tau$.—Even when the frequency of the (successive) flashing ν is substantially smaller than $1/\tau$, the quantity of the reaction is still affected by ν in a specific manner depending on the flash intensity. This effect may be said to be due to the method itself. The general features may perhaps be summarized as follows:

A) At a constant light quantity per second, the larger ν may increase the quantity of the reaction per second more or less according to the intensity.

B) At a constant light intensity of one pulse, the quantity of reaction per each successive flash is independent of ν. However, the average quantity of reaction per flash decreases with ν.

The Effect of ν when $\tau \approx 1/\nu$.—A complicated effect due to the method itself may be anticipated.

Some Relations between I and ν Effects when a Genuine Frequency Effect exists.—For example, the case in which X absorbs light and induces an additional reaction will be considered.

I. The Establishment of the Steady State

Let us consider the case in which no net reaction takes place and yet an intermediate, X, with a suitable lifetime, τ, is produced. Upon successive flashes, the concentration of X increases until $X^o{}_n$ and $X^f{}_n$ practically reach the constant value (see Fig. 1).

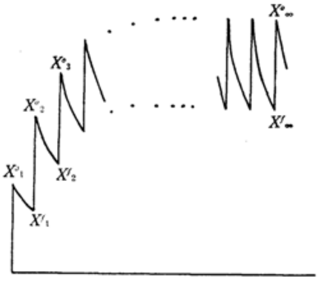

Fig. 1. Change in the concentration of X when no net reaction occurs.

The number of flashes necessary to realize this situation can be derived as follows: Put the initial concentration of dye as C_o and the concentrations of dye immediately after each flash and just before the next flash, respectively, as $C^o{}_n$ and $C^f{}_n$.

$$\left.\begin{array}{l} C_o \to C^o{}_1 \to C^o{}_2 \to \cdots\cdots \\ \phantom{C_o \to{}} X^o{}_1 \to X^o{}_2 \to \cdots\cdots \end{array}\right\}$$

$$\left.\begin{array}{l} C^f{}_1 \to C^f{}_2 \to \cdots\cdots \\ X^f{}_1 \to X^f{}_2 \to \cdots\cdots \end{array}\right\}$$

If $(1-f)$ fraction of dye is changed to X by each flash and if the ratio of $X^f{}_n$ to $X^o{}_n$ is g, the following relations hold:

1st pulse

$$C^o{}_1 = C_o f \qquad X^o{}_1 = C_o(1-f)$$
$$C^f{}_1 = C_o - X^f{}_1 \qquad X^f{}_1 = C_o(1-f)g$$
$$= C_o(1-g+fg)$$

2nd pulse

$$C^o{}_2 = C_o\{1-(1-f)g\}f$$
$$X^o{}_2 = C_o\{1-(1-g+fg)f\}$$
$$C^f{}_2 = C_o\{1-g+fg(1-g)+f^2g^2\}$$
$$X^f{}_2 = gX^o{}_2$$

3rd pulse

$$C^o{}_3 = C^f{}_2 f$$
$$X^o{}_3 = C_o[1-\{1-g+fg(1-g)+f^2g^2\}f]$$
$$C^f{}_3 = C_o[(1-g)+fg(1-g) + f^2g^2(1-g)+f^3g^3]$$
$$X^f{}_3 = gX^o{}_3$$

n-th pulse

$$C^f{}_n = C_o\{(1-g)+fg(1-g)+\cdots \cdots+(fg)^{n-1}(1-g)+f^ng^n\}$$
$$= \frac{C_o}{1-fg}\{(1-f)f^ng^{n+1}+(1-g)\}$$

Changing $(1-f)$ to f for convenience:

$$C^f{}_n = \frac{C_o\{(1-f)^ng^{n+1}f+(1-g)\}}{1-(1-f)g} \tag{1a}$$

$$X^f{}_n = \frac{C_o fg\{1-(1-f)^ng^n\}}{1-(1-f)g} \tag{1b}$$

$$C^o{}_n = \frac{C_o\{(1-f)(1-g)+(1-f)^ng^n\}}{1-(1-f)g} \tag{1c}$$

$$X^o{}_n = \frac{C_o f\{1-(1-f)^ng^n\}}{1-(1-f)g} \tag{1d}$$

For $n \to \infty$:

$$C^f{}_\infty=\frac{1-g}{1-(1-f)g}C_o \qquad (1'\text{a})$$

$$C^o{}_\infty=\frac{(1-f)(1-g)}{1-(1-f)g}C_o \qquad (1'\text{c})$$

$$X^f{}_\infty=\frac{C_ofg}{1-(1-f)g} \qquad (1'\text{b})$$

$$X^o{}_\infty=\frac{C_of}{1-(1-f)g} \qquad (1'\text{d})$$

If X returns to the ground state dye according to the first order reaction, then $g=\exp(-k/\nu)$, where k is a rate constant and ν, the frequency of the flash.

If the light absorption is proportional to $C\varepsilon$ (assuming the cell length to be 1 cm.), f can be written as $\Phi\varepsilon\alpha$, where α is a fraction of the excited dye which reaches X, and Φ is the light quantity per pulse (see II).

As an example, let us consider the case when $f=0.1$ and $k\approx 10\,\text{sec}^{-1}$. For 100 pulses per sec. (100 pps),

$$g=e^{-k/\nu}\approx 0.9 \qquad X^f{}_\infty\approx 0.47C_0$$

It can be estimated that the second term in Eqs. 1a, b, c and d becomes less than 1 % of the first term when $n=20$. For 10 pps, g is ca. 0.4, $X^f{}_\infty$ is ca. 6 % of C_o, and two or three flashes would be enough for X^f to get within 10 % of this $X^f{}_\infty$ value.

If $f=0.01$, $k\approx 10\,\text{sec}^{-1}$, and $\nu=100$, $X^f{}_\infty$ would be about 8 % of the concentration of the ground state dye, and the second term in Eq. 1b becomes one per cent of the first term when n equals 40.

II. Intensity Effect ($\nu\ll 1/\tau$)

The high intensity of the flash is favorable to a large reaction rate. However, if it is too large, the absorption of light is so close to the saturation point that a quantitative treatment is rather troublesome. What kind of effect may be expected when the intensity approaches the saturation value? How is it influenced by the frequency of the flash? What is the largest possible intensity which is not accompanied with complicating effects? These questions must be answered before we can deal with our problem quantitatively.

Let us take the case when the reaction proceeds through X with a rather long τ. At first, however, only the $\nu\ll 1/\tau$ region, where no genuine kinetic effect is expected, will be considered. The scheme is written as follows:

$$\begin{tikzcd} \text{D} \arrow[r] & \text{D}^* \arrow[r] & \text{X} \arrow[r, "k_d"] \arrow[d, "k_r"] & \text{D}, \qquad k_s=k_r+k_d \\ & & \text{Product} & \end{tikzcd}$$

a) The 1 pulse per sec., total light quantity; Φ_o (photons per cm²).

In case the absorption is more or less close to the saturation ($1000\,\Phi_o\varepsilon\alpha\lesssim 1$; see below), the fractions of light absorbed are a little different in the earlier and in the later stages of one flash, although its duration is as short as several microseconds. Differentiating Φ_o into small parts, one can put

$$\text{d}\Phi_{ab}=\varepsilon C\text{d}\Phi_o$$

assuming C to be small enough. If α part of the molecules excited is transferred to X,

$$\alpha\text{d}\Phi_{ab}=-\text{d}C/1000$$

Hence:

$$-\text{d}C=1000\,\alpha C\varepsilon\text{d}\Phi_o$$

Integration gives

$$\ln\frac{C_o}{C}=1000\,\alpha\varepsilon\Phi_o$$

Putting the decrease of C during the flash as $\varDelta C$,

$$\varDelta C=\alpha\Phi_{ab}=C_o(1-e^{-1000\Phi_o\alpha\varepsilon})$$

The quantity of reaction by one flash (R_o) is

$$R_o=\Phi_{ab}\ \alpha\frac{k_r}{k_s}=C_o\frac{k_r}{k_s}(1-e^{-1000\Phi_o\alpha\varepsilon}) \qquad (2)$$

Now let us treat the case in which the following approximation holds, i. e., the case in which f in I, where f is approximated by $\Phi_o\alpha\varepsilon$, must be replaced by $f-f^2/2$. Besides, $1000\Phi_o$ will be replaced by Φ from now on.

$$R_o=\Phi_{ab}\alpha\frac{k_r}{k_s}\approx C_o\frac{k_r}{k_s}\left\{\Phi\alpha\varepsilon-\frac{(\Phi\alpha\varepsilon)^2}{2}\right\}$$
$$=C_o\frac{k_r}{k_s}\left(f-\frac{f^2}{2}\right) \qquad (3)$$

b) The ν times illumination for one second with the flash of Φ.

For the first flash:

$$\varDelta C=C_o\frac{k_r}{k_s}\left(f-\frac{f^2}{2}\right)=C_of'$$

For each successive flash, the initial concentration, C_n, and the quantity of reaction, R_n, may be given as follows:

Flash No.	Initial concn.	R_n*	$\sum R_n$**
1	C_o	C_of'	C_of'
2	$C_o(1-f')$	$C_o(1-f')f'$	$\{C_of'(1-f')+1\}$
3	$C_o(1-f')^2$	$C_o(1-f')^2f'$	$\{C_of(1-f')^2+(1-f')+1\}$
4	$C_o(1-f')^3$	$\vdots$	$\vdots$
$\vdots$	$\vdots$	$\vdots$	$\vdots$
ν	$C_o(1-f')^{\nu-1}$	$C_o(1-f')^{\nu-1}f'$	$C_o(1-(1-f')^\nu)$

* R_n: Quantity of reaction to each flash

** $\sum R_n$: Total quantity of the reaction

The total quantity of the reaction for one second when $\nu f'<1$:

$$\sum_{n=1}^{\nu} R_n = C_0\{1-(1-f')^{\nu}\}$$

$$= C_0\left\{\nu f' - \frac{\nu(\nu-1)}{2!}f'^2 + \frac{\nu(\nu-1)(\nu-2)}{3!}f'^3 + \cdots\right\}$$

and

$$\nu f' = \nu\frac{k_r}{k_s}\left(f - \frac{f^2}{2}\right)$$

$$= \nu\frac{k_r}{k_s}\left\{\Phi\alpha\varepsilon - \frac{(\Phi\alpha\varepsilon)^2}{2}\right\}$$

$$\frac{\nu(\nu-1)}{2!}f'^2 = \frac{\nu(\nu-1)}{2}\left(\Phi^2\,\alpha^2\,\varepsilon^2\frac{k_r^2}{k_s^2} + \cdots\right)$$

Hence,

$$\sum_{n=1}^{\nu} R_n \doteqdot \nu\frac{k_r}{k_s}C_0\left[\Phi\alpha\varepsilon - \frac{(\Phi\alpha\varepsilon)^2}{2}\left\{1+(\nu-1)\frac{k_r}{k_s}\right\}\right] \tag{4}$$

In order for $\sum_{n=1}^{\nu} R_n$ to be proportional to the light intensity (within 10 %), the second term must be less than 10 % of the first term.

So,

$$\Phi\alpha\varepsilon < \frac{0.2}{1+(\nu-1)\dfrac{k_r}{k_s}} \tag{5}$$

This shows that the limit for the linearity largely depends on k_r/k_s. For small values of k_r/k_s, the critical value of Φ does not depend on ν, and for the value of k_r/k_s close to 1, it approaches to $1/\nu$ of that for 1 pps. For instance, in the case of 100 pps, $\Phi_o\varepsilon\alpha$ must be less than 0.004 when $k_r/k_s \approx 0.5$. It is desirable to perform the experiment in the Φ region where the linearity holds approximately irrespective of ν. In the region of Φ treated here, $(1/\nu)\sum_{n=1}^{\nu} R_n$ decreases with the larger ν, and so a correction is needed to get a genuine effect if it is observed.

For example, in the case of 100 pps,

$$\sum_{n=1}^{\nu} R_n = 100\frac{k_r}{k_s}\Phi\alpha\varepsilon C_0\left[1-\frac{1}{2}\left\{1+99\frac{k_r}{k_s}\right\}\Phi\alpha\varepsilon\right] \tag{6}$$

and in case of 10 pps,

$$\sum_{n=1}^{\nu} R_n = 10\frac{k_r}{k_s}\Phi\alpha\varepsilon C_0\left[1-\frac{1}{2}\left\{1+9\frac{k_r}{k_s}\right\}\Phi\alpha\varepsilon\right] \tag{6'}$$

c) The light quantity per second $I_o=\nu\Phi$ is kept constant.

The critical intensity (light quantity per second) below which the linearity holds, increases remarkably with the value of ν. Putting the light quantity per second as $I_o=\nu\Phi$, the quantity of reaction per second, $\sum_{n=1}^{\nu} R_n$, is given by:

$$\sum_{n=1}^{\nu} R_n = C_0\frac{k_r}{k_s}I_0\alpha\varepsilon\left[1-\frac{I_0\alpha\varepsilon}{2\nu}\left\{1+(\nu-1)\frac{k_r}{k_s}\right\}\right] \tag{7}$$

Thus, for 1 pps,

$$\sum_{n=1}^{\nu} R_n = C_0\frac{k_r}{k_s}I_0\alpha\varepsilon\left\{1-\frac{1}{2}I_0\alpha\varepsilon\right\}$$

for 10 pps,

$$\sum_{n=1}^{\nu} R_n = C_0\frac{k_r}{k_s}I_0\alpha\varepsilon\left\{1-\frac{I_0\alpha\varepsilon}{10}\left(\frac{1}{2}+\frac{9}{2}\ \frac{k_r}{k_s}\right)\right\}$$

for 100 pps,

$$\sum_{n=1}^{\nu} R_n = C_0\frac{k_r}{k_s}I_0\alpha\varepsilon\left\{1-\frac{I_0\alpha\varepsilon}{100}\left(\frac{1}{2}+\frac{99}{2}\ \frac{k_r}{k_s}\right)\right\}$$

III. Specific Effect When the Lifetime of X is Comparable with $1/\nu$

Even when no genuine kinetic effect is present, a certain frequency effect may be expected when the lifetime of X is comparable with $1/\nu$. Therefore, it is necessary to examine such an effect before the quantitative investigation can be made. It is, however, perhaps impossible to get an exact expression generally applicable to all cases. Here one has to be satisfied with treating two problems approximately.

a) An approximate expression for the quantity of reaction by n pulses when $nf<1$.

b) An appoximate expression for the quantity of reaction in unit time as a function of ν when $f_o=\nu f=$const. (<1).

a) X produced by each flash goes to the product by the fraction $q=k_r/k_s$. The remaining portion returns to the original dye step by step according to the flashing condition and contributes further to the total quantity of reaction. Thus, if X_n represents the quantity of X produced by the nth flash, then $(1-q)(1-g)X_n$ goes back to the original dye before the commencement of the $(n+1)$th flash. gX_n represents the portion of X_n at the commencement of the $(n+1)$th flash. In the same way, $gX_n(1-g)(1-q)$ returns to the original dye during the period between $(n+1)$-th and the $(n+2)$th flash. These processes continue until the end of all flashings; the situations are similar for all X_n.

On the basis of the above reasoning, one gets a general expression for X_n produced*

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* The meaning of X_n is different from $X^o{}_n$ or $X^f{}_n$.

by the nth flash. For the sake of simplicity, $(1-g)(1-q)$ is set as r.

For the 1st flash,

$$X_1=C_of$$

for the 2nd flash

$$X_2=\{C_of(1-f)+X_1fr\}$$

for the 3rd flash,

$$\begin{aligned}X_3=&\{C_of(1-f)^2+X_1f(1-f)r+X_1fgr\}\\&+X_2fr\end{aligned}$$

for the 4th flash,

$$\begin{aligned}X_4=&C_of(1-f)^3\\&+X_1fr\{(1-f)^2+g(1-f)+g^2\}\\&+X_2fr\{(1-f)+g\}+X_3fr\end{aligned}$$

for the 5th flash,

$$\begin{aligned}X_5=&C_of(1-f)^4\\&+X_1fr\{(1-f)^3+g(1-f)^2\\&\qquad+g^2(1-f)+g^3\}\\&+X_2fr\{(1-f)^2+g(1-f)+g^2\}\\&+X_3fr\{(1-f)+g\}+X_4fr\end{aligned}$$

Hence, for the nth flash,

$$\begin{aligned}X_n=&C_of(1-f)^{n-1}\\&+X_1fr\{(1-f)^{n-2}+g(1-f)^{n-3}\\&\qquad+g^2(1-f)^{n-4}+\cdots+g^{n-2}\}\\&+X_2fr\{(1-f)^{n-3}+g(1-f)^{n-4}\\&\qquad+g^2(1-f)^{n-5}+\cdots+g^{n-3}\}\\&\quad\vdots\\&+X_{n-2}fr\{(1-f)+g\}\\&+X_{n-1}fr\end{aligned}$$

This is simplified as follows:

$$\begin{aligned}\mathrm{X}_n=&C_of(1-f)^{n-1}\\&+rf\Big[X_1\frac{\{(1-f)^{n-1}-g^{n-1}\}}{1-f-g}\\&+X_2\frac{\{(1-f)^{n-2}-g^{n-2}\}}{1-f-g}\\&\cdots+X_{n-2}\frac{\{(1-f)^2-g^2\}}{1-f-g}\\&+X_{n-1}\frac{\{(1-\mathrm{f})-g\}}{1-f-g}\Big]\end{aligned}\tag{8}$$

Similarly,

$$\begin{aligned}X_{n-1}=&C_of(1-f)^{n-2}\\&+rf\Big[X_1\frac{\{(1-f)^{n-2}-g^{n-2}\}}{1-f-g}\\&+X_2\frac{\{(1-f)^{n-3}-g^{n-3}\}}{1-f-g}\\&\cdots+X_{n-3}\frac{\{(1-f)^2-g^2\}}{1-f-g}\\&+X_{n-2}\frac{(1-f-g)}{1-f-g}\Big]\end{aligned}$$

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$$\begin{aligned}X_3=&C_of(1-f)^2\\&+rf\Big[X_1\frac{\{(1-f)^2-g^2\}}{1-f-g}+X_2\frac{1-f-g}{1-f-g}\Big]\end{aligned}$$

$$X_2=C_of(1-f)+rfX_1\frac{(1-f-g)}{1-f-g}$$

$$X_1=C_of$$

To get a simple expression, one has to draw attention to the condition $nf<1$ and has to cut down all the terms higher than f^3.

Then, $X_n=C_of\,(1-f)^{n-1}$

$$\begin{aligned}&+C_orf^2\Big[\frac{(1-f)^{n-1}-g^{n-1}}{1-f-g}\\&+\frac{(1-f)\{(1-f)^{n-2}-g^{n-2}\}}{1-f-g}\\&+\frac{(1-f)^2\{(1-f)^{n-3}-g^{n-3}\}}{1-f-g}\\&+\cdots+(1-f)^{n-2}\frac{(1-f-g)}{(1-f-g)}\Big]\end{aligned}$$

This is reduced to the following equation:

$$\begin{aligned}X_n=&C_of(1-f)^{n-1}\\&+\frac{C_orf^2}{1-f-g}\Big\{(n-1)(1-f)^{n-1}\\&+\frac{g^n-g(1-f)^{n-1}}{1-f-g}\Big\}\end{aligned}$$

In the same way,

$$\begin{aligned}X_{n-1}=&C_of(1-f)^{n-2}\\&+\frac{C_orf^2}{1-f-g}\Big\{(n-2)(1-f)^{n-2}\\&+\frac{g^{n-1}-g(1-f)^{n-2}}{1-f-g}\Big\}\end{aligned}$$

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$$\begin{aligned}X_3=&C_of(1-f)^2\\&+\frac{C_orf^2}{1-f-g}\Big\{2(1-f)^2+\frac{g^3-g(1-f)^2}{1-f-g}\Big\}\end{aligned}$$

$$\begin{aligned}X_2=&C_of(1-f)\\&+\frac{C_orf^2}{1-f-g}\Big\{(1-f)+\frac{g^2-g(1-f)}{1-f-g}\Big\}\end{aligned}$$

$$\mathrm{X}_1=C_of$$

By means of the formula of the geometric progression, one gets

$$\begin{aligned}\sum X_n = {} & C_o\{1-(1-f)^n\} \\ & + \frac{C_o r f^2}{1-f-g}\left[\frac{(1-f)-(n-1)(1-f)^n}{f}\right. \\ & + \frac{(1-f)^2-(1-f)^n}{f^2} \\ & + \frac{g^2-g^{n+1}}{(1-f-g)(1-g)} \\ & \left. - \frac{g(1-f)\{1-(1-f)^{n-1}\}}{(1-f-g)f}\right] \end{aligned} \tag{9a}$$

and the quantity of the reaction, R, is given by:

$$R \equiv q\sum X_n \tag{9b}$$

It is to be added that when $g=0$, the above equation leads to

$$q\sum X_n = C_o\left\{nfq - \frac{n(n-1)}{2}f^2q^2\right\} \tag{10}$$

This is just the expression obtained from $C_o\{1-(1-f)^n\}$, which is the quantity of reaction when the interval of flash is long enough. From Eq. 9a one can easily calculate the quantity of reaction by n flashes for arbitrary values of f, g and q. These calculations must be performed for a set of successive flashes irrespective of the time spent by n flashes. For example, if one sets $f=0.001$, $n=101$, $g=0.5$, and $q\approx 0$, then the quantity of reaction is about 5 % smaller than when $g=0$. Thus, it is expected generally that the shorter the period of flash, the less the quantity of the reaction. It is worth mentioning here that the above formulas (9) hold only when $nf \ll 1$; a much larger effect would be expected if f is larger.*

b) The quantity of reaction per second when $f_o=\nu f=$const. (<1), where ν is the frequency of flash, is easily obtained by an extension of the treatment given in a). The case in which ν is very small need not be considered, since the situations are just the same as with a). When ν is large, g is approximately equal to 1 and is written as follows:

$$g=e^{-k_s/\nu}\approx 1-\frac{k_s}{\nu}, \quad 1-g=\frac{k_s}{\nu}$$

Further, one can replace $(1-f)^\nu$ by e^{-f_o}. Starting from Eq. 8, one can derive following expression by substituting the above relations. (It should be added that all terms higher than f^3 are disregarded.)

$$\begin{aligned} q\sum_{n=1}^{\nu} X_n = {} & C_0\{1-\mathrm{e}^{-f_o}\}q + \frac{C_o q(1-q)k_s f_o^2(\nu-1)}{2(k_s-f_o)\nu} \\ & - \frac{C_o q(1-q)k_s f_o^2(\nu-1)}{2\nu(k_s-f_o)}\left\{1+\frac{k_s f_o}{\nu(k_s-f_o)}\right\} \end{aligned} \tag{11}$$

If ν is large enough, Eq. 11 is simplified as follows (in the approximation to f_o^2):

$$q\sum_{n=1}^{\nu} X_n = C_o\{1-\mathrm{e}^{-f_o}\}q \doteqdot C_o\left\{f_o q - \frac{f_o^2}{2}q\right\} \tag{12}$$

This is to be compared with the quantity of reaction per second obtained under the assumption of a steady state illumination, when X and the product, P, are respectively, produced according to the following relations:

$$\frac{\mathrm{d}X}{\mathrm{d}t} = \alpha\varepsilon I_o C = k_s X \tag{13}$$

$$\frac{\mathrm{d}P}{\mathrm{d}t} = -\frac{\mathrm{d}C}{\mathrm{d}t} = k_r X \tag{14}$$

Equation 13 is restricted to the case where $\alpha\varepsilon C$ is small enough. When I_o is moderately large, the quantity of the reaction per second, R, may be approximately given as follows:

$$\begin{aligned} R &= C_o\left\{\frac{k_r}{k_s}I_o\alpha\varepsilon - \frac{1}{2}\frac{k_r^2}{k_s^2}I_o^2\alpha^2\varepsilon^2\right\} \\ &= C_o\left\{f_o q - \frac{1}{2}f_o^2 q^2\right\} \end{aligned} \tag{15}$$

Thus, when ν is large enough, the quantity of reaction per second is $(1/2)f_o^2 q(1-q)$ less than that of the steady illumination. It is to be noted that Eq. 15 is different from Eq. 12 in the f_o^2 term and that it is equal to Eq. 10 if one replaces n with ν and takes it large enough. Comparing Eq. 15 with Eq. 7, one can say that when $\tau<1/\nu$, the quantity of reaction per second (when $I_o=\nu\Phi=$const.) for the frequency ν is $(1/2\nu)(1-k_r/k_s)I_o^2\alpha^2\varepsilon^2(k_r/k_s)$ less than that of the steady illumination at I_o.

Summing up the results obtained in III and II, one can say as follows. As the frequency of flashing is made larger under the condition $\nu f=f_o=$const., then the quantity of reaction per second increases and tends to the value of the steady illumination in the $\tau<1/\nu$ region, but it decreases when τ becomes larger than $1/\nu$. Further, one can say that when $f_o\approx 0.1$, the ordinary kinetic treatment may be used as in the steady illumination. Thus, it would be better to deal with the rate constant evaluated by the usual method rather than with the quantity of reaction per pulse or per second. The condition for linearity is more stringent for the latter (see IV).

IV. A Model Case

One model case will be considered as an example in which a genuine kinetic frequency effect is to be expected. It is the case in which X absorbs light and then reacts. For this case, an argument similar to that given in III can be made.

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* f represents $\Phi\alpha\varepsilon$, but this is an approximation. An exact expression for $(1\text{-}f)$ is e^{-f}.

The first flash produces the intermediate X in the amount $X_1 = C_0 f$. During the dark period, the fraction of X_1 which goes to the product is $(1-g)q$ and $r=(1-g)(1-q)$ returns to the ground state. The second flash then produces X in the amount $C_0 f(1-f)+X_1 rf$. The situations up to this point are just the same as in III. The difference appears during the second flash, in which the remaining fraction of X_1, i.e., gX absorbs light and some portion of it contributes to the reaction. Thus the g included explicitly in Eq. 8 is reduced to some extent and should be replaced by such a quantity as $g'=g(1-\varepsilon'\alpha'\Phi)$ (when $\varepsilon'\alpha'\Phi$ is small enough). This implies that the fraction $g\varepsilon'\alpha'\Phi$ goes to the product by the absorption of light. Analogous processes go on to the end of all the flashings and the situations are similar for all X_n.

However, the above situations are too complicated to be considered exactly; one must here be content with the treatment of the extreme case in which all the gX reacts upon the absorption of light. In this case one has only to put $g=0$ in Eq. 9. The contribution of X_n to the quantity of reaction is in general given by $X_n\{(1-g)q+g\}$. Another point to be noted, however, is that the summation must be done to the $(n-1)$th flash, because X_n produced by the last flash goes to the product by the amount of $X_n q$.

Thus, the quantity of the product is given by;

$$R' = \sum_{1}^{n-1} X_{n-1}\{(1-g)q+g\} + X_n q$$

By applying Eq. 9 (putting $g=0$) and Eq. 8, one gets:

$$\begin{aligned} R' = {} & \mathrm{C}_0\{1-(1-f)^n\}q + C_0\{1-(1-f)^{n-1}\} \\ & \times g(1-q) + C_0 r f^2 q\left\{\frac{1-(n-2)(1-f)^{n-2}}{f}\right. \\ & \left. + \frac{(1-f)-(1-f)^{n-2}}{f^2} + (n-1)(1-f)^{n-2}\right\} \\ & + C_0 r f^2 g(1-q)\left\{\frac{1-(n-2)(1-f)^{n-2}}{f}\right. \\ & \left. + \frac{(1-f)-(1-f)^{n-2}}{f^2}\right\} \end{aligned} \tag{16}$$

Apart from f^2 terms, one gets from Eqs. 16, 9 and 10:

$$\begin{aligned} R'-R &= C_0\{1-(1-f)^{n-1}\}g(1-q) \\ &\fallingdotseq (n-1)C_0 f g(1-q) \end{aligned} \tag{17}$$

and

$$\frac{R'-R}{R} = \frac{n-1}{n}\,\frac{g(1-q)}{q} \tag{18}$$

The above two formulas are, of course, the maximum values possible for given g and q values, but they make some general features clear. Thus, according to them, the effect is zero when $q=k_r/k_s=1$ and increases with the value of g. Since $g=\exp(-k_s/\nu)$, the effect becomes apparent in the frequency region where $\nu \gtrsim k_s$. Equation 17 does not, however, indicate the intensity effect correctly. This is natural since the above treatment concerns only the extreme case when the light absorption by X is large enough. If one treats the general case, a complicated function involving $g\varepsilon'\alpha'\Phi$ in both denominator and numerator would result.

The situations will be clarified, at least approximately, by the steady state treatment. Thus, if one assumes that $\alpha'\varepsilon' I_0 X (=k'\varepsilon' I_0 X)$ of X undergoes the photo-reaction, then

$$I_0\alpha\varepsilon(C-X) = k_s X + \alpha'\varepsilon' I_0 X$$

and if one assumes X is very small compared with C,

$$\frac{-\mathrm{d}C}{\mathrm{d}t} = \frac{I_0\alpha\varepsilon C_0(k_r + k'' I_0)}{k_s + k'' I_0} \tag{19}$$

In the absence of any extra reaction,

$$\frac{-\mathrm{d}C}{\mathrm{d}t} = I_0\alpha\varepsilon C_0 \frac{k_r}{k_s} \tag{20}$$

Hence, the ratio R'/R in this case is given approximately by

$$\frac{R'}{R} = \frac{1+(k''/k_r)I_0}{1+(k''/k_s)I_0} \tag{21}$$

and

$$\frac{R-R'}{R} = \frac{k'' I_0(1/k_r - 1/k_s)}{1+(k''/k_s)I_0} \tag{22}$$

These values are, in general, not independent of I_0. To sum up, the genuine effect begins to appear at such a frequency when $\nu \gtrsim k_s$ and, in addition, $k'' I_0 (=\alpha'\varepsilon' I_0)$ should be at least comparable with k_r. The intensity exponent for $R'-R$ lies between the first and the second order.

Summary

The method of intermittent illumination by means of flashes of very short duration has been criticized, particularly with regard to the frequency and intensity of the flash. It has been concluded that when f_0 (the fractional decrease of the starting substance per second due to the absorption of light) is less than 0.1, the kinetics for the steady illumination will hold within a few per cent. A model case in which a certain intermediate absorbs light and causes an addition reaction has been discussed.

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