CCII.—*On the Connexion between Absorbed Energy and Velocity in Photochemical Reactions of the* $I^{0\cdot5}$ *Type.*

By ARTHUR JOHN ALLMAND.

SINCE the discovery that the rate of reaction between aqueous solutions of potassium oxalate and iodine in light is proportional to the square root of the intensity (Berthoud and Bellenot, *Helv. Chim. Acta*, 1924, 7, 307), a number of similar cases have been investigated, in the majority of which either bromine or iodine is the absorbing reactant. In reactions in which the velocity is proportional to the first power of the intensity, the quantum efficiency at a given temperature for light of a given wave-length has frequently a definite significance characteristic of the reaction (chain reactions excepted), being independent of intensity, thickness of reaction vessel, and, within certain limits, the concentration of the absorbing reactant. On the other hand, the quantum efficiency for a reaction depending on the square root of the incident light (termed $I^{0\cdot5}$ reactions in what follows) is essentially a function of all these variables.

It therefore becomes of interest to inquire whether there is not some constant which is as characteristic of such a reaction to the same degree as γ is of the $I^{1\cdot0}$ reactions, *i.e.*, a function of wavelength and temperature, but independent of light intensity, concentration of absorbing reactant, and thickness of reaction cell.

It is suggested that constants analogous to the *photochemical susceptibility* (σ) of Henri and Wurmser (*J. Physique*, 1913, **3**, 305) and of Boll (*Ann. Physique*, 1914, **2**, 5, 226) and the *coefficient of utilisation* (Γ) of Tian (*Ann. Physique*, 1916, **5**, 248), developed for $I^{1\cdot0}$ reactions, are suitable for the purpose. σ is merely the proportionality constant k_I of the old "intensity formulation" of photochemical change (*e.g.*, Gros, *Z. physikal. Chem.*, 1901, **37**, 157), according to which the rate is given by the expression

$$-dx/dt = k_I I_0 c^n \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where c is the concentration of the absorbing reactant and I_0 the incident intensity, whilst Γ is the proportionality constant k_A of the old "absorption formulation" of photochemical change (Luther, *Z. Elektrochem.*, 1908, **14**, 445), which wrote

$$-dx/dt = k_A \times \text{(absorbed light)} \quad . \quad . \quad . \quad . \quad (2)$$

and originally assumed that the kinetic order of a light-absorbing substance (n in Equation 1) was always unity. In this case, it can readily be shown that $k_A = k_I/\alpha$, or $\Gamma = \sigma/\alpha$, where α represents the extinction coefficient of the absorbing reactant, the general expression being $\Gamma = \sigma c^{n-1}/\alpha$. If $-dx/dt$ is expressed in molecules and the absorbed light in quanta, Γ becomes of course identical with the quantum efficiency (γ).

Photochemical reactions of the $I^{0\cdot5}$ type can be regarded from the same two points of view. On the intensity formulation, we can write that, at any point in the photolyte,

$$\text{Rate} = k_I I^{0\cdot5} c^n \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where n is usually found in practice to be 0·5. Using the absorption formulation, we have, again for any given volume element of the photolyte,

$$\text{Rate} = k_A \times \text{(rate of absorption of light)}^{0\cdot5} \quad . \quad . \quad (4)$$

The following table contains expressions for (i) rate of reaction, (ii) rate of reaction per unit absorption of energy, derived from Equation 4. It is assumed that insolation is effected by a beam of parallel light normal to the surface of the reaction vessel. I_0 is the incident flux per unit area, and l represents the distance of any particular point in the photolyte measured from the front of the cell.

	Amount transformed per unit time.	Amount transformed per unit time per unit absorption of energy.
(*a*) In a layer of thickness *dl*,		
(i) for any value of *l*.	$k_A . I_0^{\frac{1}{2}} . e^{-\frac{acl}{2}} . c^{\frac{1}{2}} . a^{\frac{1}{2}} . dl$	$\dfrac{k_A}{I_0^{\frac{1}{2}} . e^{-\frac{acl}{2}} . c^{\frac{1}{2}} . a^{\frac{1}{2}}} = \dfrac{k_A}{\left(\text{rate of absorption of light per unit volume}\right)^{\frac{1}{2}}}$
(ii) for $l = 0$.	$k_A . I_0^{\frac{1}{2}} . c^{\frac{1}{2}} . a^{\frac{1}{2}} . dl$	
(*b*) In a layer of finite thickness *l*,		
(i) general expression.	$k_A . I_0^{\frac{1}{2}} . c^{\frac{1}{2}} . a^{\frac{1}{2}} . \int_0^l e^{-\frac{acl}{2}} . dl$ $= k_A . I_0^{\frac{1}{2}} . \dfrac{2}{c^{\frac{1}{2}}a^{\frac{1}{2}}} . (1 - e^{-\frac{acl}{2}})$	$\dfrac{2k_A}{I_0^{\frac{1}{2}} . c^{\frac{1}{2}} . a^{\frac{1}{2}} . (1 + e^{-\frac{acl}{2}})}$
(ii) *acl* very small, very slight absorption.	$k_A . I_0^{\frac{1}{2}} . a^{\frac{1}{2}} . c^{\frac{1}{2}} . l$	$\dfrac{k_A}{I_0^{\frac{1}{2}} . c^{\frac{1}{2}} . a^{\frac{1}{2}}} = \dfrac{k_A}{\left(\text{rate of absorption of light per unit volume}\right)^{\frac{1}{2}}}$
(iii) *acl* very large, complete absorption.	$k_A . I_0^{\frac{1}{2}} . \dfrac{2}{c^{\frac{1}{2}} . a^{\frac{1}{2}}}$	$\dfrac{2k_A}{I_0^{\frac{1}{2}} . c^{\frac{1}{2}} . a^{\frac{1}{2}}}$

It can readily be shown that $k_A = k_I . c^n/c^{\frac{1}{2}}\alpha^{\frac{1}{2}}$, and from this relation the corresponding "intensity formulation" expressions can be derived. Thus, the rate of reaction in a layer of thickness l when absorption is complete is $k_I . I_0^{\frac{1}{2}} . c^n\frac{2}{\alpha c}$.

Discussion.

An examination of the above table leads to the following conclusions.

(*a*) For any wave-length (characterised by definite values of k_A and of α), the quantum efficiency, whilst always being inversely proportional to the square root of the incident intensity, is only inversely proportional to the square root of the rate of absorption of energy if αcl is very small.

(*b*) If, for a definite wave-length, incident intensity and depth of cell, the concentration be continually increased from a very small figure until absorption is practically complete, the quantum efficiency does not alter inversely proportionally with the increase in $c^{\frac{1}{2}}$ during this transition, but less rapidly. In fact, $\gamma c^{\frac{1}{2}}$ rises to double its initial value as c increases indefinitely, $k_A/I_0^{\frac{1}{2}}\alpha^{\frac{1}{2}}$ becoming $2k_A/I_0^{\frac{1}{2}}\alpha^{\frac{1}{2}}$.

(*c*) If, for a definite wave-length, incident intensity and concentration, the thickness be continually increased from a very small figure until absorption is practically complete, the limiting value of γ obtained in very thick layers is double that got with a very thin layer.

(*d*) In $I^{1 \cdot 0}$ reactions, although the absorbed energy can readily be calculated from I_0 on the assumption of the validity of the Beer–Lambert law, most workers prefer to measure it where possible. In the case of $I^{0 \cdot 5}$ reactions, this measurement would appear pointless in view of the non-characteristic nature of the γ value calculated from it. A more rational proceeding would seem to be (i) to measure I_0; (ii) to follow the rate of reaction; (iii) to calculate k_A from one of the last three expressions in column 2 of the above table, knowing c, l, and α. As already indicated, if I_0 is expressed in terms of quanta and the decomposition in terms of molecules, the value obtained for k_A will be such as to allow of the immediate calculation of γ for any particular set of I_0, α, c and l values.

The introduction of the constant k_A has proved useful in connexion with the results of experiments in monochromatic light carried out in this laboratory on two photochemical reactions of the $I^{0 \cdot 5}$ type, *viz.*, the oxidation of aqueous potassium oxalate by iodine and the decomposition of aqueous hydrogen peroxide solutions (hitherto always reported as being of the $I^{1 \cdot 0}$ type). When quantum efficiencies were calculated in the ordinary way, the results appeared anomalous. In the first case, under our particular experimental conditions, γ passed through a maximum in the green. In the second reaction, which is in any event a more complex one, γ_{365} was found, in certain circumstances, to be greater than either γ_{313} or γ_{275}. When, however, the relative k_A values were calculated, in both instances they were found to increase with frequency, just as is normally the case for $I^{1 \cdot 0}$ reactions.

UNIVERSITY OF LONDON,
KING'S COLLEGE.

[*Received, May* 18*th*, 1929.]