# IODINATION. PART IV. STUDIES ON THE PHOTO-IODINATION OF DIFFERENT UNSATURATED ORGANIC COMPOUNDS IN LIGHT OF DIFFERENT FREQUENCIES IN NON-POLAR SOLVENTS.

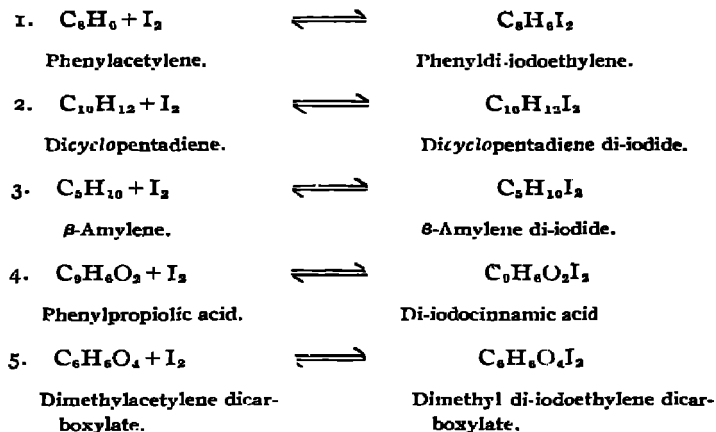BY S. K. BHATTACHARYYA.

Photochemical iodination of phenylacetylene, dicyclopentadiene, dimethylace-tylene dicarboxylate, β-amylene and phenylpropiolic acid in 546, 436 and 366μμ in solutions of $Cl_4$ has been described. The reaction is unimolecular with respect to iodine. The rate of reaction has a small temperature coefficient  The quantum efficiency of the reaction has been worked out to be high in the case of phenylacetylene and dicyclopenta-diene but small in other cases.

Instances of photochemical iodination in non-polar solvents are rarely met with in literature. A short note on the photochemical formation of ethylene iodide in red light in solution of carbon tetrachloride published by De, Right and Wiig (*J. Amer. Chem. Soc.*, 1936, **58**, 693), the photo-chemical decomposition of ethylene iodide studied by Schumacher and co-workers (*Z. physikal. Chem.*, 1930, **B 11**, 45 ; 1931, **B 12**, 348), the photo-chemical iodination of butene, propylene and ethylene at very low tempera-ture in 644, 546 and 436 $\mu\mu$ in solutions of chloroform and carbon tetrachloride studied by Forbes and Nelson (*J. Amer. Chem., Soc.*, 1936, **58**, 182; 1937, **59**, 693) and the vapour phase photoreaction between *cyclo*propane and iodine at temperature a range of 180°-230°, studied by Ogg and Priest (*J. Chem. Phys.*, 1939, **7**, 736), are the only instances known. All these authors found that the reaction in light was simple and proceeded by a chain reaction started by iodine atoms formed by absorption of light.

In this part the results of investigations made on the photochemical iodination of phenylacetylene, dicyclopentadiene, dimethylacetylene dicar-boxylate, β-amylene and phenylpropiolic acid in 546, 436 and 366μμ in solutions of carbon tetrachloride have been described. It is to be pointed out here that the above reactions are reversible and do not proceed to completion except the photoreaction between iodine and phenylacetylene in

solution of carbon tetrachloride which goes almost to completion. The reactions may be represented according to the following equations :—

1.   $C_8H_6 + I_2$      $\rightleftharpoons$      $C_8H_6I_2$

    Phenylacetylene.                  Phenyldi-iodoethylene.

2.   $C_{10}H_{12} + I_2$      $\rightleftharpoons$      $C_{10}H_{12}I_2$

    Dicyclopentadiene.            Dicyclopentadiene di-iodide.

3.   $C_5H_{10} + I_2$      $\rightleftharpoons$      $C_5H_{10}I_2$

     β-Amylene.                     β-Amylene di-iodide.

4.   $C_9H_6O_2 + I_2$      $\rightleftharpoons$      $C_9H_6O_2I_2$

    Phenylpropiolic acid.          Di-iodocinnamic acid

5.   $C_8H_6O_4 + I_2$      $\rightleftharpoons$      $C_8H_6O_4I_2$

    Dimethylacetylene dicar-        Dimethyl di-iodoethylene dicar-
      boxylate.                        boxylate.

## E X P E R I M E N T A L.

The light source was a quartz-mercury point-o-lite lamp run at 2·1 amperes from a battery of 30 volts. Parallel beams of light were obtained by using quartz convex lenses of different focal lengths. Monochromatic radiations of 546, 436 and 366μμ were obtained by using as filters, a dilute solution of copper sulphate (2%) in combination with the corresponding "Schott and Gen" monochromatic filters.

The reaction cell ($4 \times 4 \times 0·5$ c.c. or $4 \times 4 \times 0·3$ c.c.) made of glass plates fused into one another with a stopper at the top was placed inside a double jacketted metal box with a window in front. The temperature of the box was kept constant by circulating, with the aid of a pump, water through the annular space of the box.

*Reagents.*—Merck's extra pure carbon tetrachloride and iodine were purified as in Part I of the series (*J. Indian Chem. Soc.* 1941, **18**, 171). B. D. H. purest phenylacetylene and β-amylene, further purified by distillation, and B.D.H. purest phenylpropiolic acid, further purified by crystallisation, were used. Light's dicyclopentadiene and Kahlbaum's dimethylacetylene dicarboxylate were used after distillation in vacuum. It may be mentioned here that dicyclopentadiene in contact with air forms peroxides (Schulze, *J. Amer. Chem. Soc.*, 1934, **56**, 1552) which affect the kinetic measurements. β-Amylene also forms peroxides in contact with air. So fresh solutions

were prepared with freshly distilled acceptors after every 2 days so that no appreciable amount of peroxides were formed to vitiate our results.

*Measurement of Intensity.*—The intensity of incident radiation was measured by means of a Moll galvanometer and a Moll thermopile, calibrated by means of a standard lamp supplied by the "Bureau of Standards". The energy of absorbed radiation was calculated according to the equation,

$$I_{abs.} = I_0 \times (1 - 10^{-\epsilon.c.d})$$

where $\epsilon$ = molecular extinction coefficient,
$c$ = concentration of iodine in gram mols per litre, and
$d$ = thickness of the reaction cell in cm.

The values of $\epsilon$ at different wave-lengths were found experimentally by intensity measurements in the following way. The deflections in the galvanometer were noted, first of all, with the solvent ($CCl_4$) alone and secondly with iodine solution in $CCl_4$ of known concentration. The molecular extinction coefficient ($\epsilon$) of iodine in $CCl_4$ was then calculated according to the equation,

$$\epsilon = \frac{1}{c \times d} \log_{10} \frac{I_0}{I_t}$$

where $c$ and $d$ have their usual significance as mentioned before. $I_0$ and $I_t$ are the incident and transmitted radiations measured. The values of $\epsilon$ for different wave-lengths ($\lambda$), *e.g.*, 546, 436 and 366$\mu\mu$ are recorded in Table I.

TABLE I.

| $\lambda(\mu\mu)$ | ... | 366 | 436 | 546 |
|---|---|---|---|---|
| | ... | 8·9 | 33·9 | 723·5 |

*Determination of the Velocity of Reaction.*—The velocity of reaction was determined by taking out 1·13 c.c. of the reaction mixture in a micropipette and titrating iodometrically with 0·01$N$-thiosulphate solution by means of a microburette.

The reactions were done at temperatures between 24° and 40°. The concentrations of iodine and the acceptor were so chosen that no measurable dark reaction was observed during the period of investigation. Dicyclopentadiene forms a precipitate with iodine solution having concentrations greater than 0·02$M$ and so the compositions of the reaction mixtures were so chosen that the concentration of iodine was always far less than 0·02$M$. Iodine reacts with $\beta$-amylene even in the dark when the concentrations of the former are high. The thermal reaction was discussed in Parts I and II (*vide* pp. 245, 253).

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The experimental data are recorded in Tables II to XXI. The values of $k_a$, which are recorded, have been derived from the simple monomolecular equation,

$$k_a = \frac{2\cdot3}{t} \log_{10} \frac{a}{a-x}$$

where $a$, is the initial concentration of iodine in gram mols per litre and $x$, the concentration of the iodo product in gram mols per litre, formed in time $t$ seconds. In other words, the reactions are all unimolecular with respect to iodine. But the quantity $k_a$ is not a constant, but depends on $(I_{abs.}^{\frac{1}{2}})$ and [A]. It is thus only a quantity to be calculated which is perhaps convenient to handle but it is not the velocity constant.

The values of $k_a$ were found to diminish very slightly with time. This may be due to two causes, $viz.$, (1) there is a photostationary state, the iodo product formed gives a reverse reaction and (2) with the disappearance of iodine the absorbed energy for the same incident intensity continually diminishes. This happens only in $436\mu\mu$ and $366\mu\mu$ where $\epsilon$ is very small.

The absorbed energy may be considered to be practically constant and the iodo product formed may be regarded as negligible when the concentrations of iodine does not change by more than 10 to 15%. Hence values of $k_a$ as measured above may be regarded as derived under conditions of constant light absorption and negligible amount of iodo product formed.

In the sixth vertical column of Tables II to VI, are given the values of $k_a$ and in the 7th column are given the values of $k_a/I_{abs.}^{\frac{1}{2}}$ It will be seen from these tables that $k_a/I_{abs.}^{\frac{1}{2}}$ have always got the same value for the same monochromatic radiation, but with increase in the magnitude of the quantum absorbed by iodine, the values of $k_a/I_{abs.}^{\frac{1}{2}}$ increase.

### R E S U L T S.

#### *Effect of varying the Concentration of Iodine.*

The notations used in the following tables are given below :

$\theta$ = temperature.

$d$ = thickness of the reaction cell in cm.

$\lambda$ = wave-length.

$a, b$ = initial concentrations of iodine and the acceptor respectively in gram mols per litre.

$I_o$ = intensity of incident radiation in ergs per sq. cm. per sec.

$I_{abs.}$ = number of quanta absorbed by iodine per c.c. per sec.

$\gamma$ = quantum efficiency.

## TABLE II.

Acceptor = Phenylacetylene. $\theta = 24°$. $d = 0.5$ cm.

| λ | a. | b. | $I_0$. | $I_{abs.} \times 10^{-12}$. | $k_\theta \times 10^4$. | $k_\theta \times 10^{12}/I_{abs}^{\frac{1}{2}}$ | γ. |
|---|---|---|---|---|---|---|---|
| 366μμ | 0·005M | 0·05M | 679·2 | 12·54 | 4·3 | 121·5 | 104·0 |
| ,, | 0·03 | ,, | ,, | 63·58 | 10·1 | 126·7 | 248·8 |
| ,, | 0·005 | 0·1 | ,, | 12·54 | 8·7 | 245·8 | 210·2 |
| 436 | 0·005 | 0·05 | 51·0 | 4·01 | 2·3 | 115·5 | 174·7 |
| ,, | 0·0238 | ,, | ,, | 13·74 | 4·3 | 116·1 | 451·4 |
| ,, | 0·005 | 0·1 | ,, | 4·01 | 3·4 | 172·5 | 260·7 |
| 546 | 0·009 | 0·05 | 138·5 | 76·9 | 4·2 | 48·0 | 29·9 |
| ,, | 0·0225 | ,, | ,, | ,, | ,, | ,, | 78·2 |
| ,, | 0·01 | 0·1 | ,, | ,, | 6·8 | 77·5 | 53·6 |

## TABLE III.

Acceptor = Dicyclopentadiene. $\theta = 29°$. $d = 0.3$ cm.

| | a. | b. | $I_0$. | $I_{abs.} \times 10^{-12}$. | $k_\theta \times 10^4$. | $k_\theta \times 10^{12}/I_{abs}^{\frac{1}{2}}$ | γ. |
|---|---|---|---|---|---|---|---|
| 366 | 0·005M | 0·05M | 700·96 | 13·1 | 6·3 | 17·5 | 14·6 |
| ,, | 0·015 | ,, | ,, | 39·2 | 11·0 | 17·8 | 26·2 |
| ,, | 0·005 | 0·1 | ,, | 13·1 | 12·5 | 34·5 | 28·5 |
| 436 | 0·005 | 0·05 | 761·53 | 62·3 | 10·0 | 12·7 | 4·9 |
| ,, | 0·015 | ,, | ,, | 167·2 | 17·3 | 13·4 | 9·4 |
| ,, | 0·005 | 0·1 | ,, | 62·3 | 19·5 | 24·7 | 9·5 |
| 546 | 0·0049 | 0·05 | 121·15 | 102·15 | 7·5 | 7·4 | 2·2 |
| ,, | 0·0123 | ,, | ,, | 112·20 | 7·5 | 7·0 | 4·9 |
| ,, | 0·0049 | 0·1 | ,, | 102·5 | 12·7 | 12·5 | 3·7 |

## TABLE IV.

Acceptor = β-amylene. $\theta = 23°$. $d = 0.5$ cm.

| | a. | b. | $I_0$. | $I_{abs.} \times 10^{-12}$. | $k_\theta \times 10^4$. | $k_\theta \times 10^{12}/I_{abs}^{\frac{1}{2}}$ | γ. |
|---|---|---|---|---|---|---|---|
| 366 | 0·01M | 0·05M | 709·6 | 25·8 | 2·1 | 4·1 | 4·9 |
| ,, | 0·02 | ,, | ,, | 48·9 | 2·7 | 3·9 | 6·8 |
| 436 | 0·01 | 0·05 | 900·0 | 120·3 | 3·3 | 3·0 | 1·7 |
| ,, | 0·02 | ,, | ,, | 217·3 | 4·2 | 2·9 | 2·4 |
| 546 | 0·01 | 0·05 | 1800·0 | 1000·0 | 4·6 | 1·5 | 0·3 |
| ,, | 0·02 | ,, | ,, | ,, | ,, | ,, | 0·6 |

## TABLE V.

Acceptor = Phenylpropiolic acid. $\theta = 30°$. $d = 0.5$ cm.

| | a. | b. | $I_0$. | $I_{abs.} \times 10^{-12}$. | $k_\theta \times 10^4$. | $k_\theta \times 10^{12}/I_{abs}^{\frac{1}{2}}$ | γ. |
|---|---|---|---|---|---|---|---|
| 366 | 0·01M | 0·03M | 147·1 | 5·4 | 5·4 | 2·3 | 6·2 |
| ,, | 0·032 | ,, | ,, | 15·4 | 8·9 | 2·3 | 11·3 |
| 436 | 0·01 | 0·03 | 311·5 | 44·7 | 7·0 | 1·0 | 0·9 |
| ,, | 0·032 | ,, | ,, | 98·7 | 10·9 | 1·1 | 2·2 |
| 546 | 0·01 | 0·03 | 86·5 | 48·1 | 6·1 | 0·9 | 0·8 |
| ,, | 0·02 | ,, | ,, | ,, | 5·6 | 0·8 | 1·4 |

## TABLE VI.

Acceptor = Dimethylacetylene dicarboxylate.    $\theta = 30°$.    $d = 0\cdot3$ cm.

| λ. | a. | b. | $I_0$. | $I_{abs.} \times 10^{-12}$. | $k_\theta \times 10^6$. | $k_\theta \times 10^{12}/I_{abs.}^{\frac{1}{2}}$ | γ. |
|---|---|---|---|---|---|---|---|
| 366μμ | 0·0059M | 0·125M | 597·1 | 13·2 | 3·3 | 0·9 | 0·9 |
| ,, | 0·0339 | ,, | ,, | 69·6 | 8·1 | 1·0 | 2·4 |
| 436 | 0·0297 | 0·165 | 106·2 | 39·5 | 5·7 | 0·9 | 2·6 |
| ,, | 0·0695 | ,, | ,, | 63·2 | 7·2 | 0·9 | 4·8 |
| 546 | 0·0063 | 0·125 | 119·0 | 105·5 | 5·2 | 0·5 | 0·2 |
| ,, | 0·0252 | ,, | ,, | 110·2 | 5·1 | 0·5 | 0·7 |

*Effect of varying the Concentration of the Acceptor.*

## TABLE VII.

Acceptor = Phenylacetylene.    $\theta = 24°$.    $d = 0\cdot5$ cm.

| | a. | b. | $I_0$. | $I_{abs.} \times 10^{-12}$. | $k_\theta \times 10^4$. | γ. |
|---|---|---|---|---|---|---|
| 366 | 0·01M | 0·025M | 679·2 | 24·6 | 3·3 | 81·2 |
| ,, | ,, | 0·05 | ,, | ,, | 6·4 | 158·9 |
| ,, | ,, | 0·1 | ,, | ,, | 11·9 | 295·5 |
| ,, | ,, | 0·15 | ,, | ,, | 17·3 | 429·6 |
| 436 | 0·015 | 0·025 | 51·0 | 10·04 | 2·6 | 234·0 |
| ,, | ,, | 0·05 | ,, | ,, | 3·7 | 336·3 |
| ,, | ,, | 0·1 | ,, | ,, | 5·3 | 484·5 |
| 546 | ,, | 0·033 | 138·46 | 76·9 | 3·8 | 45·5 |
| ,, | ,, | 0·066 | ,, | ,, | 5·1 | 60·3 |
| ,, | ,, | 0·132 | ,, | ,, | 7·5 | 88·7 |

## TABLE VIII.

Acceptor = Dicyclopentadiene.    $\theta = 29°$.    $d = 0\cdot3$ cm.

| | a. | b. | $I_0$. | $I_{abs.} \times 10^{-12}$. | $k_\theta \times 10^6$. | γ. |
|---|---|---|---|---|---|---|
| 366 | 0·01M | 0·25M | 700·96 | 26·2 | 4·9 | 11·5 |
| ,, | ,, | 0·05 | ,, | ,, | 9·3 | 21·6 |
| ,, | ,, | 0·1 | ,, | ,, | 18·3 | 42·7 |
| ,, | ,, | 0·2 | ,, | ,, | 35·0 | 81·5 |
| 436 | ,, | 0·025 | 761·53 | 117·8 | 7·3 | 3·7 |
| ,, | ,, | 0·05 | ,, | ,, | 14·6 | 7·5 |
| ,, | ,, | 0·1 | ,, | ,, | 29·0 | 15·0 |
| 546 | 0·0123 | 0·0167 | 121·15 | 112·2 | 3·5 | 2·3 |
| ,, | | 0·033 | ,, | ,, | 5·6 | 3·7 |
| ,, | ,, | 0·083 | ,, | ,, | 8·3 | 5·5 |

## TABLE IX.

Acceptor = β-amylene.   θ = 24°.   d = 0·5 cm.

| λ. | a. | b. | $I_0$. | $I_{abs.} \times 10^{-12}$. | $k_a \times 10^6$. | γ. |
|---|---|---|---|---|---|---|
| 366μμ | 0·01M | 0·025M | 709·6 | 25·8 | 1·1 | 2·5 |
| ,, | ,, | 0·1 | ,, | ,, | 3·9 | 9·3 |
| ,, | ,, | 0·2 | ,, | ,, | 8·0 | 18·9 |
| 436 | ,, | 0·025 | 900·0 | 120·3 | 1·7 | 0·9 |
| ,, | ,, | 0·05 | ,, | ,, | 3·3 | 1·7 |
| ,, | ,, | 0·1 | ,, | ,, | 6·9 | 3·5 |
| 546 | ,, | 0·025 | 588·5 | 327·0 | 1·3 | 0·2 |
| ,, | ,, | 0·05 | ,, | ,, | 2·6 | 0·4 |
| ,, | ,, | 0·1 | ,, | ,, | 5·5 | 1·0 |

## TABLE X.

Acceptor = Phenylpropiolic acid.   θ = 30°.   d = 0·5 cm.

| | a. | b. | $I_0$. | $I_{abs.} \times 10^{-12}$. | $k_a \times 10^6$. | γ. |
|---|---|---|---|---|---|---|
| | 0·01M | 0·01M | 147·1 | 5·4 | 1·8 | 2·0 |
| ,, | ,, | 0·02 | ,, | ,, | 3·4 | 3·8 |
| ,, | ,, | 0·04 | ,, | ,, | 7·5 | 8·4 |
| 436 | ,, | 0·02 | 311·5 | 44·7 | 5·0 | 0·7 |
| ,, | ,, | 0·03 | ,, | ,, | 7·0 | 0·9 |
| ,, | ,, | 0·04 | ,, | ,, | 9·8 | 1·3 |
| 546 | ,, | 0·01 | 86·5 | 48·1 | 2·1 | 0·3 |
| ,, | ,, | 0·02 | ,, | ,, | 4·1 | 0·5 |
| ,, | ,, | 0·04 | ,, | ,, | 8·3 | 1·1 |

## TABLE XI.

Acceptor = Dimethylacetylene dicarboxylate.   θ = 30°   d = 0·3 cm.

| | a. | b. | $I_0$. | $I_{abs.} \times 10^{-12}$. | $k_a \times 10^6$. | γ. |
|---|---|---|---|---|---|---|
| 366 | 0·0115M | 0·125M | 597·1 | 25·5 | 4·8 | 1·3 |
| ,, | ,, | 0·375 | ,, | ,, | 14·4 | 3·9 |
| 436 | 0·0152 | 0·0825 | 318·5 | 69·9 | 3·2 | 0·4 |
| ,, | ,, | 0·495 | ,, | ,, | 21·0 | 2·8 |
| 546 | 0·0126 | 0·125 | 119·0 | 110·2 | 5·2 | 0·4 |
| ,, | ,, | 0·375 | ,, | ,, | 16·0 | 1·2 |

From Tables VII to XI it appears that velocity constant varies nearly proportionally with the concentration of the acceptor.

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*Effect of varying the Intensity of Absorbed Radiation.*

### TABLE XII.

**Acceptor = Phenylacetylene.** $\theta = 24°$.   $d = 0.5$ cm.

| λ. | a. | b. | $I_{abs.} \times 10^{-12}$. | $k_e \times 10^6$. | $k_e \times 10^{12}/I_{abs.}^{\frac{1}{2}}$. | γ. |
|---|---|---|---|---|---|---|
| 366μμ | 0.01M | 0.05M | 24.6 | 6.4 | 129.0 | 158.9 |
| ,, | ,, | ,, | 12.3 | 4.5 | 128.6 | 221.7 |
| 436 | 0.01 | 0.05 | 7.33 | 3.1 | 114.8 | 256.0 |
| ,, | ,, | ,, | 2.44 | 1.8 | 115.4 | 446.7 |
| 546 | 0.015 | 0.05 | 76.9 | 4.2 | 48.0 | 49.7 |
| ,, | ,, | ,, | 29.0 | 2.7 | 49.6 | 83.7 |

### TABLE XIII.

**Acceptor = Di*cyclo*pentadiene.**   $\theta = 29°$.   $d = 0.3$ cm.

| | a. | b. | $I_{abs.} \times 10^{-12}$. | $k_e \times 10^6$. | $k_e \times 10^{12}/I_{abs.}^{\frac{1}{2}}$. | γ. |
|---|---|---|---|---|---|---|
| 366 | 0.01M | 0.1M | 26.2 | 18.3 | 35.7 | 42.3 |
| ,, | ,, | ,, | 4.5 | 7.7 | 36.2 | 103.0 |
| 436 | 0.01 | 0.1 | 96.3 | 25.0 | 25.5 | 15.7 |
| ,, | ,, | ,, | 10.7 | 8.3 | 25.5 | 47.2 |
| 546 | 0.0099 | 0.1 | 112.2 | 12.8 | 12.1 | 6.8 |
| ,, | ,, | ,, | 56.1 | 9.3 | 12.4 | 9.9 |

### TABLE XIV.

**Acceptor = β-amylene.** $\theta = 24°$.   $d = 0.5$ cm.

| | a. | b. | $I_{abs.} \times 10^{-12}$. | $k_e \times 10^6$. | $k_e \times 10^{12}/I_{abs.}^{\frac{1}{2}}$. | γ. |
|---|---|---|---|---|---|---|
| 366 | 0.01M | 0.1M | 25.8 | 3.9 | 9.5 | 9.3 |
| ,, | ,, | ,, | 6.5 | 2.1 | 9.6 | 19.3 |
| 436 | 0.01 | 0.1 | 120.3 | 6.9 | 6.3 | 3.5 |
| ,, | ,, | ,, | 6.7 | 1.7 | 6.5 | 15.3 |
| 546 | 0.01 | 0.1 | 327.0 | 5.6 | 3.1 | 1.0 |
| ,, | ,, | ,, | 24.1 | 1.5 | 3.1 | 3.8 |

### TABLE XV.

**Acceptor = Phenylpropiolic acid.** $\theta = 30°$.   $d = 0.5$ cm.

| | a. | b. | $I_{abs.} \times 10^{-12}$. | $k_e \times 10^6$. | $k_e \times 10^{12}/I_{abs.}^{\frac{1}{2}}$. | γ. |
|---|---|---|---|---|---|---|
| 366 | 0.01M | 0.03M | 5.4 | 5.4 | 2.3 | 6.2 |
| ,, | ,, | ,, | 2.2 | 3.9 | 2.6 | 10.0 |
| 436 | 0.01 | 0.03 | 44.7 | 7.0 | 1.0 | 1.0 |
| ,, | ,, | ,, | 13.9 | 3.8 | 1.0 | 1.7 |
| 546 | 0.01 | 0.03 | 48.1 | 6.0 | 0.9 | 0.8 |
| ,, | ,, | ,, | 24.0 | 4.2 | 0.9 | 1.1 |

## TABLE XVI.

Acceptor = Dimethylacetylene dicarboxylate.   $\theta = 30°$.   $d = 0.3$ cm.

| $\lambda$. | $a$. | $b$. | $I_{abs.} \times 10^{-12}$. | $k_6 \times 10^n$. | $k_6 \times 10^{12}/I_{abs.}^{\frac{1}{2}}$. | $\gamma$. |
|---|---|---|---|---|---|---|
| $366\mu\mu$ | $0.0115M$ | $0.125M$ | $25.5$ | $4.8$ | $1.0$ | $1.3$ |
| ,, | ,, | ,, | $12.7$ | $3.5$ | $2.0$ | $1.9$ |
| $436$ | $0.015$ | $0.165$ | $69.9$ | $6.9$ | $0.8$ | $0.9$ |
| ,, | ,, | ,, | $23.4$ | $4.0$ | $0.8$ | $1.5$ |
| $546$ | $0.0126$ | $0.125$ | $110.2$ | $5.2$ | $0.5$ | $0.4$ |
| ,, | ,, | ,, | $35.1$ | $3.7$ | $0.5$ | $0.5$ |

From Tables XII to XVI the velocity constant appears to be directly proportional to the square root of the intensity of absorbed radiation.

### *Effect of Varying the Temperatures*

## TABLE XVII.

Acceptor = Phenylacetylene.   $d = 0.5$ cm.

| $\lambda$. | $a$. | $b$. | $I_0$. | $I_{abs.} \times 10^{-12}$. | $k_6 \times 10^6$ | | $v$. |
|---|---|---|---|---|---|---|---|
| | | | | | $\theta = 24°$. | $\theta = 34°$. | |
| $366\mu\mu$ | $0.01M$ | $0.05M$ | $679.2$ | $24.6$ | $6.4$ | $6.5$ | $1.01$ |
| $436$ | ,, | ,, | $51.0$ | $7.3$ | $2.9$ | $3.1$ | $1.07$ |
| $546$ | $0.015$ | $0.066$ | $138.5$ | $76.9$ | $5.1$ | $5.7$ | $1.1$ |

## TABLE XVIII.

Acceptor = Dicyclopentadiene.   $d = 0.3$ cm.

| $\lambda$. | $a$. | $b$. | $I_0$. | $I_{abs.} \times 10^{-12}$. | $k_6 \times 10^5$ | | $v$. |
|---|---|---|---|---|---|---|---|
| | | | | | $\theta = 29°$. | $\theta = 39°$. | |
| $366$ | $0.01M$ | $0.1M$ | $700.96$ | $26.2$ | $18.3$ | $18.3$ | $1.0$ |
| $436$ | ,, | $0.05$ | $747.2$ | $117.8$ | $14.6$ | $15.2$ | $1.04$ |
| $546$ | $0.0099$ | $0.05$ | $121.15$ | $112.2$ | $7.4$ | $8.4$ | $1.13$ |

## TABLE XIX

Acceptor = $\beta$-amylene.   $d = 0.5$ cm.

| $\lambda$. | $a$. | $b$. | $I_0$. | $I_{abs.} \times 10^{-12}$. | $k_6 \times 10^5$ | | $v$. |
|---|---|---|---|---|---|---|---|
| | | | | | $\theta = 24°$. | $\theta = 34°$. | |
| $366$ | $0.01M$ | $0.05M$ | $709.6$ | $25.8$ | $2.1$ | $2.1$ | $1.0$ |
| $436$ | ,, | ,, | $900.0$ | $120.3$ | $3.3$ | $3.4$ | $1.03$ |
| $436$ | | ,, | $43.3$ | $24.1$ | $0.8$ | $0.9$ | $1.12$ |

## TABLE XX.

Acceptor = Phenylpropiolic acid.    $d = 0.5$ cm.

| λ. | a. | b. | $I_0$. | $I_{abs.} \times 10^{-13}$. | $k_6 \times 10^6$ | | v. |
|---|---|---|---|---|---|---|---|
| | | | | | $\theta = 24°$. | $\theta = 34°$. | |
| 366μμ | 0.01M | 0.03M | 147.1 | 5.4 | 5.4 | 5.4 | 1.0 |
| 436 | ,, | ,, | 311.5 | 44.7 | 7.0 | 7.2 | 1.03 |
| 546 | ,, | ,, | 86.5 | 48.1 | 6.1 | 6.6 | 1.09 |

## TABLE XXI.

Acceptor = Dimethylacetylene dicarboxylate.    $d = 0.5$ cm.

| λ. | a. | b. | $I_0$. | $I_{abs.} \times 10^{-13}$. | $k_6 \times 10^6$ | | v. |
|---|---|---|---|---|---|---|---|
| | | | | | $\theta = 30°$ | $\theta = 40°$ | |
| 366 | 0.0223M | 0.125M | 597.1 | 47.2 | 6.7 | 6.9 | 1.03 |
| 436 | 0.0152 | 0.165 | 318.5 | 69.9 | 6.9 | 7.3 | 1.05 |
| 546 | 0.0126 | 0.126 | 119.0 | 110.2 | 5.2 | 5.5 | 1.07 |

$v$ = Temperature coefficient for 10° rise.

From Tables XVII to XXI we see that the temperature coefficient is nearly unity.

### Quantum Efficiency of the Process.

Calculation of the quantum efficiency has not much theoretical significance in these reactions, because the velocity observed is really due to reaction chains started by the iodine atoms which attain a definite value at the stationary state. However, the quantum efficiency has been calculated here only to have some idea of the mechanism of the reaction.

A typical method of calculation is given below :—

At the beginning of the reaction we may take it that the reaction is represented by the equation

$$\Delta x = k_6 [I_2] \, \Delta t.$$

The significance of this equation will be found from the discussion.

Taking the concentration of phenylacetylene = 0.1M ; the concentration of iodine = 0.01M and $k_6 = 6.8 \times 10^{-4}$, and $\lambda = 546 \mu\mu$,

we get    $\dfrac{\Delta x}{\Delta t} = k_6 [I_2] = 6.8 \times 10^{-4} \times 0.01 \times 10^{-3}$ mols per c.c. per sec.

$= 6.8 \times 10^{-1} \times 0.01 \times 10^{-3} \times 6.06 \times 10^{23}$ molecules of iodine per c.c. per sec.

$= 41.208 \times 10^{14}$ molecules of iodine per c.c. per sec.

Again, when the intensity of incident radiation $= 138\cdot5$ ergs per sq. cm. per sec. and the thickness of the cell $= 0\cdot5$ cm., the intensity of absorbed radiation $= 277\cdot0$ ergs per c.c. per sec.

Therefore, the number of quanta absorbed by 1 c.c. of solution per sec.

$$(I_{abs.}) = \frac{277\cdot0}{h\nu} = \frac{277\cdot0}{3\cdot6 \times 10^{-12}} = 76\cdot9 \times 10^{12}.$$

Hence $\gamma =$ quantum efficiency $= \dfrac{41\cdot208 \times 10^{14}}{76\cdot9 \times 10^{12}} = 53\cdot6.$

All the other calculations are made in the same way.

## Discussion.

The reactions have the following characteristics :—

1. They are unimolecular with respect to iodine. Of course, it is quite wrong in photochemical reactions to search for velocity constants of the first, second or any order. The quantity $k_6$ which has been calculated according to the equation,

$$k_6 = \frac{2\cdot3}{t} \log_{10} \frac{a}{a-x}$$

is not a constant, but depends on $I_{abs.}^{\frac{1}{2}}$ and on $[A]$. It is thus only a quantity to be calcuated which is perhaps convenient to handle but it is not the velocity constant.

2. The quantity $k_6$ diminishes slightly with the progress of the reaction, and is directly proportional to the square root of the intensity of the absorbed radiation. It increases nearly proportionally with the increase in the concentration of the acceptors. At $546\ \mu\mu$, where the absorption of iodine is complete with very dilute solutions, $k_6$ is independent of the initial concentrations of iodine. At $436$ and $366\mu\mu$, where iodine has weak absorption, $k_6$ increases with increasing concentration of iodine. In fact $k_6 \times 10^{12}/I_{abs.}^{\frac{1}{2}}$ remains always constant for a particular wave-length but increases with the increase in the magnitude of the quanta absorbed by iodine.

The temperature coefficient is small, nearly unity. The quantum efficiency is very high in the case of phenylacetylene and dicyclopentadiene, but in other cases it is very small.

The experimental data recorded above can be explained by the following addition reactions:

$$I_2 + h\nu = I + I \qquad \ldots \qquad \ldots \qquad \ldots \quad (i)$$
$$I + I = I_2 \qquad \ldots \qquad \ldots \qquad \ldots \quad (ii)$$
$$I + A = AI \qquad \ldots \qquad \ldots \qquad \ldots \quad (iii)$$
$$AI = I + A \qquad \ldots \qquad \ldots \qquad \ldots \quad (iv)$$
$$AI + I_2 = AI_2 + I \qquad \ldots \qquad \ldots \qquad \ldots \quad (v)$$

where A represents the acceptor molecule. In these reactions the concentration of iodine atoms per c.c. in the stationary state is given by the relation

$$[I] = \left( \frac{1}{k_2} \cdot I_{abs.} \right)^{\frac{1}{2}}$$

where $I_{abs.}$ = number of quanta absorbed by iodine per c.c. per sec. Hence the above mechanism given for

$$k_6 = - \frac{1}{[I_2]} \cdot \frac{d[I_2]}{dt} = k_5 \cdot \frac{k_3}{k_4} \left( \frac{1}{k_2} \cdot I_{abs.} \right)^{\frac{1}{2}} [A]$$

$$= k'(I_{abs.})^{\frac{1}{2}} [A] \qquad \qquad \ldots \quad (a)$$

The equation (a) agrees very well with the experimental observations recorded in Tables XII to XVI that $k_6$ varies directly as the square root of the energy of absorbed radiation.

From equation (a) it also follows that $k_6$ is directly proportional to the concentration of the acceptor, which has been approximately found to be the case.

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