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An Infinite Optical Path Photoreactor and a Filter for the Isolation of Light at 366 NM

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Abstract : It is well known that the conventional optical bench photoreactors have many shortcomings such as inefficient utilisation of light, calibration of absorbed light intensity, etc. A new reactor, namely, the infinite optical path photoreactor, which eliminates most of the shortcomings is discussed. A theory for this reactor is derived. A new chemical filter for the isolation of light at 366 nm is shown to be effective.

1. Introduction

A photochemical reaction system differs from a normal chemical system in that the former has an additional feature which allows the exposure of the reaction mixture to a monochromatic light of definite intensity. Therefore, the design of a photochemical reaction system requires special attention as to

(i) the proper choice of construction material and filter,

(ii) the proper positioning of the light source,

(iii) the thermostating of the reaction vessel to prevent the temperature of the reaction system rising due to continued irradiation,

(iv) precautions for the prevention of loss of light due to reflection,

(v) the maximum light utilization efficiency.

The conventional (optical bench) photoreactor suffers from the following drawbacks :

(i) Inefficient utilization of light due to collimation difficulties.

(ii) Calibration of the absorbed light intensity is not possible as it is a function of the reactants.

(iii) Correction for the reflection and scattering of light at the glass-reactants interface is necessary.

(iv) Gradual variation of intensity of light absorbed within the reaction mixture, due to the consumption of the reactants, may cause changes in mechanism.

(v) Gradual variation of intensity with distance may cause different mechanisms to operate at different points in the solution.

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An 'infinite optical path photoreactor' (Figure 1) was designed which partially removed the above said defects. The unique feature of the reactor is its 100% light absorption and as a consequence of this, the following advantages are accomplished :

(i) Increased power utilization efficiency.

(ii) Easy calibration by only one actinometry experiment.

(iii) There is no variation of absorbed intensity (at any point in the reaction mixture) with time, because emitted light is totally absorbed by the reaction mixture, whatever its concentration, due to the infinite optical path available for absorption.

(iv) The variation of absorbed intensity with position is less marked (than in an optical bench photoreactor) due to the averaging effect caused by the periodic retracing of the path of a given ray due to multiple reflections.

(v) The correction for reflection at interface is irrelevant in this case due to the fact that there is no provision for light loss due to the geometry of the reactor.

2. Theoretical

The most spectacular feature of the reactor is its infinite optical path. The condition under which this photoreactor is of infinite optical path will be derived below.

Let the source be designated by 0 and the first reflection at the wall by 1, the second reflection at the wall by 2 and the third reflection by 3, etc.

Let α, β and γ be the optical densities of the filter system, reaction mixture and the pyrex wall of the reaction vessel, respectively, where

$$\alpha = \varepsilon_f C_f l_f + \varepsilon_{CA} C_{CA} l_{CA} + \varepsilon_{MB} C_{MB} l_{MB}$$

as the filter system (in this case) is made of two concentric cylindrical compartments containing chrome alum (CA) and methylene-blue (MB) separately (Figure 2).

$$\beta = \varepsilon_r C_r l_r \text{ (for the reaction mixture)}$$

$$\gamma = \varepsilon_\omega C_\omega l_\omega$$

where f = filter (pyrex) glass

r = reaction mixture

ω = pyrex glass wall

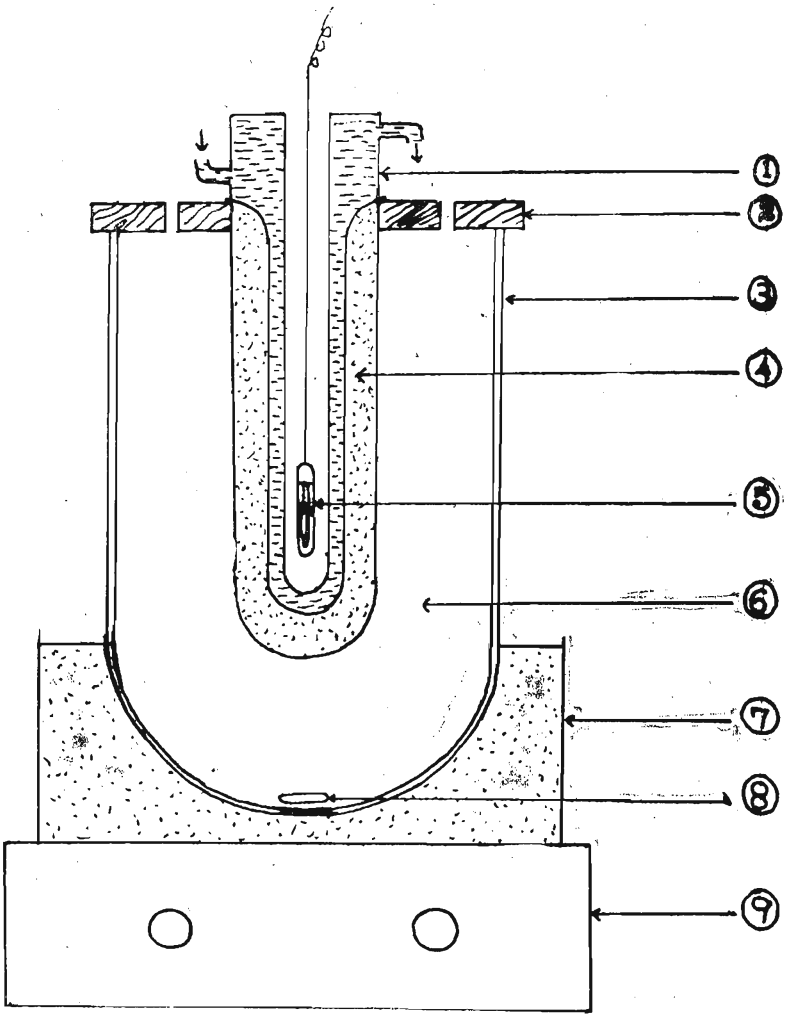

Figure 1. Infinite optical path photoreactor

1. Water jacket
2. Wooden lid
3. Thermos flask
4. Filter solution (CA)
5. Mercury lamp (medium pressure)
6. Reaction mixture
7. Regiform box
8. Magnetic needle
9. Magnetic stirrer

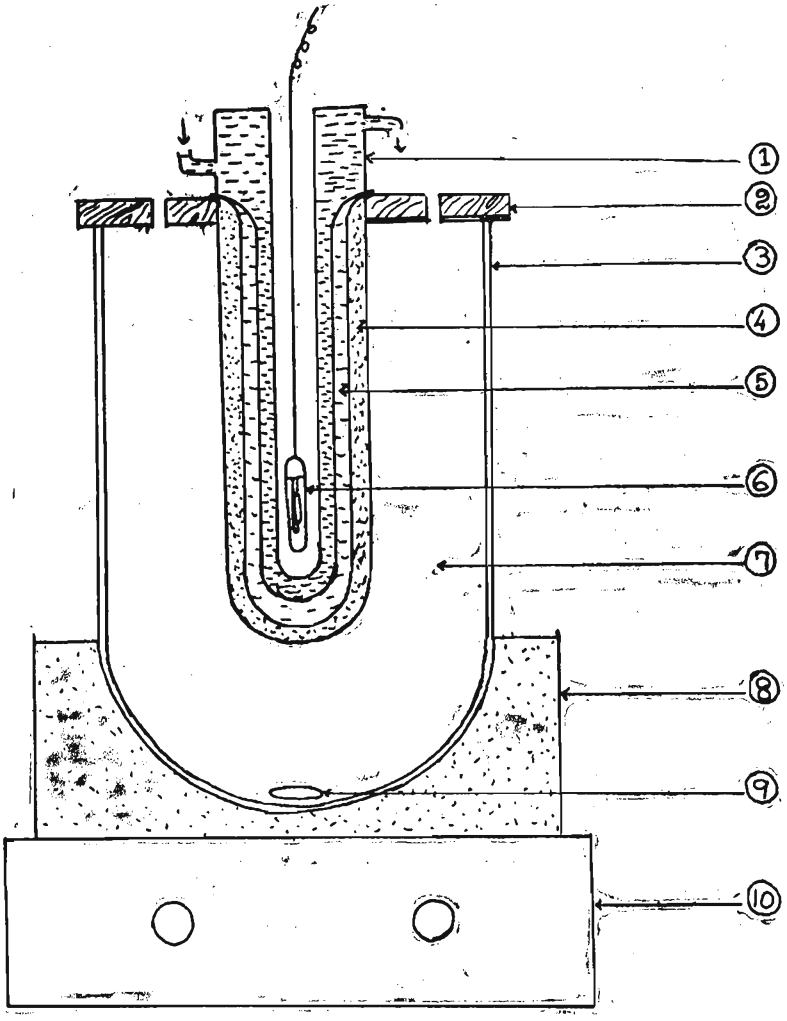

Figure 2. Infinite optical path photoreactor

1. Water jacket
2. Wooden lid
3. Thermos flask
4. Filter solution (MB)
5. Filter solution (CA)
6. Mercury lamp (medium pressure)
7. Reaction mixture
8. Regiform box
9. Magnetic needle
10. Magnetic stirrer

Let I_{ij} be the intensity of light absorbed by the reaction mixture when the light travels from i to j where

$i = 0, 1, 2.....$ and $j = i + 1$ (i.e. $i \varepsilon N$)

Assuming that there is no reflection at the interfaces and losses through the opening (Figure 2),

by Beer-Lambert's law,

$I_{oi} = I_o(\lambda)\ 10^{-\alpha}\ (1 - 10^{-\beta})$ where

$I_o(\lambda)$ is the intensity of light emitted at λ *nm*

$$I_{12} = I_o(\lambda)\, 10^{-(\alpha+\beta)}\, 10^{-\gamma}\,(1 - 10^{-\beta}) + I_o(\lambda)\, 10^{(3\alpha+\beta+\gamma)}\,(1 - 10^{-\beta})$$

$$I_{23} = I_o(\lambda)\, 10^{-(3\alpha+2\beta+\gamma)}\,(1 - 10^{-\beta}) + I_o(\lambda)\, 10^{-(5\alpha+3\beta+2\gamma)}\,(1 - 10^{-\beta})$$

$$I_{34} = I_o(\lambda)\, 10^{-(5\alpha+4\beta+3\gamma)}\,(1 - 10^{-\beta}) + I_o(\lambda)\, 10^{-(7\alpha+5\beta+2\gamma)}\,(1 - 10^{-\beta})$$

Total intensity of light absorbed by the reaction mixture (I_{abs}) is given by the following equation

$$I_{abs} = \sum_{i=0} I_{ij} \quad (j = i + 1)$$

$$I_{abs} = I_o(\lambda)\, 10^{-\alpha}\,(1 - 10^{-\beta}) \left\{ 1 + \frac{1}{10^{(\beta+\gamma)}} + \frac{1}{10^{(2\alpha+\beta+\gamma)}} \cdots\cdots \right.$$

$$\left. + \frac{1}{10^{(2\alpha+2\beta+2\gamma)}} + \frac{1}{10^{(4\alpha+3\beta+2\gamma)}} \right\} + \cdots\cdots$$

It can be easily seen that $I_{abs} = I_o(\lambda)$ only when $\alpha = 0$ and β and/or γ are very large. For 100% absorption of light by the reactants, the wall should not absorb any light but should reflect it. Therefore $\lambda = 0$ in order to satisfy the requirement.

In short, α and γ should be zero and β should be very large for the 100% absorption by the reaction mixture and for infinite optical pathlength. In other words, the infinite optical path photoreactor functions with 100% efficiency when, and only when, the glass and filter solutions do not absorb any light and the mixture absorbs it strongly.

In order to make $\alpha = 0$, we must find a filter which possesses 100% transmission at the wavelength concerned. To make $\gamma = 0$, a noble metal surface can be used.

3. Chemical Filter

Chemical filters are often used with medium pressure mercury lamps to provide an intensity of monochromatic light which is often higher than those obtainable from conventional photochemical monochromator systems.

The main interest has been the mechanistic study of photochemical benzpinacolization. Benzophenone reduction in the presence of a hydrogen donor requires an irradiation of light of wavelength 366 nm, because, the energy gap between the first excited singlet of benzophenone ($^1S_1$) and ground state ($^1S_0$) matches the energy of light of wavelength 366 nm. For any quantitative and easily interpretative measurement, one should have a monochromatic light. Firstly, the construction of a near perfect monochromatic 'chemical filter' will be considered.

In the early stages of the investigation of the photoreduction of benzophenone, an aqueous solution of chrome alum had been used[4] as a chemical filter which transmits light in the region $450 < \lambda < 550$ nm within which is a Hg band at 546 nm (Figures 3 and 5). So the filter is not monochromatic and should therefore be modified. Attempts were made to improve both the monochromaticity and transmittance of the filter. A study of transmittance characteristics of various compounds was made. The selection of the filter compounds was based on the criterion that a violet aqueous solution was obtained with transmission in the region $350 < \lambda < 400$ nm. Some of them were aqueous solutions of crystal violet, chrome alum, gentian violet, bromothymol blue and methylene blue. None of the above mentioned solutions gave a transmittance peak having a maximum close to $\lambda = 366$ nm. However the transmission spectrum of methylene blue (Figure 4) is noteworthy. Although it transmits light at 400 nm and 435 nm, where there are Hg bands, (Figure 5), it does not transmit light at 546 nm. Further, this does not have transmission in the region $\lambda < 350$ nm and $\lambda > 500$ nm. A desirable feature of methylene blue is that one of its maxima is at $\lambda = 375$ nm which is very close to 366 nm. Therefore, it was expected that a mixture of CA and MB would yield a near perfect filter. Using the transmission versus wavelength plot (Figure 3) of chrome alum and assuming Beer-Lambert's law, the optimum concentration of chrome alum was calculated by maximising the transmission at 366 nm and minimising the transmission at 540 nm. The optimum concentration was estimated to be 0·28 moles l^{-1} (with 10% transmission at 310 nm and 366 nm, and 0·05% transmission at 540 nm).

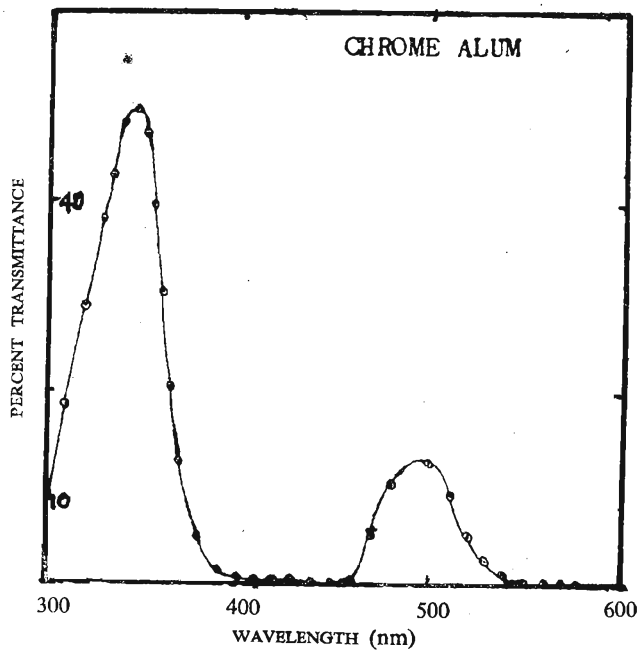

Figure 3

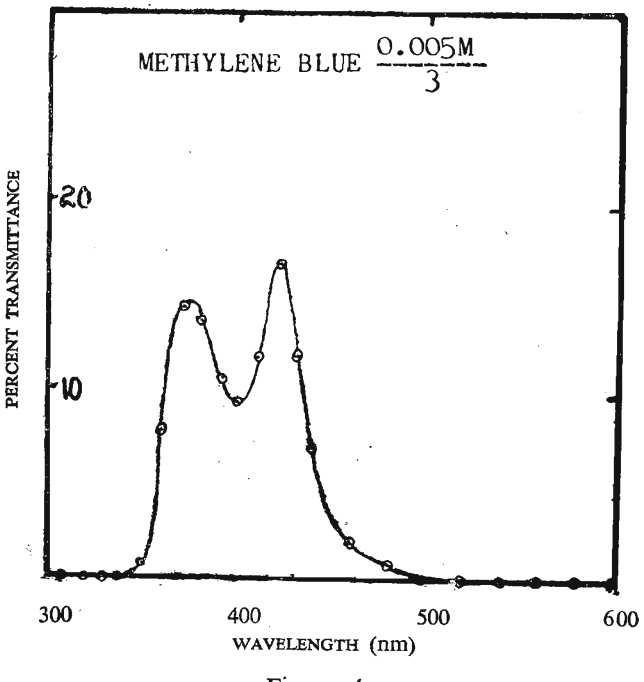

Figure 4

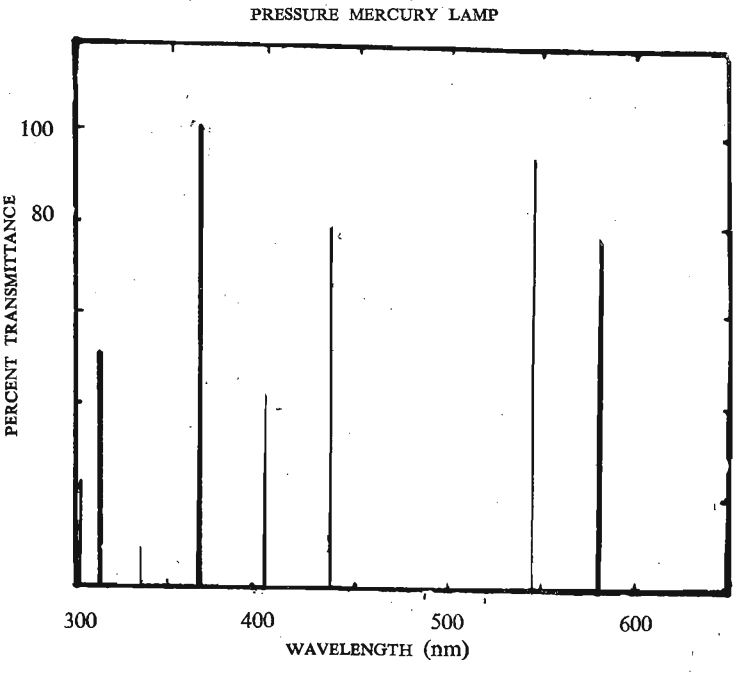

Figure 5. Relative energy distribution in Medium Pressure Mercury Lamp

Transmittance characteristics of the following mixtures were studied (Figure 6).

TABLE 1

Mixture	*Concentration of chrome alum (moles* l^{-1})	*Concentration of methylene blue (moles* l^{-1})
I	0·28	0·0016
II	0·28	0·0008
III	0·28	0·0005
IV	0·14	0·0006

Transmission spectrum of mixture I (Figure 6) shows 1·5% transmission at $\lambda = 366$ nm. Transmission characteristics of mixtures II and III show that the reduction in concentration of methylene blue causes a hypsochromic shift.

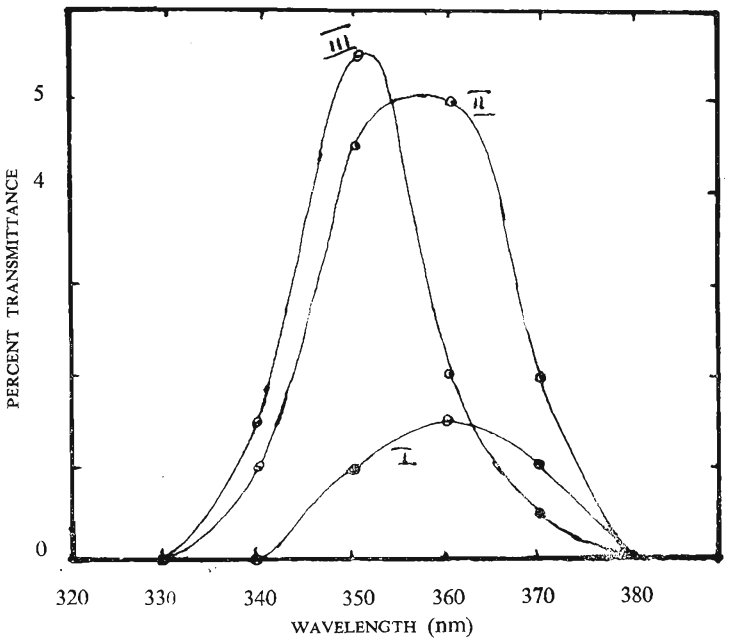

Figure 6

It is easily seen (Figure 7) that mixture IV (0·14M in chrome alum and 0·0006M in methylene blue) constituting a monochromatic filter has a transmittance of 11% at 362 nm. Thus, we have achieved a near perfect monochromatic filter for 366 nm.

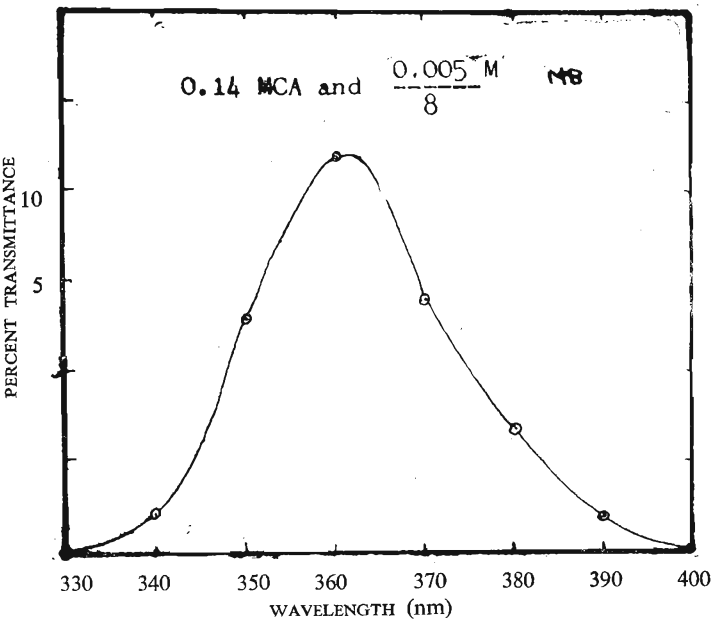

Figure 7

4. Experimental

Lamp : medium pressure mercury lamp (90W).

Filter : 'CAMB' filter 0·25M in chrome alum and 0·0011M in methylene blue, concentrations are adjusted to give the same transmission, as the transmission was measured in an 1CM cell whereas the filter pathlength here is 0·55 CM.

Reactor : Reactor I

4.1. Experiment 1 : The total volume 640 ml (0·15M in ferric ammonium sulphate and 0·06M in $K_2C_2O_4$) was made by adding the appropriate volumes of stock solutions. Ferric ammonium sulphate was added at time zero to a thermally equilibrated mixture of the rest. 10 ml samples were drawn out (and replaced by 10 ml of water) and the following reagents were added in succession :

(i) 10 ml of buffer,

(ii) 2 ml of 0·1% 1, 10 phenanthroline

and the total volume was made up to 50 ml.

The resulting mixture was subjected to the analysis as described by Calvert and Pitts.[2] Photosensitive solutions were handled in the dark. (Temperature at which the experiment was done = 29°C ± 1°C).

4.2. Experiment 2 :

Lamp : Medium pressure mercury lamp. (90W)

Filter : "CA/MB" but concentrations of chrome alum and methylene blue were adjusted in accordance with the filter pathlength to get the same transmission as with 1 CM cell. Concentration of chrome alum is 0·7M and that of methylene blue is 0·006M.

Experiment 1 was repeated in reactor II (Figure 2).

4.3. Experiment 3 : The total volume 640 ml (0·05M in $H_2C_2O_4$ and 0·01M in uranyl sulphate) was made up by mixing appropriate volumes of $H_2C_2O_4$ (0·8M) and uranyl sulphate (0·08M) and water. 10 ml. of samples were drawn (and replaced by 10 ml of water) at intervals and subjected to permanganate titrations (temperature 30°C ± 1°C).

5. Results

5.1. Experiment 1 :

TABLE 2

No.	*Time (min)*	*O.D. (optical density)*	*corrected optical density*
1	3.17	0·055	0·055
2	10.50	0·175	0·178
3	14.00	0·245	0·253
4	18.00	0·265	0·278
5	23.00	0·295	0·315

5.2. Experiment 2: The reaction was immeasurably fast and optical density measurements were impossible.

5.3. Experiment 3 :

TABLE 3

No.	*Time (min)*	*Vi (ml)*	V_i^{corr} *(ml)*
1	0	103·70	103·70
2	20	102·10	102·10
3	40	99·00	100·58
4	60	96·00	99·07
5	80	92·80	97·35
6	100	89·30	95·28

6. Calculation

6.1. Experiment 1 :

The appropriate equation for the evaluation of light flux or intensity output emitted by the lamp filter system is given by

$$I = \frac{50}{10} \cdot \frac{V}{\phi \varepsilon l} \left\{ \frac{d\,(O.D.)^{corr}}{dt} \right\} \qquad (1)$$

where I is the intensity output by the lamp filter system,

ϕ : is the quantum yield of the actinometer reaction,

ε : is the extinction coefficient of $Fe(phen)_3^{2+}$ at 510 nm,

l : pathlength of absorption cell, and

V : total volume in litres, when the results are subjected to least square treatment.

$$\frac{d\,(O.D^{corr})}{dt} = 1.68 \times 10^{-2}\ \text{min}^{-1}$$

and substitution of appropriate values into the equation (1) yields

$$I = \frac{50 \times 0.640 \times 1.68 \times 10^{-2} \times 6.023 \times 10^{23}}{10 \times 1.20 \times 1.1 \times 10^{4}}$$

$$= 6.25 \times 10^{18}\ \text{quanta min}^{-1}$$

6.2. Experiment 3 : When the results of Experiment 3 are subjected to least square analysis, we get

$$\frac{dV^{corr}_{KMnO_4}}{dt} = -\ 0.068\ \text{ml min}^{-1}.$$

where $V^{corr}_{KMnO_4}$ is the corrected volume of $KMnO_4$ required at time t, with coefficient of correlation (r^2) = 0.9964 which shows how suitable the results are for linear regression.

The zero time datum gives

$$N^{KMnO_4} = 0.0096\ \text{eq l}^{-1}.$$

$$-\frac{d[OX]}{dt} = \frac{-d\left[V^{corr}_{KMnO_4}\right]}{dt} \cdot \frac{N_{KMnO_4}}{10\ \text{ml} \times 2\ \text{eq mole}^{-1}}$$

The equation for the determination of absorbed intensity (I) is given by the following equation :

$$I = \frac{V}{\phi}\left[\frac{-d[OX]}{dt}\right]$$

$$I = \frac{0.640 \times 0.068 \times 0.0096 \times 6.023 \times 10^{23}}{0.49 \times 10 \times 2}$$

$$= 2.57 \times 10^{19}\ \text{quanta min}^{-1}.$$

7. Discussion

Consider the lamp-filter system of reactor I. Measurement shows that the total thickness of glass through which the light travels before coming into contact with the reaction mixture is 0.62 cm and the filter pathlength is 0.55 cm. Figure 8 shows the transmission characteristics of 0.62 cm thick pyrex glass from which the transmission at 365 nm is 64.8%. Effectively, the relative intensity felt by the reaction mixture is $\frac{64.8}{100} \times 10.25 = 6.6\%$ at 365 nm.

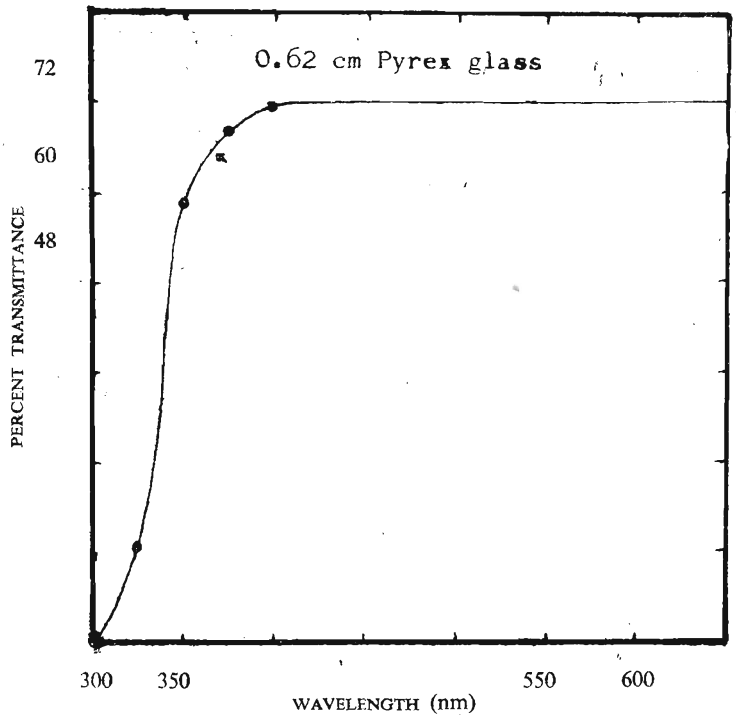

Figure 8

If the percent transmittance of the lamp-filter system was 6.6%, an intensity of 10^{19} quanta min^{-1} order(deduced on the basis of experimental results[4] obtained in previous work at the laboratory) should have been observed. The reduction in intensity was suspected to be due to the interaction of chrome alum and methylene blue at higher intensities as interaction has been shown to be absent[5] at low intensities.

Therefore chrome alum and methylene blue were kept in two separate concentric cylindrical compartments and Experiment 2 was carried out in reactor II. Measurements show that the total thickness of glass through which the light passes before coming into contact with the reaction mixture is 0.78 cm. The transmission characteristics of pyrex glass of 0.78 cm thickness is shown in Figure 9, from which the relative intensity output by the lamp-filter system can be shown to be $\frac{10.25 \times 62}{1000} = 6.35\%$ which is comparable to the relative intensity output (6.60%) of the former filter system (CAMB filter).

In Experiment 2, observation of ferrous oxalate precipitation before any measurements could be made indicates that the reaction was complete in a short period of time. It obviously implies that the intensity has been increased greatly.

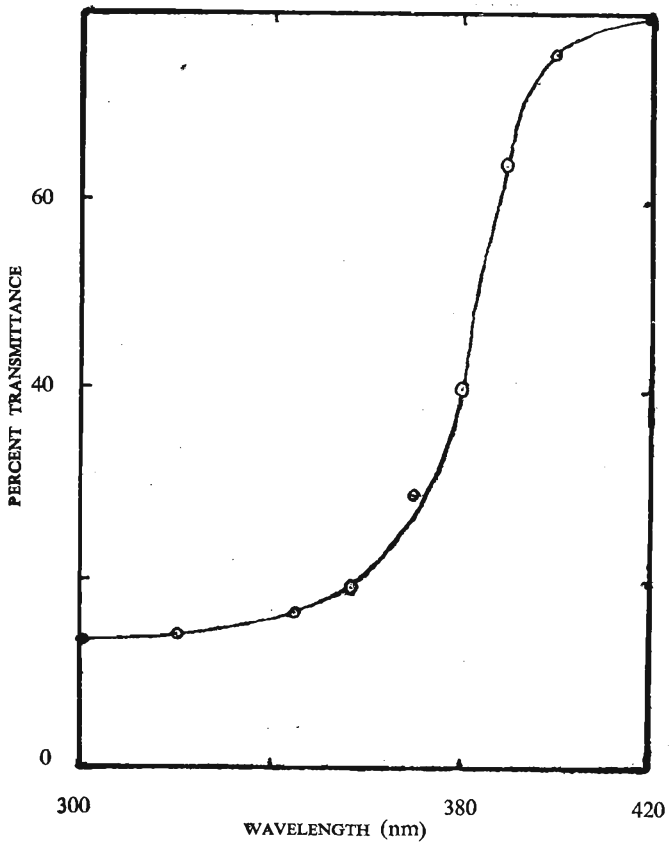

Figure 9

As uranyl oxalate actinometry is most suitable for high flux of light, Experiment 3 was performed, (the results of which are shown in Table 3,) from which the intensity turns out to be 2.57×10^{19} quanta min^{-1}.

The use of two filter compartments results in a four-fold increase in intensity. From this increase in percentage transmission with high analyzing light intensity when chrome alum and methylene blue are isolated from each other, it may be concluded that an association complex is formed between either one or more excited species and ground state species of chrome alum and methylene blue.

Since methylene blue is well known as a photosensitizer,[6] we can cautiously suggest that the first excited triplet of methylene blue is interacting with the Cr^{3+} or in other words, it may be a case of exciplex formation. But what is significant about this is the fact that one of the components is an inorganic species.

Thus a highly monochromatic lamp-filter system has been achieved emitting a reasonably high intensity. We shall now compare some of the reported values with the intensity output and properties of the filter.

Hammond obtained 3×10^{19} quanta min^{-1} in the 365 nm region from a 800W showing a power utilization efficiency (PUE) of 3.75×10^{16} quanta min^{-1} W^{-1}. 2.57×10^{19} quanta min^{-1} from 90W lamp was obtained showing a PUE of 2.85×10^{17} quanta min^{-1} which is eight times as large as Hammond's and also the light is more monochromatic than in the case of Hammond's experiment, since the half band width is 25 nm, whereas it was 50 nm in Hammond's case.

Calvert and Pitts[1] recommend a filter for the isolation of light at 366 nm. The comparison of this with the filter used is given below (Table 4).

TABLE 4

Calvert-Pitts (*Figure* 10)		*"CA/MB" filter* (*Figure* 11)	
Components	*Pathlength*	*Components*	*Pathlength*
1. Components			
(i) aqueous $CuSO_4$ solution 50 gl^{-1}	10 cm	(i) aqueous solution of chrome allum (0.7 mole l^{-1})	0·2 cm
(ii) Corning glass 7-37 (5800)	0·5 cm	(ii) aqueous solution of methylene blue (0·006 mole l^{-1})	0·1 cm
(iii) 2, 7 dimethyl 3, 6 diazo cyclopepta 1,6 diene perchlorate (0·1 gl^{-1})	1 cm		
2. Testing time : 113 h		Length of time is immaterial	
3. Light stability : Increase in transparency observed in the first four hours		No change in transparency	
4. Half band width : 30 nm		Half band width : 25 nm	
5. Maximum transmittance : 25%		6·5%	

The above table shows the relative advantages of the filter over the other except the fact that the maximum transmission in this case is nearly four times less than Calvert's and Pitt's.

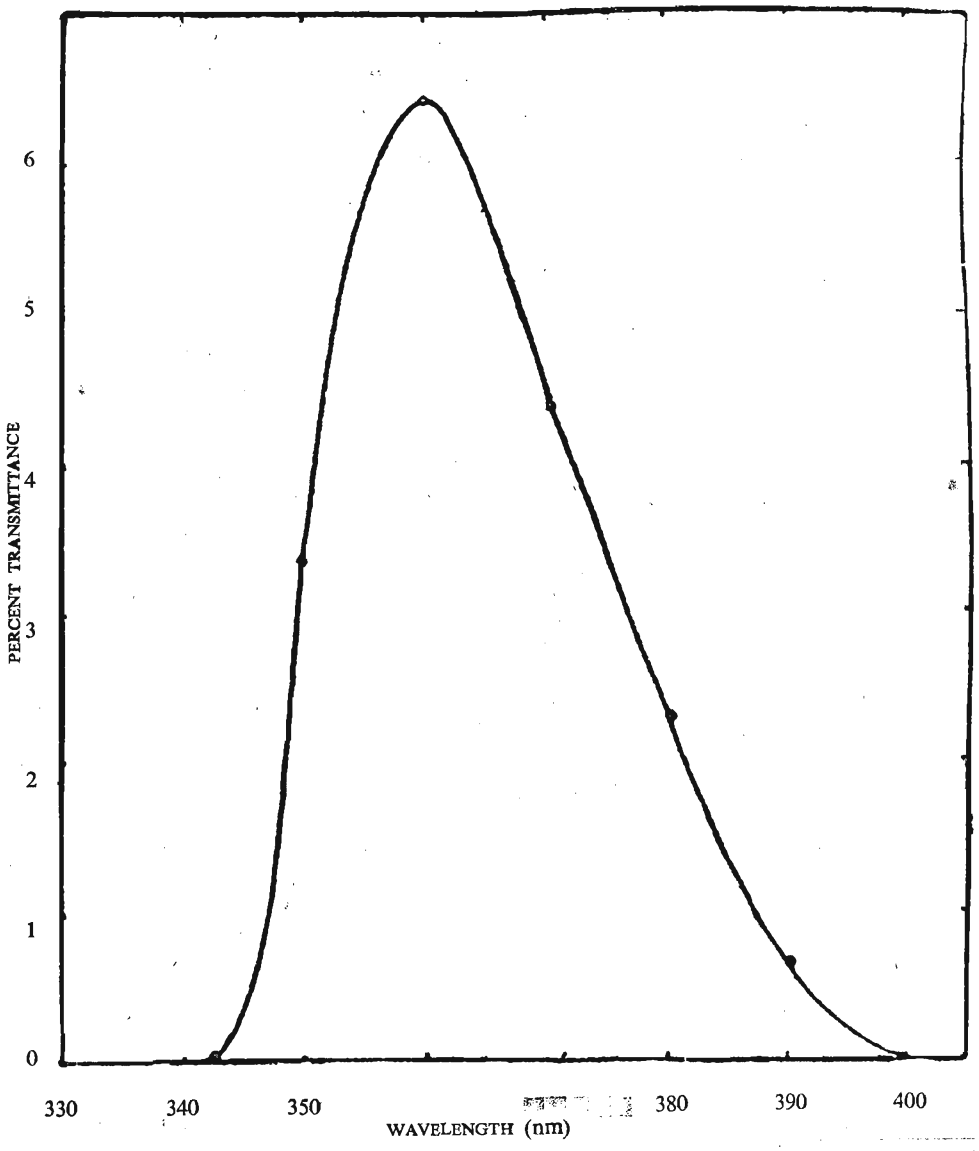

Figure 10. Percent light transmission after passing through the lamp filter system.

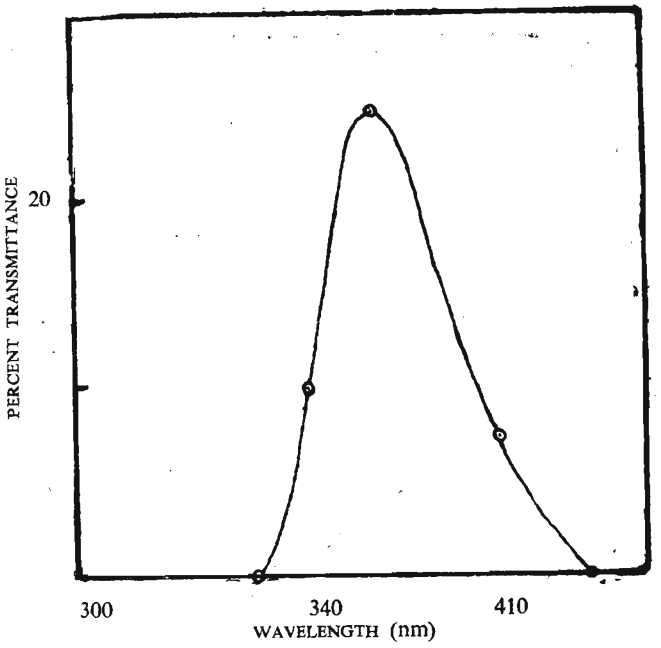

Figure 11. Transmission of filter combination for isolation of 365–366 nm region

It is expected that further experimentation with relative concentrations of two components will no doubt enable an attainment of a higher percentage of transmittance. Further experimentation in improving the filter and detection and elucidation of the structure of highly absorbing intermediates in the irradiated benzophenone-iso-propanol system are the current main interests.

Addendum

In Experiments 1, 2 and 3, each sample of reaction mixture was replaced by an equal volume of water in order to prevent the error due to the decrease in volume. The error due to dilution is very much smaller than that due to a drop in volume. A correction can be made for this artificial dilution. It can be shown that

$$(O.D_i^{corr}) = \frac{V}{V - \sum_{i=1}^{i=1}(i-1)\mathcal{V}} O.D_i$$

where V is the total volume of reaction mixture,

$\mathcal{V}$ is the volume of sample,

$O.D_i^{corr}$: corrected $O.D.$ for the i^{th} sample,

$O.D_i$: $O.D.$ for the i^{th} sample.

Similarly

$$V_{i\,KMnO_4}^{corr} = \frac{V}{V - \sum_{i=1}^{i=1}(i-1)\mathcal{V}} V_{i\,KMnO_4}$$

Abbreviations

1. "CAMB" filter : an aqueous solution containing chrome alum and methylene blue.
2. "CA/MB" filter : aqueous solutions of chrome alum and methylene blue kept in separate compartments.

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