Notes

Aqueous Solutions of Glucose & Sucrose as Actinometers

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Acetone-sensitized photolysis of glucose solution can be used as an actinometer for short irradiation time whereas unsensitized glucose and sucrose solutions can be used for long irradiation time.

POTASSIUM ferrioxalate[1] and uranyl oxalate[2] solutions are commonly used as chemical actinometers. The former is sensitive even to visible light. In dilute solutions in which these are used, they are suitable only for low intensity of light while many organic substances have to be irradiated with high intensity of light for longer periods of time. It was therefore considered necessary to investigate some system which can be used only in 200-300 nm region and has a low and reproducible quantum yield.

The photolysis of aqueous carbohydrate solutions have been studied earlier[3] and malonaldehyde has been identified as one of the products of photolysis. In the present study it has been shown that by determining the malonaldehyde yield from the photolysed glucose or sucrose solution it can be used as an actinometer. The quantum yield of malonaldehyde from only sugar solution was very low and hence sensitization of the reaction with acetone has been carried out in this study. Malonaldehyde can be conveniently estimated spectrophotometrically after reacting with 2-methylindole[4].

Glucose, sucrose and acetone were BDH analytical reagents. 2-Methylindole (Schuchardt) and 1,1,3,3-tetraethoxypropane (Fluka AG) were used as such.

A Hanovia medium pressure mercury lamp (450 watt) was placed in a water cooled quartz container which was surrounded by a cylindrical pyrex jacket containing the solution. Filter sleeves of vycor or pyrex fit around the lamp and cut off light of wavelength shorter than 200 nm and 300 nm respectively.

Aqueous solution of glucose and sucrose of required concentration were prepared in distilled water and 200 ml of the solution was photolysed. In the case of acetone sensitized solutions, required amount of acetone was added by an Hamilton microsyringe. In each experiment 200 ml of solution were photolysed.

Potassium ferrioxalate actinometer was used in order to find the photon flux. When H_2SO_4 solution of $K_3Fe(C_2O_4)_3$ was irradiated, reduction of the ferric ion to the ferrous state occurred. The quantum yield for Fe^{2+} formation is known to be 1·25. Fe^{2+} was estimated as the red coloured 1,10-phenanthroline-Fe^{2+} complex. The photon flux was calculated and found to be $4{\cdot}8\times10^{17}$ quanta/sec.

A known amount of 1,1,3,3-tetraethoxypropane was hydrolysed with water to malonaldehyde in a volumetric flask. This solution was diluted suitably to give solutions of malonaldehyde in the range of 0-2 μg/ml. One ml of the solution was incubated for 45 min at room temperature with 2 ml of 0·1% (w/v) solution of 2-methylindole in a 25% (w/v) of HCl in ethyl alcohol. A pink colour developed and its optical density was read at 555 nm. A calibration curve of OD vs [MA] was drawn and the amount of malonaldehyde in the photolysed product estimated from the linear plot (linear behaviour up to 2 mg/litre). The photolysed solution was treated identically and unphotolysed solution was used as a blank.

Five percent solution of Glucose (5%) when photolysed for a period of 30 min using a pyrex filter did not give any malonaldehyde thus showing that light >300 nm is not effective in the photolysis of sugar solution.

Fig. 1 gives the optical density versus time of photolysis of glucose and sucrose solutions. Fig. 2 shows the optical density versus time of photolysis of glucose solution in presence of sensitizer acetone. The quantum yield for the formation of MA resulting from the photolysis of glucose and sucrose solution have been calculated from the slopes of the curves in Figs. 1 and 2. Table 1 shows the quantum yield of MA from the photolysis of 5% and 1% solutions of glucose and 5% solution of sucrose for 15-90 min of photolysis.

It is evident from Fig. 2 that the formation of MA is linear from 15-90 min of photolysis. The formation of MA was not detected when the solution was photolysed for time shorter than 10 min. The quantum yield of malonaldehyde from the photolysis of unsensitized solution can be compared with

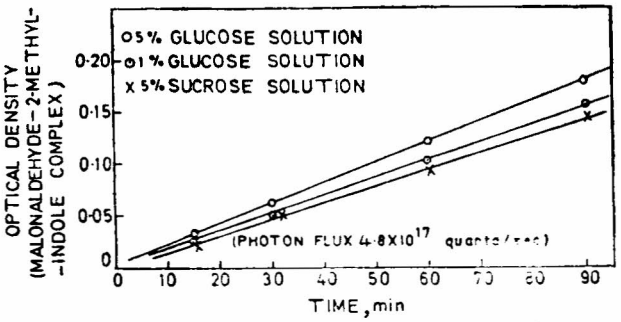

Fig. 1 — Plot of optical density versus time of photolysis of glucose or sucrose solutions

the sensitized solutions (Table 2). For 10^{-2} and $10^{-3}M$ acetone in 5 and 1% glucose solution, the plot of OD vs time of photolysis is linear for 5-30 min of photolysis. But for $10^{-1}M$ sensitizer concentration, it is linear only upto 15 min of photolysis. There is considerable increase in the quantum yield of MA when glucose solution is photolysed using the sensitizer. For hundred-fold decrease in the sensitizer concentration there is only about 50% change in MA quantum yield.

The results show that acetone sensitized photolysis of glucose solution can be used as an actinometer for short irradiation times whereas unsensitized glucose and sucrose solution can be used for long irradiation times. Malonaldehyde formation from the photolysis of glucose and sucrose solution can be used as a chemical actinometer for $14{\cdot}4\times10^{19}$ quanta to $25{\cdot}9\times10^{20}$ quanta of light in the 200-300 nm range.

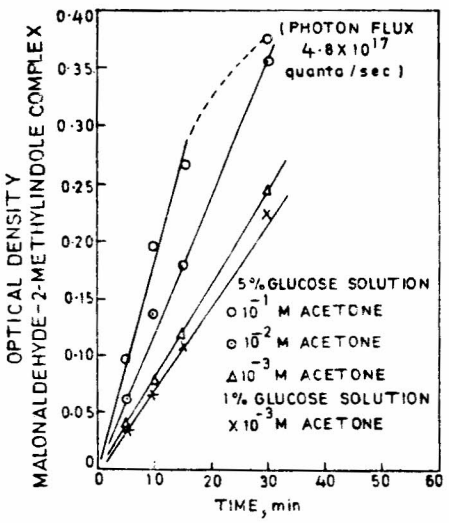

Fig. 2—Plot of optical density versus time of photolysis in the acetone-sensitized photolysis of glucose and sucrose solutions

TABLE 1 — YIELD OF MALONALDEHYDE WITH GLUCOSE AND SUCROSE SOLUTION

	Quantum yield of malonaldehyde $\times10^3$ after photolysis for			
	15 min	30 min	1 hr	1½ hr
Glucose				
5% solution	0·32	0·34	0·33	0·32
1% solution	0·27	0·23	0·25	0·27
Sucrose				
5% solution	0·23	0·27	0·24	0·26

TABLE 2 — YIELD OF MALONALDEHYDE WITH VARYING SENSITIZER CONCENTRATION AND VARYING GLUCOSE CONCENTRATION

	Quantum yield of manonaldehyde $\times10^2$ after photolysis for			
	5 min	10 min	15 min	30 min
Glucose (5%) + acetone				
$10^{-1}M$	0·33	0·34	0·30	0·21
$10^{-2}M$	0·21	0·23	0·21	0·20
$10^{-3}M$	0·12	0·13	0·14	0·14
Glucose 1% + acetone $10^{-3}M$	0·097	0·11	0·12	0·13

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Effect of Surfactants on the Fluorescence Intensity of 9,10-Diphenylanthracene

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The effect of some nonionic, cationic and anionic surfactants on the fluorescence intensity of 9,10-diphenylanthracene has been studied. It has been found that there is a marked enhancement in the fluorescence intensity on adding the surfactants. The effect of varying ethanol concentration is also studied.

PADHYE and Padhye[1] have found that some non-ionic and anionic surfactants increase the fluorescence intensity of optical brightening agents. Ghosh[2] has studied the effect of sodium lauryl sulphate on absorption spectrum and fluorescence intensity of methylene blue. Similarly Harada and Toya[3] have reported that fluorescence intensity of certain dyes are influenced by the addition of long chain fatty acids and esters.

We wish to report in this note the results of preliminary investigation on the effect of some anionic, viz. dodecylbenzene sodium sulphonate (DBSS) and dioctyl sodium sulphosuccinate (DSSS); non-ionic, viz. Triton X-100 (T_x-100), polyoxyethylene 23-laurylsulphate (Brij-35) and polyoxyethylene mono-o'eate (Tween-80) and cationic, viz. cetyltrimethylammonium bromide (CTAB) surfactants on the fluorescence intensity of 9,10-diphenylanthracene (9,10-DPA). Notable increase in fluorescence intensity occurs for all the surfactants, specially on the addition of some non-ionic surfactants (Table 1). However, increase in fluorescence intensity also occurs on increasing ethanol concentration in the absence of surfactants. Further the fluorescence intensity reaches a maximum at 50% ethanol concentration (Table 2). Observations in total absence of ethanol could not be made due to the insolubility of 9,10-DPA in pure water. Further work is in progress.

At the moment it is difficult to give a theoretical explanation for the enhancement in fluorescence. It is likely that micelle formation is occurring in solution resulting in enhancement of fluorescence, since a limiting value is being approached in all the cases.

Carl-Zeiss spectrophotometer "SPEKOL" with fluorescence attachment was used for fluorescence studies in which a mercury lamp was employed as the light source. Appropriate filters were used for