Appendix-Actinometry

There are a variety of chemical actinometry that have been developed over the years. In this section, a few of the actinometers are described.

0.1 Potassium ferrioxalate actinometry

The governing chemical reaction is represented as ferrous ions + oxalate gives rise to ferrous ions and carbon dioxide i.e., $2Fe^{+++} + C_2O_4{}^{2-} = 2Fe^{++} + 2CO_2$ The ferrous ion thus formed is estimated spectrophotoetrically as its phenanthraline complex at 510 nm. Ferric ions form only weak complex with Phenanthraline and is transparent at 510 nm. This actinometer has some advantages and also some disadvantages. The possible advantages are (1) The method is easy and can be adopted and used quickly (2) Does not depend on difference reading between large numbers to determine the amount of conversion (3) Quantum Yields are accurately known (4) Can be adopted to the blue region of the visible spectrum. The major disadvantages of this method are (1) Only short irradiation is enough (2)High absorption neceessitates light filtering or corrections have to be applied.

0.2 Solutions required

1,10 Phenanthroline (0.2 pcercent by weight) in water 2. Buffer solution (82 grams of sodium acetate + 10 ml of concentrated sulphuric acid dilited to 1000 ml with water. 3. Ferric sulphate solution (100 grams of ferric sulphate hydrated + 55ml concentrated sulphuric acid diluted to 1000 with water. 4.Standardised 0.1M EDTA 5.0.08M FeSO$_4$ in 0.1M sulphuric acid 6.Standard 0.1N potassium chromate solution 7. One percent diphenylamine in concentrated sulphuric acid [Solutions 5-6 are required only to determine the extinction coefficient of ferrous phenonthroline complex. One can also use a reported value of 1.11 X 10^4

0.3 Extinction coefficient of ferrous phenanthraline complex

The following sequence of steps may be followed for this determination.

1. Titrate of 0.08M ferrous sulphate solution in 0.1 sulphuric acid with a standard 0.1N potassium chromate using a few drops of diphenylamine solution as indicator.

2. Dilute 0.08 M ferrous sulphate solution 20 times with 0.1 N sulphuric acid to get 4 x 10^{-4} M solution of ferrous sulphate.

3. To a series of six 25 ml volumetric flasks add 0,1,3,5,7,9 mls respectively the solution in 2

4. Add enough 0.1N sulphuric acid to each of these solutions in 3 to bring the volume approximately 12.5 ml

5. To each of these solutions in 4 add 2 ml of the 0.2

6. Add six ml of buffer solution to each of the volumetric flasks and dilute to the mark.

7. Measure the absorption of each of these solutions at 510 nm in a 1 cm cell versus a solution prepared as above without ferrous sulphate.

8. Plot the absorption values obtained versus complex concentration and determine the extinction coefficient from the slope.

0.4 Prepartion of actinometer solution

1. Titrate 0.2N ferric sulphate solution with standard EDTA using 0.2 g of salicylic acid in 100 ml solution as indicator and buffered with0.3 g glycine/100 ml solution to a pH of 3 to 4.

2. prepare a standard solution of $K_2C_2O_4$ such that its molarity is six times that of ferric sulphase solution.

3. When actinometer solution is required, pipete 5 ml ofthe ferric sulphate solution, add 5 mls of the oxalate into a 100 ml volumetric flask and dilute to the mark with water.

0.5 Measurment of the intensity

1. Pipete out into the reaction vessel a volume of $K_3Fe(C_2O_4)_3$ necessary to be irradiated.

2. Irradiate the solution a definite time period.

3. Mix the irradiated solution and then pipete one ml of the actnometer sotion into a 10 ml volumetric flask.

4. Add 2 ml of 0.2 phenanthroline solution.

5. Add a volume of buffer equal to half of the aliquot of actinometer solution taken.

6. Make up to the mark.

7. Prepare a blank solution following steps 3-6 with a nonirradiated volume of actinometer taken.

8. Measure the absorption of the solutions 6 and 7 versus water at 510 nm and note the difference.

0.6 Calculation of Light Intensity

From the values given in Table 1 select the appropriate quantum yield for ferrous production Using the absorption obtained, calcuate the light intensity from the following formula I(in Einsteins/min) = $AV_2V_3/tV_1\varepsilon\phi_\lambda$ where A is absorption of irradiated actinometer solution corrected for absorption of the blank; V_1 in mls of the irradiated actinometer solution; V_2 is volume of the actinometer

solution irradiated; v_3 is the volume of volumetric flask used for dilution of irradiated aliquot solution;ε is the extinction coefficient of ferrous phenonthroline complex at 510 nm(1.11 x 10^4); ϕ_λ is quantum yield of ferrous production at the wavelength of light used and t is time of irradiation in minutes.

Table 1 Quantum yields of ferrous production from potassium ferrioxalate[The data have been reproduced from C.G.Hatchard and C.A.Parker, Proc.Roy.Soc., (London)A235,518 (1956)]

$\lambda(nm)$	concentration(moles/litre)	Quantum yield
254	0.006	1.25
297	0.006	1.24
313	0.006	1.24
334	0.006	1.24
361	0.006	1.21
405	0.006	1.14
436	0.006	1.11

0.7 B.Uranyl oxalate actinometry

0.7.1 solutions

1. 0.01M Uranyl sulphate in 0.05M oxalic acid solution

2. Standardised 0.04M $KMnO_4$ solution.

0.7.2 Procedure

1. Titrate an approxmate volume of the actinometer solution with the standardised permanganate solution. Titrate at 333K in 1n sulphuric acid solution of the oxalate

2. Irradiate the desired volume of actinometer for appropriate time period.

3. Titrate the irradiated solutionn with permanganate

4. Calculate the light intensity

Table 2 Quantum yields of oxalate disappearance for uranyl oxalate [W.G.Leighton and G.S.Forbes, J.Am.Chem.Soc., 52,313 (1930)]

λ(nm)	Quantum yield
254	0.602
265	0582
302	0.570
313	0.561
366	0492
405	0.563
436	0.584

0.8 C.Benzophenone-Benzhydrol actinometry

0.8.1 net reaction

ϕ_2(CO)+ϕ-CH(OH)-$\phi \Rightarrow [m]$ ϕ-CH(OH)-CH(OH)-ϕ
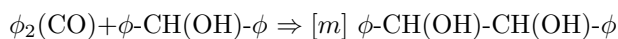
0.8.2 Discussion

The rate expression for the system is $(1/\phi_{Ph_2(CO)} = 1 + k_1/k_2(BH_2)$. If this is multiplied by the quantum yield of disappearance of benzophenone at a specific [BH$_2$] concentration, then the expression is $\phi_a/\phi_{Ph_2CO} = \phi_a + \phi_a k_1/k_2(BH_2)$. A Plot of the relative quantum yield ratio ϕ_a/ϕ_{2CO} versus reciprocal of the benzhydrol concentration gives an intercept of ϕ_a and the light intensity can be calculated from this value.

Procedure

1. Prepare 0.1M ϕ_2CO solution in benzene containing varying concentrations of benzhydrol (e.g. 0.3, 0.1, 0.07 and0.05M)

2. Degas with freeze thaw cycles and then irradiate

3. Dilute each tube 25 times andcompare the absorption of each to diluted non irradiated samples

4. Plot $\phi_a/\phi_P h_2$CO versus 1/[BH$_2$] where [BH$_2$] is the average of the initial and final benzhydrol concentrations.

5. Determine ϕ_a from the intercept

6. Calcualte the light intensity I= $\Delta(\phi_2$CO/$\phi_a)$

0.9 2-hexanone actinometry

2-hexanone undergoes Norrish type II photochemical reaction to yield acetone (which can be determined by GC)or the disappearance of 2-hexanone or the formation of propene can also be determined

0.9.1   Procedure

1. Irradiate an approximate volume of a 1M solution of 2-hexanone in pentane, hexane or cyclohexane.

2. Analyse in a carbowax or similar column and compare chromatographic peak areas to those obtained from a standard acetone solution

Table 3 Quantum yields for 2-hexanone Reactions in hydrocarbon solvent [D.R.Coulson and N.C.Yang, J.Am.Chem.Soc., 88,4511 (1968)]

ϕ-hexanone	0.327
$\phi_{acetone}$	0.252
$\phi_{propene}$	0.25
$\phi_{cyclobutanol}$	0.075

For more details on this topic, the reader is requested to refer the book by Steven L Murov "Handbook of Photochemistry",Marcel Dekker Inc, 1973.