

# INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

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## CHEMICAL ACTINOMETRY

Prepared for publication by

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# Chemical actinometry

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## I. LIST OF ACTINOMETERS

*This compilation lists chemical systems that have been shown suitable for the integration of incident light by chemical conversion. Emphasis is mainly on gas and liquid phase systems which photochemists are most frequently dealing with. In addition, some solid phase actinometers and convenient electronic devices are mentioned. Actinometric systems or procedures that are marked by an asterisk (\* = well established) in the following list have been used over years by different authors in several laboratories and can thus be recommended. All other systems appear to be not yet widely used and may be labelled as still under discussion. Systems fallen into discredit are given at the bottom of this list under the heading Disproved. Order is with increasing wavelength.*

Abbreviations: E = Electronic Device, S = Solid Phase, G = Gas Phase, L = Liquid Phase.

WR = Wavelength Range,  $\Phi_{\lambda}$  = Quantum Yield at irradiation wavelength  $\lambda$ .

S = Sensitivity ( $\epsilon \cdot \Phi_{\lambda}$ , with  $\epsilon$  or  $\Delta\epsilon$  at the photometric wavelength, where  $\epsilon$  is the molar (decadic) absorption coefficient), AM = Analytical Method.

PP = Procedure, Precautions, Comments, Lit. = Literature

**Readers are invited to send complementary information, corrections and comments.**

### I.1 Chemical systems

*Several physical means for the calibration of light sources are known. With chemical systems, however, it is much easier to mimic the experimental situation of the sample. By choosing strictly identical experimental set-ups for standard and sample, any experimental errors due to differences in shape, surface, and spatial arrangement of the reaction vessel, filters, lenses etc. can be avoided without much effort. If possible, even the same solvent and about equal absorbances should be chosen for actinometry and reaction under study.*

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### 1.1.1. Solid phase chemical actinometers

S01: *1-Ethyl-1,4-dihydro-7-methyl-4-oxo-1,8-naphthyridine-3-carboxylic acid, or nalidixic acid.*

UV-A film dosimeter

WR: 280 - 360 nm

AM: absorbance change at 330 nm

Lit.: 1) T.J.Tate, B.L.Diffey, A.Davis, *Photochem.Photobiol.* 31, 27 (1980);

2) N.K.Gibbs, A.R.Young, *Photochem.Photobiol.* 37, 345 (1983).

S02: *Azoxybenzene*  $\rightarrow$  2-hydroxyazobenzene. cf. L09.

WR: 300 - 400 nm; poly(methyl methacrylate) block:  $\phi = \sim 10^{-3}$

AM: absorbance at 420 nm

Lit.: 1) N.J.Bunce, J.J.Smith, *J.Photochem.* 23, 219 (1983);

2) N.J.Bunce, G.G.Debrabandere, K.B.Jacobs, M.E.Lemke,

C.R.Montgomery, J.S.Nakai, E.J.Stewart, *J.Photochem.* 34, 105 (1986).

S03: *o-Nitrobenzaldehyde*  $\rightarrow$  *o*-nitrosobenzoic acid photoisomerization.

Also applicable in gas or liquid phase.

WR: 310 - 400 nm; KBr pellet:  $\phi \sim 0.5$

WR: 280 - 410 nm; poly(methyl methacrylate);  $\phi = 0.5 \pm 0.06$

AM: IR  $1530 \text{ cm}^{-1}$  ( $\text{NO}_2$ )

Lit.: 1) J.N.Pitts, jr., J.K.S.Wan, E.A.Schuck, *J.Am.Chem.Soc.* 86, 3606 (1964);

2) G.W.Cowell, J.N.Pitts, jr., *J.Am.Chem.Soc.* 90, 1106 (1968);

3) P.Leighton, F.A.Lucy, *J.Chem.Phys.* 2, 756 (1934);

4) C.B.Roy, S.C.Das, *Indian J.Chem.* 14A, 653 (1976).

S04: *Polysulfone* UV-B film dosimeter.

WR:  $\leq 315 \text{ nm}$

AM: absorbance at 300 nm

Lit.: A.Davis, B.L.Diffey, T.K.Tate, *Photochem.Photobiol.* 34, 283 (1981).

S05: *3'-[p-(Dimethylamino)phenyl]spiro[fluorene-9,4'-oxazolidine]-2'.5'-dione*, photoelimination of carbon dioxide and monoxide.

Sunburn dosimeter (polycarbonate film matrix).

WR:  $\leq 350 \text{ nm}$ ;

AM: visual color matching; absorbance at 480 nm

Lit.: A.Zweig, W.A.Henderson, jr., *Photochem.Photobiol.* 24, 543 (1976).

S06: *1,4,4a,8a-Tetrahydro-4a,7-dimethyl-1,4-methanonaphthalene-5,8-dione* (Diels-Alder adduct of 2,5-dimethylbenzoquinone and cyclopentadiene) photoisomerization in a dry silica matrix.

Irradiation apparatus described for adsorbed substances.

WR:  $362 \pm 5 \text{ nm}$ ;  $\phi = 1.0$  (also in solution)

AM: absorbance, GC

Lit.: S.Lazare, P.de Mayo, W.R.Ware, *Photochem.Photobiol.* 34, 187 (1981).

S07: *2-(2-Quinolyl)-1,3-indanedione, or quinophthalon*, photofading.

Plastic plates.

WR: 366 - 436 nm;  $\phi = 2 \cdot 10^{-5}$

AM: absorbance at 420 nm

Lit.: H.Okabe, *Appl.Opt.* 20, 4054 (1981).

## 1.1.2. Gas phase chemical actinometers

G01: Rare gases photoionization.

WR: 44 Å - 1022 Å

AM: He or Ne ion current measurement, extrapolation to zero pressure

Lit.: J.A.R.Samson, G.N.Haddad, *J.Opt.Soc.Amer.* 64, 47 (1974).

G02: Nitric oxide (NO).

WR:  $\leq$  134 nm

AM: ion yield

Lit.: K.Watanabe, F.M.Matsunaga, H.Sakai, *Appl.Opt.* 5, 391 (1967).

G03\*: Nitrous oxide ( $N_2O$ ) photolysis.

WR: 147 - 185 (138 - 210) nm;  $\phi_{\Delta n} = 1.00 \pm 0.05$ ;  $\phi_{N_2} = 1.44 \pm 0.1$  at moderate pressure near r.t.;  $\phi = 1.18$  at 123.6 nm;  $\phi_{\Delta n} \sim 0.8$  at 105 - 120 nm  $N_2$

AM:  $N_2$  analysis, pressure measurement

PP: low absorbance at 150 - 170 nm ( $\leq 30 \text{ l mol}^{-1} \text{ cm}^{-1}$ ); separation of  $N_2$  from NO and  $O_2$  or very accurate pressure measurement.

Lit.: 1) cf. J.G.Calvert, J.N.Pitts,jr., *Photochemistry*, Wiley, New York 1966. p.782:

2) M.Zelikoff, L.M.Aschenbrand, *J.Chem.Phys.* 22, 1685 (1954):

3) W.E.Groth, H.Schierholz, *Planet.Space Sci.* 1, 333 (1959):

4) N.R.Greiner, *J.Chem.Phys.* 47, 4373 (1967):

5) A.M.Pravilov, I.O.Shul'pyakov, *High Energy Chem.* 19, 351 (1985):

6) H.C.Dodge, J.Heicklen, *Int.J.Chem.Kinet.* 3, 269 (1971).

G04: Oxygen photolysis.

WR: 130 - 190 nm;  $\phi = 2.0$

AM: absorbance of iodine-iodide complex (formed from ozone and KI solution) at 353 nm

Lit.: 1) cf. J.G.Calvert, J.N.Pitts,jr., *Photochemistry*, Wiley, New York 1966. p.782:

2) J.N.Driscoll, P.Warneck, *Photochem.Photobiol.* 13, 283 (1971):

3) G.R.Powell, D.S.Sethi, *Int.J.Chem.Kinet.* 10, 1161 (1978):

4) A.K.Davies, K.A.Khan, J.F.McKellar, G.O.Phillips, *Mol.Photochem.* 7, 389 (1976).

G05: Hexafluoroacetone photolysis.

WR: 147 nm;  $\phi = 0.97 \pm 0.05$

AM: CO

Lit.: 1) J.J.Magenheimer, R.B.Timmons, *J.Chem.Phys.* 52, 2790 (1970):

2) G.R.Powell, D.S.Sethi, *Int.J.Chem.Kinet.* 10, 1161 (1978).

G06: Ethylene photolysis.

WR: 147, 163, 185 nm;  $\phi \sim 0.4$

AM:  $H_2$  analysis, pressure measurement

Lit.: 1) L.C.Glasgow, P.Potzinger, *J.Phys.Chem* 76, 138 (1972):

2) P.Potzinger, L.C.Glasgow, G.von Büнау, *Z.Naturf.* 27a, 628 (1972).

G07: Trimethylamine photoionization.

WR: 147 nm;  $\phi = 0.38$

AM: ion saturation current, very precise

Lit.: D.Salomon, A.A.Scala, *J.Chem.Phys.* 62, 1469 (1975).

G08: Carbon dioxide photolysis.

WR: below 170 nm;  $\phi = 1.0$ , dependent on  $\lambda$

AM: CO analysis, oxygen formed besides

Lit.: 1) cf. J.G.Calvert, J.N.Pitts,jr., *Photochemistry*, Wiley, New York 1966, p.782:

2) P.Warneck, *J.Opt.Soc.Amer.* 56, 408 (1966).

G09\*: *Hydrogen bromide* photolysis.

WR: 180 - 250 nm;  $\phi = 1.0$  at 100 mm, 25 °C, at low conversion

AM: H<sub>2</sub> analysis, Hg interferes

Lit.: 1) cf. J.G.Calvert, J.N.Pitts,jr., *Photochemistry*, Wiley, New York 1966, p.782;

2) R.M. Martin, J.E.Willard, *J.Chem.Phys.* 40, 2999 (1964).

G10: *Nitrosyl chloride* photolysis.

WR: 230 - 630 nm;  $\phi \sim 2.0$

AM: NO analysis

Lit.: 1) cf. J.G.Calvert, J.N.Pitts,jr., *Photochemistry*, Wiley, New York 1966, p.782;

2) F.I.Vilesov, L.G.Karpov, A.S.Kozlov, A.M.Pravilov, L.G.Smirnova, *High Energy Chem.* 12, 468 (1978);

3) A.M.Pravilov, S.E.Ryabov, *High Energy Chem.* 16, 331 (1982).

G11.1\*: *Acetone* photolysis.

WR: 250 - 320 nm;  $\phi_{\text{CO}} = 1.0$  at  $\geq 125$  °C and  $\leq 50$  mm Hg

AM: pressure measurement and GC (CO and CH<sub>4</sub>) after freezing down at -196 °C

Lit: cf. J.G.Calvert, J.N.Pitts,jr., *Photochemistry*, Wiley, New York 1966, p.782.

G11.2: *Acetone/hydrogen chloride* photolysis.

WR: 285, 300, 313 nm;

$\phi_{\text{CH}_4} / \phi_{\text{CO}} = 2$  at  $P_{\text{acetone}} = 5 - 60$  mm Hg,

$P_{\text{HCl}} = 1 - 8$  mm Hg, 130 °C

AM: GC or MS for CH<sub>4</sub> and CO

Lit: A.Horowitz, *J.Photochem.* 37, 241 (1987).

G12\*: *3-Pentanone* photolysis.

as G11.1, simple pressure measurement for CO after freezing down at -196 °C

G13: *2-Butene*, Hg sensitized photoisomerization.

WR: 254 nm;  $\phi_{\text{cis} \rightarrow \text{trans}} = \phi_{\text{trans} \rightarrow \text{cis}} = 0.50 \pm 0.02$  at  $P \geq 30$  Torr

AM: GC

Lit.: 1) R.B.Cundall, T.F.Palmer, *Trans.Faraday Soc.* 56, 1211 (1960);

2) R.B.Cundall, *Progr.Reaction Kinetics* 2, 165 (1964);

3) M.Termonia, G.R.De Maré, *Chem.Phys.Letters* 25, 402 (1974).

G14: *Propane*, Hg sensitized photolysis.

WR: 254 nm;  $\phi_{\text{H}_2} = 0.581$  at  $P = 300$  Torr

AM: pressure H<sub>2</sub> measurement

Lit.: 1) Y.Rousseau, *Thesis*, University of Alberta 1963;

2) T.L.Pollock, *Thesis*, University of Alberta 1971.

G15: *Perfluoroacetic anhydride*.

WR: 254, 265 nm;  $\phi = 0.29$  at 25 °C, 0.34 at 200 °C

AM: CO measurement

Lit.: G.A.Chamberlain, E.Whittle, *J.Chem.Soc.Faraday Trans.1* 71, 1978 (1975).

G16: *Perfluoropropionic anhydride*.

WR: 254, 265 nm;  $\phi = 0.24$  at 26 °C, 0.29 at 200 °C

AM: CO measurement

Lit.: as G15.

G17: *Azomethane*.

WR: 270 - 410 nm;  $\phi = 1$

AM:  $N_2$  besides  $CH_4$

Lit.: H.Okabe, *Photochemistry of small molecules*, Wiley-Interscience, New York etc., 1978, p.128.

G18: *Chlorine/hydrogen* photoinitiation.

WR: 280 - 380 nm;  $\phi \sim 15 \dots 16$

Lit.: E.Cremer, H.Margreiter, *Z.physikal.Chem.* 199, 90 (1952).

G19: *Chlorine monofluoride*.

WR: vacuum UV up to 320 nm

Lit.: N.F.Chebotarev, *Russ.J.Phys.Chem.* 60, 1105 (1986); C.A. 105, 87729c (1986).

### 1.1.3. Liquid phase chemical actinometers

L01\*: *cis-Cyclooctene cis-trans* photoisomerization.

WR: 185 nm;  $\phi_{cis \rightarrow trans} = 0.34 \pm 0.02$  in n-pentane (0.02 M)

AM: *trans*-cyclooctene analysis (GC, Ag complex)

PP: the 254 nm Hg line is ineffective; wavelength and temperature dependence of  $\phi$  have not yet been investigated

Lit.: 1) R.Srinivasan, J.A.Ors, *J.Am.Chem.Soc.* 100, 7089 (1978);

2) H.-P.Schuchmann, C.von Sonntag, R.Srinivasan, *J.Photochem.* 15, 159 (1981);

3) F.Weeke, E.Bastian, G.Schomburg, *Chromatographia* 7, 163 (1974);

4) W.Adam, T.Oppenländer, *Photochem.Photobiol.* 39, 719 (1984).

L02\*: *Ethanol* photolysis (*Farkas actinometer*).

WR: 185 nm;  $\phi_H = 0.4$  in 5 M aqueous solution

AM:  $H_2$  analysis <sup>2</sup>(GC)

PP: Solution must be free of H atom scavengers like  $O_2$  and acetaldehyde which implies low conversions ( $\leq 0.1\%$ );  $\phi$  depends on the ethanol concentration; the 254 nm Hg line is ineffective; no temperature dependence in the +15 - 40 °C range

Lit.: 1) C. von Sonntag, H.-P.Schuchmann, *Adv.Photochem.* 10, 59, 81 (1977) and lit. cited therein;

2) C. von Sonntag, *Z.physikal.Chem.N.F.* 69, 292 (1970);

3) H.-P.Schuchmann, C. von Sonntag, *J.Photochem.* 16, 289 (1981);

4) F.Weeke, E.Bastian, G.Schomburg, *Chromatographia* 7, 163 (1974);

5) A.K.Davies, K.A.Khan, J.F.McKellar, G.O.Phillips, *Mol.Photochem.* 7, 389 (1976).

L03: *Hydrogen azide, or hydrazoic acid*, photolysis.

WR: 200 - 260 nm;  $\phi = 1.00 \pm 0.05$  in water

AM: absorbance ( $HN_3$ ),  $N_2$ ,  $NH_2OH$

PP:  $HN_3$  (CAUTION, EXPLOSIVE) was prepared in solution from  $NaN_3$  and  $HClO_4$  immediately before irradiation and no thermal decomposition was observed under the conditions applied

Lit.: D.Shapira, A.Treinin, *J.Phys.Chem.* 77, 1195 (1973).

L04: *Glucose* photolysis.

WR: 200 - 300 nm;  $\phi \sim 0.33$  in 5% aqueous solution

AM: absorbance of malonaldehyde/2-methylindole complex at 555 nm

Lit.: R.K.Datta, K.N.Rao, *Indian J.Chem.* 14A, 122 (1976).

L05\*: *Uranyl oxalate* photolysis.

WR: 200 - 500 nm;  $\phi \sim 0.5 \dots 0.6$

AM:  $KMnO_4$  titration; absorbance at 320 nm after incubation (80 °C, 10 min) with Ce(IV) sulfate in  $H_2SO_4$  (versus unirrad. blank); GC for  $CO$ ,  $CO_2$ .

PP: use of commercial ceric sulfate is not recommended, ammonium nitrate impurities may limit the

stability of the standardized solution, preparation cf. ref.14); method critically depends on Ce(IV) concentration which should not be less than equivalent to and not higher than twice the oxalate concentration of the blank.

- Lit.: 1) W.G.Leighton, G.S.Forbes, *J.Am.Chem.Soc.* 52, 3139 (1930);  
 2) F.P.Bracket, G.S.Forbes, *J.Am.Chem.Soc.* 55, 4459 (1933);  
 3) C.A.Parker, *Proc.Roy.Soc.(London)*, A220, 104 (1953);  
 4) C.G.Hatchard, C.A.Parker, *Proc.Roy.Soc.(London)*, A235, 518 (1956);  
 5) J.N.Pitts, jr., J.D.Margerum, R.P.Taylor, W.Brim, *J.Am.Chem.Soc.* 77, 5499 (1955);  
 6) C.A.Discher, P.F.Smith, I.Lippman, R.Turse, *J.Phys.Chem.* 67, 2501 (1963);  
 7) D.H.Volman, J.R.Seed, *J.Am.Chem.Soc.* 86, 5095 (1964);  
 8) J.G.Calvert, J.N.Pitts, jr., *Photochemistry*, Wiley, New York 1966, p. 787;  
 9) S.L.Murov, *Handbook of Photochemistry*, Dekker, New York 1966, p.124;  
 10) L.J.Heidt, G.W.Tregay, F.A.Middleton, jr., *J.Phys.Chem.* 74, 1876 (1970);  
 11) H.A.Taylor in: *Analytical Photochemistry and Photochemical Analysis*, ed. by J.M.Fitzgerald, Dekker, New York 1971, p. 91;  
 12) D.F.Eaton, *Ph.D.Thesis*, Calif. Institute of Technol., 1972, p.120;  
 13) P.deMayo, H.Shizuka, *Creation and Detection of the Excited State*, ed. W.R.Ware, 4, 140 (1976), Dekker, New York.  
 14) G.F.Smith, W.H.Fly, *Anal.Chem.* 21, 1233 (1949).

L06\*: 4-(Dimethylamino)- $\alpha$ -[4-(dimethylamino)phenyl]- $\alpha$ -phenylbenzeneacetonitrile, or malachite green leucocyanide, photoionization.

WR: 225 - 289 nm;  $\phi = 0.91 \pm 0.01$

AM: absorbance at 620 nm

- Lit.: 1) J.G.Calvert, H.J.L.Rechen, *J.Am.Chem.Soc.* 74, 2101 (1952);  
 2) G.J.Fisher, J.C.LeBlanc, H.E.Johns, *Photochem.Photobiol.* 6, 757 (1967);  
 3) H.A.Taylor in: *Analytical Photochemistry and Photochemical Analysis*, ed. by J.M.Fitzgerald, Dekker, New York 1971, p. 91;  
 4) *on paper*: L.Chalkley, *J.Opt.Soc.Amer.* 42, 387 (1952);  
 5) *in gelatine matrix*: A.Kantz, K.Humpherys, *Radiat.Curing* 5, 4 (1978).

L07.1\*: Azobenzene (Actinochrome 2R (245/440) photoisomerization (reusable).

WR: 230 - 460 nm;  $\phi_{\text{cis} \rightarrow \text{trans}} = 0.4 \dots 0.5$ ;  $\phi_{\text{trans} \rightarrow \text{cis}} = 0.1 \dots 0.2$  in methanol or *i*-octane; different for the two bands; S = about  $10^3 \text{ M}^{-1} \text{ cm}^{-1}$

AM: absorbance at 358 nm; HPLC

PP:  $6.4 \cdot 10^{-4} \text{ M}$  in  $\text{CH}_3\text{OH}$ ;  $\phi_{\text{trans} \rightarrow \text{cis}} = 0.14$  in  $\text{CH}_3\text{OH}$ , 0.24 in *i*-octane;  $\phi_{\text{cis} \rightarrow \text{trans}} = 0.48$  in  $\text{CH}_3\text{OH}$ , 0.55 in *i*-octane; commercial p.A. quality is sufficient, no side products, conversion limit 20% (total absorption); no wavelength dependence of  $\phi$  for the  $\text{trans} \rightarrow \text{cis}$  reaction; no temperature dependence; thermal  $\text{cis} \rightarrow \text{trans}$  regeneration at 60 °C possible; reproducibility better than 2%; also applicable for lasers

- Lit.: 1) G.Zimmerman, L.-Y. Chow, U.-J. Paik, *J.Am.Chem.Soc.* 80, 3528 (1958);  
 2) G.Gauglitz, *J.Photochem.* 5, 41 (1976);  
 3) S.Hubig, Diplomarbeit, Tübingen 1980; Dissertation, Tübingen 1984;  
 4) G.Gauglitz, S.Hubig, *J.Photochem.* 15, 255 (1981);  
 5) G.Gauglitz, S.Hubig, DP 3242489.2;  
 6) G.Gauglitz, S.Hubig, *J.Photochem.* 30, 121 (1985);  
 7) J.Drabek, I.Cepciansky, J.Poskocil, *Chem.Listy* 78, 94 (1984);  
 8) G.Gauglitz, S.Hubig, *Z.Phys.Chem.N.F.* 139, 237 (1984);  
 9) G.Persy, J.Wirz, *EPA Newsletter* No. 29, 45 (1987);  
 10) *Note: Quantum yields for the cis  $\rightarrow$  trans reaction at 313 nm in various solvents were redetermined recently by two groups*, cf. N.Siampiringue, G.Guyot, S.Monti, P.Bortolus, *J.Photochem.* 37, 185 (1987).

L07.2: 2,2',4,4'-Tetraisopropylazobenzene.

WR: 350 - 390 nm;  $\phi_{\text{trans} \rightarrow \text{cis}} = 0.112 \pm 0.04$  in heptane

AM: absorbance at 365 nm

Lit.: R.Frank, G.Gauglitz *J.Photochem.* 7, 355 (1977).

L08\*: 8H,16H-4b,12b-Epidioxydibenzo[a,j]perylene-8.16-dione, or heterocoerdianthrone endoperoxide, or Actinochrome 1R (248/334), photoreversible photodissociation.

WR: 248 - 334 nm for the dissociation;  $\phi = 0.27 \pm 0.01$  in  $\text{CH}_2\text{Cl}_2$  ( $2 \cdot 10^{-3}$  M) independent of  $\lambda$  between 253 and 302 nm;  $S = 7770 \pm 200 \text{ M}^{-1}\text{cm}^{-1}$  between 253 and 302 nm,  $S = 7050, 6740, 4630$  at 248, 313, and 334 nm;  $23 \pm 2$  °C

AM: absorbance at 572 nm

PP: temperature coefficient  $+0.2\% / \text{°C}$ ; conversion limit  $\leq 1\%$ ; suitable as polychromatic quantum counter; solutions recover on exposure to sunlight behind a 455 nm cut-off filter and may be reused  $\sim 100$  times without loss in accuracy.

Lit.: 1) H.-D.Brauer, R.Schmidt, *Photochem.Photobiol.* 37, 587 (1983);

2) R.Schmidt, H.-D.Brauer, *J.Photochem.* 25, 489 (1984);

3) Note: Actinometric use of the reverse reaction (cf. H.-D.Brauer, W.Drews, R.Schmidt, G.Gauglitz, S.Hubig, *J.Photochem.* 20, 335 (1982)) is no longer recommended by the authors, since there are more convenient systems available for this wavelength region, cf. L35 or L39.

L09.1: Azoxybenzene  $\rightarrow$  2-hydroxyazobenzene photorearrangement, in solid phase cf. S02

WR: 250 - 350 nm;  $\phi \sim 0.02$  in ethanol, modestly dependent on  $\lambda$

AM: absorbance at 458 nm in ethanolic KOH

PP: no concentration dependence; no temperature dependence up to at least 45 °C;

Lit.: 1) N.J.Bunce, J.LaMarre, S.P.Vaish, *Photochem.Photobiol.* 39, 531 (1984);

2) cf. H.Mauser, G.Gauglitz, F.Stier, *Liebigs Ann.Chem.* 739, 84 (1970).

L09.2: 1,1'-Azoxy-naphthalene.

WR: 350 nm;  $\phi = 0.022$  at 350 nm in 95% ethanol

AM: absorbance at  $\geq 500$  nm

PP: more pronounced spectral shift from reactant to product than with azoxybenzene but more difficult to prepare

Lit.: N.J.Bunce, G.G.Debrabandere, K.B.Jacobs, M.E.Lemke, C.R.Montgomery, J.S.Nakai, E.J.Stewart, *J.Photochem.* 34, 105 (1986).

L10: Hydrogen peroxide photolysis sensitized by uranyl sulfate.

WR: 250 - 450 nm;  $\phi \sim 1.3$ , temperature coefficient  $+0.0095 / \text{°C}$

AM:  $\text{O}_2$  volumetric,  $\text{H}_2\text{O}_2$  consumption

Lit.: 1) G.O.Schenck, W.Haubold, cited in G.O.Schenck, *Angew.Chem.* 69, 579 (1957);

2) G.Folcher, J.Paris, E.Saito, *Nouv.J.Chim.* 7, 703 (1983).

L11: 1,2,3,4-Tetraphenylcyclobutane photolysis.

WR: 260 nm continuous light or 265 nm laser flashes;  $\phi = 0.27$  in butyl chloride

AM: absorbance at 300 nm (trans-stilbene)

Lit.: S.Takamuku, G.Beck, W.Schnabel, *J.Photochem.* 11, 49 (1979).

L12: Chloroacetic acid photohydrolysis.

WR:  $\leq 270$  nm;  $\phi = 0.31$  at 254 nm, 25 °C, temperature coefficient  $+0.009 / \text{°C}$

AM: potentiometry, polarography, turbidimetry,  $\text{Cl}^-$  ion specific electrode

Lit.: 1) R.N.Smith, P.A.Leighton, W.G.Leighton, *J.Am.Chem.Soc.* 61, 2299 (1939);

2) L.B.Thomas, *J.Am.Chem.Soc.* 62, 1879 (1940);

3) W.Kemula, A.Grabowska, *Roczn.Chemii* 29, 834 (1955):



- 4) H.A.Taylor in: *Analytical Photochemistry and Photochemical Analysis*, ed. by J.M.Fitzgerald, Dekker, New York 1971, p. 91;  
 5) M.Neumann-Spallart, N.Getoff, *Radiat.Phys.Chem.* 13, 101 (1979).

L13: 1,2-Dimethoxy-4-nitrobenzene  $\Rightarrow$  2-methoxy-5-nitrophenolate anion, photohydrolysis.

WR: 254 - 365 nm;  $\phi$  0.116  $\pm$  0.002 in 0.5M aqueous KOH

AM: Absorbance at 450 nm

Lit.: L.Pavlickova, P.Kuzmic, M.Soucek, *Coll.Czech.Chem.Comm.* 51, 368 (1986).

L14\*: Potassium tris(oxalato)ferrate(III), or potassium iron(III) oxalate,  $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ , photoreduction (Hatchard-Parker actinometer).

WR: 250 - 500 nm;  $\phi = 1.25 \dots 0.9$

AM: absorbance at 510 nm of Fe(II)-1.10-phenanthroline complex in buffered acidic solution

PP: all work must be done under dark red light; pure solid green  $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ . recryst. from water is stable in the dark; 0.006 ... 0.20 M solutions have been used; only freshly prepared and mixed solutions should be used; make sure that there is total absorption; sufficient stirring is essential; complexation should be done immediately after irradiation; add irradiated solution to pre-mixed buffer-phenanthroline solution; complete complexation takes about an hour; phenanthroline solution is sensitive to UV (fluorescent room lights) and should be stored in the dark; in case of high conversion there may not be sufficient phenanthroline to complex all Fe(II); test for the linearity of the results with irradiation time; for use with lasers see Lit 23; no problems at 60 °C without deoxygenation.

Note: In view of the numerous different and often contradictory observations and recommendations given in the literature concerning the adequate use of the ferrioxalate actinometer it is suggested that publications should contain a short but unequivocal indication as to which experimental conditions have been applied. Lit.:

- 1) C.G.Hatchard, C.A.Parker, A new sensitive chemical actinometer. II. Potassium ferrioxalate as a standard chemical actinometer, *Proc.Roy.Soc.(London)*, A235, 518 (1956); part I: C.A.Parker, *Proc.Roy.Soc.(London)*, A220, 104 (1953);
- 2) J.H.Baxendale, N.K.Bridge, The photoreduction of some ferric compounds in aqueous solution, *J.Phys.Chem.* 59, 783 (1955);
- 3) C.E.Bricker, S.S.Schonberg, Photonometric determination of vanadium and chromium, *Anal.Chem.* 30, 922 (1958);
- 4) J.Lee, H.H.Seliger, Quantum yield of the ferrioxalate actinometer, *J.Chem.Phys.* 40, 519 (1964);
- 5) J.Calvert, J.N.Pitts, *Photochemistry*, Wiley, New York 1966, p. 783;
- 6) E.W.Wegner, A.W.Adamson, Photochemistry of complex ions. III. Absolute quantum yields for the photolysis of some aqueous chromium(III) complexes. Chemical actinometry in the long wavelength visible region, *J.Am.Chem.Soc.* 88, 394 (1966);
- 7) H.P.Wolf, J.J.Bohning, P.A.Schnieper, K.Weiss, Apparatus for the measurement of quantum yields and rates of photochemical reactions, *Photochem.Photobiol.* 6, 321 (1967);
- 8) C.A.Parker, *Photoluminescence of Solutions, with Applications to Photochemistry and Analytical Chemistry*, Elsevier, Amsterdam 1968, p. 208;
- 9) H.A.Taylor, Analytical methods and techniques for actinometry, p. 91 in *Analytical Photochemistry and Photochemical Analysis*, J.M.Fitzgerald, ed., Dekker, New York 1971;
- 10) K.C.Kurien, A modification to the ferrioxalate actinometer, *J.Chem.Soc.* B1971, 2081;
- 11) M.Wrighton, S.Witz, Stability of Fe(II) in ferrioxalate solutions, *Mol.Photochem.* 3, 387 (1972);
- 12) S.L.Murov, *Handbook of Photochemistry*, Dekker, New York 1973, p. 119;
- 13) E.I.Aleksandrov, T.A.Lopasova, *Sov.J.Quant.Electron.* 4, 813 (1974);
- 14) P. de Mayo, H.Shizuka, Measurement of reaction quantum yields, *Creation and Detection of the Excited State*, W.R.Ware, ed. 4, 164 (1976);
- 15) W.D.Bowman, J.N.Demas, Ferrioxalate actinometry. A warning on its correct use, *J.Phys.Chem.* 80, 2434 (1976);
- 16) D.E.Nicodem, M.L.P.F.Cabral, J.C.N.Ferreira, The use of 0.15M potassium ferrioxalate as a chemical actinometer, *Mol.Photochem.* 8, 213 (1977);

- 17) P.Thomas, M.Benedix, H.Hennig, Zur Synthese und Photolyse von Trisphenanthrolinium-trisoxalatoeisen(III) und seiner Eignung als Aktinometersubstanz, *Z.Chem.* 17, 114 (1977);
- 18) R.Frank, G.Gauglitz, *Chemieanlagen Verfahren* 1978, 19;
- 19) E.Fernandez, J.M.Figuera, A.Tobar, Use of the potassium ferrioxalate actinometer below 254 nm, *J.Photochem.* 11, 69 (1979);
- 20) A.D.Baker, A.Casadavell, H.D.Gafney, M.Gellender, Photochemical reactions of tris(oxalato)iron (III), a first-year chemistry experiment, *J.Chem.Educ.* 57, 314 (1980);
- 21) J.S.Connolly, T.H.Meyer, A convenient irradiation cell for ferrioxalate actinometry, *Photochem.-Photobiol.* 34, 145 (1981);
- 22) E.W.Vitz, E.Boschmann, The ferrioxalate actinometer: A lecture demonstration, *J.Chem.Educ.* 58, 655 (1981);
- 23) J.N.Demas, W.D.Bowman, E.F.Zalewski, R.A.Velapoldi, Determination of the quantum yield of the ferrioxalate actinometer with electrically calibrated radiometers, *J.Phys.Chem.* 85, 2766 (1981);
- 24) C.H.Langford, C.A.Holubov, Wavelength and temperature dependence in the photolysis of the chemical actinometer, potassium trisoxalatoferrate(III), at longer wavelengths, *Inorgan.Chim.Acta* 53, L59 (1981);
- 25) E.A.Wolfenden, A.D.Q.Agnew, D.R.Causton, A photochemical light meter suitable for oecological survey, *Acta Oecolog., Oecol.Plant.* 3, 101 (1982);
- 26) D.E.Nicodem, O.M.V.Aquilara, Standardization of the potassium ferrioxalate actinometer over the temperature range 5 - 80 °C, *J.Photochem.* 21, 189 (1983);
- 27) A.D.Kirk, C.Namasivayam, Errors in ferrioxalate actinometry, *Anal.Chem.* 55, 2428 (1983);
- 28) G.Gauglitz, Modern chemical actinometry, *EPA Newsletter No.19*, 49 (1983);
- 29) E.Fischer, Ferri-oxalate actinometry, *EPA Newsletter No.21*, 33 (1984);
- 30) A.M.Braun, M.-T. Maurette, E.Oliveros, Technologie Photochimique, *Presses Polytechniques Roman-des*, Lausanne 1986, p. 43 - 96;
- 31) L.Vincze and S.Papp, Individual quantum yields of  $\text{Fe}^{3+}\text{OX}_n^{2-}\text{H}_m^+$  complexes in aqueous acidic solutions ( $\text{OX}^{2-} \equiv \text{C}_2\text{O}_4^{2-}$ ,  $n = 1-3$ ,  $m = 0,1$ ), *J.Photochem.* 36, 289 (1987).

L15: 3-(2-Hydroxyphenyl)-2-propenoic acid, or o-coumaric acid, dianion photoisomerization.  
cis $\rightarrow$ trans reaction

WR: 254 - 300 nm:  $\phi = 0.52 \pm 0.05$ ; 313 - 400 nm:  $\phi = 0.75 \pm 0.05$  (G.Guyot)

trans $\rightarrow$ cis reaction

WR: 254 - 300 and 350 - 400 nm:  $\phi = 0.10 \pm 0.01$  (G.Guyot)

AM: absorbance, fluorescence at 492 nm (G.Guyot)

Lit.: G.Perbet, L.-M.Coulangeon, P.Boule, J.Lemaire, *J.Chim.Phys.* 75, 1096 (1978).

L16: Iodomethane photoexchange with  $^{131}\text{I}_2$ .

WR: 254 nm;  $\phi = 1.0$

AM: radiochemical

Lit.: 1) G.M.Harris, J.E.Willard, *J.Am.Chem.Soc.* 76, 4678 (1954);

2) J.R.Majer, J.P.Simons, *Adv.Photochem.* 2, 137 (1964).

L17: 1,3-Dimethyluracil photohydration.

WR: 254 nm;  $\phi = 0.0130 \pm 0.0007$  in water

AM: absorbance at 266 nm

Lit.: N.Numao, T.Hamada, O.Yonemitsu, *Tetrahedron Lett.* 1977, 1661.

L18: 1,3-Cycloheptadiene photoisomerisation.

WR: 254 nm;  $\phi = 0.48 \pm 0.01$  in ethanol

AM: absorbance at 246 nm

Lit.: N.Numao, T.Hamada, O.Yonemitsu, *Tetrahedron Lett.* 1977, 1661.

L19: *Stilbenes cis-trans photoisomerization*

WR: 254 - 366 nm; quantum yields depend on substitution and solvent

AM: absorbance, GC

Lit.: 1) J.Saltiel, A.Marinari, D.W.-L.Chang, J.C.Mitchener, E.D.Megarity, *J.Am.Chem.Soc.* 101, 2982 (1979);2) J.Saltiel, J.L.Charlton, in: *Rearrangements in Ground and Excited States*, ed. P.de Mayo, Vol.3, 25, Academic Press, New York 1980;3) H.Görner, *Ber.Bunsenges.Phys.Chem.* 88, 1199 (1984)4) T.-I.Ho, T.-M.Su, T.-C.Hwang, *J.Photochem.Photobiol.* 41A, 293 (1988).L20: *Phenylglyoxylic acid photodecarboxylation*.WR: 254 - 405 nm;  $\phi = 0.6 \dots 0.8$  in acidic  $\text{CH}_3\text{CN} - \text{H}_2\text{O}$  (3:1 v/v) solution;

AM: absorbance at 360 - 390 nm, potentiometry, HPLC, NMR

PP: moderately dependent on  $\lambda$ ; strongly dependent on pH and water content, but reproducibility better than  $\pm 0.05$ ; correction for benzaldehyde content at  $\lambda_{\text{obs}} \leq 370$  nm necessary; not to be used above 45 °C; temperature coefficient  $\Delta\phi/\Delta t = 0.0029 \pm 0.0007/^\circ\text{C}$ ; conversion limit ~20%; no significant dependence on air, concentration or light intensity; freshly recryst. acid should be used;

Lit.: 1) A.Defoin, R.Defoin-Straatmann, K.Hildenbrand, E.Bittersmann, D.Kreft,

H.J.Kuhn, *J.Photochem.* 33, 237 (1986);2) A.Defoin, H.J.Kuhn, *EPA Newsletter No.26*, 23 (1986).

## L21: Laser pulse actinometry via standard transients.

WR: 265 nm (*anthracene, naphthalene*); 353 nm (*all-trans-retinal*)Lit.: 1) R.Bensasson, C.R.Goldschmidt, E.J.Land, T.G.Truscott, *Photochem. Photobiol.* 28, 277 (1978);2) *benzophenone*: L.V.Romashov, Yu.I.Kiryukhin, Kh.S.Bagdasar'yan,*High Energy Chem.* 12, 132 (1978);3) J.K.Hurley, N.Sinai, H.Linschitz, *Photochem.Photobiol.* 38, 9 (1983).L22: *2,3-Dimethyl-2-butene*, sensitized photooxygenation.

Especially designed for high-power pulse and cw lasers.

WR: 280 - 560 nm;  $\phi = 0.76$  with methanolic  $\text{Ru}(\text{bipy})_3^{2+}$  chloride and *2,3-dimethyl-2-butene* as acceptorAM:  $\text{O}_2$  consumption, volumetricPP: slight dependence of  $\phi_{\text{obs}}$  on TME concentration and  $\text{P}_{\text{oxygen}}$ Lit.: 1) J.N.Demas, E.W.Harris, R.P.McBride, in: *Lasers in Physics, Chemistry, and Biophysics, Proc.-Int.Meet.Soc.Chim.Phys.* 27th, ed. J.Joussot-Dubien, Elsevier, Amsterdam, 1975, p.477;2) J.N.Demas, R.P.McBride, E.W.Harris, *J.Phys.Chem.* 80, 2248 (1976).L23: *Iodide photooxidation*.

WR: Rose Bengal sensitization

AM: polarography, redox titration of iodine

Lit.: 1) C.Sánchez-Pedreño, T.Pérez-Ruiz, C.Martinez-Lozano, M.Hernández-Córdoba,

*Analyt.Chim.Acta* 104, 397 (1979);2) cf. A.E.H.Meyer, E.O.Seitz, *Ultraviolette Strahlen*, de Gruyter, Berlin 1949, p.200.L24: *Benzophenone/benzhydrol photoreduction*.WR: 300 - 390 nm; relative method, no predetermined  $\phi$ 

AM: differential absorbance

Lit.: 1) W.M.Moore, G.S.Hammond, R.P.Foss, *J.Am.Chem.Soc.* 83, 2789 (1961);2) W.M.Moore, M.Ketchum, *J.Am.Chem.Soc.* 84, 1368 (1962);3) S.L.Murov, *Handbook of Photochemistry*, Dekker, New York 1973, p. 125.

## L25.1: 2-Hexanone photolysis.

WR: 313 nm;  $\phi = 0.22$  (acetone), 0.25 (propene), 0.075 (cyclobutanol), 0.33 (2-hexanone consumed) in pentane solution

AM: GC

Lit.: 1) D.R.Coulson, N.C.Yang, *J.Am.Chem.Soc.* **88**, 4511 (1966);

2) P.J.Wagner, *Tetrahedron Lett.* **1968**, 5795;

3) S.L.Murov, *Handbook of Photochemistry*, Dekker, New York 1973, p.126.

## L25.2: Butyrophenone photolysis.

Lit.: J.N.Pitts, L.D.Hess, E.J.Baum, E.A.Schuck, *Photochem.Photobiol.* **4**, 305 (1965).

## L25.3: Valerophenone photolysis.

Lit.: 1) P.J.Wagner, A.Kelso, A.E.Kemppainen, J.M.McGrath, N.H.Schott, R.G.Zepp, *J.Am.Chem.Soc.* **94**, 7495 (1972);

2) W.Amrein, J.Gloor, K.Schaffner, *Chimia* **28**, 185 (1974).

## L25.4: 2-Methyl-2-phenylpropanal photolysis.

Lit.: 1) W.Amrein, J.Gloor, K.Schaffner, *Chimia* **28**, 185 (1974).

2) H.Küntzel, H.Wolf, K.Schaffner, *Helv.Chim.Acta* **54**, 868 (1971).

## L26: 1,3-Pentadiene photoisomerization sensitized by benzophenone.

WR: 313, 366 nm;  $\phi_{\text{cis} \rightarrow \text{trans}} = 0.55$ ;  $\phi_{\text{trans} \rightarrow \text{cis}} = 0.44$

AM: GC

Lit.: 1) S.L.Murov, *Handbook of Photochemistry*, Dekker, New York 1973, p. 128;

2) G.F.Vesley, *Mol.Photochem.* **3**, 193 (1971).

## L27: 1,3-Cyclohexadiene, sensitized photodimerization.

WR: 313, 366 nm:  $\phi = 0.97$  in benzene

AM: GC

Lit.: G.F.Vesley, G.S.Hammond, *Mol.Photochem.* **5**, 367 (1973).

## L28.1\*: Fulgide photoisomerization (photoreversible)

(E)-[1-(2,5-dimethyl-3-furyl)ethylidene](isopropylidene)succinic anhydride, or Aberchrome 540  $\leftrightarrow$  7,7a-dihydro-2,4,7,7a-pentamethylbenzo[b]furan-5,6-dicarboxylic anhydride, or Aberchrome 540P.

WR: 310 - 375 nm (reversible with white light);  $\phi = 0.20$  in toluene solution;  $S = 1640 \text{ M}^{-1} \text{ cm}^{-1}$  at 494 nm, 1214 at 343 nm;

WR: back reaction 435 - 535 nm;  $\phi = 0.073$  at 436 nm, 0.0594 at 494 nm, 0.0470 at 546 nm, linearly dependent on wavelength; 30000 cycles possible;  $S = 487$  at 494 nm;

AM: absorbance at 494 nm ( $\epsilon = 8200 \text{ dm}^3 \text{ Mol}^{-1} \text{ cm}^{-1}$ ) or 343 nm ( $\epsilon = 6077$ )

PP: reproducibility  $\pm 1\%$  (back reaction  $\pm 0.5\%$ ); precision  $\pm 3\%$  (back reaction  $\pm 1\%$ ); also applicable to one- and two-laser experiments; other solvents possible; degassing desirable while not essential; no conversion limit, but only small A changes necessary; a nonreversible side process interferes  $\leq 313$  nm.

Lit.: 1) H.G.Heller, *Chem.Ind.* **1978**, 193; Brit. Patent 7/1464603, USA Patent 9/719.254;

2) H.G.Heller, J.R.Langan, *J.Chem.Soc.Perkin Trans.1* **1981**, 341;

3) H.G.Heller, J.R.Langan, *EPA Newsletter* Oct. **1981**, 71;

4) V.Wintgens, L.J.Johnston, J.C.Scaiano, *J.Am.Chem.Soc.* **110**, 511 (1988).

## L28.2: 7,7a-Dihydro-4,7,7,7a-tetramethyl-2-phenylbenzo[b]thiophene-5,6-dicarboxylic anhydride, or Aberchrome 999P.

WR: 435 - 640 nm; linear dependence of  $\phi$  on wavelength.  $\phi = 0.0351$  at 436 nm, 0.0240 at 546 nm, 0.0210 at 575 nm in toluene.  $S = 288 \text{ M}^{-1} \text{ cm}^{-1}$  at 546 nm.

AM: absorbance at 546 nm ( $\epsilon = 12000 \text{ dm}^3 \text{ M}^{-1} \text{ cm}^{-1}$ )

PP: reproducibility  $\pm 0.5\%$ ; precision  $\pm 1\%$ ; no conversion limit; reversible on exposure to 366 nm;

Note: Reuse of the solution not recommended because some degradation takes place during recolouring.

Lit.: 1) private communication by H.G.Heller;

2) for similar compounds cf. A.P.Glaze, S.A.Harris, H.G.Heller, W.Johncock, S.N.Oliver, P.J.Strydom, J.Whittal, *J.Chem.Soc.Perkin Trans. 1* 1985, 957.

L29\*: Potassium diamminetetraacyanatochromate(III), or potassium Reineckate,  $K[Cr(NH_3)_2(CNS)_4]$ , photoaquation in dilute acidic solution.

WR: 316 - 750 nm;  $\phi \sim 0.3$ , dependent on  $\lambda$ ; only slightly dependent on temperature; no significant dependence on light fluence;  $S = 30.5$  at 520 nm;  $\epsilon_{520} = 110.7 \pm 2.3$ ,  $\epsilon_{452} = 36.2 \pm 1.7$ ,  $\epsilon_{392} = 96.3 \pm 2.5$  (Hubig)

AM: absorbance at 450 nm of Fe(III) thiocyanate complex

PP:  $\phi = 0.291$  at 316 nm, 0.388 at 350 nm, 0.335 at 366 nm, 0.316 at 392 nm, 0.310 at 416 nm, 0.311 at 452 nm, 0.299 at 504 nm, 0.286 at 520 nm, 0.282 at 545 nm, 0.270 at 577 and 585 nm, 0.276 at 600 nm, 0.271 at 676 nm, 0.284 at 713 nm, 0.302 at 735 nm, 0.273 at 750 nm (Hubig); thermal dark reaction; only weak red light  $\geq 750$  nm is admitted; the commercially available salt must be carefully recryst. in the dark from water below 80 °C to limit thermal aquation; in basic solution thermal aquation (substitution) becomes a major problem; temperature dependence is related to pH; conversion should not exceed 10%; reproducibility  $\pm 2\%$ ; precision  $\pm 5\%$ ;

Note: Actinometric use not recommended by Hubig and Gauglitz.

Lit.: 1) E.E.Wegner, A.W.Adamson, *J.Am.Chem.Soc.* 88, 394 (1966);

2) P.de Mayo, H.Shizuka, *Creation and Detection of the Excited State*, ed. W.R.Ware, 4, 139 (1976), Dekker, New York;

3) J.N.Demas, *ibidem*, 4, 1 (1976);

4) S.Hubig, *Diplomarbeit* (G.Gauglitz) Tübingen 1980.

L30: 9,10-Dimethylantracene photooxygenation.

WR: 334 - 395 nm;  $\phi = 0.58 \pm 0.02$  in air saturated Freon 113 Uvasol Merck ( $1.7 \times 10^{-3}$  M), independent of  $\lambda$ ;  $S = 630 \pm 20$  M<sup>-1</sup>cm<sup>-1</sup>

AM: absorbance at 324 nm

PP: conversion limit  $\sim 20\%$

Lit: H.-J.Adick, R.Schmidt, H.-D.Brauer, *J.Photochem.Photobiol., A: Chem.* 45, 89 (1988).

L31: 3,3,8,8-Tetramethyl-1,2,6,7-tetraazaspiro[4.4]nona-1,6-diene photolysis.

For actinometry of circularly polarized light.

WR: 345 nm

AM: CD

Lit.: R.Blume, H.Rau, O.Schuster, *J.Am.Chem.Soc.* 98, 6583 (1976)

L32: Tris(2,2'-bipyridine)ruthenium(2+)\* irreversible electron transfer quenching in an electrochemical cell.

WR: 360 - 580 nm

AM: photocurrent

Lit.: W.J.Dressick, T.J.Meyer, B.Durham, *Isr.J.Chem.* 22, 153 (1982).

L33: Tris(2,2'-bipyridine)ruthenium(2+) oxidation upon photolysis in presence of peroxodisulphate.

WR: 366, 405, 436 nm;  $\phi = 1.3$  in argon-saturated aqueous solution (140  $\mu$ M Ru(bipy)<sub>3</sub><sup>2+</sup> and 2 mM potassium peroxodisulphate, pH  $\approx$  5);  $S = 16600$  M<sup>-1</sup>cm<sup>-1</sup>

AM: absorbance at 450 nm

PP:  $\phi$  is dependent on pH and peroxodisulphate concentration; there is a slow dark reaction, therefore mixtures should not be stored; because of a reverse dark reaction absorption must be measured immediately after irradiation.

Lit.: 1) F.Bolletta, A.Juris, M.Maestri, D.Sandrini, *Inorg.Chim.Acta* 44, L175 (1980);

2) H.Görner, H.J.Kuhn, D.Schulte-Frohlinde, *EPA Newsletter* No.31, 13 (1987).

L34: Degradation of 2,2,6,6-tetramethyl-4-oxo-1-piperidylloxyl, or TAN, by photoproducted hematoporphyrin anion radicals. Actinometry in an EPR cavity.

WR: 366 - 546 nm;

AM: ESR

Lit.: J. Moan, B. Hovik, E. Wold, *Photochem. Photobiol.* 30, 623 (1979).

L35: 5,12-Diphenylnaphthacene photooxygenation.

WR: 405 - 500 nm;  $\phi = 0.762 \pm 0.015$  in air saturated Freon 113 Uvasol Merck ( $1.6 \cdot 10^{-3}$  M), independent of  $\lambda$ ;  $S = 662 \pm 18 \text{ M}^{-1} \text{ cm}^{-1}$

AM: absorbance at 383 nm

PP: conversion limit ~ 30%; suitable as polychromatic quantum counter

Lit: H.-J. Adick, R. Schmidt, H.-D. Brauer, *J. Photochem. Photobiol. A: Chem.* 45, 89 (1988).

L36: *p*-(Diethylamino)benzenediazonium tetrafluoroborate or DEAD photolysis.

WR: 405 nm;  $\phi = 0.48$  in aqueous solution

AM: absorbance at about 376 nm

Lit.: 1) A. Cox, T. J. Kemp, D. R. Payne, P. Pinot de Moira, *J. Photogr. Sci.* 25, 208 (1977);

2) H. Baumann, K. Behrmann, H. Jahnke, W. Ortmann, G. Waldmann,

*J. Signalanfz.-Mater.* 11, 385 (1983).

L37: Thiourea photooxidation.

WR: 420 - 660 nm;  $\phi \sim 0.98$  with ethyl chlorophyllide.  $\phi = 0.74$  with pheophytin or pheophorbid as sensitizers in pyridine

AM:  $\text{O}_2$  consumption, manometric

Lit.: 1) O. Warburg, V. Schocken, *Arch. Biochem.* 21, 363 (1949);

2) M. Schwartz, *BBA* 22, 175 (1956).

L38: Hexakis(urea)chromium(III) chloride.  $[\text{Cr}(\text{urea})_6]\text{Cl}_3$  photoaquation.

WR: 452 - 735 nm;  $\phi \sim 0.09 \dots 0.10$

AM: precipitation of the unreacted complex as the perchlorate salt and determination of chromium in the supernatant;

Lit.: E. W. Wegner, A. W. Adamson, *J. Am. Chem. Soc.* 88, 394 (1966).

L39\*: 7,16-Diphenyldibenzo[*a,o*]perylene, or meso-diphenylhelianthrene, or Actinochrome N (475/610) self-sensitized photooxygenation

WR: 475 - 610 nm;  $\phi = 0.224 \pm 0.004$  in air-saturated toluene ( $10^{-3}$  M) independent of  $\lambda$ ;  $S = 4080 \pm 90 \text{ M}^{-1} \text{ cm}^{-1}$  at sea level ( $S = 4030, 4000, 3970$  at 1000, 2000, and 3000 m altitude)

AM: absorbance at 429 nm

PP: conversion limit ~ 10%; reproducibility better than  $\pm 1\%$ ; irreversible; no side products; suitable as polychromatic quantum counter; no dependence on wavelength; solutions stable at  $-15^\circ\text{C}$  for at most 3 months.

Lit.: 1) G. Sauvage, *Ann. Chim.* [12], 2, 844 (1947);

2) H.-D. Brauer, R. Schmidt, G. Gauglitz, S. Hubig, *Photochem. Photobiol.* 37, 595 (1983);

3) A. Acs, R. Schmidt, H.-D. Brauer, *Photochem. Photobiol.* 38, 527 (1983);

4) W. Drews, *Dissertation* Frankfurt 1980; S. Hubig, *Dissertation* Tübingen 1984;

5) R. Schmidt, H.-D. Brauer, *J. Photochem.* 25, 489 (1984).

6) H.-J. Adick, R. Schmidt, H.-D. Brauer, *J. Photochem. Photobiol. A: Chem.* 45, 89 (1988).

L40: Cobalt(III) anionoammies photolysis.

WR: 488 nm;  $\phi \sim 10^{-4} - 5 \cdot 10^{-3}$

AM:  $\text{NH}_3$  release; absorbance at 625 nm

Lit.: R. A. Pribush, C. K. Poon, C. M. Bruce, A. W. Adamson, *J. Am. Chem. Soc.* 96, 3027 (1974).

Disproved:

L41: Decafluorobenzophenone photoreduction in 2-propanol.

WR: 290 - 370 nm;  $\phi = 0.60 \pm 0.01$

Lit.: 1) N.Filipescu, J.P.Pinion, F.L.Minn, *J.Chem.Soc.Chem.Comm.* 1970, 1413

*Two independent studies advised against the use of this system because of complex stoichiometry, wavelength-dependent  $\phi$ , and dependence on light fluence:*

2) P.Margaretha, J.Gloor, K.Schaffner, *J.Chem.Soc.Chem.Comm.* 1974, 565;

3) G.Gauglitz, U.Köfle, *J.Photochem.* 4, 309 (1975).

**I.2. Electronic devices**

*Light intensity measurements before and after or during a photochemical reaction the quantum yield of which is of interest are rather cumbersome to perform with traditional methods of chemical actinometry. Integrating electronic actinometers of the "Quantacount" type (E06, 07, 10) are designed to measure and integrate the amount of light absorbed by the sample during irradiation, largely independent of the absorbance. For that purpose, the entering monochromatic light is split into a sample beam and a reference beam. By means of a chemical quantum counter (e.g. Rhodamine B) and photodiodes (or photoelements or photomultipliers) the two light beams produce voltages that are electrically matched. During irradiation the difference of the light intensities before and behind the sample is continuously computed and converted into a frequency which is integrated, counted and displayed. The instruments allow to apply a preset amount of quanta to the sample and account for any changes of the intensity of the light source and of the absorbance of the sample. Registration of the absorbance or taking a complete absorption spectrum are comfortable options which allow to monitor the photochemical conversion. The complete optical and electronic set-up has to be calibrated by chemical or physical means determining the Einsteins per count relationship for desired wavelengths.*

E01: UV light integrator as photochemical monitor.

Lit.: R.W.Yip, D.R.Dickinson, *J.Sci.Instr.* 43, 758 (1966).

E02: Calibrated thermopile for continuous measurement of light absorption during irradiation.

Lit.: H.P.Wolf, J.J.Bohning, P.A.Schnieper, K.Weiss, *Photochem.Photobiol.* 6, 321 (1967).

E03: Quantum flux monitor consisting of a Rhodamin B solution and a photomultiplier.

Lit.: 1) J.Yguerabide, *Rev.Sci.Instr.* 39, 1048 (1968);

2) B.Schaarschmidt, *Z.Naturf.* 25b, 330 (1970).

E04: Physical light integrator.

Lit.: H.Schultze, H.-R.Vogel, *Mol.Photochem.* 5, 223 (1973).

E05: Digital quantum dose integrator with memory.

Lit.: J.N.Demas, *Chem.Instrumentation* 5, 283 (1973/74).

E06\*: Electronically integrating actinometer.

WR: 254 - 578 nm (Rhodamine B as quantum counter; photoelements)

Lit.: W.Amrein, J.Gloor, K.Schaffner, *Chimia* 28, 185 (1974)

*Note: An advanced instrument ("Quantacount") of this kind is commercially available.*

E07\*: Electronic actinometer with photomultipliers.

Lit.: H.E.Zimmerman, T.P.Cutler, V.R.Fitzgerald, T.J.Weigt, *Mol.Photochem.* 8, 379 (1977).

E08: Luminescent quantum counters.

Lit.: D.G.Taylor, J.N.Demas, *Analyt.Chem.* 51, 712, 717 (1979).

E09: MgWO<sub>4</sub> phosphor photoelectronic UV-B dosimeter for microcomputer read-out.

WR: UV-B; the emission at 420 - 560 nm is detected by a photodiode

Lit.: G.Davidson, R.B.Sluder, I.L.Kofsky, G.Goldsmith, *Photochem.Photobiol.* **34**, 287 (1981).

E10\*: Integrating electronic actinometer with automatic UV/VIS monitoring.

WR:  $\leq 365 - \geq 578$  nm (Rhodamine B as fluorescent converter; photodiodes)

Lit.: 1) H.Baumann, K.Behrmann, H.Jahnke, W.Ortmann, G.Waldmann,

*J.Signalaufz.-Maer.* **11**, 385 (1983);

2) K.Behrmann, E.Fanghänel, J.Kyziol, *Z.Chem.* **24**, 20 (1984).

## II. RECOMMENDED ACTINOMETRIC PROCEDURES

(For references and more data cf. Section I.1.3. )

L01\*: *cis-Cyclooctene* cis-trans photoisomerization.

(submitted by R.Srinivasan, C.von Sonntag, and H.-P.Schuchmann)

WR: 185 nm;  $\phi_{cis \rightarrow trans} = 0.34$ ;  $\phi_{trans \rightarrow cis} = 0.44$

2 - 4 ml of a solution of *cis*-cyclooctene in pentane ( $2 \cdot 10^{-2}$  M, total absorption) containing nonane as a GC standard are placed in a suprasil cell and deaerated by purging with a gentle stream of oxygen-free argon while the sample is kept cold to minimize solvent evaporation. A gas-tight cell assembly is necessary. Even though oxygen is not expected to interfere with the isomerization reaction, it may lead to charge-transfer absorption at longer wavelengths involving the solvent. The irradiation is performed at room temperature. It is recommended to stir the solution during purging and irradiation by a Teflon coated bar magnet. At a 185 nm photon irradiance of about  $1 \cdot 10^{18} \text{ min}^{-1}$  per sample (cross section 2 - 4 cm<sup>2</sup>), conversion after 1 minute of irradiation is easily measurable by gas chromatography.

This actinometer involves a system where the product, *trans*-cyclooctene, is photoisomerized back to the *cis* compound (side reactions are very minor).  $N$ , the number of absorbed quanta per sample volume per unit time can be calculated from

$$f([cis]) = - \frac{N \cdot [cis]_0}{N_A \cdot [cis]_\infty} \cdot \phi_{trans \rightarrow cis}$$

where  $f([cis])$  is given by the expression

$$f([cis]) = \frac{\epsilon_{cis} - \epsilon_{trans}}{\epsilon_{trans}} ([cis] - [cis]_0) + ([cis]_0 + \frac{\epsilon_{cis} - \epsilon_{trans}}{\epsilon_{trans}} [cis]_\infty) \ln \frac{[cis] - [cis]_\infty}{[cis]_0 - [cis]_\infty}$$

$[cis]$  is the molar concentration of *cis*-cyclooctene. Subscript 0 indicates zero conversion and  $\infty$  refers to the stationary state ( $[trans]_\infty/[cis]_\infty \approx 1$ ).  $[cis]_\infty/[cis]_0$  is close to 0.5.  $\epsilon_{cis} = 8500 \text{ M}^{-1} \text{ cm}^{-1}$ ,  $\epsilon_{trans} = 6000 \text{ M}^{-1} \text{ cm}^{-1}$ ,  $N_A =$  Avogadro's number,  $t =$  irradiation time (min.). Since  $f([cis])$  is in units of  $\text{mol} \cdot \text{dm}^{-3}$ ,  $N$  is obtained in  $\text{dm}^{-3} \cdot \text{min}^{-1}$ . For details and an alternative graphical method of evaluation cf. references in L01, Section I .

L02\*: *Ethanol* photolysis (*Farkas actinometer*).

(submitted by C.von Sonntag and H.-P.Schuchmann)

WR: 185 nm;  $\phi_{H_2} = 0.4$

2 - 4 ml of a 5 M aqueous solution of pure ethanol (free of acetaldehyde and oxygen) are placed in a suprasil cell and purged with a gentle stream of oxygen-free argon while the sample is kept cold in order to minimize evaporation. A gas-tight cell assembly is necessary. At a 185 nm photon irradiance of about  $1 \cdot 10^{18} \text{ min}^{-1}$  per sample (cross section 2 - 4 cm<sup>2</sup>) enough hydrogen is produced after one minute to be easily measurable by gas chromatography. Hydrogen is stripped from the sample directly into the



gas chromatograph by the carrier gas. The product-collecting procedure is the same as the purging procedure. It is recommended to stir the solution during purging, irradiation, and stripping by a Teflon coated bar magnet. As usual, the GC determination requires calibration. The hydrogen quantum yield is dependent on the concentration of ethanol; there is total absorption at concentrations  $\geq 0.5$  M.

L05\*: *Uranyl oxalate photolysis.*

(submitted by D.F.Eaton)

WR: 200 - 500 nm;  $\phi = 0.5 \dots 0.6$

*Preparation of solutions:* 0.42478 g uranyl sulfate ( $\text{UO}_2\text{SO}_4$ ) and 0.67262 g disodium oxalate ( $\text{Na}_2\text{C}_2\text{O}_4$ , primary standard grade) are dissolved in 0.2 N  $\text{H}_2\text{SO}_4$  and diluted to 1.0 L in the dark. The solution is  $5.004 \cdot 10^{-3}$  M in oxalate dianion and  $1.011 \cdot 10^{-3}$  M in uranyl ion. Store in the dark. Ceric sulfate is prepared from ammonium hexanitratocerate according to the procedure of Smith and Fly (L05\*, Lit.14). Approximately 5.5 g  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$  are dissolved in 15 ml water and treated with 100 ml 15 N  $\text{NH}_4\text{OH}$ . The resulting precipitate is washed with six portions of water (25 ml each) until neutral to pH paper. The precipitate is then dissolved in hot 2 N sulfuric acid (125 ml) and washed into a 1.0 L volumetric flask. The solution is cooled and brought to approximately 950 ml. The cerium concentration is then determined spectrophotometrically by dilution of an aliquot and measurement of the absorbance at 320.0 nm versus 0.2 N  $\text{H}_2\text{SO}_4$  in a 1.0 cm cell. The molar absorption coefficient of Ce(IV) at this wavelength is  $5.41 \cdot 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ . The concentration of cerium is then adjusted until it is slightly greater than twice the (molar) concentration of oxalate in the actinometer solution. The use of commercial ceric sulfate is not recommended, since it is contaminated by ammonium nitrate which limits the stability of standardized cerium solutions.

*Procedure:* After irradiation of two 3.0 ml aliquots of actinometer solution, a 1.0 ml aliquot is pipetted into a 10.0 ml volumetric flask. 1.0 ml of the standard Ce(IV) solution and 1.0 ml 2 N  $\text{H}_2\text{SO}_4$  are added and the solution brought to the mark with water. Both irradiated samples and an unirradiated blank are treated in this way. The solutions are then incubated at 80 °C for 10 min and allowed to cool in the dark. The absorbances of the irradiated samples are determined at 320.0 nm versus a reference of the unirradiated blank.

*Calculations:* The measured radiant power,  $P$ , is given by:

$$P = \frac{V \cdot \Delta A \cdot 10^{-2}}{\text{CF} \cdot t \cdot \phi \cdot F \cdot \epsilon}$$

where  $\Delta A$  = measured absorbance at 320.0 nm vs. unirradiated blank (1.0 cm pathlength);  $V$  = volume of irradiated actinometer solution (ml);  $10^{-2}$  = volume of dilution in liters; CF = conversion factor to convert from moles cerium analyzed to moles oxalate photolyzed:  $2 \text{ Ce(IV)} + \text{C}_2\text{O}_4^{2-} \rightarrow 2 \text{ Ce(III)} + 2 \text{ CO}_2$ ;  $t$  = time of irradiation (min);  $\phi$  = quantum yield of oxalate loss;  $F$  = fraction of incident light absorbed by actinometer solution (0.999);  $\epsilon$  = molar absorption coefficient of cerium(IV) at 320.0 nm, ( $5.41 \cdot 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ).

The formula reduces to photon flux,  $\phi_p$ .

$$\phi_p = \frac{\Delta A}{t \cdot \phi} \cdot (2.773 \cdot 10^{-6}) [\text{Einstein} \cdot \text{min}^{-1}].$$

The quantum yields for photosensitized oxalate decomposition are:

$\lambda$ (nm)	$\phi$	$\lambda$ (nm)	$\phi$	$\lambda$ (nm)	$\phi$
208	0.48	254	0.60	335	0.53
237	0.58*	265	0.58	366	0.49
243	0.60*	278	0.58	405	0.56
245	0.61	302	0.57	436	0.58
248	0.61*	313	0.56		

The values marked by \* are interpolated from the other data (due to Leighton and Forbes, and Brackett and Forbes).

*Comments:* The procedure discussed here is an improved version of one due to Pitts. The sensitivity of the method is only half of that of the conventional ferrioxalate procedure (largely because the molar absorption coefficient of Ce(IV) at the analysis wavelength is only half that of the phenanthroline-Fe(II) complex used in the analysis of the ferrioxalate procedure). Also, the success of the method outlined here depends critically on the concentration of Ce(IV): if the concentration is less than sufficient to oxidize all the oxalate in the unirradiated blank, the results will be meaningless; if the concentration is significantly greater than twice the oxalate concentration of the blank then the optical densities measured for the blank and irradiated samples will be so large as to render differential absorption techniques invalid. Considerable care must be exercised when using the uranyl oxalate actinometer, and one should always check the integrity of freshly prepared solutions by comparing intensities measured by uranyl oxalate actinometry to those obtained using ferrioxalate actinometry at a wavelength at which quantum yields are known for both systems.

L07.1\*: *Azobenzene, or Actinochrome 2R (245/440)* photoisomerization (reusable).

(submitted by G.Gaiglitz)

WR: 230 - 460 nm;  $\phi_{\text{trans} \rightarrow \text{cis}} = 0.14$ ;  $\phi_{\text{cis} \rightarrow \text{trans}} = 0.48$ ;  $S = 130 \dots 3900 \text{ M}^{-1} \text{ cm}^{-1}$

*Wavelength range 340 - 270 nm:* The absorbance  $A$  of a  $6.4 \cdot 10^{-4} \text{ M}$  methanol solution of azobenzene, stored in the dark (see below), is measured at 358 nm. A value of about 1 is recommended. Each irradiation period should cause a change in  $A_{358}$  of about 0.02 and the final value should be kept between 0.85 and 0.9. Except during irradiation, only light  $\geq 500 \text{ nm}$  is to be admitted to the sample. For regeneration a sealed cell should be stored in the dark or irradiated at 254 nm.

*Wavelength range 266 - 245 nm:* The solution is preirradiated at 313 nm. The actinometry (as above) then starts at the photostationary state ( $A_{358} \approx 0.30$ ) and the final  $A$  value should be below 0.45.

*Wavelength range 350 - 440 nm:* There is *no total absorption* in this range. Irradiation and observation wavelengths are chosen the same. For the range 375 - 440 nm, a preirradiated solution is used and the procedure starts at the photostationary state. Efficient stirring of the solution is essential in all cases.

*Evaluation:* For the range 340 - 245 nm the following formula is used, where  $\Delta A_{358}$  is the change in absorbance at 358 nm and  $\Delta t$  is the irradiation time in seconds. The factors  $F$  can be taken from the table below. Thus, the photon flux,  $E_p$  is given by

$$E_p = F_{\lambda} \cdot \Delta A_{358} / \Delta t \quad [\text{Einstein} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}]$$

$\lambda_{\text{irrad}}$ (nm)	F-value
245	$2.30 \cdot 10^{-6}$
280	$4.60 \cdot 10^{-6}$
302	$4.63 \cdot 10^{-6}$
313	$5.30 \cdot 10^{-6}$
334	$3.60 \cdot 10^{-6}$

In case the photon flow ( $\text{Einstein} \cdot \text{s}^{-1}$ ) is desired, the ratios of the irradiated volumina as well as of the front areas of actinometric and reaction cell have to be taken into consideration.

For the range 350 - 440 nm graphical or arithmetical kinetic evaluation methods have to be used (cf. Gaiglitz 1976, 1981 and other references cited). The latter is done with the aid of a computer. The graphical method uses the expression

$$E_p = \tau / Q \cdot t$$

where  $Q$  is the *pseudo total quantum yield*,  $(\phi_{\text{trans} \rightarrow \text{cis}} \cdot \epsilon_{\text{trans}} + \phi_{\text{cis} \rightarrow \text{trans}} \cdot \epsilon_{\text{cis}}) / 1000$ , with  $\epsilon$  at the irradiation wavelength.  $Q$  values are independent of time and concentration. They are listed in the literature, but should be determined for each lamp-filter combination at the irradiation wavelengths.  $\tau$  is taken from calibration graphs of the time-dependent absorbance *versus*  $\tau$ .

L08\*: 8H.16H-4b.12b-Epidioxybenzo[*a*,*j*]perylene-8.16-dione or heterocoerdianthrone endoperoxide.

or Actinochrome 1R (248/334) photoreversible photodissociation (reusable).

(submitted by R.Schmidt)

WR: 248 - 334 nm;  $\phi = 0.27$ ; S = 4630 - 7770 M<sup>-1</sup>cm<sup>-1</sup>

2.5 ml of an air-saturated stock solution of heterocoerdianthrone (2 mM in CH<sub>2</sub>Cl<sub>2</sub> Uvasol Merck) are put in a rectangular cuvette ( $l = 1$  cm) and provided with a small Teflon coated magnetic stirrer. The cuvette is closed tightly with a Teflon stopper. The accurate volume  $V$  in L is evaluated after every measurement by differential weighing.  $\rho^{20} = 1.327$  kg/L. Then the solution is placed in a box, which has a cut-off filter (cut-off between 420 and 480 nm, e.g. Schott GG 455) as a window, and is exposed to sunlight until complete decolouration occurs. The colourless solution is then stored in the dark at room temperature. Before irradiation the absorbance at 572 nm,  $A_{572}$ , is determined. In the case of irradiation at 334 nm,  $A_{334}$  is also measured. Then the cuvette is exposed to the desired radiation under continuous stirring for a time interval  $\Delta t$  until a maximum value of  $A_{572} \approx 0.3$  is reached.  $A_{572}$  is determined again and the total number of photons,  $\phi_{P\lambda} \cdot \Delta t$ , or the spectral photon flow,  $\phi_{P\lambda}$ , entering the cuvette, are calculated by

$$\phi_{P\lambda} \cdot \Delta t = \frac{\Delta A_{572} \cdot V}{\epsilon_{572} \cdot \phi_{\lambda} \cdot A_{\lambda} \cdot l} \quad [\text{mole photons}]$$

where  $\epsilon_{572}$  is the molar absorption coefficient of the product heterocoerdianthrone at 572 nm, and  $A_{\lambda}$  is the mean absorption at irradiation wavelength  $\lambda$  during time interval  $\Delta t$ , equalling 1 (total absorption) except at 334 nm; here,  $A_{\lambda} = 1 \cdot 10^{-A_{334}}$ .  $\epsilon_{572} \cdot \phi = 7770 \pm 200$  M<sup>-1</sup>cm<sup>-1</sup> for 253 - 302 nm, and 7050, 6740, and 4630 for 248, 313, and 334 nm, respectively, at  $23 \pm 2$  °C. After decolouration as described the solution is ready for reuse. About 100 cycles are possible without loss in accuracy.

L14\*: Potassium tris(oxalato)ferrate(III), or potassium iron(III) oxalate, K<sub>3</sub>[Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>] · 3H<sub>2</sub>O, photoreduction (Hatchard-Parker actinometer).

(Submitted by G.Gauglitz and S.Hubig)

WR: 250 - 500 nm;  $\phi = 1.25 \dots 0.9$ ; S = 13900 ... 9990 M<sup>-1</sup>cm<sup>-1</sup>

All is done under red safe-light. Green crystals of K<sub>3</sub>Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub> · 3H<sub>2</sub>O are prepared by mixing 3 vol. 1.5 M K<sub>2</sub>C<sub>2</sub>O<sub>4</sub> with 1 vol. 1 M FeCl<sub>3</sub> solution, recrystallized three times from warm water, dried at 45 °C and kept in the dark. 0.006, 0.012, or 0.15 M ( $\geq 405$  nm) solutions can be used for actinometry. A 0.006 M solution is prepared by dissolving 2.947 g of the crystals in 100 ml 1 N H<sub>2</sub>SO<sub>4</sub> and dilution with distilled water to 1 L. Take an absorption spectrum of the solution and look for total absorption at the desired irradiation wavelength and optical pathlength. E.g., 3 ml ( $V_1$ ) solution are irradiated under efficient stirring. 1 ml ( $V_2$ ) of the irradiated solution is given into a 10 ml ( $V_3$ ) volumetric flask containing a mixture of 4 ml 0.1 % 1.10-phenanthroline solution (store in the dark!) and 0.5 ml buffer (stock solution: 82 g NaOAc, 10 ml conc. H<sub>2</sub>SO<sub>4</sub>, diluted to 1 L with distilled water) which is then diluted to the mark with distilled water. It is essential that the irradiation time measurement (electronic shutter) as well as the pipetting is done very precisely. A reference is prepared in the same way except that it has not been irradiated. Both solutions are kept in the dark (about an hour) until full colour development is achieved, and the absorbance of the first minus that of the second sample is measured at 510 nm (1 cm pathlength,  $\epsilon = 11100$  dm<sup>3</sup> mol<sup>-1</sup>cm<sup>-1</sup>).  $A_{510}$  should be kept within the range 0.4 - 1.8. Conversion should not exceed 5%. The evaluation uses for the photon flow,  $\phi_p$ ,

$$\phi_p = \frac{\Delta A \cdot V_1 \cdot 10^{-3} \cdot V_3}{\phi_{\lambda} \cdot \epsilon_{510} \cdot V_2 \cdot l} \quad [\text{Einstein} \cdot \text{s}^{-1}]$$

where  $l$  is in seconds.  $\phi_{\lambda}$  at room temperature equals 1.20 - 1.26 (0.006 M) for the wavelength range 254 - 366 nm, 1.14 at 405 nm, 1.11 (0.006 M) at 436 nm, 1.12 (0.01 M) at 458 nm, 1.08 (0.08 M)

at 488 nm, 0.93 (0.20 M) at 514 nm. There is no total absorption above 450 nm even in 0.15 M solution. In this case the value for the photon flow must be divided by the fraction of absorbed light at the irradiation wavelength,  $(1 \cdot 10^{-A})$ .

The procedure described in Murov's Handbook of Photochemistry (L14\*, ref.12) is also recommended, but the precautions listed above should be obeyed. Note that due to its high S-value L14\* is not really an integrative system, i.e. periodical fluctuations in light intensity may not be "seen" during the rather short irradiation periods.

L28.1\*: *Fulgide* photoisomerization (photoreversible).

(E)-/l-(2.5-dimethyl-3-furyl)ethylidene]isopropylidene)succinic anhydride, or *Aberchrome 540*  $\leftrightarrow$  7.7a-dihydro-2.4.7.7.7a-pentamethylbenzo[b]furan -5.6-dicarboxylic anhydride, or *Aberchrome 540P*.

(submitted by H.G.Heller)

WR: 310 - 375 nm;  $\phi = 0.2$ ; S = 1640 M<sup>-1</sup>cm<sup>-1</sup>

A ca.  $5 \cdot 10^{-3}$  molar solution is prepared by dissolving 25 mg *Aberchrome 540* in 20 ml toluene. An accurately measured volume (e.g. 3 ml) of this solution is pipetted into a cuvette and the absorbance (if any) at 494 nm is noted. The stirred solution is then irradiated for a known period. A magnetic stirrer is recommended. Care should be taken to prevent the magnetic follower from entering the light beam. It is essential that the solution absorbs all the uv light falling upon it. After irradiation in a 1 cm cell and mixing, the absorbance at 494 nm is measured. The increase in absorbance ( $\Delta A_{494}$ ) enables the photon flow to be calculated from

$$\phi_p = \frac{\Delta A \cdot V \cdot N_A}{\phi \cdot \epsilon_{494} \cdot t} \quad [\text{photons} \cdot \text{s}^{-1}]$$

where  $V$  = irradiated volume in dm<sup>3</sup>,  $N_A$  = Avogadro's number,  $\phi = 0.20$  from 310 - 375 nm,  $\epsilon_{494} = 8200 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ,  $t$  = time in seconds. The coloured form is reversed with white light and the solution is ready for reuse.

L39\*: 7.16-Diphenyldibenzo[a.o]perylene, or *meso-diphenylhelianthrene*, or *Actinochrome N (475/610)* self-sensitized photooxygenation.

(submitted by G.Gauglitz and R.Schmidt)

WR: 475 - 610 nm;  $\phi = 0.224$ ; S = 4080 M<sup>-1</sup>cm<sup>-1</sup>

A  $10^{-3}$  M solution in air-saturated toluene is used for the ranges 475 - 520 nm and 580 - 610 nm while a  $5 \cdot 10^{-4}$  M solution is used for the range 520 - 580 nm. Total absorption, vigorous shaking in order to achieve air saturation before irradiation, as well as sufficient stirring during irradiation are essential. Fresh solutions are recommended (storage at -15 °C in the dark for no longer than three months). Only red light  $\geq 640$  nm must be admitted during preparation of the solution and actinometry. Absorbance at 429 nm before and after irradiation in a 1 cm cuvette should be about 0.7 and not much higher than 1.5, respectively. The evaluation follows

$$\phi_p = \frac{\Delta A_{429} \cdot V}{\Delta \epsilon_{429} \cdot \phi \cdot \Delta t \cdot l} \quad [\text{Einstein} \cdot \text{s}^{-1}]$$

where  $\phi_p$  = quantum flow entering the cuvette in Einstein  $\cdot$  s<sup>-1</sup>,  $\Delta A_{429}$  = difference in absorbance at 429 nm before and after irradiation,  $\Delta t$  = irradiation time in seconds,  $V$  = volume of the solution in L (density = 0.867 g  $\cdot$  cm<sup>-3</sup>),  $l$  = optical pathlength,  $\Delta \epsilon_{429} \cdot \phi = 4080 \pm 90 \text{ M}^{-1} \text{ cm}^{-1}$  at sea level, 4030 at 1000 m altitude (oxygen concentration depends on partial pressure of O<sub>2</sub>),  $\phi = 0.224 \pm 0.004$  independent of wavelength. The system may be used as polychromatic quantum counter.

Note: *Aberchromes* (L28.1, L28.2) and *Actinochromes* (L07.1, L08, L39) as well as the *Quantacount* instrument (E06) are commercially available.

## Appendix

Additional references concerning calculation of quantum yields

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### III. GENERAL CONSIDERATIONS ON CHEMICAL ACTINOMETRY

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#### III.1 Pros and cons of chemical actinometry

According to the "Glossary of Terms Used in Photochemistry", an actinometer is a chemical system or a physical device by which the number of photons in a beam can be determined integrally or per unit time<sup>1)</sup>. In a chemical actinometer (CA) photochemical conversion is directly related to the number of photons absorbed. Chemical actinometry is employed in photochemistry as a relatively simple and accurate method for radiation measurement since about 50 years<sup>2)</sup>.

Due to the recent progress in the development of radiation detectors, semiconductors and electronic equipment, physical devices furnished with a direct readout become more and more popular among photochemists for the measurement of radiation. For the case of simple irradiation geometries physical devices are often preferred to CAs because of their easy, fast and precise performance.

However, these outstanding properties are inherent in only a small number of electrically calibrated radiometers (ECRs) available in a few highly equipped laboratories. ECRs are special thermopiles<sup>3)</sup> or piezoelectric radiometers<sup>4,5)</sup>, which can be calibrated in an absolute manner by electrical substitution without the need of any standard. The majority of physical detectors, like usual thermopiles, piezoelectric joulemeters or photodiodes are only secondary standards, the response of which can be subject to changes.

The sensitivity of a joulemeter may decrease with use due to surface damage by high power radiation. The same is valid for thermopiles. The spectral sensitivity of the widespread silicium photodiodes is even altered without use, just by aging. The extent of this effect depends on the wavelength range in which the detector will be used. An 18% decrease in sensitivity at 300 nm in one year was reported to be a typical value<sup>6)</sup>. Visually unnoticeable damage of photodiodes occurs during exposure to high irradiation levels (generally more than 10 mW/cm<sup>2</sup> for silicium photodiodes in continuous wave experiments) resulting in an irreversible decrease of sensitivity and severe inhomogeneities in the surface. Consequently, occasional recalibration of radiation detectors against a standard is strongly recommended.

In contrast to the physical detectors, well established CAs lead to accurate absolute radiation measurements, if employed according to the recommended procedures. These CAs have been proven reproducible and do not demand any recalibration.

### III.2 Quality marks of a chemical actinometer

An established CA should meet the following requirements:

The photochemical system should be simple and well studied. The photoreaction must be reproducible under well defined and easily controllable experimental conditions. Quantum yields should be accurately known for a large number of wavelengths. A wide useful spectral range and wavelength-independent quantum yields are desired.

The chemical components should be thermally stable to exclude complications due to dark reactions.

The analytical methods should be simple. Direct spectrophotometric analysis is preferred.

The system should display large sensitivity.

The handling of the photochemical system and the evaluation of the number of photons absorbed should be simple and straightforward.

The actinometric material should be easy to synthesize and purify. Preferably it should be commercially available.

The CAs offered in the present list fulfill the requirements mentioned above in various degrees. Each system suffers also from disadvantages and a careful selection among the CAs is appropriate, depending on the intended photochemical experiment.

### III.3. Fields of application of chemical actinometry

It is important to mention that chemical actinometry covers only the  $130 \text{ nm} \leq \lambda \leq 750 \text{ nm}$  wavelength range.

In photochemical experiments involving a complex irradiation geometry (*e.g.* photoreactors of the merry-go-round type) CAs serve best for the purpose of absolute radiation measurement and are unrivalled by physical devices. In any case, in photobiological and photochemical laboratories with less sophisticated equipment but where workers are experienced in chemical techniques, chemical actinometry is the standard procedure for radiation measurement.

Photochemists using physical equipment for radiation measurements need standards for the occasional recalibration of their detectors. CAs are the first choice for this procedure. For detectors with wavelength-independent response like thermopiles and joulemeters the calibration by CAs is particularly easy since calibration at only one wavelength is sufficient.

Measurements of laser pulse energies can conveniently be done by joulemeters. At high laser powers most CAs will probably lose accuracy and sensitivity due to multiple photon processes occurring at high photon densities. However, if linearity of the joulemeter readout is guaranteed, a periodically repeated calibration by CAs at reduced laser power is an easy way of controlling the accuracy of the power meter. For this purpose those CAs can be used as standards which have been investigated especially at high photon flows using laser excitation <sup>7)</sup>.

### III.4. Potential errors in chemical actinometry

The detailed description of the chemical system, the limitations and the possible sources of errors for each CA should be explicated in every publication. In the following only general aspects are discussed.

#### III.4.1. Refractive index

A CA yields the radiant power  $P_0$  entering the sample cell. For the determination of the radiant power of the irradiation beam  $P_B$ , a correction for the reflection losses  $R$  should be performed:  $P_B = P_0 / (1 - R)$ .

Assuming that the incident radiation strikes the sample surface at a right angle, the reflection loss at the boundary between two materials of refractive indices  $n_1$  and  $n_2$  can be calculated through the Fresnel law:

$$R = \left( \frac{n_1 - n_2}{n_1 + n_2} \right)^2$$

While entering a quartz sample cell the radiation passes the boundaries air/quartz and quartz/solution suffering reflections at each boundary. Approximately,  $R$  is the sum of the reflection losses at both boundaries whereby the second contribution is smaller than the first. Consequently, only the wavelength dependence of the refractive index of quartz determines the wavelength dependence of  $R$ . At 250 nm  $(1 - R)$  amounts for 2,2,2-trifluoroethanol ( $n = 1.29$ ) to 0.955, for toluene ( $n = 1.49$ ) to 0.959 and for  $\text{CS}_2$  ( $n = 1.63$ ) to 0.956. At 400 nm and 800 nm these values are higher by 0.005 and 0.007, respectively.

Thus, a mean value of  $1 - R = 0.96$  can be applied for the calculation of  $I'_B$  introducing an additional error of 0.5% at most. From the above estimation it follows that when comparing a photochemical system with a CA in different solvents an error of at most 0.4% will be introduced should the correction be omitted.

#### III.4.2. Temperature

The influence of temperature variation has been investigated only for a small number of CAs. Temperature may influence an actinometric system through the temperature dependency of the quantum yield, of the density of solvents, and of possible competing dark reactions.

Photochemical quantum yields usually do not depend on temperature or only do so slightly. The temperature induced changes in density lead to a corresponding change in concentration and consequently to an apparent change in chemical conversion. This effect can easily be cancelled out by measuring the conversion at the temperature of CA calibration or by calculation using tabulated density values. However, a large variation of the influence of eventual dark reactions may take place with changing temperature. Therefore, actinometric measurements at temperatures different from the recommended range should be avoided.

#### III.4.3. Absorption by photoproducts

Ideally, in the wavelength range of a particular CA photoproducts should not absorb. In this case a high dynamic range of the actinometric measurement (photon dose, photon flow) can be expected. If photoproducts do absorb an inner filter will develop, this leading to a reduced conversion range. This difficulty should be considered with great care and extrapolation of the data to infinitely low conversion is recommended.

#### III.4.4. Degree of absorption by the CA

Some CAs are designed for incomplete absorption of the actinic light. This arrangement is particularly advantageous for the case of high photon flows, since the irradiated volume can be large, thus avoiding inhomogeneity problems during photoreaction. Since in this case additional errors are introduced by light reflections and the necessary measurements of transmission during irradiation, these systems are unfavourable for the measurement of low levels of radiation.

CAs exhibiting complete absorption of the radiation allow convenient measurement and easy evaluation and are thus preferred. At high absorbance the penetration depth of irradiation is small. Therefore, at the high photon flows met *e.g.*, in laser beams, severe inhomogeneity problems arise, which cannot be overcome even by effective stirring. This possible source of error is insufficiently discussed in the literature. Since at high absorbances the photoreaction occurs only in a very small reaction volume multiple photonic processes can be expected at high photon flows and have already been reported<sup>7)</sup>.

#### III.4.5. Polychromatic quantum counters

CAs with wavelength-independent quantum yields allow polychromatic quantum counting in the specified wavelength range provided complete absorption is maintained. In this case, each photon entering the actinometric solution causes chemical conversion with the same probability regardless of its energy. Polychromatic quantum counters are particularly accurate due to their wavelength independent conversion yield.

**References to section III**

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