The Photolysis of Simple Inorganic Anions in Solution

By Malcolm F. Fox
SCHOOL OF CHEMISTRY,* CITY OF LEICESTER POLYTECHNIC,
LEICESTER, LE1 9BH

1 Introduction

Ultraviolet irradiation of deaerated aqueous solutions of potassium iodide causes decomposition to hydrogen and iodine, the hydrogen evolved originating from the water of the solution. The overall process is part of a general two-electron equivalent exchange reaction,

$$2X_{aq}^- + 2H_{aq}^+ \rightarrow H_2 + X_2 \qquad (1)$$

where X_{aq}^- may be either charged or neutral. In this review attention is focused upon the case where X^- is a simple anion, *e.g.* halide, pseudo-halide or oxy-anion of Groups 4—7. A clear distinction is drawn between this case and the photolysis of co-ordination compounds, the latter being based upon ligand field absorption bands.[1]

The photolysis of simple anions prior to 1953 has been reviewed and only essential points are recalled here.[2] Iodide is a good example because its photochemistry and spectroscopy have been studied extensively. The initial step in the irradiation of iodide solutions,[3] (1), was thought to be the ejection of an electron from the anion into the solution to become a 'free solution electron'.[4] The energy of the spectroscopic transition, E_{max}, is given by:

$$E_{max} = E_X + \Delta H_s^{\theta -} - \Delta H_s^{\theta} + \chi - B \qquad (2)$$

where $\Delta H_s^{\theta -}$ and ΔH_s^{θ} are the heats of solvation of the ion and radical respectively. χ represents the Franck–Condon strain; the solvent molecules around the radical are in the same position as previously around the parent anion, the position of these dipoles being unaltered during the transition. The electron was assumed to be completely photoionised and ejected into the solution where it was bound by its solvation energy, B, which arises from the electric polarisation of surrounding water molecules. E_X is the electron affinity of the radical produced. The value of χ can be estimated but B could not. However, experimental evidence did not support the existence of 'free solution electrons' and in a further reaction

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*Present address: Pioneering Research Laboratories, U.S. Army Natick Laboratories, Natick, Massachusetts, 01760, U.S.A.

[1] A. W. Adamson, *et al.*, *Chem. Rev.*, 1969, **69**,

[2] L. E. Orgel, *Quart. Rev.*, 1954, **8**, 422.

[3] E. Warburg and W. Rump, *Zeits. f. Physik*, 1928, **47**, 305.

[4] J. Franck and G. Scheibe, *Zeits. f. physik. Chemie.*, 1928, **A139**, 22.

scheme[5] the electron was transferred to a water molecule, in some way intimately associated with the ion, the water molecule instantly dissociating:

$$I^-.(H_2O) \xrightarrow{h\bar{\nu}} I^\cdot + H^\cdot + OH^- \qquad (3)$$

The product quantum yield, ϕ, is defined as the number of molecules of a product formed per quantum of incident radiation absorbed by the iodide ion. An important feature of anion photolysis is the strong pH-dependence of this quantum yield,[3,6,7] and mechanism (3) cannot account for this effect. The initial transition was then formulated, (4), as the transfer of an electron from the hydrated anion to one specific water molecule, followed by one of two processes, either thermal deactivation returning the electron to the radical, (5), or further migration and reaction with a proton to give a hydrogen atom, (6).

$$I^-(H_2O) \xrightarrow{h\bar{\nu}} I^\cdot(H_2O)^- \qquad (4)$$

$$I^\cdot(H_2O) \rightarrow I^-(H_2O) \qquad (5)$$

$$(H_2O)^- + H^+ \rightarrow H_2O + H^\cdot \qquad (6)$$

The radicals dimerise to give molecular products. This scheme fitted the limited quantitative results available at the time and excludes a dependence of ϕ upon iodide concentration. However, the quantum yield depends upon both iodide and hydrogen ion concentrations[8] and a mechanism to explain these effects, (7) and (8), envisaged the formation of hydrogen and iodine atoms formed from (3) together with a new species, H_2^+.

$$H^\cdot + H^+ \rightarrow H_2^+ \qquad (7)$$

$$H_2^+ + I^- \rightarrow I^\cdot + H_2 \qquad (8)$$

The experimental evidence for choosing between these mechanisms is less than compelling. Many difficulties are experienced in interpreting the photolysis of the simple anions; theoretical models are required for the initial spectroscopic transition, together with the mechanism of subsequent formation of reactive species (indeed, which reactive species!) and a detailed physical model of ionic environment.

2 Experimental Techniques

A. Steady State.—The basic experimental procedures of photochemistry are well described by Pitts and Calvert.[9] The irradiation sources in anion photolysis are usually element resonance lamps; low and medium pressure mercury and

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[5] J. Franck and F. Haber, *Sitz. ber. Preuss. Akad. Wiss.*, 1931, 250.
[6] A. Farkas and L. Farkas, *Trans. Faraday Soc.*, 1938, **34**, 1113.
[7] A. Farkas and L. Farkas, *Trans. Faraday Soc.*, 1938, **34**, 1120.
[8] T. Rigg and J. J. Weiss, *J. Chem. Soc.*, 1952, 4198.
[9] J. N. Pitts and J. G. Calvert, 'Photochemistry', Wiley, New York, 1966.

cadmium–brass lamps with high emission intensities concentrated into relatively narrow bandwidths at 254 and 185 nm (Hg) and 229 nm (Cd–brass) are the most common. These lamps are particularly convenient since most anions of interest have broad absorption bands in the region covered by these emission lines.

Resonance lamps have both short and long term stability problems which affect the accuracy of quantum yield values. The most serious short term instability arises from variation in the temperature of the lamp envelope, and thermostatting to within 1 K is necessary to achieve less than 1 % variation.[10] The most stable wall temperature is in the region of 310 K, depending slightly upon current. The intensity dependences at 254 and 185 nm of a low pressure mercury resonance lamp on rare gas pressure, positive column input power and surface temperature are complicated. Direct current operation of a lamp leads to migration of the plasma (cataphoresis) and is thus inherently less stable than a.c. operation, which is to be preferred.[11,12] Only when a reactive intermediate has a half-life comparable to the emission half-cycle time of the lamp should d.c. operation be considered. The long-term stability of a lamp is determined by solarisation of the silica tube wall. Alternate or consecutive actinometry with sample irradiation is essential to obtain accurate quantum yields.

Hydrogen peroxide,[13] uranyl oxalate,[9] and ferrioxalate[9] systems have well-established quantum yields and are suitable for actinometry at 254 nm. The quantum yield of the hydrogen peroxide actinometer is very temperature dependent and thermostatting to within 0·2 K is necessary. The spectral response of the actinometer and sample are generally different, and the lamp source will have other emission lines which will affect the first, but not the second, and a correction is necessary.[14] The 229 nm radiation intensity can be measured using the ferrioxalate or uranyl oxalate actinometers.[15] Because of high absorbance values of the irradiated sample solutions the system must be stirred otherwise reaction products build up in the first millimetre of solution.[14]

Quantum yield values for 185 nm actinometry have been the subject of controversy. A long-established value of 0·8 for the quantum yield of hydrogen production from 5M aqueous ethanol[16] (specific for 185 nm radiation) was based on a chain of three unsatisfactory determinations. The corresponding quantum yields for the photolysis of several anions were greater than unity and this was unacceptable. A new actinometer, aqueous nitrous oxide, has a quantum yield of unity which is relatively unaffected by 254 nm radiation.[17]

The quantum yield of hydrogen from 5M aqueous ethanol related to the nitrous oxide actinometer is 0·40. This is the most convenient actinometer for 185 nm

[10] T. B. Read, *J. Appl. Phys.*, 1964, **15**, 837.
[11] M. A. Cayless, Proc. Fifth Int. Conf. Ionization Phenomena in Gases, Munich, 1961, 261.
[12] T. B. Read, *J. Sci. Instr.*, 1967, **44**, 273.
[13] J. H. Baxendale and J. A. Wilson, *Trans. Faraday Soc.*, 1957, **53**, 344.
[14] F. S. Dainton and S. R. Logan, *Proc. Roy. Soc.*, 1965, **287A**, 281.
[15] M. Ottolenghi, *J. Amer. Chem. Soc.*, 1963, **85**, 3557.
[16] L. Farkas and Y. Hirschberg, *J. Amer. Chem. Soc.*, 1937, **59**, 2450.
[17] F. S. Dainton and P. Fowles, *Proc. Roy. Soc.*, 1965, **287A**, 295.

radiation and the value of 0·40 for the quantum yield is well established.[18,19] A reinvestigation gave 0·63 for the hydrogen quantum yield from 5M ethanol,[20] but if the quantum yield for ammonia photolysis is taken as 0·14 instead of 0·25,[17] a value of 0·35 is obtained. All quantum yields are referred to 0·40 for 5M ethanol and this reduces the apparent discrepancies between published values.

B. Flash Photolysis.—The technique of flash photolysis[21] has been successfully extended to the far-u.v. region for solutions.[22] An interesting combination of steady state and flash photolysis techniques measures the absorption spectra of transient radicals.[23] The u.v. exciting radiation absorbed by the anion is modulated at 100 Hz, and if the half-lives of the intermediates formed by the exciting radiation are very much less than 10^{-2}s, then the concentration of these species will closely follow the light source variation. If stable continuum radiation is passed through the solution, the transmitted light will contain a 100 Hz component at frequencies where the intermediate absorbs. Essentially, the 100 Hz component is transferred from the exciting light to the analysing light with a spectral response characteristic of the absorption spectrum of the intermediate. This apparatus enables concentrations of strongly absorbing species such as solvated electrons to be detected down to 5×10^{-12}M.

3 The Theory of C.T.T.S. Spectra

The u.v. absorption spectra of simple inorganic anions show intense ($f \sim 0{\cdot}1$), broad, structureless bands which are characterised as charge-transfer-to-solvent, (c.t.t.s.) (Figure 1).[24] The absorption spectra of polyatomican ions show internal, in addition to c.t.t.s., transitions. The solvent plays an important part in defining the excited state of a c.t.t.s. transition and theoretical models are more manageable when the Franck–Condon principle is extended to include the ion and the solvent molecules immediately around it. These dipolar molecules are oriented and relatively immobilised by interaction with the intense potential field of the ion and correspond to zone A of the Frank–Wen model of ion solvation.[25] The difficulty of calculating B, the excited state electron binding energy of equation (2) was overcome by Franck and Platzman who used a spherically symmetrical excited state centred on the parent anion site.[26] B is then the sum of two contributions, E_e and S_e, where E_e arises from the polarisation of the oriented water molecules around the ion giving a coulomb field with effective charge of $Z_{eff} = 1/D_{op} - 1/D_s$. The calculated mean radius, r_e, of the excited state electron shows

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[18] J. Barrett, M. F. Fox, and A. L. Mansell, *J. Chem. Soc.* (*A*), 1966, 489.

[19] N. Getoff, *Monatsh.*, 1968, **99**, 136.

[20] A. Bernas, M. Bonard, and D. Saghattchian, *J. Chim. Phys.*, 1965, 1418.

[21] G. Porter, 'Technique of Organic Chemistry,' 2nd. Edn. **8**, Pt. 2. 1055. Interscience, New York, 1963.

[22] J. R. Huber and E. M. Hayon, *J. Phys. Chem.*, 1968, **72**, 3820; (*a*) E. Hayon, private communication.

[23] R. Devonshire and J. J. Weiss, *J. Phys. Chem.*, 1968, **72**, 3815.

[24] M. J. Blandamer and M. F. Fox, *Chem. Revs.*, 1970, **70**, 59.

[25] H. S. Frank and W-Y Wen, *Discuss. Faraday Soc.*, 1957, **24**, 133.

[26] J. Franck and R. L. Platzman, *Z. Physik.*, 1954, **138**, 411.

extensive delocalisation into the solvent and justifies the use of bulk solvent properties. S_e arises from the electronic polarisation of the solvent by the excited state electron. For aqueous solutions at 298 K and a hydrogen-like 2*s* orbital, B (approx. 146 kJ mol^{-1}) and r_e (580 pm) are effectively independent of anion. The solvation enthalpies of the anions, $\Delta H_s^{\theta-}$, and of the radicals, ΔH_s^{θ}, were calculated. Equation (2) gives good agreement between predicted and observed E_{max} for the halide ions.[26]

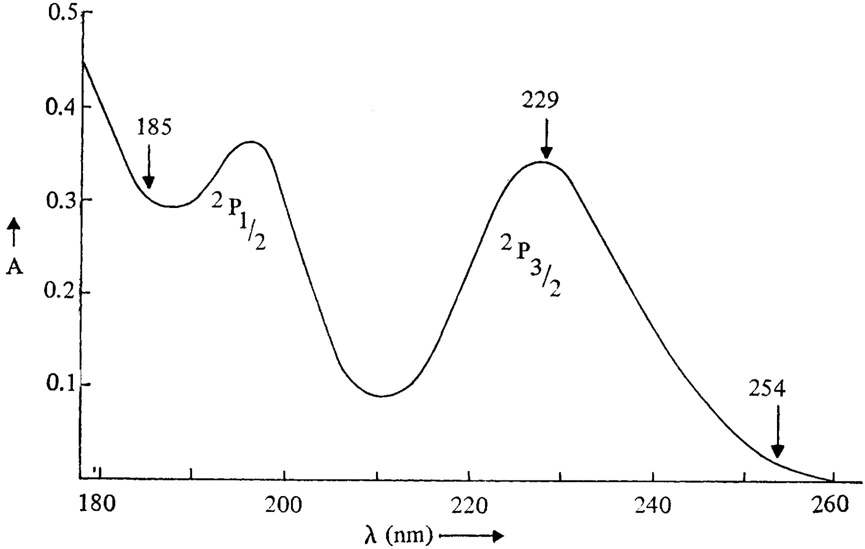

Figure 1 *A typical c.t.t.s. absorption spectrum*: *iodide in water at* 274 K, *showing irradiation frequencies* (M. F. Fox, unpublished work)

Whilst this theory predicts E_{max} well, it does not readily predict the effect on E_{max} of such changes as solvent, added co-solvent, added electrolyte, pressure, and temperature.[27,28] The temperature coefficient, dE_{max}/dT, is an order of magnitude greater, and opposite in sign, to that predicted by the Franck–Platzman theory. A new theory was proposed using a model of an electron in a potential well of variable radius.[27] E_{max} depends upon the ionisation potential and the excited state potential well radius, (9).

$$E_{max} = I_{X^-} + h^2/8mr_c^2 \qquad (9)$$

This radius parameter does not correspond to any known property of the anion, being the distance between the centre of the ion and the inner edge of the potential well. This theory uses a 'confined' model for the excited state. Changes

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[27] M. Smith and M. C. R. Symons, *Discuss. Faraday Soc.*, 1957, **24**, 206.

[28] G. Stein and A. Treinin, *Trans. Faraday Soc.*, 1959, **55**, 1087, 1091; *ibid*, 1960, **56**, 1393.

in $E_{\max}$ arise from changes in r_c, *i.e.* the excited state. This theory was primarily developed and tested for the halide ions in a variety of solvents.

The Franck–Platzman model was combined with the variable radius parameter in the diffuse model which was able to predict both absolute values of $E_{\max}$ and environmental effects.[28] The radius parameter, r_d, is defined as the spectroscopically effective cavity radius of the anion in solution and is close to $1{\cdot}25\ r_i$, where r_i is the crystallographic radius of the anion. The radius r_d characterises the ground state and corresponds closely to ionic radii predicted from analyses of partial molar volume and electrostriction effects. The theory was generalised by Treinin to include polyatomic multivalent anions,[29] where the transition corresponds to the process $X^{z}_{aq} \xrightarrow{h\nu} [X^{(z-1)} + e^{-}]_{aq}$, and for divalent aqueous anion at 298 K:

$$E_{\max} = I_{X^-} + 1945/r_i - 121{\cdot}4/r_i^3 - 146{\cdot}4 \qquad (10)$$

where I_{X^-} is now the vertical ionisation potential of the anion. Application of the diffuse model leads to negative ionisation potentials for some anions and, further, when applied to pseudohalides,[30] gives values which are markedly different from those derived from other techniques such as the magnetron method.[31] Jorgenson[32] has proposed a Rydberg transition model but this has not been developed in detail.

A semi-empirical approach to 12 c.t.t.s. transitions of 9 anions proposes a simple shell-type acceptor orbital for the excited state centred on the parent anion site and bounded by the solvent molecules.[33] The anion is regarded as a donor and this, with the acceptor orbital, forms a donor–acceptor complex. Applying Mulliken theory for donor–acceptor complexes leads to the transition energy $E_{\max}$, (11).

$$E_{\max} = I_{X^-} - E_{H_2O} + \frac{\sigma^2}{I_{X^-} - E_{H_2O}}(1/2r_i) \qquad (11)$$

E_{H_2O} is the electron affinity of a group of solvent molecules (not that for an isolated molecule), σ is the overlap term which depends on the overlap integral and polarisation terms and r_i is the crystallographic radius of the ion. Good agreement is observed between predicted and observed transition energy values for this set of anions in both methyl cyanide and aqueous solution.

The underlying unity of these theories lies in the strong spectroscopic evidence for an excited state which is either completely or predominantly defined by the solvent and centred on the parent anion site. Addition of a wide range of electrolytes and non-electrolytes, including those used as scavengers in anion photolysis, shows that even at very high concentrations the nature of the transition is un-

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[29] A. Treinin, *J. Phys. Chem.*, 1963, **67**, 893-897.

[30] E. Gusarsky and A. Treinin, *J. Phys. Chem.*, 1965, **69**, 2176.

[31] F. M. Page, 'Electron Affinities of Inorganic Radicals,' AD 434912; *Chem. Abs.*, 1963, **63**, 15662*c*.

[32] C. K. Jorgenson, *Adv. Chem. Phys.*, 1963, **5**, 33.

[33] M. F. Fox and T. F. Hunter, *Nature*, 1969, **223**, 177.

altered. The added solutes act indirectly through solvent–solvent interactions to stabilise/destabilise the ground or excited states. The solutes do not interact directly with the excited state.

4 Photochemistry

The photochemistry of simple anions is summarised in the Table. The chemistry of the c.t.t.s. excited state controls the photochemistry of the halides and those polyatomic anions where no bond fission occurs, *e.g.* SO_4^{2-}. Some anions have both c.t.t.s. and internal transitions, *e.g.* $S_2O_3^{2-}$, and others only the latter, *e.g.* NO_3^-. The diversity of photolysis products from the anions (see Table) can be examined in terms of the initial photolytic process and then the scavenging kinetics which lead to final products.

Table

Anion	*Irradiation Source (nm)*	*Scavenger System*	*Product*	*Reference*
Cl^-	185	N_2O	ϕ_e 0·43(288)	*a*
	185	H^+/alc.	ϕ_e 0·43(288)	*a*
	185	H^+/alc.	ϕ_e 0·49(308)	*b*
Br^-	185	N_2O	ϕ_e 0·35(298)	*a*
	185	H^+/alc.	ϕ_e 0·34(298)	*a*
	185	H^+/alc.	ϕ_e 0·36(308)	*b*
	229	H^+/alc.	ϕ_e 0·55(308)	*b*
I^-	229	N_2O	ϕ_e 0·42(323)	*a*
	229	H^+/alc.		
	254	N_2O	ϕ_e 0·36(328)	*a*
		N_2O(up to 1·2 M)	ϕ_e 0·36(298) (± 0·06)	*c*
		H^+/alc.	ϕ_e 0·36(310)	*b*
	185	H^+/alc.	ϕ_e 0·25(298)	*b*
OH^-	185	N_2O	ϕ_e 0·11(298)	*a*
		MeOH	ϕ_e 0·105(298)	*d*
CNS^-	229/254	phosphate/alcohol		
		allyl alcohol	CN^-, sulphur	*e*
N_3^-	229		N_2	*m*
NO_3^-	185		ONO_2^- (298)	*f*
			OH,NO_2	
	229, 300		NO_2^-, O_2	
	335		O_2	
$H_2PO_4^-$/ HPO_4^{2-}	185		ϕ_e = 0·50	*g*
HSO_4^-	185	H^+/alc.	ϕ_e 0·55	*h*
SO_4^{2-}	185	H^+/alc.	ϕ_e 0·64 ± 0·02	*h*
		N_2O	ϕ_e 0·67	
$S_2O_3^{2-}$	229	N_2O	ϕ_e = 0·08, H_2S, SO_3^{2-}	*i*

(continued overleaf)

Anion	*Irradiation Source (nm)*	*Scavenger System*	*Product*	*Reference*
BrO_n^-	uv		$BrO^-_{n-1} + O$	*j*
XO_3^- (X = halogen)				
	uv		$\phi_{O_2} = 0{\cdot}15$	*k*
Ferrocyanide				
	214	N_2O	$\phi = 0{\cdot}88$	*l*
	229	N_2O	$\phi_e = 0{\cdot}89$	*l*
	254	N_2O	$\phi_e = 1{\cdot}00$	*l*
	265	N_2O	$\phi_e = 0{\cdot}40$	*l*
	300	N_2O	$\phi_e = 0{\cdot}00$	*l*

[a]F. S. Dainton and P. Fowles, *Proc. Roy. Soc.*, 1965, **A287,** 295; [b]J. Jortner, M. Ottolenghi, and G. Stein, *J. Phys. Chem.*, 1964, **68,** 247; [c]G. Czapski, J. Ogdan, and M. Ottolenghi, *Chem. Phys. Lett.*, 1969, **3,** 383; [d]J. Barrett, M. F. Fox, and A. L. Mansell, *J. Chem. Soc.* (*A*), 1966, 489; [e]M. Luria and A. Treinin, *J. Phys. Chem.*, 1968, **72,** 305; [f]U. Shuali, M. Ottolenghi, J. Rabani, and Z. Yelin, *J. Phys. Chem.*, 1969, **73,** 3445; M. Daniels, R. V. Meyers, and E. V. Belardo, *J. Phys. Chem.*, 1968, **72,** 389; [g]M. Halmann and I. Platzner, *J. Phys. Chem.*, 1966, **70,** 2281; [h]see refs. a and d; [i]A. Treinin, *J. Phys. Chem.*, 1963, **67,** 893, 897. [j]O. Amichai, G. Czapski, and A. Treinin, *Israel J. Chem.*, 1969, **7,** 351; G. V. Buxton and F. S. Dainton, *Proc. Roy. Soc.*, 1968, **A304,** 427; [k]A. Treinin and M. Yaacobi, *J. Phys. Chem.*, 1964, **68,** 2487; [l]M. Shirom and G. Stein, *Nature*, 1964, **204,** 778; [m]E. M. Hayon and M. Simic, unpublished work.

A. The Primary Photolytic Process.—Flash photolysis of deaerated aqueous halide ion solutions, X_{aq}^-, gives X_2^- transient radical ions with λ_{max} at 385, 360, and 350 nm for I_2^-, Br_2^- and Cl_2^- respectively with a common subsidiary band at 300 nm.[34] When specific scavengers for these transient radicals, such as 0·2M methanol, are added, a broad transient absorption band is produced in the visible region with λ_{max} at approximately 670 nm.[35] Substitution of air/argon (1:50), nitrous oxide, or H^+ as scavenger gives either partial or complete suppression of the visible band in a manner identical to that of the solvated electron produced in the pulse radiolysis of water.[36] Concentrations are arranged such that the incident radiation is absorbed almost entirely by the anion and not by the water or scavengers.[24] The solvated electrons are produced in the photolysis of these solutions through a c.t.t.s. excited state, (12).

$$Cl_{aq}^- \xrightarrow{h\nu} Cl^{\cdot} + e_{aq}^- \tag{12}$$

Flash photolysis of deaerated aqueous bromide, iodide, thiocyanate, hydroxide, and ferricyanide ions gives similar results.[35] No distinction could be made between direct photo-ionisation of the electron into the solvent or a solvent relaxation mechanism releasing only a certain fraction of the electrons.

If the solvated electron is produced in close proximity to the parent anion site then the other dissociation product might be expected to influence it, particularly when a radical ion is formed. The close proximity of the radical ion would asym-

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[34] L. I. Grossweiner and M. S. Matheson, *J. Phys. Chem.*, 1957, **61,** 1089.

[35] M. S. Matheson, W. A. Mulac, and J. Rabani, *J. Phys. Chem.*, 1963, **67,** 2613.

[36] E. J. Hart and J. W. Boag, *J. Amer. Chem. Soc.*, 1962, **84,** 4090.

metrise the potential well containing the solvated electron, whose spectrum would then be modified. The spectra of both radical and solvated electron have been obtained from the flash photolysis and modulated photo-excitation of a range of anions.

The steady state photochemistry of phosphate anions gives hydrogen when electron and hydrogen atom scavengers are added. Medium intensity c.t.t.s. bands are found below 200 nm with only extremely weak internal transitions above 200 nm.[24] Thus, when aqueous oxygen saturated HPO_4^{2-} solutions are irradiated at pH 8·9 a transient absorption band, λ_{max} 480 nm with a shoulder at 575 nm, is obtained, which is assigned to the HPO_4^- radical anion (Figure 2a).[23]

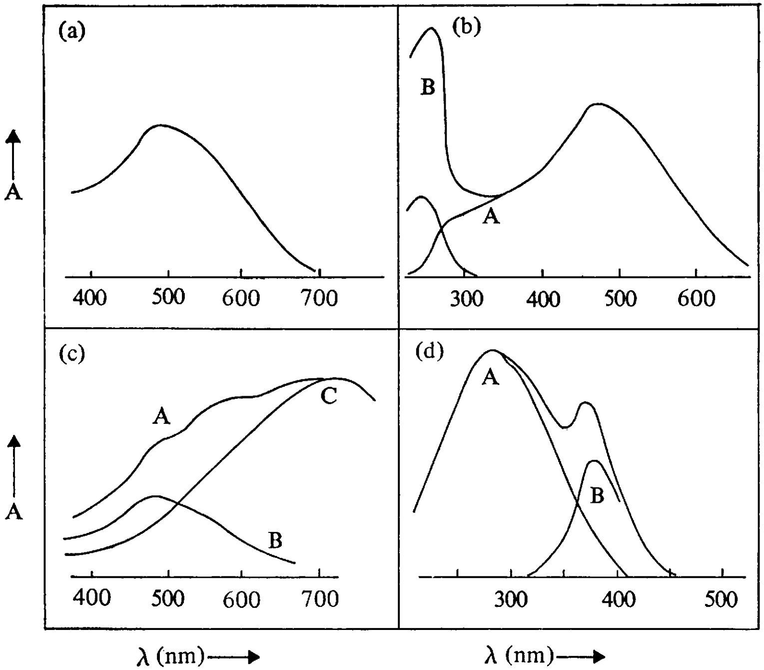

Figure 2 (a) *Phosphate radical ion spectrum from oxygen-saturated aqueous* 6·7 × 10^{-3}M Na_2HPO_4,pH 8·9 (ref. 22) (b) *transient absorption spectrum from* A, *air-free, and* B, *oxygen-saturated,* $H_2PO_4^-$ (ref. 22); (c) *transient absorption from* A, *argon-saturated* 6·7 × 10^{-3}M Na_2HPO_4, pH 8·9, B, HPO_4^- *radical spectrum from* (a) *above and* C, *difference spectrum,* (a)-(b) (ref. 23); (d) *transient absorption spectrum from the flash photolysis of thiosulphate ion,* A, $S_2O_2^-$, B, $S_2O_3^-$ (ref. 45).

Flash photolysis experiments give good corroboration of this spectrum and the derived ϵ_{max} is 600 ± 50 M^{-1} cm^{-1}.[22] Photolysis of $H_2PO_4^-$ ion at pH 4·5 gives an almost identical transient spectrum. λ_{max} 500 nm with ϵ_{max} = 650 ± 50 $M^{-1}cm^{-1}$. The close similarity between the spectra of these species and also their decay rates gives a strong indication that these radicals are the same, *i.e.* HPO_4^-, the H_2PO_4 radical probably dissociating *via* (13); the further dissociation to PO_4^{2-} has also been measured, (13).[22a]

$$H_2PO_4 \underset{}{\overset{pK=5\cdot9}{\rightleftarrows}} HPO_4^- + H^+ \overset{pK=10\cdot7}{\rightleftarrows} PO_4^{2-} + 2H^+ \qquad (13)$$

Air or oxygen saturation of these solutions removes the solvated electron as O_2^-, $k(e_{aq}^- + O_2) = 1\cdot9 \times 10^{10}\ \text{M}^{-1}\text{s}^{-1}$,[37] with λ_{max} at 240 nm, $\epsilon_{max} = 900\ \text{M}^{-1}\ \text{cm}^{-1}$ (Figure 2b), but these constants are being re-evaluated.[37a] When argon-saturated HPO_4^{2-} solutions are irradiated a complex spectrum is observed (Figure 2c), but when the spectrum of either the solvated electron or the HPO_4^- radical ion (Figure 2b), is subtracted, the spectrum of the other remains.[23] A short-lived species with λ_{max} at 700 nm is observed in the flash photolysis of deaerated HPO_4^{2-} and is assigned to the solvated electron.[22] The solvated electron cannot be detected when deaerated aqueous $H_2PO_4^-$ solutions are irradiated because the solvated electron reacts with this ion to form hydrogen atom and HPO_4^- radical with a rate constant $k(e_{aq}^- + H_2PO_4^-) = 7\cdot7 \times 10^6\ \text{M}^{-1}\ \text{s}^{-1}$.[36] The lifetime of the solvated electron in these solutions is approximately 10^{-3} s. Flash photolysis of pyrophosphate ion gives essentially similar results.[22] The pulse radiolysis of aqueous phosphorous oxyanions gives identical spectra to those produced in the photochemical work.

Solvated electrons are not observed in the photochemistry of anions which have transitions other than c.t.t.s. processes. In the flash photolysis of aqueous nitrate ion no transient absorption is observed in the 400—700 nm region[38] but this is by no means conclusive evidence, since the solvated electron could be scavenged by the nitrate ion, NO_3^{2-} (λ_{max} 245 nm),[38a] being a proposed intermediate in the radiolysis of nitrate solutions.[39] When ferrocyanide is irradiated under identical conditions in the presence of nitrate ion, solvated electrons are produced which have sufficiently long lifetimes for their decay to be measured. Solvated electron production can be ruled out and this is confirmed by the proposed initial π–π^* and n–π^* transitions.[40] A relatively longlived product in neutral aerated solutions, λ_{max} 300 nm, is assigned to the peroxynitrite ion, O–N–O–O.[41]

Other flash and steady-state photolysis studies of the 195 nm (high intensity) and the 300 nm (low intensity) bands show that four independent processes occur.[42] Firstly, pernitrite is formed in a process whose mechanism is obscure. Secondly, hydroxyl radical and nitrogen dioxide are formed.

$$NO_3^- \xrightarrow{h\nu} NO_2 + O^- \qquad (14)$$

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[37] M. Anbar, and P. Neta, *J. Appl. Rad. Isotopes*, 1967, **18**, 493; (*a*) M. Anbar and P. Neta, *J. Phys. Chem.*, 1969, **73**, 3736.

[38] F. Barat, B. Hickel, and J. Sutton, *Chem. Comm.*, 1969, 125; (*a*) M. Simic and E. Hayon to be published.

[39] S. Gordon, E. J. Hart, M. S. Matheson, J. Rabani, and J. K. Thomas, *Discuss. Faraday. Soc.*, 1963, **38**, 193; J. K. Thomas, S. Gordon, and E. J. Hart, *J. Phys. Chem.*, 1964, **68**, 1524.

[40] D. Meyerstein and A. Treinin, *Trans. Faraday Soc.*, 1961, **57**, 2104.

[41] G. Yagil and M. Anbar, *J. Inorg. Nuclear. Chem.*, 1964, **26**, 453.

[42] U. Shuali, M. Ottolenghi, J. Rabani, and Z. Yelin, *J. Phys. Chem.*, 1969, **73**, 3445.

Subsequent reactions of O^- with thiocyanate, carbonate, and oxygen produces the appropriate radicals. This process occurs for both 195 and 300 nm irradiation.[42,43] Thirdly, the residual yield for nitrite for both 300 and 229 nm irradiation is assigned to an 'internal recombination' mechanism which leads to direct evolution of oxygen. Finally, there is good evidence for a reaction, *via* an unknown intermediate, which leads to simultaneous formation of nitrite and oxygen. A proposed reaction scheme involving oxygen atoms for the last process[43] has been rejected for two reasons. Firstly, the observation of significant yields of nitrite from 335 nm irradiation indicates that excited oxygen atoms are not formed and, secondly, specific scavengers for various electronic states of solvated oxygen atoms do not detect these species.[38] The mechanism of nitrite and oxygen formation at the higher wavelengths is not clear.[42]

The oxyhalogen anions absorb only by internal processes above 200 nm,[24] and the flash photolysis of oxybromine ions in oxygen-saturated solutions shows a transient absorption at $\lambda_{\max}$ 430 nm, assigned to the O_3^- ion,[44] from (15) and then (16).

$$BrO_n^- \xrightarrow{h\nu} O^- + BrO_{n-1} \qquad (15)$$

$$O^- + O_2 \rightarrow O_3^- \qquad (16)$$

No solvated electron formation is observed. Other primary processes may compete with (15), *e.g.* internal recombination and subsequent reaction *e.g.*

$$BrO_3^- \xrightarrow{h\nu} BrO^- + O_2 \qquad (17)$$

This illustrates the similarity between the photochemistry of oxybromine and nitrate anions.

The absorption spectra of sulphite, thiosulphite, thiocyanate, and azide ions in solutions are characterised by overlap of internal and c.t.t.s. transitions.[24] Irradiation at a given frequency into these bands could give one of two reaction pathways depending upon the frequency. Thiosulphate is a typical example of this group for, following flash photolysis, two transients are observed.[45] These are a relatively shortlived intermediate at $\lambda_{\max}$ 380 nm, B, and a longlived intermediate at $\lambda_{\max}$ 280 nm, A (Figure 2d). Both are formed in acid, neutral, or alkaline solution, in the presence or absence of oxygen and at concentrations up to 10^{-2}M thiosulphate.

The transient with $\lambda_{\max}$ 380 nm (B in Figure 2d), is intensified by 50% when nitrous oxide-saturated solutions are irradiated relative to nitrogen- or oxygen-saturated thiosulphate solutions. This arises from reaction of solvated electrons, produced by the photo-ionisation of thiosulphate ion, (18), with nitrous oxide to produce hydroxyl radicals, (19), which react with thiosulphate ion, (20).

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[43] M. Daniels, R. B. Meyers, and E. V. Belardo, *J. Phys. Chem.*, 1968, **72**, 389.

[44] O. Amichai, G. Czapski, and A. Treinin, *Israel J. Chem.*, 1969, **7**, 351; G. V. Buxton and F. S. Dainton, *Proc. Roy. Soc.*, 1968, **A304**, 427.

[45] L. Dogliotti and E. Hayon, *J. Phys. Chem.*, 1968, **72**, 1800.

$$S_2O_{3aq}^{2-} \rightarrow S_2O_3^- + e_{aq}^- \qquad (18)$$

$$e_{aq}^- + N_2O \rightarrow N_2 + OH^- + OH\cdot \qquad (19)$$

$$OH\cdot + S_2O_3^{2-} \rightarrow S_2O_3^- + OH^- \qquad (20)$$

The intensity of this transient is reduced, relative to oxygen- or nitrogen-saturated solutions, by 50% when 10^{-1}M ethanol is added in the presence or absence of nitrous oxide and this acts by removing the hydroxyl radicals, (21).

$$OH^{\cdot} + CH_3CH_2OH \rightarrow H_2O + CH_3CHOH \qquad (21)$$

This lower level of transient absorption intensity corresponds to (18), and another process, independent of nitrous oxide, must contribute the additional 50% absorption of this radical in oxygen- or nitrogen-saturated solutions. The overall reaction scheme for the production of this radical is consistent with an initial c.t.t.s. process followed by solvated electron and radical ion formation.

The $S_2O_3^-$ radical decays in neutral or alkaline solution by a bimolecular process in the absence of oxygen and possibly forms $S_4O_6^{2-}$ ion. In the presence of oxygen the decay of the $S_2O_3^-$ radical is pseudo-first order. The bimolecular decay is not affected by the presence of carbonate ion, allyl or ethyl alcohols.

When filters with cutoffs at 237 and 215 nm respectively are used in the flash photolysis of thiosulphate solutions the intensities of the transient species are significantly reduced. The filters reduce the 380 nm transient intensity by 50% and 20% whereas the second transient at 280 nm is reduced by 80% and 100%. The first transient at 380 nm must arise from a transition above 200—210 nm and this would correspond to the c.t.t.s. band at 205 nm.[23] Pulse radiolysis of these solutions gives an almost identical transient radical spectrum, λ_{max} 375 nm, arising from a reaction such as (20).[46]

The transient absorption at 280 nm, A in Figure 2d, is formed by a process independent of that described above, the intensity of this transient being unaffected by the presence or absence of oxygen, nitrogen, or nitrous oxide. The effect of filters indicates the transition giving rise to this transient to be below 200 nm. The band below 200 nm is an allowed *n*–*π** transition, the nonbonding electron being on oxygen. Photolysis leads to sulphur–oxygen bond fission and the formation of $S_2O_2^-$ radical anion, (22).

$$S_2O_3^{2-}aq \xrightarrow{h\nu} S_2O_2^- + OH + OH^- \qquad (22)$$

The hydroxyl radical contributes to the formation of $S_2O_3^-$ by (20) and accounts for the decrease of approximately 50% in 380 nm intensity when ethanol is added. The primary quantum yields of (18) and (22) are roughly equal and the $S_2O_2^-$ radicals decay by a second order process independent of alcohol. carbonate, or oxygen. Sulphur, hydrogen sulphide, and sulphite ion are also produced as reaction products in the flashed solutions. Essentially similar results are found for the flash photolysis of sulphite and thiocyanate solutions.[45]

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[46] G. E. Adams, J. W. Boag, and B. D. Michael, *Trans. Faraday Soc.*, 1965, **61**, 1674.

Solvated electrons are also formed in the flash photolysis of aromatic compounds and the yields are dramatically increased when the compounds are ionised, *e.g.* as phenolate or naphtholate.[47] No c.t.t.s. transitions have been observed above 210 nm for these ions and the absorption process is assigned to an allowed π–π^* transition. These ions fluoresce in solution and as the pH of the solutions are raised, the fluorescence intensities decrease. The solvated electron formation and fluorescence originate from the same excited state and compete with each other.

Thus, π–π^* transitions of organic anions can lead to solvated electron formation without c.t.t.s. transitions but n-π^* and π–π transitions of inorganic anions lead to dissociation. Simple inorganic anions form solvated electrons only through c.t.t.s. transitions. Where solvated electron formation follows irradiation of inorganic anions the spectra are the same in each case and therefore independent of the radical formed with it.

The differing natures of the radicals formed indicate that the radical and solvated electron must be well separated from each other and in the bulk of the solution. This is supported by the almost identical spectra of the same radicals produced in the pulse radiolysis of these solutions. The primary photolytic process following the formation of a c.t.t.s. excited state is the formation of a solvated electron and radical which then move apart and are found independent of each other in the solution. When the transition is an internal process, irradiation gives dissociation of the anion.

B. Radical Scavenging.—The radicals formed in the primary photolytic process will either recombine, dimerise, or be scavenged by added solutes. Much effort has been expended in determining the primary quantum yield of the initial process using a large range of scavengers. These approaches use competition kinetics to relate the observed yields to the primary quantum yield.

Specific scavengers for solvated electrons include nitrous oxide, acetone, monochloracetic acid, 1,2-dichloroethane and Brönsted acids such as H^+, HF, $H_2PO_4^-$, and NH_4^+.[48] The last group are thought to react with solvated electrons in accord with the Bronsted general acid catalysis law[49] but a detailed investigation finds that other Brönsted acids in the same pK range do not react with solvated electrons at all.[48] A proton transfer mechanism is rejected in favour of incorporation of the electron into the scavenger to form an intermediate radical or radical anion.[48] This radical may then decompose to give other radicals which will be scavenged by further specific scavengers; *e.g.* solvated electrons will be scavenged by $H_2PO_4^-$ to give HPO_4^- and hydrogen atom, the latter then being scavenged by an aliphatic alcohol.[50] The rate constants for the electron +

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[47] G. Stein, 'The Solvated Electron', ACS 50, American Chem. Soc., Washington, D.C., 1965, p. 230.

[48] M. Anbar, 'The Solvated Electron'., ACS 50, American Chem Soc., Washington, D.C. 1965, p. 55.

[49] J. Jortner, M. Ottolenghi, J. Rabani, and G. Stein, *J. Chem. Phys.*, 1962, **37**, 2488.

[50] J. Rabani, 'The Solvated Electron', ACS 50, American Chem. Soc., Washington D.C. 1965, p. 242.

scavenger reactions are not always diffusion controlled;[48] the predicted solvated electron + hydrogen ion reaction rate constant is $1{\cdot}1 \times 10^{11}\ \text{M}^{-1}\text{s}^{-1}$ but the observed value is $2{\cdot}3 \times 10^{10}\,\text{M}^{-1}\text{s}^{-1}$ in both water and ethanol. The rate of encounter according to diffusion theory[51] depends on the relative permittivity of the solution and that for ethanol is very much different from that for water. The absence of a solvent effect shows the reaction not to be diffusion controlled, despite the high diffusion coefficient of H^+ in solution.

Solvated electrons are converted into hydrogen molecules by some Brönsted acids, principally H^+ and $H_2PO_4^-$,[50] and alcohol scavenging systems; when alcohols are used alone in neutral solution the primary quantum yields calculated depend upon which alcohol is used.[18,52] Hydrogen molecules are formed by hydrogen abstraction from the α-carbon of the alcohol, the resulting radical either dimerising to give a glycol or disproportionating to give an aldehyde/ketone and alcohol.[52]

Nitrous oxide is used as a specific scavenger for solvated electrons because of the high rate constant, $k(e_{aq}^- + N_2O) = 8{\cdot}7 \times 10^9\ \text{M}^{-1}\text{s}^{-1}$;[48] nitrogen molecule and hydroxyl radical are produced. The nitrogen evolved may be used as a direct measure of the solvated electron quantum yield. The N_2O^- intermediate has a finite lifetime of approximately 10^{-7} s and can act as a strong oxidising or mild reducing agent. The hydroxyl radicals are not formed from an immediate, dissociative electron capture of the N_2O.[48]

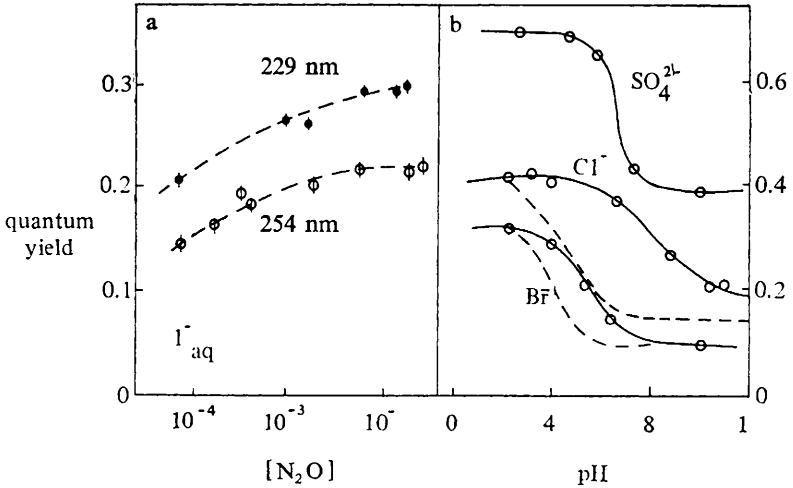

Figure 3 *Plot of quantum yield for* (a) 5×10^{-3}M KI *photolysed at* 229 nm *and* 10^{-1}M KI *photolysed at* 254 nm *in the presence of* N_2O, *and* (b) Cl^- (0·04M), Br^- (0·01M), *and* SO_4^{2-} (0·1M) *in the presence of* H^+ and 0·4M CH_3OH (refs. 14 and 63).

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[51] M. S. Matheson, 'The Solvated Electron', ACS 50, American Chem. Soc., Washington, D.C. 1965, p. 45.

[52] M. Halmann and I. Platzner, *J. Phys. Chem.*, 1966, **70**, 2281.

The primary quantum yield for an anion photolysis/scavenger system is obtained from the limiting initial slopes of product concentration *vs.* time plots. For all cases involving solvated electron and radical formation from anions, and also in radical pair formation where the original pair can be identified, the very marked dependence of quantum yield on scavenger concentration increases up to a limiting value (Figure 3). These limiting quantum yields are also independent of irradiation intensity and, together with the scavenger concentration effect, favour a cage, inhomogeneous, radical-scavenging mechanism and reject a homogeneous radical-recombination/radical-scavenging competition.[53] Photolysis of iodide in other solvents such as methanol (ϕ_e = 0·60), ethanol (0·66), isopropanol (0·70), and methyl cyanide (0·75) gives similar scavenger concentration/product quantum yield effects, again interpreted as a cage scavenging mechanism.[54] The increased quantum yields relative to aqueous iodide photolysis are attributed to more efficient relaxation mechanisms of electron release to the solvent. Various scavengers used in iodide photolysis give the same limiting quantum yield of electron release to a given solvent, showing the yield to be independent of the nature of the scavenger.[53] This evidence, together with the cage scavenging mechanism and the spectroscopic studies of anion/scavenger systems,[27,28] shows that the scavenger does not interact with the spectroscopic excited state and, because the quantum yield is always less than unity, does not react with the first dissociation process of the excited state.

The wavelength at which iodide is photolysed, 254 nm, is more than two half-band widths on the lower energy side of the (Gaussian) absorption band centre; the absorption band intensity of iodide at 254 nm is approximately 3% of that at ϵ_{max}.[27] Irradiation into the band centre at 229 nm gives an increased quantum yield, 0·31; further, irradiation into the high energy doublet at 185 nm (Figure 1), gives ϕ_e = 0·25.[55] The iodine radicals produced from irradiation at 254 and 185 nm and bromine radicals from 229 nm irradiation do not dehydrogenate alcohols. Bromine and chlorine radicals produced at 185 nm dehydrogenate added alcohols and the difference between the action of these radicals arises from the energy required to abstract hydrogen from a C–H bond.[55] This correlation holds except for the high energy iodine radical, which has the highest energy of all. The wavelength dependence of the quantum yields for these anions has not been investigated in depth; on the other hand, the wavelength dependence of ferrocyanide quantum yield arises from varying contributions of c.t.t.s. and ligand field bands at the irradiation wavelengths used.[56]

The large bandwidths of c.t.t.s. absorption bands, *e.g.* approximately 4200 cm^{-1} for aqueous iodide at 298 K,[24] are interpreted as a distribution of excited state electron radii and would indicate a distribution of radical-solvated electron separations. However, the ratio of quantum yields at 254 and 229 nm for aqueous iodide photolysis is constant for all N_2O scavenger concentrations up to

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[53] J. Jortner, M. Ottolenghi, and G. Stein, *J. Phys. Chem.*, 1962, **66**, 2029, 2037, 2042.
[54] J. Jortner, M. Ottolenghi, and G. Stein, *J. Phys. Chem.*, 1963, **67**, 1271.
[55] J. Jortner, M. Ottolenghi, and G. Stein, *J. Phys. Chem.*, 1964, **68**, 247.
[56] M. Shirom and G. Stein, *Nature*, 1964, **204**, 778.

and including that necessary to observe the limiting quantum yield (Figure 3a).[14] The fraction of solvated electrons scavenged is therefore independent of the number of radicals produced at each wavelength. Further, the separation of the electron and radical and electron must also be the same for each wavelength, despite the quantum energy difference of 50 kJ mol^{-1} and is consistent with the formation of the radicals in a solvent cage which is defined initially by the ground state solvation configuration.[14]

Quantum yields increase with increase in temperature;[14,55] the range covered is not extensive but there is a tendency for the quantum yield to become independent at higher temperatures (Figure 4). The variation arises from a competition between two excited-state deactivation modes, (23) and (24), *e.g.* for aqueous iodide:[14]

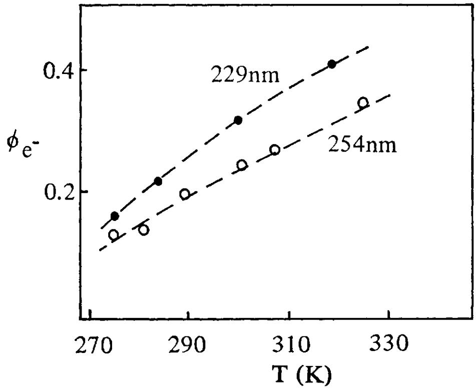

Figure 4 *Plot of quantum yield against temperature for* 5 × 10^{-3}M KI *from* 229 nm *photolysis and* 10^{-1}M KI *photolysed at* 254 nm (from ref. 14).

$$I_{aq}^{-*} \rightarrow I_{aq}^{-} \qquad (23)$$

$$I^{-*} \rightarrow I^{\cdot} + e_{aq}^{-} \qquad (24)$$

If (23) is a collisional thermal deactivation (fluorescence has never been observed from a c.t.t.s. excited state) then k_{23} will be proportional to $T^{\frac{1}{2}}$. The rate at which molecules diffuse out of the solvent cage may be related to the viscosity of the solution and an activation energy for this process defined which corresponds to the activation energy, B, for viscous flow, *i.e.*

$$\eta \text{ (viscosity)} = A\mathrm{e}^{-B/RT} \qquad (25)$$

$$k_{24} = k_{24'} \exp(-B/RT) \qquad (26)$$

The limiting quantum yield, ϕ_e, is a competition between processes (23) and (24),

$$\phi_e = \frac{k_{24}}{k_{23} + k_{24}} \tag{27}$$

An Arrhenius plot of the limiting quantum yield *vs.* temperature data for the halide ions gives B values of 19·7 and 20·5 kJ mol^{-1} for aqueous iodide photolysed at 254 nm, 20·9 and 16·8 kJ mol^{-1} for iodide and bromide at 229 nm respectively.[14] At 185 nm, values of 14·2 and 4·2 kJ mol^{-1} are obtained for bromide and chloride.[14] These values, except that for chloride, agree quite well with the average value of B from viscosity data over the same temperature range, 18·9 kJ mol^{-1},[57] and point to the role of molecular relaxations in releasing electrons from the aqueous solvent cage. It is somewhat surprising to find this correlation because B from viscosity is a bulk property and the activation energy of electron release defined above would be a property of the oriented water molecules immediate to the ion. Further, from (27), if $k_{24} \gg k_{23}$, ϕ_e will tend to a constant value of unity at the higher temperatures. This behaviour is only observed in part, for the quantum yields do tend to constant values at higher temperatures but in no case do they approach unity.

A quantitative model for the formation and diffusion into the bulk of the radicals has been developed[53] based on the work of Noyes.[58] The radicals may undergo a primary recombination, probability β', to give a ground state anion and this is indistinguishable, kinetically, from excited state thermal deactivation, (23). The relative importance of these effects has not been probed, but together they will reduce the quantum yield which can be observed below unity. The radicals that do not undergo primary recombination will diffuse apart with different diffusive properties.

The asymmetrisation process which gave rise to the radicals from the excited state will result, for a c.t.t.s. transition, in the solvation shell being centred on the electron rather than the initial anion site. A detailed Debye–Huckel treatment of results from photolysis of iodide in aqueous solutions of varying ionic strength shows that the electron moves rapidly to a distance of at least 1 nm from the initial anion site.[14] The mechanism of this movement involves rotation of water molecules and thus links the quantum yield of electron release to the solvent and the activation energy of viscous flow, (25), (26), and (27).[14]

Secondary recombination of the radicals will occur from a chance diffusive encounter of the original partners or they will diffuse separately into the bulk solution and react independently. The limiting quantum yield at a given temperature, ϕ_e, and the product quantum yield, ϕ, at scavenger concentration $[S]$, are related through,

$$\ln(1 - \phi/\phi_e) = \ln \beta' - 2a/\beta' (\pi k_S [S])^{\frac{1}{2}} \tag{28}$$

where the parameter a is related to the frequency of diffusive motions of the liquid.[53] There is good general agreement between the observed photochemical

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[57] D. Eisenberg and W. Kauzmann, 'The Structure and Properties of Water', Oxford University Press, 1969, London.

[58] R. M. Noyes, *J. Amer. Chem. Soc.*, 1955, **77**, 2042; 1956, **78**, 5486.

kinetics of simple anions and the quantitative theory of scavenging which leads to (26). This theory is known as the Jortner–Ottolenghi–Stein (J–O–S) treatment[53] and has also been successfully applied to the steady state photolysis of nitrate at 313 nm[43] and thiocyanate at 254 and 229 nm[59] in aqueous solution.

The principal discrepancy between theory and experiment is that efficient competition by the scavenger occurs at concentrations which are approximately two orders of magnitude lower than by predicted theory.[60–63] The scavenger appears to be much more efficient than predicted; a plateau is reached in quantum yield at nitrous oxide and hydrogen ion concentrations of approximately 5×10^{-3}M in iodide photolysis (Figure 3),[14] in contrast to incomplete scavenging at 0·5 M (10^{-2} mole fraction) observed in systems other than anion photolysis.[60]

The procedure of determining primary quantum yields from the initial slopes of product concentration *vs.* time plots has been re-examined and the final products shown to be formed in secondary or even tertiary steps.[60] Significant discrepancies are observed between rate data derived from competition kinetics and those from pulse radiolysis, a direct method of measurement.[48] The slope of the initial linear portion of the product concentration *vs.* time curve will not give the true yield and introduces a misleading scavenger concentration dependence.[60]

Application of steady state kinetics to results for anion photolysis, using rate constants derived from pulse radiolysis, shows that competition between scavenger and back reactions of the radicals will give rise to the observed quantum dependences in the intermediate scavenger region. In iodide photolysis, I_2^- and e_{aq}^- (or H) react homogeneously in the bulk of the solution. The intensity of primary yields for subsequent flashes of a series of negative ions in aqueous solution are independent of scavenger concentration.[60] The intensity of the primary intermediates formed increases slightly initially, because of impurity 'cleanup', and then decreases. The decrease in primary yield results from back reactions of the radicals with reaction products. Agreement between formal application of cage scavenging equations and experiment does not, therefore, act as a definitive test for cage recombination. Additional information is required such as the absolute value of the scavenging reaction rate constant, k_s, such that $k_s c_s = 10^9$–10^{10}s^{-1}, and $k_b c_p$, where k_b is the back reaction rate constant (for radical and products) and c_p is the (analysed) product concentration. Only when $k_s c_s \gg k_b c_p$ can experimental yields be taken to be true primary yields and used subsequently to test cage scavenging mechanisms.[60]

The photochemistry of aqueous iodide and bromide ions at 254 and 229 nm respectively has been re-investigated in the presence of high concentrations of nitrous oxide (2×10^{-2}M—1·2M).[64] The rate constant for solvated electrons reacting with tri-iodide is only 4—8 times that of solvated electrons reacting with nitrous oxide so that the condition $k_s c_s \gg k_b c_p$ holds. The iodide quantum yield

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[59] M. Luria and A. Treinin, *J. Phys. Chem.*, 1968, **72**, 305.
[60] G. Czapski and M. Ottolenghi, *Israel J. Chem.*, 1968, **6**, 75.
[61] G. Stein, 'The Chemistry of Ionisation and Excitation', Taylor and Francis, London, 1967.
[62] M. S. Matheson, W. A. Mulac, J. L. Weeks, and J. Rabani, *J. Phys. Chem.*, 1966, **70**, 2092.
[63] F. S. Dainton, and P. Fowles, *Proc. Roy. Soc.*, 1965, **A287**, 312.

increases with increase in nitrous oxide concentration until there is little variation in quantum yield, within experimental error, over a fourfold increase in nitrous oxide concentration. The quantum yields are independent of iodide and bromide concentrations and irradiation dose. Bromide photolysis quantum yields are independent of nitrous oxide over the same range as used for iodide.

The maximum quantum yield observed, 0·36 ± 0·06 is close to the highest observed in the temperature variation, 0·36,[14] indicating an upper limit for the quantum yield of iodide photolysis at 254 nm.

Three mechanisms were considered for the increase in iodide quantum yield at high nitrous oxide concentrations.[64] Firstly, a charge transfer complex between nitrous oxide and iodide was considered but this is ruled out by the quantum yield being independent of the iodide concentration at constant nitrous oxide concentration. The second possibility is of an excited state iodide ion reacting directly with nitrous oxide but this is ruled out by the lifetime of excited iodide being below an upper limit of about 10^{-11}s,[65] too short to react directly with nitrous oxide. This leaves a cage scavenging mechanism,

$$\begin{array}{ll} I_{aq}^- \xrightarrow{h\nu} I_{aq}^{-*} \rightarrow (I + e_{aq}^-)\ \text{cage} \xrightarrow{N_2O} I + & N_2O^- \\ & \quad\downarrow \\ & N_2 + O^{-\cdot} \end{array} \qquad (29)$$

The independence of bromide quantum yield at the higher nitrous oxide concentration, $1{\cdot}2 \times 10^{-2}$M—1·2 M, follows on directly from a region, $1{\cdot}9 \times 10^{-7}$M—$1{\cdot}67 \times 10^{-2}$ M[63] where a limiting quantum yield is observed. A larger initial separation between radical and electron may account for this effect,[64] the radicals being relatively easier to scavenge than iodide. A limiting quantum yield will therefore be observed at lower concentrations of scavenger; extrapolation to chloride photolysis predicts an even larger radical–solvated electron distance, giving an even lower concentration necessary for complete scavenging. This is observed (Figure 3b).[63] A further correlation may be drawn between the magnitude of the residual yield at pH 7, (with no electron scavenger present but in the presence of a hydrogen atom scavenger) and the limiting quantum yield as a reflection of the initial radical–solvated electron separation (Figure 3).

The quantum yield has been redefined as $\Gamma\phi_e$, where Γ is the fraction of radicals produced in the initial photo-act;[64] little is known of this factor and it is taken to be unity. ϕ_e is the fraction of radicals which escape cage recombination and may be scavenged. ϕ, the product quantum yield, varies between ϕ_e and the residual quantum yield, ϕ_r, according to the scavenger concentration. The operative scavenger concentration region depends upon the distance of initial separation of the radicals. The assignments of values close to unity for both Γ and ϕ_e in chloride photolysis is based upon incorrect values for $\phi_e(Cl_{aq}^-)$ of 0·98,[55] instead of the actinometry corrected value of 0·43.[63]

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[64] G. Czapski, J. Ogdan, and M. Ottolenghi, *Chem. Phys. Letters*, 1969, **2**, 383.

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