The Photochemistry of the Uranyl Ion

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1 Introduction

Whilst historically predating organic photochemistry, only in the last decade has inorganic photochemistry received comparable study of the nature of the primary photochemical and photophysical processes involved.[1] The important photoinduced reactions in inorganic systems (particularly those involving metal ions) are redox reactions, ligand substitutions, and molecular rearrangements.[1] The uranyl ion presents a model species for photochemical study as, in addition to the high photosensitivity of its many complexes,[2,3] the excited uranyl ion luminesces, thus providing an additional tool for the study of the excited-state processes involved. Nevertheless, the two most recent reviews on the photochemistry of this species[2,3] both indicate that many of the results are intricate and confusing, and that our understanding of the primary processes involved is far from satisfactory. In large part, these problems stem from both a lack of detailed understanding of the spectroscopy of the uranyl ion, and a lack of application of fast-reaction techniques to the study of mechanisms. We feel now, however, that this situation has been remedied sufficiently to enable a more detailed but consistent picture of the photochemistry of uranium(VI) to be presented.

Photochemical studies on uranium(VI) date back to the beginning of the nineteenth century when uranyl oxalate was found to decompose under the influence of light.[4] Detailed investigation of the photochemistry received considerable impetus both from the discovery that uranyl oxalate provides a suitable actinometer[5] and, much later, from the Manhattan project and later related

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[1] See, for example, A. W. Adamson, W. L. Waltz, E. Zinato, D. W. Watts, P. D. Fleischauer, and R. D. Lindholm, *Chem. Rev.*, 1968, **68**, 541; W. L. Waltz and R. G. Sutherland, *Chem. Soc. Rev.*, 1972, **1**, 241; or ref. 3.

[2] E. Rabinowitch and R. L. Belford, 'Spectroscopy and Photochemistry of Uranyl Compounds', Pergamon Press, Oxford, 1964.

[3] V. Balzani and V. Carassiti, 'Photochemistry of Co-ordination Compounds', Academic Press, London, 1970.

[4] A. Buchholz, *Ann. Chim. Phys.*, 1805, **56**, 142, quoted in ref. 3.

[5] See, for example, C. R. Masson, V. Bockelheide, and W. A. Noyes, jun., 'Photochemical Reactions' in 'Techniques of Organic Chemistry, Vol. II', ed. A. Weissberger, Interscience, New York, 2nd edn., 1956, p. 294,

studies, where one of the objectives was to determine methods of separating pure uranium and obtain isotopic enrichment.

Here we will concentrate on those aspects of the subject which have developed since the reviews of Balzani and Carassiti,[3] and Rabinowitch and Belford,[2] especially those which have led to a clarification of the primary processes involved, and of the mechanistic pathways leading to stable final products. However, where appropriate, references are included from these earlier reviews.

2 Structure and Bonding

The dominating structural factor in uranyl compounds is the O–U–O system, which is generally thought to be linear both in the solid state[6] and in solution.[7] Around this are co-ordinated a further 4, 5, or 6 ligands; *e.g.* in the crystal structure of uranyl nitrate dihydrate[8] (Figure 1) the metal atom exhibits an overall co-ordination number of 8, with two water molecules and two nitrate ligands co-ordinated in the plane perpendicular to the O–U–O axis. Further, the U–O bonds to the ligands are always longer than those in the UO_2 moiety, *e.g.* in the uranyl nitrate complex, U–O (nitrate) = 2.504, 2.547 Å, U–O (water) = 2.397 Å, U–O (uranyl) = 1.749, 1.770 Å. The metal–ligand bonds are thought

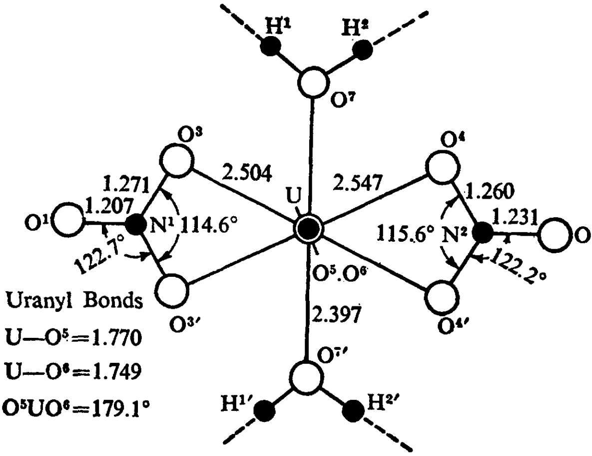

Figure 1 *Structure of* $UO_2(NO_3)_2,2H_2O$ *from ref.* 8 (O_5 *and* O_6, *the atoms in the* UO_2 *entity, are directly above and below the* U *atom and all other atoms are approximately coplanar*)
(Reproduced by permission from *Acta Cryst.*, 1965, **19**, 536)

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[6] For example, J. E. Fleming and H. Lynton, *Chem. and Ind.*, 1960, 1415.

[7] S. P. McGlynn and J. K. Smith, *J. Mol. Spectroscopy*, 1961, **6**, 164 (see also ref. 15).

[8] J. C. Taylor and M. H. Mueller, *Acta Cryst.*, 1965, **19**, 536; N. K. Dalley, M. H. Mueller, and S. H. Simonsen, *Inorg. Chem.*, 1971, **10**, 323.

to be covalent in character rather than purely electrostatic,[9] so the short U–O bond distances in the uranyl species provide good evidence for involvement of π-bonding in this group.

A number of theoretical treatments[7,10–15] have been performed on UO_2^{2+} which support the existence of π-bonding. The electronic configuration[7] of U is $5f^3 6d^1 7s^2$. In UO_2^{2+} the $6d$-orbitals of uranium are thought to be involved both in σ- and π-bonding with the $2p$-orbitals of the O atoms.[7,12–15] Evidence for f-orbital involvement is less clear. Calculations show only limited $5f$-orbital involvement[12–14] but Coulson and Lester[11] have demonstrated that $6f$-orbitals may be involved, at least in the bonding to the other ligands. Although the actual ordering of the molecular orbitals has not been settled,[7,13,14] theoretical calculations on uranyl, assuming $D_{\infty h}$ symmetry, suggest that the ground state is a singlet state ($^1\Sigma_g{}^+$) with electronic configuration[7] $(1\sigma_u{}^+)^2$ $(1\sigma_g{}^+)^2$ $(1\pi_u)^4$ $(1\pi_g)^4$. Magnetic measurements confirm that uranyl complexes are predominantly diamagnetic, with a weak temperature-independent paramagnetism.[10] The magnetic properties are discussed in more detail by Eisenstein and Pryce[10] and by McGlynn and Smith.[7] Whilst spectroscopic studies[16,17] of uranyl complexes indicate that the symmetry is often different from $D_{\infty h}$, this does not significantly affect the above picture.

Further, whilst uranyl forms complexes with a wide range of organic and inorganic ligands, and also hydrolyses in a slow, pH-dependent reaction to give polymeric species,[18] the photochemical properties in both cases can be considered to be predominantly those of the UO_2^{2+} moiety. In the hydrolysed species, the UO_2 system probably remains intact, with bonding between adjacent units *via* hydroxy bridges.[19] Fuller details on the structure of uranyl complexes are given elsewhere.[20,21]

3 Spectroscopy and Photophysics

A. Absorption Spectrum.—The electronic absorption spectrum of the uranyl ion is probably one of the most extensively studied regions of molecular spectroscopy, yet our understanding of it remains far from complete. The spectrum shows a

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[9] For a discussion, see, for example, N. W. Alcock, *J.C.S. Dalton*, 1973, 1616.
[10] J. C. Eisenstein and M. H. L. Pryce, *Proc. Roy. Soc.*, 1955, **A229**, 20.
[11] C. A. Coulson and G. R. Lester, *J. Chem. Soc.*, 1956, 3650.
[12] R. L. Belford, *J. Chem. Phys.*, 1961, **34**, 318.
[13] R. L. Belford and G. Belford, *J. Chem. Phys.*, 1961, **34**, 1330.
[14] J. B. Newman, *J. Chem. Phys.*, 1965, **43**, 1691.
[15] S. P. McGlynn, J. K. Smith, and W. C. Neely, *J. Chem. Phys.*, 1961, **35**, 105.
[16] C. Görller-Walrand and S. De Jaegere, *J. Chim. Phys.*, 1972, **69**, 726.
[17] C. Görller-Walrand and S. De Jaegere, *Spectrochim. Acta*, 1972, **A28**, 257.
[18] See, for example, H. S. Dunsmore, S. Hietanen, and L. G. Sillén, *Acta Chem. Scand.*, 1963, **17**, 2644 and other papers in this series.
[19] J. T. Bell and R. E. Biggers, *J. Mol. Spectroscopy*, 1967, **22**, 262.
[20] A. E. Comyns, *Chem. Rev.*, 1960, **60**, 115.
[21] I. I. Chernayev, 'Complex Compounds of Uranium', Israel Program for Scientific Translations, Jerusalem, 1966.

remarkable sensitivity to its environment and to temperature.[22–24] However, the main spectral features are typified by uranyl perchlorate in water[24] (Figure 2) where the absorbing species is probably $[UO_2(H_2O)_6]^{2+}$. These consist of an initial series of weak bands between 500 and 360 nm, with progressively stronger bands towards the u.v.

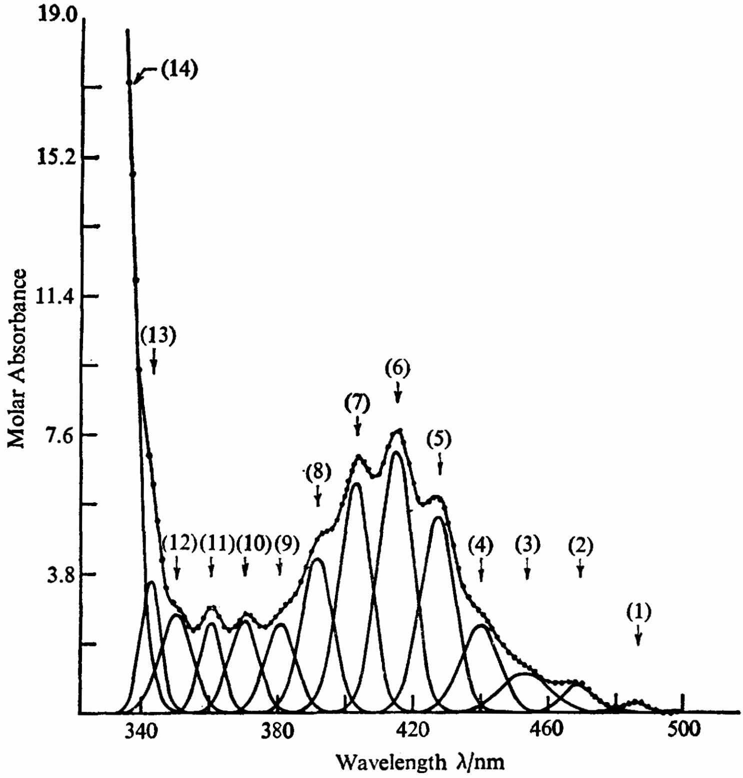

Figure 2 *Absorption spectrum of uranyl perchlorate in aqueous* $HClO_4$. *Filled circles—experimental spectrum of* $UO_2(ClO_4)_2$ (9.15 mM, $[HClO_4]$ = 1.4 mM); *full line joining circles—computer simulated spectrum; separate curves—components of simulated spectrum (Numbering scheme due to Bell and Biggers, ref.* 24)

(Reproduced by permission from *J. Mol. Spectroscopy*, 1965, **18**, 247)

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[22] G. H. Dieke and A. B. F. Duncan, 'Spectroscopic Properties of Uranium Compounds' McGraw-Hill, New York, 1949.

[23] B. Jezowska-Trzebiatowska and A. Bartecki, *Spectrochim. Acta*, 1962, **18**, 799 and other papers in this series.

[24] J. T. Bell and R. E. Biggers, *J. Mol. Spectroscopy*, 1965, **18**, 247.

Jorgensen[25] suggested that the weak visible bands are probably Laporte-forbidden, and arise from a charge-transfer transition of an electron from a ligand orbital to an empty 5*f*-orbital on the central U atom. However, most other workers interpret the transition as being completely within the UO_2^{2+} grouping.[7,26] Following the theoretical demonstration of the importance of π-bonding in uranyl, McGlynn and Smith[7] assigned the lowest-energy transition to excitation of an electron from the highest filled π-orbital to a non-bonding orbital on the uranium, and this interpretation is generally accepted. Such an excited state may be expected to possess certain free-radical character, and in fact hydrogen atom abstraction by the excited uranyl ion is observed experimentally (see Section 4B).

Assignment of the electronic states involved in the absorption spectrum is, however, rather more controversial. McGlynn and Smith[7] suggested that the lowest-energy absorption between 20 500 and 30 000 cm^{-1} results from a triplet $\leftarrow$ singlet transition to either $^3\Pi_u$ or $^3\Delta_u$ states (with a preference for the former). Because of the presence of significant spin–orbit coupling, this transition is reasonably intense ($\epsilon_{max} \sim 10\,l\,mol^{-1}\,cm^{-1}$) even though it is spin-forbidden. They argued that these bands could be divided into three groups with origins at 22 050, 24 125, and 27 000 cm^{-1} representing the three components of the triplet state which is split by the local field. Further vibronic fine structure is superimposed on these absorptions. McGlynn and Smith's assignment of the lowest excited state to a triplet state stems primarily from theoretical arguments. Support for this assignment has been proposed on the basis of magnetic circular dichroism (m.c.d.) studies on $(Bu_4N)UO_2(NO_3)_3$ in a polymer matrix at 10 K,[27] from studies of the effect of complexation on the absorption spectrum of uranyl solutions,[23,28–30] and from further theoretical analyses.[24,31–33] In a particularly detailed study, Bell and Biggers[19,24,31,32] showed that the complicated uranyl absorption could be resolved mathematically using a non-linear least-squares computer program into a series of 24 Gaussian bands in 7 groups (Figure 2). Following McGlynn and Smith's model,[7] they assigned the first 13 bands to the three components of a triplet state $^3\Pi_u$ at 21 329, 24 107, and 27 731 cm^{-1}. Brint and McCaffery[27] have argued that at least in the case of $(Bu_4N)UO_2(NO_3)_3$ the lowest-energy transition, which is parity-forbidden, is to two close-lying triplet states ($^3E_{1g}$ and $^3E_{2g}$ in their nomenclature).

Alternative assignments of the low-energy absorptions have, however, been

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[25] C. K. Jørgensen, *Acta Chem. Scand.*, 1957, **11**, 165.
[26] See, for example, Z. Libuś, *J. Inorg. Nuclear Chem.*, 1962, **24**, 619.
[27] P. Brint and A. J. McCaffery, *Mol. Phys.*, 1973, **25**, 311.
[28] M. M. Fayt, E. M. Vandeput, and S. De Jaegere, *Nature*, 1963, **200**, 355.
[29] S. De Jaegere and T. Govers, *Nature*, 1965, **205**, 900.
[30] V. Baran, *Coll. Czech. Chem. Comm.*, 1966, **31**, 2093.
[31] J. T. Bell and R. E. Biggers, *J. Mol. Spectroscopy*, 1968, **25**, 312.
[32] J. T. Bell, *J. Inorg. Nuclear Chem.*, 1969, **31**, 703.
[33] Y. J. Israeli, *Bull. Soc. chim. France*, 1965, 196.

proposed.[34–43] Volod'ko and co-workers[38] have investigated uranyl solutions and crystals at low temperatures and concluded that the absorption spectrum has four series of lines in the region 330—500 nm with substantially different characteristics which arise from transitions to four separate singlet levels, and have given an energy state diagram based on this model. Similarly, Görller-Walrand and Vanquickenborne[42,43] favour interpretation of the low-energy region in terms of singlet ← singlet transitions because of the effect of ligands on the uranyl spectrum. They find that the spectra of a large number of uranyl complexes are virtually independent of the chemical nature of the ligand, but are strongly dependent on the total symmetry of the complex. Siddall and Prohaska[35] have also questioned the assignment of the low-energy bands to a triplet ← singlet transition, following a study of solvent effects on spectra of organophosphorus and organonitrogen adducts of uranyl.

The evidence is not strong enough to allow an unambiguous assignment of the lowest excited state but we favour the triplet assignment. In support, McGlynn and Smith[7] noted that a weak paramagnetism (different from the permanent, temperature-independent paramagnetism) could be detected in an excited uranyl complex. Unfortunately, no further details on this have been forthcoming.

Similar uncertainty exists in the assignment of the upper excited states. McGlynn and Smith[7] assigned the excited states at 34 000 and 48 000 $\mathrm{cm^{-1}}$ (2nd and 3rd excited states in their classification) to the lowest excited singlet states. Israeli[33] assigned states at 29 000, 34 500, 42 600, and 53 000 $\mathrm{cm^{-1}}$ to the singlet states $^1\Delta_u$, $^1\Pi_u$, $^1\Sigma_u{}^+$, and $^1\Pi_u$. Volod'ko and co-workers[38] have indicated the difficulty of assigning states higher than 31 000 $\mathrm{cm^{-1}}$ in uranyl salt solutions where the counter-ion is nitrate, sulphate, or any other anion possessing absorptions in this region. They assign the excited states between 20 000 and 31 000 $\mathrm{cm^{-1}}$ to four singlet states. Brint and McCaffery,[27] however, on the basis of low-temperature absorption and m.c.d. studies assign the absorption between 29 000 and 36 000 $\mathrm{cm^{-1}}$ to the parity-allowed $T \leftarrow S$ transition $^3E_{1u} \leftarrow {}^1A_{1g}$. Bell and Biggers[24,31,32] overcame the problem of overlapping counter-ion absorption by using uranyl perchlorate, and produced possibly the most comprehensive analysis of the spectrum. They assigned the state at 31 367 $\mathrm{cm^{-1}}$ to the second triplet

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[34] A. N. Sevchenko, *Analele Stiint. Univ., 'A. I. Cuza', Iasi Sect. 1*, 1961, **7**, 121; *Chem. Abs.*, 1963, **59**, 2300e.

[35] T. H. Siddall and C. A. Prohaska, *Nature*, 1963, **202**, 1088.

[36] A. N. Sevchenko, *Izvest. Fiz. Inst. ANEB, Bulg. Akad. Nauk*, 1968, **17**, 69; *Chem. Abs.*, 1968, **69**, 81974v.

[37] L. V. Volod'ko, A. N. Sevchenko, and D. S. Umreiko, *Doklady Akad. Nauk S.S.S.R.*, 1967, **172**, 1303; *Chem. Abs.*, 1967, **66**, 109 903k.

[38] L. V. Volod'ko, A. I. Komyak, and L. E. Sleptsov, *Optics and Spectroscopy*, 1967, **23**, 397.

[39] D. S. Umreiko, A. N. Sevchenko, and G. G. Novitskii, *Doklady Akad. Nauk Beloruss. S.S.R.*, 1968, **12**, 884; *Chem. Abs.*, 1969, **70**, 42 522x.

[40] A. I. Komyak and L. V. Volod'ko, *Vesti Akad. Navuk Beloruss. S.S.R. Ser. Fiz.-Mat. Navuk*, 1969, 115; *Chem. Abs.*, 1969, **71**, 17311r.

[41] D. N. Sanwal and D. D. Pant, *Proc. Indian Acad. Sci., Sect. A*, 1969, **69**, 324; *Chem. Abs.*, 1970, 72 7520q.

[42] C. Görller-Walrand and L. G. Vanquickenborne, *J. Chem. Phys.*, 1971, **54**, 4178.

[43] C. Görller-Walrand and L. G. Vanquickenborne, *J. Chem. Phys.*, 1972, **57**, 1436.

state, and resolved five further excited states which, whilst possessing steadily increasing oscillator strengths, were separated by an approximately constant energy gap of 6015 ± 39 cm^{-1}.

Two groups have observed absorptions in the uranyl spectrum at energies less than 20 000 cm^{-1}. Bell[44] reported very weak bands at 507.7 and 531.0 nm, which he assigned to hot bands involving transitions from the first vibrational level of the ground state to the lowest excited state. De Jaegere and co-workers[28] found a band at 555 nm in the absorption spectrum of uranyl nitrate solution under 110 kG cm^{-2} of oxygen. This, however, is believed to result from a charge-transfer transition in a uranyl–O_2 complex.

In the presence of strongly complexing species the uranyl spectrum is significantly modified.[16,17,24,42,43,45] However, the changes are predominantly in the intensities and bandwidths of the absorptions, and only slightly, if at all, in the actual positions of the bands. Such a change has been interpreted in terms of a variation of the uranyl symmetry,[16,17] and a good correlation has been observed between the vibronic fine structure and the geometry of the UO_2 co-ordination.

In addition to these transitions within the UO_2^{2+} grouping (probably involving transitions of π-electrons to progressively higher orbitals on the U atom) there is some evidence for charge-transfer-to-metal (CTTM) transitions of fairly low energy from the surrounding ligands to the central metal atom.[46,47] In particular, a study by Barnes and Day[47] showed that with $UO_2^{2+}(H_2O)_{n-1}X$ complexes ($X = Br^-, NCS^-, S_2O_3^{2-}, SO_4^{2-}, H_2O$) there are bands between *ca.* 30 000 and 50 000 cm^{-1} which, from a comparison of similar bands in cobalt complexes, are almost certainly of a charge-transfer character. As commented by Balzani and Carassiti,[3] similar CTTM transitions should be observed in complexes with organic ligands. Indeed, such transitions appear in the uranyl chloride–tributyl phosphate complex,[17] although it is not clear whether the charge transfer is from the chloride or organic part. Similarly, Heidt and colleagues have suggested that CTTM bands are present in oxalatouranium(VI) species.[48]

B. Luminescence.—Uranyl salts exhibit a highly characteristic luminescence both in the solid state and in solution. The luminescence, which is assigned to emission from the lowest excited $^3\Pi_u$ state only[24] (and is therefore strictly an example of phosphorescence, although the majority of workers adhere to the description 'fluorescence'), displays considerable vibrational structure. Bell and Biggers[24] resolved six bands in the luminescence spectrum of uranyl perchlorate in water (see Figure 4). As with the absorption spectrum, the shape and intensity of the emission spectrum are very sensitive to the particular environment of the UO_2^{2+} species. Volod'ko and co-workers found that the luminescence decay of uranyl salts in various organic solvents at low temperatures could be divided into three

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[44] J. T. Bell, *J. Mol. Spectroscopy*, 1972, **41**, 409.

[45] R. L. Belford, A. G. Martell, and M. Calvin, *J. Inorg. Nuclear Chem.*, 1960, **14**, 169.

[46] J. L. Ryan and C. K. Jørgensen, *Mol. Phys.*, 1963, **7**, 17; J. H. Miles, *J. Inorg. Nuclear Chem.*, 1965, **27**, 1595.

[47] J. C. Barnes and P. Day, *J. Chem. Soc.*, 1964, 3886.

[48] L. J. Heidt, G. W. Tregay, and F. A. Middleton, jun., *J. Phys. Chem.*, 1970, **74**, 1876.

first-order components of species with different emission spectra, assigned to different uranyl complexes.[49]

In suitable cases the luminescence quantum yield (ϕ_F) is unity,[2,50] but in solution ϕ_F decreases markedly, possibly being influenced both by physical effects (as evinced by the decrease in ϕ_F with decreasing viscosity) and by chemical reactions of the excited state.

The luminescence of uranyl salts, either in solution or in the solid state, is affected both in intensity and in lifetime by deuteriation of the ligands; for example, the replacement of H_2O by D_2O in crystals of $UO_2SO_4,3H_2O$ increases the luminescence lifetime,[50] although with $K_2UO_2(SO_4)_2,2H_2O$, deuteriation has no effect (however, ϕ_F is unity in this case). Similarly, the luminescence yield and lifetime of UO_2^{2+} in D_2O solution is 1.7—2 times greater than in H_2O.[51,52] The reason for this isotope effect is not at present clear. Three possibilities exist:

(*i*) Intramolecular radiationless deactivation of the excited state *via* the O–H stretch modes of co-ordinated water molecules. The lower frequency of the O–D stretch vibration compared with the O–H stretch allows less efficient deactivation. Similar isotope effects have been observed in radiationless processes in organic molecules.[53]

(*ii*) Intermolecular energy transfer from excited uranyl ion to vibrational modes of solvent water molecules. Thus, with the lowest state of uranyl being at 21 000 cm^{-1}, this could energy transfer to the sixth overtone of the O–H stretch, but only to the eighth or ninth overtone of the O–D stretch vibration. Similar intermolecular energy transfer to solvent vibrations has been proposed to account for solvent effects on the fluorescence lifetimes of excited rare-earth ions,[54] and singlet oxygen.[55] However, the energy of the excited state involved is considerably lower in these cases, so that the process would be expected to be more significant than with UO_2^{2+} ion.

(*iii*) Chemical deactivation of excited uranyl by hydrogen abstraction from water, *i.e.* equation (1):

$$(UO_2^{2+})^* + H_2O \rightarrow UO_2H^{2+} + \dot{O}H \qquad (1)$$

[a similar oxidation has been suggested in the photochemistry of aqueous

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[49] L. V. Volod'ko and E. A. Turetskaya, *Zhur. priklad. Spectroskopii*, 1965, **3**, 248; *Chem. Abs.*, 1966, **64**, 7548c.

[50] D. D. Pant, D. N. Pande, and H. C. Pant, *Indian J. Pure Appl. Phys.*, 1966, **4**, 289; *Chem. Abs.*, 1966, **65**, 17926g; see also D. D. Pant and H. B. Tripathi, *Indian J. Pure Appl. Phys.*, 1969, **7**, 140; *Chem. Abs.*, 1969, **70**, 92050n; and D. D. Pant and H. C. Pant, *Indian J. Pure Appl. Phys.*, 1968, **6**, 219; *Chem. Abs.*, 1968, **69**, 63314a.

[51] J. L. Kropp, *J. Chem. Phys.*, 1967, **46**, 843.

[52] R. J. Hill, T. J. Kemp, and (in part) D. M. Allen and A. Cox, *J.C.S. Faraday I*, 1974, **70**, 847.

[53] See, for example, J. B. Birks, 'Photophysics of Aromatic Molecules', Wiley, London, 1970.

[54] See, for example, Y. Haas, and G. Stein, *J. Phys. Chem.*, 1971, **75**, 3668.

[55] P. B. Merkel and D. R. Kearns, *J. Amer. Chem. Soc.*, 1972, **94**, 7244.

> cerium(IV) solutions].[56] One would expect a primary kinetic isotope effect on equation (1). No e.s.r. signal attributed to $\dot{O}H$ is observed on photolysis of uranyl perchlorate in an aqueous glass. However, under the influence of light, uranyl ion has been shown to exchange its oxygen atoms[57] with H_2O,[18] probably *via* production of the catalytic U^V.

It is not at present possible to say definitely which of these explanations is responsible for the observed isotope effect on U^{VI}. Detailed consideration of (*i*) and (*ii*) must await theoretical study on radiationless processes in inorganic complexes. It seems likely that, at least in the solid state, the intramolecular deactivation process (*i*) is involved. In solution, however, a chemical process of type (1) could easily occur. Similar hydrogen abstraction from water by the triplet states of benzophenone[58] and quinones[59] has recently been reported and may be important in photosynthesis. The failure to observe $\dot{O}H$ radicals may merely imply rapid back reaction between $\dot{O}H$ and the U^V species in the solvent cage; indeed, radiation chemical studies indicate that the reaction between U^V and $\dot{O}H$ is rapid.[60]

Whereas in water and certain other solvents the decay of the uranyl luminescence follows good first-order kinetics,[2] in certain cases, particularly in crystals under high light intensities, non-exponential decay of the luminescence is observed.[61–63] This has been attributed to formation of colour centres in the crystals.[61] Recent flash photolysis experiments in glasses[64,65] and in solutions[52,66,67] have shown that the lowest excited state of UO_2^{2+} possesses absorptions in the visible and near-i.r. regions. For example, flash photolysis of a 2×10^{-2} M solution of uranyl perchlorate in water yields a transient absorption

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[56] J. J. Weiss and D. Porret, *Nature*, 1937, **139**, 1019; in this case, however, the photo-oxidation is suggested to proceed *via* electron transfer from water co-ordinated to Ce^{IV}.

[57] G. Gordon and H. Taube, *J. Inorg. Nuclear Chem.*, 1961, **16**, 272.

[58] M. B. Ledger and G. Porter, *J.C.S. Faraday I*, 1972, **68**, 539.

[59] K. C. Kurien and P. A. Robins, *J. Chem. Soc. B*, 1970, 855 and references therein.

[60] V. G. Firsov, *Doklady Akad. Nauk S.S.S.R.*, 1961, **138**, 1155; *Chem. Abs.*, 1962, **56**, 12459h.

[61] N. A. Tolstoi, A. P. Abramov, and I. N. Abramova, *Optics and Spectroscopy*, 1966, **20**, 415.

[62] A. M. Bonch-Bruevich, E. N. Kaliteevskaya, G. O. Karapetyan, V. P. Kolobkov, P. I. Kudryashov, T. K. Razumova, and A. L. Reishakhrit, *Optics and Spectroscopy*, 1969, **27**, 433.

[63] N. A. Tolstoi, A. P. Abramov, and I. N. Abramova, *Proc. Int. Conf. Lumin.*, 1969 (Publ. 1970), 330, ed. F. Williams, North-Holland, Amsterdam; *Chem. Abs.*, 1971, **74**, 17705.

[64] C. C. Robinson, *J. Opt. Soc. Amer.*, 1967, **57**, 4; *U.S. Dept. Comm. A.D.* 624361 (1965) (*Chem. Abs.*, 1967, **67**, 16387a); L. A. Cross and L. G. Cross, *Proc. I.E.E.E.*, 1966, **54**, 1460.

[65] N. A. Tolstoi, I. N. Abramova, and A. P. Abramov, *Optics and Spectroscopy*, 1969, **26**, 314; I. N. Abramova, A. P. Abramov, and N. A. Tolstoi, *ibid.*, 1969, **27**, 293; V. P. Gapontsev, E. I. Galant, M. E. Zhabotinskii, Y. P. Rudnitskii and E. I. Sverchkov, *Int. Conf. Microwaves Opt. Generation Amplification*, [*Proc.*], *Eighth Meeting*, 1970 (publ. 1971), 13/22; *Chem. Abs.*, 1973, **78**, 36076d.

[66] L. N. Rygalov, A. K. Chibisov, A. V. Karyakin, E. V. Bezrogova, B. F. Myasoedev, and A. A. Nemodruk, *Teor. i eksp. Khim.*, 1972, **8**, 484; *Chem. Abs.*, 1973, **78**, 130520r; G. Sergeeva, A. Chibisov, L. Levshin, and A. Karyakin, *J.C.S. Chem. Comm.*, 1974, 159.

[67] D. M. Allen, H. D. Burrows, A. Cox, R. J. Hill, T. J. Kemp, and T. J. Stone, *J.C.S. Chem. Comm.*, 1973, 59.

(Figure 3) with $\lambda_{max} \sim$ 590 nm, which is completely formed within the pulse of 50 ns from a frequency-doubled ruby laser.[52,67] The decay of this absorption (k_1 = 8.02 × 10^5 s^{-1}) parallels the decay of the luminescence as determined by single-photon counting (k_1 = 3.85 × 10^5 s^{-1})[52] and similar parallels are found for the analogous absorptions and emissions in H_2SO_4 and aqueous H_3PO_4[52,67] and rigid silicate glass solutions.[62] Vibronic structure is perceptible in most of these absorptions, *e.g.* with average band separations of 580 cm^{-1} in fluid solution[52] and 700 ± 30 cm^{-1} in U^{VI}-doped glasses.[62] The identification of the electronic level *from* which the 590 nm absorption takes place with that from which emission occurs is confirmed by the identical quenching action of methanol and [$^2H_3$]methanol upon the kinetics of both processes (Table 1).[52] This implies a triplet energy level scheme of the type shown in Figure 4. Reabsorption of uranyl luminescence by the $^3\Pi_u$ state under high-intensity excitation could account for both the observed non-exponential decay and the failure to observe significant laser action in uranyl glasses.[68] In addition, this excited-state absorption may act as an *internal* Q-switch in uranyl–Nd^{3+} glasses,[69] although the occurrence of uranium(v) impurity centres cannot be ruled out.[70]

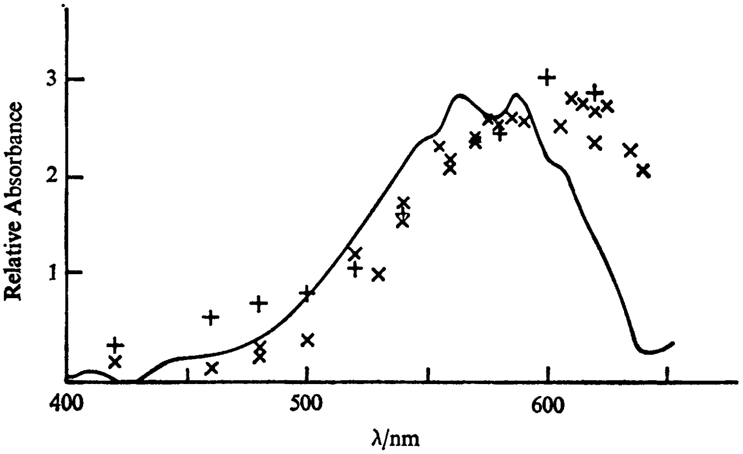

Figure 3 *Flash photolysis spectra of aqueous solutions of uranyl salts. Full line—spectrographic recording of absorption from* 2 × 10^{-2} M *uranyl perchlorate following* μs *flash*; X—*photoelectrically recorded absorptions on laser flashing* 2 × 10^{-2} M *uranyl perchlorate*, +—*analogous experiments with uranyl nitrate* (*from ref.* 67).

A curious and, as yet, unexplained fact is that the uranyl excited state can be

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[68] O. Risgin, *U.S. Dept. Comm. A.D.* 470360 (1965); *Chem. Abs.*, 1967, **67**, 16650f; H. Hartmann, G. Nitschmann, and G. Scharmann, *Z. angew. Phys.*, 1968, **24**, 69.

[69] N. T. Melamed, C. Hirayama, and P. W. French, *Appl. Phys. Letters*, 1965, **6**, 43.

[70] C. B. Greenberg and P. W. French, *J. Opt. Soc. Amer.*, 1968, **58**, 472.

Table 1 *Absolute rate constants and isotope effects for the interaction between* $(UO_2^{2+})^*$ *and alcohols measured by laser flash photolysis* (*ref.* 52)

Alcohol	*Medium*	$10^{-6}k_2/\mathrm{l\ mol^{-1}\ s^{-1}}$	$k_{C-H/C-D}$	$k_{O-H/O-D}$
CH_3OH	H_2O	6.40 ± 0.08 (k_I)	$k_I/k_{II} = 2.76$	$k_I/k_{III} = 0.98$
CD_3OH	H_2O	2.32 ± 0.10 (k_{II})		
CH_3OD	D_2O	6.50 ± 0.19 (k_{III})	$k_{III}/k_{IV} = 2.39$	$k_{II}/k_{IV} = 0.85$
CD_3OD	D_2O	2.72 ± 0.04 (k_{IV})		
$(CH_3)_2CHOH$	H_2O	85.3 ± 0.5	2.41	
$(CH_3)_2CDOH$	H_2O	35.4 ± 0.9		
cyclo-$C_6H_{11}OH$	H_2O	294 ± 9	2.31	
cyclo-$C_6D_{11}OH$	H_2O	127 ± 3		

excited by electrolysis[71] or radiolysis[72] of uranyl solutions, as indicated by the resultant characteristic luminescence.

C. Energy Transfer.—A number of studies have been performed on energy transfer involving the UO_2^{2+} ion,[73–85] with particular relevance to the use of

[71] V. P. Kazakov, *Zhur. fiz. Khim.*, 1965, **39**, 2936; *Chem. Abs.*, 1966, **64**, 12195e.

[72] C. Gopinathan, G. Stevens, and E. J. Hart, *J. Phys. Chem.*, 1972, **76**, 3698.

[73] G. I. Kobyshev, G. N. Lyalin, and A. N. Terenin, *Doklady Akad. Nauk S.S.S.R.*, 1963, **148**, 1294; *Chem. Abs.*, 1963, **59**, 127d.

[74] G. N. Lyalin and G. I. Kobyshev, *Optics and Spectroscopy*, 1963, **15**, 135.

[75] H. W. Gandy, R. J. Ginther, and J. F. Weller, *Appl. Phys. Letters*, 1964, **4**, 188; NASA Accession No. N64-27523, Rept. No. AD 441832, 1964; *Chem. Abs.*, 1965, **62**, 3777h; *Appl. Phys. Letters*, 1965, **6**, 46; *Rep. NRL Progr.*, 1966, 1; *Chem. Abs.*, 1967, **66**, 100095r; L. G. DeShazer and A. Y. Cabezas, *Proc. I.E.E.E.*, 1964, **52**, 1355; A. Kitamura, *J. Phys. Soc. Japan*, 1965, **20**, 1283; M. E. Zhabotinskii, Y. P. Rudnitskii, V. V. Tsapkin, and G. V. Ellert, *Zhur. exp. teor. Fiz.*, 1965, **49**, 1689; *Chem. Abs.*, 1966, **64**, 12058h; M. J. Vogel, U.S. P., 3 265 628/1966; *Chem. Abs.*, 1966, **65**, 13000b; Y. I. Krasilov, Y. A. Polyakov, and Y. P. Rudnitskii, *Izvest. Akad. Nauk S.S.S.R. Neorg. Materialy*, 1966, **2**, 2186; *Chem. Abs.*, 1967, **66**, 89910e; M. T. Artamonova, C. M. Briskina, and V. F. Zolin, *Zhur. priklad. Spektroskopii*, 1967, **6**, 112; *Chem. Abs.*, 1967, **67**, 59134.

[76] A. Y. Cabezas and L. G. DeShazer, U.S. P. 3 417 345/1968; *Chem. Abs.*, 1969, **70**, 42797r.

[77] M. V. Artamonova, C. M. Briskina, V. F. Zolin, and N. M. Noginova, 'Proceedings of International Conference on Luminescence', 1966 (publ. 1968), Vol. 2, p. 1699, ed. G. Szigeti, Akad. Kiado, Budapest; *Chem. Abs.*, 1969, **70**, 52786a; N. S. Belokrinitskii, M. E. Zhabotinskii, A. D. Manulskii, Y. P. Rudnitskii, M. S. Soskin, V. V. Tspakin, and G. V. Ellert, *Doklady Akad. Nauk S.S.S.R.*, 1969, **185**, 557; *Chem. Abs.*, 1969, **70**, 119857v; G. M. Gaevoi, M. E. Zhabotinskii, Y. I. Krasilov, Y. P. Rudnitskii, and G. V. Ellert, *Izvest. Akad. Nauk Arm. S.S.R., Fiz.*, 1968, **3**, 431; *Chem. Abs.*, 1969, **71**, 34378k; N. E. Alekseev, I. M. Buzhinskii, V. P. Gapontsev, M. E. Zhabotinskii, Y. P. Rudnitskii, V. V. Tspakin, and G. V. Ellert, *Izvest. Akad. Nauk S.S.S.R., Neorg. Materialy*, 1969, **5**, 1042; *Chem. Abs.*, 1969, **71**, 54715w.

[78] G. Blasse, *J. Electrochem. Soc.*, 1968, **115**, 738.

[79] M. V. Hoffman, *J. Electrochem. Soc.*, 1970, **117**, 227.

[80] F. J. Avella, U.S. P. 3 586 634/1971; *Chem. Abs.*, 1971, **75**, 69455t.

[81] N. M. Pavlushkin, M. V. Artamonova, C. M. Briskina, and G. V. Leuta, *Steklo*, 1971, **1**, 32; *Chem. Abs.*, 1971, **75**, 114430u.

[82] B. M. Antipenko and V. L. Ermolaev, *Izvest. Akad. Nauk S.S.S.R., Ser. fiz.*, 1968, **32**, 1504; *Chem. Abs.*, 1969, **70**, 15730g.

(*refs. 83—85 overleaf*)

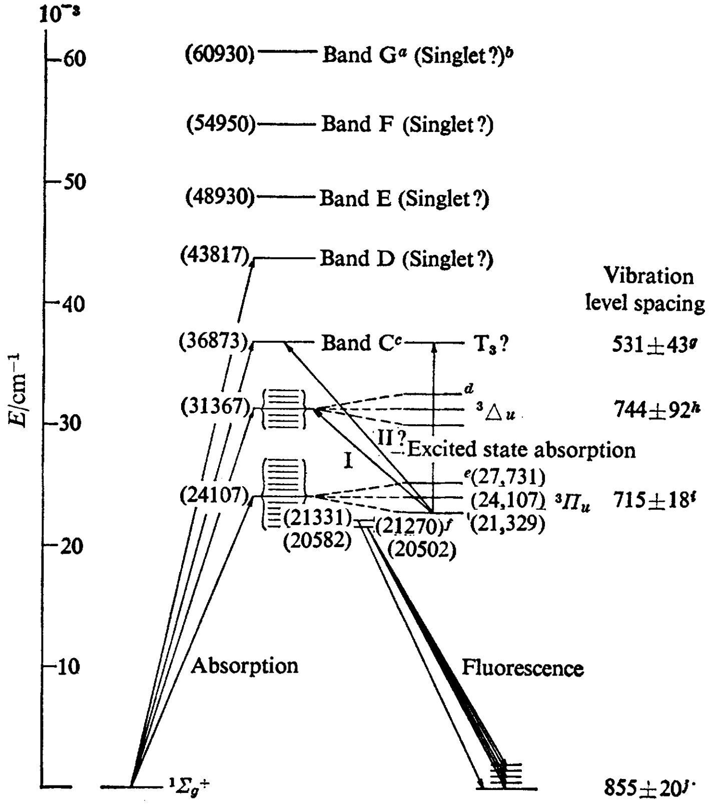

Figure 4 *Energy level diagram from* UO_2^{2+} *ion (based on the data and assignments of Bell and Biggers, refs.* 24 *and* 31)

[a] Nomenclature of u.v. bands of Bell and Biggers (ref. 31).

[b] Multiplicity suggested by Bell and Biggers.

[c] Band C displays no vibrational structure in absorption and is regarded by Bell and Biggers as a member of the (singlet) series C to G which are separated by a constant spacing of 6015 ± 39 cm^{-1}. This level may be degenerate with a triplet level (denoted T_3) which does display vibronic structure following excitation from the ground triplet state $^3\Pi_u$ with λ_{max} 574 nm (17 420 cm^{-1}); the latter absorption indicates T_3 to be positioned at 38 750 cm^{-1}, *i.e.* very near to band C at 36 873 cm^{-1}. That T_3 is triplet in character is suggested by the strong extinction of the 574 nm absorption which is clearly highly allowed. The transition depicted as I (of 10 038 cm^{-1}) may be the origin of the near-i.r. absorption band found in the flash photolysis spectra of uranyl-doped silicate glasses (ref. 62).

[d,e] The groups of levels centred around 31 367 and 24 107 cm^{-1} are regarded as triplet states $^3\Delta_u$ and $^3\Pi_u$ respectively by Bell and Biggers (ref. 31) and McGlynn and Smith (ref. 7).

[f] Assignments due to Bell and Biggers (ref. 31); emission from the 21 270 cm^{-1} level is only 4.66% of the total.

[g] Data from μs flash photolysis absorption (ref. 52).

[h,i] Fine structure due to symmetric stretching frequency in the excited state (ref. 31).

[j] Fine structure due to symmetric stretching frequency in the ground state (ref. 31).

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[83] L. I. Kononenko, N. S. Poluektov, and L. M. Burtnenko, *Optics and Spectroscopy*, 1967, **23**, 321; *Chem. Abs.*, 1968, **68**, 55191x.

[84] L. M. Burtnenko, L. I. Kononenko, and N. S. Poluektov, *Monokrist, Stsintill Org. Lyuminofory*, 1968. **4**, 246; *Chem. Abs.*, 1970, **74**, 117990g.

[85] R. Matsushima, *Chem. Letters*, 1973, 115.

UO_2^{2+} in laser systems. For example, intramolecular energy transfer has been observed from organic ligands to the uranyl ion,[83,84] whilst the latter has been shown to transfer energy to tervalent lanthanide ions in both the solid state[73–81] and solution.[51,82] Energy transfer to phthalocyanine has also been observed.[73,74] UO_2^{2+} has recently been shown to photosensitize the aquation of hexacyanocobaltate(III) ion in aqueous solution,[85] presumably *via* energy transfer to the lowest ligand field state of the Co^{III} complex.

4 Solution Photochemistry of UO_2^{2+}

UO_2^{2+} possesses a rather low redox potential ($UO_2^{2+} + e^- = UO_2^+$; $E^0 = +0.05$ V)[86] and thermal oxidations are normally comparatively slow.[87] The important processes in the photochemistry of uranyl systems are (*i*) oxidation of ligands or other species present in solution (including the solvent), usually, but not invariably, with accompanying net reduction of the uranium to U^{IV} and (*ii*) in the presence of oxygen, sensitized oxidations[2] which depend on regeneration of U^{VI} by autoxidation of reduced states of uranium. Both of these processes are thought to proceed *via* the intermediacy of U^V species. Rabinowitch and Belford[2] classified the oxidations into two types, *i.e.*

(*i*) those proceeding *via* excitation of cluster complexes between uranyl and the oxidizing species, and

(*ii*) those involving a kinetic encounter between $(UO_2^{2+})^*$ and the substrate.

We have found it convenient to use a slightly different division of the reaction types, set out below as A (excitation of complexes), B (intermolecular abstraction of a hydrogen atom), C (intermolecular electron transfer), and D (energy transfer).

A. Excitation of Complexes.—UO_2^{2+} ion readily forms complexes with a variety of ligands, including organic acids and inorganic ions. When a variety of carboxylate ions are added to solutions of uranyl ion, there is a modification in the shape and intensity of the spectrum.[17] As with inorganic ligands, this may well result from a charge-transfer transition from the ligand to the metal ion (CTTM). In all cases photolysis destroys the ligand, but there are differences from acid to acid, and we shall present the results *seriatim*.

(*i*) *Oxalic acid.* There have been a very large number of individual studies of this system,[2,5,48,88,89] particularly because of its former near-universal use as a chemical actinometer, although most contemporary groups prefer that based on potassium ferrioxalate.[90] The uranyl oxalate system is normally based on measurement of oxalate destroyed, but an ingenious development depends on the sensitive g.l.c. determination of CO released[91] (after conversion into CH_4).[92]

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[86] W. M. Latimer, 'Oxidation Potentials', 2nd edn., Prentice-Hall Inc., New York, 1952, Chapter 21.

[87] T. W. Newton and F. B. Baker, *Adv. Chem. Ser.*, No. 71, 1967, p. 268.

[88] D. H. Volman and J. R. Seed, *J. Amer. Chem. Soc.*, 1964, **86**, 5095.

[89] C. A. Discher, P. F. Smith, I. Lippman, and R. Turse, *J. Phys. Chem.*, 1963, **67**, 2501.

[90] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.*, 1956, **A235**, 518.

[91] K. Porter and D. H. Volman, *J. Amer. Chem. Soc.*, 1962, **84**, 2011.

[92] K. Porter and D. H. Volman, *Analyt. Chem.*, 1962, **34**, 748.

Studies by a number of techniques suggest that the main complexes present in aqueous solution in the pH range 1—7 are the mono- and bis-oxalato-species.[48] Unlike many other uranyl complexes, photodecomposition of the oxalato-uranium(VI) complex involves little net reduction of U^{VI} (unlike the ferrioxalate system[90] where $\phi[Fe^{II}]$ is high). The chief pathways are (2) and (3),

$$UO_2^{2+} + HO_2CCO_2H \xrightarrow{h\nu} UO_2^{2+} + CO_2 + CO + H_2O \qquad (2)$$

$$UO_2^{2+} + HO_2CCO_2H \xrightarrow{h\nu} UO_2^{2+} + CO_2 + HCO_2H \qquad (3)$$

and the redox breakdown (4) is very minor

$$UO_2^{2+} + HO_2CCO_2H \xrightarrow{h\nu} UO_2H^+ \ (\textit{i.e.}\ U^{IV}) + H^+ + 2CO_2 \qquad (4)$$

The ratio $\phi_2{:}\phi_3$ is determined by pH:[48] whereas (2) accounts for *ca.* 96% of all photodecomposition of oxalate at pH 0, at pH 3 and 7 this figure has fallen to 25% and zero respectively. CO_2 production is pH-invariant and $\phi[U^{IV}]$ increases slowly from pH 2 to pH 6, but is always low (*i.e.* between 0.0023 and 0.0063) but depends somewhat on $[U^{IV}]$.[48,93] Disregarding reaction (4) means that we are dealing with an apparent 'sensitization' reaction[2] whereby although U^{VI} is instrumental in absorbing the radiation, probably *via* a CTTM transition to give a U^V species (I) in reaction (5), the U^V is reconverted into U^{VI} rather than undergoing disproportionation to $U^{VI} + U^{IV}$.

$$(UO_2^{2+}\cdot C_2O_4^{2-}) \rightarrow \underset{\text{(I)}}{[U^V\cdot CO_2\bar{\cdot}]} + CO_2 \qquad (5)$$

The 'complexed radical' (I) acts as the source of formate at high pH by a reversal of the electron transfer (6),

$$[U^V\cdot CO_2\bar{\cdot}] + H_2O \rightarrow [U^{VI}\cdot HCO_2^-] + OH^- \qquad (6)$$

At low pH, the replacement of HCO_2^- by CO as coprincipal product with CO_2 must lie in an alternative acid-catalysed breakdown (7):

$$[U^V\cdot CO_2\bar{\cdot}] + H_3O^+ \rightarrow UO_2^{VI}OH^+ + HCO^+ \qquad (7)$$

(the formatouranyl complex itself is not decomposed at these acidities to give CO).

The quantum yield for oxalate disappearance shows a small but definite sensitivity to the wavelength of the irradiation:[89] for example $\phi(365.5\text{ nm}) = 0.492$ whereas $\phi(435.8\text{ nm}) = 0.573$ (both ± 0.002).

Two pieces of physical evidence provide support for a long-lived intermediate in this photoreaction: Parker and Hatchard have detected a long-lived but reversible optical absorption on flash photolysis of a U^{VI}-oxalate solution containing excess oxalic acid.[94] Photolysis at 77 K of concentrated aqueous oxalic

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[93] J. J. McBrady and R. Livingston, *J. Phys. Chem.*, 1946, **50**, 176.

[94] C. A. Parker and C. G. Hatchard, *J. Phys. Chem.*, 1959, **63**, 22.

acid containing uranyl perchlorate[95] yielded an e.s.r. signal displaying no hyperfine splitting but *g*-factor anisotropy with the average *g*-factor of 2.0044, which is rather high for free $CO_2^{\cdot-}$ radicals. However, in the neighbourhood of a metal atom, the value typical of free σ-radicals is likely to be increased to perturbation effects,[96] consistent with an assignment to (I).

(*ii*) *Benzilic acid.* The only product which could be identified by thin-layer chromatography was benzophenone.[97] In addition some gas (probably CO_2) is evolved. Further information on the mechanism in this case has come from e.s.r. and flash photolysis studies.[98] Upon intense photolysis of cold ethanolic benzilic acid and uranyl perchlorate in the cavity of an e.s.r. spectrometer, the e.s.r. spectrum of the diphenylketyl radical ($Ph_2\dot{C}OH$) is observed. Similarly, upon μs flash photolysis of either aqueous or ethanolic solutions of uranyl ion and benzilic acid, the very well-known spectrum of the ketyl radical is observed immediately after the flash (Figure 5). This can readily be interpreted in terms of a CTTM transition leading to oxidation of the acid. The resulting species is expected to decarboxylate very rapidly ($k_1 = 10^9$—10^{10} s^{-1})[99] to give the observed ketyl radical (8) and (9) (the two steps may possibly be concerted as the carboxyl radical is likely to be formed in an energy-rich state):

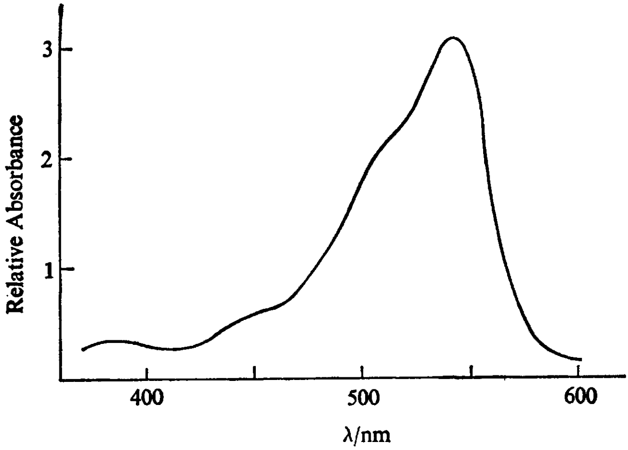

Figure 5 *Flash photolysis spectrum obtained from a solution in ethanol of* 2 mM *uranyl perchlorate and* 2 mM *benzilic acid using* $\lambda > 300$ nm *and attributed to the radical* $Ph_2\dot{C}(OH)$ (*from ref.* 98)
(Reproduced by permission from *J. Amer. Chem. Soc.*, 1971, **93**, 2539)

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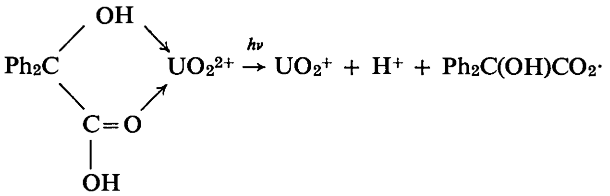
[95] D. Greatorex, R. J. Hill, T. J. Kemp, and T. J. Stone, *J.C.S. Faraday I*, 1972, **68**, 2059.
[96] P. W. Atkins, N. Keen, and M. C. R. Symons, *J. Chem. Soc.*, 1962, 2873.
[97] H. D. Burrows and T. J. Kemp, unpublished observations.
[98] H. D. Burrows, D. Greatorex, and T. J. Kemp, *J. Amer. Chem. Soc.*, 1971, **93**, 2539.
[99] L. Herk, M. Feld, and M. Szwarc, *J. Amer. Chem. Soc.*, 1961, **83**, 2998.



(8)

$$Ph_2C(OH)CO_2^{\cdot} \rightarrow Ph_2\dot{C}OH + CO_2 \qquad (9)$$

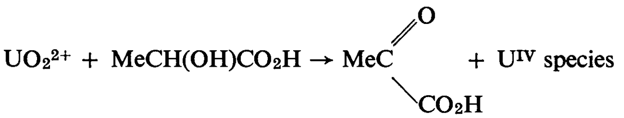
Under high metal-ion concentrations, the ketyl radical is then oxidized to the observed product, benzophenone (10):

$$Ph_2\dot{C}OH + UO_2^{2+} \rightarrow Ph_2CO + UO_2H^{2+} \qquad (10)$$

This is similar to the photo-oxidations both of benzilic acid by 'paraquat'[100] and of 2-hydroxyisobutyric acid by U^{VI} to acetone and U^{IV}.[101]

(*iii*) *Lactic acid.* Here the extent to which oxidative decarboxylation occurs depends on the medium; thus photolysis of solutions of uranyl nitrate and lactic acid in aqueous solution at high pH levels leads to the formation of acetaldehyde and carbon dioxide (11), whereas at low pH the organic product is pyruvic acid (12);[102] in both pathways U^{IV} is produced in stoicheiometric proportions.

$$UO_2^{2+} + MeCH(OH)CO_2H \xrightarrow{pH > 3.5} MeCHO + U^{IV}\text{ species} \qquad (11)$$



$$UO_2^{2+} + MeCH(OH)CO_2H \rightarrow MeC(=O)CO_2H + U^{IV}\text{ species} \qquad (12)$$

This result is readily interpreted in terms of the species present. At high pH, the spectra indicate that lactate anion is complexed to U^{VI} and decarboxylation can occur to yield initially the $Me\dot{C}HOH$ radical which is further oxidized to acetaldehyde. However, at low pH the extent of complexation is much less, and the photochemical reaction is intermolecular hydrogen atom abstraction by excited uranyl to yield the $Me\dot{C}(OH)CO_2H$ radical, which yields pyruvic acid on further oxidation. In support of this view, e.s.r. studies on frozen lactic acid solutions of U^{VI} at 77 K confirm the presence of these radicals at pH 7 and pH 1 respectively (although at pH 7 a small quantity of $Me\dot{C}(OH)CO_2H$ radical is also observed).[95] Kemp *et al.*[67] report a preliminary figure for the rate constant of U^{VI*} attack upon lactic acid of $9.8 \times 10^6\ l\ mol^{-1}\ s^{-1}$ at pH 1.5 using laser flash photolysis.

(*iv*) *Acetic acid and its homologues and dicarboxylic acids.* Heckler *et al.*[103] have

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[100] J. R. Barnett, A. S. Hopkins, and A. Ledwith, *J.C.S. Perkin II*, 1973, 80.

[101] K. Pan and W.-K. Wong, *J. Chinese Chem. Soc.* (*Taiwan*), Ser. II, 1961, **8**, 1; *Chem. Abs.*, 1962, **57**, 3003g.

[102] S. Sakuraba and R. Matsushima, *Bull. Chem. Soc. Japan*, 1970, **43**, 1950.

[103] G. E. Heckler, A. E. Taylor, C. Jensen, D. Percival, R. Jensen, and P. Fung, *J. Phys. Chem.*, 1963, **67**, 1.

carefully determined the gaseous products of anaerobic photolysis of a number of carboxylic acids and di-acids in the presence of UO_2^{2+} ion at pH values of 0.6—1.8, confirming the conclusion of earlier workers that the principal reaction is decarboxylation, *viz.*

$$RCH_2CO_2H \xrightarrow[UO_2^{2+}]{h\nu} RCH_3 + CO_2 \qquad (13)$$

Several dicarboxylic acids were selected for detailed micromanometric study (CO_2 being then the sole gaseous product) and it was found

(*i*) that there is a general increase in the rate of CO_2 evolution with increase of pH, and

(*ii*) that this rate is dependent on the concentrations of mono-ionized acid for succinic and glutaric acids and of di-ionized acid for malonic acid.

These observations imply that U^{VI}–anion complexes are the photoreactive species: at high ($\sim$10 mM) concentrations of acid anion (or dianion) the rate reaches a plateau value corresponding to essentially complete complexation of UO_2^{2+}. Absorbence measurements of U^{VI}–substrate solutions indicate the stoicheiometric compositions of the complexes to be $U^{VI}\cdot(HO_2CCH_2CH_2CO_2^-)_2$ and $U^{VI}\cdot(O_2CCH_2CO_2^-)$. Unfortunately these authors record no yields for U^{VI}, but the net reaction (13) as written involves no consumption of oxidant. Consequently, if the first step *is* one of oxidative decarboxylation of the type effected by Ce^{IV} and Pb^{IV} under irradiation, then the radical resulting from reaction (14)

$$U^{VI}\cdot RCH_2CO_2H \rightarrow U^{V}\cdot R\dot{C}H_2 + CO_2 + H^+ \qquad (14)$$

might back-react with U^V (as in the case of oxalic acid) to give RCH_2^- and thence RCH_3 (the course with Ce^{IV} and Pb^{IV} is that $RCH_2^{\cdot}$ is oxidized by a second equivalent of oxidant to yield $R\overset{+}{C}H_2$ and thence RCH_2OH). Left to itself $RCH_2^{\cdot}$ can either dimerize to RCH_2CH_2R (the dimeric product is not normally found, although there exists an early report of C_2H_6 as a major product in the U^{VI}-sensitized decomposition of acetic acid which has not been subsequently confirmed), or possibly attack further acid, especially at high substrate concentrations:

$$RCH_2 + RCH_2CO_2H \rightarrow RCH_3 + R\dot{C}HCO_2H \qquad (15)$$

The product from dimerization of $R\dot{C}HCO_2H$ is not, however, recorded in investigations that we are aware of.

E.s.r. work indicates that reaction (14) does not appear to operate significantly for 'neat' solutions at 77 K;[95] photolysis of frozen solutions of U^{VI} in neat substrate yields e.s.r. spectra of the radical corresponding to abstraction of a hydrogen atom from carbon adjacent to the CO_2H group for the following acids: acetic, propionic, isobutyric, cyclobutanecarboxylic, and cyclohexanecarboxylic. (The alkyl radical *is* obtained during photo-oxidation by Ce^{IV} under these reaction conditions.)[104] However, the alkyl radical expected from step (14) *is* found

[104] D. Greatorex and T. J. Kemp, *Trans. Faraday Soc.*, 1971, **67**, 1576.

with succinic and trifluoroacetic acids, and in the case of acetic acid both $CH_3\cdot$ and $\cdot CH_2CO_2H$ are found at 77 K, although only the latter radical survives on warming to 140 K. Irradiation of solutions of U^{VI} in neat acetic and propionic acids at 293 and 255 K respectively[105] gave well-resolved signals of $\cdot CH_2CO_2H$ and $CH_3\dot{C}HCO_2H$ in conformity with the low-temperature data. It is possible that the abstraction of an α-hydrogen atom is predominant in highly concentrated solutions whereas decarboxylation is more important in dilute aqueous solution—such a complete change in mechanism with solvent composition has been established for the U^{VI*}–methanol system (see below). Another possibility is that the entity $U^{V}\cdot R\dot{C}H_2$ in (14) is too labile even at 77 K for e.s.r. detection and that the e.s.r. signals detected refer to a relatively minor reaction pathway.

With certain other systems containing U^{VI}, an intramolecular CTTM mechanism is also likely. Thus on photolysis of uranyl iodide complexes[2,3] iodine formed may well arise from process (16), which is followed by steps (17) and (18):

$$UO_2I^+ \rightarrow UO_2^+ + I\cdot \qquad (16)$$

$$I\cdot + I^- \rightarrow I_2^{\cdot -} \qquad (17)$$

$$2I_2^{\cdot -} \rightarrow I_2 + 2I^- \qquad (18)$$

It appears that a photostationary equilibrium is attained in this system[2,3] between the reactants and U^{IV} and I_2. Wan and colleagues[106] find that irradiation of aqueous tetrabutylammonium iodide yields a black precipitate of tributyliodoammonium iodide $(C_4H_9)_3IN^+I^-$ without loss of U^{VI}, and a sensitization mechanism is invoked.

Recent studies featuring spin-trapping of radicals by benzylidene nitrone and t-nitrosobutane have shown that on photolysis of uranyl nitrate in methanol solution the immediate product radical is methoxyl ($CH_3O\cdot$).[107] This can then abstract a hydrogen from solvent methanol to yield $\cdot CH_2OH$, the radical observed upon photolysis in a glass at 77 K. The reaction can most readily be interpreted in terms of a CTTM transition from co-ordinated methanol to the U atom. The reaction, however, shows a marked solvent sensitivity. Upon photolysis of uranyl nitrate in 2:1 (v/v) water–methanol, the only radical detectable by spin-trapping is $\cdot CH_2OH$.[107] Possibly in this case only water is co-ordinated to the uranyl, such that an intermolecular mechanism must be involved (see later).

B. Intermolecular Abstraction of a Hydrogen Atom by U^{VI*}.—The quenching of the U^{VI} emission by a number of alcohols, as measured by the Stern–Volmer quenching constant K_{SV}[108–111] correlates very well with the corresponding

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[105] D. Greatorex, R. J. Hill, T. J. Kemp, and T. J. Stone, *J.C.S. Faraday I*, 1974, **70**, 216.

[106] J. K. S. Wan, E. A. Schuck, J K Foote, and J. N. Pitts, jun., *Canad. J. Chem.*, 1964, **42**, 2029.

[107] A. Ledwith, R. J. Russell, and L. H. Sutcliffe, *Proc. Roy. Soc.*, 1973, **A332**, 151.

[108] S. Sakuraba and R. Matsushima, *Bull. Chem. Soc. Japan*, 1970, **43**, 2359.

[109] S. Sakuraba and R. Matsushima, *Bull. Chem. Soc. Japan*, 1971, **44**, 2915.

[110] R. Matsushima and S. Sakuraba, *J. Amer. Chem. Soc.*, 1971, **93**, 5421.

[111] R. Matsushima, *J. Amer. Chem. Soc.*, 1972, **94**, 6010.

quantum yield[108,110,111] for the photo-oxidations determined by $\phi(U^{IV})$. Again, the *absolute* rate constants for the quenching of U^{VI} emission by CH_3OH and CD_3OH and other similar pairs of alcohols agree with those for the rates of decay of the 590 nm absorption of U^{VI*} in the presence of these added substrates[52] (Table 1). These observations imply that the quenching of U^{VI} luminescence is both chemical and collisional in nature, *viz.*

$$UO_2^{2+} \xrightarrow{h\nu} (UO_2^{2+})^* \qquad (19)$$

$$(UO_2^{2+})^* \xrightarrow{k_{nr}} UO_2^{2+} \qquad (20)$$

$$(UO_2^{2+})^* \xrightarrow{k_f} UO_2^{2+} + h\nu \qquad (21)$$

$$(UO_2^{2+})^* + RCH_2OH \xrightarrow{k_q} UO_2^{2+} + R\dot{C}HOH + H^+_{solv} \qquad (22)$$

where the subscripts refer to non-radiative, fluorescent, and quenching pathways respectively.

k_q implies a 'kinetic encounter' between $(UO_2^{2+})^*$ and the alcohol, of the type proposed by Rabinowitch and Belford.[2] That the quenching act involves intermolecular hydrogen abstraction primarily from a C–H bond of the hydroxylated carbon atom is strongly suggested by the following evidence.

(i) *Luminescence quenching*. For the series of alcohols methanol, ethanol, propan-2-ol and t-butyl alcohol, the quenching increases rapidly with the first three (with K_{SV} values of 12, 60, and 113 l mol^{-1} respectively[110]) as anticipated from the progressive reduction of the relevant C–H bond energies, but falls off sharply with t-butyl alcohol with $K_{SV} = 5$ l mol^{-1} (all K_{SV} measured at 293 K). Again substitution at the weakest bond by deuterium reduces both the value of K_{SV} and the photoreactivity of the alcohol as determined by U^{IV} production (Table 2).

(ii) *Quenching of emission lifetime*. The emission of UO_2^{2+} in water ($k_1 = 3.85 \times 10^5$ s^{-1}) is systematically reduced on addition of either CH_3OH or CD_3OH,[52] yielding second-order rate constants for the quenching process of $k(CH_3OH) = 4.48 \pm 0.08) \times 10^6$ l mol^{-1} s^{-1} and $k(CD_3OH) = (1.73 \pm 0.13) \times 10^6$ l mol^{-1} s^{-1} with $k_H/k_D = 2.59 \pm 0.24$.

(iii) *Quenching of the excited-state absorption of* U^{VI}. The characterization of the absorption spectrum of excited UO_2^{2+} ion (see above) affords a convenient direct method of determination of rate constants of its reactions utilizing laser flash photolysis. Data exist for the photo-oxidation of three alcohols, including some in D_2O for methanol[52] (Table 1).

(iv) *E.s.r. spectra of irradiated glassy and liquid alcoholic solutions of* U^{VI}. Irradiated glassy solutions of U^{VI} in alcohols at 77 K yield e.s.r. spectra[95] of $R\dot{C}HOH$ in the case of primary alcohols except for n-propanol (see later), but with secondary alcohols C–C cleavage occurs: propan-2-ol gives $CH_3^{\cdot}$ and butan-2-ol and pentan-3-ol both give $\cdot C_2H_5$. 2-phenylethanol gives the spectrum

Table 2 *Isotope effects on the Stern–Volmer quenching constants and quantum yields for* U^{IV} *production in the interaction between* $(UO_2^{2+})^*$ *and alcohols in aqueous solution*

Alcohol	K_{SV}[a]	K^H_{SV}/K^D_{SV}[a]	$\phi^H_{U^{IV}}/\phi^D_{U^{IV}}$[b]
CH_3OH	5.26	2.76	—
CD_3OH	1.90		
CH_3CH_2OH	60	2.06	2.21
CD_3CD_2OH	29		
$(CH_3)_2CHOH$	113	2.76	1.94
$(CH_3)_2CDOH$	41		
cyclo-$C_6H_{11}OH$	369	2.30	
cyclo-$C_6D_{11}OH$	160		

[a] Data from Ref. 52; [b] data from Ref. 110.

of $C_6H_5CH_2\cdot$; in this connection it is interesting to note that Ledwith *et al.*[107] spin-trapped both benzyl radical and 2-phenylethanoxyl radical $PhCH_2CH_2O\cdot$ during peroxydisulphate oxidation of 2-phenylethanol. The latter radical is considered to fragment, *viz.*

$$PhCH_2CH_2O\cdot \rightarrow PhCH_2\cdot + CH_2{=}O \qquad (23)$$

C–C cleavage is, as expected, the principal route with tertiary alcohols at 77 K:

Substrate	*Principal Radical*
$(CH_3)_3COH$	$\cdot CH_3$
$(CH_3)_2CHC(CH_3)_2OH$	$\cdot CH(CH_3)_2$
$CH_3CH_2C(CH_3)_2OH$	$\cdot CH_2CH_3$
$CH_3CH_2CH_2C(CH_3)(C_2H_5)OH$	$\cdot CH_2CH_3$
$CH_3CH_2CH(CH_3)C(CH_3)_2OH$	$\cdot CH_3$ + ?

Liquid-phase e.s.r. studies[98,105] were restricted to a narrower range of substrates: methanol, ethanol, propan-1-ol, and butan-1-ol yielded $R\dot{C}HOH$ radicals (Figure 6), but $(CH_3)_2CHCH_2OH$ gave $(CH_3)_2\dot{C}CH_2OH$, 2-phenylethanol gave benzyl radical, and propan-2-ol gave $(CH_3)_2\dot{C}OH$.

The result with CH_3OH is interesting in connection with the related spin-trapping work of Ledwith *et al.*[107] mentioned in the previous section. In liquid methanol, the principal radical spin-trapped is $CH_3O\cdot$ (and not $\cdot CH_2OH$) although the latter is predominant in aqueous methanol. Clearly direct examina-

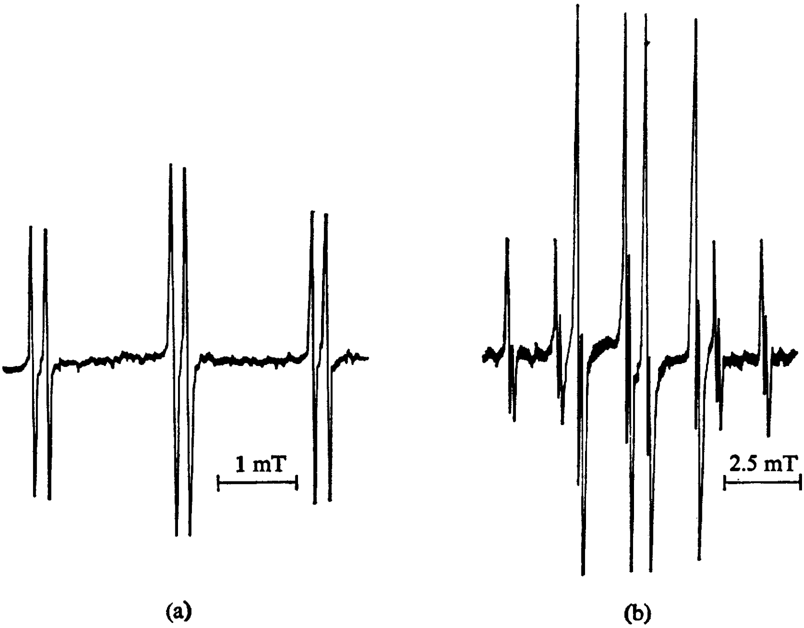

Figure 6 *Electron spin resonance spectra of irradiated fluid solutions in* (a) *methanol and* (b) *ethanol, of uranyl perchlorate* (*from R. J. Hill, Ph.D. thesis, University of Warwick,* 1974)

tion of the U^{VI}–methanol system in the solid state or liquid yields a secondary radical formed by attack of methoxyl upon solvent:

$$CH_3O\cdot + CH_3OH \rightarrow \cdot CH_2OH + CH_3OH \qquad (24)$$

With all other alcohols, the spin-trapped radical is $R\dot{C}HOH$[107] and it seems that methanol is quite atypical in its behaviour with $U^{VI}*$.

(v) *Photolysis products.* That from ethanol is acetaldehyde in conformity with fast, secondary thermal oxidation of $CH_3\dot{C}HOH$.[108]

(vi) *Substituent effect on photolysis rate.* The rate of photoreduction of U^{VI} by various aliphatic alcohols correlates well with the Taft $\sigma*$ values[110–112] (Figure 7). These studies also indicate that the polarity of the substituent is a more important factor than any steric effect on the rate of photolysis.

It is evident from these results that $(UO_2{}^{2+})*$ shares with triplet-state benzophenone, hydroxyl, and alkoxyl radicals a strong propensity to function oxidatively by abstracting hydrogen atoms from activated C–H bonds, and it seems probable that these reagents share the property of a high spin density at the

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[112] R. Venkatraman and S. B. Rao, *Indian J. Chem.*, 1971, 9, 500.

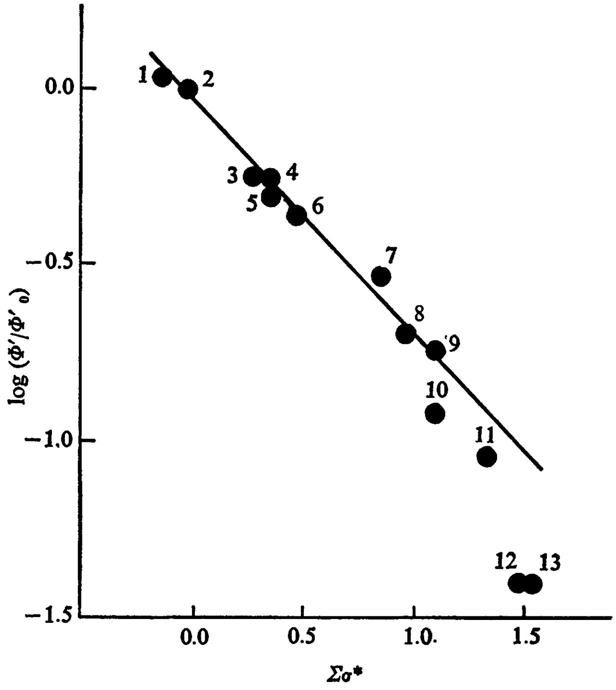

Figure 7 *Plot of* log (ϕ/ϕ_0) *as a function of* $\Sigma\sigma^*$ *where* ϕ_0 *is the quantum yield for* U^{IV} *with* $\Sigma\sigma^* = 0$ *(propan-2-ol) and* ϕ *is the formation quantum yield divided by the number of α-hydrogen atoms*

(1) s-butyl alcohol, (2) propan-2-ol, (3) i-butyl alcohol, (4) n-butanol, (5) n-propanol, (6) ethanol, (7) 3-chloropropan-1-ol, (8) methanol, (9) ethylene glycol, (10) benzyl alcohol, (11) 2-phenoxyethanol, (12) 2-bromoethanol, (13) 2-chloroethanol.

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oxygen atom. E.s.r. investigation of U^{VI}-doped glasses and crystals of organic materials following irradiation at 77 K indicates that hydrogen-atom abstraction is predominant with certain acids, esters, amides, aldehydes, ketones, and phosphorus(III) compounds.[95] However, in many cases there is a competition between hydrogen abstraction and C–C bond cleavage: for example, in photolysis of uranyl perchlorate in an acetaldehyde glass, the spectra both of $CH_3\cdot$ (indicating C–C cleavage) and of $\cdot CH_2CHO$ (due to hydrogen abstraction) are observed. Products studied on the photolysis of uranyl nitrate and acetaldehyde in dilute sulphuric acid solution indicate the formation of biacetyl,[113] suggesting yet a further reaction, *i.e.* hydrogen-atom abstraction from the carbonyl carbon, but

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[113] S. Sakuraba and R. Matsushima, *Chem. Letters*, 1972, 911.

no acetyl radical was found in the solid-state e.s.r. spectrum, in contrast to the result with photolysis of Ce^{IV} solutions in acetaldehyde.[114]

In cases where carbon–carbon bond cleavage is observed, these radicals presumably arise either from a CTTM transition between complexed substrate and U^{VI} or from intermolecular electron transfer from substrate to the excited uranyl. For example, photolysis of UO_2^{2+} in a t-butyl alcohol glass gives the e.s.r. spectrum of the methyl radical. This is the product expected from decomposition of the t-butoxy radical,[115] (25), (26):

$$(CH_3)_3COH + UO_2^{2+} \rightarrow UO_2^{+} + (CH_3)_3CO\cdot + H^+ \qquad (25)$$

$$(CH_3)_3CO\cdot \rightarrow (CH_3)_2CO + CH_3\cdot \qquad (26)$$

Similarly, as indicated above, solid-state e.s.r.[95] studies show that on photo-oxidation with UO_2^{2+}, 2-phenylethanol yields benzyl radical, *via* the intermediacy of the alkoxyl radical ($PhCH_2CH_2O\cdot$) [*cf.* equation (23)].

In all cases, the radicals observed upon C–C bond cleavage are those anticipated from the mass spectral breakdown pattern of the substrate. Thus, the mass spectrum of t-amyl alcohol[116] displays its strongest peak at *m*/*e* 59, attributed to $(CH_3)_2\overset{+}{C}OH$, which suggests loss of $C_2H_5\cdot$; similarly, on photolysis of uranyl perchlorate in t-amyl alcohol glass at 77 K, the radical observed initially is $C_2H_5\cdot$.[95] Further, the mass spectrum of ethyl methyl ketone indicates cleavage of the ethyl–carbonyl bond,[117] whereas on photolysis of a uranyl perchlorate–ethyl methyl ketone glass, the ethyl radical is observed by e.s.r.[95] In the case of n-propanol, the mass spectrum[116] shows its strongest peak at $m/e = 31$, implying loss of $C_2H_5\cdot$ and the e.s.r. spectrum of glassy n-propanol irradiated in the presence of U^{VI} shows $C_2H_5\cdot$ to be the principal radical[118] (ethanol gives no C–C fission product). Whilst the radicals observed in cases where there is C–C bond cleavage are most readily explained in terms of an electron transfer to the uranyl group, it is not at present clear whether this takes place *via* an intermolecular route, or *via* a CTTM transition in a uranyl–substrate complex.

C. Intermolecular Electron Transfer to Excited Uranyl Ion.—While there is no spectroscopic evidence for ground-state interaction between UO_2^{2+} and aromatic hydrocarbons, the latter efficiently quench uranyl fluorescence[111,119] to give good, linear Stern–Volmer plots. These afford a correlation between the quenching constant K_{SV} and the polarity of the aromatic compound as measured by the Yukawa–Tsuno σ constant for the substituent. There is no net photochemical reaction, nor is there a deuterium isotope effect on K_{SV}, and the process has been interpreted in terms of an intermediate exciplex in which charge is transferred

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[114] D. Greatorex and T. J. Kemp, *J.C.S. Faraday I*, 1972, **68**, 121.
[115] P. Gray and A. Williams, *Chem. Rev.*, 1959, **59**, 239.
[116] R. A. Friedel, J. L. Schultz, and A. G. Sharkey, jun., *Analyt. Chem.*, 1956, **28**, 926.
[117] A. G. Sharkey, jun., J. L. Schultz, and R. A. Friedel, *Analyt. Chem.*, 1956, **28**, 934.
[118] R. J. Hill, Ph.D. thesis, University of Warwick, 1974.
[119] S. Sakuraba and R. Matsushima, *J. Amer. Chem. Soc.*, 1971, **93**, 7143.

from the aromatic π-cloud to U^{VI}. This is followed either by the reverse process or by radiationless deactivation of the complex.

A number of metal ions have also been found[120] to quench U^{VI*}; where the quencher ion has a low-lying excited state then the quenching may simply result from electronic energy transfer. Some preliminary work indicates that the quenching in other cases may best be interpreted in terms of an intermolecular electron-transfer process.[121]

D. Energy Transfer.—One of the early mechanisms suggested for the photo-oxidation of oxalate by UO_2^{2+} involved energy transfer from U^{VI} to the ligand[122] but this was later discounted.[123] Energy transfer has since been observed between $(UO_2^{2+})^*$ and lanthanide ions[51,82] and also $Co(CN)_6{}^{3-}$.[85] Energy transfer from $(UO_2^{2+})^*$ to acrylamide (to give a triplet state) has been invoked to explain the photosensitization by UO_2^{2+} of the polymerization of acrylamide,[124] but it has been found that U^{VI} photo-oxidizes a number of vinyl monomers[95] to give free radicals detected by e.s.r. and a free-radical mechanism may be responsible for the observed polymerization.

5 Reactions of Intermediate Species

Following photo-oxidation of the substrate (either *via* electron- or atom-transfer) the immediate inorganic product is a uranium(V) species (probably UO_2^{+} or, in solutions of high uranyl concentration,[125] $U_2O_4^{3+}$, a species which has been identified kinetically[126]).

U^{V} is known to disproportionate rapidly in a process which depends on pH, anion concentration, and UO_2^{2+} concentration[125,127] to yield U^{VI} and U^{IV}, and normally U^{IV} is the observed end product of photo-oxidations by U^{VI}. U^{V} has also been shown to be oxidized back to U^{VI} by inorganic ions such as copper(II)[108] and mercury(II).[128] The U^{V} may also be oxidized back to U^{VI} by complexed organic radicals (see above).

The substrate radicals may undergo the following processes:

(i) *Further oxidation either by* UO_2^{2+} *or* UO_2^{+}, *e.g.*

$$Ph_2\dot{C}OH + UO_2^{2+} \rightarrow Ph_2CO + UO_2^{+} + H^{+} \qquad (27)$$

[120] M. Novák, *Jaderná Energie*, 1957, **3**, 44 (*Chem. Abs.*, 1960, **54**, 10505g); G. Alberti and A. Saini, *Analyt. Chim. Acta*, 1963, **28**, 536; I. K. Shutov and D. S. Umreiko, *Izvest. Akad. Nauk. S.S.S.R., Ser. fiz.*, 1970, **34**, 1349 (*Chem. Abs.*, 1970, **73**, 71776a); Y. Kato and H. Fukutomi, *Bull. Tokyo Inst. Technol.*, 1971, **102**, 55 (*Chem. Abs.*, 1972, **76**, 28227x); I. A. Taha and H. Morawetz, *J. Amer. Chem. Soc.*, 1971, **93**, 829 and references cited therein.

[121] H. D. Burrows, S. J. Formosinho, G. Miguel, and M. C. S. Viais, unpublished observation.

[122] W. West, R. H. Müller, and E. Jette, *Proc. Roy. Soc.*, 1928, **A121**, 294.

[123] A. H. Carter and J. J. Weiss, *Proc. Roy. Soc.*, 1940, **A174**, 351.

[124] K. Venkatarao and M. Santappa, *J. Polymer Sci., Part A-1, Polymer Chem.*, 1970, **8**, 1785, 3429.

[125] T. W. Newton and F. B. Baker, *Inorg. Chem.*, 1965, **4**, 1166.

[126] R. Bressat, B. Claudel, M. Fève, and G. Giorgio, *Compt. rend.*, 1968, **267**, *C*, 707; G. Giorgio, *Ann. Chim. (France)*, 1971, **6**, 53.

[127] J. Selbin and J. D. Ortego, *Chem. Rev.*, 1969, **69**, 657.

[128] S. Sakuraba and R. Matsushima, *J. Amer. Chem. Soc.*, 1972, **94**, 2622.

This reaction mode has been confirmed by flash photolysis.[129] Similar oxidation of aliphatic radicals by metal ions has been observed. For example, Cohen and Meyerstein[130] studied the oxidation of several aliphatic radicals in aqueous solution by $[Co(NH_3)_6]^{3+}$ and $[Ru(NH_3)_3]^{3+}$ using the pulse radiolysis technique.

(ii) *Disproportionation, e.g.*

$$2CH_3\dot{C}HOH \rightarrow CH_3CHO + CH_3CH_2OH \tag{28}$$

This reaction mode has been identified by radiation chemical studies[131] and in many cases kinetic data have been obtained from pulse radiolysis.[132] While Matsushima and Sakuraba[108,128] favour this as the main route for the formation of the organic products in photo-oxidations of alcohols by U^{VI}, based on the absence of any effect of other metal ions on ϕ (organic product) it is probable that in most cases both reactions of type (27) and (28) occur. Both yield the same final product, and the predominance of one process will be favoured by variations in the metal ion and radical concentrations.

(iii) *Dimerization.* The latter is normally important only at low metal–ion concentrations, but is most probably responsible for the formation of biacetyl in the photo-oxidation of acetaldehyde by uranyl perchlorate in dilute sulphuric acid.[113]

$$2CH_3\dot{C}O \rightarrow (CH_3CO)_2 \tag{29}$$

The processes of dimerization and disproportionation with organic radicals have recently been reviewed.[133]

(iv) *Decomposition.* This is most probably the fate of the radicals produced prior to C–C bond cleavage, *e.g.* the formation of the benzyl radical from the 2-phenylethanoxy radical [equation (23)].

(v) *Hydrogen abstraction.* This has been observed both by e.s.r. studies on glasses at 77 K[105] and, in the case of the methanoxy radical, by spin-trapping studies in solution at room temperature.[107].

(vi) *Polymerization.* Photolysis of vinyl monomers in the presence of UO_2^{2+} readily effects polymerization.[3,124,134]

6 Applications of the Photochemistry of Uranyl Compounds

A number of applications of the photochemical reactivity of U^{VI} have been suggested, of which a few representatives are as follows. The photoreduction of U^{VI} to U^{IV} by, for example, ethanol, and the subsequent precipitation of the U^{IV} as the oxysulphate, has been used as a method for separating uranium from other

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[129] H. D. Burrows and T. J. Kemp, to be published.

[130] H. Cohen and D. Meyerstein, *J. Amer. Chem. Soc.*, 1972, **94**, 6944.

[131] J. T. Allan, E. M. Hayon, and J. J. Weiss, *J. Chem. Soc.*, 1959, 3913.

[132] M. Simic, P. Neta, and E. Hayon, *J. Phys. Chem.*, 1969, **73**, 3794.

[133] M. J. Gibian and R. C. Corley, *Chem. Rev.*, 1973, **73**, 441.

[134] S. Okamura and S. Tazuke, Jap. P. 7034392/1970 (*Chem. Abs.*, 1971, **74**, 64633u); M. Amagasa, S. Kinumaki, Y. Kasuga, H. Chiba, K. Konno, H. Ueda, and H. Mukunaski, *Kobunshi Kagaku*, 1970, **27**, 718 (*Chem. Abs.*, 1971, **75**, 6401b).

metal ions.[135] Further, the photoreduction, and subsequent analysis of U^{IV}, has been used as a rapid method for determining U^{VI}, particularly at trace levels.[136]

Uranyl-ion photosensitized polymerization has been mentioned earlier. This can be used as a method for coating metal, paper, wood, or glass surfaces.[137]

A silver-free photographic process has been proposed, based on the reduction of Hg^{II} by a photolysed uranyl–organic system in a viscous polyvinyl alcohol system.[128]

Finally, mention should be made of a study of the uranyl acetate-photosensitized killing of *Escherichia coli K-12*. Neely and co-workers[138] found that under the conditions they used, the uranyl-photosensitized killing occurred only after 150 minutes. Binding of UO_2^{2+} to the cell was shown to be fairly rapid (complete within 30 minutes) and the observation was attributed to the necessity for penetration of UO_2^{2+} into the cell's interior to effect photosensitization. The photochemistry of U^{VI} may thus provide a probe into the structure of the interior of cells. Perhaps surprisingly, few other reports exist on uranyl photoreactions in biological systems, although Wacker and colleagues[139] have noted that U^{VI} can photochemically cleave thymine dimers to give thymine, and another unidentified product.

7 Some Comparisons with Other Metal Ions

Whilst UO_2^{2+} shares with several lanthanide ions the comparatively unusual phenomenon of luminescence[54,140,141] and with a number of one-equivalent oxidants such as Ce^{IV},[98,104,114] Tl^{III}, Pb^{IV},[142] Fe^{III},[143] and Cu^{II}[143] the ability to photo-oxidize a variety of substrates, it is the best-known exponent of each of these properties and the only member common to both groups. The luminescence of Eu^{3+} is *more* intense in methanol than in water, *i.e.* photochemical attack on C–H bonds by $(Eu^{3+})^*$ is imperceptible.[54,141] In the group of photo-oxidizing metal ions U^{VI} is the weakest as regards the thermodynamic energy released on the reduction process and this is reflected in its tendency to oxidize molecules like t-butyl alcohol by C–H cleavage to $\cdot CH_2C(CH_3)_2OH$ rather than by the C–C cleavage (to give $CH_3\cdot$) exhibited by Ce^{IV} on photo-oxidation. Again, U^{VI} photo-oxidation of CH_3CHO gives $\cdot CH_2CHO$ whereas the Ce^{IV} reaction yields the acyl radical $CH_3CO\cdot$.[114] Photochemical studies of Pb^{IV*} have been confined to carboxylic acid complexes[142] and the data with Fe^{III} and Cu^{II} are comparatively few,[3,143] making comparison with U^{VI} difficult at this stage.

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[135] C. R. Das and D. Patnaik, *Chem. and Ind.*, 1973, 699 and references given therein.

[136] W. M. Riggs, *Analyt. Chem.*, 1972, **44**, 390.

[137] K. Juna, H. Nakayama, and K. Asada, Ger. Offen, 2 010 867/1970; *Chem. Abs.*, 1970, **73**, 121659n.

[138] W. C. Neely, S. P. Ellis, and R. M. Cody, *Photochem. and Photobiol.*, 1971, **13**, 503.

[139] A. Wacker, H. Dellweg, L. Träger, A. Kornhauser, E. Lodemann, G. Türck, R. Selzer, P. Chandra, and M. Ishimoto, *Photochem. and Photobiol.*, 1964, **3**, 369.

[140] Y. Haas and G. Stein, *Chem. Phys. Letters*, 1972, **15**, 12.

[141] Y. Haas and G. Stein, *J. Phys. Chem.*, 1972, **76**, 1093.

[142] K. Heusler and H. Loeliger, *Helv. Chim. Acta*, 1969, **52**, 1495; H. Loeliger, *Helv. Chim. Acta*, 1969, **52**, 1516; P. B. Ayscough, J. Machová, and K. Mach, *J.C.S. Faraday II*, 1973, **69**, 750.

[143] R. J. Hill and T. J. Kemp, unpublished results.

As regards u.v. spectra, a comparison between UO_2^{2+} and other actinide oxo-cations has been made[32] and the results have been accommodated by a single molecular orbital model.

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