Physical and Chemical Quenching of Excited Uranyl Ion by Organic Molecules studied by Fluorimetric and Laser Flash Photolysis Methods

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The quenching by a large number of carboxylic acids of the luminescence of excited uranyl ion has been examined. Acetic and propionic acids display weak quenching as measured by the Stern–Volmer constant K_{SV}, but branching or lengthening of R in RCO_2H increases K_{SV} to figures of up to 15 dm^3 mol^{-1}. Cycloalkanecarboxylic acids show considerably higher K_{SV}. The introduction of halogen atoms introduces diverse effects: CF_3CO_2H and CCl_3CO_2H *increase* the luminescence intensity very strongly, $ClCH_2CO_2H$ and $BrCH_2CO_2H$ weaken it very slightly, ICH_2CO_2H powerfully quenches it (K_{SV} *ca.* 2 000 dm^3 mol^{-1}). Introduction of Cl or Br at the 2- or 3-positions of propionic acid exerts moderate to strong quenching which is ascribed to a physical, rather than a chemical mechanism, a result also indicated by studies of quenching by various alkyl halides. The introduction of alkoxy-groups increases K_{SV} by a factor of 200, but this has been found to be due to a remarkably high sensitivity of ether groups to $(UO_2^{2+})^*$ as further evinced by a high quantum yield for U^{IV} production. The introduction of C=C bonds in strategic positions also enormously increases K_{SV} (up to 1 600 dm^3 mol^{-1}) but this was also found to be due to the C=C bond itself, and a number of alkenes were found to exhibit quenching rates approaching diffusion control, presumably *via* an exciplex mechanism. Substituted benzoic acids quench $(UO_2^{2+})^*$ most effectively (K_{SV} up to 6 000 dm^3 mol^{-1}) and the rates follow a good Hammett correlation, (ρ −0.88 ± 0.04). In some instances, the quenching data have been augmented by quantum yield measurements, and absolute constants for the reaction between $(UO_2^{2+})^*$ and substrate have been obtained directly by monitoring the absorption of $(UO_2^{2+})^*$ at 590 nm using ns flash photolysis.

THE several detailed studies of the quenching of the well known, strong emission from aqueous uranyl ion (UO_2^{2+}) by a variety of aliphatic alcohols due to Matsushima and his colleagues [1-4] has enabled a comprehensive picture to be built up of the primary interaction between $(UO_2^{2+})^*$ and substrate in the photochemical reaction. The effects of structural variation and isotopic substitution indicate the quenching to be chemical in character, involving the abstraction of an α-hydrogen atom from a $\supset$CHOH or $-CH_2OH$ group to give a transient alcohol radical together with the intermediate aquouranium(V) species.[5] This mechanism has been supported by solution [6] and matrix e.s.r. experiments [7] on the UO_2^{2+}–alcohol system in addition to spin-trapping experiments [8] and laser flash photolysis studies of the absorption of $(UO_2^{2+})^*$ in this system.[9]

In view of the several previous studies of the U^{VI} photo-oxidation of carboxylic acids.[10] including product analysis,[11] and e.s.r. work,[6,7] which present quite different features from those of the alcohols, we have made a systematic examination of the quenching of the luminescence of $(UO_2^{2+})^*$ by carboxylic acids. Additional factors of interest were (i) the nature of the *primary* radical produced from RCH_2CO_2H, which might be $R\dot{C}HCO_2H$, $RCH_2CO_2\cdot$, or $RCH_2\cdot$ and (ii) the possible effect of substituents in stabilising such radicals. From the latter approach, it rapidly became apparent that $(UO_2^{2+})^*$ is subject to a whole variety of quenching processes and the study was extended to cover details of these. To establish whether quenching was physical or chemical in nature, quantum yields for the production of U^{IV} were determined in certain cases, and the absolute rate constants for quenching of particularly significant molecules were separately determined by laser flash photolysis.

EXPERIMENTAL

Materials.—These were of the highest grade available commercially. Inorganic materials were of AnalaR quality and organic materials were normally further purified by distillation or recrystallisation. Water was deionised and then doubly distilled.

Spectrofluorimetry.—In the early stages of this work, a single-beam Farrand model mark I spectrofluorimeter was used (all emission intensities being normalised with the aid of a fluor-loaded plastic block as standard). Later, a Perkin-Elmer Ltd. model MPF-3 double-beam instrument was used instead. Using the maximum of the 412 nm vibronic component of the absorption as our excitation wavelength, complete emission spectra were run in every case, and measurements taken of the intensity of the 510 nm vibronic component at its maximum. Stock solutions of uranyl nitrate in aqueous perchloric acid were maintained and portions were diluted with aliquot portions of water or aqueous carboxylic acid to maintain constant $[UO_2^{2+}]$ at 0.02M, $[H_3O^+]$ at 0.382M and ionic strength $\simeq [H_3O^+]$. Measurements were recorded at ambient temperature, 293 K. All quenching data were expressed in the form of Stern–Volmer plots, *e.g.* Figure 1.

Extinction Data.—The extinction coefficient for aquouranium(IV) in water was determined by photolysing an argon-flushed solution of uranyl nitrate (*ca.* 5 × 10^{-3}M) containing

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

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

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

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

[5] S. Sakuraba, S. Mimura, and R. Matsushima, *Bull. Chem. Soc. Japan*, 1973, **46**, 2784.

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

[7] D. Greatorex, R. J. Hill, T. J. Kemp, and T. J. Stone, *J.C.S. Faraday I*, 1972, 2059.

[8] A. Ledwith, P. J. Russell, and L. H. Sutcliffe, *Proc. Roy. Soc.*, 1973, *A*, **332**, 151.

[9] R. J. Hill, T. J. Kemp, D. M. Allen, and A. Cox, *J.C.S. Faraday I*, 1974, 847.

[10] For a review of U^{VI} photo-oxidation, see H. D. Burrows and T. J. Kemp, *Chem. Soc. Rev.*, 1974, **3**, 139.

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

the highly active reductant, dioxan (1.12M) and $HClO_4$ (various acidities) until the absorption spectrum of U^{IV} ($\lambda_{max.}$ 646 nm) measured on a Cary 14 instrument in a 2 cm cell increased no further. At 0.4 and 0.13M acidity, respectively, $\varepsilon_{max.}$ = 58 and 56.5 dm^3 mol^{-1} cm^{-1}. These compare with figures of 50 at pH 1 (ref. 12) and, reading from a graph of ε *versus* [H_3O^+], of 52.5 and 56 at 0.1 and 0.4M HCl.[13]

Irradiation and Actinometry.—The irradiation source was a high pressure mercury arc (Wotan HBO 200 W) mounted on an optical bench and powered by a constant current power supply stabilised to 0.1%. The lamp output was collimated and passed through a combination of Corning glass filters (5 850 and 4 303) which transmit maximally at 410 nm. U^{VI} concentrations in actinometry experiments were sufficiently high so that, in the 5 cm pathlength quartz cell employed (capacity 20 cm^3), complete absorption of the transmitted band at 410 nm took place. The cell was mounted in a brass thermostat equipped with optical windows, the temperature of which was stabilised by circulating tap water. Complete spectra of irradiated solutions in the 5 cm cell were run on a Cary 14 instrument, and actinometry was by the method of Hatchard and Parker;[14] irradiation intensities were of the order of 3 × 10^{-7} einstein s^{-1}.

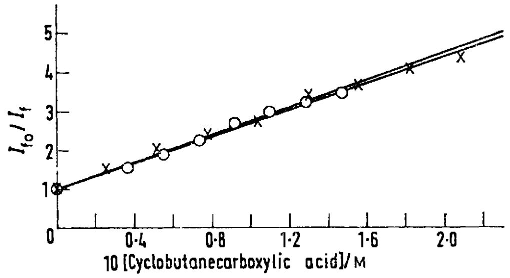

FIGURE 1 Stern–Volmer plot (two sets of solutions) for the luminescence quenching of uranyl ion in aqueous $HClO_4$ by cyclobutanecarboxylic acid. Conditions are given in footnote to Table 1: ○, gradient 17.05 ± 0.4; ×, 16.36 ± 0.4

Laser Flash Photolysis.—This was performed on two assemblies, one at the University of Salford which is similar to that described by Richards[15] and one, model K 347, latterly installed at Warwick by Applied Photophysics Ltd. Both employ ruby lasers, the 50 ns output pulses of which are frequency-doubled with an ammonium dihydrogen phosphate crystal to yield 347 nm radiation. The monitoring source is a pulsed 250 W xenon lamp and the cell is of 2 cm depth. In the K 347 equipment a collinear arrangement of the laser and analysing beams is utilised. Signals are stored in a Tetronix model 7623 oscilloscope equipped with 7B50 and 7A14A amplifiers. Traces are photographed on polaroid negative film and enlarged for analysis, which is performed using a least-squares computer program.

RESULTS

Luminescence Quenching Data.—These are tabulated in terms of particular structural variations explored (Table 1).

TABLE 1

Stern–Volmer constants for the quenching of UO_2^{2+} emission by carboxylic acids RCO_2H in aqueous ($K_{SV}^{H_2O}$) or aqueous acetone (K_{SV}^{AA}) solution (48% acetone v/v)

([UO_2^{2+}] 0.02M, [$HClO_4$] 0.382M, *T* 290 K)
(All K_{SV} are given in units of dm^3 mol^{-1})

R	$K_{SV}^{H_2O}$	K_{SV}^{AA}
(*a*) Unsubstituted aliphatic acids		
H	6.5	
CH_3	0.28	
CD_3	0.28	
CH_3CH_2	1.28	0.14
$CH_3CH_2CH_2$	1.91	0.41
$(CH_3)_2CH$	5.50	
$CH_3CH_2CH_2CH_2$		3.27
$(CH_3)_2CHCH_2$	4.87	
$(CH_3)_3C$	3.75 ± 0.05 [a]	0.81
$(CH_3CH_2)_2CH$	15.0	
$CH_3CH_2CH_2CH_2CH_2$		8.67
(*b*) Cyclic aliphatic acids [b]		
cyclo-C_3H_5	6.1 ± 1.2 [a]	
cyclo-C_4H_7	16.7 ± 0.3 [a]	
cyclo-C_5H_9	49.53 ± 0.16 [a]	
cyclo-C_6H_{11}	89.15 ± 2.34 [a]	14.5
(*c*) Halogen-substituted aliphatic acids		
$ClCH_2$	0.150	
$BrCH_2$	0.32	
ICH_2	3.6 × 10^3	550
F_3C	*c*	
Cl_3C	*c*	
CH_3CHCl	18.4	
$ClCH_2CH_2$	20.0	
CH_3CHBr	103	
$BrCH_2CH_2$	90	
ICH_2CH_2	1.96 × 10^3	
CH_3CH_2CHBr	36	
(*d*) Oxygen-substituted aliphatic acids		
$C_2H_5OCH_2CH_2$	203	71
$CH_3OCH_2CH_2$		37
(*e*) Unsaturated acids		
$CH_3CH{=}CH$	8.74	6.1
$\overbrace{-CH\cdot CH_2\cdot CH_2\cdot CH{:}CH\cdot CH_2}$		8.4
$CH_2{=}CHCH_2$	1.60 × 10^3	240
$CH_2{=}CHCH_2CH_2$		1.52 × 10^3
(*f*) Dicarboxylic acids		
HO_2CCH_2	*c*	
(*g*) Monosubstituted aromatic acids $XC_6H_4CO_2H$		
X	$10^{-3}K_{SV}^{H_2O}$	$10^{-3}K_{SV}^{AA}$
H	4.15	1.70
p-NH_3^+	0.92	
p-NO_2	0.90	
m-NO_2	0.85	
o-NO_2	0.79	
p-F	3.80	
m-Cl	2.03	
p-Br	2.90	
o-I	3.88	
p-CH_3	4.88	
m-CH_3	4.10	
o-CH_3	3.40	
p-OCH_3	6.00	
p-$C(CH_3)_3$		0.193
(*h*) Other aromatic acids		
Acid	$10^{-3}K_{SV}^{H_2O}$	$10^{-3}K_{SV}^{AA}$
Phenylacetic	3.50	
Diphenylacetic		2.26
2,3-Dimethylbenzoic		1.97
Benzilic		0.723
2,4,6-Trimethoxybenzoic	1.56	
Pentafluorobenzoic	1.02	

[a] Complete run performed in duplicate (error refers to that on averaged figure). [b] [UO_2^{2+}] 0.04M, [$HClO_4$] 0.233M.
[c] No quenching of luminescence found (for details see text).

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[12] L. J. Heidt, *J. Amer. Chem. Soc.*, 1954, **76**, 5962.

[13] K. A. Kraus and F. Nelson, *J. Amer. Chem. Soc.*, 1950, **72**, 3901.

[14] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.*, 1956, *A*, **235**, 518.

[15] R. McNeil, J. T. Richards, and J. K. Thomas, *J. Phys. Chem.*, 1970, **74**, 2290.

In the vast majority of cases examined, the effect of adding a carboxylic acid was simply to reduce the spectral intensity of the UO_2^{2+} emission with comparatively minor effects on the positions and relative intensities of the individual vibronic components. In the cases of trifluoroacetic, trichloroacetic, and malonic acids, however, replacement of water in the medium by substrate resulted in *enhancement* of the fluorescence intensity by a considerable factor.

TABLE 2

Stern–Volmer constants (in $dm^3 mol^{-1}$) for the quenching of UO_2^{2+} emission by other compounds in aqueous acetone solution (48% acetone v/v).

(Conditions as for Table 1)

(*a*) Esters	
$CH_3CH_2CO_2CH_3$	3.23
$CH_3(CH_2)_2CO_2C_2H_5$	0.47
$CH_3(CH_2)_2CO_2CH_3$	6.59
$CH_3CH{=}CHCO_2CH_3$	3.33
$BrCH_2CH_2CO_2CH_3$	53
$C_6H_5CO_2CH_3$	328
(*b*) Alkyl halides	
CCl_4	1.25
C_2H_5I	670
n-C_3H_7I	435
n-C_4H_9Br	84
C_2H_5Br	105
$CHBr_3$	87
n-C_4H_9Cl	10.8
(*c*) Alkenes	
$CH_3{-}CH{=}C(CH_3)CH_3$	800
Cycloheptatriene	2 320
Cyclopentene	240
Cyclohexene	1 320
(*d*) Unsaturated ketones	
Cyclopent-2-enone	13.3
$(CH_3)_2C{=}CHCOCH_3$	416
3,4,4-Trimethylcyclohex-2-enone	210
3,5-Dimethylcyclohex-2-enone	232
(*e*) Halogenated and hydroxylated alkenes	
$CH_2{=}CHCH_2Cl$	261
$CH_2{=}CHCH_2Br$	262
$CH_2{=}CHCH_2OH$	205

The presence of halogen atoms in the acid [Table 1(*c*)] affected K_{SV} depending on both the position and number of substituent atoms but especially on the particular atom, iodine producing quenching constants $>10^3$ $dm^3 mol^{-1}$. For this reason, the effect of halogens on the quenching of $(UO_2^{2+})^*$ luminescence by halogenoalkanes was investigated [Table 2(*b*)], although here, and in a number of other instances, it became necessary to use an acetone–water mixture as solvent. Alkoxy-groups also exerted a large quenching action [Table 1(*d*)] and to determine the effect of alkoxy-groups *per se* a number of ethers were examined (Table 3). Unsaturated carboxylic acids gave a wide range of values for K_{SV} [Table 1(*e*)] and, similarly, some alkenes and unsaturated ketones were explored [Tables 2(*c* and *d*)]. A group of aromatic acids gave very large quenching constants typical of aromatic systems [16] [Tables 1(*g* and *h*)].

TABLE 3

Stern–Volmer constants (in $dm^3 mol^{-1}$) for the quenching of UO_2^{2+} emission by ethers in aqueous ($K_{SV}^{H_2O}$) or water–acetone (K_{SV}^{AA}) solution (48% acetone v/v)

Ether	$K_{SV}^{H_2O}$	K_{SV}^{AA}
$C_2H_5OC_2H_5$		138 ± 2 [a]
$CH_3OCH_2CH_2OCH_3$	204	
$(CH_3OCH_2CH_2)_2O$	327	
1,4-Dioxan	243	
Tetrahydrofuran	547	
2-Methyltetrahydrofuran	595	
$(CH_3)_2CHOCH(CH_3)_2$		54
$C_2H_5OCH_2CO_2H$	203	71
$CH_3OCH_2CH_2CO_2H$		37
Tetrahydropyran		57
1,3-Dioxan		224

[a] Mean of two complete plots.

TABLE 4

Quantum yields for U^{IV} appearance in the photo-oxidation of organic molecules by $(UO_2^{2+})^*$

([U^{VI}] 0.04M; [$HClO_4$] 0.382M; 5 cm cell; blue filter combination)

Substrate	Concentration/M	Medium	$\varphi[U^{IV}]$
Cyclopropanecarboxylic acid	0.334	48% Acetone–H_2O	0.041
Cyclopropanecarboxylic acid	0.334	H_2O	0.037
Cyclohexanecarboxylic acid	0.150	48% Acetone–H_2O	0.075
$BrCH_2CH_2CO_2H$	0.50	H_2O	$<10^{-4}$
$C_2H_5OCH_2CH_2CO_2H$	1.20	H_2O	1.89
1,4-Dioxan	1.17	H_2O	0.76
$CH_3OCH_2CH_2OCH_3$	1.08	H_2O	0.72
$(CH_3OCH_2CH_2)_2O$	0.295	H_2O	0.67

Quantum Yields for U^{IV} *Production.*—These were obtained for a number of ethers and carboxylic acids (Table 4).

Laser Flash Photolysis.—Decays of the absorption spectrum of (UO_2^{2+}) were measured at 590 nm [9] for several substrates. In 0.382M aqueous $HClO_4$, the first-order decay constant in the absence of substrate was 4.0×10^5 s^{-1}, whilst in 48% acetone–52% water the decay constant increased to 1.14×10^6 s^{-1}. Four or five concentrations of substrate were used and the pseudo-first-order rate constant *versus* concentration plot gave a straight line with an intercept on the rate axis and a slope affording k_2, the absolute rate constant for attack of quencher upon $(UO_2^{2+})^*$. These

TABLE 5

Rate constants for the quenching of the 590 nm absorption of excited uranyl ion by added substrates

(*a*) Cycloalkanecarboxylic acids
([Uranyl nitrate] 0.04M, [$HClO_4$] 0.233M)

Substrate	$10^{-6}k_2$ [a]/ $dm^3 mol^{-1} s^{-1}$	K_{SV} [b]/ $dm^3 mol^{-1}$	$10^6K_{SV}/k_2$
Cyclopropanecarboxylic acid	2.63 ± 0.07	6.1 ± 1.2	2.3
Cyclobutanecarboxylic acid	8.23 ± 0.37	16.70 ± 0.30	2.0
Cyclopentanecarboxylic acid	37.5 ± 2.9	49.53 ± 0.16	1.3
Cyclohexanecarboxylic acid	66.6 ± 5.1	89.15 ± 2.34	1.3

(*b*) Miscellaneous substrate molecules
([Uranyl nitrate] 0.08M, [$HClO_4$] 0.382M)

Substrate	$10^{-8}k_2$ [a]/$dm^3 mol^{-1} s^{-1}$
1,4-Dioxan	1.60 [b]
3-Bromopropionic acid	1.12 [b]
Cyclohexene	15.5 [c]
Pent-4-enoic acid	12.0 [c]

[a] Mean of four determinations. [b] Aqueous solution. [c] 48% Acetone–52% water solvent.

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[16] R. Matsushima and S. Sakuraba, *J. Amer. Chem. Soc.*, 1971, **93**, 7143.

data are summarised in Table 5 together with corresponding values for K_{SV} affording an indication of the internal consistency of the two sets of data. Some typical results are presented in Figure 2.

DISCUSSION

It has long been known, albeit at a qualitative level, that photoirradiation of U^{VI} in the presence of carboxylic acids leads to decomposition of the latter.[10] Oxalic acid has been carefully studied by several groups, however, and its photodecomposition proceeds in high yield (φ 0.58) although only a small fraction of U^{VI} becomes reduced to U^{IV}, implying either a re-oxidation of intermediate U^{V} or preservation of the oxidation state of uranium as +6 throughout.[17]

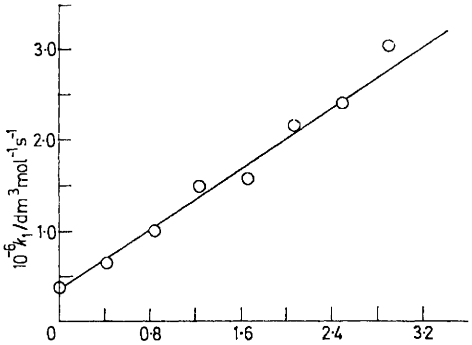

FIGURE 2 Dependence on cyclobutanecarboxylic acid concentration of the pseudo-first-order rate constant for the decay of the 590 nm transient in the laser flash photolysis of aqueous acidic uranyl nitrate. (The straight line was derived from a least squares analysis)

Heckler *et al.*[11] found a series of mono- and di-carboxylic acids to be photodecomposed by U^{VI} excited at 253.7 nm for 3—16 h to give CO_2 and RH from RCO_2H at pH values of about unity; rates were measured micromanometrically from CO_2 evolution: no U^{IV} yields were given however. Although the role of U^{VI}–substrate complexes was evaluated, no mechanism was proposed. In accordance with the time-scale of these experiments, we find the quenching of U^{VI} fluorescence by the lower members of the series to be very small, although both lengthening and branching of the chain increase K_{SV} [Table 1(*a*)]. These rate data support mechanisms either of concerted oxidative decarboxylation [equation (1)] or of hydrogen atom abstraction to give a transient carboxyl radical which rapidly decomposes [equations (2) and (3)].

The concerted pathway has been favoured for thermal and photochemical oxidation of carboxylic acids by Co^{III},[18,19] Pb^{IV},[20] Ce^{IV},[21,22] Tl^{III},[23] Mn^{III},[24] and $S_2O_8^{2-}$,[25] largely on the grounds of the rate sequence $Me_3CCO_2H > CH_3CO_2H$ which, while always pronounced, varies quantitatively with the oxidant, being least marked for the stronger oxidants, Pb^{IV} and Co^{III}, and for photochemical (compared with thermal) activation. In the case of

$$RCO_2H{\to}U^{VI} \xrightarrow{h\nu} R\cdot + CO_2 + H^+ + U^V \quad (1)$$

$$RCO_2H{\to}U^{VI} \xrightarrow{h\nu} RCO_2\cdot + H^+ + U^V \quad (2)$$

$$RCO_2\cdot \longrightarrow R\cdot + CO_2 \quad (3)$$

oxidation by $(UO_2^{2+})^*$, the reactivity ratios are sufficient to favour reaction (1) over reactions (2) and (3).

Photolysis of U^{VI} salts in *neat* acetic and propionic acids at room temperature produced[6] e.s.r. signals of the radicals $R\dot{C}HCO_2H$ (R = H and Me respectively), rather than those of $RCH_2\cdot$, but such a change of medium is known[8] to influence greatly the pathway of U^{VI*} photoreactions. Cycloalkanecarboxylic acids show an order-of-magnitude higher quenching ability towards $(UO_2^{2+})^*$, with a systematic increase of K_{SV} with ring size from C_3 to C_6 [Table 1(*b*)], and $\varphi[U^{IV}]$ also reflects this trend (Table 4). These data also reveal that at least a portion of the reaction in these instances proceeds with net production of U^{IV} rather than by a purely 'sensitisation' mechanism as for oxalic acid. U^{IV} is presumably produced *via* disproportionation of U^{V} as indicated from Heidt's work on U^{VI} photo-oxidation of methanol[12] and carbohydrates.[26] The enhancement of reactivity by introducing a cycloalkyl group parallels that found in the alcohols: K_{SV} for cyclohexanol quenching of $(UO_2^{2+})^*$ is 369 whilst that of propan-2-ol[9] is 96.5 $dm^3 mol^{-1}$.

Introduction of halogen atoms into the lower members of the homologous series RCO_2H produced some striking effects. Replacement of all three (methyl) hydrogen atoms of acetic acid by F and Cl resulted in a several-fold *enhancement* of the fluorescence intensity although the basic pattern of the emission spectrum was unchanged: clearly the trihalogenoacetato complexes so formed are more luminescent than the UO_2^{2+} ion. The only other acid to produce such enhancement was malonic acid. Substitution of single hydrogen atoms of acetic acid by either Cl or Br depresses K_{SV} still further or leaves it practically unchanged respectively. However, substitution by a single iodine atom dramatically increases K_{SV} [Table 1(*c*)], which suggests the following possibilities: (i) the operation of a heavy atom effect, (ii) a special stabilisation of the intermediate radicals by I, or (iii) a charge-transfer quenching centred on the iodine atom. A separate measurement on quenching of $(UO_2^{2+})^*$ by ethyl iodide produced a similarly large value for K_{SV} in

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

[18] S. S. Lande and J. K. Kochi, *J. Amer. Chem. Soc.*, 1968, **90**, 5196.

[19] A. A. Clifford and W. A. Waters, *J. Chem. Soc.*, 1965, 2796.

[20] J. K. Kochi, R. A. Sheldon, and S. S. Lande, *Tetrahedron*, 1969, **25**, 1197.

[21] R. A. Sheldon and J. K. Kochi, *J. Amer. Chem. Soc.*, 1968, **90**, 6688.

[22] I. M. Mathai and R. Vasudevan, *J. Chem. Soc. (B)*, 1970, 1361.

[23] J. K. Kochi and T. W. Bethea, III, *J. Org. Chem.*, 1968, **33**, 75.

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[25] D. D. Tanner and S. A. A. Osman, *J. Amer. Chem. Soc.*, 1968, **90**, 6572.

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aqueous acetone [3] [Table 2(*b*)] which supports possibilities (i) and (iii). Highly efficient quenching of a variety of excited states by compounds containing iodine atoms have been reported, *e.g.* that of triplet benzophenone by HI and iodoacetic acid [27] and of singlet excited anthracene [28] and alkanones [29] by ethyl and other iodides. Attempts to perturb the weak absorption spectrum of $\mathrm{UO_2}^{2+}$ in aqueous acetone by introducing 50% (v/v) ethyl iodide failed, and flushing a uranyl nitrate solution with xenon did not affect the excited state decay rate, both of which results imply that $(\mathrm{UO_2}^{2+})^*$ is *not* subject to heavy-atom perturbation, and that the quenching by iodine atoms (and to a lesser extent, Br and Cl) is due to charge-transfer from the halogen to $\mathrm{U^{VI}}$ to give a transient exciplex, as in the quenching of alkanones by alkyl iodides.[29]

With the substituted propionic acids, the situation is more complex. Introduction of Cl or Br atoms at the 3-position increases K_{SV} 16- and 70-fold respectively [Table 1(*c*)], which at first suggests special stabilisation of the resulting radical intermediate $\mathrm{XCH_2\dot{C}H_2}$ by a bridging mechanism of the type widely discussed [30] and for which there exists supporting evidence at least for asymmetric bridged conformations from the observed hindered rotation in e.s.r. spectra, *e.g.* of β-halogenoalkyl radicals [31,32] and also from INDO calculations on these species.[33] This possibility is, however, greatly reduced by (i) the comparable effects of analogous substitutions at the 2-position and (ii) the strong quenching by ethyl bromide and 1-chlorobutane [Table 2(*b*)]. Despite its comparatively large quenching constant, 3-bromopropionic acid reacts with $\mathrm{UO_2}^{2+}$ under irradiation at 410 nm only exceedingly slowly, giving an upper limit of φ [$\mathrm{U^{VI}}$] of 10^{-4} compared with a figure of 0.075 from cyclohexanecarboxylic acid which has almost the same K_{SV}. We therefore ascribe the quenching of the halogen-substituted acids to charge-transfer quenching with no net reduction of $\mathrm{U^{VI}}$. There are nonetheless some puzzling features here: neither the presence of Cl or Br in acetic acid itself produces any comparable quenching ability (due possibly to the proximity to the $\mathrm{CO_2H}$ group), and $\mathrm{CCl_4}$ is a remarkably weak quencher compared with 1-chlorobutane. Again, $\mathrm{CHBr_3}$ is less effective a quencher than ethyl bromide. Such fluctuations are, however, a feature of halogen-substituted quenchers, for example chloroform quenches singlet anthracene with K_{SV} of 0.07 $\mathrm{dm^3\ mol^{-1}}$, whilst $\mathrm{CCl_4}$ shows [28] K_{SV} 0.92 $\mathrm{dm^3\ mol^{-1}}$. The proficiency of Br atoms in inducing non-chemical quenching of $(\mathrm{UO_2}^{2+})^*$ has been noted with ethylene bromohydrin (K_{SV} 2 550 $\mathrm{dm^3\ mol^{-1}}$).[4]

Alkylation of the carboxylic hydrogen atom produces no startling changes in K_{SV} [Table 2(*a*)], but substitution of a hydrogen atom in a simple carboxylic acid by methoxy- or ethoxy-groups induces a very large increase in K_{SV} (Table 3), *e.g.* the introduction of a 3-ethoxy-group into propionic acid (in water) increases K_{SV} 160-fold. The increases in K_{SV} are paralleled by a large increase in the quantum yield of $\mathrm{U^{IV}}$ production (Table 4). These large figures imply high efficiency of the initial photochemical decomposition of acid followed by further rapid thermal (or photochemical) consumption of $\mathrm{U^{VI}}$ by radical and other readily oxidisable intermediates. (The exact final oxidation level of the substrate is not easily ascertained in these experiments, which render only a qualitative value to arguments based on values of $\varphi[\mathrm{U^{IV}}]$.) The effects of $\mathrm{OC_2H_5}$ and $\mathrm{OCH_3}$ again raise the question of stabilisation of radical intermediates by bridging, but this possibility is largely vitiated from the observation that simple ethers are, rather surprisingly, highly effective quenchers of $(\mathrm{UO_2}^{2+})^*$ (Table 3). It is unusual for ethers to display such a level of reactivity towards oxidising agents as compared with alcohols, as Barter and Littler [34] have pointed out: for example, the powerful one-equivalent oxidant, cerium(IV) sulphate, barely attacks either di-isopropyl ether or dioxan, and pervanadyl sulphate is similarly unreactive, whereas ethanol and cyclohexanol are attacked at an appreciable rate by these two oxidants. Hitherto, the only oxidising agents found to be particularly reactive [34] towards ethers are those capable of functioning as two-equivalent oxidants, *viz.* mercury(II) ion, bromine, and permanganate ion, and the question arises as to whether the high reactivity of ethers towards $(\mathrm{UO_2}^{2+})^*$ lies in the exceptional one-equivalent oxidising power of the latter (either by electron- or hydrogen atom-abstraction) *e.g.* equation (4), or whether, with these substrates, a *two*-electron oxidation is operative (equation 5), possibly *via* hydride ion-abstraction:

$$(\mathrm{UO_2}^{2+})^* + \mathrm{RCH_2OR} \longrightarrow \underset{\text{(I)}}{\mathrm{R\dot{C}HOR}} + \mathrm{H}^+ + \mathrm{U^V} \qquad (4)$$

$$\begin{tikzcd}(\mathrm{UO_2}^{2+})^* + \mathrm{RCH_2OR} \arrow[r] & \mathrm{RCH{=}\overset{+}{O}R} \arrow[d, "\mathrm{H_2O}"', "\text{fast}"] \\ & \mathrm{RCH{=}\,O}\end{tikzcd} \qquad (5)$$

(A two-electron process has been established in the case of chromic acid photo-oxidation of alcohols.[35,36]) That radical intermediates are involved at least to a degree in solution-phase photo-oxidation of ethers by $(\mathrm{UO_2}^{2+})^*$ is evident from the direct observation [6] of e.s.r. spectra of species (I) during photolysis, using a 1 kW source at a moderately low temperature of solutions (with ether as solvent) of $\mathrm{UO_2}^{2+}$ perchlorate in tetrahydrofuran, 1,2-dimethoxyethane, and 2-methoxyethanol: in the latter

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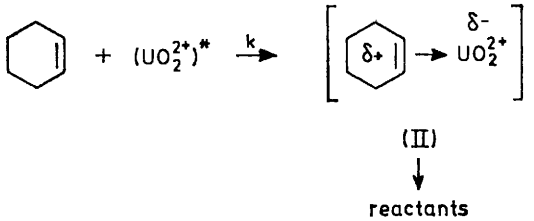
case, the major radical is that derived by abstraction of a hydrogen atom from carbon adjacent to the ether, rather than to the hydroxy-function. Accordingly, we favour a one-equivalent oxidation process, *i.e.* reaction (4).

The presence of a suitably located alkene function in the acid induces remarkable enhancement of the quenching effect [Table 1(*e*)]. The exceptionally high quenching constant for pent-4-enoic acid, compared with a value for the natural lifetime τ of $(UO_2^{2+})^*$ in the acetone–water medium, determined directly by laser flash photolysis to be 8.8×10^{-7}s (*i.e.* k_1 1.14×10^{-6} s^{-1}), predicts the absolute rate of the quenching process to be $K_{SV}/\tau = 1.73 \times 10^9$ dm^3 mol^{-1} s^{-1}. This compares with a figure of 1.20×10^9 dm^3 mol^{-1} s^{-1} obtained directly from measurements of the acceleration of the decay of the absorption of $(UO_2^{2+})^*$ in this medium at 590 nm by laser flash photolysis (Table 5).

These large values for K_{SV} are not accompanied, however, by a correspondingly large quantum yield for U^{IV} production (accurate measurements on vinylacetic acid were frustrated by precipitation of what we presume to be a polymer), suggesting another mode of physical quenching, and an investigation was made of simple alkenes to assess the effectiveness of quenching by isolated and conjugated double bonds. All alkenes investigated [Table 2(*c*)] gave large values for K_{SV}, whether cyclic or acyclic, conjugated or unconjugated, but the effectiveness of the highly conjugated cycloheptatriene was greater than that of the monoalkenes. The figure for cyclohexene in aqueous acetone yields a predicted figure for the quenching rate of 1.50×10^9 dm^3 mol^{-1} s^{-1} in good agreement with experiment (Table 5). Energy transfer from $(UO_2^{2+})^*$ to alkene is ruled out because the singlet energy levels of the latter, typically at 52 000 cm^{-1}, are far higher than that of $(UO_2^{2+})^*$ at 20 500 cm^{-1}. The quenching probably originates, therefore, in an excited state charge-transfer or (' exciplex ') interaction (6) of the type proposed by Matsushima [4,16] for the quenching of $(UO_2^{2+})^*$ fluorescence by aromatic molecules. No net chemical change results from the de-excitation of the ' exciplex ' (II). For electron-rich alkenes, as with arenes,[4,16] the rate constant k of 1.5×10^9 dm^3 mol^{-1} s^{-1}, approaches the value for diffusion control as there is little activation barrier for formation of (II). However, K_{SV} for alkenes is extremely sensitive to the presence of substituent groups, as evinced by the diminution of K_{SV} on conjugation both with carbonyl and carboxy-groups [Table 1(*e*) and 2(*d*)]. Substitution by Br, Cl, and OH reduce K_{SV}, the allyl halides and allyl alcohol all yielding K_{SV} between 200 and 260 dm^3 mol^{-1}.



(6)

Benzoic acid and its ring-substituted analogues show very high quenching ability of the type noted for benzene itself by Matsushima.[4,16] In water quenching constants approach 6.0×10^3 dm^3 mol^{-1} (for *p*-methoxybenzoic acid) implying an experimental quenching rate of 2.4×10^3 dm^3 mol^{-1} s^{-1}, *i.e.* near to diffusion control. Experimental rate constants of this magnitude k_{obs} require correction for local concentration gradients according to the treatment of Noyes [37] [reaction (7) where σ refers to the

$$k_{obs} = 4\pi\ \sigma\ D/(1 + 4\pi\ \sigma\ D/k_{corr}) \qquad (7)$$

collision diameter and D to the relative diffusion coefficient]. For aqueous solutions σ and D are typically 5×10^{-10} m and 10^{-5} cm^{-2} s^{-1} respectively, and the values of k_{corr} so obtained have been utilised in the Hammett plot (Figure 3) which demonstrates the systematic reduction of quenching rate by electron-withdrawing substituents. The σ_{meta} and σ_{para} values of Brown and Okamoto [38] yielded a reaction constant ρ of -0.88 ± 0.04 which compares with a figure of -0.83 obtained by Matsushima and Sakuraba [16] utilising the multi-parameter Yukawa–Tsuno [39] relation for substituted benzenes in 10% acetone–90% water medium. (More complicated forms of the Hammett equation, and the use of σ^+ parameters, gave no improved correlation with our results.) Such a figure indicates only a modest degree of transfer of charge from the aromatic to uranyl ion in the quenching process, in accordance with an exciplex mechanism rather than one of complete (but reversible) electron-transfer to give a caged ArH^+U^V pair.

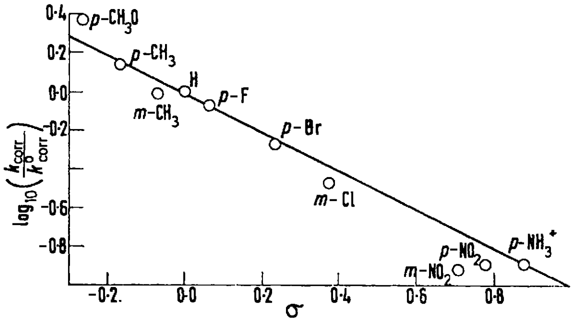


FIGURE 3 Hammett plot for the quenching of uranyl fluorescence by a series of benzoic acids in dilute aqueous perchloric acid solution [data from Table 1(*g*)]

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