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Acidity Effects on the Luminescence of the Uranyl Ion in Aqueous Acidic Solution

M. D. MARCANTONATOS

Department of Inorganic and Analytical Chemistry, University of Geneva, 1211 Geneva 4, Switzerland

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In a previous work [1], it was shown that the luminescent state of the linear uranyl ion can be quenched chemically by water, leading to the excited hydrogenated $(UO_2H^{2+})^*$ species which, as $(UO_2^+)^*$, has the conditional oxydation state U(V). Dual luminescence from 406 nm irradiated aqueous acidic solutions of UO_2^{2+} was also reported and was attributed to an exciplex, probably having the composition $(U_2O_4H^{4+})^*$.

Although the formation of the excited complex was strongly supported by its significant contribution to the total luminescence, by the characteristics of its emission spectrum [1] and by the peculiar variation of the Stern–Volmer constant with uranyl concentration, in the quenching of $(UO_2^{2+})^*$ by Ag^+ [2, 3] and MeOH [3], the $(UO_2H^{2+})^*$ species was only suggested by the well known particular photochemical behaviour of UO_2^{2+} and from the fitting of the experimental data by a kinetic scheme which assumed its formation [1].

In the present work, further evidence for the excited-state formation of the $(UO_2H^{2+})^*$ and $(U_2O_4H^{4+})^*$ species is presented. It can be shown that the very low emission efficiency of $(UO_2H^{2+})^*$ and its conversion to the non-emitting $(UO_2^+)^*$ species are the principal degradative processes of the $(OUO^{2+})^*$ $(5f, \delta_u \text{ or } \phi_u)^1\pi_u^3$ luminescent state, and this justifies some reconsideration of uranyl photochemistry.

In fact, the previously reported luminescence data for uranyl solutions of concentration higher than 10^{-2} *M* and constant pH = 1.94, revealed that the apparent luminescence efficiency $\zeta_{(2,3)}$, at $\lambda(2)$ = 544 and $\lambda(3)$ = 554 nm, varies with the intensity of the exciting light (406 nm) [1].

This was shown to be the result of exciplex formation. The emission of this excited complex of probable composition $(U_2O_4H^{4+})^*$ was found to be superimposed on that of the linear $(OUO^{2+})^*$ and its contribution was visible at high excitation intensities. Under these conditions, sufficient population of the lowest excited states of $(OUO^{2+})^*$ and $(UO_2H^{2+})^*$ was achieved, thus resulting in detectable concentrations of the exciplex formed by the interaction of $(UO_2H^{2+})^*$ with OUO^{2+}.

The above behaviour is shown in Fig. 1a, which shows that the logarithmic plot of the emission intensity $I_{L\lambda(3)}$ at $\lambda(3)$ = 554 nm *vs.* the absorbed intensity I_m at 406 nm, is characterised by two intersections ($\ln\zeta_{(3)}$) for $\ln I_m = 0$ [1]. Fig. 1b shows, however, that a pH increase from 1.94 (for curve a)

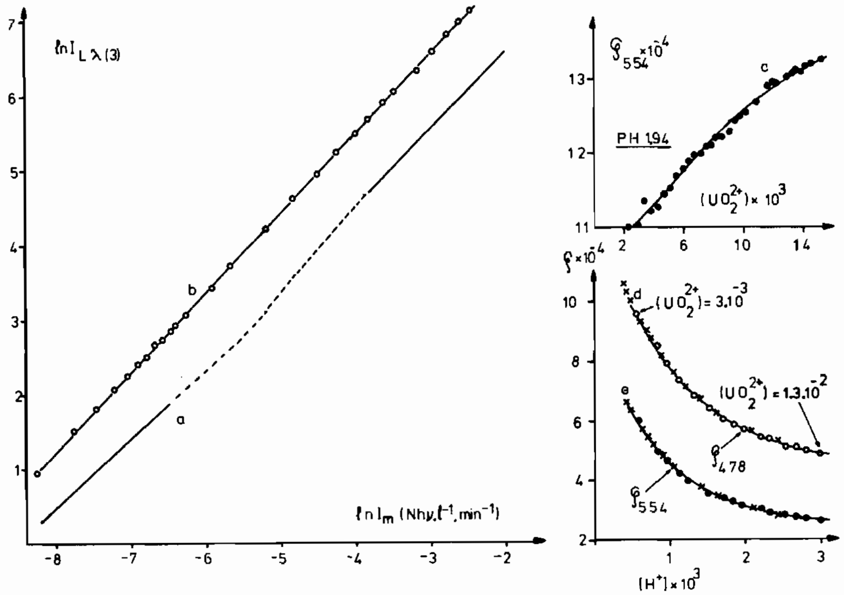


Fig. 1. Logarithmic plot of UO_2^{2+} luminescence intensity I_L *vs.* I_m (exc.: 406, em: 554 nm). 1a) pH = 1.94. 1b) pH = 2.7 (HNO_3); $[UO_2^{2+}] = 3 \times 10^{-2}$. Apparent luminescence efficiency ζ variations: 1c) with uranyl activity at constant pH ($I_0' = 9.6 \times 10^{-6}$ Nh/min). 1d) and 1f) with both uranyl and proton concentration ($I_0' = 9.6 \times 10^{-6}$ Nhν/min for 1d; $I_0 = 6.2 \times 10^{-4}$ Nhν/min for 1e; ex.: 406 nm). ●, ○, experimental; ×, calculated by (10). Each point is the mean of four independent determinations.

to 2.70, results in a totally linear dependence of $\ln I_{L(3)}$ upon $\ln I_m$ (Fig. 1b), indicating either that the formation of the exciplex E* is strongly inhibited or that E* is actively decomposed.

The quenching of the E* emission by increasing pH is further evidenced by comparing the ζ_{554} variations with uranyl activity (U) (for their role see in [1]), at constant (Fig. 1c) and varying pH (Fig. 1e). As previously shown [1], at constant pH = 1.94 and low (U), $\zeta_{(2)}$ at $\lambda(2) = 544$ nm varies with (U) roughly as $\zeta_{(1)}$ (at $\lambda(1) = 478$ nm), the latter being essentially the efficiency ζ_{rU} of $(\mathrm{OUO^{2+}})^*$. However, as (U) increases further and E* becomes appreciable, $\zeta_{(2)}$ changes to $\zeta_{rU} + \zeta_{rE}$ and therefore increases. By using 406 nm irradiation sixty-five times more intense, this increase at $\lambda = 554$ starts, obviously, for lower uranyl activities (Fig. 1c), but as seen from Fig. 1e, for the same excitation intensity, this increase is suppressed for pH higher than 1.94. As expected ($\mathrm{p}K_A = 6.1$ for $\mathrm{UO_2^{2+} + H_2O \rightleftharpoons UO_2(OH)^+ + H^+}$ [4]), there was no indication of any static quenching by $\mathrm{UO_2^{2+}}$ suffering appreciable solvolysis in the $2.52 \leqslant \mathrm{pH} \leqslant 3.24$ range (no detectable change in the absorption spectrum in this pH range and $\epsilon_{357} = 3.16 \pm 0.02$, $\epsilon_{406} = 7.37 \pm 0.04$, $\epsilon_{436} = 4.21 \pm 0.03$ from 26 absorbance measurements of $5 \times 10^{-3} \leqslant [\mathrm{UO_2^{2+}}] \leqslant 5 \times 10^{-2}$ solutions) and therefore quenching of the E* emission must result from excited-state proton transfer paths.

Exciplex formation was argued [1] to take place via:

$$\underset{U^*}{(\mathrm{UO_2^{2+}})^*} + \mathrm{H_2O} \underset{k'_{UX}}{\overset{k'_{XU}}{\rightleftharpoons}} \underset{X^*}{(\mathrm{UO_2H^{2+}})^*} \qquad (1)$$

$$(\mathrm{UO_2H^{2+}})^* + \mathrm{UO_2^{2+}} \underset{k_{XE}}{\overset{k_{EX}}{\rightleftharpoons}} \underset{E^*}{(\mathrm{U_2O_4H^{4+}})^*} \qquad (2)$$

with competing processes:

$$(\mathrm{UO_2^{2+}})^* \xrightarrow{k_U(=k_{rU} + k_{nrU})} \mathrm{UO_2^{2+}} + h\nu(1) \qquad (3)$$

$$(\mathrm{UO_2H^{2+}})^* \xrightarrow{k_X(=k_{rX} + k_{nrX})} \mathrm{UO_2^+} + \mathrm{H^+}; \qquad k_{nrX} \gg k_{rX}, \qquad (4)$$

and the E* degradation:

$$(\mathrm{U_2O_4H^{4+}})^* \xrightarrow{k_E(=k_{rE} + k_{nrE})} \mathrm{UO_2^{2+}} + \mathrm{UO_2^+} + \mathrm{H^+} + h\nu(2) \qquad (5)$$

Thus possible participants in hydrolytic paths may be all or any of the above excited uranyl species.

Considering first the linear uranyl ion, it is doubtful whether there is any increase in the acidity of $\mathrm{OUO^{2+}}$ in its luminescent state. One electron occupancy of either of the virtually atomic 5f components of the $\delta_u\mathrm{MO}(f_{z(x^2-y^2)}, f_{xyz})$ or of the $\phi_u\mathrm{MO}$-$(f_{x(x^2-3y^2)}, f_{y(3x^2-y^2)})$, cannot result in any appreciable change in the acidity of $\mathrm{OUO^{2+}}$ in its lowest excited state. Moreover, if there is even a weak involvement of the $\phi_u\mathrm{MO}$ (by its $f_{x(x^2-3y^2)}$ component) in the equatorial aquo-ligation, its occupancy must result in some decrease of $\mathrm{OUO^{2+}}$ acidity in this state.

The involvement of $(\mathrm{U_2O_4H^{4+}})^*$ in the spontaneous path:

$$(\mathrm{U_2O_4H^{4+}})^* \xrightarrow{\mathrm{H_2O}} \mathrm{OUO^{2+}} + \mathrm{UO_2^+} + \mathrm{H_3O^+}$$

competing with the characteristic emission of the above exciplex or the possible proton transfer:

$$(\mathrm{U_2O_4H^{4+}})^* + \mathrm{H_2O} \rightleftharpoons (\mathrm{U_2O_4^{3+}})^* + \mathrm{H_3O^+}$$

with $(\mathrm{U_2O_4^{3+}})^*$ degradating without radiation, appear as extreme alternatives and lead, in fact, to luminescence efficiency ζ expressions which do not fit the experimental data. This is also the case when the excited linear uranyl is taken as a possible candidate involved in a solvolytic path. On the contrary, excited-state hydrolysis of the species $(\mathrm{UO_2H^{2+}})^*$:

$$\underset{X^*}{(\mathrm{UO_2H^{2+}})^*} + \mathrm{H_2O} \underset{k'_{XY}}{\overset{k'_{YX}}{\rightleftharpoons}} \underset{Y^*}{(\mathrm{UO_2^+})^*} + \mathrm{H_3O^+} \qquad (6)$$

going from the conditional oxydation state U(V) to the state U(V), and thus suggesting some tendency of oxygens in X* to restore electron density taken by uranium in the E.T. absorption process of $\mathrm{UO_2^{2+}}$, is a possible path which does account for our results.

With this latter assumption and as far as $1/k'_{YX}$-$[\mathrm{H_2O}] + k'_{XY}[Y^*] + [\mathrm{H_3O^+}]$) (or $1/k_{YX} + k_{XY}$, at a given $[\mathrm{H_3O^+}]$) is comparable to the lifetime of X*, path (6), with Y* decaying without irradiation:

$$(\mathrm{UO_2^+})^* \xrightarrow{k_{nrY}} \mathrm{UO_2^+}, \qquad (7)$$

together with processes (1) to (5), lead to the following expression for the concentration of X*:

$$[X^*] = k_{XU}[U^*]/k_{UX} + k_{nrY} + k_{nrY}K_Y[\mathrm{H_3O^+}]^{-1} + k_E K_E(U) \qquad (8)$$

where $k_{XU} = k'_{XU}[\mathrm{H_2O}]$, $k_{UX} = k'_{UX}[\mathrm{OH^{\cdot}}]$, $K_E = k_{EX}/k_{XE} + k_E$ and $K_Y = [Y^*][\mathrm{H_3O^+}]/[X^*]$
I_m (the rate of light absorption) being:

$$I_m = (k_U + k_{XU})[U^*] - k_{UX}[X^*],$$

$$\frac{I_m}{[U^*]} = \frac{k_U(k_{UX} + k_{nrX}) + k_{XU}k_{nrX} + (k_U + k_{XU})k_{nrY}K_Y[H_3O^+]^{-1} + (k_U + k_{XU})k_EK_E(U)}{k_{UX} + k_{nrX} + k_{nrY}K_Y[H_3O^+]^{-1} + k_EK_E(U)}$$

and the apparent luminescence efficiency ζ is given by:

$$\zeta = \frac{qk_{rU}(k_{UX}+k_{nrX}+k_{nrY}K_Y[H_3O^+]^{-1})+qk_{rU}k_EK_E(U)}{k_U(k_{UX}+k_{nrX}+k_{nrY}K_Y[H_3O^+]^{-1}) + k_{XU}(k_{nrX}+k_{nrY}K_Y[H_3O^+]^{-1})+(k_U+k_{XU})k_EK_E(U)} \qquad (9)$$

$$= \frac{A + B(U)}{C + D(U)} = qk_{rU}[U^*]\,I_m^{-1} = q\phi_{rU}$$

As can be seen from (9), for low pH and rather high uranyl activities, ζ is undoubtedly a function of both $[H_3O^+]$ and (U), but as $[H_3O^+]$ decreases and for relatively low uranyl activities, ζ is expected to become a function of $[H_3O^+]$ only and its expression (9) to be simplified to:

$$\zeta = \frac{qk_{rU}k_{nrY}K_Y + qk_{rU}(k_{UX}+k_{nrX})[H_3O^+]}{(k_{UX} + k_{XU})k_{nrY}K_Y + [k_U(k_{UX} + k_{nrX}) + k_{XU}k_{nrX}]\,[H_3O^+]}$$

$$= \frac{a + b[H_3O^+]}{c + d[H_3O^+]}, \qquad (10)$$

reflecting the fact that under these conditions exciplex formation via (2) is actively quenched by path (6).

Obviously, this can account for the suppression of the exciplex contribution to the total emission and in order to check quantitatively (10), this relation is taken in the form:

$$(\zeta_{554} - ac^{-1})[H_3O^+]^{-1} = S = bc^{-1} - \zeta_{554}dc^{-1} \quad (11)$$

$$(ac^{-1}) = \lim \zeta_{554} \text{ for } [H_3O^+] \rightarrow 0)$$

Since S (Fig. 2a) and therefore ζ_{554} as well ζ_{478} (Fig. 2b) are well obeyed functions (note the S validity for low (U) and $[H^+]$ as expected for the reduction of (9) to (10)), the parameter:

$$bd^{-1} = q_{478}k_{rU}/k_U + k_{XU}k_{nrX}(k_{UX} + k_{nrX})^{-1} = 1.58 \times 10^4$$

obtained from $S = 1.88 \times 10^7 - 1.19 \times 10^3\,\zeta_{478}$, can be compared to:

$$BD^{-4} = q'_{478}k_{rU}/k_U + k_{XU},$$

which from previous data [1] is 4.22×10^4 (from $Z_{(1)} = 5.45 \times 10^6 - 1.29 \times 10^2\,\zeta_{478}$ [1]).

As for the present results (see Fig. 2b) $q_{478} = q'_{478}/3.05$,

$$(k_U + k_{XU})/(k_U + k_{XU}Q) = 1.14,$$

$$\text{where } Q = k_{nrX}/k_{UX} + k_{nrX}, \qquad (12)$$

and $k_{XU}/k_U = 0.14(1 - 1.14\,Q)^{-1}$.

Now, since (see (12)):

$$0 < Q < 1,\ k_{XU}/k_U > 0.14,$$

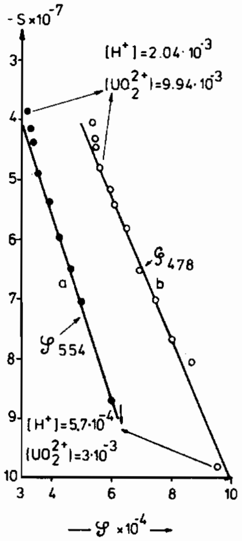


Fig. 2. The S *vs.* ζ variation according to relation (11).

and this indicates that the photoexcited linear uranyl ion can abstract a hydrogen from water.

This result may not at all be surprising [5, 6]. As we shall show in a further paper, there is a dramatically good linear correlation between rate constants, in aqueous solutions, of hydrogen abstraction by $OH^{\cdot}$ from alcohols and the constants k_q of the quenching of $(UO_2^{2+})^*$ by these compounds. This correlation shows that $OH^{\cdot}$ is roughly twelve times more reactive than $(UO_2^{2+})^*$ and it may not be implausible to anticipate a same order of reactivity in a H abstraction from water, since other resemblances between $(UO_2^{2+})^*$ and $OH^{\cdot}$ have already been [3, 7] and will be reported [8].

Rate constants $k_{OH(x)}$ of hydrogen abstraction by $OH^{\cdot}$ from x in aqueous solutions are 4.2×10^7 (x = H_2), 1.6×10^7 (x = D_2) [9] and energies of H–H, D–D and H–OH are 104.2, 105, 116 Kcal/mol respectively, so that even if $k_{OH(H_2O)}$ is taken to be as low as 6×10^5 (fifty times lower than $k_{OH(x)}$), $k'_{XU} \sim 5 \times 10^4$ and $k_{XU} \sim 3 \times 10^6$ sec^{-1} which is, of course, comparable to k_U (8×10^5 sec^{-1} [10]).

Another point of interest in relation to the ζ variation is the value of $k_{UX} + k_{nrX}/k_{nrY}K_Y$, given by b/a ((10)) and being $1.2 \times 10^2\ M^{-1}$. Introduced in the equation (9), ζ becomes:

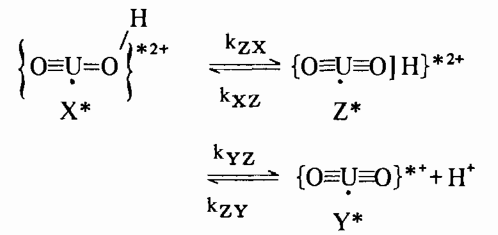
$$\zeta = \frac{qk_{rU}[(120 + H_3O^+]^{-1})k_{nrY}K_Y + k_EK_E(U)]}{k_U(k_{UX} + k_{nrX}) + k_{XU}k_{nrX} + (k_U + k_{XU})[k_{nrY}K_Y[H_3O^+]^{-1} + k_EK_E(U)]}$$

and it can readily be seen that if (UO_2^{2+}), in acid media, remains constant and pH decreases, ζ has to increase, since the relative decrease of $(120 + [H_3O^+]^{-1})k_{nrY}K_Y$ is far less important than that of $[H_3O^+]^{-1}k_{nrY}K_Y$.

To avoid changes in the structural constitution of the medium, we compared the luminescence of UO_2^{2+} solutions in aqueous HNO_3, having an ionic strength of 0.74 (added $NaNO_3$) and an uranyl ion activity $(U) = 1.19 \times 10^{-3}$, and there was indeed about two-fold increase in the quantum yield from 10^{-2} to $5 \times 10^{-1}\ M\ HNO_3$.

This, then, can rationalize the observation that life-time τ_0 increases from aqueous perchlorate solutions (1.25 μs) [10], to 0.67 M H_3PO_4 (10 μs) [11] and to 1 M H_3PO_4 (169 μs) [12], as being principally due to a solvated proton effect. Recently [13], this effect was shown to be also in part responsible for the discrepant values of the Stern–Volmer constants given in the literature, for the $(UO_2^{2+})^*$ quenched by Ag^+.

Now, one may be quite embarrassed by the bimolecularity, as given in (6), of the reverse reaction, which corresponds to an intermolecular reduction of the solvated proton by the excited $(UO_2^+)^*$ species. In fact, it is unlikely that the excited-state formation of $(UO_2^+)^*$ takes place in the manner given by (6). In OUO^{2+}, oxygens are negatively charged and a strong electrostatic field must rise owing to their proximity to the uranium atom. In the $(\pi_u)^4$, (5f, δ_u or $\phi_u)^1$ state of $(UO_2^+)^*$, axial oxygens are certainly even more negatively charged, so that possibly the interaction of $(UO_2H^{2+})^*$ with solvent proceeds as:



$$\left\{O{=}\underset{\bullet}{U}{=}O\overset{H}{\diagup}\right\}^{*2+}_{X^*} \underset{k_{XZ}}{\overset{k_{ZX}}{\rightleftharpoons}} \{O{\equiv}\underset{\bullet}{U}{\equiv}O]H\}^{*2+}_{Z^*} \underset{k_{ZY}}{\overset{k_{YZ}}{\rightleftharpoons}} \{O{\equiv}\underset{\bullet}{U}{\equiv}O\}^{*+}_{Y^*} + H^+ \quad (12)$$

connecting X* to Z* by a more plausible intramolecular redox reaction.

Note, however, that such a mechanism does not change the form of the ζ expression (9), since, with mechanism (12), it can be readily seen that $K_Y[H_3O^+]^{-1}$ in (9) becomes $K_1K_2[H_3O^+]^{-1}$, where

$$K_1 = [Z^*]/[X^*] \text{ and } K_2 = [Y^*][H_3O^+]/[Z^*]$$

Finally, it should be noticed that suppression of the second emittive component of the uranyl luminescence by increasing the pH in aqueous acidic solution, definitely excludes the connection of this second emission to an excited UO_2^{2+} state other than the f, π_u one, previously shown to be [1,3,13] unlikely.

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References

1 M. D. Marcantonatos, *Inorg. Chim. Acta, 26,* 41 (1978).
2 H. D. Burrows, S. J. Formoshinho, M. da G. Miguel and F. Pinto Coelho, *J. Chem. Soc. Faraday Trans., 72 I,* 163 (1976).
3 M. D. Marcantonatos, *Inorg. Chim. Acta, Letters, 24,* 37 (1977).
4 R. L. Gustafson, C. Richard and A. E. Martell, *J. Am. Chem. Soc., 82,* 1526 (1960).
5 H. D. Burrows and T. J. Kemp, *Chem. Soc. Rev., 3,* 139 (1974).
6 P. Benson, A. Cox. T. J. Kemp and Q. Sultana, *Chem. Phys. Letters, 36,* 195 (1975).
7 D. Greatorex, R. J. Hill, T. J. Kemp and T. J. Stone, *J. Chem. Soc. Faraday Trans., 68 I,* 2059 (1972).
8 M. D. Marcantonatos, to be published.
9 E. T. Denisov, "Liquid-Phase Reaction Rate Constants", IFI/Plenum, New York (1974) p. 200.
10 R. J. Hill, T. J. Kemp and (in part) D. M. Allen and A. Cox, *J. Chem. Soc. Faraday Trans., 70 I,* 847 (1974).
11 R. Matsushima, J. Fujimori and S. Sakuraba, *J. Chem. Soc. Faraday Trans., 70 I,* 1702 (1974).
12 G. I. Sergeev, A. K. Chibisov, L. V. Levshin and A. V. Karyakin, *J. Photochem., 5,* 253 (1976).
13 M. D. Marcantonatos, *Inorg. Chim. Acta, 25,* L87 (1977).