Inorganica Chimica Acta, 24 (1977) L37–L39
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The Exciplex Formation between Uranyl Species Further Evidenced by Quenching Data of the UO_2^{2+} Luminescence

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Received June 22, 1977

In a recent investigation of the electron-transfer quenching of the UO_2^{2+} luminescent state by metal ions [1], Burrows *et al.* found that the Stern–Volmer constant for the Ag^+ quencher (k_{SV}^{Ag}) is a function of ionic strength (μ) and of uranyl ion concentration ([U]). The μ dependency was attributed to salt effects, while the variation with [U] was suspected to result from the formation of a non-emitting excimer [1].

More recently, we observed dual luminescence from 10^{-2} *M* nitric acid solutions of UO_2^{2+} and gave evidence that the second component is the emission of the uranyl $(U_2O_4H^{4+})^*$ exciplex, formed and being degradated according to [2]:

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

$$(UO_2^{2+})^* + H_2O \underset{k'_{UX}}{\overset{k_{XU}}{\rightleftharpoons}} \underset{X^*}{(UO_2H^{2+})^*} + OH\cdot \qquad (2)$$

$$(UO_2H^{2+})^* \xrightarrow{k_{nrX}} UO_2H^{2+} \xrightarrow{OH\cdot} UO_2^{2+} + H_2O \qquad (3)$$

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

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

Moreover, in a ϕ_{rU} *vs.* $[UO_2^{2+}]$ study of self-quenching, very significant dependencies of the apparent luminescence efficiency of the linear uranyl ion ϕ_{rU} upon ionic strength were revealed and it was definitely shown that ϕ_{rU} is effectively a function of uranyl ion activity (U), owing to path (4) [2]. Excimer $(U_2O_4^{4+})^*$ formation could, of course, also account for this result, but kinetic schemes assuming this formation were unable to fit our experimental data [2].

In [2], Burrows *et al.* data of k_{SV}^{Ag}, for different low $[UO_2^{2+}]$ and various μ, were briefly argued to be consistent with the above (1) to (5) processes and with the ϕ_{rU} expression derived from the above scheme. It was then of interest, since the dependence of k_{SV}^{Ag} upon $[UO_2^{2+}]$ was shown to be due to $(U_2O_4H^{4+})^*$, to check the k_{SV} variations in the case of another perturber, quenching the luminescent state of UO_2^{2+} by a different mechanism.

Methanol was chosen as quencher, since in contrast to Ag^+, the result of the collisional process gives a net chemical change which must enhance the yield of $(UO_2H^{2+})^*$.

Table I gives the SV data, obtained by exciting (at 406 nm) the uranyl solutions with a very low intensity in order to avoid distortion of the $h\nu(1)$ radiation intensity by $h\nu(2)$ (see [2]). Figures 1a and

TABLE I. Stern–Volmer data for MeOH[a,b].

$[UO_2^{2+}] \times 10^2$	$(UO_2^{2+})^c \times 10^3$	λ_{em}(nm)	r^d	$y^e + k_{SV}^f$
0.5	2.64	544	0.999	0.98 + 10.44
0.8	3.85	544	0.997	1.04 + 9.65
1	4.56	544	0.998	1.03 + 9.23
		478	0.998	1.02 + 9.43
1.5	6.10	488	0.999	1.00 + 8.35
2	7.39	544	0.998	0.99 + 8.42
		488	0.998	1.03 + 8.06
2.5	8.50	544	0.998	1.07 + 8.23
3	9.48	544	0.998	1.02 + 7.65
		478	0.998	1.04 + 7.83
4	11.10	544	0.997	1.06 + 7.97
		478	0.999	1.00 + 7.90
5	12.46	544	0.996	1.00 + 7.60
		488	0.996	1.00 + 7.49

[a] In 10^{-2} HNO_3. [b] Fifteen different concentrations from 2×10^{-2} to 3.2×10^{-1}. [c] Calculated as in [2]. [d] Linear regression coefficient. [e] Intercept. [f] From thirty independent determinations.

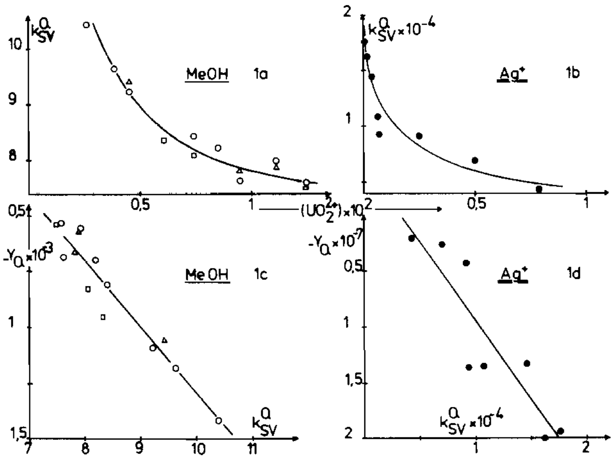

Figure 1. k_{SV}^Q *vs.* uranyl activity. 1a, Q = MeOH (pH = 1.94); 1b, Q = Ag^+ (Burrows *et al.* data, pH ~ 2 [1]); exc: 406 nm; em: ○ - 544, □ - 488, △ - 478, ● - 510 nm. 1c and 1d, linearisation of the functions (17) (see (19)) (linear regression coefficient 1c: 0.954, 1d: 0.901).

1b show the variation of k_{SV} with (U) in the case of MeOH and Ag^+ (Burrows *et al.* data).

There are four interesting features in these variations: (i) in both cases k_{SV} is a decreasing monotonic function of uranyl activity (U) and (ii) for any (U), k_{SV}^{Ag} is far more important than k_{SV}^{MeOH}. For low (U), (iii) $dk_{SV}^{Ag}/d(U)$ is greater than the corresponding slope for MeOH and (iv) as (U) decreases, the increase in $dk_{SV}^{Ag}/d(U)$ (in absolute value) is more important than the increase of $dk_{SV}^{MeOH}/d(U)$.

All the above features can be explained by the scheme (1) to (5), completed in the presence of Ag^+ by:

$$(UO_2^{2+})^* \xrightarrow{k_q^{Ag},\ Ag^+} UO_2^{2+} \qquad (6)$$

and by:

$$(UO_2^{2+})^* + CH_3OH \xrightarrow{k_q^{MeOH}} (UO_2H^{2+})^* + \dot{C}H_2OH \quad (7)$$

$$(2\dot{C}H_2OH \longrightarrow CH_2O + CH_3OH),$$

in methanol/water.

In fact, and as already reported in [2], $(UO_2H^{2+})^*$ suffers hydrolysis and recent results [3] strongly suggest this path, so that the scheme (1) to (5) must be completed by:

$$(UO_2H^{2+})^* \underset{k_{XY}}{\overset{k_{YX}}{\rightleftharpoons}} (UO_2^+)^* + H^+ \qquad (2')$$

$$(UO_2^+)^* \xrightarrow{k_{nrY}} UO_2^+ \qquad (2'')$$

Also recent data [3] further support a $U_2O_4H^{4+}$ composition of the emitting exciplex, since its emission (observed for $[UO_2^{2+}] > 10^{-2}$ in 10^{-2} HNO_3 and high excitation intensities) is found, under exactly the same conditions, to be considerably reduced when H_2O is replaced by D_2O.

In the absence of quencher and according to the photophysical and chemical processes (1) to (5) and (2′), (2″), the concentrations of species of interest and the emission intensity I_L of the linear uranyl unperturbed by the $(U_2O_4H^{4+})^*$ emission (present experimental conditions) are:

$$[U^*] = I_m[A + k_EK_E(U)]/D \qquad (8)$$

$$[X^*] = k_{XU}[U^*]/A + k_EK_E(U) \qquad (9)$$

$$[E^*] = I_mk_{XU}K_E(U)/D \qquad (10)$$

$$I_L = qk_{rU}I_m[A + k_EK_E(U)]/D \qquad (11)$$

with I_m: absorbed intensity, q : an apparatus constant,

$$K_E = k_{EX}/k_{XE} + k_E,\ K_Y = k_{YX}/k_{XY} + k_{nrY},$$

$$A = k_{UX} + k_{nrX} + k_{nrY}K_Y[H^+]^{-1} \qquad (12)$$

$$B = k_{nrX} + k_{nrY}K_Y[H^+]^{-1} \qquad (13)$$

$$D = k_UA + k_{XU}B + (k_U + k_{XU})k_EK_E(U) \qquad (14)$$

I_L/I_L^Q takes then the form:

$$I_L/I_L^{MeOH} = 1 + [B + k_EK_E(U)]\,k_q^{MeOH}D^{-1}[MeOH] \qquad (15)$$

$$I_L/I_L^{Ag} = 1 + [A + k_EK_E(U)]\,k_q^{Ag}D^{-1}[Ag^+], \qquad (16)$$

and for either quencher (see (14)):

$$k_{SV}^Q = [m + m'(U)][d + d'(U)]^{-1} \qquad (17)$$

Also, as $[E^*] = K_E(U)[X^*]$ (see also (15), (16), (10)):

$$k_{SV}^Q = [m + m'(U)](I_mk_{XU})^{-1}[X^*]$$

which, for low uranyl concentrations and constant excitation intensity, becomes:

$$k_{SV}^Q \cong [m + m'(U)]\ [Gk_{XU}(U)]^{-1}[X^*]$$
$$\cong p\,[X^*](U)^{-1} + g[X^*] \qquad (18)$$

where p and g are constants.

Figures 1c and 1d show that relation (17), taken in the form:

$$\frac{k_{SV}^Q - (md^{-1})}{(U)} = Y_Q = m'd^{-1} - d'd^{-1}k_{SV}^Q = f(k_{SV}^Q), \qquad (19)$$

is satisfied for both quenchers, thus further suggesting (see [2]) that the monotonous decrease (see also (18)) of k_{SV}^Q with (U) comes from the E* exciplex formation between uranyl species.

Parameters m/d and m′/d′ in (19) or p and g in (18) are of course much higher for Ag^+ than for MeOH, the former being, as is well known, a far more effective quencher ($k_q^{Ag} \gg k_q^{MeOH}$) of the uranyl luminescent state.

It is our opinion that both quenchers form transient exciplexes with the linear excited uranyl and that the primary act is a simultaneous overlap of the π_u M.O. and of one of the virtually atomic components ($f_{x,y,z}$ or $f_{z(x^2-y^2)}$ of the σ_u M.O. of $(UO_2^{2+})^*$ $\pi_u^3(5f, \sigma_u)^1$, by an appropriate orbital of the quencher (*i.e.* $d_{y,z}$ of Ag^+ or the group M.O. π_{CH_3} [4] of MeOH). The efficiency of quenching must then be controlled by the expansion and energy (E) of the overlapping orbital of the quencher.

For Ag^+, radius (r_m) of d maximum density is 0.25 a.u. and E = –0.756 a.u. while for MeOH E (π_{CH_3}) = –0.624, E (π'_{CH_3}) = –0.669 a.u. and r_m must be much higher than that of Ag^+. Nevertheless, in the case of MeOH, the primary act is followed by H-abstraction and obviously MeOH behaves as a far less effective quencher.

Parenthetically, it is interesting to note that hydroxylic H-abstraction would require overlap of $(UO_2^{2+})^*$ π_u, ($5f$, σ_u) M.O.'s by some appropriate COH M.O., but in this case the closeness of the methanolic oxygen to that of $(UO_2^{2+})^*$ and, therefore, the O-----O repulsion would make this overlap small.

In fact, hydroxylic H is inaccessible to $(UO_2^{2+})^*$, not only in the case of alcohols but also in that of carboxylic acids [5]. Significantly enough, the hydroxyl radical abstracts H from alcohols in the same position [6] as $(UO_2^{2+})^*$ does.

From the same point of view, one would also expect the quenching efficiency of alkyl halides to decrease with increasing halogen electronegativity. Indeed $k_{SV}(RX)$: n-C_3H_7I: 670, n-C_4H_9Br: 84, n-C_4H_9Cl = 10.8, while assuming (as in [5]) charge transfer by 5f, π_u overlap with a X non bonding n orbital or some other group M.O. containing a n component, the same order could be argued, but unfortunately k_{SV}: C_2H_5Br: 105, $CHBr_3$: 87 and CCl_4: 1.25.

It is, therefore, our impression that collisions for efficient overlap between $(UO_2^{2+})^*$ and quencher M.O.'s require special orientations, with the $(UO_2^{2+})^*$ oxygen (the axial extremity where π_u is practically delocalised) avoiding highly negative centers and preferring π_{CH_n} manifolds.

For halides X^-, $(UO_2^{2+})^*$ has no sterical choice and quenching efficiency has to be ruled by expansion and energy of the overlapping M.O. of the quencher.

Considering, now, $dk_{SV}^Q/d(U)$, one obtains from (18), with $k_{SV}^Q = f((U), [X^*])$ and $[X^*] = v((U))$:

$$dk_{SV}^{Q}/d(U) = p\,[(U)[X^*]]^{-1}([1 + g(U)p^{-1}]\,[X]^*d[X^*]/d(U) - (U)^{-1}) = -p(U)^{-2}[X^*]^{-1} \quad (20)$$

so that at any low (U) $dk_{SV}^{Ag}/d(U) > dk_{SV}^{MeOH}/d(U)$, since $p^{Ag} > p^{MeOH}$ (Figs. 1a and 1b).

It is, moreover, noteworthy that, as (U) decreases (low (U)), $dk_{SV}^Q/d(U)$ (in absolute value) increases more rapidly in the case of Ag^+ than of MeOH, for which the enhancing X* step (7) slows down this increase in accordance with (19). This indicates that chemical quenching by MeOH is far more important than its physical one, since otherwise curve 1a should parallel curve 1b.

Finally, it has to be noticed that, according to processes (1) to (5) and (2′), (2″), photoexcitation of (UO_2^{2+}) in aqueous acidic media must produce U(IV) species by UO_2^+ disproportionation (see (2″) and (5)):

$$2UO_2^+ + 4H^+ \longrightarrow UO_2^{2+} + U^{4+} + 2H_2O$$

and, very interestingly, recent results [7] revealed that photoexcitation of UO_2^{2+} in concentrated phosphoric acid and phosphate glasses leads indeed to U^{4+} species formation.

Acknowledgements

The author is grateful to Professors C. K. Jørgensen and R. Reisfeld for helpful discussions. X^α calculations on Ag^+ by J. Weber and experimental work by Mrs. Y. Zakaria are gratefully acknowledged.

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