Deactivation Pathways of Excited Uranyl Ions in Solutions

By Galina Sergeeva, Alexander Chibisov,* Leonid Levshin, and Arkadii Karyakin

(*Vernadsky Institute of Geochemistry and Analytical Chemistry, Academy of Sciences, Moscow, and Moscow State University Physical Department, U.S.S.R.*)

Summary Deactivation pathways of excited uranyl ions in solutions have been studied by flash photolysis and the production of U^{5+} has been shown to occur *via* exciplex formation as a result of donor–acceptor interaction between U^{6+*} and electron donors.

It is known that uranyl ions in solution are characterized by intensive luminescence with a lifetime of 10^{-4} s.

Flash excitation (1×10^{-5} s, 1000 J) of deaerated pure aqueous solutions of uranyl ions[1] produces a luminescent afterglow (10^{-4} s), and a short-time absorption (10^{-4} s) with λ_{max} 590 nm[2] at 300 K. These results have been confirmed recently.[3] A comparative study of the kinetics of the decay of both the short-time absorption and the afterglow of uranyl ions measured by absorption and emission with and without various quenchers has shown that the rate constants of deactivation of the uranyl ions coincide. This shows that emission and absorption occur from the same excited level of uranyl ions.

Table

Rate constants for the 'physical' and 'chemical' deactivations of excited uranyl ions

Alcohol	'Physical' quenching $K_2 \times 10^{-7}$ l mol^{-1} s^{-1}	'Chemical' quenching $K_3 \times 10^{-7}$ l mol^{-1} s^{-1}
t-Butyl	8·19	<0·007
Methyl	57·4	14·0
Ethyl	112·0	28·4
Isopropyl	176·0	55·0

The lower excited level of uranyl ions is a singlet, shown by the equal life-times of uranyl ion excited states measured with and without O_2 and by the absence of a typical T–T absorption for such acceptors as anthracene-α-sulphonic acid, Rhodamine 6G, and 3,3′-diethylthiocarbocyanine in the experiments carried out on T–T energy transfer from excited uranyl ions.

Observed changes in absorption (Figure) on flash excitation of uranyl ions are the result of transitions between the first excited singlet level of the uranyl ion (S_1^*) and higher levels (S_n^*). The maxima of the absorption bands (shown in the Figure with arrows) were calculated using uranyl ion transition energies[4] between various electronic states and were in good agreement with experimental data.

Organic substances such as aliphatic alcohols, aliphatic acids, aniline, diphenylamine, β-naphthylamine, phenol, β-naphthol, and hydroquinone were shown to be efficient quenchers of the U^{6+*} species. The quenchers were selected so that the energy transfer from the excited uranyl ions to molecules of the quenchers is impossible.

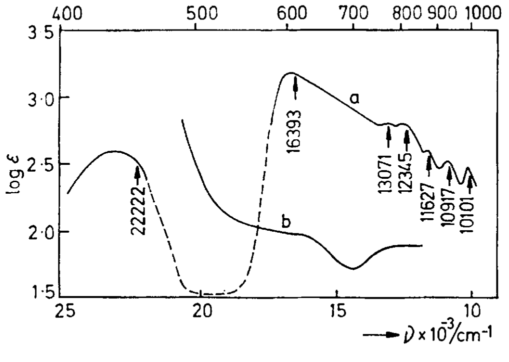

Figure. Absorption spectra of U^{6+*} (a) and U^{5+} (b) in 1M H_3PO_4.

In the presence of the quenchers (10^{-3}—10^{-2} M) new absorption bands were observed in the visible range due to formation of U^{5+} (Figure) and cation-radicals of the quenchers. The U^{5+} absorption spectrum measured compares well with that previously obtained.[5]

To explain the deactivation of excited uranyl ions in solutions with organic quenchers (Q) present we suggest Scheme 1 where equations (2) and (3) represent 'physical' and 'chemical' deactivations respectively.

$$U^{6+} + h\nu \xrightarrow{k_0} U^{6+*} \tag{0}$$

$$U^{6+*} \xrightarrow{k_1} U^{6+} + h\nu_{fl} \tag{1}$$

$$U^{6+*} + Q \xrightarrow{k_2} U^{6+} + Q \tag{2}$$

$$U^{6+*} + Q \xrightarrow{k_3} U^{5+} + \dot{Q}^{+} \tag{3}$$

Scheme 1

To determine the values of the rate constants for U^{6+*} deactivation, kinetic calculations were made which gave equation (4).

$$\frac{[U^{6+*}]_0}{[U^{5+}]_{max}} = \frac{k_2 + k_3}{k_3} + \frac{k_1}{k_3} \times \frac{1}{[Q]} \qquad (4)$$

The Table contains the values of the rate constants for the 'physical' and 'chemical' deactivations of excited uranyl ions when they are quenched with various aliphatic alcohols in 1M H_3PO_4. The considerable increase of the quenching rate constants in passing from t-butyl to isopropyl alcohol can be associated with the different reactivity of these alcohols.

Assuming that 'physical' and 'chemical' deactivations of U^{6+*} occur *via* the uranyl exciplex ($[U^{6+} \ldots Q]^*$) according to Scheme 2 equations (8) and (9) can be derived. From equations (8) and (9) assuming $k_5 = k_{diff.} = 7{\cdot}7 \times 10^9$ l mol^{-1} s^{-1}, $(k_{-5} + k_6 + k_7)^{-1} = \tau_{exciplex} \leqslant 10^{-6}$ s, one can estimate $k_6 \geqslant 7 \times 10^4$ s^{-1}, $k_7 \leqslant 2 \times 10^4$ s^{-1}, $k_{-5} \geqslant 9 \times 10^5$ s^{-1}, $K = k_5/k_{-5} \geqslant 8 \times 10^3$ M^{-1} for aqueous solution of uranyl ions with methanol.

$$U^{6+*} + Q \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} [U^{6+} \ldots Q]^* \qquad (5)$$

$$[U^{6+} \ldots Q]^* \xrightarrow{k_6} U^{6+} + Q \qquad (6)$$

$$[U^{6+} \ldots Q]^* \xrightarrow{k_7} U^{5+} + \dot{Q}^+ \qquad (7)$$

SCHEME 2

$$k_2 = \frac{k_5 \,.\, k_6}{(k_{-5} + k_6 + k_7)} \qquad (8)$$

$$k_3 = \frac{k_5 \,.\, k_7}{(k_{-5} + k_6 + k_7)} \qquad (9)$$

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