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Bright chemiluminescence during the solid-phase reaction of uranium(IV) sulfate and sodium perxenate powders

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The reaction of powders resulting in the excitation of uranyl ions occurs anomalously quickly for a solid-phase reaction.

It is well known that the brightness I of chemiluminescence (CL) is proportional to its yield η and reaction rate v. In turn, η is the product of excitation yield η_e by radiation yield η_r of the photon emitter

$$I = \eta v = \eta_e \eta_r v.$$

The oxidation of tetravalent uranium ions in acidic aqueous media with xenon difluoride or xenon trioxide is accompanied by CL; however, its high excitation yield does not at all imply a high radiation yield of the excited $^*UO_2^{2+}$ ion[1–3] due to high-probability radiationless deactivation processes. For example, the life time of the $^*UO_2^{2+}$ ion in an excited state in a solution of perchloric acid decreases by almost two orders of magnitude in comparison with the corresponding solid perchlorate. Accordingly, the yields of luminescence and hence CL decrease by three orders. The same applies to the luminescence of other actinides. In fact, ions or neptunium and plutonium brightly fluoresce in crystals activated by these ions but do not fluoresce in solutions.[4,5] In view of this, the oxidation of an uranium(IV) salt with xenon compounds in a solid phase should result in an increase in the yield of CL (and hence its brightness) by several orders of magnitude in comparison with solutions.

Solid-phase redox reactions of actinides are known; they usually occur at high temperatures.[6–8] The thermal deactivation under these conditions is so strong that there is no chance to detect the radiation of photons, even if a reaction produces excited actinide ions. In this context, xenon compounds are attractive as their reduction results in gaseous xenon. Hence, one could expect that the surfaces of crystals would be renewed due to their breakdown as a result of gas liberation; hence, we had a reason to expect that the reaction would occur at lower temperatures.

It is dangerous to carry out a solid-phase reaction of an uranium(IV) salt with the solid trioxide XeO_3 due to its well-known brisant explosive properties. Salts of octavalent xenon are more stable. Thus, it could be assumed that gradual reduction of octavalent xenon to Xe(0) would pass through the hexavalent state, which is well known to undergo chemiluminescent reactions with tetravalent uranium.[1]

We found that the simple mixing of $U(SO_4)_2 \cdot 4H_2O$ and $Na_4XeO_6 \cdot 8H_2O$ salts with a glass spatula without trituration (!) resulted in greenish luminescence visible by unaided eye even in a slightly darkened room. At 18 and 26 °C, the dependence of CL intensity I on time can be very well linearised in the $1/\sqrt{I} - t$ (time) coordinates (Figure 1). This type of dependence is typical of the CL of recombination processes.

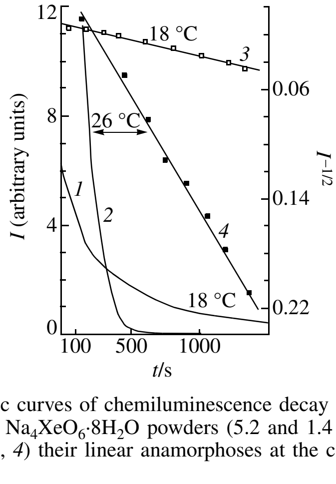

Figure 1 Kinetic curves of chemiluminescence decay for the reaction of $U(SO_4)_2 \cdot 4H_2O + Na_4XeO_6 \cdot 8H_2O$ powders (5.2 and 1.4 mg) at (*1*) 18 and (*2*) 26 °C and (*3*, *4*) their linear anamorphoses at the corresponding temperatures.

The rate constants obtained from these curves are effective values since not only the elementary steps of formation of excited ions but also the valence states of xenon compounds involved in the limiting steps are unknown. Nevertheless, for such crystal sizes, the values of the rate constants give an idea about the time required for the reaction to be completed, which is from 1 to 1.5 h. An estimate of the activation energy in such a small temperature range gives a value of ≈ 22(±3) kcal. Presumably, the activation processes of redox processes themselves are overlaid by structural, relaxation or phase transitions either in the perxenate salt or in uranium sulfate. In the case of gradual heating, two maxima at 28 and 41 °C appear on the temperature dependence of the CL intensity (Figures 2 and 3). In order to provide a uniform temperature distribution in the bulk of the mixture, we used a massive copper furnace (in comparison with the weighed sample), small samples (3–6 mg) distributed as a thin layer at the ampoule bottom (5 mm in diameter), slow heating (13 K min^{-1}) and a maximum heater power of 20 W. The temperature was monitored using a copper–constantan thermo-

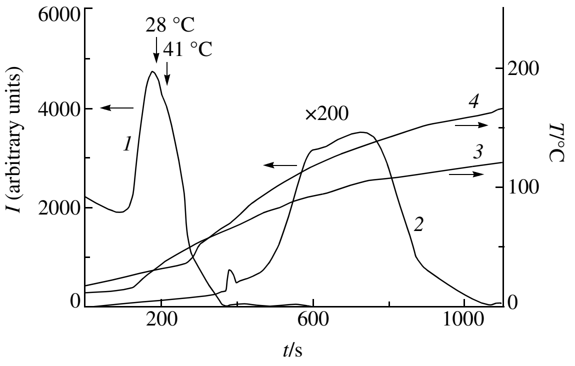

Figure 2 Variation of CL intensity in time during the gradual heating of (*1*) $U(SO_4)_2{\cdot}4H_2O + Na_4XeO_6{\cdot}8H_2O$ powders (5.2 and 1.4 mg) and (*2*) $UO_2SO_4{\cdot}3H_2O + Na_4XeO_6{\cdot}8H_2O$ powders (2.5 and 1 mg). (*3*, *4*) Temperature variation in time.

couple (the diameter of the conductors was 0.1 mm).

The activation energy determined at the initial part of luminescence growth, where the change in the amount of the reacted compound can still be neglected, is close to the activation energy in the first region of the kinetic curve evaluated under isothermal conditions at the two temperatures. Note that the thermal decomposition[9] of pure perxenate occurs only above 300 °C hence the changes in the curve are totally determined by the redox reactions of uranium ions with different valence forms of xenon compounds.

Figure 4 shows the photoluminescence and excitation spectra for the reaction products of $U(SO_4)_2{\cdot}4H_2O + Na_4XeO_6{\cdot}8H_2O$ powders and for $UO_2SO_4{\cdot}3H_2O$. The CL spectrum obtained for the reaction of $U(SO_4)_2{\cdot}4H_2O$ and $Na_4XeO_6{\cdot}8H_2O$ powders confirms the fact that it is the excited uranyl ion $^*UO_2^{2+}$ that is the radiation emitter in the entire kinetic region studied. The CL spectrum for the reaction of $U(SO_4)_2{\cdot}4H_2O + Na_4XeO_6{\cdot}8H_2O$ powders was recorded using sharp-cutoff light filters. The spectral analysis of CL was carried out using a MZD-2 monochromator as the spectrometer; the slit opening had the maximum value (the optical width was 25 nm). Such a slit width does not allow the typical radiation structure of the uranyl ion to be resolved, but its spectral region is matched very well. The spectral scanning rate was 20 nm s^{-1}.

The luminescence observed upon mixing $U(SO_4)_2{\cdot}4H_2O$ with $Na_4XeO_6{\cdot}8H_2O$ totally ceases after the complete decomposition of sodium perxenate at 300 °C. It is known that the decomposition products of pure sodium perxenate are Xe, O_2 and Na_2O. On the other hand, reduction with a hydrated uranium(IV) salt can give other products. In particular, sodium hydroxide can be produced instead of sodium oxide. Additionally, it is likely that a smaller quantity of molecular oxygen will be formed. However, evolution of xenon certainly occurs. Brightly fluorescing crystals of the uranyl salt are visible under a luminescent microscope with UV excitation. The photoluminescence spectrum of these crystals and the excitation spectrum of uranyl sulfate are shown in Figure 4. The good agreement of these spectra may additionally confirm that uranyl sulfate is a product of the reaction between $U(SO_4)_2{\cdot}4H_2O$ and $Na_4XeO_6{\cdot}8H_2O$.

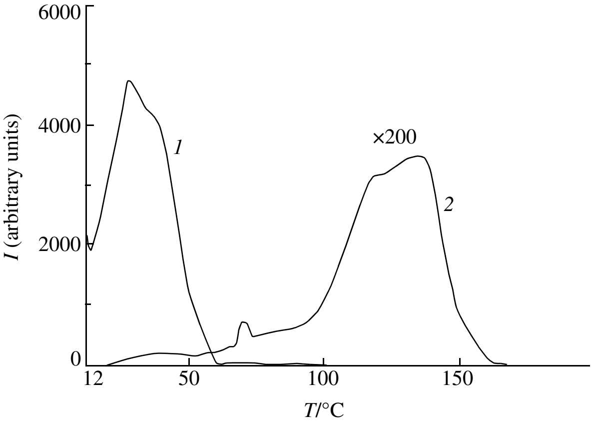

Figure 3 Temperature dependence of CL intensity during gradual heating of (*1*) $U(SO_4)_2{\cdot}4H_2O + Na_4XeO_6{\cdot}8H_2O$ powders (5.2 and 1.4 mg) and (*2*) $UO_2SO_4{\cdot}3H_2O + Na_4XeO_6{\cdot}8H_2O$ powders (2.5 and 1 mg).

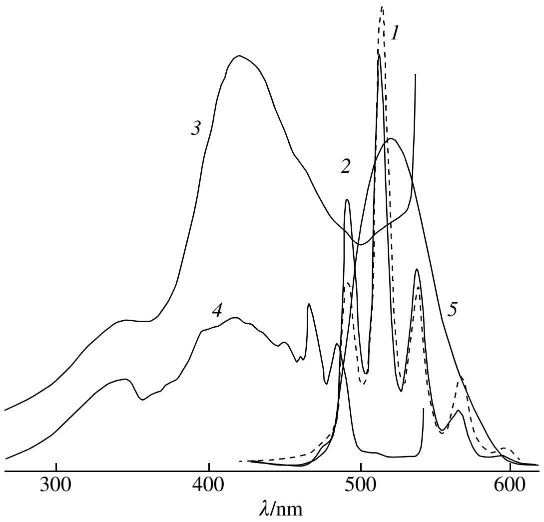

Figure 4 (*1*, *2*) Photoluminescence and (*3*, *4*) excitation spectra for the reaction products of (*1*, *3*) $U(SO_4)_2{\cdot}4H_2O + Na_4XeO_6{\cdot}8H_2O$ powders (7 and 1.5 mg) ($\lambda_{ex} = 380$ nm, $\lambda_{obs} = 570$ nm) and (*2*, *4*) $UO_2SO_4{\cdot}3H_2O$ ($\lambda_{ex} = 350$ nm, $\lambda_{obs} = 560$ nm); 18 °C. (*5*) Chemiluminescence spectrum for the reaction of $U(SO_4)_2{\cdot}4H_2O + Na_4XeO_6{\cdot}8H_2O$ powders recorded using light filters; 18 °C.

It should be noted that no noticeable irradiation was detected during gradual heating of pure sodium perxenate (the detection threshold was ≥ $5{\times}10^3$ photons). If powders of sodium perxenate and uranyl sulfate are mixed, a noticeable acceleration of CL occurs (Figures 2 and 3). The most likely origin of this acceleration is that uranyl ions can be reduced by hydrogen peroxide formed as a reaction product between crystal water and xenon compounds, which under these unusual conditions can reduce the uranyl ion to a pentavalent state with its subsequent reverse oxidation by other forms of xenon and with the formation of an excited ion.

Let us note in conclusion that the vigorous gas evolution is undoubtedly the main reason for the fast reaction between $U(SO_4)_2{\cdot}4H_2O$ and $Na_4XeO_6{\cdot}8H_2O$. This is accompanied by the decomposition of sodium perxenate crystals and renewal of the contact surface. Probably, rather an important role belongs to crystal water, which is also involved in the reaction with the perxenate ion; this also results in the destruction of crystals. On the whole, twelve water molecules are liberated from both reacting compounds: eight molecules from the hydrated xenon salt and four molecules from tetravalent uranium sulfate. These molecules can form a surface water microphase on the surface of the reacting crystals, which considerably accelerates the redox reactions.

It is interesting to note that the reaction of uranium dioxide with sodium perxenate does not result in a noticeable light emission in the temperature range 20–300 °C.

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