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Chemiluminescence during the solid-phase interaction of uranium(IV) hydrophosphate and xenon difluoride powders

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The solid-phase reaction of uranium(IV) hydrophosphate and xenon difluoride powders resulted in chemiluminescence accompanied by an exothermal effect and intense evolution of a liquid phase.

A considerable increase in the fluorescence (FL) yield of UO_2^{2+} ions on transition to solid salts is a significant factor that allows one to observe chemiluminescence (CL) during the solid-phase oxidation of uranium(IV) salts by xenon compounds. Previously, bright CL was observed during the reaction of uranium(IV) sulfate with octavalent xenon compounds.[1] Light emission, albeit with a smaller intensity, also occurred during the oxidation of uranium(IV) hydroxide with sodium perxenate or xenon difluoride.[2] The brightness observed during the oxidation of uranium(IV) sulfate with xenon difluoride is several orders of magnitude smaller.[3]

We have found that the CL brightness and the reaction rates depend considerably on the chemical nature of the coordination environment. Although the reaction of xenon difluoride with uranium(IV) sulfate occurs rather slowly, the mixing of xenon difluoride powders with uranium(IV) hydrophosphate $U(HPO_4)_2 \cdot 4H_2O$ is accompanied by violent liberation of a liquid phase and strong self-heating.

The powders of $U(HPO_4)_2 \cdot 4H_2O$ and XeF_2 with a 1.5-fold excess of the oxidant (by equivalent mass) were rapidly stirred with a glass rod in a small Teflon cell and the mixture was then transferred into a CL cell in order to record light emission. An intensity burst was observed, followed by an intensity drop.

The reaction progress was visually controlled using an Altami SM-II stereoscopic microscope equipped with a video camera. We observed that intense interaction of the powders started as they approached each other: the mechanochemical motion of crystals was distinctly visible at the contact boundary, which most likely occurred due to adhesion forces. As the powders contact, a liquid phase starts to form and white vapour is evolved intensely. There is an impression that uranium(IV) hydrophosphate as if 'sucks in' XeF_2 crystals. Further, the 'sucked-in' XeF_2 reacted with a great excess of uranium(IV) hydrophosphate. In a few minutes after the reaction start, the reaction mixture looked like a 'boiling' dark-green mass.

A liquid phase might be formed due to the liberation of crystallisation water in a free form at the interface. An abrupt increase in temperature takes place immediately after the crystals are mixed. Measurements with a copper–constantan thermocouple showed that the temperature reached 97 °C at the very beginning of the reaction. After that it decreased, so the shape of the decrease plot resembled a CL drop curve. At this temperature, XeF_2 starts to sublime, and the observed white vapour most likely consists of HF, a xenon difluoride decomposition product, and vapours of the oxidant. Taking into account the oxidant loss, we always used a 1.5-fold excess of the oxidant. Figure 1 shows the temperature variation upon mixing $U(HPO_4)_2 \cdot 4H_2O$ and XeF_2 powders, along with the kinetics of CL accompanying the reaction. The kinetic curves could not be linearized in first- and second-order coordinates. Meantime, the kinetic curves of the oxidation of uranium(IV) sulfate with sodium perxenate can be linearized in the $1/\sqrt{I_{CL}} - t$ (time) coordinates;[1] this behaviour is typical of CL in recombination processes. Our attempts to linearize the curves in these coordinates failed, suggesting the reaction of interest has a more complex nature. Gaseous xenon is liberated during the reaction, which results in the renewal of the reaction mixture surface owing to continuous gas evolution. An interesting feature of the reaction is that it occurs in a pulse mode. This is demonstrated by the fact that the temperature changes in a stepwise rather than smooth manner.

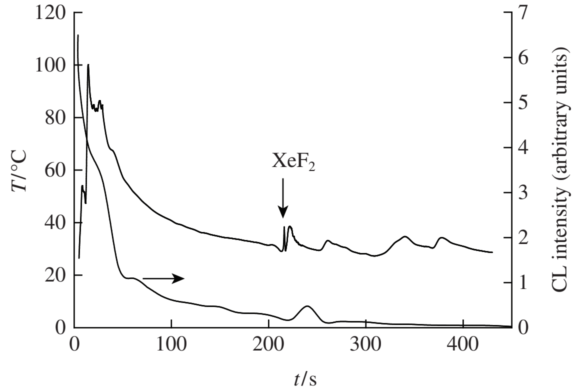


Figure 1 CL kinetic curve for the reaction of $U(HPO_4)_2 \cdot 4H_2O$ with XeF_2 (1 : 1.5 equiv.) and accompanying temperature variations during the reaction. The time of introducing an additional XeF_2 crystal is marked with an arrow.

If a few more crystals of the oxidant are added during light emission drop, the temperature increases again. This suggests that not all uranium(IV) has reacted by that instant.

A comparison of diffusion reflection spectra for $U(HPO_4)_2 \cdot 4H_2O$ and $UF_4 \cdot 2.5H_2O$ with those of the reaction products shows that the changes mainly involve a hypsochromic shift of the absorption maxima, which is typical of uranium(IV) compounds when its complex form changes (Figure 2). For example, λ_{max} = 648 nm for U^{4+}_{aq}, whereas λ_{max} = 610 nm for UF_4. We assume that a considerable fraction of uranium(IV) is converted in the starting period of the reaction to give a fluoride-phosphate complex, which is

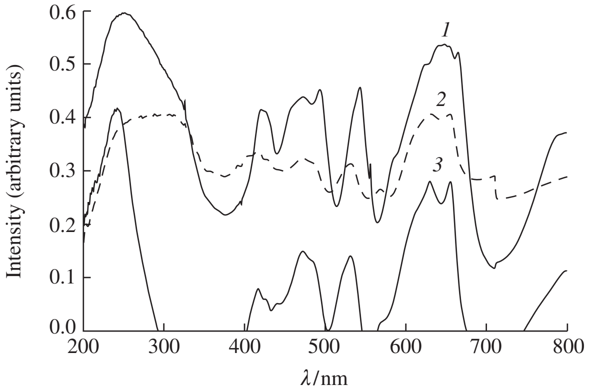


Figure 2 Diffusion reflection spectra: (*1*) pure $U(HPO_4)_2 \cdot 4H_2O$, (*2*) $U(HPO_4)_2 \cdot 4H_2O + XeF_2$ reaction product and (*3*) $UF_4 \cdot 2.5H_2O$ at 25 °C (MgO is used as the reference material).

resistant against oxidation, as suggested by the characteristic bands of uranium(IV) in the diffusion reflection spectrum after mixing $U(HPO_4)_2 \cdot 4H_2O$ with the oxidant.

A blue component was found at 340 nm[1] in the reflection spectrum during the oxidation of uranium(IV) sulfate with sodium perxenate; this component is typical of complex uranium(IV) carbonates and oxalates, *i.e.*, uranium(IV) complexes where the ligands contain an anion of a weak acid. We believe that the changes in the reflection spectra result from the formation of an uranium(IV) complex perxenate rather than the oxidation of uranium(IV). The subsequent reaction steps can occur within such a complex due to the oxidation of the complexing agent with the ligand. Apparently, an intermediate of xenon difluoride with uranium(IV) is formed in our reaction; however, we cannot detect it by spectrophotometry as it quickly undergoes further reactions.

The solid-phase reaction of uranium sulfate and sodium perxenate powders[1] is inferior to the reaction of $U(HPO_4)_2 \cdot 2H_2O$ and XeF_2, in terms of both reaction intensity and liquid phase evolution. The main difference is that, in our reaction, at such reagent ratios we did not observe a colour change from green to yellow that would suggest that all uranium(IV) was completely oxidized. However, the major fraction of uranium(IV) is oxidized, and FL emission spectra (Figure 3) contain bands typical of uranyl ions. This is accompanied by a 6 nm shift towards the blue region in comparison with pure $UO_2HPO_4 \cdot 2H_2O$. Based on the spectra obtained, one can assume that solid-phase oxidation of uranium(IV) hydrophosphate with xenon difluoride results in a fluoride-phthalate complex of uranyl, *i.e.*, the oxidation product 'inherits' the coordination environment of the original valent state. Uranium(IV) is a well-known quencher of excited states of the uranyl ion; it is reasonable to explain by this fact why characteristic uranyl lines are absent from the FL excitation spectrum of the reaction products, although they are readily detectable for crystalline uranyl phosphate.[4]

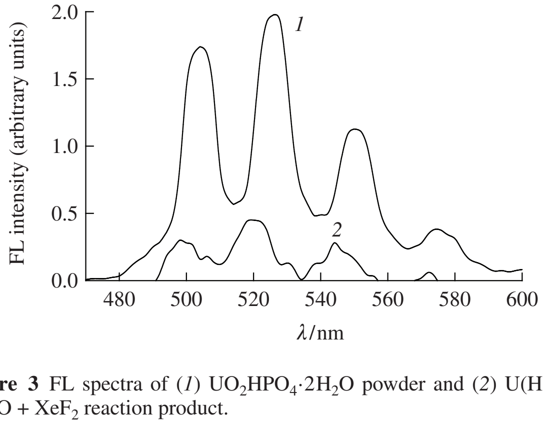
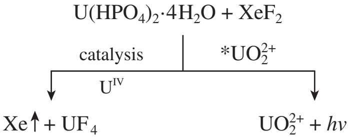


Figure 3 FL spectra of (*1*) $UO_2HPO_4 \cdot 2H_2O$ powder and (*2*) $U(HPO_4)_2 \cdot 4H_2O + XeF_2$ reaction product.

Based on the above, we can conclude that two processes run in parallel during the reaction of $U(HPO_4)_2 \cdot 4H_2O$ with XeF_2: the oxidation of a fraction of uranium(IV) to uranyl and a catalytic reaction of xenon difluoride decomposition (Scheme 1). In other words, uranium(IV) ions also act as a catalyst, since they are strong acceptors of fluoride ions. The catalytic character of the reaction is also corroborated by the fact that the solid-phase reaction of xenon difluoride with thorium(IV) nitrate, which does not participate in redox reactions but is a catalyst of xenon difluoride hydrolysis in solutions,[5] is also accompanied by a small temperature increase (48 °C). Thus, we can say that the decomposition of xenon difluoride in a solid phase occurs with heat liberation in the presence of metals that are fluoride ion acceptors and it is strongly accelerated if the metal additionally undergoes oxidation.



Scheme 1

A comparison with the previously studied reactions[1–3] shows that they are inferior to the observed reaction of $U(HPO_4)_2 \cdot 2H_2O$ with XeF_2, in terms of both reaction intensity and liquid phase evolution. We assume that the reason for such a significant difference of this reaction is that there is a non-substituted proton in the uranium(IV) coordination environment. This agrees with published data on the catalysis of xenon difluoride degradation with protic acids. Furthermore, the reaction of xenon difluoride with the HPO_4^{2-} anion in the coordination environment of uranium(IV) should not be ruled out; it can produce an intermediate unstable xenon(II) fluorophosphate followed by its fast degradation.[6] Note that the intensity of FL (and hence the yield of uranyl ion emission) considerably increased upon coordination to the phosphate anion. As a consequence, the intensity of CL can be higher in the reaction of XeF_2 with the phosphate complex of uranium(IV), as compared with other reactions.

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