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Multi-emitter chemiluminescence in the solid-phase interaction of xenon difluoride with uranyl hydrogen phosphate

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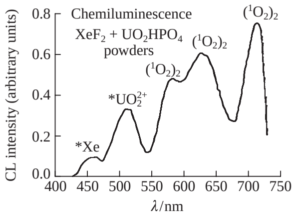
Chemiluminescence (CL) was found in the solid-phase interaction of xenon difluoride with uranyl hydrogen phosphate; the CL emitters are *Xe, UO_2^{2+} and the singlet oxygen dimole $(^1O_2)_2$.



The study of chemiluminescence (CL) makes it possible to reveal the unit event of electron excitation (*) generation in chemical processes regardless of the phase state of the reaction system.[1,2]

The interaction of inorganic reagents[3–5] accompanied by CL has not been adequately studied. Inorganic CL processes in a solid state are much more seldom phenomena. In this context, CL in the solid-phase oxidation reactions of uranium(IV) hydroxide[6] and hydrogen phosphate[7] with xenon difluoride deserves attention because the uranyl ion is both the end product and the light emitter in these reactions. Xenon difluoride is an effective oxidant,[8] and its reactivity sharply increased in the presence of fluoride ion acceptors, in particular, SiO_2.[9,10] In the solid-phase decomposition of XeF_2 on the surface of silica gel in the absence of U^{IV}, we found CL and identified gaseous electron excited products, *Xe (465 nm), $*Xe^+$ (415, 540 and 580 nm) and singlet oxygen.[10]

The basis of the given research was the unexpected appearance of bright CL in the solid-phase interaction of xenon difluoride with U^{VI} hydrogen phosphate, which has the highest oxidation state one order of magnitude higher than that in a redox reaction of XeF_2 with U^{IV}. In this work, we studied spectral-luminescent properties to reveal the emitters of CL in the solid-phase interaction of xenon difluoride with UO_2^{2+} hydrogen phosphate, which can optionally be both the CL activator and the initiator of XeF_2 decomposition due to accepting F^- anions.†

When the finely dispersed polycrystalline salts of UO_2^{2+} (HPO_4^-, NO_3^-, SO_4^- and F^-) were mixed with xenon difluoride, the CL in the green spectral region was visually detected. The most intense luminescence was observed in the interaction of uranyl hydrogen phosphate with xenon difluoride.

When the course of the solid-phase reaction of an equimolar powder mixture of XeF_2 (17 mg) and $UO_2HPO_4{\cdot}4H_2O$ (44 mg) was monitored by microscopy, both explosive decomposition and intense movement of crystals were observed due to chemoresponsive reactions of crystals with gas products.[11] The formation of molecular oxygen, Xe, XeF and HF was confirmed by mass spectrometry. The reaction occurred within about 10 min, and its kinetics is given in Figure 1. The end product was a vitreous mass, which self-heated to 320 K in the reaction.

The visually detected CL in the solid-phase interaction of XeF_2 with $UO_2HPO_4{\cdot}4H_2O$ is caused by the fact that UO_2^{2+} is a strong acceptor of fluoride anions [stability constant $\lg K_1(UO_2F^+) = 4.93$],[12] and it can initiate xenon difluoride decomposition.

Immediately after the mixing of $UO_2HPO_4{\cdot}4H_2O$ and XeF_2 powders, CL was detected: a low-intensity band at about 460 nm, bright luminescence in the green region of the spectrum with a maximum at 520 nm, and long-wave maxima at 580, 630 and 709 nm (Figure 1, spectrum *2*).

Published data[10,13,14] on the radiative transitions of *Xe (462–467 nm) indicate that CL at 460 nm can be assigned to xenon atom luminescence. The spectra of *Xe emission and UO_2^{2+} absorption overlap, and this circumstance provides both nonradiative energy transfer and CL activation with the uranyl ion with an intense radiative transition at 520 nm. The fluorescence (FL) spectrum of $UO_2HPO_4{\cdot}4H_2O$ is given in Figure 2. Therefore, in this reaction, the uranyl ion is both a CL activator and the initiator of XeF_2 decomposition due to the acceptance of F^- anions.

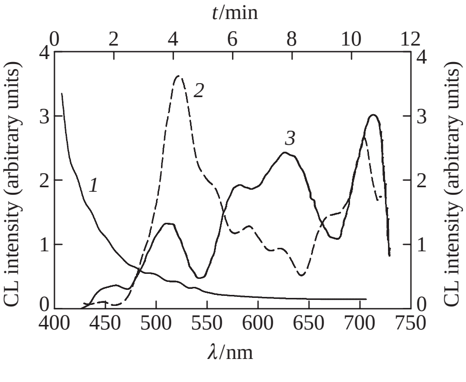


Figure 1 (*1*) CL kinetics in interaction of powders of $UO_2HPO_4{\cdot}4H_2O$ (44 mg) and XeF_2 (17 mg). CL spectra in solid-phase reaction of XeF_2 with $UO_2HPO_4{\cdot}4H_2O$ (*2*) in the beginning of reaction and (*3*) after 2 min (325 K).

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† The CL and FL spectra were measured on a Solar CM-2203 spectrofluorimeter. The absorption spectra were recorded on a Specord M400 spectrophotometer, and the mass spectra were taken on a ThermoFinnigan MAT 95XP instrument. XeF_2 and $UO_2HPO_4{\cdot}4H_2O$ were synthesized according to published procedures.[19,20] $UO_2F_2{\cdot}2.5H_2O$ was prepared by the dissolution of a weighed portion of UO_3 in hydrofluoric acid under heating with an IR lamp. The crystal water content was determined by thermogravimetry on a Q-1000 derivatograph. The salts of UO_2^{2+} were purified by double recrystallization from twice-distilled water.

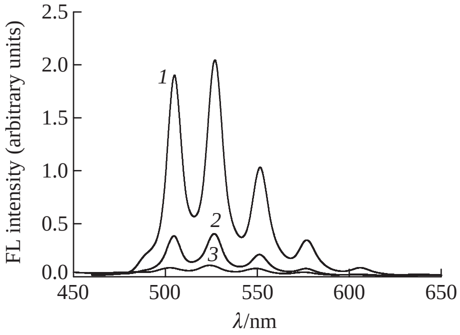

Figure 2 FL spectra of polycrystalline powders: (*1*) $UO_2HPO_4{\cdot}4H_2O$; (*2*) reaction product of XeF_2 with $UO_2HPO_4{\cdot}4H_2O$; and (*3*) $UO_2F_2{\cdot}2.5H_2O$ (λ_{ex} = 450 nm, 298 K).

Previously, we have detected the formation of singlet $^1O_2(^1\Delta_g)$ in the solid-phase interaction of XeF_2 on silica gel,[10] which was explained by the adsorption destruction of O_3[16] generated in the reaction. In the test system, the elimination of O_3 was also detected spectrophotometrically (257 nm). The literature and experimental data suggest that CL at 580–709 nm is caused by the radiation of singlet oxygen dimole $(^1O_2)_2$. The fine correlation of the CL maxima observed at 580, 630 and 709 nm with the reported data on the radiative transitions of $(^1O_2)_2$ (578, 633 and 703 nm)[17] confirms this supposition.

Note that 2 min after the powders of $UO_2HPO_4{\cdot}4H_2O$ and XeF_2 were mixed, the CL intensities were redistributed over the entire spectral range (Figure 1, spectrum *3*). When the CL at 520 nm due to $^*UO_2^{2+}$ decreased, the radiation of *Xe (460 nm) became pronounced and the luminescence in the region of $(^1O_2)_2$ (580–709 nm) emission increased.

Figure 2 shows the luminescence spectra of polycrystalline specimens of $UO_2HPO_4{\cdot}4H_2O$, the reaction product of XeF_2 with $UO_2HPO_4{\cdot}4H_2O$, and $UO_2F_2{\cdot}2.5H_2O$, whose light sums corresponding to the quantum yields (φ) of FL are 73, 17 and 6, respectively. Because φ of FL of the reaction product of XeF_2 with $UO_2HPO_4{\cdot}4H_2O$ takes an intermediate position between those for UO_2^{2+} hydrogen phosphate and fluoride, it is reasonable to suppose the formation of uranyl phosphate-fluoride complexes. In turn, the complexation of the F^- anion with uranyl leads to induced xenon difluoride decomposition.

Because the solid-phase reaction of XeF_2 with $UO_2HPO_4{\cdot}4H_2O$ was carried out in a sealed quartz cell and the lifetime of $^1O_2$ monomole in a gas phase was 72 min,[18] the rise in CL intensity in the region of 580–709 nm can be explained by the accumulation of singlet oxygen dimole in the bulk. Really, after depressurization and blowing the reactor with air, luminescence in the region of $(^1O_2)_2$ emission was not detected.

Therefore, UO_2^{2+} hydrogen phosphate is both the initiator of the solid-phase decomposition of xenon difluoride due to accepting F^- anion and the activator of CL according to the mechanism of nonradiative energy transfer from electron-excited atomic *Xe. We found that Xe (460 nm), $^*UO_2^{2+}$ (520 nm) and singlet oxygen dimole $(^1O_2)_2$ are responsible for CL in the solid-phase interaction of XeF_2 with $UO_2HPO_4{\cdot}4H_2O$.

The experiments were performed on the equipment of the ‘Khimiya’ Centre of Collective Use at the Ufa Institute of Chemistry of the Russian Academy of Sciences.

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