ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

Mendeleev Commun., 2015, **25**, 375–376

Mendeleev Communications

Chemiluminescence emitters in the solid-phase decomposition of xenon difluoride on a silica gel surface

Gul'shat A. Masyagutova,* Alexander V. Mamykin and Sergey S. Ostakhov

Ufa Institute of Chemistry, Russian Academy of Sciences, 450054 Ufa, Russian Federation.
Fax: +7 3472 356 066; e-mail: masgul@anrb.ru

DOI: 10.1016/j.mencom.2015.09.020

Chemiluminescence (CL) has been detected on the solid-phase decomposition of XeF_2 on a SiO_2 surface, where Xe, Xe^+ and singlet oxygen acted as CL emitters.

Xenon difluoride is an efficient oxidant[1] and fluorinating agent.[2] The reactivity of XeF_2 increases abruptly in the presence of fluoride ion acceptors[3] such as SiO_2 to give intermediate oxidants, namely, XeF^+ and Xe^+.

Chemiluminescence (CL) is an efficient method for the detection and study of the kinetics of these labile oxidants generated in XeF_2 reactions. Previously,[4] it was reported that moisture sorption from atmospheric air by crystalline XeF_2 was accompanied by light emission. However, the spectral composition of CL was not recorded due to its low intensity. CL intensity increased significantly in the presence of uranium(IV) ions, but the emitters of CL have not been identified.[5] Weak light emission at 350–500 nm was also observed in the hydrolytic reduction of XeF_2 in acidic aqueous solutions.[6,7] The addition of pulverized glass to an aqueous XeF_2 solution was shown[8] to favor a considerable increase in CL intensity. However, the nature of luminescence emitters in XeF_2 reactions was not determined.

It is known that, unlike in solutions, short-lived intermediates are stabilized and the quantum yield of luminescence increases in a solid phase. Based on this fact and on the effect of surface on CL intensity during the hydrolytic reduction of xenon difluoride in aqueous solutions,[8] we assumed that it would be possible to reliably identify light emitters during solid-phase decomposition of XeF_2 on SiO_2 surface.[†]

As expected, CL manifests high intensity during the solid-phase decomposition of XeF_2 on a SiO_2 surface, and its kinetics after reagent mixing demonstrates a plot with an extremum (Figure 1, curve *1*).

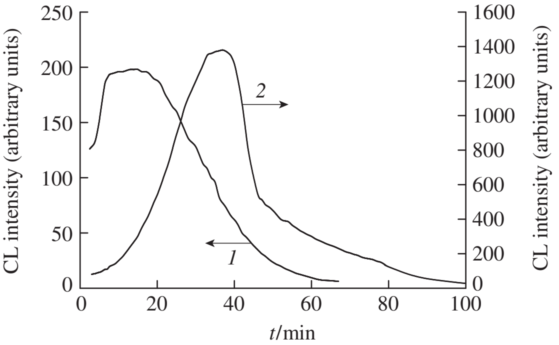

Figure 1 CL kinetics during XeF_2 decomposition on the surfaces of SiO_2 with grain sizes of (*1*) 0.125–0.160 mm and (*2*) 7.5 μm (294 K).

We believe that the growth in CL intensity, which reaches a maximum ~20 min after the onset of reaction, is due to the diffusion and adsorption of XeF_2 on the SiO_2 surface (particle size, 0.125–0.160 mm), after which a decrease in luminescence intensity is observed. As the SiO_2 particle size decreased (7.5 μm), the time required to reach a maximum on the kinetic curve increased (~40 min) and the CL intensity considerably rose (by almost an order of magnitude) (Figure 1, curve *2*). These effects are caused by an increase in the specific surface area of SiO_2 and hence in the amount of adsorbed XeF_2.

Note that the CL of XeF_2 on the SiO_2 surface is detected in both thoroughly dried and undried silica gel samples, though the luminescence kinetics and intensity differ. It means that generation of electron-excited intermediates can be due to both XeF_2 reduction with adsorbed water[6] and the catalysis of XeF_2 decomposition by a silica gel surface due to weakening of the Xe–F bond upon adsorption.[3] The results reported here were obtained for undried samples.

The high CL intensity during XeF_2 decomposition on SiO_2 surface allows the luminescence spectral composition to be reliably recorded (Figure 2, spectrum *1*).

Chemiluminescence maxima are observed at 415, 465, 540 and 580 nm. Comparison with published data[11,12] for radiative transitions of electronically excited Xe* in the region of 462–467 nm and Xe^{+*} at 418, 542 and 567 nm makes it possible to assign the CL maxima at 465 nm and those at 415, 540 and 580 nm to Xe* and Xe^{+*}, respectively.

This assignment agrees with data obtained using other excitation methods, *e.g.*, in xenon sonoluminescence (470, 540 and 570 nm)[13] and triboluminescence (TL) of crystalline cerium sulfate in a xenon atmosphere (475, 540 nm).[14] Mechanodestruction of xenon difluoride crystals was also accompanied by clearly

---

[†] CL spectra were recorded using a set-up described previously,[7] equipped with edge light filters in the visible (FEU-119 photomultiplier, 330–700 nm) and IR (FEU-83, 400–1300 nm) spectrum regions after fast (2–5 s) mixing of weighed samples of XeF_2 (9 nm) and SiO_2 (80 mg) in a quartz cell.

In TL studies, a weighed sample of XeF_2 crystals (200–250 mg) was placed in a cylindrical steel cell 25 mm in diameter with a quartz bottom. TL was excited using a four-blade mixer of PTFE (1000 rpm). Luminescence was recorded while grinding the crystals with the stirrer on the cell bottom in air atmosphere. TL spectra were recorded with an Aminco-Bowman J4-8202 fluorimeter using a Hamamatsu R3896 photomultiplier as a light detector.

Absorption spectra of gaseous products formed in the reaction of crystalline XeF_2 and SiO_2 were recorded in a sealed quartz cell (l = 10 cm) using a Specord M-40 spectrophotometer.

Xenon difluoride was synthesized using reported techniques[9,10] by exposing a xenon–fluorine mixture to electric discharge. SiO_2 (Lachema) with a grain size of 0.125–0.160 mm and 7.5 μm was used.

The UV and CL spectra were recorded at the Chemistry Center for Collective Use of the Ufa Institute of Chemistry of the Russian Academy of Sciences.

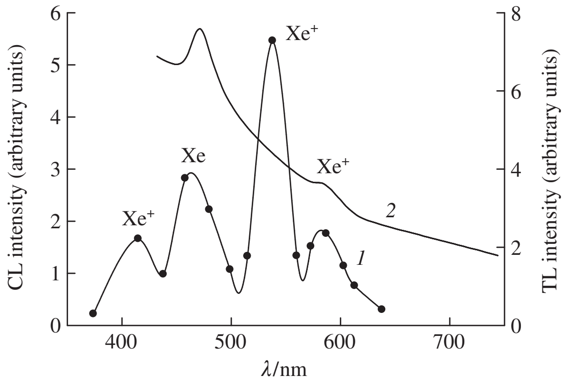

Figure 2 (*1*) CL spectrum during XeF_2 decomposition on SiO_2 surface; (*2*) TL spectrum of crystalline XeF_2 (294 K).

detectable luminescence corresponding to the radiation of atomic xenon, Xe*, at 470 nm, whereas the TL of Xe^{+*} cations is only observed as a low-intensity line at 580 nm (Figure 2, spectrum *2*).

In addition to the gaseous products previously detected in XeF_2 reactions, namely, Xe and F,[1,2] as well as atomic and molecular oxygen,[15,16] we also observed ozone evolution, which could be detected spectrophotometrically (257 nm). Ozone is probably formed in the reaction $O + O_2 \rightarrow O_3$ of crystalline XeF_2 with SiO_2.[17] After mixing the reagents in a sealed quartz cell ($l = 10$ cm), the concentration of ozone initially increased to reach a maximum in 40 min, followed by its decrease due to catalytic decomposition by silica gel surface.

It was previously found[18] that adsorption decay of ozone on silica gel gives oxygen in a singlet-excited state ($^1O_2$). This fact initiated a search for $^1O_2$ luminescence ($\lambda = 1270$ nm) in the test reaction. In fact, CL was detected in this region during XeF_2 grinding on a Schott filter surface (SiO_2). It follows from the results obtained that the highly efficient oxidant XeF_2 initiates the formation of another oxidant, $^1O_2$, which plays an important role in both chemistry and biochemistry.

Thus, high CL quantum yields and stabilization of short-lived electron-excited intermediates in solid-phase XeF_2 reactions allowed us to obtain data on the nature of luminescence emitters. We demonstrated that the gaseous products Xe* (470 nm), Xe^{+*} (415, 540, 580 nm) and singlet oxygen are responsible for CL during the solid-phase decomposition of xenon difluoride on the SiO_2 surface.

References

1 N. Bartlett and F. O. Sladky, *Chem. Commun. (London)*, 1968, 1046.
2 F. O. Sladky, P. A. Bulliner and N. Bartlett, *J. Chem. Soc. A*, 1969, 2179.
3 J. I. Steinfeld, *Chem. Rev.*, 1989, **89**, 1291.
4 S. P. Kuleshov, G. P. Parshin, V. D. Klimov and V. P. Kazakov, *Izv. Akad. Nauk, Ser. Khim.*, 1981, 1931 (in Russian).
5 G. A. Masyagutova, A. V. Mamykin, I. G. Tananaev,V. P. Kazakov and B. F. Myasoedov, *Mendeleev Commun.*, 2011, **21**, 7.
6 V. P. Kazakov, G. A. Tolstikov, S. V. Lotnik, A. V. Mamykin and L. A. Khamidullina, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1984, **33**, 2592 (*Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984, 2829).
7 R. G. Bulgakov, V. P. Kazakov and G. A. Tolstikov, *Khemilyuminestsentsiya metalloorganicheskikh soedinenii (Chemiluminescence of Organometallic Compounds)*, Nauka, Moscow, 1989 (in Russian).
8 S. V. Lotnik, L. A. Khamidullina and V. P. Kazakov, *Radiokhimiya*, 1993, **35**, 50 (in Russian).
9 *Nobel-gas Compounds*, ed. H. H. Hyman, The University of Chicago Press, Chicago, London, 1963, p. 404.
10 P. Groz, J. Kiss, A. Reverz and T. Siros, *J. Inorg. Nucl. Chem.*, 1966, **28**, 909.
11 A. R. Striganov and N. S. Sventitskii, *Tablitsy spektral'nykh linii neitral'nykh i ionizirovannykh atomov (Tables of Spectral Lines of Neutral and Ionized Atoms)*, Atomizdat, Moscow, 1966 (in Russian).
12 E. B. Saloman, *J. Phys. Chem. Ref. Data*, 2004, **33**, 765.
13 D. J. Flannigan and K. S. Suslick, *Phys. Rev. Lett.*, 2005, **95**, 044301.
14 A. A. Tukhbatullin, G. L. Sharipov, A. M. Abdrakhmanov and M. R. Muftakhutdinov, *Opt. Spectrosc.*, 2014, **116**, 691 (*Optika i Spektroskopiya*, 2014, **116**, 747).
15 V. A. Legasov, V. N. Prusakov and B. B. Chaivanov, *Zh. Fiz. Khim.*, 1968, **42**, 1167 (in Russian).
16 E. H. Appelman and J. G. Malm, *J. Am. Chem. Soc.*, 1964, **86**, 2297.
17 C. D. Razumovskii, *Kislorod – elementarnye formy i svoistva (Oxygen – Elementary Forms and Properties)*, Khimiya, Moscow, 1979 (in Russian).
18 A. I. Voloshin, G. L. Sharipov, V. P. Kazakov and G. A. Tolstikov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1986, **35**, 2397 (*Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 2613).

Received: 26th February 2015; Com. 15/4575