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Mass-spectrometric study of the solid-phase reaction of Na$_4$XeO$_6$·8H$_2$O with U(SO$_4$)$_2$·4H$_2$O

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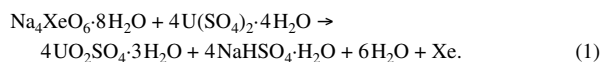
A mass-spectrometric study of gaseous products evolved during the solid-phase reaction of uranium(IV) sulfate (tetrahydrate) with sodium perxenate (octahydrate) at 20–170 °C revealed xenon, its oxides in intermediate oxidation states (II, IV, VI), oxygen and water; pulsed stepwise gas evolution was noted in this reaction.

Previously,[1] we found bright chemiluminescence (CL) accompanying the solid-phase reaction of sodium perxenate (octahydrate) with uranium(IV) sulfate (tetrahydrate). The green luminescence of the UO$_2^{2+}$ ion excited during the reaction could be observed with naked eye even at room temperature upon mixing the powders with a glass rod. The reaction of uranium sulfate and sodium perxenate occurs anomalously quickly for a solid-phase reaction. Presumably, it involves vigorous gas evolution accompanying the destruction of the crystals and surface renewal.

We found spectroscopically that the oxidation of uranium(IV) with sodium perxenate gives uranyl sulfate as the solid-phase product.

Mass spectra were recorded with a ThermoFinnigan MAT 95XP chromatograph–mass spectrometer using a system for direct sample introduction. The ionisation energy was 70 eV. Exact measurements of the mass numbers of the ions formed in the source were carried out using the peak alignment procedure (the resolution was 10000 at 10% height). Perfluorokerosene was used as a reference. Aluminium or glass cells were used. The solid-phase reaction was carried out using uranium sulfate powders of chemically pure grade. The reagents were taken in equivalent amounts in accordance with the assumed reaction stoichiometry

$$Na_4XeO_6 \cdot 8H_2O + 4U(SO_4)_2 \cdot 4H_2O \rightarrow$$
$$4UO_2SO_4 \cdot 3H_2O + 4NaHSO_4 \cdot H_2O + 6H_2O + Xe. \quad (1)$$

Equation (1) belongs to the overall reaction, which takes place at room temperature and does not reflect the multistage character of reaction.

To prevent the test reaction from occurring too early, that is, before the reagents have been placed into the mass spectrometer ion source, the powders were cooled to about –20 °C before mixing. The mixing was also carried out at ~ –20 °C. A specimen was heated to 270 °C at a rate of 22 K min^{-1} in the direct insertion system.

We have found that, like thermal decomposition of sodium perxenate, the thermal solid-phase reduction of Na$_4$XeO$_6$·8H$_2$O with U(SO$_4$)$_2$·4H$_2$O gives the following major products: xenon as expected and, surprisingly, oxygen. The formation of the latter is recorded at temperatures above 100 °C. On the other hand, xenon is liberated in the entire range where ionic current is detected as the temperature is gradually increased from 50
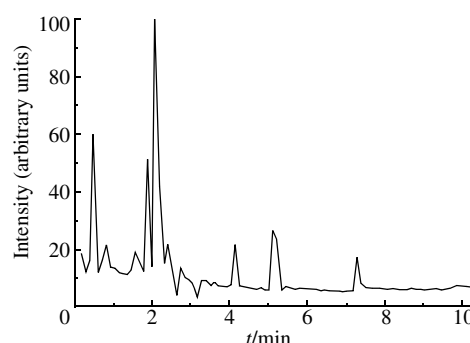

Figure 1 Dependence of the total ionic current detected by the mass spectrometer in the reaction of a mixture of Na$_4$XeO$_6$·8H$_2$O and U(SO$_4$)$_2$·4H$_2$O powders at 20 °C demonstrating its pulsed character.

to 270 °C. The maximum evolution of xenon is detected above 100 °C. Furthermore, H$_2$O is also detected. The character of the curve of water evaporation from the reaction mixture matches the dehydration behaviour in the differential thermal analysis (DTA) curve for sodium perxenate crystal hydrate obtained elsewhere.[2] Complete dehydration occurs only above 250 °C. The fact that the reaction occurs so readily suggests that it probably involves crystal water, which possibly forms a quasi-liquid microphase facilitating the fast reaction.

Mass-spectroscopic measurements revealed that the evolution of gaseous products occurs in a pulsed stepwise mode (Figure 1). This phenomenon is especially pronounced if the reaction is carried out at room temperature. At higher temperatures, it is also possible to notice traces of the pulsed process, but they are considerably smoothed out due to the high reaction rate (Figure 2). However, the curve always has a somewhat 'saw-tooth' shape. The amplitudes of the teeth exceed considerably the background fluctuations. Apparently, we encounter a new phenomenon, *viz.*, a pulsed reaction mode.

The same products, namely Xe, O$_2$ and H$_2$O, were detected mass-spectrometrically upon heating both a mixture of uranyl sulfate (trihydrate) and sodium perxenate (octahydrate) powders and pure crystalline Na$_4$XeO$_6$·8H$_2$O powder. Note that the mass spectra contain not only signals attributable to xenon, oxygen and water but also small signals of other components. At the starting heating stage, CO$_2$ is detected; it is evolved throughout almost the entire range of spectrum recording, up to 300 °C.
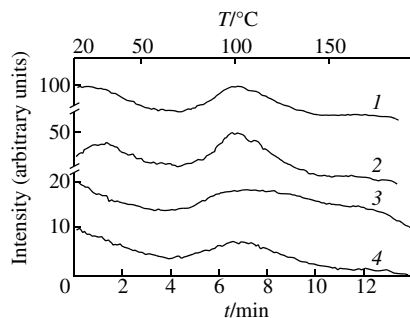
Figure 2 Plots of ionic current for separate gaseous reaction products during gradual heating of a specimen from 20 to 170 °C at a rate of 13 K min^{-1}: (*1*) total ionic current from all gaseous products; (*2*) H$_2$O; (*3*) Xe and (*4*) O$_2$.

The positions of CO$_2$ evolution maxima almost coincide with water evaporation maxima. Presumably, CO$_2$ appears due to an impurity of sodium carbonate in Na$_4$XeO$_6$·8H$_2$O, which was obtained by an alkaline method. Oxidation of the reference additive (fluorinated hydrocarbon) with sodium perxenate can be the second reason.

Previously, the thermal stability of sodium perxenate[3] and the temperature dependence of gas evolution[2] were studied by DTA, thermogravimetric analysis (TGA), differential thermo-gravimetric analysis (DTGA), IR spectroscopy and radioemana-tion analysis. It was found that the thermal decomposition of Na$_4$XeO$_6$·6H$_2$O occurs in the range 360–380 °C. In the range 20–200 °C, dehydration of sodium perxenate crystal hydrate occurs, but no noticeable evolution of xenon occurs in this temperature range. Insignificant gas evolution presumably cor-responding to xenon was observed in the range 200–350 °C; it reached a maximum at 375±5 °C.

We expected that reduction of perxenate both at room tem-perature and on heating in the range 50–360 °C would follow equation (1). According to this equation, the reaction should give uranyl sulfate (as confirmed by photoluminescence spectra).

It was expected that the maximum rate of xenon evolution would match the maximum of chemiluminescence intensity. However, we did not observe the anticipated correlation. It is likely that this relationship does not exist since CL is a result of numerous reactions involving different-valence forms of both xenon (from 8 to 0) and uranium (4–6) and various possible phase transitions of these compounds with an increase in the temperature.

It was unexpected that the mass spectra contained a relatively high amount of oxygen, which was absent if the reaction was carried out at 20 °C and the amount of which increased to 50% of the xenon amount with an increase in the temperature.

We detected the presence of xenon in intermediate oxidation states (XeO$_3^+$, XeO$_2^+$ and XeO$^+$) (Figure 3).

The contribution of these ions to the total ionic current is about 0.3%. It is most likely that the presence of oxygen in the gas phase is due, at least partially, to decomposition of these
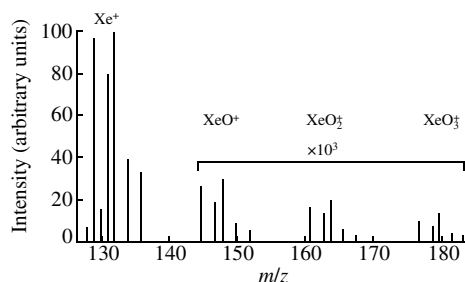
Figure 3 Mass spectrum of xenon oxides in intermediate oxidation states (II, IV, VI) formed during the reaction of uranium(IV) sulfate with sodium perxenate (20–170 °C, heating rate of 13 K min^{-1}).
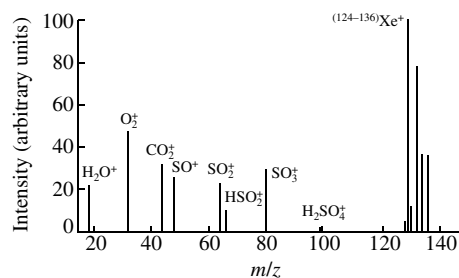
Figure 4 Mass spectra of reaction products of uranium(IV) sulfate with sodium perxenate (50–170 °C, heating rate of 13 K min^{-1}).

intermediate products. The highest intensity of O$_2$ evolution was noted when the evolution of xenon was maximal. In the future, we plan to perform a more detailed mass-spectrometric study in order to compare the formation kinetics of these intermediates with the kinetic behaviour of CL. This is highly important in order to reveal the reaction mechanism, since it is impossible to observe intermediates directly in most cases.

Note that gaseous reaction products formed at temperatures above 100 °C also contain small amounts of by-products such as SO$_3^+$, SO$_2^+$, SO$^+$, HSO$_2^+$ and H$_2$SO$_4^+$ (Figure 4). However, it is unlikely that they play a considerable role in the reaction in question.

It is possible that the solid-phase reaction of UO$_2$SO$_4$·3H$_2$O and Na$_4$XeO$_6$·8H$_2$O powders occurs *via* the formation of uranyl perxenate Na$_{10}$(UO$_2$)$_3$(XeO$_6$)$_4$·nH$_2$O, as reported previously:[3,5] thermal decomposition of the latter results in uranyl ion excita-tion (as confirmed by photoluminescence spectra) and oxygen evolution. According to published data, uranyl perxenate starts to decompose at about 100 °C.[4] A decrease in the heating rate (in the range 20 to 170 °C) to 13 K min^{-1} results in a small shift in peak positions and only a minor redistribution of intensities of the spectral lines, whereas the elementary composition of ions in the mass spectra varied quite insignificantly.

Undoubtedly, crystal water plays an important role in the reaction under study, its role being emphasized for other com-pounds reaction.[6]

Thus, the formation of xenon oxides in intermediate oxidation states (II, IV, VI) was detected by mass-spectrometric methods. The products of the reactions under consideration in a gas phase are xenon, oxygen and water.

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