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Thermal Decomposition of Xenon Tetroxide at 490–780 K

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Abstract—The decomposition of XeO_4 was studied over the temperature range 490–780 K. A reaction mechanism was proposed. A conclusion on the high vibrational excitation of O_2 molecules formed in the elementary reaction $O + XeO_4 \longrightarrow O_2 + XeO_3$ and the branched-chain character of the decomposition with branching in the reaction $O + XeO_3 \longrightarrow 2O + O_2 + Xe$ was drawn.

INTRODUCTION

The XeO_4 molecule has a very high energy content: considerable energy (up to 152 kcal/mol) can be released on its decomposition depending on the composition of final products. Thus, it is of interest to find at which steps of the decomposition reaction mechanism energy is released. This work was devoted to a study of the thermal decomposition of XeO_4 molecules at temperatures of up to 780 K. This work is a continuation of our studies on gas-phase XeO_4 reactions [1–5].

EXPERIMENTAL

The experimental setup included (1) a generator of XeO_4, (2) a vessel for preparing gas mixtures, and (3) a reactor with a helical heater. Xenon tetroxide was prepared immediately before each particular experiment by the reaction of sodium hexaoxoxenonate with concentrated sulfuric acid [1]. The resulting XeO_4 was passed from the reactor to the mixing vessel—a 93-cm^3 quartz tube section 4.5 cm in diameter equipped with flat end windows for the inlet and outlet of radiation from a probing source. The mixture of XeO_4 and a diluent gas, which was prepared in the vessel, was pumped out through the heated reactor with a calibrated orifice at the outlet. The orifice determined the flow rate of the mixture and thereby the linear velocity of the gas flow in the reactor. The characteristic time of pumping the mixture was 16 s, and the linear velocity of the flow in the course of pumping was constant and equal to 15 cm/s in the unheated portion of the reactor. The initial concentration of XeO_4 in the mixing vessel and the flow rate of the mixture were monitored by the absorption of light from the probing source at a wavelength of 253.6 nm with the use of previously found XeO_4 absorption cross sections [2]. A low-pressure mercury lamp served as the probing source, and an F-29 photoelectric cell served as a detector. More than 99% radiation from the mercury lamp accounted for the line at 253.6 nm. Radiation of other lines from the lamp (less than 1%) gave a negligibly small contribution to the photodetector signal because of its low sensitivity in the corresponding region of the spectrum. This allowed us to use the detection system without filters and (or) a monochromator.

A quartz tube ~10 cm in length with an internal diameter of 0.7 cm served as the reactor. At an end, the reactor had a flat window for observing luminescence in the decomposition reaction. The spectral composition of luminescence was studied with the use of a monochromator equipped with a photomultiplier tube. A heater of densely coiled Nichrome wire was placed outside the reactor. Heaters with coiling lengths of 1.2 and 3 cm were used. The output power of the heater varied over a range of 10–100 W; however, it was usually equal to 40 W. Temperatures at different points of the inner surface of the reactor were measured in special experiments with the use of a thermocouple. The temperature in the central portion of the heated surface was 550–740 or 490–780 K for the short or long heater, respectively, depending on the input power. On the supply of a flow to the reactor, the temperature of reaction walls decreases because of heat losses by gas heating. According to estimations, the decrease in the temperature of wall heating for this reason is no greater than 2%. On the other hand, the gas is heated because of heat release in the course of XeO_4 decomposition. If it is believed that the decomposition corresponds to the stoichiometric equation $XeO_4 \longrightarrow 2O_2 + Xe + 152$ kcal/mol with the maximum heat release and is complete, then the increase in the gas temperature with respect to the temperature of wall heating is no higher than 1%.

The initial pressure of XeO_4 in the mixing vessel was no higher than 2 torr, and the pressure of the diluent gas (usually Ar) was 540 torr. It is well known that heterogeneous decomposition of XeO_4 occurs at room temperature [3]. The characteristic time of heterogeneous XeO_4 decomposition in the mixing vessel was measured to be $\sim 4 \times 10^3$ s. The characteristic time of XeO_4 decomposition under the action of UV radiation from a probing lamp was ~700 s under experimental conditions. A typical experiment lasted for ~3 min and included the following stages: the addition of XeO_4

(<30 s) and a diluent gas (a few seconds) to the mixing vessel, the stirring of the mixture (~2 min), and the pumping of the prepared mixture (~1 min). Thus, the consumption of XeO_4 as a result of heterogeneous decomposition during the experiments could be ignored. The mercury-lamp radiation was closed during the stirring of the mixture; therefore, the consumption of XeO_4 because of photochemical decomposition could also be ignored.

RESULTS AND DISCUSSION

The reaction of XeO_4 decomposition was accompanied by luminescence and formation of a white film-like deposit as a distinct ring ~5 mm wide at a distance (1.5–2 cm) from the heated zone. In the case of the short heater, the formation of a ring was observed over the entire range of reactor wall temperatures, whereas it was observed at wall temperatures of no higher than 670 K in the case of the long heater (see below). A study of the spectral composition of radiation, which was performed using a monochromator (spectral slit width of 0.25 nm), demonstrated that it corresponded to the yellow doublet of sodium at 589 and 589.6 nm (the states $Na(^2P_{3/2})$ and $Na(^2P_{1/2})$). It is likely that trace sodium entered the system on the decomposition of sodium hexaoxoxenonate. Because the temperature in the reaction zone was no higher than 780 K, it is evident that the luminescence of sodium is nonequilibrium. The atoms of Na can undergo electronic excitation in multiquantum vibrational-energy transfer from a vibrationally excited partner on collision (see [6] and references therein). The probability of this transfer is as high as unity per collision. The detected luminescence indicates that highly vibrationally excited products are formed at the steps of the XeO_4 decomposition mechanism.

Using chemical analysis, we found that the deposit on the reactor walls consisted of XeO_3. Elementary steps in which XeO_3 can be formed are the steps of heterogeneous and (or) homogeneous generation of O atoms

$$XeO_4 + \text{wall} \longrightarrow O + XeO_3, \qquad (I)$$

$$XeO_4 + M \longrightarrow O + XeO_3 + M \qquad (II)$$

and of O atom decay

$$O + XeO_4 \longrightarrow O_2 + XeO_3 + 96\ \text{kcal/mol}. \qquad (III)$$

Energy released in reaction (III) is sufficient for the excitation of O_2 molecules to the vibrational levels $v \geq 12$, from which Na atoms can be excited to the state ^2P, which is higher than the ground state ^2S by 2.1 eV: $O_2(v \geq 12) + Na(^2S) \longrightarrow Na(^2P) + O_2(v')$. The fact that O_2 molecules excited to the maximally possible level $v = 27$ [7] were observed in the analogous reaction $O + O_3 \longrightarrow O_2(v) + O_2$ (the O–XeO_3 and O–O_2 bond energies are similar in values) provides indirect evidence for the possibility of formation of highly vibrationally excited O_2 molecules in reaction (III).

Because of the short radiation lifetime of $Na(^2P)$ (16 ns), the size of the reaction zone can be judged from the length of the luminescence zone. The luminescence zone was no greater than the size of the short heater over the entire temperature range tested. The majority of experiments with the short heater was performed at a wall temperature of ~680 K. In this case, the emission reached a maximum ~8 s after supplying the mixture to the reactor and then decayed with a characteristic time close to the characteristic time of pressure decrease in the reactor. The occurrence of the maximum was due to the dependence of the conversion of XeO_4 on the pressure of the mixture in the reactor. At a pressure higher than 330 torr, which was observed in the reactor before the emission reached a maximum after 8 s (the pressure of the mixture at the beginning of pumping was 540 torr, and the characteristic time of pumping was 16 s), the mixture had no time to be sufficiently heated within the time of passing the heated zone because of the low rate of heat transfer, and the conversion of XeO_4 was incomplete. At a pressure of the mixture equal to ~330 torr, XeO_4 was completely converted into products within the residence time in the heated zone because of accelerated heat and mass transfer. As a result, the concentration of emitting species increased, even though the pressure decreased. The subsequent decrease in the emission intensity at complete XeO_4 conversion resulted from a decrease in the concentration of emitting species with a further decrease in the total pressure of the mixture on pumping. As estimated, ~80% parent XeO_4 was converted in the course of an experiment.

As follows from the above consideration, the decomposition of XeO_4 to final products did not occur with the short heater. The use of the long heater allowed us to determine the characteristic time of the complete decomposition of XeO_4. In the experiments with the long heater, we found minimum temperatures of the reactor walls at which XeO_3 underwent complete decomposition, which corresponded to the absence of a visible deposit in the cold portion of the reactor. The experimental results are given below.

Surface temperature, K	490	540	573	607	673	715	780
Presence (+) and absence (–) of a ring	+	+	+	+	–	–	–

In all cases, the initial pressure of the diluent gas (Ar) in the mixing vessel was 540 torr, and the pressure of XeO_4 was 2 torr. We can conclude that the complete decomposition of XeO_4 occurred at a reactor wall temperature of ≥670 K in a time of ~0.1 s (which depends on (1) the gas velocity, which, in the heated part of the reactor, is almost twice as high as that in the cold part if it is assumed that the gas temperature differs only slightly from the wall temperature, and (2) the size of the reaction zone, which is approximately equal to the heater length because of the rapid decrease in the temperature outside the heater). Let us estimate the gas temperature in the reactor. The reduced average temperature over the reactor cross section can be determined from the equation [8]

$$\begin{aligned}\theta(x) &= (T_w - T(x))/(T_w - T_1)\\ &\approx 0.82\exp(-14.62ax/wd^2).\end{aligned} \qquad (1)$$

Here, a is the temperature conductivity coefficient, cm^2/s; w is the average flow velocity, cm/s; d is the reactor diameter, cm; T_w is the wall temperature; $T(x)$ is the cross-sectional average gas temperature; T_1 is the gas temperature at the reactor inlet; and x is the distance along the flow from the beginning of the heated portion of the reactor, cm.

At room temperature and an atmospheric pressure of Ar, $a = 0.29$ cm^2/s. At another temperature, $a(T) = a(300)(T/300)^{3/2}$. If we assume that the gas temperature differs from the wall temperature only slightly (for example, by no more than 10%), we have $a = 1.15$ or 1.95 cm^2/s at $T_w = 670$ K and a pressure of 540 or 330 torr, respectively. With the use of Eq. (1), we obtain $\theta(1.2, 540) = 0.21$ for $x = 1.2$ cm (short heater) at $P = 540$ torr; that is, the gas temperature is lower than the wall temperature, on average, by 80 K. At $P = 330$ torr, $\theta(1.2, 330) = 0.08$; that is, the gas temperature is lower than the wall temperature, on average, by 30 K. At $x = 1.5$ and 3 cm (in the middle and at the end of the heated portion with the long heater) and the pressures specified above, $\theta(1.5, 540) = 0.15$, $\theta(1.5, 330) = 0.046$, $\theta(3, 540) = 0.028$, and $\theta(3, 330) = 0.0027$. As can be seen, in the three last-named cases, the gas temperature was only slightly different from the wall temperature.

The decomposition of XeO_4 under the conditions of the experiments can be roughly separated into the following two steps: initially, XeO_3 is formed from XeO_4; next, XeO_3 is converted into final products. According to estimations, the decomposition of XeO_4 in reactions analogous to steps (I) and (II) is impossible because of the strength of the $O–XeO_2$ bond (~60 kcal/mol [9]). In that case, the conversion of XeO_3 is described by the process

$$\begin{aligned}O + XeO_3 &\longrightarrow 2O + O_2 + Xe\ (a),\\ &\hookrightarrow 2O_2 + Xe\ (b).\end{aligned} \qquad (IV)$$

The mechanism of decomposition should be supplemented with the conceivable processes of the decay of O atoms

$$O + O_2 + M \longrightarrow O_3 + M, \qquad (V)$$

$$O + \text{wall} \longrightarrow \text{decay}, \qquad (VI)$$

$$O + O_2 \longrightarrow 2O_2. \qquad (VII)$$

An analysis of the reaction scheme that includes processes (IV)–(VII) demonstrated that the fraction of channel (a) in process (IV) should be higher than 50% for the complete conversion of XeO_3; that is, the decomposition of XeO_3 should be a branching chain reaction. The branching chain reaction is insensitive to the "inoculating" concentration of O atoms, which is unknown. For this reason, the rate constant of reaction (IV) can be determined despite the absence of data on the "inoculating" concentration of O atoms. An analysis suggests that $k_4 = (1–5) \times 10^{-14}$ cm^3/s at $T = 670$ K and the fraction of channel (a) varies within the range 0.6–1.

We experimentally found that the ring of adsorbed XeO_3 molecules rapidly moved toward colder parts of the reactor. The ring migration dynamics was studied in the case of the short heater. At a heater power of 40 W, the temperature that corresponds to the edge of a freshly formed ring closest to the heater was 344 K. After the migration of the ring by ~1 cm, the movement of the ring was almost stopped. In this case, the temperature that corresponds to the ring edge closest to the heater was 314 K. The linear velocity of the ring decreased from ~2 mm/min initially to ~0.5 mm/min shortly before coming to a complete stop. The overall process of ring migration took ~10 min. Evidently, the migration was associated with a temperature gradient along the reactor wall and with the temperature dependence of the equilibrium XeO_3 vapor pressure. According to the Clausius–Clapeyron equation, this pressure is $\sim\exp(-\Delta H/RT)$, where ΔH is the heat of sublimation of XeO_3. The known thermodynamic data $\Delta H(s) = 96$ kcal/mol [10] and $\Delta H(g) = 116$ kcal/mol [9] (the heats of formation of XeO_3 in solid and gaseous states, respectively) suggest that $\Delta H = \Delta H(g) - \Delta H(s) = 20$ kcal/mol. The concentration distribution of XeO_3 molecules in a gas phase $n(x)$ throughout the length in a situation when a gas flow along the reactor is stopped because of the equalization of pressure before and after the calibrated orifice can be described by the equation

$$Dd^2n(x)/dx^2 + (\varepsilon V/4d)(n(x) - n_\infty(x)) = 0. \qquad (2)$$

The surface concentration of XeO_3 molecules $n_s(x)$ at the point x is given by the equation

$$dn_s(x)/dt = (\varepsilon V/4)(n(x) - n_\infty(x)). \qquad (3)$$

Here, V is the thermal velocity of XeO_3 molecules, ε is the probability of the adsorption of XeO_3 molecules on collision with the surface, D is the diffusion coefficient of XeO_3 molecules, and $n_\infty(x)$ is the equilibrium concentration of XeO_3 molecules at the temperature at point x.

The set of Eqs. (2) and (3) should satisfy the edge conditions $dn(x)/dx = 0$ at the ends of the test interval $x = x_0$ and $x = 1$ cm; x_0 is the shift of the ring after which we can consider that the gas flow in the reactor has stopped. If we assume that the temperature linearly changes in the range $x = 0$ ($T = 344$ K), $x = 1$ cm ($T = 314$ K), then $x = x_0$ $T(x_0) = 344 - 30x_0$ at the point $x = x_0$. The solution of the set of Eqs. (2) and (3) gives the transformation of the time distribution of the surface concentration of XeO_3 molecules, that is, the ring velocity, depending on the parameters that enter into the equations. In the calculations, we assumed that $V = 2 \times 10^4$ cm/s, $D = 500$ cm^2/s, $\varepsilon = 0.1$–1, and $x_0 = 0.5$ cm. We considered that all 80% of the XeO_4 that underwent decomposition was completely converted into XeO_3. A decrease in the equilibrium vapor pressure at an insufficient surface coverage with XeO_3 molecules was taken into account using the factor $1 - \exp(-n_s(x)/10^{15})$, where 10^{15} cm^{-2} is the surface concentration of particles, which corresponds to a monolayer. Solutions consistent with experimental data (in the units of pressure) were obtained at n_∞ ($T = 300$ K) $= 4 \times 10^{-5}$ and n_∞ ($T = 300$ K) $= 2 \times 10^{-4}$ torr if $\varepsilon = 1$ and 0.1, respectively. The other parameters that enter into Eqs. (1) and (2) are characterized by greater definiteness, and an analysis demonstrated that possible errors in these parameters insignificantly affected the result. Previously, in studies of the photolysis of XeO_4 with UV light (reactions $XeO_4 + H_2$ or CS_2) [1–5]), we did not take into account reactions with the participation of XeO_3 molecules in the analysis of reaction schemes, as we believed that the saturated vapor pressure of XeO_3 is low. The data of this work provide support for this assumption.

CONCLUSIONS

The experiments suggest that the thermal decomposition of XeO_4 proceeds through the following steps:

$$XeO_4 + \text{wall} \longrightarrow O + XeO_3, \qquad \text{(I)}$$

$$XeO_4 + M \longrightarrow O + XeO_3 + M, \qquad \text{(II)}$$

$$O + XeO_4 \longrightarrow O_2 + XeO_3, \qquad \text{(III)}$$

$$\begin{array}{ll} O + XeO_3 \longrightarrow 2O + O_2 + Xe \text{ (a)}, & \\ \qquad\quad\ \ \llcorner\!\longrightarrow 2O_2 + Xe \text{ (b)}. & \text{(IV)} \end{array}$$

The contribution of processes (I) and (II) to the generation of O atoms depends on temperature. Highly vibrationally excited O_2 molecules ($v \geq 12$) are formed in reaction (III). The fraction of channel (a) in reaction (IV) is no lower than 50%. The constant k_4 ($k_4 = (1$–$5) \times 10^{-14}$ cm^3/s) at $T = 670$ K and the saturated vapor pressure of XeO_3 ($4 \times 10^{-5} - 2 \times 10^{-4}$ torr) at room temperature were estimated.

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