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# Kinetics and Mechanism of the Reaction of Xenon Tetroxide with Carbon Disulfide

**N. N. Aleinikov, G. K. Vasil'ev, S. A. Kashtanov, E. F. Makarov, and Yu. A. Chernyshev**

*Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow oblast, 142432 Russia*

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**Abstract**—The dependence of the rate of the reaction of $XeO_4$ with $CS_2$ on the concentrations of reactants and diluent gases He, $O_2$, and $CO_2$ was studied at room temperature. A reaction mechanism was proposed.

## INTRODUCTION

Reactions with the participation of sulfur and carbon compounds are not clearly understood yet. As a rule, they occur via complex mechanisms, and data on the rate constants of elementary reactions involving carbon- and sulfur-containing species are absent. This work, which was devoted to the reaction of $XeO_4$ with $CS_2$, is a part of the series of our studies on gas-phase reactions of $XeO_4$ with various compounds [1–3]. Data on the reaction of $XeO_4$ with $CS_2$ are absent from the literature.

## EXPERIMENTAL

The course of the reaction was monitored using a spectroscopic technique. The concentration of $XeO_4$ was determined by measuring light absorption at 253.6 nm with the use of our previous data [2] on the absorption cross sections of $XeO_4$ in the UV region. The experimental setup included a quartz reactor (4.5 cm in diameter and 5 cm in length) a light source (low-pressure mercury lamp), a monochromator, and a detection system (photomultiplier tube; chart recorder). Xenon tetroxide was prepared by a procedure described elsewhere [1]. Carbon disulfide was used after double degassing at liquid nitrogen temperature. To perform an experiment, xenon tetroxide was admitted to the evacuated reactor from a $XeO_4$ generator. Then, the gas supply lines were shut off and evacuated. Then, a specially prepared mixture of $CS_2$ with a diluent gas was admitted to a metering tank in an amount that provided the required total pressure and partial pressure of $CS_2$ after transferring the mixture to the reactor.

## RESULTS

The rate of the gas-phase reaction of $XeO_4$ with $CS_2$ at room temperature was studied as a function of concentrations of reactants and added gases (He, $O_2$, and $CO_2$). The gas pressures were varied over the following ranges (torr): $XeO_4$, 0.05–0.5; $CS_2$, 0.05–3; He, $O_2$, and $CO_2$, 0–400. We found previously that $XeO_4$ was slowly decomposed in the reactor in the absence of $CS_2$. This decomposition was heterogeneous, as evidenced by the dependence of the rate of decomposition on the pretreatment of the reactor with decomposition products. In a “fresh” reactor, the rate of thermal decomposition of $XeO_4$ was reasonably high. However, after performing one or two experiments for ~0.5 h each, the rate decreased and became well reproducible. Figure 1 shows the experimental dependence of the degree of $XeO_4$ decomposition in a treated reactor, which was calculated by the equation $\Delta\eta = \Delta[XeO_4]/[XeO_4]_0$, where $\Delta[XeO_4]$ is the change in $XeO_4$ concentration and $[XeO_4]_0$ is the initial concentration of $XeO_4$, on the reaction time. The slope of the straight line corresponds to the characteristic time of decomposition equal to $8 \times 10^3$ s.

All experiments with $XeO_4$ + $CS_2$ mixtures were performed in the pretreated reactor. It was found in experiments with mixtures containing $CS_2$ that the rate of thermal decomposition of $XeO_2$ remained unchanged in the treated reactor. Special tests demonstrated that a photochemical contribution to $XeO_4$ decomposition due to light from the mercury lamp could be neglected.

The concentration of $XeO_4$ rapidly decreased after the admission of $CS_2$ to the reactor. For example, at initial $XeO_4$ and $CS_2$ pressures of 0.5 torr, the concentration of $XeO_4$ halved even after ~10 s. Figure 2 shows typical curves for the relative concentration of xenon tetroxide $\eta = [XeO_4]_t/[XeO_4]_0$, where $[XeO_4]_t$ is the current concentration of $XeO_4$, plotted against the reaction time at various initial concentrations $[XeO_4]_0$ and a constant initial concentration $[CS_2]_0$ of carbon disulfide, which was present in an excess. It can be seen that the kinetic curves are almost coincident up to high degrees of $XeO_4$ conversion; that is, in these experiments, the quantity $\eta$ is only time dependent. Figure 3 demonstrates the characteristic time $\tau$ of the reaction as a function of $[CS_2]_0$, which was obtained in experiments with an excess of carbon disulfide. Obviously, the quantity $1/\tau$ is a linear function of $[CS_2]_0$.

Let us consider the $XeO_4$ reaction kinetics in terms of the formal equation $-\frac{d[XeO_4]}{dt} = k[XeO_4]^n[CS_2]^m$. We believe that $[CS_2] = [CS_2]_0$ in experiments with excess carbon disulfide. In this case, $\eta$ is independent of $[XeO_4]_0$ only at $n = 1$ (see Fig. 2). Then, the above equation has the following solution: $\eta = \exp(-k[CS_2]_0^m t) = \exp(-t/\tau)$. It is evident that $1/\tau$ is a linear function of $[CS_2]_0$ only at $m = 1$ (see Fig. 3). Thus, the reaction rate obeys the rate law $-\frac{d[XeO_4]}{dt} = k[XeO_4][CS_2]$. The stoichiometric coefficient of the reaction (that is, the ratio between the consumption of both of the reactants $\alpha = \Delta[CS_2]/\Delta[XeO_4]$) should be known to describe the reaction kinetics, which was followed by measuring the consumption of one of the reactants. To determine $\alpha$, experiments were performed at an initial pressure of $CS_2$ lower than the initial pressure of $XeO_4$. In this case, after the complete conversion of carbon disulfide, $\Delta[CS_2] = [CS_2]_0$ and $\alpha = [CS_2]_0/\Delta[XeO_4]$. According to experimental data (see the table), on the average, $\alpha = 0.7$.

Figure 4 shows typical curves of $\eta$ plotted against the reaction time in experiments with equal initial pressures of $XeO_4$ and $CS_2$ at different pressures of oxygen added. It can be seen that an increase in the pressure of $O_2$ led to some decrease in the reaction rate. The addition of He or $CO_2$ has an even smaller effect on the reaction rate.

At initial $CS_2$ pressures of ~3 torr or higher, the reaction was accompanied by luminescence. To reveal the nature of this luminescence (i.e., thermal or nonthermal), experiments were performed at constant initial $XeO_4$ and $CS_2$ pressures of 0.4 and 3 torr, respectively, and at a variable total pressure of the mixture, which was increased up to 240 torr by adding helium. Luminescence was observed in all cases.

## DISCUSSION

The following experimental facts should be taken into account in the consideration of the reaction mechanism:

(1) The high reaction rate;

(2) The linear dependence of the reaction rate on $XeO_4$ and $CS_2$ concentrations, which was observed up to high conversions of $XeO_4$;

(3) The weak effects of buffer gases added in large excess on the reaction rate;

(4) The average consumption of 0.7 molecules of $CS_2$ per one molecule of $XeO_4$ in the reaction;

(5) The luminescence observed in the course of the reaction in highly diluted mixtures.

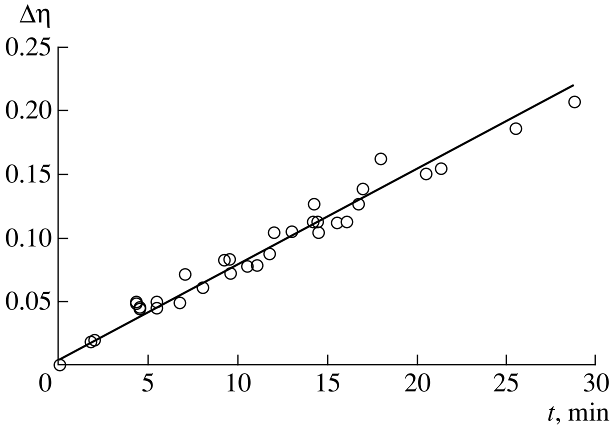


**Fig. 1.** Conversion of $XeO_4$ as a function of reaction time on thermal decomposition.

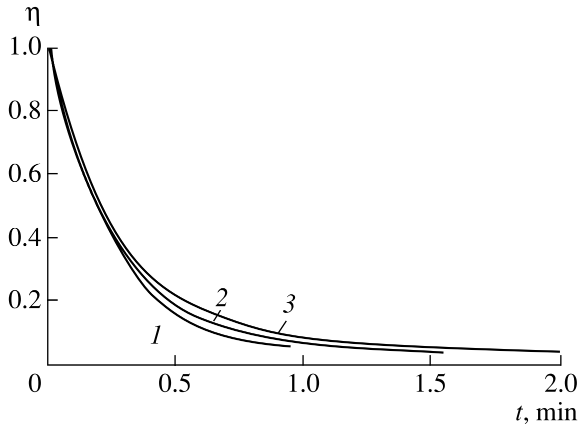


**Fig. 2.** Relative $XeO_4$ concentration as a function of time in the course of the reaction $XeO_4 + CS_2$. The initial pressure of $CS_2$ was 0.3 torr. The initial pressure of $XeO_4$ was (*1*) 0.056, (*2*) 0.090, or (*3*) 0.174 torr.

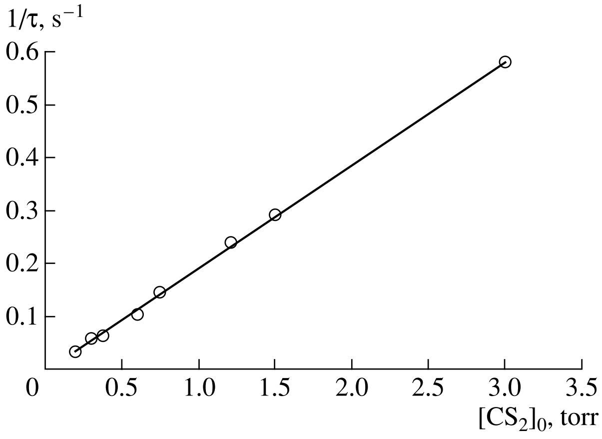


**Fig. 3.** Characteristic time of the reaction $XeO_4 + CS_2$ as a function of the initial pressure of $CS_2$.

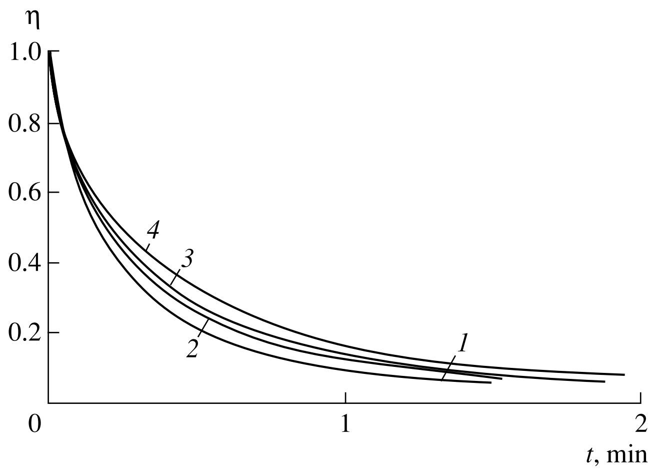


**Fig. 4.** Relative $XeO_4$ concentration as a function of time in the course of reaction in $XeO_4 + CS_2 + O_2$ mixtures. The initial pressures of $XeO_4$ and $CS_2$ were 0.17 and 0.46 torr, respectively. The pressure of $O_2$ was (*1*) 46, (*2*) 92, (*3*) 184, or (*4*) 370 torr.

Published data on the carbon–sulfur–oxygen system allowed us to suggest active species that participate in the reaction. These are O, SO, CS, and S. In experiments with the addition of $O_2$, the probabilities of decay of the O and SO species changed from relatively low (under standard experimental conditions) to relatively high values (at a maximum pressure of $O_2$) because the termolecular processes

$$O + O_2 + O_2 \longrightarrow O_3 + O_2 \text{ and}$$

$$SO + O_2 + O_2 \longrightarrow SO_3 + O_2.$$

were added to the reactions

$$O + CS_2 \longrightarrow CS + SO \text{ and}$$

$$SO + XeO_4 \longrightarrow \text{product}$$

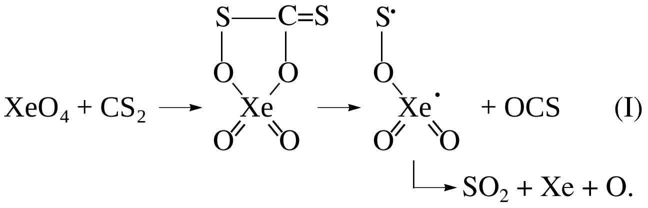
as the concentration of $O_2$ increased.

Stoichiometric coefficient of the reaction of $XeO_4$ with $CS_2$

| $[XeO_4]_0$, torr | $[CS_2]_0$, torr | α |
|---|---|---|
| 0.45 | 0.30 | 0.83 |
| 0.45 | 0.20 | 0.69 |
| 0.45 | 0.15 | 0.66 |
| 0.45 | 0.10 | 0.74 |
| 0.45 | 0.075 | 0.62 |
| 0.20 | 0.10 | 0.74 |
| 0.20 | 0.05 | 0.67 |

The weak inhibition of the mixtures by oxygen suggests that either short chains are formed in the reaction or the reaction occurs via a completely nonchain mechanism. Thus, the heterogeneous decomposition of $XeO_4$ with the formation of O atoms cannot be responsible for the generation of active species: the rate of $XeO_4$ conversion in the presence of $CS_2$ is higher than that in the absence of this reactant by three or more orders of magnitude. That is, the formation of chains including 1000 or more steps should be suggested in this case to explain the high rate of reaction between $XeO_4$ and $CS_2$. Moreover, analysis showed that in this mode of generation of active centers the reaction rate should be almost independent of the concentration of $CS_2$; however, this is inconsistent with experimental data.

We believe that active centers are generated by the direct collisions of $XeO_4$ with $CS_2$. The following reaction mechanism is conceivable:



The $CS_2$ molecule adds to $XeO_4$ to form a complex. Then, C–S and Xe–O bonds are ruptured, and the OCS molecule is eliminated. The rearrangement and fragmentation of the remaining species resulted in the $SO_2$ molecule and the unstable XeO species (the ground state of XeO is unbound [4]), which decomposes into Xe and O. The possibility of reaction (I) and its reasonably high rate can be explained by the easy transition of Xe from the octavalent to the hexavalent state. Consequently, the $XeO_4$ molecule will exhibit the properties of a biradical in some sense. The O atoms react with $CS_2$ and $XeO_4$ molecules:

$$O + CS_2 \longrightarrow SO + CS\ (k_2 = 3.6 \times 10^{-12}\ \text{cm}^3/\text{s [5]}), \quad \text{(II)}$$

$$\begin{gathered} O + XeO_4 \longrightarrow O_2 + XeO_3 \\ (k_3 \le 4.5 \times 10^{-16}\ \text{cm}^3/\text{s [1]}). \end{gathered} \quad \text{(III)}$$

The SO and CS radicals react with $XeO_4$ molecules. Of all possible channels of these reactions, the following ones do not cause chain propagation:

$$SO + XeO_4 \longrightarrow SO_2 + XeO_3, \quad \text{(IV)}$$

$$CS + XeO_4 \longrightarrow OCS + XeO_3. \quad \text{(V)}$$

We neglect the reactions of sulfur atoms because these atoms are formed in the radical–radical reactions

$$\mathrm{O + CS \longrightarrow CO + S},$$

$$\mathrm{SO + CS \longrightarrow OCS + S},$$

and their concentrations cannot be high. Reactions with the participation of $XeO_3$ molecules can also be ignored because these molecules are less reactive than $XeO_4$. These molecules cannot be accumulated in detectable amounts because $XeO_3$ exhibits a low vapor pressure and hence undergoes rapid adsorption on the reactor walls. Active species can decay on the surface

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

$$\mathrm{SO + wall \longrightarrow decay}, \quad \text{(VII)}$$

$$\mathrm{CS + wall \longrightarrow decay}, \quad \text{(VIII)}$$

or in the termolecular processes in the bulk on the addition of $O_2$

$$\mathrm{O + O_2 + O_2 \longrightarrow O_3 + O_2} \quad (k_9 = 6.2 \times 10^{-34}\ \mathrm{cm^6/s}\ [5]), \quad \text{(IX)}$$

$$\mathrm{SO + O_2 + O_2 \longrightarrow SO_3 + O_2} \quad (k_{10} = 1.4 \times 10^{-34}\ \mathrm{cm^6/s}\ [6]). \quad \text{(X)}$$

In the presence of $O_2$, the following reaction can also occur:

$$\mathrm{SO + O_2 \longrightarrow SO_2 + O} \quad (k_{11} = 6.7 \times 10^{-17}\ \mathrm{cm^3/s}\ [5]). \quad \text{(XI)}$$

In the quasi-steady-state approximation, the following expressions can be derived from the reaction scheme including processes (I)–(XI):

$$-\frac{d[\mathrm{XeO_4}]}{dt} = k_1[\mathrm{XeO_4}][\mathrm{CS_2}](1 + fg), \quad (1)$$

$$-\frac{d[\mathrm{CS_2}]}{dt} = k_1[\mathrm{XeO_4}][\mathrm{CS_2}](1 + f), \quad (2)$$

where

$$f = \left(\frac{k_4[\mathrm{XeO_4}] + k_7 + k_{10}[\mathrm{O_2}]^2}{k_4[\mathrm{XeO_4}] + k_7 + k_{10}[\mathrm{O_2}]^2 + k_{11}[\mathrm{O_2}]} + \frac{k_3[\mathrm{XeO_4}] + k_6 + k_9[\mathrm{O_2}]^2}{(k_2[\mathrm{CS_2}])}\right)^{-1},$$

and

$$g = \frac{k_3[\mathrm{XeO_4}]}{k_2[\mathrm{CS_2}]} + \frac{k_4[\mathrm{XeO_4}]}{k_4[\mathrm{XeO_4}] + k_7 + k_{10}[\mathrm{O_2}]^2 + k_{11}[\mathrm{O_2}]} + \frac{k_5[\mathrm{XeO_4}]}{k_5[\mathrm{XeO_4}] + k_8}.$$

Under standard experimental conditions, $k_2[\mathrm{CS_2}] \gg k_3[\mathrm{XeO_4}]$, $k_6$, and $k_9[\mathrm{O_2}]^2$. If a plausible assumption is made that $k_4[\mathrm{XeO_4}] \gg k_7$ and $k_5[\mathrm{XeO_4}] \gg k_8$ even at low $XeO_4$ concentrations, which correspond to considerable conversions, $f = 1$ and $g = 2$. Then, we obtain from Eqs. (1) and (2) that

$$-\frac{d[\mathrm{XeO_4}]}{dt} = 3k_1[\mathrm{XeO_4}][\mathrm{CS_2}], \quad (3)$$

$$-\frac{d[\mathrm{CS_2}]}{dt} = 2k_1[\mathrm{XeO_4}][\mathrm{CS_2}]. \quad (4)$$

It follows from Eqs. (3) and (4) that the rate of consumption of $XeO_4$ is a linear function of reactant concentrations, and 0.67 molecules of $CS_2$ is consumed per molecule of $XeO_4$ as was observed experimentally. The slope of the straight line in Fig. 3 corresponds to the value $3k_1 = 6 \times 10^{-18}$ cm$^3$/s; that is,

$$k_1 = 2 \times 10^{-18}\ \mathrm{cm^3/s}.$$

At high $O_2$ concentrations when $k_9[\mathrm{O_2}]^2 \gg k_3[\mathrm{XeO_4}] + k_6$ and $k_{10}[\mathrm{O_2}]^2 \gg k_4[\mathrm{XeO_4}] + k_7 + k_{11}[\mathrm{O_2}]$, we have $f = (1 + k_9[\mathrm{O_2}]^2/k_2[\mathrm{CS_2}])^{-1}$. If the pressure of $O_2$ is 400 torr, and the pressure of $CS_2$ is equal to 0.5 torr, as it usually is, $f \simeq 0.5$, $g = 1$; and, according to Eq. (1), $\frac{d[\mathrm{XeO_4}]}{dt} \simeq 1.5k_1[\mathrm{XeO_4}][\mathrm{CS_2}]$. A comparison of this expression with Eq. (3) demonstrates that, at a maximum concentration of $O_2$, the reaction rate decreases by a factor of two or lower as was observed experimentally. Note that the rate of mixing decreases and becomes comparable to the rate of reaction as the total pressure in the mixture increases; this results in an apparent decrease in the reaction rate. The effect of large additives of He and $CO_2$ can be explained by this phenomenon.

Because the reaction luminescence was retained in the mixtures of $XeO_4$ with $CS_2$ at high dilution with helium, we believe that it is chemiluminescence. It is most likely that reaction (IV) is responsible for the luminescence. Energy (108 kcal/mol) released in this reaction is sufficient for transferring $SO_2$ into an electronically excited state. Note that chemiluminescence was also observed in the gas-phase reactions of ozone with simple sulfides such as $H_2S$, $CH_3SH$, $(CH_3)_2S$, or $(CH_3S)_2$ [7, 8]. This chemiluminescence was ascribed to the electronically excited $SO_2$ species formed in the reaction $\mathrm{SO + O_3 \longrightarrow SO_2 + O_2}$, which is similar to reaction (IV) in terms of energy.

Thus, the proposed reaction scheme fully describes the mechanism of reaction of $XeO_4$ with $CS_2$ and explains all experimental data. According to this mechanism, active centers are generated in direct collisions of $XeO_4$ and $CS_2$ molecules (the reaction rate constant $k_1 = 2 \times 10^{-18}$ cm$^3$/s). Thereafter, a short chain of at most two steps is formed. The high rate of chain initiation renders the mixtures of $XeO_4$ with $CS_2$ fundamentally unstable.

## ACKNOWLEDGMENTS

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