

# Mechanism of the Reaction of Xenon Tetraoxide with Hydrogen: A Photochemical Reaction

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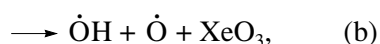
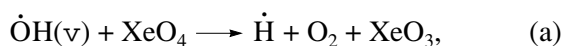
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**Abstract**—The dependence of the rate of a photochemical reaction of  $\text{XeO}_4$  with  $\text{H}_2$  on the concentrations of  $\text{H}_2$  and the diluent gases He and  $\text{CO}_2$  is studied at room temperature. The results are compared with the data for the dark reaction. A mechanism with the elementary energetic branched-chain reaction  $\dot{\text{O}}\text{H}(\nu) + \text{XeO}_4 \longrightarrow \text{OH} + \dot{\text{O}} + \text{XeO}_3$  is proposed to explain the results of the study.

## INTRODUCTION

Previously [1], we found that the dark reaction of  $\text{XeO}_4$  with  $\text{H}_2$  occurs via a chain mechanism and that the reaction of the vibrationally excited radical  $\dot{\text{O}}\text{H}(\nu)$  with the  $\text{XeO}_4$  molecule is a key step in the reaction mechanism. The addition of efficient  $\dot{\text{O}}\text{H}(\nu)$  deactivators (such as  $\text{CO}_2$  and  $\text{O}_2$ ) in small amounts to the reaction mixture dramatically decreased the rate of the reaction of  $\text{XeO}_4$  with  $\text{H}_2$ . In principle, the reaction of  $\dot{\text{O}}\text{H}(\nu)$  with  $\text{XeO}_4$  can occur via the following three channels:



where reaction (a) is chain propagation, reaction (b) is chain branching, and reaction (c) is chain termination because of the low activity of the  $\text{H}\dot{\text{O}}_2$  radical. Questions as to which of these reactions occur and in what proportion are very important because this proportion governs the reaction mechanism: either a linear chain reaction or a branched-chain reaction takes place. In this work, we examined a photochemical reaction of  $\text{XeO}_4$  with  $\text{H}_2$ . In this case, the rate of generation of active centers can be much higher than in the dark reaction. A comparison between the rates and paths of the reaction of  $\text{XeO}_4$  with  $\text{H}_2$  in these two cases can provide an answer to this issue.

## EXPERIMENTAL

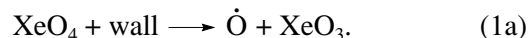
The experiments were performed using a previously described setup [2]. The setup included a quartz reactor, a UV-radiation source (deuterium arc lamp) for initiating the chemical reaction, a probing radiation

source (low-pressure mercury lamp with an emission wavelength of 253.6 nm), and a generator of  $\text{XeO}_4$ . The reaction was followed by monitoring the consumption of  $\text{XeO}_4$ , as determined by changes in the absorption of probing radiation in the reactor [3].  $\text{XeO}_4$  was prepared immediately before each particular experiment by the reaction of sodium hexaoxoxenonate with concentrated sulfuric acid. The  $\text{O}_2$  concentration in  $\text{XeO}_4$  was ~30% with respect to the  $\text{XeO}_4$  formed [1]. The initial pressure of  $\text{XeO}_4$  in the reactor was 0.3 or 0.4 torr. The pressure of  $\text{H}_2$  in diluted reactant mixtures was varied from 0.5 to 4 torr. Helium and carbon dioxide were used as diluent gases. The pressures of He and  $\text{CO}_2$  were varied from 4 to 400 torr and from 4 to 60 torr, respectively. The experiments with undiluted mixtures were performed at three fixed  $\text{H}_2$  pressures of 2.0, 2.5, and 3.8 torr.

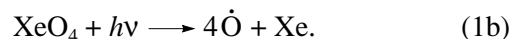
The rate of  $\text{XeO}_4$  conversion depended on the number of experiments performed in the reactor. The results were reproducible after stabilizing the state of reactor walls by treatment with reaction products [1]. The data considered below were obtained under these conditions.

## RESULTS

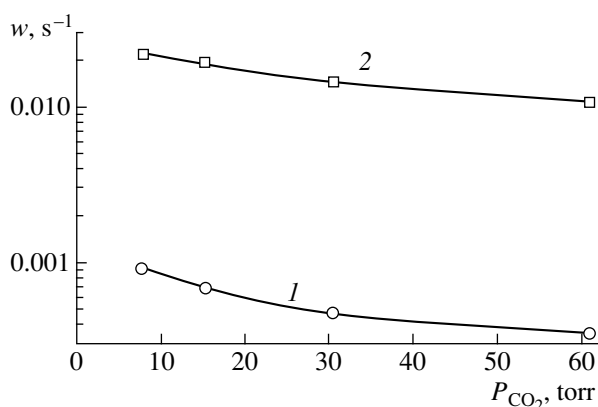
In the dark reaction, chains are initiated in the heterogeneous decomposition of  $\text{XeO}_4$  [1]



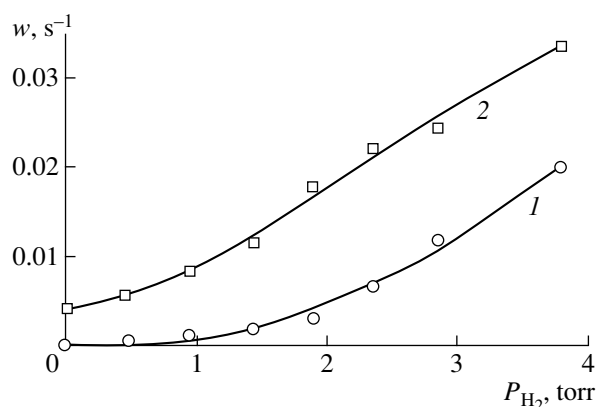
In the photochemical reaction, chains are initiated by the photodissociation of  $\text{XeO}_4$ , which forms O atoms mostly in the ground state [2]:



The ratio between the specific rate constants (per one  $\text{XeO}_4$  molecule) of thermal ( $k_{1\text{a}}$ ) and photochemical ( $k_{1\text{b}}$ ) chain initiation was determined from experi-



**Fig. 1.** Specific rates of (1) dark and (2) photochemical reactions as functions of CO<sub>2</sub> pressure. The pressures of XeO<sub>4</sub> and H<sub>2</sub> are 0.4 and 3.8 torr, respectively.



**Fig. 2.** Specific rates of (1) dark and (2) photochemical reactions as functions of H<sub>2</sub> pressure. The total pressure was 7.6 torr;  $P_{\text{XeO}_4} = 0.4$  torr; and the balance was He.

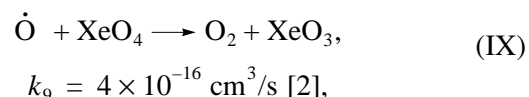
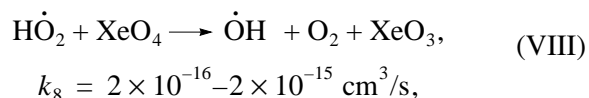
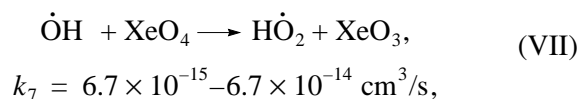
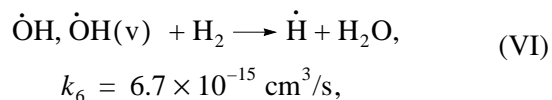
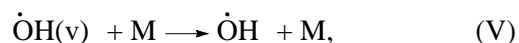
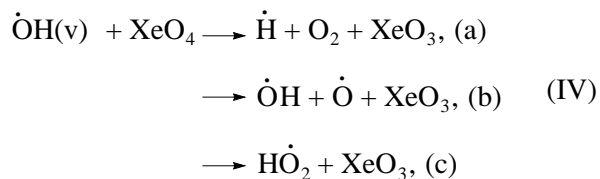
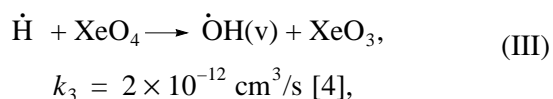
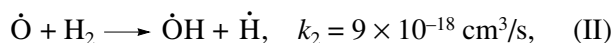
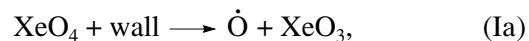
ments on the thermal and photochemical degradation of XeO<sub>4</sub>. If experiments were performed under identical conditions at low pressures (when the decay of O atoms on the walls and (or) in the reaction  $\dot{\text{O}} + \text{XeO}_4 \rightarrow \text{O}_2 + \text{XeO}_3$  play the main role),  $k_{1b}/k_{1a} = w_{1b}/w_{1a}$ , where  $w_{1a}$  and  $w_{1b}$  are the specific rates of thermal and photochemical decomposition of XeO<sub>4</sub>, respectively. We found from the results of measurements that  $w_{1a} = 10^{-4} \text{ s}^{-1}$  and  $w_{1b} = 5 \times 10^{-3} \text{ s}^{-1}$ ; that is, the rate of photochemical chain initiation is higher than the rate of thermal chain initiation by a factor of 50, all other conditions being the same.

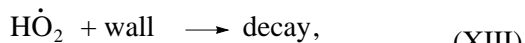
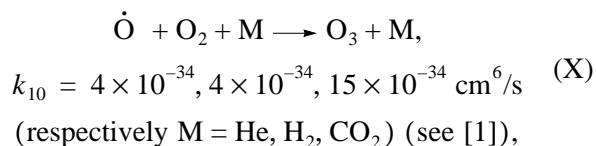
The specific rate of the reaction of XeO<sub>4</sub> with H<sub>2</sub>,  $w = -\frac{1}{[\text{XeO}_4]} \frac{d[\text{XeO}_4]}{dt}$  was determined from the initial portions of kinetic curves at XeO<sub>4</sub> conversions lower than 30%. The rate was characterized by the  $w$  value that provided the best fit to the initial portion.

Figures 1 and 2 illustrate the typical dependence of the reaction rate on the pressures of CO<sub>2</sub> and H<sub>2</sub>, respectively. The ratio between the rates of photochemical and dark reactions in experiments with mixtures containing CO<sub>2</sub> was ~30 (see Fig. 1). In experiments without adding diluent gases, the ratio between the rates of photochemical and dark reactions was strongly affected by the H<sub>2</sub> amount: the difference was great at small amounts of H<sub>2</sub> (as well as in the mixtures with CO<sub>2</sub>), whereas the rates became commensurable at maximum H<sub>2</sub> amounts (see Fig. 2). For example, at  $P_{\text{H}_2} = 3.8$  torr, the rate of the photochemical reaction was higher than the rate of the dark reaction by a factor less than two. The addition of helium had a weak effect on the ratio between the rates of photochemical and dark reactions.

## DISCUSSION

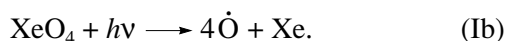
Previously [1], we proposed a mechanism for the dark reaction, which involved the following elementary steps:



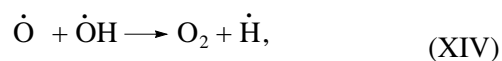


$$k_{11}, k_{12}, k_{13} = 1\text{--}10 \text{ s}^{-1}.$$

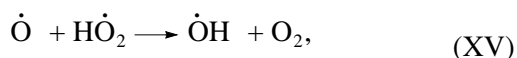
In the photochemical reaction, chain is initiated by the reaction:



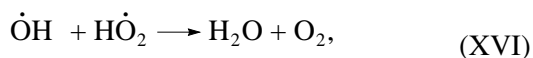
At high concentrations of active centers, which can be attained, for example, in the photochemical or fast dark reaction, the following reactions between radicals should be taken into account:



$$k_{14} = 3.3 \times 10^{-11} \text{ cm}^3/\text{s},$$



$$k_{15} = 5.7 \times 10^{-11} \text{ cm}^3/\text{s},$$



$$k_{16} = 1.1 \times 10^{-10} \text{ cm}^3/\text{s}.$$

The set of reactions (I)–(XVI) was taken as a basis for our analysis. Data on the reaction rate constants were taken from [5], unless otherwise indicated in the scheme. The constants  $k_7, k_8, k_{11}, k_{12}$ , and  $k_{13}$  were varied within the limits specified in the scheme. For  $k_7$  and  $k_8$ , the values of the rate constants of the corresponding processes in the reaction of  $\text{O}_3$  with  $\text{H}_2$  were taken as a basis.

Using the method of quasi-steady-state concentrations with respect to the species  $\text{H}$ ,  $\dot{\text{O}}\text{H}(\text{v})$ ,  $\dot{\text{OH}}$ ,  $\text{H}\dot{\text{O}}_2$ , and  $\dot{\text{O}}$ , and with reasonable assumptions valid under experimental conditions, we obtained

$$k_1[\text{XeO}_4] + \alpha k_6[\text{H}_2][\dot{\text{OH}}]$$

$$= (A + k_{14}[\dot{\text{OH}}] + k_{15}[\text{H}\dot{\text{O}}_2])[\dot{\text{O}}], \quad (1)$$

$$2k_2[\text{H}_2][\dot{\text{O}}] = (k_{13} + 2k_{16}[\dot{\text{OH}}])[\text{H}\dot{\text{O}}_2], \quad (2)$$

$$(k_7[\text{XeO}_4] + \beta k_6[\text{H}_2])[\dot{\text{OH}}]$$

$$= (k_8[\text{XeO}_4] + k_{13} + k_{15}[\dot{\text{O}}])[\text{H}\dot{\text{O}}_2], \quad (3)$$

$$w = k_2[\dot{\text{O}}] + k_8[\text{H}\dot{\text{O}}_2] + (\gamma k_6[\text{H}_2]/[\text{XeO}_4] + k_7)[\dot{\text{OH}}], \quad (4)$$

where

$$A = k_2[\text{H}_2] + k_9[\text{XeO}_4] + k_{10}[\text{O}_2][\text{M}] + k_{11},$$

$$\alpha = k_{4b}[\text{XeO}_4]/((k_{4b} + k_{4c})[\text{XeO}_4] + k_5[\text{M}]),$$

$$\beta = k_{4c}[\text{XeO}_4]/((k_{4b} + k_{4c})[\text{XeO}_4] + k_5[\text{M}]),$$

$$\gamma = (2k_4[\text{XeO}_4] + k_5[\text{M}])/((k_{4b} + k_{4c})[\text{XeO}_4] + k_5[\text{M}]),$$

$k_1$  is the specific rate of  $\dot{\text{O}}$  formation in the course of initiation ((Ia) or (Ib));  $k_1 = 10^{-4}$  or  $5 \times 10^{-3} \text{ s}^{-1}$  for the dark or photochemical reaction, respectively (see above).

Initially, we analyzed the experiments with mixtures containing  $\text{CO}_2$ . In this case, the reaction scheme is simplified because processes involving  $\dot{\text{OH}}(\text{v})$  radicals should not be taken into account since deactivation by  $\text{CO}_2$  molecules is rapid. Consequently,  $\alpha = \beta = 0$  and  $\gamma = 1$ . It is evident that at a low rate of generation of active centers, when quadratic processes (XV) and (XVI) can be neglected, the reaction rate  $w$  is a linear function of the rate constant of generation  $k_1$ . At a sufficiently high rate of initiation, when the rates of quadratic processes (XV) and (XVI) are higher than the rates of linear processes (VIII) and (XIII), we obtain the following relations from Eqs. (2) and (3):

$$k_2[\text{H}_2][\dot{\text{O}}] = k_{16}[\dot{\text{OH}}][\text{H}\dot{\text{O}}_2], \quad (5)$$

$$k_7[\text{XeO}_4][\dot{\text{OH}}] = k_{15}[\dot{\text{O}}][\text{H}\dot{\text{O}}_2]. \quad (6)$$

It follows from Eqs. (5) and (6) that the concentration of  $\text{H}\dot{\text{O}}_2$  approaches the limit  $[\text{H}\dot{\text{O}}_2]_0 = \sqrt{k_2 k_7 [\text{H}_2] [\text{XeO}_4] / k_{15} k_{16}}$ . This behavior is a consequence of a rapid increase in the rate of process (XV) with an increase in the concentration of active centers. From Eq. (1), taking into account Eq. (5), we obtain

$$k_1[\text{XeO}_4] = (A + k_{14}[\dot{\text{OH}}]) \quad (7)$$

$$+ k_{15}[\text{H}\dot{\text{O}}_2]_0 k_{16}[\dot{\text{OH}}][\text{H}\dot{\text{O}}_2]_0 / k_2[\text{H}_2].$$

The rate of reaction, which primarily depends on the last term in Eq. (4), is proportional to  $k_1$  at  $k_{14}[\dot{\text{OH}}] < A + k_{15}[\text{H}\dot{\text{O}}_2]_0$  in Eq. (7) or proportional to  $\sqrt{k_1}$  with a further increase in the rate of initiation when  $k_{14}[\dot{\text{OH}}] > A + k_{15}[\text{H}\dot{\text{O}}_2]_0$ . The intermediate dependence of  $w$  on  $k_1$  was observed experimentally: the reaction rate increased by a factor of 30 with an increase in the rate of initiation by a factor of 50.

In mixtures without  $\text{CO}_2$ , the rates of photochemical and dark reactions were little different at a high pressure of  $\text{H}_2$  ( $P > 2$  torr, see Fig. 2). This can be explained assuming that the reaction mixtures occurred in a

branching region. In this case, external initiation weakly affects the concentrations of active species and hence the rate of reaction. An initial exponential increase in the concentrations of active species becomes slower because of the acceleration of the quadratic processes of chain termination with an increase in the concentrations of atoms and radicals and because of the accumulation of products that facilitate chain termination (water molecules, which are efficient quenchers of the  $\dot{\text{O}}\text{H}(\text{v})$  radicals, are formed in the reaction [6]). A nonexplosive reaction (with characteristic times of tens of seconds or longer) is a consequence of this. A similar situation was observed in the study of the branched-chain reaction of  $\text{F}_2$  with  $\text{H}_2$  to form HF as the end product. This product, being an efficient deactivator of vibrationally excited species responsible for the step of branching, dramatically decreased the rate of reaction [7]. For the fast dark reaction, we ignored the terms  $k_1[\text{XeO}_4]$  in Eq. (1) and  $k_{13}$  in Eqs. (2) and (3), which are insignificant at high concentrations of active species. Then, we obtain from Eqs. (2) and (3)

$$[\dot{\text{O}}\text{H}] = k_8[\text{XeO}_4][\dot{\text{H}}\text{O}_2]/(k_7[\text{XeO}_4] + \beta k_6[\text{H}_2] - k_{15}k_{16}[\dot{\text{H}}\text{O}_2]^2/k_2[\text{H}_2]). \quad (8)$$

It follows from Eq. (8) that the concentration of  $\dot{\text{H}}\text{O}_2$  cannot be higher than the value  $[\dot{\text{H}}\text{O}_2]_0 = \sqrt{(k_7[\text{XeO}_4] + \beta k_6[\text{H}_2])k_2[\text{H}_2]/k_{15}k_{16}}$ . In this case, the concentration of  $\dot{\text{O}}\text{H}$  dramatically increases in the vicinity of  $[\dot{\text{H}}\text{O}_2]_0$ . Therefore, we can take  $[\dot{\text{H}}\text{O}_2] = [\dot{\text{H}}\text{O}_2]_0$  for reactions in the branching region, which is characterized by the high concentration of  $\dot{\text{O}}\text{H}$ . Then, we obtain from Eqs. (1) and (2) using the above assumptions

$$\alpha k_6[\text{H}_2] = k_7[\text{XeO}_4] + \beta k_6[\text{H}_2] + (A + k_{14}[\dot{\text{O}}\text{H}])k_{16}[\dot{\text{H}}\text{O}_2]_0/k_2[\text{H}_2]. \quad (9)$$

It follows from Eq. (9) that  $k_7[\text{XeO}_4]/k_6[\text{H}_2] < \alpha - \beta$ . Considering the expressions for  $\alpha$  and  $\beta$  (see above) and taking into account that  $\alpha - \beta < 1$ , we obtain

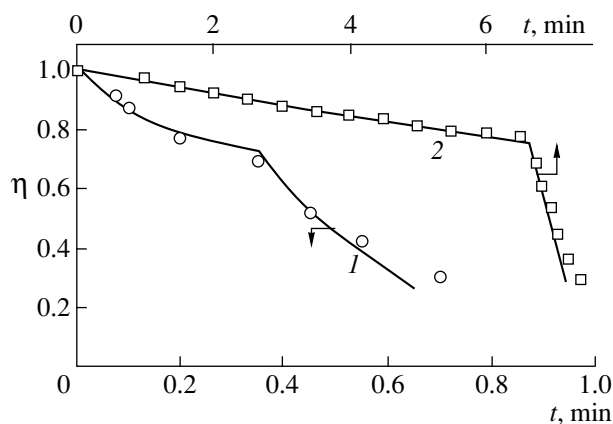
$$k_7[\text{XeO}_4]/k_6[\text{H}_2] < (k_{4b} - k_{4c}) \times [\text{XeO}_4]/((k_{4b} + k_{4c})[\text{XeO}_4] + k_5[\text{M}]) < 1.$$

It follows from the above inequalities that (1)  $k_{4b} > k_{4c}$ ; that is, the fraction of reaction (IVb) is greater than the fraction of reaction (IVc) and (2)  $k_7 < k_6[\text{H}_2]/[\text{XeO}_4] = 10k_6 = 7 \times 10^{-14} \text{ cm}^3/\text{s}$ ; that is the rate constant of step (VII) is lower than the rate constant of an analogous reaction of the  $\dot{\text{O}}\text{H}$  radical with  $\text{O}_3$ .

The reaction was analyzed in more detail by computer simulations. To describe quantitatively the exper-

iments with mixtures containing  $\text{CO}_2$ , we varied the unknown rate constants of the heterogeneous decay of active species (reactions (XI)–(XIII)) and the rate constants of chain propagation (VII) and (VIII) involving  $\text{XeO}_4$ . The values of  $k_{11}$ – $k_{13}$  were varied over the range  $1$ – $10 \text{ s}^{-1}$  (this range was chosen based on the analysis of a great body of published data on the heterogeneous decay of  $\dot{\text{O}}$ ,  $\dot{\text{O}}\text{H}$ , and  $\dot{\text{H}}\text{O}_2$ ). The values of  $k_7$  and  $k_8$  were varied over the ranges  $0.1$ – $1.0$  of the rate constants of the corresponding processes in the reaction of  $\text{O}_3$  with  $\text{H}_2$ . We found that, at a simultaneous tenfold change in  $k_{11}$ – $k_{13}$ , the rates of the dark and photochemical reactions changed by a factor of less than two and by less than 10%, respectively. The low sensitivity of the rate of the photochemical reaction to changes in the rate constants of heterogeneous decay results from an increasing part of quadratic processes. Variations in  $k_7$  and  $k_8$  over the specified range provided that  $k_7/k_8 \gg 1$  (in the reaction between  $\text{O}_3$  and  $\text{H}_2$ , the corresponding ratio is equal to 30 [5]) resulted in less than twofold changes in the rates of dark and photochemical reactions. An analysis demonstrated that preferable values of the constants  $k_7$ ,  $k_8$ , and  $k_{11}$ – $k_{13}$  cannot be chosen because various combinations of them adequately describe the experimental data as a consequence of the weak effect of these constants on the reaction rate. At the same time, the strong effect of the rate of generation of active centers on the reaction rate, which was observed experimentally, was described by calculated data.

To quantitatively describe the experiments without  $\text{CO}_2$ , we additionally varied the reaction parameters associated with the participation of  $\dot{\text{O}}\text{H}(\text{v})$ , namely, the parameter  $r = k_4/k_5$  ( $\text{M} = \text{O}_2$ ), where  $k_5$  ( $\text{M} = \text{O}_2$ ) is the rate constant of relaxation of  $\dot{\text{O}}\text{H}(\text{v})$  on  $\text{O}_2$ , and the proportions between variants of reaction (IV)  $r_{4a} = k_{4a}/k_4$ ,  $r_{4b} = k_{4b}/k_4$ , and  $r_{4c} = k_{4c}/k_4$ . In a similar reaction system of  $\text{O}_3$  with  $\text{H}_2$ ,  $\dot{\text{O}}\text{H}$  radicals are formed in the reaction  $\dot{\text{H}} + \text{O}_3$  primarily on the level of  $\text{v} = 9$  (see [8]). The rate constant of the reaction  $\dot{\text{O}}\text{H}(\text{v} = 9) + \text{O}_3$  is equal to  $2 \times 10^{-10} \text{ cm}^3/\text{s}$  [9], and the rate constant of deactivation of  $\dot{\text{O}}\text{H}(\text{v} = 9)$  by  $\text{O}_2$  molecules is equal to  $1.7 \times 10^{-11} \text{ cm}^3/\text{s}$  [10]; that is, the parameter analogous to  $r$  is  $\approx 10$ . Reaction (III) exhibits the same energetics as the reaction  $\dot{\text{H}} + \text{O}_3$ . Therefore, we took  $r = 10$  as an upper limit in variations and the variation range  $r = 1$ – $10$ . The relative constants of  $\dot{\text{O}}\text{H}(\text{v})$  deactivation in other species were taken from [6]. Data on the dark and photochemical reactions were adequately described at  $r = 3$ – $10$  over a wide range of  $r_{4b}$  values up to  $r_{4b} = 1$ . At the same time, it follows from the calculations that  $r_{4a}$  cannot be higher than  $r_{4b}$ . Thus, the proportions between channels in reaction (IV) cannot presently be unambiguously deter-



**Fig. 3.** Relative (reduced to the initial)  $\text{XeO}_4$  concentration ( $\eta$ ) as a function of time. Points and curves refer to the experimental and calculated data, respectively: (1) total pressure, 7.6 torr;  $P_{\text{XeO}_4} = 0.4$  and  $P_{\text{H}_2} = 3.8$  torr; and the balance He; (2) total pressure, 15 torr;  $P_{\text{XeO}_4} = 0.4$  and  $P_{\text{H}_2} = 3.8$  torr; and the balance  $\text{CO}_2$ .

mined because data for a number of processes are absent. However, we can state the relation  $r_{4b} > r_{4a}, r_{4c}$ . Taking into account the above relation between the variants of reaction (IV) and the range of possible  $r$  values, we can estimate the lower limit  $k_{4b} \geq k_5$  ( $M = \text{O}_2$ )  $\sim 10^{-11}$  cm<sup>3</sup>/s. Previously [1], analyzing the scheme of the dark reaction in a linear approximation, we found that the fraction of reaction (IVa) can be as high as 100%. Analysis of data on the photochemical reaction with consideration for nonlinear processes, which was performed in this work, allowed us to determine that the fraction of reaction (IVa) is at most 50%.

Figure 3 compares the experimental kinetic curves for two experiments (with and without  $\text{CO}_2$ ) to the curves calculated for a possible set of parameters ( $d = 0.1$ ,  $r = 10$ ,  $r_{4a} = 0$ ,  $r_{4b} = 0.7$ ,  $r_{4c} = 0.3$ , and  $k_{11} = k_{12} = k_{13} = 1$  s<sup>-1</sup>). The presented data refer to combined experiments in which the dark reaction initially took place. Then, after turning on the deuterium lamp (bends in the curves correspond to the instant of turning on), the pho-

tochemical reaction occurred. It can be seen that the experimental results are everywhere adequately described by the calculated data.

## CONCLUSIONS

(1) The reaction of  $\text{XeO}_4$  with  $\text{H}_2$  occurs via a branched-chain mechanism involving an energetic branched-chain reaction in elementary step (IVb).

(2) For the variants of reaction (IV), the relation  $r_{4b} > r_{4a}, r_{4c}$  is true.

(3) The rate constant of reaction (VII) is lower than the rate constant of an analogous reaction of the  $\dot{\text{O}}\text{H}$  radical with  $\text{O}_3$ .

(4) The experimentally observed effects associated with the dependence of the reaction rate on external conditions (the rate of initiation and composition of reactant mixtures) are adequately described by the suggested scheme.

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