MECHANISM OF COMBUSTION OF MIXTURES OF H₂ WITH O + O₂,
H₂O₂, AND HNO₃

V. Ya. Basevich and S. M. Kogarko

On the basis of qualitative considerations, we can assume that the mechanisms of combustion of mixtures of H₂ with O + O₂ [1, p. 419], H₂O₂, and HNO₃ are similar. The purpose of the present paper is quantitative verification of this assumption and elucidation of specific characteristics of the combustion of H₂ with these oxidizing agents. In addition, we have refined the rate constants of some elementary combustion reactions.

EXPERIMENTAL

The experiments were carried out in a jet unit [2] making it possible to obtain kinetic curves without distortions introduced by diffusion processes. Reagents diluted with Ar were fed to the reactor separately, heated rapidly, and stirred. The initial concentrations of the O (and H) atoms were created by passing O₂ (H₂) through a discharge; H₂O₂ and HNO₃ vapors were fed into the stream with a bubbling device. Together with the H₂O₂ vapors, H₂O and O₂ also entered the reactor. The content of H₂ and O₂ in the initial mixture and in the reaction products was measured by gas chromatography in samples withdrawn with a cooled gas sampler. The concentrations of O and H atoms and OH hydroxyl were determined by EPR (the sensitivity thresholds were 10¹⁸, 10¹⁴, and 10¹¹ l/cm³, respectively). After accumulation in a trap cooled with liquid N₂, H₂O₂ was determined by titration; NO₂ was determined spectroscopically. In all the experiments, the pressure was 1 kPa, except for the experiments with H₂O₂, where the pressure was 1.34 kPa.

Beforehand, the rate constant of the process H₂ + O → OH + H (5) in a wide temperature range was refined. For this, jets of H₂ + Ar and O + O₂ + Ar were mixed. At constant

![Figure 1. Rate constant of the reaction O + H₂ → OH + H. The hatched field denotes the region of values, and the broken line denotes the average value [3, p. 64]. The points and the solid line denote our measurements [Eq. (2)].](image)


1050 0568-5230/80/2907-1050$07.50 © 1981 Plenum Publishing Corporation
The products of the reaction $\text{H}_2 + (0 + 0_2) + \text{Ar}$. $[0]_o = 0.5\%$, $[0_2]_o = 0.82\%$, 1160°K, $\tau = 2.5$ msec.

The products of the reaction $(\text{H} + \text{H}_2) + 0_2 + \text{Ar}$ (a) and $(\text{H} + \text{H}_2) + (0 + 0_2) + \text{Ar}$ (b). $[\text{H}]_o = 0.11$, $[\text{H}_2]_o = 6.25$, $[0]_o = 0.041-0.107\%$, 293°K, $\tau = 20$ msec.

initial concentrations of $[0]_o$ and $[0_2]_o$ of 0.5% and 0.85%, respectively, and with variation of the $[\text{H}_2]_o$ concentration from 0 to 12.5%, the value of which should change little during the process, the rate constant of (5) could be determined according to the decrease of atomic oxygen $[0]$ from the approximate expression

$$k_5 = \frac{\ln [0]_o}{B [\text{H}_2]_o \tau}$$  \hspace{1cm} (1)

where $\tau$ is the reaction time, and $B \approx 2$ is a stoichiometric coefficient taking into account the change in the $[0]$ concentration in secondary reactions. In the range of 293-1160°K, the obtained values of $k_5$ (Fig. 1) could be approximated with the expression

$$k_5 = 10^{31.7 \pm 0.7} \exp (-600 \pm 600/RT)$, cm$^3$/molecule $\cdot$ sec  \hspace{1cm} (2)

The temperature dependence of $k_5$ is not described by a straight line in log $k$ vs $1/T$ coordinates mainly because of the relatively large value of $k_5$ at 293°K, something which was also noted previously by other authors. In the range of 450-1160°K, the temperature dependence of $k_5$ could be approximated by the Arrhenius equation

$$k_5 = 10^{30.4 \pm 0.6} \exp (-8900 \pm 400/RT)$, cm$^3$/molecule $\cdot$ sec  \hspace{1cm} (2a)

or by the equation

$$k_5 = 10^{31.2 \pm 0.5} \exp (-8200 \pm 380/RT)$, cm$^3$/molecule $\cdot$ sec  \hspace{1cm} (2b)

The products of the reaction of $\text{H}_2$ with $0 + 0_2$ were studied at 1160°K and $\tau = 2.5$ msec in greater detail (Fig. 2).

The mechanism of the recombination processes was also studied at 20°C, when we could ignore the processes with high activation energy. To determine the rate constant of the process $\text{H} + 0_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$ (7), $\text{H} + \text{H}_2 + \text{Ar}$ and $0_2 + \text{Ar}$ jets were mixed. The rate constant was determined at constant initial concentrations of $[\text{H}]_o$ and $[\text{H}_2]_o$ of 0.11% and 6.25%,