Reports of the Academy of Sciences of the USSR

V. P. Balakhnin, Yu. M. Gershenzon, Academician V. N. Kondrat' ev,

1964

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR

1964. Volume 154, No. 4

Physical Chemistry

V. P. Balakhnin, Yu. M. Gershenzon, Academician V. N. Kondrat’ ev,
A. B. Nalbandyan

Measurement of the Concentrations of Atomic Oxygen and Hydrogen in a Rarefied Hydrogen Flame by the E.P.R. Method

In the combustion of hydrogen, chain propagation and branching are effected by the following generally accepted sequence of elementary reactions:

$$OH + H_2 \rightarrow H_2O + H, \tag{1}$$
$$H + O_2 \rightarrow OH + O, \tag{2}$$
$$O + H_2 \rightarrow OH + H. \tag{3}$$

If for the rate constant of reaction (2) one may adopt the formula $k_2 = 1.3 \cdot 10^{-10} \cdot e^{-15900/RT}$ cm^3·molecule^{-1}·sec^{-1}, with which, within the limits of measurement error, the data obtained by various authors agree, then for the rate constants of reactions (1) and (3) the data of different authors differ substantially. For the rate constant of process (3) we adopt the formula $k_3 = 0.9 \cdot 10^{-10} \cdot e^{-11700/RT}$ cm^3· molecule^{-1} · sec^{-1}, obtained at the Institute of Chemical Physics (^{1}), which we consider the most reliable. As for the constant k_1, at present there are two formulas which in the region of 1000° K give values differing by several times ($^{2-4}$). At $T = 900°$ K, $k_1 > k_3 > k_2$. For a stoichiometric mixture at this temperature

$$\frac{1}{k_1(H_2)} : \frac{1}{k_2(O_2)} : \frac{1}{k_3(H_2)} = \frac{1}{80} : 1 : \frac{1}{16}.$$

These quantities characterize the lifetime of the OH radical and of the H and O atoms, and to some extent make it possible to judge the relationship between their concentrations (^{5}). It is clear, for example, that for a stoichiometric mixture (H) > (O) > (OH). It can be shown that for mixtures poor in hydrogen, (O) > (H) > (OH).

The present work is devoted to the detection of atomic oxygen and to the measurement of the concentrations of O and H atoms in a rarefied hydrogen flame from electron paramagnetic resonance (E.P.R.) spectra. For this purpose a jet apparatus was used, analogous to that described earlier (^{6,7}). In contrast to previous work, the reactor was located directly in the resonator, which made it possible to determine the concentrations of H and O atoms directly in the combustion zone. The reactor heater consisted of platinum filaments arranged along the reactor walls and enclosed in a quartz sheath (^{8}). This type of arrangement of the heater filaments practically did not lead to a decrease in the Q factor (^{9}). However, when a direct current of 3 amp was passed, the amplitude of the derivative signal from a sample located at a distance of 1.5 cm from the center of the resonator decreased by a factor of 2-4, which is explained by the inhomogeneity of the magnetic field introduced by the heater and leading to line broadening. Thus the sensitivity of the instrument was somewhat reduced.

For an accurate determination of the concentration of atoms it is necessary to select such a combustion regime that the most intense part of the flame is located at the center of the resonator. At constant pressure, temperature, and mixture composition this was achieved by the appropriate choice of jet velocity. In Fig. 1···

the dependence of the concentrations of atomic oxygen and hydrogen on the volumetric flow rate (W) at $T = 580°\text{C}$, $p = 6$ mm Hg, and a ratio $H_2/O_2 = 1$ is shown. As is seen from the graph, at flow rates of 50 cm^3/min and higher the EPR signal practically does not change. A volumetric flow rate of 60 cm^3/min proved suitable for all mixtures except those poor in oxygen. For mixtures of 70% H_2 + 30% O_2 and 80% H_2 + 20% O_2, flow rates of 40 cm^3/min and 30 cm^3/min, respectively, were chosen in analogous fashion. A volumetric flow rate of 60 cm^3/min corresponds, under flame conditions, to a linear velocity of 7.6 m/sec, at which the contact time is 4.2 msec (inner tube diameter 8 mm, resonator length 32 mm). It should be noted that the signals from O and H atoms are recorded at the flame temperature, whereas determination of the number of particles responsible for the signal is carried out by comparison with a reference sample at room temperature. According to the Curie–Weiss law, the observed concentration must be multiplied by the temperature factor T/T_0 (T is the flame temperature, T_0 is the temperature of the reference sample). In addition, it should be borne in mind that, so long as the distribution of particles in the flame, or at least the approximate dimensions of the flame zone, is unknown, one must speak not of concentration, but of the number of particles giving the EPR signal of the value obtained [10].

Fig. 1. Dependence of the concentrations of hydrogen and oxygen atoms in a rarefied hydrogen flame on the jet volumetric flow rate ($T = 580°\text{C}$, $p = 6$ mm Hg, $H_2 : O_2 = 1$)

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

From the fact that the EPR signal of O and H atoms under the chosen experimental conditions does not depend on the jet velocity, it may be concluded that the distribution of active centers along the length of the resonator is uniform, and that the dimensions of the flame zone are greater than the length of the resonator. Therefore, to determine concentrations it is necessary to introduce a factor $2/V$ [10], where V is the volume of the tube enclosed in the resonator. With an inner diameter of 0.8 cm and a resonator length of 3.2 cm, this factor is 1.25 cm^{-3}.

First, the rarefied flame of a mixture containing 5% H_2 and 95% O_2 was studied. In the flame of this mixture, large amounts of atomic oxygen were registered (up to $6 \cdot 10^{15}$ particles). The concentration of atomic hydrogen in this case lies at the sensitivity limit of the instrument ($1\text{-}2 \cdot 10^{14}$ particles). When the hydrogen concentration was increased from 5 to 10%, the concentration of H atoms rose to $3 \cdot 10^{15}$ particles; the concentration of atomic oxygen increased by more than a factor of two. The dependence of the concentrations of atomic oxygen and hydrogen on the mixture composition is presented in Fig. 2. As is seen from the graph, the number of oxygen and hydrogen atoms is the same for a mixture containing 33% H_2 and 67% O_2. The region of predominant formation of atomic oxygen lies in mixtures containing 15 percent hydrogen or less. A detailed study of flames of various composition showed that atomic oxygen is detected in appreciable quantities in a mixture containing 75% H_2 and 25% O_2. The region of predominant formation of atomic hydrogen corresponds to mixtures containing more than 70% molecular hydrogen.

Fig. 2. Dependence of the concentrations of hydrogen and oxygen atoms in a rarefied hydrogen flame on the mixture composition ($T = 580°\mathrm{C}$, $p = 6$ mm Hg)

From consideration of the temperature dependence of the ratio $k_2(O_2) : k_3(H_2)$, it follows that, with increasing temperature, the ratio $(O)/(H)$ should increase. Below we give the values of $(O)/(H)$ obtained at several temperatures in the flame of an equimolecular mixture at $p = 5.5$ mm Hg, $W = 40$ cm^3/min.

t, °C	460	530	580	680
$(O) : (H)$	0.33	0.36	0.43	0.6

From the values presented it is seen that, as the temperature increases from 460 to 680° C, the ratio $(O)/(H)$ does indeed increase. If it is assumed that the ratio $(O)/(H)$ is linearly related to the ratio of the rates of reactions (2) and (3), then in the coordinates $(\lg(O)/(H),\ 1/T)$ the data given lie well on a straight line, from which the difference in activation energies of processes (2) and (3) is found to be approximately 5 kcal/mole—a value practically coinciding with the difference of the accepted values of the activation energies of these processes (4.2 kcal/mole).

It should be noted that, in determining the absolute concentrations of hydrogen and oxygen atoms, no account was taken of the difference in the magnitudes of their magnetic moments, as a result of which the concentrations of atomic oxygen obtained are overestimated by a factor of 4.5.

Institute of Chemical Physics
Academy of Sciences of the USSR

Received
9 X 1963

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Note: Figure translations are in progress. See original paper for figures.