V. Ya. Basevich and S. M. Kogarko

1961

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

V. Ya. Basevich and S. M. Kogarko

THE EFFECT OF OXYGEN ATOMS ON COMBUSTION AT LOW PRESSURES

(Presented by Academician V. N. Kondrat’ ev, 12 V 1961)

Between the acceleration of combustion processes observed at atmospheric pressure under the action of atoms and radicals (1−5), and the long-known rarefied atomic flames (6), one can discern a commonality in the mechanism of the phenomenon. If in the first case additions of atoms and radicals accelerate the oxidation process, then in the second, under low-temperature conditions, the reactions of atoms and radicals with the fuel are the basis of the process. An analogous phenomenon also occurs in spontaneous ignition (7−9).

In work (10) it was observed that, for acetylene with oxygen, there is a region in which atomic flames, obtained at relatively high pressures of several millimeters of mercury, and ordinary flames, when combustion can already develop independently, coexist. Proceeding from the idea of the unity of the mechanism of atomic and ordinary flames and of the role in it of the initial concentrations of the active reaction centers, we set as the task of the present work the investigation of the action of atomic oxygen on the velocity of flame propagation at low pressures, and also the elucidation of the possibility of lowering the pressure limit of combustion to the region in which atomic flames exist.

Method. Oxygen atoms were obtained from a glow discharge by the generally known method; only in the present case, in order to extend the region of ignition of the discharge upward in pressure, provision was made for working with small distances between the electrodes (Fig. 1). Oxygen from a cylinder, after a measuring diaphragm and a discharge tube, passed through an expanding nozzle 4 mm in diameter into a reservoir 60×110 mm in diameter. The combustible gas (technical propane—butane), after a measuring diaphragm, passed into the reservoir through an annular opening 1 mm wide, concentric with the nozzle. In the reservoir there were central and side electrodes for igniting the mixture by a spark of constant energy, approximately 0.45 J. On the central electrode a frame with a mesh of $15\ \mu$ wire could be fastened, entering inside the nozzle and serving for the recombination of oxygen atoms formed in the discharge. Instead of the side electrode, a thermocouple 0.2 mm in diameter could be installed; it measured either the heat of recombination or—when the mesh was installed—the temperature of the gas issuing from the nozzle. The reservoir was evacuated through a receiver by a fore-vacuum pump; the pressure was measured with a

Fig. 1. Schematic of the apparatus.

Figure 1: Fig. 1. Schematic of the apparatus.

Fig. 2. Visible flame propagation velocities under spark ignition.

Figure 2: Fig. 2. Visible flame propagation velocities under spark ignition.

calibrated vacuum gauge. The visible velocity of flame propagation was recorded through a slit on a photoregister. In some control experiments, photographs of the shape of the flame front were taken. Since the degree of expansion due to outflow from the reservoir and heat removal to the walls could not be determined, the work compared the visible flame velocities. In determining the combustion pressure limit, the occurrence of a flash was recorded throughout the entire volume of the reservoir.

The experiments were carried out: 1) with the glow discharge switched off, 2) with the glow discharge switched on, but with a mesh installed in the nozzle for recombination

and 3) with the discharge switched on without a grid. In the second case either partial or complete recombination occurred, depending on the discharge current and pressure. This could be established from the presence or absence in the reservoir of the afterglow of NO_2^*, formed as a result of the presence in the oxygen of a certain amount of nitrogen, and also from the thermocouple readings: heating of the junction at maximum discharge currents in the tube ($i_2 \leqslant 900$ mA)

Fig. 1. Schematic of the apparatus. 1 –electrical circuit for the glow discharge, 2 –generator for spark ignition, 3 –discharge tube, 4 –reservoir, 5 –vacuum gauge, 6 –slit, 7 –photographic recorder, 8 –fore-vacuum pump

was $\leqslant 60^\circ$ C. In the absence of the grid in the latter case, the junction temperature rose to 420°, which makes it possible to estimate the maximum oxygen concentration at the nozzle section as being of the order of 10%.

Fig. 2. Visible flame propagation velocities under spark ignition: 1 –discharge, 2 –discharge with a grid in the nozzle, 3 –without discharge: a –as a function of composition, $P = 43$ mm Hg; b –as a function of pressure, $\alpha = 3$; c –as a function of current, $P = 43$ mm Hg, $\alpha = 3$.

Apparently, the temperature of the gas entering from the glow discharge was close to room temperature (see also (6)) and in any case was not lower in the case of the discharge with a grid than without a grid, since fractions of a second are required to heat a grid made of 15-μ fibers.

Results and discussion. In the first series of experiments the distance between the electrodes of the glow discharge was 170 mm. Comparison-

visible flame-propagation velocities from the spark. In this series of experiments

Fig. 3. Limits of combustion with respect to pressure. Spark ignition: 1 —discharge, 2 —discharge with a grid in the nozzle, 3 —without discharge, 4 —self-ignition

Figure 3: Fig. 3. Limits of combustion with respect to pressure. Spark ignition: 1 —discharge, 2 —discharge with a grid in the nozzle, 3 —without discharge, 4 —self-ignition

the mean flow velocity from the nozzle did not exceed 1 m/sec. Figure 2a presents the values of the flame velocity U_{v} at pressures $P = 43$ mm Hg for different coefficients of oxygen excess α. It is seen that in the presence of oxygen atoms the flame velocity in the region of lean mixtures increases very substantially. The strength of the discharge current in the tube was chosen so that, when switched on, it would not cause self-ignition of the mixture in the reservoir. Therefore it varied depending on the composition of the mixture: it was greater for lean mixtures and smaller when the mixture was enriched up to $\alpha = 0.75$. The apparently small effect of oxygen atoms on U_{v} in the region of rich mixtures is explained by the small permissible discharge-current strength. Figure 2b gives velocity values at different pressures, at an oxygen-excess coefficient $\alpha = 3$, with analogous selection of the discharge current. Increasing the discharge current, which leads to an increase in the concentration of oxygen atoms, increases the visible flame velocity (Fig. 2b). Measurements showed that increasing the rate of gas admission from the discharge tube into the reservoir very noticeably increases the flame velocity above the values indicated above. With a discharge with a grid and without a discharge, an analogous change in the flow velocity does not cause changes in the flame velocity. In the experiments, a strong increase in flame luminosity was observed in the presence of atomic oxygen.

Fig. 3. Limits of combustion with respect to pressure. Spark ignition: **1** —discharge, **2** —discharge with a grid in the nozzle, **3** —without discharge, **4** —self-ignition.

In the second series of experiments, the possibility was investigated of lowering the combustion limit with respect to pressure that is obtained under the conditions of the apparatus described (Fig. 3). In this series of experiments the flow rates of oxygen and combustible gas were increased almost twofold, and the distance between the electrodes was increased to 1000 mm. As can be seen, the limit with spark ignition is about 10 mm Hg; with preliminary switching on of a glow discharge ($i_2 \leq 400$ mA), but in the presence of a grid, it is about 9 mm Hg; and in the absence of the grid it decreases to 4.5 mm Hg. By increasing the strength of the discharge current in the tube to 900 mA it is possible to cause self-ignition in the reservoir at a pressure of 2 mm Hg, which already corresponds to the region of existence of atomic flames. Apparently, by increasing the pumping speed and the distance between the electrodes, this limit can be lowered to the pressures at which work with atomic flames is ordinarily carried out, 0.1-4 mm Hg. (6,10).

Institute of Chemical Physics
Academy of Sciences of the USSR

Received
12 V 1961

CITED LITERATURE

1. S. W. Churchill, A. Weir, K. L. Gealer, K. I. Kelley, *Ind. and Eng. Chem.*, **49**, 1419 (1957).
2. S. M. Kogarko, M. I. Devishev, V. Ya. Basevich, *ZhFKh*, **33**, 2345 (1959).
3. S. M. Kogarko, M. I. Devishev, V. Ya. Basevich, *DAN*, **127**, 137 (1959).
4. V. Ya. Basevich, M. I. Devishev, S. M. Kogarko, *Izv. AN SSSR, OTN, Energetika i Avtomatika*, No. 3, 138 (1960).
5. S. M. Kogarko, V. V. Mikheev, V. Ya. Basevich, *ZhFKh*, **35**, No. 10 (1961).
6. P. Harteck, U. Kopsch, *Zs. phys. Chem.*, **B12**, 327 (1931).
7. H. H. Semenov, F. I. Dubovitskii, A. B. Nalbandyan, *Trans. Farad. Soc.*, **29**, 606 (1933).
8. A. Nalbandjan, *Acta Physicochem. USSR*, **1**, 305 (1934).
9. A. B. Nalbandyan, *Phys. Zs. Sowjetunion*, **4**, 747 (1933).
10. A. G. Gaydon, H. G. Wolfhard, *Proc. Roy. Soc.*, **A213**, 366 (1952).

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