PHYSICAL CHEMISTRY

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Abstract

Full Text

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DETECTION OF ATOMIC OXYGEN IN THE COLD-FLAME OXIDATION OF CARBON DISULFIDE BY MOLECULAR OXYGEN

The cold flame of low-temperature combustion of carbon disulfide is a classical example of "cold flames," the mechanism of which has not yet been sufficiently studied.

Earlier investigations aimed at detecting intermediate products in this reaction were based chiefly on optical spectroscopy, and their result was the detection and study of certain properties of such intermediate substances as CS ([1–8]), SO ([2,8,9]), and S_2O ([8]). However, these studies did not lead to the detection of atomic active chain centers, whereas these same spectroscopic investigations gave grounds for assuming the presence and significant role of atoms, above all oxygen atoms. Indeed, it was found ([3,10]) that at ratios $\alpha = [O_2]/[CS_2] > 2.5$, when the flame has a violet coloration, an intense continuum is detected in the ultraviolet absorption spectrum; moreover, its intensity increases as α increases from 3 to 6 ([10]). Analysis of the properties of this continuum shows ([10]) that neither SO_2, nor SO_3, nor O_3 can be responsible for its appearance.

As noted in Kondrat' ev' s work ([3]), this continuous spectrum should be attributed to recombination processes of intermediate active centers. On the basis of energetic considerations, it may be assumed that these recombining particles must be very active, i.e., they are most likely atoms. It is known from the literature ([3]) that the formation of S_2 in this reaction occurs only at $\alpha < 2.5$, with its maximum at $\alpha \simeq 1.5$. At values $\alpha > 2.5$, S_2 is not formed. If one proceeds from the fact that S_2 is formed with the participation of S atoms, then at $\alpha > 2.5$ the concentration of S atoms must be insignificant, and consequently the continuum in the ultraviolet spectrum is not associated with reactions of sulfur atoms. Atomic oxygen, with whose participation rapid oxidative processes with molecular oxygen usually occur, could be responsible for the continuous spectrum, as is the case in the oxidation of carbon monoxide ([11–14])*.

For the purpose of detecting atomic oxygen and studying the dependence of its concentration on the experimental conditions, the method of electron paramagnetic resonance was used in the present work. An EPR radiospectrometer IKF-2 with a cylindrical resonator and wave type H_{011} was used. The experiments were

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

carried out in a jet vacuum apparatus. The experimental procedure is described essentially in ([14]). As the reaction vessel in different experiments, two different quartz tubes passing through the spectrometer resonator were used.

To obtain a flame in the resonator zone, one of these tubes was wound with platinum wire fed by direct current, as described in ([15,16]). Carbon disulfide and oxygen were fed separately into the gas jet. The O_2 feed rate was determined by means of a rheometer, and the carbon disulfide feed rate by the change in pressure in the flask from which it was supplied. The temperature in the reactor was measured with a chromel-copel thermocouple. Experiments in this tube were carried out at a temperature of 269-271°

* The conclusion that atomic oxygen is present in the reacting system with S_2-O_2 is also drawn in ([11]), where the continuum in the ultraviolet spectrum is associated with reactions of O atoms.

and pressure of 5-6 mm Hg. The volumetric flow rate of the mixture was 14-16 cm^3/min. In different experiments the value of α was varied from 0.8 to 14. With increasing α, a sharp change in the color of the flame was observed, from greenish-gray to violet, when α reached values lying between 2.2 and 2.5. At $\alpha \geq 2.5$, under flame conditions, we recorded the EPR signal of atomic oxygen (Fig. 1). Identification of the spectrum was carried out from the value of the g-factor, which proved to be 1.50, and from the fine structure of the spectrum, which we were able to obtain by lowering the pressure of the gas mixture in the flame to 2 mm (the minimum pressure in our experiments at which the flame had not yet gone out). As is known ([14,17,18]), the EPR spectral lines of O atoms due to transitions in the $^3P_2$ state merge into one at pressures above 1-1.5 mm Hg. The distance between the two components of the $^3P_1$ state, however, is sufficiently large (10.88 oersted) ([18–20]) that they do not merge as a result of broadening. These components are also split in the spectrum shown. Thus, both the form of the spectrum and its numerical characteristics are in good agreement with the available literature data on the spectrum of atomic oxygen ([17–20]).

Fig. 1. EPR spectrum of atomic oxygen, recorded at $\alpha = 5$, $P = 2$ mm, $T = 270°$

Fig. 2. Lines of the EPR spectrum of the hydroxyl radical, due to electric-dipole transitions $(m_j)^+ \leftrightarrow (m_j - 1)^-$ in the ground state $^2\Pi_{3/2}$. The spectrum was recorded in a flame of CS_2 and O_2 containing 10% H_2, $P = 2$ mm, $T = 420°$

The assignment of this spectrum to atomic oxygen is also confirmed when molecular hydrogen is added to the CS_2+O_2 mixture and, in the presence of a flame, signals of atomic hydrogen and of the OH radical are recorded along with the

Fig. 3

Figure 2: Fig. 3

EPR signal of O atoms; these appear in the combustion zone owing to the reaction:

$$O + H_2 = H + OH.$$

For detection of hydroxyl radicals, another reaction vessel was used, expanding in the resonator and encompassing both the magnetic and the electric components of the microwave field in the resonator ([21,22]). In this case the flame was produced in the upper part of the tube, above the resonator, and propagated into the wide part located in the resonator. The initial content of molecular hydrogen reached 10% of the O_2 content; the mixture pressure was 2 mm Hg, and the flame temperature was 420°.

Figure 2 shows the EPR spectrum of the hydroxyl radical obtained by us, recorded in fields of 5850-5880 oersted (ν_{mw} = 9375 MHz). This doublet is due to electric-dipole transitions $(m_j)^+ \leftrightarrow (m_j - 1)^-$ in the ground state ($^2\Pi_{3/2}$, $J = 3/2$) ([21]). Each component of the doublet consists of three lines, which could not be resolved under the conditions of our experiments because of broadening due to the relatively high pressure. The characteristics of this spectrum are also in good agreement with literature data ([21,22]). As specially designed experiments showed, under the above conditions the mixture $0.1H_2 + O_2$ does not ignite. This indicates that, in these experiments, O atoms are supplied by the CS_2–O_2 system, and not by the H_2–O_2 system.

It was also noted that, upon addition of molecular hydrogen to the system under study, the concentration of O atoms decreases markedly. Thus, do

the addition of H_2 in an amount of 5% of the initial molecular oxygen content leads to a decrease in atomic oxygen by a factor of 3.

We also studied the dependence of the concentration of O atoms on α in mixtures of CS_2 and O_2. As is seen from Fig. 3, which presents the results of one series of experiments, at $\alpha < 2.2$, i.e., in the region where the flame has a greenish-gray coloration, O atoms are not detected. Atomic oxygen begins to be registered at $\alpha = 2.2 \div 2.5$, and with a further increase in α its concentration rises sharply; moreover, an increase in the O_2 content by only 3% leads to an increase in the concentration of O atoms by a factor of 2.5. In this region the color of the flame also changes sharply, becoming violet. The further decrease in the concentration of O atoms is connected with a decrease in the burning intensity due to the low content of fuel, which is also observed visually from the decrease in the intensity of the glow.

Fig. 3. Dependence of the concentration of atomic oxygen on

$\alpha = [O_2]/[CS_2]$.
$T = 369 \div 371^\circ$, $P = 5$—6 mm

It is interesting to note that, according to Kondrat'ev's data ([3]), obtained under conditions identical with ours, at $\alpha < 2.5$ the CS radical is not detected in this system. It begins to be registered starting from $\alpha \simeq 2.5$, and with a further decrease in α its concentration rises sharply, passing through a maximum. Thus, the dependences of the concentrations of O atoms and CS radicals on α are of opposite character, and when α is changed the disappearance of one of them (upon reaching $\alpha \simeq 2.5$) leads to the appearance of the other.

In the course of the work it was found that, with the same adjustment of the instrument, the introduction of quartz tubes into the resonator strongly decreases the sensitivity of the instrument. In the case of cylindrical tubes of constant diameter (10–12 mm) the sensitivity of the instrument decreases by a factor of 2-3; in the case of tubes having an expansion in the resonator, this decrease is still more considerable. Since the sensitivity changes strongly even in different tubes of the same shape and with the same diameter, when determining the concentration of paramagnetic particles in the gas phase it is necessary to place the standard sample precisely in the tube in which the measurements are carried out. In this connection, the results of ([23]) should be attributed only to the ideal case.

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