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Abstract

Full Text

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DETECTION OF FREE HYDROXYL IN A RAREFIED HYDROGEN FLAME BY THE E.P.R. METHOD

The principal elementary acts of branching and chain propagation in a rarefied hydrogen flame are:

$$\mathrm{OH} + \mathrm{H_2} \to \mathrm{H_2O} + \mathrm{H}, \tag{1}$$

$$\mathrm{H} + \mathrm{O_2} \to \mathrm{OH} + \mathrm{O}, \tag{2}$$

$$\mathrm{O} + \mathrm{H_2} \to \mathrm{OH} + \mathrm{H}. \tag{3}$$

Recently (^{1}), the concentrations of O and H were determined by the e.p.r. method; they considerably exceed the equilibrium values and reach 25% of the initial molecular O_2 and H_2.

Fig. 1. E.p.r. spectrum of free hydroxyl: *a* –spectrum $^2\Pi_{3/2}$, $J = 3/2$, $(m_j)^+ \to (m_j - 1)^-$; *b* –spectrum $^2\Pi_{3/2}$, $J = 5/2$, $(m_j)^+ \to (m_j - 1)^-$.
5933 gauss; 4864 gauss.

The measured dependence of the concentrations of O and H on the composition of the mixture shows that, over a rather wide range of composition variation, the concentrations of O and H are comparable, and only for mixtures poor in H_2 or O_2 do the concentrations of O or H, respectively, prevail. If it is assumed that the ratio of the concentrations of OH and O can be estimated from the ratio of quantities close to their lifetimes (^{2}),

$$\frac{1}{K_1(\mathrm{H_2})} : \frac{1}{K_3(\mathrm{H_2})},$$

then for $T = 900°\mathrm{K}$,

$$K_1 = 2 \cdot 10^{-10} e^{-10000/RT},$$

$$K_3 = 0.9 \cdot 10^{-10} e^{-11700/RT},$$

we obtain

$$\frac{\mathrm{OH}}{\mathrm{O}} \simeq \frac{1}{5}.$$

The microwave absorption spectrum of OH was first studied by Dousmanis, Sanders, and Townes (^{3}) in an electric discharge in H_2O vapor, and the Zeeman absorption e.p.r. spectrum of free hydroxyl was studied by Radford (^{4,5}). The authors of these investigations showed that the microwave absorption spectrum of OH is due to electric dipole transitions, whose intensity considerably exceeds the intensities of the lines of ordinary e.p.r. caused by magnetic dipole transitions. The authors pointed out the considerable broadening of the lines by pressure.

It follows from the foregoing that, at low pressures in a flame of H_2 with O_2, signals of paramagnetic absorption of free hydroxyl can be detected; moreover, detection of OH is possible only when the particles are placed in the antinode of the microwave electric field (^{6}). For this purpose the reactor was manu-

made of quartz in such a way that the absorption cell completely filled the resonator. This design made it possible to observe a spectrum due to electric and magnetic dipole transitions. The reaction furnace was located above the resonator, and the active centers were drawn into the absorption cell. Figure 1 shows the EPR spectrum of free hydroxyl obtained at p = 2 mm Hg and T = 640°C. The linear velocity of the jet was 2.5 m/sec. Spectrum (a) is a doublet in fields = 5933 Oe (ν_{svch} = 9475 MHz), the distance between the centers of whose components is 30.4 Oe, and the line width of an individual component is 0.7 of the distance between the centers of the doublet (7). As Redford showed, it is due to electric dipole transitions

$$(m_j)^+ \to (m_j - 1)^-$$

in the ground state $^2\Pi_{3/2},\ J = 3/2$ (the signs + and − refer to different levels of the λ-doubling). Each component of the doublet consists of three lines, which could not be resolved under the conditions of our experiment.

Figure 2 graph

Figure 2: Figure 2 graph

Fig. 2. Dependence of the H and OH signals on the composition of a hydrogen-oxygen flame mixture. $\mathrm{OH_I}$—spectrum with center in the field $H = 4864$ Oe, $\mathrm{OH_{II}}$—spectrum with center in the field $H = 5933$ Oe ($\nu_{\mathrm{svch}} = 9475$ MHz).

Spectrum (b) is a single line about 90 Oe wide, with its center in the field $H = 4864$ Oe. This spectrum is due to electric dipole transitions

$$(m_j)^+ \to (m_j - 1)^-$$

in the first rotationally excited level ${}^2\Pi_{3/2},\ J = 5/2$, and consists of 10 lines. When the pressure is lowered to 0.8 mm Hg, only partial resolution of spectrum (b) can be achieved. Raising the furnace 4 cm above the resonator in order to reduce the temperature in the absorption cell does not lead to any noticeable improvement in the resolution of spectra (a) and (b).

The remaining spectra of free hydroxyl due to electric dipole transitions (${}^2\Pi_{3/2},\ J = 3/2,\ (m_j)^- \to (m_j - 1)^+$ and ${}^2\Pi_{3/2},\ J = 5/2,\ (m_j)^- \to (m_j - 1)^+$), as well as the spectra corresponding to more highly excited levels ${}^2\Pi_{3/2},\ J = 7/2,\ 9/2$, lie in fields above 6000 Oe, and their observation is impossible on the EPR-2M instrument.

Redford was able (4) to observe the following three OH spectra:

1) ${}^2\Pi_{3/2},\ J = 3/2,\ (m_j)^+ \to (m_j - 1)^-$ (spectrum 1a)
2) ${}^2\Pi_{3/2},\ J = 3/2,\ (m_j)^- \to (m_j - 1)^+$
3) ${}^2\Pi_{3/2},\ J = 7/2,\ (m_j)^- \to (m_j - 1)^+$

Their relative intensities are $15 : 5 : 1$, respectively. As for spectrum 1b, Redford was unable to study it and estimate its intensity because of electron cyclotron resonance under discharge conditions.

An absolute determination of the hydroxyl concentrations was not carried out. However, a qualitative consideration of the dependence of the amplitude of the derivative of the OH absorption signal on the mixture composition, and comparison of it with the analogous dependence of the H signal, is of interest. The latter, with the reactor of the type used in the present work, could also be observed; moreover, under these conditions the hydrogen doublet is considerably less intense than the OH spectrum. In mixtures poor in hydrogen (starting from 5% and above), only the hydroxyl signal is observed; the atomic-hydrogen signal appears only in mixtures containing not less than 20% H_2.

The dependence of the intensity of the H and OH signals (in arbitrary units) is given in Fig. 2.

As the H_2 content is increased, the OH signal slowly increases, reaching a maximum value at an H_2 content of 60%, whereas the H signal

increases more sharply, reaching a maximum value at 70% H_2. The subsequent decrease in the OH signals follows the decrease in the H signals.

Under the conditions of our experiment, the signal of atomic oxygen was not observed, since it was completely suppressed by the signal from molecular oxygen, whose amplitude at the low temperature of the absorption cell considerably exceeds the O signal. However, the concentrations of O that we observed earlier ([1]) in mixtures poor in H_2 considerably exceed the concentrations of atomic hydrogen (by 60–80 times).

The data of Fig. 2, as well as earlier ([1]) measurements of the concentrations of O and H, show that in rarefied oxygen flames of hydrogen one cannot use the approximation of a single active center for all compositions.

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