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Abstract

Full Text

PHYSICAL CHEMISTRY

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DETECTION OF HO_2 RADICALS BY THE E.P.R. METHOD

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For a comparatively long time the existence of the HO_2 radical was postulated in many oxidation reactions. With the development of new experimental techniques it was shown that the HO_2 radical does indeed exist. Thus, in the work of Foner and Hudson ([1]), the formation of HO_2 upon interaction of H atoms with molecular oxygen was demonstrated by means of a mass spectrometer. The H atoms were obtained in a discharge in H_2.

Fig. 1. E.p.r. spectrum of the HO_2 radical, frozen at 77° K

The study of elementary reactions of the HO_2 radical raises the problem of finding methods simpler than the mass-spectrometric one for the analysis of this radical. Such a simpler method proved to be the method of electron paramagnetic resonance (e.p.r.). In the literature there are no data in which an e.p.r. signal would unquestionably have been ascribed to the HO_2 radical. In our experiments the HO_2 radical was obtained by the interaction of H atoms with an O_2 molecule at room temperature under jet conditions at a total pressure of 60 mm Hg. The linear velocity of the jet was 90 cm/sec. The H atoms were obtained in a silent discharge in H_2 in an ozonizer-type tube. This tube was connected with the reaction vessel through a nozzle. Molecular oxygen was fed into the reaction vessel behind the nozzle. The dependence of the rate of formation of HO_2 on pressure indicates that the reaction is termolecular, i.e., proceeds in the volume. A detailed description of the apparatus and the results of kinetic studies of the reaction

$$H + O_2 + M$$

will be published later. The HO_2 radicals were frozen out in a thin tube cooled with liquid nitrogen. Cooling with liquid nitrogen was carried out at a distance of 4 cm from the place where H was mixed with O_2. After the reaction had been carried out, the tube together with the cooling vessel was sealed off and

transferred to the instrument for recording the e.p.r. spectrum.* The e.p.r. spectrum was recorded on a 3-centimeter radiospectrometer with double modulation of the magnetic field, type -2 ([2]). Figure 1 shows the appearance of the e.p.r. spectrum of the HO_2 radical obtained in the gas phase and frozen at 77° K. As is seen from Fig. 1, the signal has an asymmetric shape. The total width of the signal between points A and B is 23–26 oersted. The g-factor of the HO_2 radical practically coincides with the g-factor of diphenylpicrylhydrazyl.

* The e.p.r. spectra were recorded by G. A. Kapralova, to whom the authors express their gratitude.

Heating the vessel followed by cooling again to 77°K leads to the disappearance of the signal. In experiments without the addition of oxygen (blank experiments), no signal is observed. In parallel with recording the EPR spectrum, a chemical analysis of the reaction products was carried out. In experiments in which the EPR signal of the HO_2 radical was detected, after the tube was opened H_2O_2 was found. In blank experiments, in which no signal was observed, H_2O_2 was absent.

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