



Paramagnetic Resonance in Semiquinone lons of Substituted oBenzoquinones

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FIG. 1. Experimental arrangement.

periments the inner surface of the reactor was coated with phosphoric acid. A Teflon liner could be inserted in the cylindrical reaction region to check the effect of surface condition on the room temperature reaction, low temperature experiments being prevented by the poor thermal contact between the Teflon liner and the liquid nitrogen bath.

In the room temperature, low-pressure (~ 1 mm) reaction between hydrogen atoms and oxygen molecules, independent of surface conditions, water was observed as the principal product with no measurable amount of H2O2, in agreement with the results of Boehm and Bonhoeffer,1 Geib and Harteck,2 Frost and Oldenberg,⁴ and Badin,⁵ although in disagreement with the recent mass spectrometric experiments of Robertson.⁶ While no HO₂ radicals were found under these conditions (i.e., HO_2 less than 0.01% of O₂), substantial quantities of OH radicals, approximately 1% of the O2 concentration, were observed. Since OH radicals are observed even at very low pressures and cannot be formed in bimolecular reactions for energetic reasons, they must be produced in a surface reaction, quite possibly by the mechanism proposed by Badin⁵: $H+O_2+W\rightarrow HO_2+W$ on the wall, followed by $H+HO_2+W\rightarrow [HO-OH]^*+W$, the excited peroxide complex dissociating into OH radicals when the wall temperature is above 200°K.

In our original experiments on HO2 production7 at much higher pressures (\sim 30 mm) the occurrence of OH radicals was puzzling because OH formation in the gas phase apparently required the presence of unstabilized HO2* complexes which reacted with hydrogen molecules according to: $H_2+HO_2^*\rightarrow OH+H_2O$, the excitation energy of the HO2* being used to overcome the activation barrier for the reaction. Since much more OH was produced than HO2, this required in addition that collisional deactivation of HO₂* was a slo process. The most plausible explanation for the OH radicals measured at high pressures, in light of the experiments reported here, is that they were likewise formed on the surface of the reactor and diffused back into the gas stream. Since HO₂ was present in the gas phase, it is, of course, possible that some OH was also produced in the homogeneous reaction:

$H+HO_2\rightarrow [H_2O_2]^*\rightarrow 2OH.$

At low pressures, cooling the reactor to liquid nitrogen tempera ture causes the OH intensity to drop to zero and only the consumption of hydrogen and oxygen is measured by the mass spectrometer. The integrated production of H₂O₂ at liquid nitrogen temperature was obtained by warming up the reactor and recording the evolution of H₂O₂. A plot of H₂O₂ intensity after running the discharge tube about 20 minutes is shown in Fig. 2. The pressure in the reactor was 1.7 mm consisting of O2=0.15 mm, H2=0.70 mm. about 10% of the hydrogen being dissociated, and He = 0.85 mm.



FIG. 2. Hydrogen peroxide production at liquid nitrogen temperature measured by warming up reactor to room temperature.

Helium was added to the hydrogen stream to prevent back diffusion of reactants into the discharge tube. The gas velocity in the reactor was about 500 cm/sec. The average production rate of $\mathrm{H_2O_2}$ at liquid nitrogen temperature is at least 150 times the room temperature rate. The high yield of H2O2 at liquid nitrogen temperature is in accord with independent chemical observations.^{1,2,5} The observed H_2O_2 production can be accounted for by assuming that most of the hydrogen atoms react at low temperature to form peroxide.

The color and phase change of the glassy deposits trapped at liquid nitrogen temperature have been ascribed⁸ to HO₂ radicals condensed from the vapor phase and stabilized on the cold surface. Our experiments indicate that if HO₂ is present in the glassy deposit, it is formed on the surface.

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Paramagnetic Resonance in Semiquinone Ions of Substituted o-Benzoguinones

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HE detection of the semiquinone ions of o- and p-benzoquinone by the technique of paramagnetic resonance has recently been reported by Blois.1 The hyperfine structure reported by Venkataraman and Fraenkel² for the p-benzosemiquinone ion in alkaline alcoholic solution was not observed by Blois¹ for either the o- or the p-benzosemiquinone ion in aqueous solution. We wish to report observations made on o-benzosemiquinone ions derived from the air oxidation of some substituted 1,2-benzenediols in alkaline alcoholic solution. The paramagnetic resonance experiments were carried out at a frequency of about 9000 mc/sec using a magic-T bridge. The absorptions were detected by the method of magnetic field modulation. The magnetic field is believed to have



FIG. 1. Derivative of the absorption spectrum of the o-benzosemiquinone ion

been homogeneous to better than 0.1 oersted over the area of the sample.

The derivative of the absorption spectrum of o-benzosemiquinone, the semiguinone ion derived from 1,2-benzenediol, is shown in Fig. 1. It is seen to consist of three sets of three lines each. The splitting is attributed to hyperfine interaction of the unpaired electron spin with the protons on the ring. The two equivalent protons para to the oxygens split the line into three parts with relative intensities (1,2,1). These three lines are further split into three lines each by the two equivalent protons ortho to the oxygens again with relative intensity ratios (1,2,1). The interval for the para-proton splitting is 4.0 oersteds and for the ortho-proton splitting is 1.0 oersted. The assignment of the larger splitting to the para-protons is made on the basis of the observations made on the substituted compounds below.

The spectrum of the semiquinone ion of 4-tert. butyl-1,2benzenediol is shown in Fig. 2. The spectrum is seen to consist of a broad doublet envelope of incompletely resolved smaller splittings. The doublet splitting is about 4.1 oersteds and is attributed to the proton on position 5. The further splitting is due to the remaining two ring protons and the protons on the substituted group. Incomplete resolution prevents an exact assignment of the individual peaks. We have also examined the spectra of the semiquinone ions of 4-phenyl-1,2-benzenediol and 3,6dially-4-tert. butyl-1,2-benzenediol. These spectra (not shown) also show a doublet envelope of incompletely resolved smaller splittings. The doublet splitting amounts to 3.4 oersteds in the former and 3.6 oersteds in the latter.

The semiquinone ion of 3-phenyl-1,2-benzenediol exhibits three groups of lines as shown in Fig. 3. The central group is a triplet and the outer groups are doublets. This pattern can be explained if the splitting by the three ring protons is in the ratio of (1,4,5); the smallest splitting being 0.7 oersted. This model predicts seven



FIG. 2. Derivative of the absorption spectrum of the semiquinone ion derived from 4-tert. butyl-1,2-benzenediol.



FIG 3. Derivative of the absorption spectrum of the semiquinone ion derived from 3-phenyl-1,2-benzenediol.

lines in three groups with relative intensities (1,1) (1,2,1) (1,1). It seems reasonable, on the basis of the above spectra, to attribute the smallest splitting to the proton para to the phenyl group, but no conclusion can be drawn from the spectrum alone as to which of the remaining two protons contributes the larger splitting.

In Figs. 1 and 2 it will be noted that the intensity of the spectrum is not symmetrical about the center of gravity of the spectrum. This is due to a decrease in the concentration of free radicals in the sample during the time taken to sweep the magnetic field through the resonance. This time is of the order of three minutes.

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Thermoluminescence of Zinc Sulfide Phosphors **Doubly Activated with Copper and Manganese** Shigeo Shionoya

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HE emission of manganese incorporated in zinc sulfide is sensitized by copper incorporated as a sensitizer, as has been mentioned in the previous letter.¹ZnS: (Cu+Mn) phosphors have two kinds of the excitation band, similar to ZnS: Cu phosphors, the one due to the absorption of host crystal (located near 3400 A) and the other due to the absorption of Cu impurity (located about 3800 A); and Mn emission is caused by the absorption of Cu as well as that of the host crystal. In this letter, the thermoluminescences were studied for both the Cu and Mn emissions after the excitation by both the host and Cu absorption.

The samples used were the same as used in the previous letter. An ordinary 100 w tungsten incandescent lamp was used as the excitation source, selecting only the necessary wavelength region for the host or Cu excitation with filters; namely, Matsuda UV-D1 plus nickel sulfate solution filter, which transmits 3000-3750 A, for the host excitation, and Matsuda UV-D1 plus V-B2, which transmits 3700-4000 A, for the Cu excitation. The thermoluminescences were measured with a specially designed Dewar vessel, using liquid air as a coolant. The phosphors were excited up to the saturated emission intensities at a liquid air temperature, and then heated with a constant rate 0.22°K/sec after allowing the emission to decay for 6 min, detecting glow intensities with a photomultiplier attached to a sensitive amplifier. The Cu and Mn emissions were isolated from each other with filters; namely, Matsuda V–Y1 plus V–B2 for Cu and V–O2 or V–R3 for Mn.