EPR spectra of hydroquinone derivatives

dr Krzysztof Kazimierczuk, mgr Mateusz Urbańczyk, mgr Saurabh Kumar Saxena

Faculty of Chemistry UW

Introduction/Goal

The goal of the experiment is to investigate the reaction of hydroquinone derivatives by observing the signal form their intermediate, which is the free radical. The measurement is performed using the miniaturized spetrometer EPR Benchtop Micro-ESR with the sweep range of magnetic field 1180-1262G and frequency 3.5GHz.

System quinone/hydroquinone

Hydroquinone (benzo-1,4-diol) subjected to the oxidants can be oxidated in two stages to quinone (Figure 1) This reaction is important element of various biological mechanisms, and is also used as the part of film developer in classic photography.

The intermediate of the reaction is the semiquinone readical, which is characterized by the yellowish color. In the alkaline enviroment is created the more stable radical ion (Figure 2), which is characterized by the red color. The hydroquinone derivatives differs by stability and color of intermediate radicals.

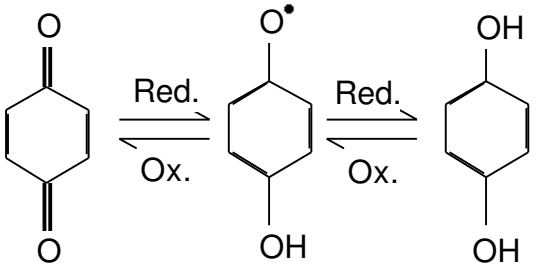

Figure 1: Two-stage reaction of oxidation of hydroquinone

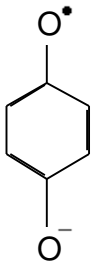

Figure 2: Radical ion created from semiquinone radical in alkaline enviroment

Procedure

1. Turn on the spectrometer by clicking the button on the back side of the machine
2. After loading the OS start the program μESR Control Software
3. Prepare 5ml 1M solution of hydroquinone in isopropanol. Measure off 1ml in to separate vial.
4. Prepare 1ml of isopropanol in the second vial.
5. In the program menu type down the sample name and comment
6. Change the Run Type in to Baseline and the Number of Scans in to 1.
7. Change the sweep range in to 1180-1220 G.
8. Click "Start Sweep". Ensure that the resonance chamber is empty and click OK.
9. Spectrometer will autocalibrate. After that insert the sample and press OK.

10. The measured spectrum will be saved as the baseline file .BAS
11. Change the run type in to "N Sweeps"
12. Start the oxidation reaction by adding 20 μl concentrated (10M) solution of KOH in to prepared before solution of hydroquinone. Mix it up. The solution should be yellowish.
13. Quickly transfer 150 μl of the mixture in to EPR-tube. Do not put it to the spectrometer!
14. Click "Start sweep". Wait until the autocalibration is over. After that insert the tube and press "OK"
15. After measuring the spectrum go to tab "Baseline Subtraction". Calibrate the baseline parameters. Click Save.
16. Turn off the autocalibration mode and register the spectra in 90 seconds intervals. Perform 20 measurements. Be aware of the changes in the multiplet intensity.
17. In the same time observe the change of the color in the reaction mixture.

If time allows repeat the experiment with different derivatives of hydroquinone, or with different solvent (methanol)

Report

For every compund:

1. Write down the spectrometer setup and interpret the spectra.
2. What splitting pattern would we predict for each radical? Which of them are observable on the spectra? What can we say about the electronic structure?
3. Determine the hyperfine coupling constant and Lande g-factor. Using the McConnel relation determine the spin density of the electron on the carbon atom in benzene ring.
4. Prepare the plot of radical concentration in the function of time. Comment the results using possible mechanisms of the radical decay

Required knowledge

- Electronic Magnetic Dipole Moment (spin and orbital), g-factor, Lande equation
- Selection rule for EPR, resonance condition.
- Electron spin-nuclear spin coupling, Fermi mechanism, and dipole-dipole mechanism.
- Hyperfine structure of EPR signal. McConnel relation.
- Construction and work of EPR spectrometer
- Types of paramagnetic centres
- Selectivity and sensitivity of EPR spectroscopy. Boltzmann distribution
- Oxidadtion of hydroquinone. Effect of pH.

Literature

- P.W. Atkins,Physical Chemistry, Oxford Higher Education; 7th edition (December 13, 2001), sections 14.1-14.3, 14.14-14.16