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COMMENTS

Comments on “Redox and Acidity Properties of 2,2′- and 4,4′-Biphenols and Corresponding Phenoxyl Radicals”

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In a recent paper,[1] Jonsson et al. reported the redox and acid−base properties of 2,2′- and 4,4′-biphenols in aqueous solutions. We disagree with the reported first and second acidity constants (pK_{a1} and pK_{a2}, respectively) of 4,4′-biphenol.[1] It may be noted that we have recently published a paper[2] on the photophysical properties of 2,2′- and 4,4′-biphenols, where we have discussed in detail the pK_{a1} and pK_{a2} values of the two biphenols. The pK_{a1} and pK_{a2} values were determined following the changes in the absorption spectra of these molecules with the pH/H_- (basicity function)[3] of the solutions. The detailed spectral changes with pH/H_- of the solutions are also discussed in Figures 1A,B in the paper.[2] In our work, pK_{a1} and pK_{a2} values for 2,2′-biphenol have been estimated to be 7.5 and 14.7 and those for 4,4′-biphenol have been estimated to be 9.4 and 14.1, respectively.[2] The differences in the pK_{a1} and pK_{a2} values of 2,2′- and 4,4′-biphenols have been rationalized on the basis of the presence and absence of intramolecular hydrogen bonding in the two respective biphenols.[2] The fluorescence characteristics of the two biphenols at different pH conditions also correspond nicely with the measured pK_{a1} and pK_{a2} values of these molecules.[2] For 4,4′-biphenol, pK_{a1} and pK_{a2} values have also been measured independently to be 9.4 and 14.1, respectively, in the paper published on the pulse radiolytic oxidation of the biphenol,[4] which also matches results reported in our earlier paper.[2] In the paper of Jonsson et al.[1] both the pK_{a1} and pK_{a2} values for 4,4′-biphenol have been argued to be the same, i.e., 9.7. This seems to be quite unusual, as normally the different acidic groups of a polybasic acid dissociate in stages with increasing pH. Jonsson et al.[1] gave a support for the same pK_{a1} and pK_{a2} values for 4,4′-biphenol from the final solution pH value of 11.2 obtained by dissolving 10^{-2} M 4,4′-biphenol in 2×10^{-2} M NaOH. It was argued that if the pK_{a2} value of 4,4′-biphenol was 14.1, the solution pH would have been close to ∼12. We have repeated the same experiment more carefully making a stock solution of NaOH (after washing the NaOH pallets several times by distilled water to remove the carbonate layer)[5] and adjusting its pH to 12.3, the expected pH for 2×10^{-2} M NaOH. The adjustment of the solution pH to 12.3 was necessary as NaOH is not a primary standard, and thus it was not possible to make an exact 2×10^{-2} M NaOH solution just by weighing. Though the pH meter (Orion Ionalyser, model 901, fitted with a combination electrode, cat. no. 91-2) was calibrated with standard buffer solutions (pH = 7.0 from Beckman Instruments Inc. USA and pH = 10.01, from Radiometer, Copenhagen NV, Denmark), we have yet to check the performance of the pH meter near pH ∼12. The OH^- concentration in the above NaOH solution (pH = 12.3) was estimated by volumetric titration using two standard acid solutions, namely, oxalic acid (0.01 M) and phthalic acid (0.02 M).[5] The OH^- concentration was thus estimated to be 2.2×10^{-2} M, indicating that the pH meter reads the solution pH (expected pH = 12.34) quite satisfactorily. On dissolving 10^{-2} M 4,4′-biphenol in the above NaOH solution (pH = 12.3), the resultant pH of the solution has been measured to be 11.9, which is very close to the expected pH value of ∼12 on the basis of the pK_{a1} and pK_{a2} values of 9.4 and 14.1, respectively, for the biphenol. Similarly, we have also dissolved 10^{-2} M 2,2′-biphenol in the same stock NaOH solution (pH = 12.3). The pH of the resultant solution has then been measured to be 12.1, which is again in support of the fact that the pK_{a2} value of 2,2′-biphenol is >14. As reference experiments, we have also dissolved 10^{-2} M phenol and 10^{-2} M *p*-cresol separately in the same NaOH solution (pH = 12.3). Both phenol and *p*-cresol have single phenolic OH groups, with their pK_a values close to ∼10. Thus for both of these reference solutions the pH was expected to be close to ∼12. In our measurements the pH for these solutions has been found to be ∼12.1. All these results clearly show that the pK_{a2} values of both 2,2′- and 4,4′-biphenols are >14. On the basis of these measurements and the observed spectral changes with pH/H_- of the solutions reported earlier,[2] we are confident that the pK_{a2} of both 2,2′- and 4,4′-biphenols are ≥14. To be noted here that in relation to the one-electron reduction potential of 4,4′-$^-$O−Ph−Ph−O$^\bullet$ Jonsson et al.[1] infer that “the 4-phenolate substituent in the para position appears to be strongly electron donating.” If this is so, it will naturally cause the pK_{a2} value of 4,4′-biphenol to be much higher than its pK_{a1} value, as are also indicated from our results.[2]

Additionally, if both pK_{a1} and pK_{a2} values of 4,4′-biphenol are indeed the same,[1] it would be very difficult to conceive the reduction potential $E°(1)$ reported by Jonsson et al., which corresponds to the redox couple (4,4′-$^-$O−Ph−Ph−O$^\bullet$/4,4′-HO−Ph−Ph−O$^-$). If pK_{a1} is equal to pK_{a2} for 4,4′-biphenol, one cannot realize the above redox couple, as there will be no pH condition where the monoanionic form of the biphenol can exist. In relation to eq 5 in the paper of Jonsson et al.,[1] it is not clear why and how one can correlate $E°(1)$ and $E°(2)$ values without considering the effect of the solution pH and the pK_{a1} of the biphenol.[6] While the redox results from the previous study were compared,[4] it would have been appropriate if the authors had measured the reduction potentials in solutions for a wide range of pH to conclude that the redox potential of 4,4′-biphenol is independent of pH. In pulse radiolysis technique, the redox measurements always have an error of about ±20 mV, especially when the kinetic method is used to estimate the equilibrium constant for the redox couples.[7] As can be seen from the data points in Figure 4 given by Jonsson et al.,[1] there is a scope of substantial error in estimating the slopes and intercepts. Thus, merely from the measurements of two closely placed pH conditions (pH 12 and 13) it might not be justified to comment that the reduction potentials of 4,4′-biphenol are independent of pH and the pK_{a1} and pK_{a2} values of the biphenol are the same.

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