Reply to Comment on "Redox and Acidity Properties of 2,2′- and 4,4′-Biphenols and the Corresponding Phenoxyl Radicals"

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Pal and Das[1] disagree with the first and second acidity constants of 4,4′-biphenol reported by us in a previous paper.[2] In addition, they question some of the methods that were used as well as the reasoning behind some of the results. We will address the points raised by Pal and Das here. However, we first would like to discuss the acidity constants of biphenols in general. The pK_a's reported by us are 7.6 and 13.7 for 2,2′-biphenol and 9.7 and 9.7 for 4,4′-biphenol. The corresponding values reported by Pal and Das are 7.5 and 14.7 for 2,2′-biphenol and 9.4 and 14.1 for 4,4′-biphenol. Qualitatively, our reported values and the values reported by Pal and Das on the acidity of 2,2′-biphenol are in agreement. The observed pK_a splitting can be attributed to stabilization of the monoanionic form due to the formation of an intramolecular hydrogen bond. This explains why the first pK_a is ca. 2.5 units lower than the pK_a for phenol and the second pK_a is 3.7−4.7 units higher than that of phenol. This type of pK_a splitting has been observed for a number of diacids where intramolecular hydrogen bonds can stabilize the monoanionic form. In the case of 4,4′-biphenol the formation of an intramolecular hydrogen bond between −OH and −O$^-$ is structurally impossible. Hence, the only rationale for a pK_a splitting would be by way of inductive and/or resonance effects of the substituent. It is well established that electron-withdrawing para substituents lower the pK_a of phenols significantly, whereas electron-donating substituents only increase the pK_a marginally. The most relevant example in this particular case is 1,4-hydroquinone. The first pK_a of 1,4-hydroquinone is 10.0 (i.e., identical to that for phenol) and the second pK_a is 11.5.[3] Consequently, the effect of the 4-O$^-$ substituent is an increase in pK_a by merely 1.5 units. It should be noted that −O$^-$ is one of the strongest electron-donating substituents we know. Pal and Das suggest that the second pK_a for 4,4′-biphenol is 4.1 units higher than that of phenol. This implies that the electron-donating capability of the 4-Ph−O$^-$ substituent is by far superior to anything previously reported in the chemical literature.

As stated in our paper, we found that the first and second pK_a for 4,4′-biphenol are "nearly identical", which meant that we could not separate two different pK_a:s in our earlier experiments. To settle this issue, we have now titrated 4,4′-biphenol. The solubility of the neutral substance is too low to permit a titration with the phenol fully dissolved. A slurry containing 10^{-2} mol/dm^3 of 4,4′-biphenol in CO_2-free water was titrated with 0.110 mol/dm^3 NaOH (calibrated against $KIO_3 \cdot HIO_3$). Both pH and turbidity were monitored and each aliquot (0.01 equiv) of NaOH was added only after the pH electrode had become stable. The sample became transparent when 1.8 OH$^-$ per phenol had been added. When the titration was finished 2 OH$^-$ per 4,4′-biphenol had been consumed. We could only observe one pK_a, its value being 10.5 ± 0.2. The need for more than one equivalent OH$^-$ to dissolve the undissociated phenol is due to its low solubility. By combining equilibria 1−3, we obtain equlibrium 4.

$$H_2A + OH^- \leftrightarrow HA^- + H_2O \tag{1}$$

$$HA^- + OH^- \leftrightarrow A^{2-} + H_2O \tag{2}$$

$$H_2A(s) \leftrightarrow H_2A \tag{3}$$

$$2\,HA^- \leftrightarrow H_2A(s) + A^{2-} \tag{4}$$

Precipitation forces eq 4 to the right, and there is almost no HA$^-$ present in the system. pK_{a1} cannot be determined and hence the observed pK_a is pK_{a2}.

By UV spectroscopy we do see changes both in peak positions and heights below pH 10, yielding a pK_{a1} of ca. 9.7.

To make sure that the delivered substance was really 4,4′-biphenol, we checked its identity using NMR. The proton NMR confirmed that our substance was indeed 4,4′-biphenol.

As pointed out by Pal and Das, we state that the 4-phenolate substituent in the para position appears to be strongly electron donating. This statement is based on the observed effect on the one-electron reduction potential of the phenoxyl radical (4,4′-$^-$O−Ph−Ph−O$^\bullet$). As discussed in our paper, the 4-phenolate substituent is considerably less electron-donating than the −O$^-$ substituent. Consequently, as discussed above, we would not expect the 4-phenolate substituent to affect the second pK_a more than does the 4-O$^-$ substituent.

The potential for the redox couple 4,4′-HO−Ph−Ph−O$^\bullet$/4,4′-HO−Ph−Ph−O$^-$ is indeed impossible to measure, and this is also clearly stated in our paper. However, this experimentally inaccessible potential is of interest when considering the effect of the 4-HO−Ph substituent. What we are interested in is the aqueous analogue of the electron affinity of 4,4′-HO−Ph−Ph−O$^\bullet$.

Concerning eq 5 in our paper, Pal and Das claim that we neglect the role of pK_{a1} and that an appropriate derivation or a suitable reference is missing. This equation is simply an application of Hess' law and can easily be derived from the thermochemical cycle presented in Figure 3. The pH of the solution is not considered because the potentials we are using are pH-independent formal potentials (aqueous analogues of electron affinities).

Finally, Pal and Das question our study of the pH effect on the phenoxyl radical reduction potential for 4,4′-biphenol. Indeed, we have only determined the potential at pH 12.3 and 13.3, but it should be noted that what we actually measure is the redox equilibrium constant between the redox couple of interest and a reference redox couple. The relation between the equilibrium constant and the difference in potential between the two redox couples is given by Nernst's equation ($\Delta E^\circ = 0.059 \log K$ at room temperature). As the potential is given by the logarithm of the equilibrium constant, a relatively large uncertainty or difference in equilibrium constant gives a relatively small change in potential. In our case, the difference in redox equilibrium constant at pH 12.3 and at pH 13.3 is less than 10%. Had the second pK_a been 14.1, we would expect a difference in redox equilibrium constant by 1 order of magnitude going from pH 12.3 to pH 13.3. We feel confident to state that the potential is pH independent. Furthermore, the equilibrium

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constants determined from kinetic measurements and equilibrium concentrations are in excellent agreement for the 4,4′-biphenol/4-MeO−PhOH system (Table 1). In addition, Pal and Das claim that there must be quite a substantial error involved in extracting the slopes and intercepts (Figure 4) from which the equilibrium constant is calculated. The uncertainties in the slope and intercept are 3% and 4% for the equilibrium concentration measurement and 3% and 12% for the kinetic measurement. The correlation coefficients (r^2) are 0.993 and 0.995, respectively. This is not what we would refer to as a substantial error.

In conclusion, the results presented in paper 1 are internally consistent and well in line with what one would expect from the numerous studies on phenols and phenoxyl radicals published in the chemical literature.

References and Notes

(1) Pal, H.; Das, T. N. *J. Phys. Chem. A* **2003**, *107*, 5876.

(2) Jonsson, M.; Lind, J.; Merényi, G. *J. Phys. Chem. A* **2002**, *106*, 4758.

(3) Serjeant, E. P.; Dempsey, B. In *Ionisation Constants of Organic Acids in Aqueous Solution*; Pergamon Press: Oxford, U.K., 1979.