

Reply to Comment on "UV Spectrum and Kinetics of Hydroxycyclohexadienyl Radicals"

Palle Pagsberg

*Environmental Science and Technology Department,
Riso National Laboratory, DK-4000 Roskilde, Denmark*

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The main controversy is the interpretation of our experimental results.¹ Thus, the proposed reaction 1b, $\text{OH} + \text{C}_6\text{H}_6 \rightarrow \text{H} + \text{C}_6\text{H}_5\text{OH}$ with a yield of about 25%, has been identified by the well-known UV spectrum of phenol (Figure 6) and the kinetic trace (Figure 5a) which was analyzed in terms of a composite absorption due to $\text{HO}-\text{C}_6\text{H}_6$ and $\text{C}_6\text{H}_5\text{OH}$, which are produced simultaneously. The experimental curve has been reproduced by computer modeling of reactions 1a and 1b and the subsequent radical-radical reactions, $2\text{HO}-\text{C}_6\text{H}_6 \rightarrow \text{products}$ and $\text{HO}-\text{C}_6\text{H}_6 + \text{H}-\text{C}_6\text{H}_6 \rightarrow \text{products}$. After adjustment of the relative yields of 75% (1a) and 25% (1b) as well as the rates of the radical-radical reactions, the model curve expressed by $5.5 \times 10^4[\text{HO}-\text{C}_6\text{H}_6] + 1.05 \times 10^5[\text{C}_6\text{H}_5\text{OH}]$ was found to reproduce Figure 5a within the experimental signal-to-noise ratio. As pointed out in the text, we have considered other possible sources, e.g., $\text{OH} + \text{C}_6\text{H}_5 \rightarrow \text{C}_6\text{H}_5\text{OH}$ and $\text{OH} + \text{HO}-\text{C}_6\text{H}_6$

$\rightarrow \text{H}_2\text{O} + \text{C}_6\text{H}_5\text{OH}$. However, none of these reactions could account for the experimental results. We have to admit that the proposed reaction 1b deserves further experimental studies, and we intend to employ tunable infrared diode laser spectroscopy for the detection of phenol without interference from other molecules.

Another source of controversy is our interpretation of the kinetic features shown in Figure 9. By addition of oxygen, we observe an increase in the transient absorption signal which we ascribe to the formation of the peroxy radical, $\text{HO}-\text{C}_6\text{H}_6-\text{O}_2$. The UV spectrum of this radical was first observed in aqueous solution (ref 33). Recently, the formation of peroxy radicals has been proposed to be an important step in the atmospheric photooxidation of aromatics, $\text{OH} + \text{Ar} + \text{O}_2 \rightarrow \text{HO}-\text{Ar}-\text{O}_2$.² Subsequent reactions of the peroxy radical, i.e., cyclization and ring fragmentation, account for the observed products, e.g., glyoxal and other carbonyl compounds. Thus, we believe that our assignment of the observed transient species to the aromatic peroxy radical is correct.

References and Notes

- (1) Bjergbakke, E.; Sillesen, A.; Pagsberg, P. *J. Phys. Chem.* **1996**, *100*, 5729–5736.
- (2) Andino, J. M.; Smith, N.; Flagan, C.; Goddard, III, W. A.; Seinfeld, J. H. *J. Phys. Chem.* **1996**, *100*, 10967–10980.