COMMENTS

Comment on "UV Spectrum and Kinetics of Hydroxycyclohexadienyl Radicals"

R. Koch

Fraunhofer Institut Toxikologie und Aerosolforschung, Abteilung Atmosphärische Chemie, Nikolai-Fuchs Strasse 1, D-30625 Hannover, Germany

Bjergbakke, Sillesen, and Pagsberg (BSP) presented interesting pulse radiolysis experiments on the OH-initiated oxidation of benzene[1] and ruled out several product channels of the reaction of NO_2 with the benzene−OH adduct (hydroxycyclohexadienyl, HCHD). At issue, however, is reaction 1b, OH + benzene → H + phenol (25% yield), which BSP invoked to explain the supposed early formation of phenol in their experiments. This reaction is in contradiction not only to high-temperature measurements of the reverse reaction (as BSP noted) but also to the following: (i) low decay rates of OH in equilibrium with HCHD (reaction 1a) have been observed,[2] (ii) the apparent OH reactivity of benzene (slope of OH decay rate vs benzene concentration) is unchanged in the presence of NO_2 (to convert H to OH) (our data, not shown), and (iii) the OH kinetics observed in benzene/O_2/NO mixtures[3] are well explained by the simple kinetic triangle OH → HCHD → HO_2 → OH. (The formation of HO_2 from H atoms would be much faster than via HCHD.) The crucial point, however, is that the experimental data presented by BSP (UV absorption time profiles a−d of Figure 5) indicate a delayed rather than prompt formation of phenol.

For a semiquantitative analysis, note that the OH radicals are consumed (by reaction 1, OH + benzene → HCHD) on a 10 μs time scale (see also Figure 4) and that formation of cyclohexadienyl radicals (H + benzene → CHD) can be neglected on that time scale. Thus, trace b (292 nm) is mainly due to HCHD. Since the absorption cross section of HCHD is larger at 275 nm (trace a) than at 292 nm (trace b, see Figure 3 for the spectra), part of the difference (a) − (b) is also due to HCHD. The remaining part of the difference (probably due to phenol) emerges mainly after $t = 50$ μs, well after reaction 1.

As possible sources of phenol, BSP considered (and dismissed) phenyl + OH → phenol and HCHD + OH → phenol + H_2O but discussed neither the reaction HCHD + benzene → phenol + CHD nor the self- and cross-reactions HCHD + (H)CHD → phenol + (hydroxy)cyclohexadiene. (Note that the spectrum in Figure 6 indicating phenol was recorded with a delay of 200 μs, when most of the HCHD radicals have been consumed by secondary reactions.)

Recently, it has been shown that phenol is the main product of the (fast) photolysis of benzene oxide/oxepin[4] and that the latter is a probable primary product of the OH-initiated oxidation of benzene.[3,4] Thus, the phenol observed in chamber experiments on benzene[5] may also be a secondary product.

Another important point of the BSP paper is the assignment of a rapidly emerging extra absorption upon addition of O_2 (Figure 9) to the peroxy radical formed by the reaction of HCHD with O_2. This reaction, together with the (fast) back-decomposition to HCHD in competition with a (slow) isomerization to a bicyclic radical, has been discussed[6] on the basis of thermochemical arguments and chamber experiments on toluene and cresol. Provided this mechanism is true (see, however, refs 3 and 4), the effective reaction rate (consumption of HCHD) is of first order in [O_2] at low levels of O_2, where the peroxy radical to HCHD ratio is proportional to [O_2] but independent of O_2, when the equilibrium is at the right-hand side. While this equilibrium has been observed in the liquid phase[7] ($K_{eq} = 4.3 \times 10^{-17}$ cm^3/molecule at room temperature), the stability of the peroxy radical has to be lower in the gas phase since pseudo-first-order kinetics of HCHD (linear in O_2 up to 1.5×10^{17} cm^{-3}) have been observed[3] at 269 K. Thus, under the conditions of the BSP experiment (5×10^{17} cm^{-3} of O_2, 320 K), the equilibrium should be on the left-hand side, and the peroxy radical would have to be an unlikely strong absorber to cause the observed extra absorption.

References and Notes

(1) Bjergbakke, E.; Sillesen, A.; Pagsberg, P. *J. Phys. Chem.* **1996**, *100*, 5729.

(2) Knispel, R.; Koch, R.; Siese, M.; Zetzsch, C. *Ber. Bunsen-Ges. Phys. Chem.* **1990**, *94*, 1375.

(3) Koch, R.; Zetzsch, C. *Proceedings of the EUTROTRAC Symposium '96*; SPB Academic Publishing: The Hague, The Netherlands, in press.

(4) Klotz, B.; Barnes, I.; Becker, K.-H. Paper presented at the joint EC-EUTROTRAC Workshop, HALIPP/LACTOZ Working Group, Strasbourg, France, Sept 25−26, 1995 (in press as Air Pollution Research Report by the EC). Barnes, I.; Becker, K.-H.; Klotz, B. *Proc. of the EUTROTRAC Symposium '96*; SPB Academic Publishing: The Hague, The Netherlands, in press.

(5) Molar yields of phenol of 0.24 and 0.15 have been reported by respectively: Atkinson, R.; Aschmann, S. M.; Arey, J.; Carter, W. P. L. *Int. J. Chem. Kinet.* **1989**, *21*, 801. Moschonas, N.; Danalatos, D.; Glavas, S. *Monatsh. Chem.*, in press.

(6) Atkinson, R.; Lloyd, A. C. *J. Phys. Chem. Ref. Data* **1984**, *13*, 315. See also: Bartolotti, L. J.; Edney, E. O. *Chem. Phys. Lett.* **1995**, *245*, 119. Lay, T. H.; Bozzelli, J. W.; Seinfeld, J. H. *J. Phys. Chem.* **1996**, *100*, 6543.

(7) Pan, X.-M.; von Sonntag, C. *Z. Naturforsch.* **1990**, *45B*, 1337. See also: Fang, X.; Pan, X.; Rahmann, A.; Schuchmann, H.-P.; von Sonntag, C. *Chem. Eur. J.* **1995**, *1*, 423 and references therein.