

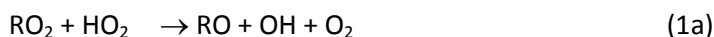
On the importance of OH-forming channels in the reactions of HO₂ with RO₂ radicals generated from the OH-initiated oxidation of aromatic hydrocarbons

Michael E. Jenkin^{1,2}

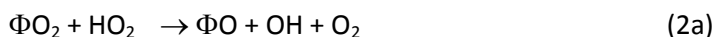
¹ Atmospheric Chemistry Services, Okehampton, Devon, EX20 1FB, UK;

² School of Chemistry, University of Bristol, Cantock's Close, Bristol, BS8 1TS, UK.

As commented on in this paper by Nehr et al. (2014), a number of studies have reported measurements of branching ratios (k_{1a}/k_1) for OH-forming channels of the reactions of HO₂ with RO₂ radicals possessing oxygenated functional groups (Hasson et al., 2004, 2012; Jenkin et al., 2007; 2008; 2009; Dillon and Crowley, 2008; Gross et al., 2014):



Birdsall et al. (2010) and Birdsall and Elrod (2011) have proposed that OH-forming channels may also be important for the analogous reactions of bicyclic RO₂ radicals formed during the OH-initiated oxidation of aromatic hydrocarbons (denoted ΦO_2 here):



This was to help explain the inferred level of OH regeneration in their systems under NO_x-free conditions, although the precise mechanism could not be confirmed. The present results of Nehr et al. (2014) are stated to be consistent with the proposal of Birdsall et al. (2010) and Birdsall and Elrod (2011), but with the conditions of their system not being sufficiently sensitive to reaction (2) to provide quantitative information. It is noted that these studies have therefore been unable to confirm that OH regeneration at low NO_x in aromatic systems actually results from reaction (2a), which remains a proposal requiring confirmation or refutation.

The purpose of this comment is to highlight some published information that has tended to be overlooked in previous discussions. The detection of the bicyclic hydroperoxide species, ΦOOH , in a number of aromatic systems by Birdsall et al. (2010) and Birdsall and Elrod (2011) suggests that reaction (2) proceeds at least partially via a terminating channel producing ΦOOH and O₂, indicating that $k_{2a}/k_2 < 1$ in the relevant systems. Our previous studies of reaction (1) for CH₃C(O)O₂, CH₃C(O)CH₂O₂, CH₃OCH₂O₂ and HOCH₂O₂ in the Ford chamber (Jenkin et al., 2007; 2008; 2009) also provided some additional information that is relevant to this issue. In those studies, benzene was used to scavenge OH radicals, and the resultant formation of phenol was used to quantify k_{1a}/k_1 for the target RO₂ radical. As a result, the relevant benzene-derived bicyclic ΦO_2 radicals were also formed in the system, under conditions when they likely react mainly with HO₂. Section 3.4 of Jenkin et al. (2007) therefore provided a discussion and assessment of the possible magnitude of OH formation from the reaction of the benzene-derived ΦO_2 with HO₂, because this could have a direct impact on the quantification of k_{1a}/k_1 for the target RO₂ (CH₃C(O)O₂ in that study). Based on the failure to detect glyoxal formation (which would be expected to be produced from the chemistry of ΦO , formed in conjunction with OH in channel (2a)) using FTIR, we reported a conservative upper limit of $k_{2a}/k_2 \leq 0.5$ for the reaction of HO₂ with the benzene-derived ΦO_2 , providing some quantitative level of restriction on the importance of channel (2a). As indicated above, this supplementary result has tended to be overlooked in subsequent discussions.

As discussed in Jenkin et al. (2007), use of this upper limit value for k_{2a}/k_2 would require our reported value of $k_{1a}/k_1 = (0.43 \pm 0.10)$ for CH₃C(O)O₂ to be reduced to (0.37 ± 0.09) , to correct for the

additional formation of phenol resulting from OH regeneration from the benzene chemistry. Until recently, these values were both consistent with other reported determinations of k_{1a}/k_1 for $\text{CH}_3\text{C}(\text{O})\text{O}_2$, including the value of (0.5 ± 0.2) reported by Dillon and Crowley (2008), based on direct measurements of OH formation. However, Gross et al. (2014) have recently reported an improved direct determination of $k_{1a}/k_1 = (0.62 \pm 0.09)$ for $\text{CH}_3\text{C}(\text{O})\text{O}_2$, which supersedes the value of Dillon and Crowley (2008) from the same laboratory. The unadjusted value of $k_{1a}/k_1 = (0.43 \pm 0.10)$ reported by Jenkin et al. (2007) is therefore only just consistent with that of Gross et al. (2014), suggesting that little reduction in this estimate of k_{1a}/k_1 can now be supported if the quoted error limits accurately quantify the experimental uncertainties. If so, this would suggest that $k_{2a}/k_2 \leq 0.1$ for the reaction of HO_2 with the benzene-derived ΦO_2 .

In summary, our previous work provided an upper limit measurement of $k_{2a}/k_2 \leq 0.5$ (Jenkin et al., 2007) for the benzene-derived ΦO_2 , with broader (more indirect) considerations suggesting that the value might be somewhat lower than this upper limit. It would therefore seem that dedicated product studies of the reactions of HO_2 with ΦO_2 radicals derived from the OH-initiated oxidation of a series of aromatic hydrocarbons are ideally required, in agreement with the general conclusion of Birdsall and Elrod (2011). Until such confirmatory studies are available, a possible major role for reaction (2a) remains speculative, and should probably be stated with qualification (as is the case in the present paper of Nehr et al., 2014).

References

- Birdsall, A. W. and Elrod, M. J.: Comprehensive NO-dependent study of the products of the oxidation of atmospherically relevant aromatic compounds, *J. Phys. Chem. A*, 115, 5397–5407, 2011.
- Birdsall, A. W., Andreoni, J. F., and Elrod, M. J.: Investigation of the role of bicyclic peroxy radicals in the oxidation mechanism of toluene, *J. Phys. Chem. A*, 114, 10655–10663, 2010.
- Dillon, T. J. and Crowley, J. N.: Direct detection of OH formation in the reactions of HO_2 with $\text{CH}_3\text{C}(\text{O})\text{O}_2$ and other substituted peroxy radicals, *Atmos. Chem. Phys.*, 8, 4877–4889, 2008.
- Hasson, A. S., Tyndall, G. S., and Orlando, J. J.: A product yield study of the reaction of HO_2 radicals with ethyl peroxy ($\text{C}_2\text{H}_5\text{O}_2$), acetyl peroxy ($\text{CH}_3\text{C}(\text{O})\text{O}_2$), and acetonyl peroxy ($\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}_2$) radicals, *J. Phys. Chem. A*, 108, 5979–5989, 2004.
- Gross, C. B. M., Dillon, T. J., Schuster, G., Lelieveld, J., and Crowley, J. N.: Direct kinetic study of OH and O_3 formation in the reaction of $\text{CH}_3\text{C}(\text{O})\text{O}_2$ with HO_2 , *J. Phys. Chem. A*, 118, 974–985, 2014.
- Hasson, A. S., Tyndall, G. S., Orlando, J. J., Singh, S., Hernandez, S. Q., Campbell, S., and Ibarra, Y.: Branching ratios for the reaction of selected carbonyl-containing peroxy radicals with hydroperoxy radicals, *J. Phys. Chem. A*, 116, 6264–6281, 2012.
- Jenkin, M. E., Hurley, M. D., and Wallington, T. J.: Investigation of the radical product channel of the $\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{HO}_2$ reaction in the gas phase, *Phys. Chem. Chem. Phys.*, 9, 3149–3162, 2007.
- Jenkin, M. E., Hurley, M. D., and Wallington, T. J.: Investigation of the radical product channel of the $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}_2 + \text{HO}_2$ reaction in the gas phase, *Phys. Chem. Chem. Phys.*, 10, 4274–4280, 2008.
- Jenkin, M. E., Hurley, M. D., and Wallington, T. J.: Investigation of the radical product channel of the $\text{CH}_3\text{OCH}_2\text{O}_2 + \text{HO}_2$ reaction in the gas phase, *J. Phys. Chem. A*, 114, 408–416, 2010.
- Nehr, S., Bohn, B., Dorn, H.-P., Fuchs, H., Häsel, R., Hofzumahaus, A., Li, X., Rohrer, F., Tillmann, R., and Wahner, A.: Atmospheric photochemistry of aromatic hydrocarbons: OH budgets during SAPHIR chamber experiments, *Atmos. Chem. Phys. Discuss.*, 14, 5535-5560, 2014.