Supplementary information: Kinetics and mechanism of the reaction of OH with 1,3,5-trimethylbenzene – Experimental evidence for the formation of adduct isomers

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S1 Analytical solutions for model-1

The reaction scheme R1a /-1a, R1b, R2 and R3 in the main paper is leading to a system of two differential equations,

$$d[OH]/dt = -a [OH] + b [add]$$
(S1)

$$d[add]/dt = c [OH] - d [add]$$
(S2)

that has a general solution:

$$[OH] = C_1 \exp(\lambda_1 t) + C_2 \exp(\lambda_2 t)$$
 (S3)

$$[add] = C_3 \exp(\lambda_1 t) + C_4 \exp(\lambda_2 t)$$
 (S4)

The coefficients $\lambda_{1,2}$ are the roots of the characteristic polynomial:

$$P(\lambda) = (-a - \lambda)(-d - \lambda) - b \ c = 0$$
 (S5)

$$\lambda_{1,2} = -\frac{a+d}{2} \pm \sqrt{(\frac{a+d}{2})^2 - ad + bc}$$
(S6)

Instead of the $\lambda_{1,2}$, decay rate coefficients or reciprocal lifetimes $\tau_{1,2}^{-1}$ of OH are usually used in equation S3 and S4. Moreover, the argument of the root function can be simplified:

$$\tau_{1,2}^{-1} = -\lambda_{1,2} = \frac{a+d}{2} \pm \sqrt{(\frac{a-d}{2})^2 + bc}$$
(S7)

This equation is identical to that obtained previously¹ and has been used in a number of studies before, also for other chemical systems^{2–7}. Note that equation IIa by Koch *et al.*⁶ is incorrect. To derive the rate coefficients *a*, *d* and the product *bc* from experimental decay curves, also the relations from Vieta's root theorem (Francois Viete, 1540–1603) proved useful:

$$\tau_1^{-1} + \tau_2^{-1} = a + d \tag{S8}$$

$$\tau_1^{-1}\tau_2^{-1} = ad - bc \tag{S9}$$

To determine the coefficients $C_1 - C_4$ of the general solutions, the equations were differentiated and inserted into the differential equations:

$$d[OH]/dt = -\tau_1^{-1} C_1 \exp(-\tau_1^{-1}t) - \tau_2^{-1} C_2 \exp(-\tau_2^{-1}t)$$

= $-a (C_1 \exp(-\tau_1^{-1}t) + C_2 \exp(-\tau_2^{-1}t))$
 $+b (C_3 \exp(-\tau_1^{-1}t) + C_4 \exp(-\tau_2^{-1}t))(S10)$

$$d[add]/dt = -\tau_1^{-1} C_3 \exp(-\tau_1^{-1}t) - \tau_2^{-1} C_4 \exp(-\tau_2^{-1}t)$$

= +c (C₁ exp(-\tau_1^{-1}t) + C_2 exp(-\tau_2^{-1}t))
-d (C_3 exp(-\tau_1^{-1}t) + C_4 exp(-\tau_2^{-1}t))(S11)

That can be rearranged:

$$C_1 \ \tau_1^{-1} = a \ C_1 - b \ C_3 \tag{S12}$$

$$C_2 \ \tau_2^{-1} = a \ C_2 - b \ C_4 \tag{S13}$$

$$C_3 \tau_1^{-1} = d C_3 - c C_1 \tag{S14}$$

$$C_4 \tau_2^{-1} = d C_4 - c C_2 \tag{S15}$$

Moreover, the general boundary conditions can be defined as follows:

$$C_1 + C_2 = [OH]_0 \tag{S16}$$

$$C_3 + C_4 = [\text{add}]_0 \tag{S17}$$

Rearrangements led to expressions for C_1 – C_4 :

$$C_1 = [OH]_0 - C_2 \tag{S18}$$

$$C_2 = \frac{[\text{add}]_0 b + [\text{OH}]_0(\tau_1^{-1} - a)}{\tau_1^{-1} - \tau_2^{-1}}$$
(S19)

$$C_3 = [add]_0 - C_4$$
 (S20)

$$C_4 = \frac{[\text{OH}]_0 c + [\text{add}]_0 (\tau_1^{-1} - d)}{\tau_1^{-1} - \tau_2^{-1}}$$
(S21)

These equations together with the $\tau_{1,2}^{-1}$ can be used to simulate decay curves of OH and the adduct under all conditions.

Under typical experimental conditions with $[add]_0=0$, i.e. pulsed formation of OH at *t*=0, the expressions C_1-C_4 further

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simplify:

$$C_1 = [OH]_0 \frac{a - \tau_2^{-1}}{\tau_1^{-1} - \tau_2^{-1}}$$
(S22)

$$C_2 = [OH]_0 \frac{\tau_1^{-1} - a}{\tau_1^{-1} - \tau_2^{-1}}$$
(S23)

$$C_3 = -[OH]_0 \frac{c}{\tau_1^{-1} - \tau_2^{-1}}$$
(S24)

$$C_4 = [OH]_0 \frac{c}{\tau_1^{-1} - \tau_2^{-1}}$$
(S25)

Finally, for the initial ratio $C_{1/2}$ of the exponential functions alternative equations apply:

$$C_1/C_2 = C_{1/2} = \frac{a - \tau_2^{-1}}{\tau_1^{-1} - a} = \frac{\tau_1^{-1} - d}{d - \tau_2^{-1}}$$
 (S26)

The last term was obtained utilizing equation S8. Previously published equations for $C_{1/2}$ were more complicated but also correct. For example, an alternative expression ^{1,6} for $C_{1/2}$ can be converted to equation S26 using the Vieta formulas in equations S8 and S9:

$$C_{1/2} = \frac{(\tau_1^{-1} - d)^2}{bc} = \frac{(\tau_1^{-1} - d)^2}{ad - \tau_1^{-1}\tau_2^{-1}}$$
$$= \frac{(\tau_1^{-1} - d)^2}{(\tau_1^{-1} + \tau_2^{-1} - d)d - \tau_1^{-1}\tau_2^{-1}} = \frac{\tau_1^{-1} - d}{d - \tau_2^{-1}}$$
(S27)

With equations S7 and S26 the curve parameters of a biexponential OH decay can be calculated from the coefficients a, bc and d related to the rate constants of the chemical system. This is the basis to directly fit the rate constants from the decay curves as was done in this work for model-1.

On the other hand, also the analytical expression of a, bc and d as a function of the curve parameters may be useful as was outlined briefly in the Results section of the main paper. Equation S26 can be directly converted accordingly,

$$a = \frac{\tau_1^{-1} C_{1/2} + \tau_2^{-1}}{1 + C_{1/2}}$$
(S28)

$$d = \frac{\tau_2^{-1} C_{1/2} + \tau_1^{-1}}{1 + C_{1/2}}$$
(S29)

From equations S26 and S9 also bc can be calculated:

$$bc = \frac{C_{1/2}(\tau_1^{-1} - \tau_2^{-1})^2}{(1 + C_{1/2})^2}$$
(S30)

S2 Analytical solutions for model-2

The reaction scheme R11a/-11a, R12a/-12a, R1b, R2, R31, and R32 in the main paper is leading to a system of three dif-

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ferential equations :

 $d[OH]/dt = -a [OH] + b [add_1] + e [add_2]$ (S31)

$$d[add_1]/dt = c [OH] - d [add_1]$$
(S32)

$$d[add_2]/dt = f [OH] - g [add_2]$$
(S33)

That has a general solution:

r

τ

$$[OH] = C_1 \exp(\lambda_1 t) + C_2 \exp(\lambda_2 t) + C_3 \exp(\lambda_3 t) \quad (S34)$$

$$[add_1] = C_4 \exp(\lambda_1 t) + C_5 \exp(\lambda_2 t) + C_6 \exp(\lambda_3 t) \quad (S35)$$

$$[add_2] = C_7 \exp(\lambda_1 t) + C_8 \exp(\lambda_2 t) + C_9 \exp(\lambda_3 t) \quad (S36)$$

The coefficients λ_{1-3} are again the roots of the characteristic polynomial:

$$P(\lambda) = (-a - \lambda)(-d - \lambda)(-g - \lambda)$$
$$-bc(-g - \lambda) - ef(-d - \lambda) = 0$$
(S37)

Expressions for λ_{1-3} can be derived from textbook formulas but are rather complicated. The normal form of the polynomial is $y = x^3 + rx^2 + sx + u = 0$. In terms of the τ_{1-3}^{-1} these parameters are:

$$a = -a - d - g \tag{S38}$$

$$s = ad + dg + ag - bc - ef$$
(S39)

$$u = bcg + efd - adg \tag{S40}$$

Setting x = y - r/3 leads to the reduced form of the polynomial: $y^3 + py + q = 0$, where $p = s - r^2/3$ and $q = 2r^3/27 - sr/3 + u$. For the so-called "casus irreducibilis" where three real solutions exist, as in the case discussed here, formulas for the polynomial roots were derived by Vieta. With $\phi = \arccos((-q/2)/\sqrt{-(p/3)^3})$ and $\rho = \sqrt{-(p/3)^3}$, the solutions are:

$${}^{-1}_{1} = 2\sqrt[3]{\rho} \cos(\phi/3) - r/3$$
 (S41)

$$\tau_2^{-1} = 2\sqrt[3]{\rho} \cos(\phi/3 + 2\pi/3) - r/3 \qquad (S42)$$

$$\tau_3^{-1} = 2\sqrt[3]{\rho} \cos(\phi/3 + 4\pi/3) - r/3 \qquad (S43)$$

It was checked that these formulas obey the Vieta equations for third-order polynomials:

$$\tau_1^{-1} + \tau_2^{-1} + \tau_3^{-1} = -r = a + d + g$$
(S44)

$$\begin{aligned} & \tau_1^{-1}\tau_2^{-1} + \tau_1^{-1}\tau_3^{-1} + \tau_2^{-1}\tau_3^{-1} = s \\ & = ad + dg + ag - bc - ef \end{aligned} \tag{S45}$$

$$\tau_1^{-1}\tau_2^{-1}\tau_3^{-1} = -u = adg - bcg - efd$$
(S46)

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To obtain the coefficients C_{1-9} the general solutions were again differentiated and inserted into the differential equations, as shown above. These equations were then rearranged:

$$C_1 \tau_1^{-1} = a C_1 - b C_4 - e C_7 \tag{S47}$$

$$C_2 \tau_2^{-1} = a C_2 - b C_5 - e C_8$$
(S48)
$$C_2 \tau_2^{-1} = a C_2 - b C_5 - e C_8$$
(S48)

$$C_3 \tau_3^{-1} = a C_3 - b C_6 - e C_9$$
 (S49)
$$C_1 \tau_3^{-1} = d C_4 - c C_9$$
 (S50)

$$C_4 t_1 = d C_4 - c C_1$$
(S50)
$$C_5 t_2^{-1} = d C_5 - c C_2$$
(S51)

$$C_{5} v_{2}^{-1} = d C_{5} - c C_{3}$$
(S52)

$$C_{7} \tau_{1}^{-1} = g C_{7} - f C_{1}$$
(S53)

$$C_8 \tau_2^{-1} = g C_8 - f C_2$$
(S54)

$$C_9 \tau_3^{-1} = g C_9 - f C_3$$
 (S55)

Moreover, generally the boundary conditions can be defined as follows:

$$C_1 + C_2 + C_3 = [OH]_0 \tag{S56}$$

$$C_4 + C_5 + C_6 = [\text{add}_1]_0 \tag{S57}$$

$$C_7 + C_8 + C_9 = [\text{add}_2]_0 \tag{S58}$$

Equations S50–S52 and S53–S55 were solved for C_4 – C_9 and the results were inserted into equations S47–S49. Together with equations S56–S58 this gave three equations for the three parameters C_1 – C_3 . The following expressions were obtained by rearrangement:

$$C_{1} = (d - \tau_{1}^{-1})(g - \tau_{1}^{-1}) \times$$
(S59)
$$\left[\frac{[add_{1}]_{0}f(d - \tau_{2}^{-1})(d - \tau_{3}^{-1})}{cf(d - g)(\tau_{1}^{-1} - \tau_{2}^{-1})(\tau_{3}^{-1} - \tau_{1}^{-1})} - \frac{c\left\{[add_{2}]_{0}(g - \tau_{2}^{-1})(g - \tau_{3}^{-1}) + f[OH]_{0}(d - g)\right\}}{cf(d - g)(\tau_{1}^{-1} - \tau_{2}^{-1})(\tau_{3}^{-1} - \tau_{1}^{-1})}\right]$$

$$C_{2} = (d - \tau_{2}^{-1})(g - \tau_{2}^{-1}) \times$$
(S60)
$$\left[\frac{[add_{1}]_{0}f(d - \tau_{1}^{-1})(d - \tau_{3}^{-1})}{cf(d - g)(\tau_{1}^{-1} - \tau_{2}^{-1})(\tau_{2}^{-1} - \tau_{3}^{-1})} - \frac{c\left\{[add_{2}]_{0}(g - \tau_{1}^{-1})(g - \tau_{3}^{-1}) + f[OH]_{0}(d - g)\right\}}{cf(d - g)(\tau_{1}^{-1} - \tau_{2}^{-1})(\tau_{2}^{-1} - \tau_{3}^{-1})}\right]$$

$$\begin{split} C_{3} &= (d - \tau_{3}^{-1})(g - \tau_{3}^{-1}) \times \\ \left[\frac{[\mathrm{add}_{1}]_{0}f(d - \tau_{1}^{-1})(d - \tau_{2}^{-1})}{cf(d - g)(\tau_{1}^{-1} - \tau_{3}^{-1})(\tau_{3}^{-1} - \tau_{2}^{-1})} \right. \\ &\left. - \frac{c\left\{ [\mathrm{add}_{2}]_{0}(g - \tau_{1}^{-1})(g - \tau_{2}^{-1}) + f[\mathrm{OH}]_{0}(d - g)\right\}}{cf(d - g)(\tau_{1}^{-1} - \tau_{3}^{-1})(\tau_{3}^{-1} - \tau_{2}^{-1})} \right] \end{split}$$

Also the $C_4 - C_9$ can be calculated using equations S50–S52 and equations S53–S55. These formulas are rather complicated but should, together with the reciprocal lifetimes τ_{1-3}^{-1} , allow to simulate OH and adduct decay curves under all boundary conditions.

The following treatment will again focus on conditions with $[add_1]_0 = [add_2]_0 = 0$. The expressions for C_{1-3} then simplify:

$$C_{1} = \frac{[\mathrm{OH}]_{0}(d - \tau_{1}^{-1})(g - \tau_{1}^{-1})}{(\tau_{1}^{-1} - \tau_{2}^{-1})(\tau_{1}^{-1} - \tau_{3}^{-1})}$$
(S62)

$$C_2 = \frac{[\text{OH}]_0(d - \tau_2^{-1})(g - \tau_2^{-1})}{(\tau_1^{-1} - \tau_2^{-1})(\tau_3^{-1} - \tau_2^{-1})} \tag{S63}$$

$$C_{3} = \frac{[\text{OH}]_{0}(d - \tau_{3}^{-1})(g - \tau_{3}^{-1})}{(\tau_{1}^{-1} - \tau_{3}^{-1})(\tau_{2}^{-1} - \tau_{3}^{-1})}$$
(S64)

The ratios are therefore given by:

$$C_{1/2} = C_1/C_2 = \frac{(d - \tau_1^{-1})(g - \tau_1^{-1})(\tau_3^{-1} - \tau_2^{-1})}{(d - \tau_2^{-1})(g - \tau_2^{-1})(\tau_1^{-1} - \tau_3^{-1})}$$
(S65)

$$C_{3/2} = C_3/C_2 = \frac{(d - \tau_3^{-1})(g - \tau_3^{-1})(\tau_2^{-1} - \tau_1^{-1})}{(d - \tau_2^{-1})(g - \tau_2^{-1})(\tau_1^{-1} - \tau_3^{-1})}$$
(S66)

Together with the reciprocal lifetimes τ_{1-3}^{-1} these ratios are the basis to fit the rate constants of model-2 in this work.

Expressions for the coefficients *a*, *d*, *g*, *bc* and *ef* as a function of the curve parameters were also derived for model-2. These are necessary for example to evaluate single triexponential decay curves. Under the assumption $[add_1]_0 = [add_2]_0 = 0$ equations S47–S49 can be summarized and identified with $[OH]_0$ from equation S56:

$$C_1 \tau_1^{-1} + C_2 \tau_2^{-1} + C_3 \tau_3^{-1} = a(C_1 + C_2 + C_3) = a[OH]_0$$
 (S67)

That can be rearranged to an expression for the parameter *a*:

$$a = \frac{C_{1/2}\tau_1^{-1} + C_{3/2}\tau_3^{-1} + \tau_2^{-1}}{1 + C_{1/2} + C_{3/2}}$$
(S68)

Formulas for the coefficients d and g are more difficult to obtain. Equations S65 and S66 are not unambiguous with regard to d and g which is also evident from the following relation that was derived from these equations:

$$1 + C_{1/2} + C_{3/2} = \frac{(\tau_1^{-1} - \tau_2^{-1})(\tau_3^{-1} - \tau_2^{-1})}{(d - \tau_2^{-1})(g - \tau_2^{-1})}$$
(S69)

Equation S69 can be used to derive an expression for the product dg:

$$dg = \frac{C_{1/2}\tau_2^{-1}\tau_3^{-1} + C_{3/2}\tau_1^{-1}\tau_2^{-1} + \tau_1^{-1}\tau_3^{-1}}{1 + C_{1/2} + C_{3/2}}$$
(S70)

Moreover, equations S44 and S68 give the sum d + g:

$$d+g = \frac{C_{1/2}(\tau_2^{-1} + \tau_3^{-1}) + C_{3/2}(\tau_1^{-1} + \tau_2^{-1}) + \tau_1^{-1} + \tau_3^{-1}}{1 + C_{1/2} + C_{3/2}}$$
(S71)

With the assumption d > g equations S70 and S71 have solutions:

$$d,g = \frac{1}{2} \frac{C_{1/2}(\tau_2^{-1} + \tau_3^{-1}) + C_{3/2}(\tau_1^{-1} + \tau_2^{-1}) + \tau_1^{-1} + \tau_3^{-1} \pm \sqrt{D}}{1 + C_{1/2} + C_{3/2}}$$
(S72)

with

$$D = C_{1/2}^{2} (\tau_{2}^{-1} - \tau_{3}^{-1})^{2}$$

$$+ 2C_{1/2} (\tau_{3}^{-1} - \tau_{2}^{-1}) \{C_{3/2} (\tau_{1}^{-1} - \tau_{2}^{-1}) - \tau_{1}^{-1} + \tau_{3}^{-1}\}$$

$$+ \{C_{3/2} (\tau_{1}^{-1} - \tau_{2}^{-1}) + \tau_{1}^{-1} - \tau_{3}^{-1}\}^{2}$$
(S73)

Expressions for *bc* and *ef* as a function of *d* and *g* were obtained by solving equation S50–S55 for C_4 – C_9 and insertion into equation S47 -S49:

$$\tau_1^{-1} = a - \frac{bc}{d - \tau_1^{-1}} - \frac{ef}{g - \tau_1^{-1}}$$
(S74)

$$\tau_2^{-1} = a - \frac{bc}{d - \tau_2^{-1}} - \frac{ef}{g - \tau_2^{-1}}$$
(S75)

$$\tau_3^{-1} = a - \frac{bc}{d - \tau_3^{-1}} - \frac{ef}{g - \tau_3^{-1}}$$
(S76)

These equations were rearranged as follows (*a* was eliminated by using equation S45):

$$bc = \frac{(d - \tau_1^{-1})(d - \tau_2^{-1})(d - \tau_3^{-1})}{g - d}$$
(S77)

$$ef = \frac{(g - \tau_1^{-1})(g - \tau_2^{-1})(g - \tau_3^{-1})}{d - g}$$
(S78)

S3 Analytical solutions for model-3

Inclusion of the isomerization reactions (R12/R21, main paper) leads to the following system of differential equations,

$$d[OH]/dt = -a [OH] + b [add_1] + e [add_2]$$
 (S79)

$$d[add_1]/dt = c [OH] - d [add_1] + h [add_2]$$
(S80)

$$d[add_2]/dt = f [OH] + i [add_1] - g [add_2]$$
(S81)

that has the same general solutions as model-2, i.e. equation S34–S36. However, the characteristic polynomial is different and the parameters s and u of the normal form are also different (compare to equations S39 and S40):

$$s = ad + dg + ag - bc - ef - hi$$
 (S82)

$$u = bcg + efd - adg + eic + hia + fbh$$
(S83)

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As was outlined in the main paper, the products *eic* and *fbh* can be expressed in terms of the product *hi*, the single, additional parameter of model-3:

$$fbh + eic = 2\sqrt{bc\,ef\,hi} \tag{S84}$$

The calculation of the reciprocal lifetimes τ_{1-3}^{-1} based on the parameters *r*, *s* and *u* is the same as for model-2, i.e. equation S41–S43.

Differentiation of the general solutions and insertion into the differential equations led to equations relating the coefficients C_{1-9} after rearrangement:

$$C_1 \tau_1^{-1} = a C_1 - b C_4 - e C_7 \tag{S85}$$

$$C_2 \ \tau_2^{-1} = a \ C_2 - b \ C_5 - e \ C_8 \tag{S86}$$

$$C_3 \ \tau_3^{-1} = a \ C_3 - b \ C_6 - e \ C_9 \tag{S87}$$

$$C_4 \ \tau_1^{-1} = d \ C_4 - c \ C_1 - h \ C_7 \tag{S88}$$

$$C_5 \ \tau_2^{-1} = d \ C_5 - c \ C_2 - h \ C_8 \tag{S89}$$

$$C_6 \tau_3^{-1} = d C_6 - c C_3 - h C_9$$
 (S90)

$$C_7 \ \tau_1^{-1} = g \ C_7 - f \ C_1 - i \ C_4 \tag{S91}$$

$$C_8 \ \tau_2^{-1} = g \ C_8 - f \ C_2 - i \ C_5 \tag{S92}$$

$$C_9 \ \tau_3^{-1} = g \ C_9 - f \ C_3 - i \ C_6 \tag{S93}$$

The general method to further simplify the expressions is similar to that explained for model-2 and also the boundary conditions are the same as for model-2, i.e. equation S56–S58. Expressions for the C_1 – C_9 under all boundary conditions can be obtained but were not derived here because they are expected to be extremely bulky. Also the C_1 – C_3 under conditions with [add₁]₀=0 and [add₂]₀=0 are rather complicated. We therefore only give equations for the ratios $C_{1,2}$ and $C_{3,2}$ of the coefficients that are necessary to analyze the OH decays:

$$C_{1/2} = \frac{(\tau_3^{-1} - \tau_2^{-1})(\sqrt{bc\,hi} + \sqrt{ef}(d - \tau_1^{-1}))}{(\tau_1^{-1} - \tau_3^{-1})(\sqrt{bc\,hi} + \sqrt{ef}(d - \tau_2^{-1}))} \times$$
(S94)

$$\frac{(\sqrt{efhi} + \sqrt{bc}(g - \tau_1^{-1}))(\sqrt{hi}(d + g - \tau_1^{-1} - \tau_3^{-1}) - \sqrt{bc\,ef})}{(\sqrt{efhi} + \sqrt{bc}(g - \tau_2^{-1}))(\sqrt{hi}(d + g - \tau_2^{-1} - \tau_3^{-1}) - \sqrt{bc\,ef})}$$

No attempt was made to directly convert the five curve parameters of triexponential decay curves to the six coefficients a, d, g, bc, ef and hi because no unique relationship is possible for all of them. An exception is *a* where equation S68 also applies for model-3. Basically this explains why the k_{OH} and k_2 were found to be identical for model-2 and model-3, as outlined in the main paper.

Note that by setting hi = 0 in equations S94 and S95, equations S65 and S66 are obtained, while setting ef = 0 gives slightly different expressions for the limiting case where add₂ is formed only by isomerization:

$$C_{1/2} = \frac{(d - \tau_1^{-1} + g - \tau_3^{-1})(g - \tau_1^{-1})(\tau_3^{-1} - \tau_2^{-1})}{(d - \tau_2^{-1} + g - \tau_3^{-1})(g - \tau_2^{-1})(\tau_1^{-1} - \tau_3^{-1})}$$
(S96)

$$C_{3/2} = \frac{(d - \tau_3^{-1} + g - \tau_1^{-1})(g - \tau_3^{-1})(\tau_2^{-1} - \tau_1^{-1})}{(d - \tau_2^{-1} + g - \tau_1^{-1})(g - \tau_2^{-1})(\tau_1^{-1} - \tau_3^{-1})}$$
(S97)

S4 Fit functions

As described in the Experimental section of the main paper, the recorded data were count numbers N of photons binned into variable time intervals $[t_1, t_2]$ after the initial formation of OH. The OH concentration is proportional to a timedependent count rate S, i.e. $S(t) \propto [OH](t)$. The background is determined by a time-independent count rate S_B . For a biexponential curve (model-1) this leads to:

$$N(t_{1},t_{2}) = \int_{t_{1}}^{t_{2}} S(t) + S_{B} dt$$
(S98)
= $\int_{t_{1}}^{t_{2}} S_{1} \exp(-t/\tau_{1}) + S_{2} \exp(-t/\tau_{2}) + S_{B} dt$
= $\frac{S_{1}}{\tau_{1}^{-1}} \exp(-t_{2}/\tau_{1}) \{\exp(\Delta t/\tau_{1}) - 1\}$ (S99)
+ $\frac{S_{2}}{\tau_{2}^{-1}} \exp(-t_{2}/\tau_{2}) \{\exp(\Delta t/\tau_{2}) - 1\} + S_{B} \Delta t$

 Δt is the interval $t_2 - t_1$. Moreover, the terms contain a factor $S_0 = S_1 + S_2 \propto C_1 + C_2 = [OH]_0$ that can be cancelled out:

$$N(t_{2},\Delta t) = S_{B}\Delta t + S_{0} \times$$

$$\left[\frac{C_{1/2}}{1+C_{1/2}}\frac{\exp(-t_{2}/\tau_{1})}{\tau_{1}^{-1}}\{\exp(\Delta t/\tau_{1})-1\}$$

$$+\frac{1}{1+C_{1/2}}\frac{\exp(-t_{2}/\tau_{2})}{\tau_{2}^{-1}}\{\exp(\Delta t/\tau_{2})-1\}\right]$$
(S100)

The factors S_0 and S_B , are two additional fit parameters for each curve. The interval width Δt was introduced here explicitly because of the data compression that led to an increase of Δt with t_2 (1.2 ms at the very beginning and stepwise increasing exponentially up to 0.6 s until the end of the observation at 5 s). Normally, a constant Δt can be cancelled out in good approximation if it is small against the lifetimes τ_i :

$$\frac{\exp(\Delta t/\tau_i) - 1}{\tau_i^{-1}} \approx \Delta t \quad \text{for} \quad \Delta t/\tau_i \ll 1$$
 (S101)

In the case of a triexponential curve (e.g. model-2) a corresponding equation applies:

$$N(t_{2},\Delta t) = S_{B}\Delta t + S_{0} \times$$
(S102)
$$\left[\frac{C_{1/2}}{1 + C_{1/2} + C_{3/2}} \frac{\exp(-t_{2}/\tau_{1})}{\tau_{1}^{-1}} \{\exp(\Delta t/\tau_{1}) - 1\} + \frac{1}{1 + C_{1/2} + C_{3/2}} \frac{\exp(-t_{2}/\tau_{2})}{\tau_{2}^{-1}} \{\exp(\Delta t/\tau_{2}) - 1\} + \frac{C_{3/2}}{1 + C_{1/2} + C_{3/2}} \frac{\exp(-t_{2}/\tau_{3})}{\tau_{3}^{-1}} \{\exp(\Delta t/\tau_{3}) - 1\}\right]$$

S5 Numerical simulations

The absolute differences of the fitted model-1 and model-2 curves in Fig. 1 of the main paper are admittedly minor. On the other hand, the observed values of χ^2 /DOF clearly indicate the advantage of model-2 and model-3 fits. To rule out that these improvements were caused by the greater flexibility of triexponential curves to compensate the effects of interfering radical-radical reactions or diffusion processes, we made numerical simulations with a FACSIMILE based IDL application⁸. These simulations were also used to learn more about mutual dependencies of fit parameters and their errors.

S5.1 Radical-radical reactions

An extended, partly hypothetical mechanism was applied to consider the effects of radical-radical reactions. Corresponding rate constants are summarized in Table S1. The underlying base mechanisms B1 and B2 refer to model-1 and model-2 under conditions of experiment 10 (Table 1, main paper), leading to ideal biexponential and triexponential decay curves, respectively. Radical-radical reactions were considered by the extended mechanism E in Table S1. Literature data for reactions E04–E06 and E09–E16 were not available and were assumed to be fast, with a rate constants of $5 \times 10^{-11} \text{ cm}^3 \text{s}^{-1}$.

Inclusion of the reactions of E at starting concentrations $[OH]_0=[H]_0=1\times10^{10}$ cm⁻³ and also taking into account photolysis products of 1,3,5-TMB (Experimental section, main paper), led to slightly different OH decay behaviour, dependent on 1,3,5-TMB concentrations. In order to assess these differences quantitatively in terms of the fit procedure applied in this work, we further processed the calculated OH concentration data to simulate the actual measurements as follows. First, the OH concentrations were converted to count rates matching those of experiment 10 including the measured background count rate. Second, count rates were interpolated to measurement times and multiplied by interval widths to obtain count numbers. Third, random noise was added dependent on count numbers according to the Poisson distribution.

Fourth, the procedure was repeated and count numbers were accumulated to simulate repeated measurements. The resulting data for different 1,3,5-TMB concentrations were then analyzed using the same fitting procedure as for the experimental data. It was found that repeated simulations of that kind led to some variations in fit parameters and fit qualities, as would also be the case for real measurements. Measurement simulations and fits were therefore repeated 100 times to obtain mean values and standard deviations of all fit parameters. These results are listed in Table S2.

In a first test the data from the base mechanism B1 in Table S1 were used. Model-1 and model-2 fits gave the same results in accordance with the simulation inputs (compare B1 entries for model-1 and model-2 in Table S2). Differences of fit results and qualities were insignificant. Thus model-2 fits converged to model-1 because experimental scatter cannot be compensated by the additional adjustable parameters of model-2. However, occasionally model-2 fits failed to converge to physically meaningful values, i.e. positive rate constants. The results χ^2 /DOF \approx 1.0 for both models confirm that the simulated experimental scatter was considered correctly in the fits.

In a second test the data from the mechanism B1+E including radical-radical reactions were fitted. Model-1 and model-2 gave similar results with minor differences (Table S2). The fit quality of model-1 was somewhat poorer with $\chi^2/\text{DOF}\approx 1.1$ and fitted rate constants were lower than the simulation inputs by 3-4%. Thus, we cannot exclude that radical-radical reactions could have a minor influence under the conditions of this work. The model-2 fit results show that the small deviations produced by the radical-radical reactions can indeed be compensated by model-2 as indicated by the unchanged fit quality for B1+E. The result corresponds to an about 4% yield of an apparent second adduct with a slower loss rate constant. However, the effect is much too small to explain the experimentally found differences of OH rate constants and fit qualities. This is demonstrated in Fig. S1, where the resulting residuals of measured and simulated decay curves are plotted. These residuals correspond to the differences between measurements (or simulations) and fits as in Fig. 1 of the main paper. In contrast to the experimental residuals obtained with model-1 (left hand, upper panel), the effect of the radical-radical reactions on the simulated model-1 curves (left hand, middle panel) is minor in accordance with the small increase of χ^2 /DOF.

In a third test the data from the base mechanism B2 were fitted. In this case the fit quality of model-1 decreased strongly to $\chi^2/\text{DOF}\approx 2.3$ while that for model-2 expectedly remained at unity and gave the correct results. Finally, the data of the B2+E mechanism were used. This led to a further slight decrease of the fit quality of model-1 while that of model-2 remained unchanged, i.e. the effects of radical-radical reactions were again compensated by model-2. However the rate constants changed insignificantly compared to those obtained with B2. Thus, radical-radical reactions are unlikely to produce the strong deviations observed in the case of model-1 and the estimated effects are well within the experimental error limits. Note also that the experimental residuals for model-1 fits were reproduced very well by the B2 simulations as shown in the lower, left hand panels of Fig. S1.

S5.2 Diffusion processes

To simulate diffusion effects, we assumed a two-dimensional Gaussian type cylindrical concentration profile of OH produced by the flash lamp at t=0 (Experimental section, main paper). This distribution had an estimated FWHM of 5 cm and was constrained to a diameter of 5 cm in the plane of detection caused by the limited size of the entrance window. Only molecular diffusion processes were considered because on the time scale of the experiments, where OH was detectable for less than 1 s, advection was estimated to be negligible at flow velocities well below 1 cm s⁻¹.

A constraint of the numerical model was that only one diffusion coefficient could be applied for all species. We therefore made the worst case assumption that all species exhibit a diffusion coefficient as large as OH in helium under the lowest pressure employed in this work, corresponding to a diffusion coefficient⁹ of about $2.3 \text{ cm}^2\text{s}^{-1}$. Moreover, we assumed that only the centre of the distribution corresponds to the detection zone determined by the overlap of the volume illuminated by the resonance lamp and that observed by the detector. To verify the numerical procedure, we first made simulations for a simpler chemical model producing monoexponential decays in the absence of diffusion. The resulting decay curves including diffusion, based on unlimited one-, two- and three-dimensional Gaussian-type starting distributions, agreed with known analytical solutions for this scenario¹⁰.

The simulations including diffusion were evaluated as described in the previous section. The results are listed in Table S2 and marked with B+D. It turned out that the influence of diffusion on the OH decays is significant but that the fitted rate constants of the base mechanisms B1 and B2 were hardly affected except for the first order loss rate constants of OH and the adducts that were increased by up to 1 s^{-1} . Thus under the employed conditions diffusion losses in good approximation led to an increase of the first-order background loss rate constants but do not alter the overall result by pretending a different chemical mechanism. Finally, simulating diffusion and radical-radical reactions together (B+E+D) by chance resulted in slightly better agreements with the base mechanisms because of apparently compensating effects.

Table S1 Reaction mechanism for numerical simulations to investigate the potential influence of radical-radical reactions on OH decays under conditions of experiment 10 (Table 1). Boundary conditions were $[OH]_0=[H]_0=1\times10^{10}$ cm⁻³ and $[BENZ]_0=1\times10^{-4}\times[TMB]$ from photolysis of H₂O and 1,3,5-TMB, respectively. BENZ = dimethylbenzyl radical, HADD = dimethyl cyclohexadienyl radical from H + TMB. Rate constants of radical-radical reactions that are not available from literature were assumed to be 5×10^{-11} cm³s⁻¹.

| | reaction | rate constant | reference/note |
|-----|--------------------------------------|---|--|
| | Base mechanism B1 (model- | 1) | |
| B11 | $OH + TMB \rightarrow ADD$ | $4.4 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ | Table 1 |
| B12 | $OH + TMB \rightarrow BENZ$ | $2.2 \times 10^{-12} \text{cm}^3 \text{s}^{-1}$ | Table 1, Atkinson ¹¹ |
| B13 | $ADD \rightarrow OH + TMB$ | 40 s^{-1} | Table 1 |
| B14 | $OH \rightarrow prod.$ | 5.0 s^{-1} | Table 1 |
| B15 | ADD \rightarrow prod. | $3.0 \ s^{-1}$ | Table 1, Table 4 |
| | Base mechanism B2 (model-2 | 2) | |
| B21 | $OH + TMB \rightarrow ADD1$ | $4.7 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ | Table 2 |
| B22 | $OH + TMB \rightarrow ADD2$ | $5.5 \times 10^{-12} \text{cm}^3 \text{s}^{-1}$ | Table 2 |
| B23 | $OH + TMB \rightarrow BENZ$ | $2.2 \times 10^{-12} \text{cm}^3 \text{s}^{-1}$ | Table 2, Atkinson ¹¹ |
| B24 | $ADD1 \rightarrow OH + TMB$ | 57 s^{-1} | Table 2 |
| B25 | $ADD2 \rightarrow OH + TMB$ | $6 \mathrm{s}^{-1}$ | Table 2 |
| B26 | $OH \rightarrow prod.$ | 5.0 s^{-1} | Table 2 |
| B27 | ADD1 \rightarrow prod. | 3.0 s^{-1} | Table 2, Table 4 |
| B28 | ADD2 \rightarrow prod. | 3.0 s^{-1} | Table 2, Table 4 |
| | Extended mechanism E (mod | el-1, model-2) | |
| E01 | $OH + OH \rightarrow prod.$ | $5.2 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1} a$ | Sander <i>et al.</i> ¹² |
| E02 | ADD1,2 + ADD1,2 \rightarrow prod. | $5.0 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ b | Bohn ¹³ |
| E03 | BENZ + BENZ \rightarrow prod. | $4.0 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ | Müller-Markgraf and Troe ¹⁴ |
| E04 | OH + ADD1,2 \rightarrow prod. | $5.0 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ | assumed |
| E05 | $OH + BENZ \rightarrow prod.$ | $5.0 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ | assumed |
| E06 | ADD1,2 + BENZ \rightarrow prod. | $5.0 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ | assumed |
| E07 | $\rm H + TMB {\rightarrow} \rm HADD$ | $7.0 \times 10^{-13} \text{cm}^3 \text{s}^{-1} d$ | Sauer and Mani ¹⁵ , Triebert et al. ¹⁶ |
| E08 | $H + BENZ \rightarrow prod.$ | $5.0 \times 10^{-10} \text{cm}^3 \text{s}^{-1}$ | Baulch et al. 17, Ackermann et al. 18 |
| E09 | $H + OH \rightarrow prod.$ | $1.1 \times 10^{-12} \text{cm}^3 \text{s}^{-1}$ | Baulch <i>et al.</i> ¹⁷ |
| E10 | $H + H \rightarrow prod.$ | $1.0 \times 10^{-13} \text{cm}^3 \text{s}^{-1} e$ | Baulch <i>et al.</i> ¹⁷ |
| E11 | $H + HADD \rightarrow prod.$ | $5.0 \times 10^{-11} \text{cm}^3 \text{s}^{-1}$ | assumed |
| E12 | H + ADD1,2 \rightarrow prod. | $5.0 \times 10^{-11} \text{cm}^3 \text{s}^{-1}$ | assumed |
| E13 | HADD + OH \rightarrow prod. | $5.0 \times 10^{-11} \text{cm}^3 \text{s}^{-1}$ | assumed |
| E14 | HADD + ADD1, $2 \rightarrow$ prod. | $5.0 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ | assumed |
| E15 | HADD + BENZ \rightarrow prod. | $5.0 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ | assumed |
| E16 | HADD + HADD \rightarrow prod. | $5.0 \times 10^{-11} \text{cm}^3 \text{s}^{-1}$ | assumed |
| E17 | $H \rightarrow prod.$ | 5.0 s^{-1} | assumed |
| E18 | HADD \rightarrow prod. | 3.0 s^{-1} | assumed |
| E19 | $BENZ \rightarrow prod.$ | 3.0 s^{-1} | assumed |

^{*a*} Rate constant for N₂ buffer gas. ^{*b*} Rate constant for OH-toluene adducts. ^{*c*} Rate constant for benzyl radicals. ^{*d*} Estimated from benzene, toluene and xylene rate constants. ^{*e*} Literature data range between 0.5×10^{-13} and 2×10^{-13} cm³s⁻¹.

Table S2 Model-1 and model-2 fit results and standard deviations from simultaneous fits to six simulated OH decay curves according to the reaction mechanisms in Table S1 at different 1,3,5-TMB concentrations under conditions of experiment 10 (Table 1, main paper). Standard deviations result from fits to 100 simulated measurements with random noise for each set of simulated OH decay curves. The agreement of the fits with the input is taken as a validation of the respective model. B = base mechanism, B+E = base + extended mechanism, B+D = base mechanism + diffusion, B+E+D = base + extended mechanism + diffusion.

| model-1 | <i>k</i> ₂ | $k_{1a} + k_{1b}$ | $k_{1a}k_{-1a}$ | _ | $k_{-1a} + k_3$ | _ | |
|-----------------------|-----------------------|--|--|--|---------------------|---------------------|-----------------|
| model-2 | k_2 | $k_{11a} + k_{12a} + k_{1b}$ | $k_{11a}k_{-11a}$ | $k_{12a}k_{-12a}$ | $k_{-11a} + k_{31}$ | $k_{-12a} + k_{32}$ | |
| | / s ⁻¹ | $/ 10^{-11} \mathrm{cm}^3 \mathrm{s}^{-1}$ | $/ 10^{-10} \mathrm{cm}^3 \mathrm{s}^{-2}$ | $/ 10^{-10} \mathrm{cm}^3 \mathrm{s}^{-2}$ | $/ { m s}^{-1}$ | $/ { m s}^{-1}$ | χ^2 /DOF |
| input B1 ^a | 5.0 | 4.62 | 17.6 | _ | 43.0 | _ | |
| | model-1 | | | | | | |
| B1 | $5.01 {\pm} 0.05$ | $4.59{\pm}0.08$ | $17.5 {\pm} 0.5$ | _ | $43.1{\pm}0.5$ | _ | $1.00{\pm}0.09$ |
| B1+E | $5.03{\pm}0.05$ | $4.46{\pm}0.08$ | $16.0 {\pm} 0.4$ | _ | $41.4{\pm}0.5$ | _ | $1.09{\pm}0.08$ |
| B1+D | $5.99 {\pm} 0.06$ | $4.65 {\pm} 0.07$ | $18.1 {\pm} 0.4$ | — | $44.9{\pm}0.5$ | _ | $1.00{\pm}0.08$ |
| B1+E+D | $6.00{\pm}0.06$ | $4.52{\pm}0.08$ | $16.6{\pm}0.6$ | _ | $43.1 {\pm} 0.5$ | _ | $1.01{\pm}0.08$ |
| | model-2 | | | | | | |
| B1 | $5.03{\pm}0.05$ | $4.59{\pm}0.08$ | $17.5 {\pm} 0.5$ | $-0.00{\pm}0.01$ | $43.0{\pm}0.6$ | $0.6{\pm}1.5$ | $0.99{\pm}0.08$ |
| B1+E | $5.02{\pm}0.05$ | $4.60 {\pm} 0.09$ | $17.3 {\pm} 0.6$ | $0.2{\pm}0.3$ | 45.1±1.6 | $11.0{\pm}4.5$ | $1.00{\pm}0.07$ |
| B1+D | $6.01{\pm}0.06$ | $4.65 {\pm} 0.07$ | $18.2 {\pm} 0.5$ | $0.3{\pm}0.3$ | $45.0{\pm}0.6$ | $0.1 {\pm} 0.9$ | $1.00{\pm}0.08$ |
| B1+E+D | $6.02{\pm}0.07$ | $4.54{\pm}0.09$ | $16.9{\pm}0.6$ | $0.1{\pm}0.6$ | 44.1±1.9 | $3.3{\pm}5.9$ | $1.00{\pm}0.08$ |
| input B2 ^a | 5.0 | 5.47 | 26.8 | 0.33 | 60.0 | 9.0 | |
| | model-1 | | | | | | |
| B2 | $5.05{\pm}0.06$ | $4.65 {\pm} 0.11$ | $17.7 {\pm} 0.7$ | _ | $43.8{\pm}0.7$ | _ | $2.29{\pm}0.15$ |
| B2+E | $5.09{\pm}0.06$ | $4.61 {\pm} 0.11$ | $17.0 {\pm} 0.7$ | _ | $43.6{\pm}0.7$ | _ | $2.48{\pm}0.13$ |
| B2+D | $6.03 {\pm} 0.07$ | $4.91 {\pm} 0.09$ | $20.1 {\pm} 0.7$ | _ | $48.1 {\pm} 0.7$ | _ | $1.58{\pm}0.11$ |
| B2+E+D | $6.06{\pm}0.08$ | $4.79 {\pm} 0.10$ | $18.8{\pm}0.7$ | _ | $47.2{\pm}0.8$ | _ | $1.72{\pm}0.11$ |
| | model-2 | | | | | | |
| B2 | $5.01 {\pm} 0.06$ | $5.46 {\pm} 0.13$ | $26.9{\pm}1.1$ | $0.35{\pm}0.07$ | $60.4{\pm}1.5$ | $9.2{\pm}0.8$ | $0.99{\pm}0.07$ |
| B2+E | $5.04{\pm}0.06$ | 5.47±0.13 | $26.8 {\pm} 1.1$ | $0.34{\pm}0.06$ | $61.4{\pm}1.5$ | $8.7{\pm}0.7$ | $1.00{\pm}0.08$ |
| B2+D | $5.99{\pm}0.07$ | $5.45 {\pm} 0.13$ | 26.6±1.3 | $0.30{\pm}0.10$ | 60.1±2.3 | 9.8±1.7 | $1.01{\pm}0.09$ |
| B2+E+D | $6.02{\pm}0.08$ | $5.40{\pm}0.12$ | $26.0{\pm}1.2$ | $0.32{\pm}0.10$ | $60.9 {\pm} 2.2$ | 9.6±1.5 | $1.00{\pm}0.10$ |

^{*a*} Rate constant input to numerical simulation, Table S1.

1–15



Fig. S1 Normalized residuals of four curves of experiment 10 with 1,3,5-TMB (323 K, 380 mbar). The differences between all data points and fitted curves as shown in Fig. 1 (main paper) were plotted as a function of time. Upper panels: model-1 and model-2 fits to experimental data. Middle panels: model-1 and model-2 fits to simulated data of base mechanism B1+E, including radical-radical reactions (Table S1). Lower panels: model-1 and model-2 fits to simulated data of base mechanism B2+E, including radical-radical reactions (Table S1). Lower panels: model-1 and model-2 fits to simulated data of base mechanism B2+E, including radical-radical reactions (Table S1). The corresponding fit parameters and qualities are given in Table S2, see B1+E and B2+E entries. The chosen examples correspond to the listed means in Table S2.

S5.3 Parameter correlations and error estimates

The simulated measurements of base mechanisms B1 and B2 were also used to investigate the mutual dependencies of the fit parameters and to check if the error estimates obtained from the experimental data are reasonable. Table S3 and S4 contain the correlation matrices of the parameters obtained from fits to 100 simulated experiments each. These data show that except for k_2 the parameters are highly correlated with positive coefficients. Consequently, also the error limits listed in Tables 1 and 2 of the main paper are not independent of each other. In the further data analysis where ratios of the parameters were evaluated, we therefore considered maximum and minimum values together in order to avoid an overestimate of the influence of the error limits.

As to the error estimates themselves, that were derived as described in the Data Analysis section of the main paper, it was found that their means are roughly a factor of three greater than the standard deviations listed in Table S2 for B1 (model-1) and B2 (model-2). The error estimates in Tables 1 and 2 are therefore conservative and should cover additional uncertainties connected with single measurements, as well as any effect associated with radical-radical reactions or diffusion effects.

S6 1,2,3-TMB and 1,2,4-TMB measurements

With the other two TMB isomers similar sets of measurements were performed as for 1,3,5-TMB. Experimental conditions, as well as model-1 and model-2 fit results are listed in Tables S5 and S6 and plotted in Figs. S2 and S3. Qualitatively the improvement of fit qualities with model-2 at temperatures above about 300 K is comparable to that obtained with 1,3,5-TMB. Moreover, the decrease of OH rate constants with temperature is again much less pronounced for model-2 leading to differences of up to a factor of two at the highest temperatures employed. The model-2 k_{OH} temperature dependencies can be described by the Arrhenius expressions given in Table 3 of the main paper. As was also indicated in the main paper, the apparently effective triexponential OH decays for 1,2,3-TMB and 1,2,4-TMB can be rationalized by the assumption that two groups of adduct isomers with different properties are be formed. However, given the fact that already the two adduct isomers of 1,3,5-TMB made the data analysis extremely complicated and partly ambiguous, no further interpretation of the fit results for 1,2,3-TMB and 1,2,4-TMB was attempted. On the other hand, the k_{OH} are expected to be insensitive towards minor adjustments associated with the presence of more than two adduct isomers.

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| parameter | <i>k</i> ₂ | $k_{1a} + k_{1b}$ | $k_{1a}k_{-1a}$ | $k_{-1a} + k_3$ |
|-----------------------|-----------------------|-------------------|-----------------|-----------------|
| <i>k</i> ₂ | 1.0 | -0.20 | -0.15 | -0.11 |
| $k_{1a} + k_{1b}$ | -0.20 | 1.0 | 0.94 | 0.67 |
| $k_{1a}k_{-1a}$ | -0.15 | 0.94 | 1.0 | 0.89 |
| $k_{-1a} + k_3$ | -0.11 | 0.67 | 0.89 | 1.0 |

Table S3 Correlation matrix of model-1 parameters obtained from fits to 100 simulated measurements of the B1 base mechanism.

Table S4 Correlation matrix of model-2 parameters obtained from fits to 100 simulated measurements of the B2 base mechanism.

| parameter | k_2 | $k_{11a} + k_{12a} + k_{1b}$ | $k_{11a}k_{-11a}$ | $k_{12a}k_{-12a}$ | $k_{-11a} + k_{31}$ | $k_{-12a} + k_{32}$ |
|------------------------------|-------|------------------------------|-------------------|-------------------|---------------------|---------------------|
| k2 | 1.0 | -0.29 | -0.23 | -0.14 | -0.18 | -0.11 |
| $k_{11a} + k_{12a} + k_{1b}$ | -0.29 | 1.0 | 0.94 | 0.29 | 0.63 | 0.20 |
| $k_{11a}k_{-11a}$ | -0.23 | 0.94 | 1.0 | 0.41 | 0.83 | 0.31 |
| $k_{12a}k_{-12a}$ | -0.14 | 0.29 | 0.41 | 1.0 | 0.74 | 0.97 |
| $k_{-11a} + k_{31}$ | -0.18 | 0.63 | 0.83 | 0.74 | 1.0 | 0.65 |
| $k_{-12a} + k_{32}$ | -0.11 | 0.20 | 0.31 | 0.97 | 0.65 | 1.0 |

| | T/K | <i>p/</i> hPa | [aromatic]/ | т | <i>k</i> ₂ | $k_{1a} + k_{1b}$ | $k_{1a}k_{-1a}$ | $k_{-1a} + k_3$ | | |
|-----------------------|----------|---------------|-------------------------|----|-----------------------|--|--|-----------------------|-----|---------------|
| # | | | $10^{12} {\rm cm}^{-3}$ | | $/ { m s}^{-1}$ | $/ 10^{-11} \mathrm{cm}^3 \mathrm{s}^{-1}$ | $/ 10^{-10} \mathrm{cm}^3 \mathrm{s}^{-2}$ | $/ { m s}^{-1}$ | DOF | χ^2 /DOF |
| | 1,2,3-tr | imethylb | enzene | | | | | | | |
| 1 | 275.7 | 750 | 0.5-5.7 | 7 | 12.9±1.3 | $3.49\pm^{0.16}_{0.15}$ | $0.29\pm^{0.28}_{0.16}$ | $8.4\pm^{9.1}_{4.9}$ | 409 | 1.29 |
| 2 | 283.2 | 380 | 0.5-5.2 | 8 | $12.9{\pm}1.2$ | $3.15\pm^{0.13}_{0.12}$ | $0.38\pm^{0.14}_{0.11}$ | $5.7\pm^{2.5}_{1.8}$ | 468 | 1.85 |
| 3 | 289.8 | 380 | 0.5-5.2 | 8 | $10.8{\pm}0.9$ | $3.09\pm^{0.11}_{0.11}$ | $0.57\pm^{0.13}_{0.11}$ | $6.6\pm^{1.5}_{1.3}$ | 468 | 1.71 |
| 4 | 295.0 | 380 | 0.5-5.7 | 7 | $8.7{\pm}0.9$ | $3.05\pm^{0.12}_{0.12}$ | $0.66\pm^{0.18}_{0.14}$ | $7.8\pm^{2.2}_{1.7}$ | 409 | 1.39 |
| 5 | 295.5 | 750 | 0.5-5.7 | 7 | $9.5{\pm}0.8$ | $3.02\pm^{0.11}_{0.10}$ | $0.74\pm^{0.18}_{0.15}$ | $8.4\pm^{2.0}_{1.6}$ | 409 | 1.43 |
| 6 | 297.3 | 380 | 1.0-5.7 | 6 | 9.8±1.3 | $2.88\pm^{0.10}_{0.10}$ | $0.83\pm^{0.14}_{0.12}$ | $9.4\pm^{1.6}_{1.4}$ | 350 | 1.55 |
| 7 | 297.4 | 750 | 0.5-3.8 | 8 | $7.8 {\pm} 1.0$ | $2.78\pm^{0.13}_{0.12}$ | $0.69\pm^{0.19}_{0.14}$ | $8.0\pm^{2.1}_{1.7}$ | 468 | 1.28 |
| 8 | 302.2 | 380 | 0.5-5.2 | 8 | $8.5{\pm}0.7$ | $2.66\pm^{0.09}_{0.09}$ | $0.81\pm^{0.13}_{0.11}$ | $7.5\pm^{1.1}_{1.0}$ | 468 | 2.18 |
| 9 | 309.9 | 380 | 0.5-5.2 | 8 | $7.8{\pm}0.7$ | $2.38\pm^{0.10}_{0.09}$ | $0.95\pm^{0.12}_{0.11}$ | $7.3\pm^{0.8}_{0.7}$ | 468 | 3.22 |
| 10 | 317.8 | 380 | 0.5-5.2 | 8 | $7.2{\pm}0.5$ | $2.07\pm^{0.09}_{0.09}$ | $1.27\pm^{0.14}_{0.13}$ | $9.4\pm^{0.7}_{0.7}$ | 468 | 3.12 |
| 11 | 324.3 | 750 | 0.5–4.7 | 11 | $5.9{\pm}0.3$ | $1.93\pm^{0.08}_{0.08}$ | $1.93\pm^{0.18}_{0.17}$ | $14.4\pm^{0.8}_{0.8}$ | 645 | 2.12 |
| 12 | 331.1 | 750 | 0.5–4.8 | 10 | $5.8{\pm}0.2$ | $1.76\pm^{0.08}_{0.08}$ | $2.87\pm^{0.29}_{0.25}$ | $23.0\pm^{1.2}_{1.1}$ | 586 | 1.90 |
| 13 | 337.4 | 750 | 0.5-5.0 | 6 | $5.8{\pm}0.2$ | $1.71\pm^{0.11}_{0.11}$ | $4.70\pm^{0.65}_{0.55}$ | $37.5\pm^{2.3}_{2.2}$ | 350 | 1.38 |
| 14 | 338.3 | 380 | 0.9–4.8 | 11 | $6.0{\pm}0.2$ | $1.62\pm^{0.08}_{0.08}$ | $4.54\pm^{0.48}_{0.43}$ | $38.1\pm^{2.0}_{1.9}$ | 645 | 2.14 |
| | 1,2,4-tr | imethylb | enzene | | | | | | | |
| 1 | 273.4 | 380 | 0.5–5.3 | 12 | $13.2{\pm}1.3$ | $3.80\pm^{0.17}_{0.17}$ | $0.28\pm^{0.28}_{0.14}$ | $5.7\pm^{8.4}_{3.4}$ | 704 | 1.16 |
| 2 | 278.6 | 380 | 0.5-5.2 | 6 | $12.6{\pm}1.3$ | $3.75\pm^{0.15}_{0.15}$ | $0.45\pm^{0.17}_{0.13}$ | $5.9\pm^{2.6}_{1.9}$ | 350 | 1.25 |
| 3 | 283.8 | 380 | 0.5-5.2 | 6 | $12.3 {\pm} 1.2$ | $3.66\pm^{0.15}_{0.14}$ | $0.49\pm^{0.13}_{0.10}$ | $4.1\pm^{1.4}_{1.1}$ | 350 | 1.26 |
| 4 | 289.7 | 380 | 0.5-5.2 | 6 | $9.2{\pm}1.0$ | $3.52\pm^{0.14}_{0.14}$ | $0.84\pm^{0.15}_{0.12}$ | $5.8\pm^{1.0}_{0.9}$ | 350 | 1.22 |
| 5 | 292.6 | 380 | 0.5-5.2 | 6 | $9.5{\pm}0.8$ | $3.40\pm^{0.12}_{0.12}$ | $1.05\pm^{0.15}_{0.13}$ | $6.8\pm^{0.9}_{0.8}$ | 350 | 1.42 |
| 6 | 297.9 | 380 | 0.8–5.5 | 7 | 8.1±1.3 | $3.12\pm^{0.13}_{0.12}$ | $1.37\pm^{0.18}_{0.16}$ | $9.0\pm^{1.0}_{0.9}$ | 409 | 1.60 |
| 7 | 297.9 | 750 | 0.8–5.7 | 16 | $7.2{\pm}1.1$ | $2.98\pm^{0.11}_{0.10}$ | $1.40\pm^{0.15}_{0.13}$ | $9.0\pm^{0.9}_{0.8}$ | 940 | 1.50 |
| 8 ^{<i>a</i>} | 304.2 | 750 | 0.7–5.6 | 8 | 6.1±1.3 | $2.58\pm^{0.21}_{0.20}$ | $1.64\pm^{0.36}_{0.29}$ | $9.7\pm^{1.6}_{1.3}$ | 468 | 2.06 |
| 9 | 314.0 | 750 | 0.7–5.6 | 8 | $6.7{\pm}0.8$ | $1.98\pm^{0.19}_{0.17}$ | $1.96\pm^{0.43}_{0.36}$ | $13.9\pm^{1.9}_{1.6}$ | 468 | 8.05 |
| 10 | 321.3 | 380 | 0.8–5.4 | 7 | $7.1 {\pm} 0.7$ | $1.66\pm^{0.17}_{0.15}$ | $2.13\pm^{0.46}_{0.37}$ | $17.6\pm^{1.9}_{1.8}$ | 409 | 5.18 |
| 11 | 332.4 | 750 | 0.7–5.5 | 8 | $6.2{\pm}0.4$ | $1.25\pm^{0.04}_{0.28}$ | $3.14\pm^{0.24}_{1.27}$ | $33.9\pm^{1.7}_{7.0}$ | 468 | 3.24 |
| 12 | 337.8 | 380 | 1.6–9.2 | 7 | $7.6{\pm}0.6$ | $1.22\pm^{0.14}_{0.12}$ | $4.31\pm^{1.01}_{0.80}$ | $48.1\pm^{4.8}_{4.4}$ | 409 | 2.21 |
| 13 | 340.7 | 380 | 0.8–5.3 | 7 | $6.9{\pm}0.3$ | $1.10\pm^{0.10}_{0.15}$ | $3.47\pm^{0.70}_{0.94}$ | $45.7\pm^{4.3}_{6.0}$ | 409 | 2.15 |

Table S5 Summary of experimental conditions and biexponential model-1 fit results for experiments with 1,2,3-TMB and 1,2,4-TMB. Right: Temperatures T, total pressures p of He, range of reactant concentrations, and number m of OH decay curves recorded. Left: Fit results and estimated error limits from simultaneous fits to the m decay curves at different aromatics concentrations.

^a flash-lamp energy lowered by a factor of two

| | k_2 | $k_{11a} + k_{12a} + k_{1b}$ | $k_{11a}k_{-11a}$ | $k_{12a}k_{-12a}$ | $k_{-11a} + k_{31}$ | $k_{-12a} + k_{32}$ | | |
|-----------------------|------------------|---|--|--|-------------------------|------------------------|-----|---------------|
| # | $/ { m s}^{-1}$ | $/10^{-11} \mathrm{cm}^3 \mathrm{s}^{-1}$ | $/ 10^{-10} \mathrm{cm}^3 \mathrm{s}^{-2}$ | $/ 10^{-10} \mathrm{cm}^3 \mathrm{s}^{-2}$ | $/ { m s}^{-1}$ | $/ { m s}^{-1}$ | DOF | χ^2 /DOF |
| | 1,2,3-trime | thylbenzene | | | | | | |
| 4 | $8.7{\pm}0.8$ | $3.13\pm^{0.13}_{0.12}$ | $0.89\pm^{0.38}_{0.25}$ | $0.13\pm^{0.15}_{0.07}$ | $16.0\pm^{11.9}_{5.5}$ | $2.1\pm^{2.0}_{1.4}$ | 407 | 1.18 |
| 5 | $9.5{\pm}0.8$ | $3.07\pm^{0.12}_{0.12}$ | $0.89\pm^{0.27}_{0.21}$ | $0.09\pm^{0.14}_{0.05}$ | $13.2\pm^{7.2}_{4.0}$ | $1.7\pm^{2.2}_{1.3}$ | 407 | 1.26 |
| 6 | 9.9±1.3 | $2.93\pm^{0.10}_{0.10}$ | $0.94\pm^{0.21}_{0.21}$ | $0.11\pm^{0.23}_{0.08}$ | $14.6\pm^{9.1}_{3.9}$ | $2.6\pm^{2.9}_{2.2}$ | 348 | 1.33 |
| 7 | $7.7{\pm}0.9$ | $2.92\pm^{0.21}_{0.16}$ | $1.06\pm^{1.29}_{0.47}$ | $0.26\pm^{0.25}_{0.18}$ | $24.8\pm^{39.5}_{12.3}$ | $4.1\pm^{2.5}_{2.2}$ | 466 | 1.15 |
| 8 | $8.5{\pm}0.6$ | $2.81\pm^{0.11}_{0.11}$ | $1.23\pm^{0.37}_{0.25}$ | $0.23\pm^{0.13}_{0.10}$ | $19.4\pm^{8.6}_{5.4}$ | $3.1\pm^{1.1}_{1.1}$ | 466 | 1.46 |
| 9 | $7.7{\pm}0.5$ | $2.66\pm^{0.11}_{0.10}$ | $1.71\pm^{0.43}_{0.31}$ | $0.33\pm^{0.11}_{0.09}$ | $22.9\pm^{7.1}_{5.0}$ | $3.7\pm^{0.7}_{0.7}$ | 466 | 1.54 |
| 10 | $6.9{\pm}0.3$ | $2.55\pm^{0.18}_{0.15}$ | $3.32\pm^{1.55}_{0.92}$ | $0.71\pm^{0.14}_{0.15}$ | $44.9\pm^{17.2}_{12.2}$ | $6.6\pm^{0.7}_{0.8}$ | 466 | 1.43 |
| 11 | $5.7 {\pm} 0.3$ | $2.51\pm^{0.26}_{0.21}$ | $5.62\pm^{3.87}_{2.04}$ | $1.30\pm^{0.22}_{0.26}$ | $73.9\pm^{33.5}_{23.7}$ | $11.6\pm^{1.0}_{1.1}$ | 643 | 1.21 |
| 12 | $5.7 {\pm} 0.2$ | $2.32\pm^{0.51}_{0.34}$ | $7.72\pm^{14.1}_{4.36}$ | $2.12\pm^{0.48}_{1.20}$ | $110\pm^{101}_{67.5}$ | $19.8\pm^{1.8}_{4.7}$ | 584 | 1.44 |
| 13 | $5.7 {\pm} 0.2$ | $2.20\pm^{1.42}_{0.47}$ | $10.1\pm^{82.3}_{6.78}$ | $3.45\pm^{1.30}_{3.44}$ | $150\pm^{383}_{110}$ | $32.8\pm^{4.2}_{29.0}$ | 348 | 1.27 |
| 14 | $5.8{\pm}0.4$ | $2.20\pm^{0.57}_{0.63}$ | $11.8\pm^{26.3}_{7.34}$ | $3.18\pm^{0.98}_{3.17}$ | $155\pm^{186}_{117}$ | $32.5\pm^{3.6}_{30.5}$ | 643 | 1.70 |
| | 1,2,4-trime | thylbenzene | | | | | | |
| 5 | 14.7±0.9 | $3.36\pm^{0.12}_{0.12}$ | $1.27\pm^{0.18}_{0.17}$ | $0.11\pm^{0.04}_{0.04}$ | $8.4\pm^{1.3}_{1.1}$ | $0.6\pm^{0.2}_{0.2}$ | 348 | 1.22 |
| 6 | $9.8{\pm}1.1$ | $3.24\pm^{0.13}_{0.13}$ | $1.69\pm^{0.25}_{0.21}$ | $0.15\pm^{0.14}_{0.08}$ | $14.4\pm^{3.8}_{2.4}$ | $2.4\pm^{1.3}_{1.0}$ | 407 | 1.07 |
| 7 | $7.3{\pm}1.0$ | $3.10\pm^{0.11}_{0.11}$ | $1.75\pm^{0.24}_{0.21}$ | $0.22\pm^{0.17}_{0.10}$ | $15.8\pm^{4.5}_{2.8}$ | $3.0\pm^{1.3}_{1.1}$ | 938 | 1.05 |
| 8 ^{<i>a</i>} | $5.9{\pm}1.0$ | $2.95\pm^{0.21}_{0.20}$ | $3.05\pm^{0.77}_{0.58}$ | $0.21\pm^{0.12}_{0.08}$ | $21.5\pm^{5.3}_{4.0}$ | $2.8\pm^{0.9}_{0.8}$ | 466 | 1.12 |
| 9 | 6.1±0.4 | $2.73\pm^{0.14}_{0.13}$ | $5.79\pm^{0.87}_{0.73}$ | $0.29\pm^{0.06}_{0.05}$ | $38.3\pm^{4.2}_{3.7}$ | $4.7\pm^{0.5}_{0.5}$ | 466 | 1.30 |
| 10 | $6.6{\pm}0.4$ | $2.68\pm^{0.25}_{0.22}$ | $9.56\pm^{2.77}_{2.0}$ | $0.62\pm^{0.16}_{0.14}$ | $65.6\pm^{13}_{10}$ | $9.0\pm^{1.1}_{1.1}$ | 407 | 1.33 |
| 11 | $6.0{\pm}0.4$ | $2.30\pm^{0.14}_{0.95}$ | $19.0\pm^{3.84}_{14.5}$ | $1.02\pm^{0.36}_{0.88}$ | $134\pm^{25}_{83}$ | $20.1\pm^{3.2}_{10.5}$ | 466 | 1.62 |
| 12 | $6.9{\pm}0.6$ | $2.44\pm^{0.90}_{0.58}$ | $28.9 \pm ^{35.6}_{14.9}$ | $2.01\pm^{1.09}_{0.98}$ | $203\pm^{113}_{76}$ | $32.7\pm^{5.9}_{7.1}$ | 407 | 1.30 |
| 13 | $6.7{\pm}0.5$ | $2.20\pm^{0.90}_{1.22}$ | $25.0\pm^{37.2}_{22.1}$ | $1.30\pm^{0.90}_{1.29}$ | $183\pm^{123}_{140}$ | $29.5\pm^{6.9}_{28.9}$ | 407 | 1.62 |

Table S6 1,2,3-TMB and 1,2,4-TMB triexponential model-2 fit results and estimated error limits from simultaneous fits to *m* decay curves at different aromatics concentrations at T > 290 K. See Table S5 for *m* and experimental conditions.

^{*a*} flash-lamp energy lowered by a factor of two



Fig. S2 Rate constant related fit parameters and fit qualities χ^2 /DOF for 1,2,3-TMB using model-1 (red) and model-2 (black, blue). Open symbols refer to measurements at 380 mbar and filled symbols at 750 mbar. Full lines in the upper three panels correspond to fitted Arrhenius expressions except for the red line in the first panel that shows a previous parametrization from literature.¹⁹. The dashed blue line in the first panel is an Arrhenius fit using model-2 data above 290 K together with model-1 data below 290 K. In the second panel temperature independent contributions of background loss rate constants were assumed. The dashed blue lines on top of the red line in the fourth panel indicate that models converged towards low temperatures. The dashed black line shows a theoretical optimum.



Fig. S3 Rate constant related fit parameters and fit qualities χ^2 /DOF for 1,2,4-TMB using model-1 (red) and model-2 (black, blue). Open symbols refer to measurements at 380 mbar and filled symbols at 750 mbar. Full lines in the upper three panels correspond to fitted Arrhenius expressions except for the red line in the first panel that shows a previous parametrization from literature.¹⁹. The dashed blue line in the first panel is an Arrhenius fit using model-2 data above 290 K together with model-1 data below 290 K. In the second panel temperature independent contributions of background loss rate constants were assumed. The dashed blue lines on top of the red line in the fourth panel indicate that models converged towards low temperatures. The dashed black line shows a theoretical optimum.