

Oxidation of the Benzyl Radical: Mechanism, Thermochemistry, and Kinetics for the Reactions of Benzyl Hydroperoxide

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Abstract: Oxidation of the benzyl radical plays a key role in the autoignition, combustion, and atmospheric degradation of toluene and other alkylated aromatic hydrocarbons. Under relevant autoignition conditions of moderate temperature and high pressure, and in the atmosphere, benzyl reacts with O₂ to form the benzylperoxy radical, and the further oxidation reactions of this radical are not yet fully characterized. In this contribution, we further develop the reaction chemistry, thermodynamics, and kinetics of benzyl radical oxidation, highlighting the important role of benzyl hydroperoxide and the benzoyl (benzyloxy) radical. The benzylperoxy + H reaction mechanism is studied using computational chemistry and statistical reaction rate theory. High-pressure limit rate constants in the barrierless benzylperoxy + H association are obtained from variational transition state theory calculations, with internal rotor contributions. The benzylperoxy + H reaction is seen to produce an activated benzyl hydroperoxide adduct that has 87 kcal mol⁻¹ excess energy over the ground state. We show that this activated adduct proceeds almost exclusively to the benzoyl radical + OH across a wide range of temperature and pressure conditions. Minor reaction paths include benzyl + HO₂, α -hydroxybenzyl + OH, and benzaldehyde + H₂O, each constituting around 1% of the total reaction rate at higher temperatures. Thermal decomposition of benzyl hydroperoxide, formed by hydrogen abstraction reactions in the benzylperoxy radical and at low temperatures in the benzylperoxy + H and benzyl + HO₂ reactions, is also investigated. Decomposition to benzoyl + OH is fast at temperatures of 900 K and above. The contribution of benzyl hydroperoxide chemistry to the ignition and oxidation of alkylated aromatics is discussed. Benzyl radical oxidation chemistry achieves the conversion of toluene to benzaldehyde, aiding autoignition via processes that either release large amounts of energy or form reactive free radicals through chain-branching.

Introduction

Alkylated aromatic hydrocarbons are a major and growing component of liquid transportation fuels, including gasoline and jet fuel. It is important that we understand the ignition and oxidation chemistry of these fuel components across the

range of temperature and pressure conditions encountered in spark ignition and jet engines. Particular uncertainties remain with regards to the chemistry taking place during the autoignition of these alkylated aromatics, where high pressures (tens of atmospheres) and moderate temperatures (ca. 800–1200 K) are encountered. Modeling autoignition behavior is important, for example, in understanding engine knock and NO_x formation and in designing advanced homogeneous charge compression ignition (HCCI) engines. Understanding the low-temperature oxidation chemistry of

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alkylated aromatics in the atmosphere is also of significance, as these compounds are a major component of air pollution in urban environments.

As the parent alkylated aromatic, much attention has been paid to the oxidation of toluene (methylbenzene). It is well-known that the initial stages of toluene oxidation predominantly result in the formation of the benzyl radical.¹ The benzyl radical is thermally stable,² and at low to moderate temperatures it is removed from combustion systems by oxidation reactions with species such as O₂,³ OH,⁴ O,⁵ and HO₂.⁶ Benzyl associates with O₂ to form the benzylperoxy radical in a mildly exothermic reaction (ca. 20 kcal mol⁻¹),³ and the benzylperoxy adduct has little excess energy to go into forward reactions to new, dissociated products. At higher temperatures, the activated benzylperoxy adduct does form some phenol + OH, but it predominantly dissociates back to benzyl + O₂. At lower temperatures and higher pressures, the activated benzylperoxy adduct is stabilized by bath gas collisions and is available to participate in further bimolecular reactions. The benzylperoxy radical is known to undergo a self-reaction to products including two benzoyl radicals + O₂ or to react with HO₂ to form benzyl hydroperoxide + O₂ (an important process in the atmospheric oxidation of toluene).⁷ Benzylperoxy can also abstract a H atom from surrounding hydrocarbons or react with free H atoms to produce the benzyl hydroperoxide molecule. Benzyl hydroperoxide decomposes to the benzoyl radical + OH with a relatively low barrier,⁶ and the benzoyl radical then undergoes chain-propagating decomposition reactions, mainly to benzaldehyde + H.⁸ In competition with bimolecular reactions, the benzylperoxy radical will decompose to benzyl + O₂ with an activation (dissociation) energy of around 20 kcal mol⁻¹. Bimolecular reactions are expected to dominate at low temperatures, where benzylperoxy radical lifetimes are large with respect to thermal decomposition, but they may also be important at higher temperatures, where an equilibrium concentration of benzylperoxy should be established.

In this study, we investigate the kinetics and products of the benzylperoxy + H reaction, using theoretical thermochemical kinetic techniques. The reaction of benzylperoxy with free H atoms should be of significance to fuel-rich flames, where H atoms are found at relatively high concentrations. Kinetics of the benzylperoxy + H association reaction are treated using variational transition state theory. Further reaction of the activated benzyl hydroperoxide adduct is studied as a function of temperature and pressure in master equation simulations, with RRKM theory for $k(E)$, providing branching ratios and apparent rate constants for input to kinetic models. The role of benzyl hydroperoxide chemistry in the oxidation and autoignition of alkylated aromatic hydrocarbons is discussed.

Computational Methods

The G3B3 composite theoretical method is used to study all species.⁹ The G3B3 method uses B3LYP/6-31G(d)-optimized structures and frequencies, with higher-level corrections for accurate energies. All electronic structure calculations are performed using Gaussian 03.¹⁰ G3B3 results for benzyl

hydroperoxide and its decomposition products are taken from a previous study,⁶ while the benzylperoxy radical and transition state structures for H addition are newly studied here. The G3B3 calculations represent a compromise between accuracy and computational efficiency for the relatively large species studied here (nine heavy atoms). Using the G2/97 test set the G3B3 method reproduces a range of thermochemical properties with a root-mean-square error of ± 1.0 kcal mol⁻¹.⁹ Our reported reaction enthalpies and barrier heights are thought to be accurate to ± 2 kcal mol⁻¹ (around two standard deviations). Optimized structures and vibrational frequencies are provided in the Supporting Information for benzylperoxy, benzyl hydroperoxide, and the transition state structures **TS1–TS4**.

The standard enthalpy of formation of the benzylperoxy radical is calculated from an atomization work reaction. Here, the 0 K reaction energy for formation of the atomic constituents in their ground state is first determined, and then the 0 K benzyl hydroperoxide heat of formation is obtained using atom reference enthalpies of 69.977, 51.634, 58.984 kcal mol⁻¹ for the C, O, and H,¹¹ as recently recommended.¹² The 0 K heat of formation is adjusted to 298 K using enthalpy corrections ($H_{298} - H_0$) of 0.251, 1.037, and 1.010 kcal mol⁻¹, for C, O, and H. Entropy and heat capacity values are obtained using statistical mechanics techniques, with the rigid rotor–harmonic oscillator (RRHO) approximation. Vibrational frequencies for rotation about C₆H₅–CH₂OO and C₆H₅CH₂–OO bonds in the benzylperoxy radical were removed from the RRHO analysis and treated as hindered internal rotors using B3LYP/6-31G(d) rotor potentials.

The kinetics of H addition to the peroxy radical site in benzylperoxy is evaluated using variational transition state theory.¹³ The minimum energy potential (MEP) for H addition is calculated at the B3LYP/6-31G(d) level of theory and scaled by the G3B3 reaction enthalpy. Rate constants are calculated as a function of temperature for structures at 0.1 Å intervals along the MEP according to canonical transition state theory, in the program ChemRate.¹⁴ The C–C and C–O internal rotors in the transition state structures are modeled using rotor potentials from the benzylperoxy radical, while the O–O rotor is treated as being similar to that in benzyl hydroperoxide (a single-fold rotor with 6.3 kcal mol⁻¹ barrier).⁶ Rate constants are minimized as a function of position along the MEP to obtain the canonical variational rate constant at each temperature. All structures on the MEP possess a single imaginary frequency, with the mode of vibration corresponding to motion along the bond-breaking coordinate. The use of canonical transition state theory in the variational analysis neglects conservation of angular momentum and is thus expected to provide an upper limit to the true addition rate constant.

Apparent rate constants in the activated benzylperoxy + H reaction mechanism are obtained from master equation simulations, with RRKM theory for $k(E)$, in the ChemRate program. Simulations are performed for pressures between 0.001 and 1000 atm and temperatures between 300 and 2000 K. Collisional energy transfer is described using an exponential-down model, with $\Delta E_{\text{down}} = 500$ cm⁻¹, and the bath gas is N₂. Lennard-Jones parameters used for the C₇H₈O₂

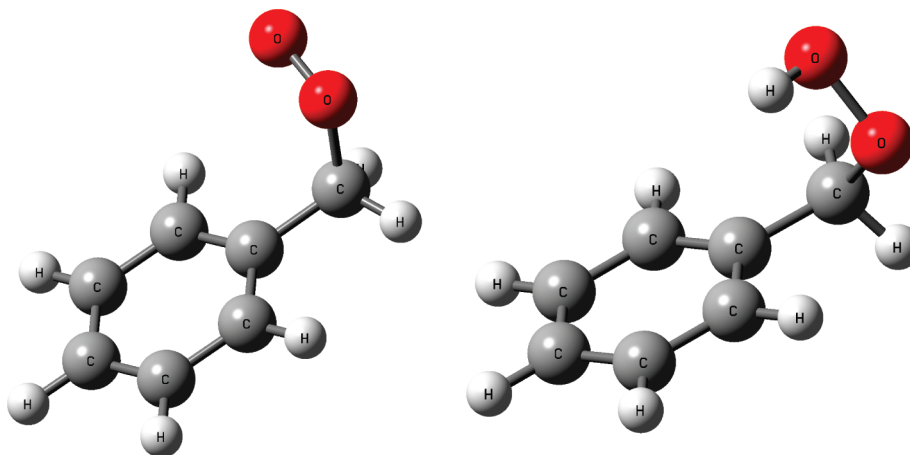


Figure 1. Optimized structures for the benzylperoxy radical and benzyl hydroperoxide (B3LYP/6-31G(d)).

Table 1. Vibrational Frequencies (cm^{-1}) of the Benzylperoxy Radical [B3LYP/6-31G(d)]^a

38.33	89.66	142.48
296.97	319.25	416.74
473.09	512.91	611.95
635.67	712.10	764.54
829.92	855.97	859.73
935.16	969.48	999.90
1005.61	1019.60	1058.54
1121.95	1171.11	1194.77
1215.62	1237.28	1278.88
1361.38	1369.22	1379.85
1503.17	1505.45	1547.22
1645.97	1665.05	3095.08
3156.55	3180.64	3188.42
3198.85	3208.27	3215.64

^a Values listed in bold correspond to internal rotational modes.

species are $\sigma = 7 \text{ \AA}$ and $\epsilon/k_b = 500 \text{ K}$. All rate constants quoted in this study are in s^{-1} or $\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ units, with activation energies in kcal mol^{-1} and temperatures in K.

Results and Discussion

Properties of the Benzylperoxy Radical. The optimized benzylperoxy radical structure is illustrated in Figure 1, compared to that for benzyl hydroperoxide. Vibrational frequencies for benzylperoxy are listed in Table 1. The 38.33 cm^{-1} vibration is attributed to internal rotation about the $\text{C}_6\text{H}_5\text{--CH}_2\text{O}_2$ bond, while the 89.66 cm^{-1} vibration corresponds to rotation around $\text{C}_6\text{H}_5\text{CH}_2\text{--O}_2$, although both internal rotational modes appear significantly coupled. Rotor profiles obtained from relaxed B3LYP/6-31G(d) scans about these C–C and C–O bonds are presented in Figure 2.

Thermochemical properties [$\Delta_f H^\circ_{298}$, S°_{298} , $C_p(T)$] are reported in Table 2 for the benzylperoxy radical, as well all other C_7 and C_6 species in the benzylperoxy + H mechanism (from ref ⁶). Smaller decomposition fragments are modeled using literature thermochemistry.^{15–18} The G3B3 benzylperoxy heat of formation is calculated as $29.6 \text{ kcal mol}^{-1}$, while Fenter et al.^{3b} report a relatively similar value of $28.0 \pm 1.4 \text{ kcal mol}^{-1}$. According to our reported thermochemistry, the benzylperoxy + H reaction is $86.7 \text{ kcal mol}^{-1}$ exothermic. This high exothermicity means that the benzyl hydroperoxide adduct produced in this association process

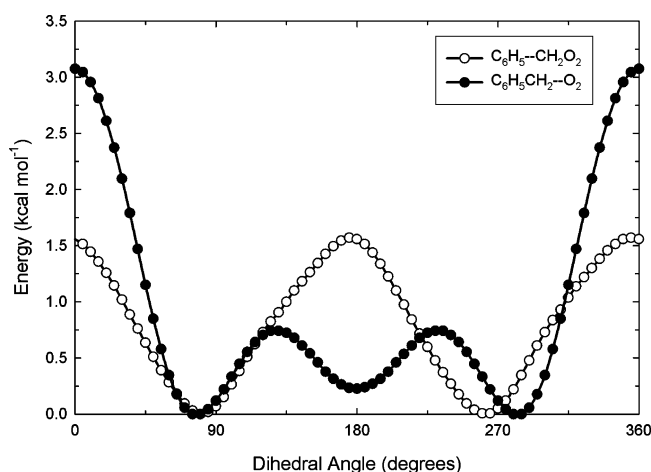


Figure 2. Internal rotor potentials in the benzylperoxy radical [B3LYP/6-31G(d)].

will be highly activated, with more than enough energy to proceed on to new decomposition products.

Variational Analysis. Rate constants for the barrierless benzylperoxy + H addition reaction and the reverse dissociation process have been calculated according to canonical variational transition state theory. The general procedure employed here has been successfully used to calculate rate constants in barrierless H association^{2d,19} and other^{13,20} reactions.

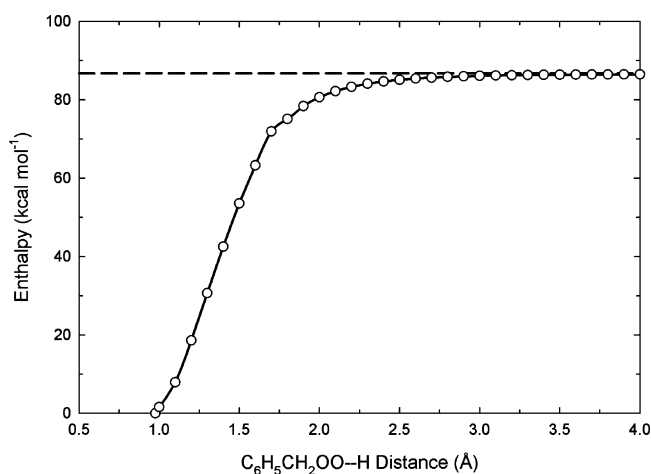
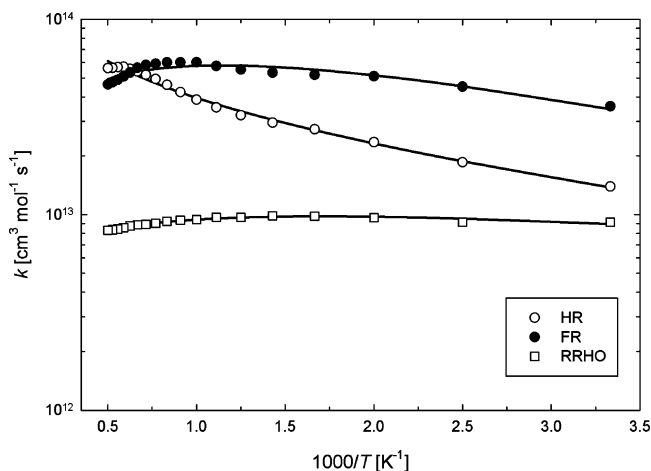
A minimum energy profile for H addition to benzylperoxy, at the G3B3//UB3LYP/6-31G(d) level of theory, is depicted in Figure 3. The dissociation reaction has a loose transition state structure, with energies within 1 kcal mol^{-1} of the dissociated products at O–H bond lengths of 2.8 \AA and greater. A very loose structure is not unexpected for this radical recombination reaction, given the large enthalpy change. Rate constants calculated at each contributing transition state structure are listed in the Supporting Information. The association reaction is found to be controlled by a very loose 3.0 \AA structure at 300 K , tightening to the 2.0 \AA structure at 2000 K . At 2.0 \AA , the transition state energy is $6.1 \text{ kcal mol}^{-1}$ below that of the dissociated products, while at 3.0 \AA it is only $0.7 \text{ kcal mol}^{-1}$ below. Fitting the minimum rate constants to a three-parameter modified Arrhenius equation using a least-squares procedure, we obtain the rate

Table 2. Enthalpies of Formation ($\Delta_f H^\circ_{298}$, kcal mol⁻¹), Entropies (S°_{298} , cal mol⁻¹ K⁻¹), and Heat Capacities [$C_p(T)$, $T = 300$ –2000 K, cal mol⁻¹ K⁻¹] for Selected Species in the Benzylperoxy + H Reaction Mechanism

	$\Delta_f H^\circ_{298}$	S°_{298}	$C_p(300)$	$C_p(400)$	$C_p(500)$	$C_p(600)$	$C_p(800)$	$C_p(1000)$	$C_p(1500)$	$C_p(2000)$
benzylperoxy	29.6	93.218	30.993	39.746	47.207	53.241	62.103	68.231	77.257	81.759
benzyl hydroperoxide	-5.0	93.275	32.699	42.050	50.181	56.802	66.439	72.940	82.225	86.756
benzaldehyde	-8.3	79.021	25.984	33.933	40.804	46.441	54.806	60.557	68.717	72.543
benzynes	111.1	69.075	18.851	24.536	29.302	33.128	38.715	42.553	48.161	50.937
benzoxyl	31.1	84.277	27.994	36.292	43.419	49.233	57.856	63.856	72.685	77.062
α -hydroxybenzyl	11.1	82.855	29.443	37.990	45.069	50.696	58.870	64.536	72.997	77.185

expression k [cm³ mol⁻¹ s⁻¹] = $1.81 \times 10^{12} T^{0.48} \exp(-0.21/T)$ [the reverse rate expression is k [s⁻¹] = $6.97 \times 10^{14} T^{0.01} \exp(-43.73/T)$].

The variational rate constant for benzylperoxy + H is plotted in Figure 4, as a function of temperature. In addition to the hindered rotor (HR) treatment of low-frequency vibrations used here, this rate constant has also been calculated using free rotor (FR) and RRHO treatments, with the results included in Figure 4. The FR rate constants are

**Figure 3.** Minimum energy potential for O–H bond dissociation in benzyl hydroperoxide at the G3B3//UB3LYP/6-31G(d) level. The dashed line indicates the energy of infinitely separated products.**Figure 4.** Variational rate constants for the barrierless benzylperoxy + H reaction, calculated using hindered rotor (HR), free rotor (FR), and rigid rotor–harmonic oscillator (RRHO) treatments. Solid lines represent three-parameter Arrhenius fits.

obtained by treating the C₆H₅CH₂O–OH internal rotor in benzyl hydroperoxide and in the transition state structures as a free rotation, with all remaining modes treated as vibrational frequencies. Because the C–O and C–C rotations are conserved in the reactants, transition states, and products, their treatment should have only a minor effect on the rate constant. In Figure 4 we show that the RRHO treatment provides rate constants that are consistently around 10¹³ cm³ mol⁻¹ s⁻¹ from 300 to 2000 K, with the FR rate constants being higher by around a factor of 5. Rate constants obtained with the HR treatment are intermediate between the other results, being close to the RRHO rate constants at low temperatures (around 2×10^{13} cm³ mol⁻¹ s⁻¹), increasing to be similar to the FR rate constants at higher temperatures (around 5×10^{13} cm³ mol⁻¹ s⁻¹). The HR results are used further in our RRKM modeling of the benzylperoxy + H reaction. We note that, in the temperature range of interest (ca. 1000 K and above), both free and hindered rotor treatment of the internal rotational modes provide rate constants of similar magnitude.

Benzylperoxy + H Kinetics. The benzylperoxy + H reaction process is evaluated using the energy surface depicted in Figure 5 (transition state structures are shown in Figure 6). The activated benzyl hydroperoxide adduct is seen to have sufficient energy to proceed to a range of products, which have been discussed in detail elsewhere.⁶ The lowest-energy pathway available is for the concerted formation of benzoxyl + OH, where the barrier height is 41.1 kcal mol⁻¹ below the entrance channel. Because this is a simple dissociation, without any intrinsic activation barrier, the reaction is entropically favored with a loose transition state structure (i.e., large pre-exponential factor). A second higher-energy pathway to benzoxyl + OH is also depicted (TS1 in Figure 6), which proceeds in a stepwise mechanism via the 3-methoxy-4-hydroxy-2,5-cyclohexadien-1-yl radical, although this reaction channel is not expected to contribute significantly to benzoxyl formation. The next most energetically favored pathway, behind concerted formation of benzoxyl + OH, is H₂O elimination to benzaldehyde (TS2). This reaction requires a barrier that is 40.6 kcal mol⁻¹ below the entrance channel, although the tight transition state structure results in a small pre-exponential factor. Other product sets considered include α -hydroxybenzyl (C₆H₅C•HOH) + OH (TS3), benzyne (C₆H₄) + HCHO + H₂O (TS4, which proceeds to the unstable C₆H₄CH₂O intermediate), and benzyl + HO₂. The reaction to benzyl + HO₂ requires the largest barrier of any of the forward reaction paths (26.3 kcal mol⁻¹ below the entrance channel); however,

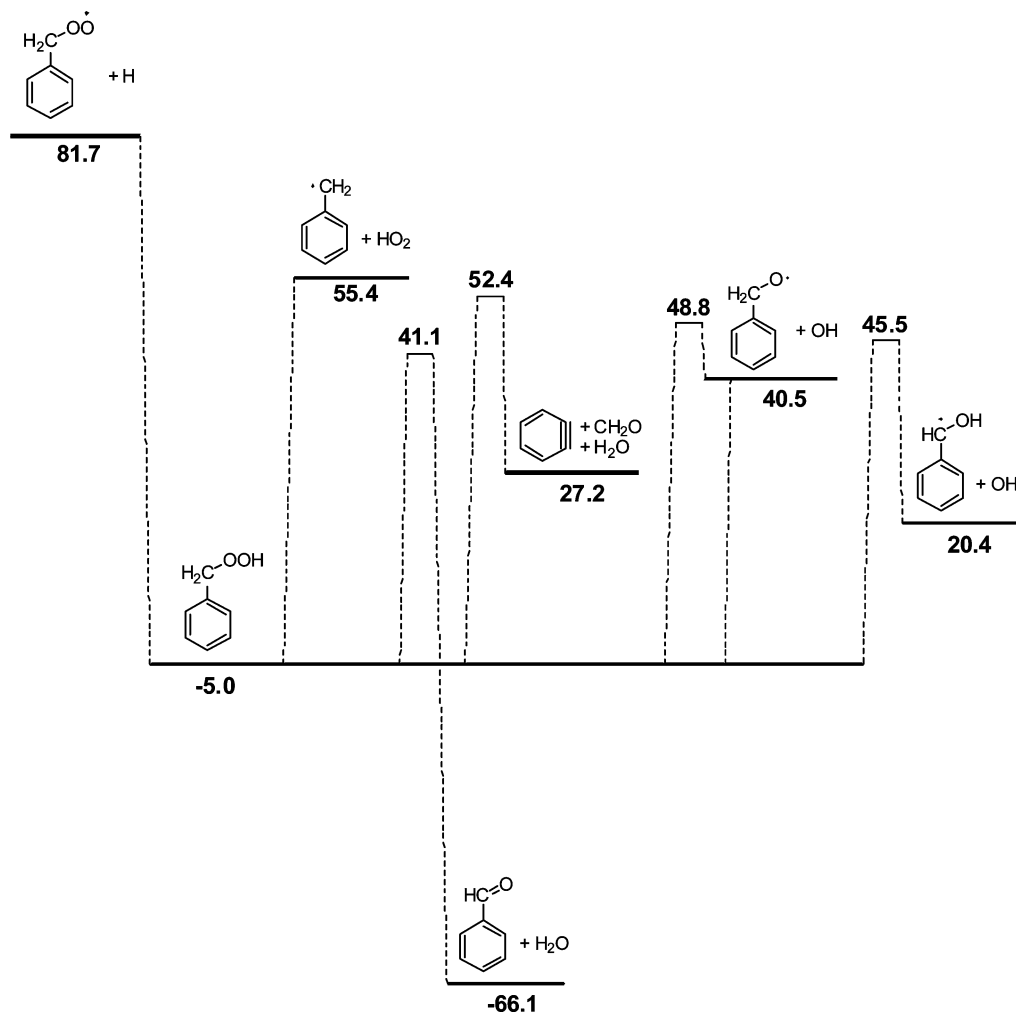


Figure 5. Energy diagram for the benzylperoxy + H reaction mechanism (G3B3 298 K enthalpies).

the loose (barrierless) transition state structure for C—OOH dissociation results in a favorable pre-exponential factor.

Fitted rate constants to important products in the benzylperoxy + H reaction, at pressures between 0.01 and 100 atm, are listed in Table 3. Rate constants to all considered product sets in the benzylperoxy + H mechanism are plotted in Figure 7, at 10 atm pressure (typical of autoignition conditions, where this reaction is expected to be of most significance). Collisional stabilization of benzyl hydroperoxide is the dominant channel at low temperatures, but it becomes unimportant at temperatures of 800 K and above, even at these relatively high pressures. From around 700 K and above, benzoyl + OH (via barrierless O—OH dissociation) are by far the dominant products, due to the favorable enthalpy and entropy of this path. Even at high temperature, the benzoyl + OH product is formed with rate constant close to 2 orders of magnitude higher than that of any other product set. At higher temperatures, the formation of benzyl + HO_2 plays a small role, contributing around 2% of the total products at 1500 K and above. The α -hydroxybenzyl + OH product set is the next most important, accounting for around 1% of the forward reaction at higher temperatures, followed by benzaldehyde plus H_2O . The reaction to benzaldehyde + H_2O and all slower reactions are deemed to be unimportant and are not considered further.

It is clear from our results that under relevant autoignition conditions the dominant products of the benzylperoxy + H reaction are benzoyl + OH. The potential significance of this reaction in toluene oxidation is discussed later in this contribution. For 10 atm we predict some formation of benzyl hydroperoxide at temperatures below 800 K, and the potential importance of these products is considered here. Figure 8 shows a plot of the branching ratio to benzyl hydroperoxide collisional stabilization in the benzylperoxy + H reaction, as a function of temperature and pressure. At pressures below 1 atm, benzyl hydroperoxide is never an important reaction product, even at very low temperatures (e.g., 500 K). At between 10 and 100 atm, representative of ignition conditions in an SI engine, quenching of the benzyl hydroperoxide adduct is significant at up to moderate temperatures, but drops away rapidly as we approach 800 K, which is at the lower end of ignition temperatures. Similar results were found previously for benzyl hydroperoxide formed in the benzyl + HO_2 mechanism.

We have investigated the effect of collisional energy transfer on benzyl hydroperoxide formation, simulating the reaction kinetics with ΔE_{down} values of between 500 and 3000 cm^{-1} . While N_2 (which we used as the buffer gas in our simulations) is a poor collider, the presence of more efficient colliders like toluene and other hydrocarbons in an actual

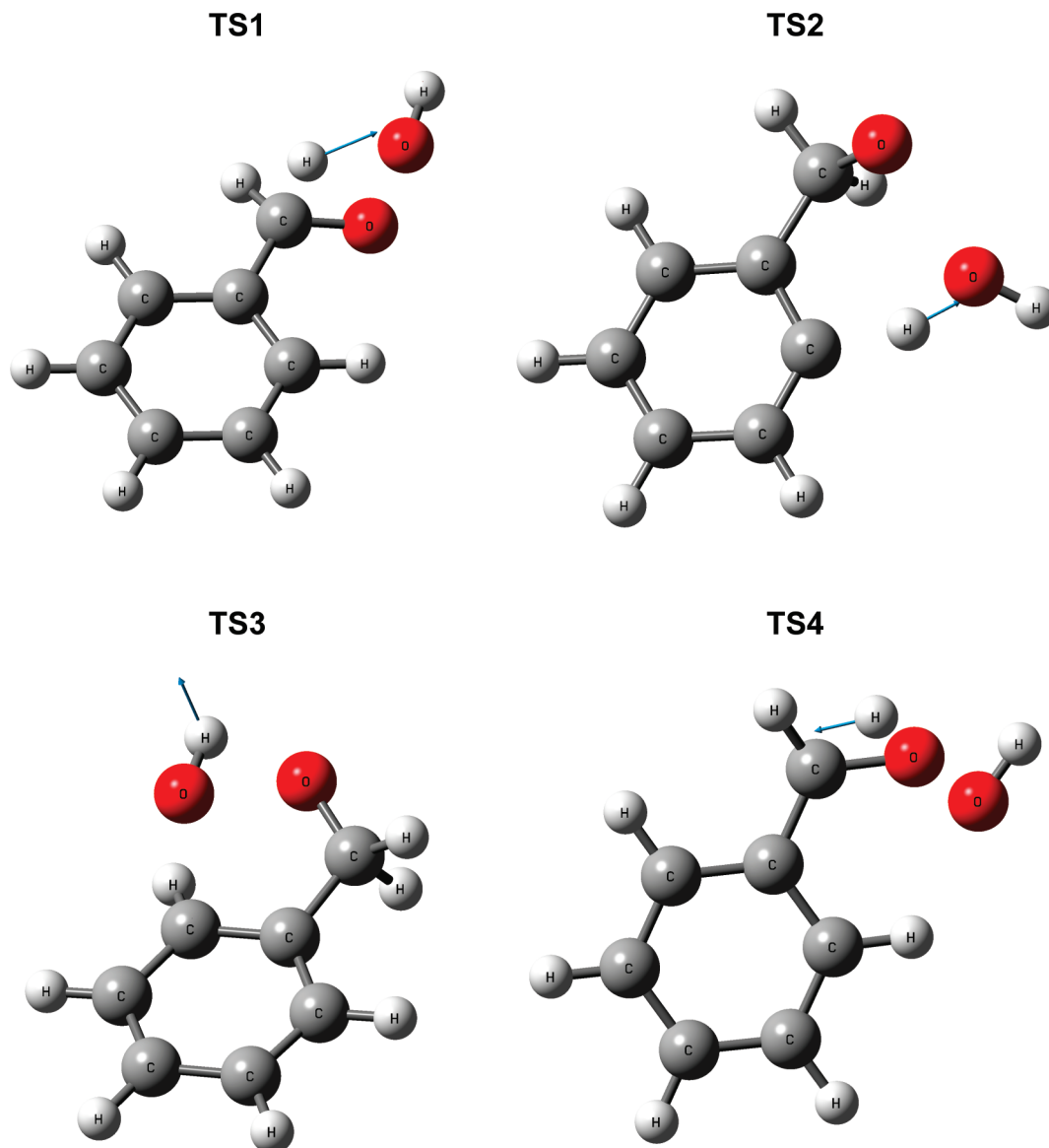


Figure 6. Transition state structures for reactions in the benzylperoxy + H mechanism: benzaldehyde + H₂O (TS1), benzyne + HCHO + H₂O (TS2), 3-methoxy-4-hydroxy-2,5-cyclohexadien-1-yl (TS3), and α -hydroxybenzyl + OH (TS4). B3LYP/6-31G(d) level; displacement vectors illustrated.

flame can lead to improved collisional energy transfer. This phenomenon may be the reason why ΔE_{down} values on the order of 2000 cm^{-1} were required to reproduce experimental falloff behavior in several unimolecular reactions that we recently studied.^{2d,21} Branching ratios to benzyl hydroperoxide formation, as a function of ΔE_{down} , are plotted in Figure 9; while large values of ΔE_{down} increase the yield of benzyl hydroperoxide at low temperatures, this product still becomes negligible for 800 K and above. At these temperatures, the benzyl hydroperoxide adduct lifetime is short toward decomposition to benzoyl + OH, relative to collision stabilization, and cannot be quenched in any appreciable quantity. Accordingly, benzyl hydroperoxide formed via the benzylperoxy + H reaction (or benzyl + HO₂) is unlikely to play a role in toluene oxidation.

Benzyl Hydroperoxide Decomposition. Our kinetic simulations demonstrate that chemically activated benzyl hydroperoxide formed in the benzylperoxy + H association reacts to new products, with negligible collisional stabilization. The

same applies for the benzyl + HO₂ reaction. Benzyl hydroperoxide can form, however, via other routes. Particularly, benzylperoxy will abstract a H atom from HO₂,⁷ toluene, and other molecules with benzylic or allylic C–H bonds, forming benzyl hydroperoxide. While the C₆H₅CH₂OO–H bond in benzyl hydroperoxide is weak ($86.7 \text{ kcal mol}^{-1}$), the C₆H₅CH₂–H bond in toluene is similar ($91.7 \text{ kcal mol}^{-1}$), making this abstraction reaction almost thermoneutral (5 kcal mol^{-1} endothermic). Reaction of benzylperoxy with HO₂ is an important process in the atmospheric degradation of toluene and should also be of some significance in combustion systems.⁷

Benzyl hydroperoxide decomposes to benzoyl + OH according to the high-pressure limit rate expression $k [\text{s}^{-1}] = 3.29 \times 10^{13} T^{0.42} \exp(-20.08/T)$. This corresponds to an activation energy of $39.89 \text{ kcal mol}^{-1}$ and a pre-exponential factor ($A'T''$) of $6 \times 10^{14} \text{ s}^{-1}$ at 1000 K. Rate constants have been calculated for this decomposition reaction from a steady-state solution of the master equation, at pressures

Table 3. Apparent Rate Parameters to Important Product Sets in the Benzylperoxy + H Reaction as a Function of Pressure

	A' ($\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$)	n	E_a (kcal mol^{-1})
benzylperoxy + H \rightarrow benzoxyl + OH (0.01 atm)	2.90×10^{12}	0.41	0.47
benzylperoxy + H \rightarrow benzoxyl + OH (0.1 atm)	1.49×10^{13}	0.21	0.87
benzylperoxy + H \rightarrow benzoxyl + OH (1 atm)	3.80×10^{14}	-0.19	1.89
benzylperoxy + H \rightarrow benzoxyl + OH (10 atm)	1.36×10^{17}	-0.87	4.49
benzylperoxy + H \rightarrow benzoxyl + OH (100 atm)	8.26×10^{15}	-0.42	5.83
benzylperoxy + H \rightarrow benzyl hydroperoxide (0.01 atm, <700 K)	5.66×10^{48}	-14.95	2.82
benzylperoxy + H \rightarrow benzyl hydroperoxide (0.01 atm, \geq 700 K)	1.49×10^{252}	-84.99	13.99
benzylperoxy + H \rightarrow benzyl hydroperoxide (0.1 atm, <700 K)	1.39×10^{57}	-16.16	6.39
benzylperoxy + H \rightarrow benzyl hydroperoxide (0.1 atm, \geq 700 K)	1.28×10^{141}	-51.10	-44.94
benzylperoxy + H \rightarrow benzyl hydroperoxide (1 atm, <700 K)	4.35×10^{60}	-15.92	11.40
benzylperoxy + H \rightarrow benzyl hydroperoxide (1 atm, \geq 700 K)	4.65×10^{125}	-46.44	-60.47
benzylperoxy + H \rightarrow benzyl hydroperoxide (10 atm, <700 K)	1.91×10^{31}	-5.87	4.98
benzylperoxy + H \rightarrow benzyl hydroperoxide (10 atm, \geq 700 K)	4.77×10^{287}	-95.60	6.05
benzylperoxy + H \rightarrow benzyl hydroperoxide (10 atm, <700 K)	2.25×10^{31}	-5.90	5.00
benzylperoxy + H \rightarrow benzyl hydroperoxide (100 atm, \geq 700 K)	4.78×10^{307}	-101.60	15.47
benzylperoxy + H \rightarrow benzyl + HO ₂ (0.01 atm)	5.73×10^1	3.18	-0.33
benzylperoxy + H \rightarrow benzyl + HO ₂ (0.1 atm)	8.48×10^3	2.55	0.81
benzylperoxy + H \rightarrow benzyl + HO ₂ (1 atm)	1.96×10^4	2.47	1.43
benzylperoxy + H \rightarrow benzyl + HO ₂ (10 atm)	1.63×10^9	1.07	5.06
benzylperoxy + H \rightarrow benzyl + HO ₂ (100 atm)	5.23×10^1	3.38	3.79
benzylperoxy + H \rightarrow α -hydroxybenzyl + OH (0.01 atm)	9.76×10^0	3.30	-0.87
benzylperoxy + H \rightarrow α -hydroxybenzyl + OH (0.1 atm)	8.90×10^1	3.03	-0.31
benzylperoxy + H \rightarrow α -hydroxybenzyl + OH (1 atm)	4.22×10^3	2.56	0.93
benzylperoxy + H \rightarrow α -hydroxybenzyl + OH (10 atm)	2.17×10^5	2.12	3.15
benzylperoxy + H \rightarrow α -hydroxybenzyl + OH (100 atm)	1.43×10^1	3.44	3.36

between 0.01 and 100 atm; the results are plotted in Figure 10, with fitted rate expressions listed in Table 4. Benzyl hydroperoxide lifetimes are shorter than 1 ms at temperatures of around 900 K and above for all pressures, making this reaction likely to proceed in an internal combustion engine. At temperature and pressure conditions relevant to the troposphere (1 atm and 300 K), the lifetime of benzyl hydroperoxide toward unimolecular decomposition is around 1×10^{15} s, making this reaction unimportant. Instead, benzyl hydroperoxide will be photolyzed, or will participate in bimolecular reactions with, for example, OH radicals. Several pathways to benzoxyl other than benzyl hydroperoxide decomposition are available at ambient conditions (for example, benzylperoxy + NO and the benzylperoxy self-reaction). Benzoxyl formed via these processes will decom-

pose to benzaldehyde + H with a lifetime of around 1 s,⁸ and this should be the dominant mechanism for benzoxyl radical removal in the troposphere.

Discussion

It is apparent, from work presented here and elsewhere, that benzyl hydroperoxide and the benzoxyl radical are key intermediates in benzyl radical oxidation, particularly under conditions relevant to autoignition and atmospheric oxidation. Scheme 1 depicts the major reaction pathways expected to take place in benzyl radical oxidation under ignition and/or atmospheric conditions, based upon our current understanding (some species are formed as transient activated adducts and/or as stable quenched intermediates). Another potential

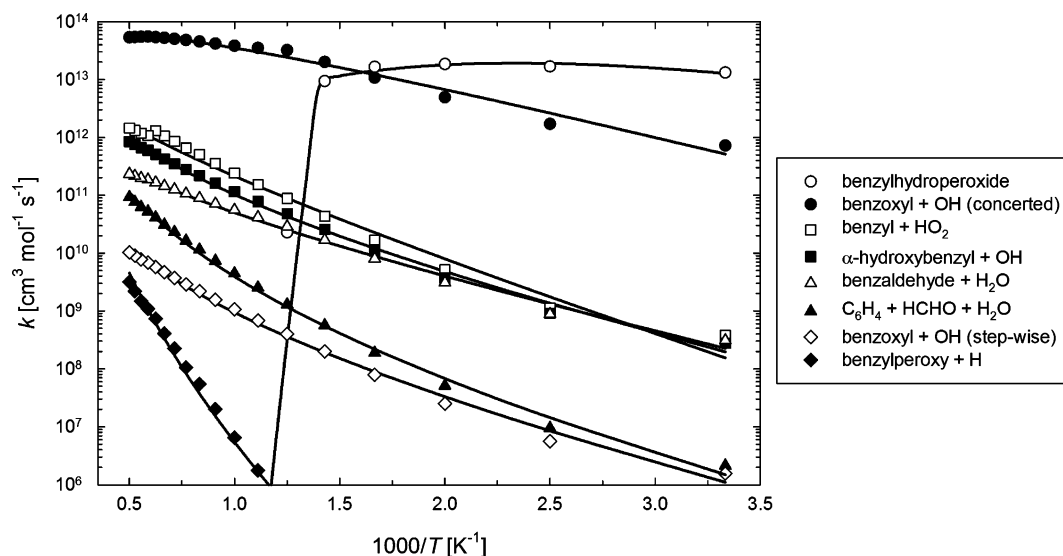


Figure 7. Apparent rate constants at 10 atm to all considered product sets in the benzylperoxy + H reaction mechanism. Solid lines represent three-parameter Arrhenius fits.

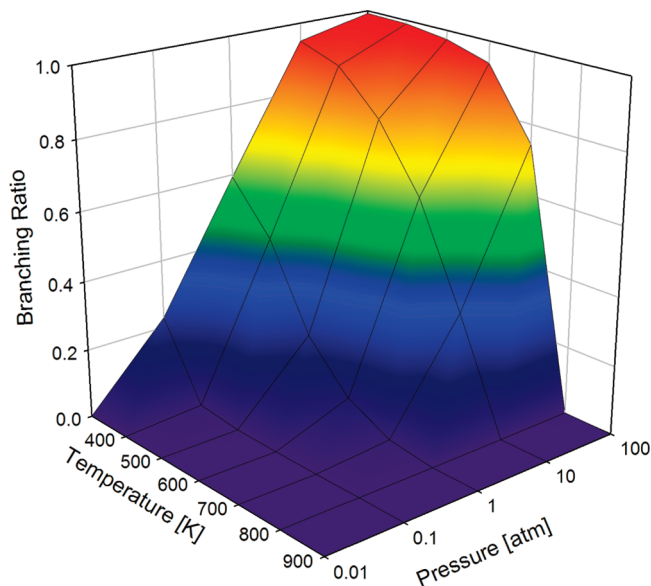


Figure 8. Branching ratios to benzyl hydroperoxide as a function of temperature and pressure in the benzylperoxy + H reaction mechanism.

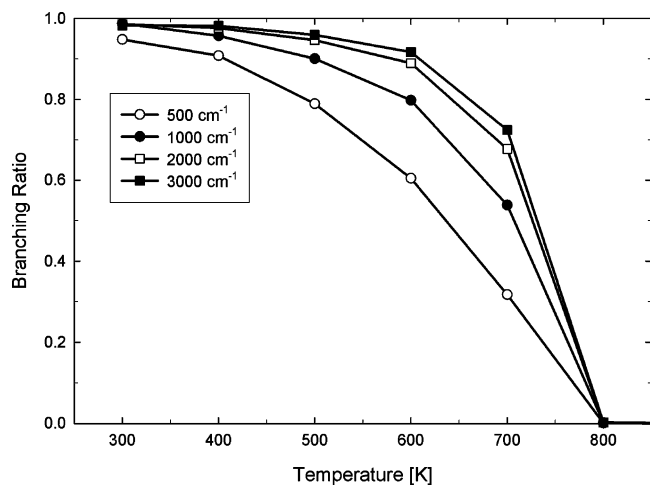


Figure 9. Branching ratios to benzyl hydroperoxide at 10 atm, as a function of ΔE_{down} .

reaction not illustrated in Scheme 1 is that of benzylperoxy with OH, which should form benzoxyl + HO₂ (such reactions are known to be significant in alkyl radical oxidation kinetics).²² Benzyl hydroperoxide will also react with OH via an addition mechanism. Ipso addition is expected to result in the formation of phenol plus the hydroperoxymethyl radical (CH₂OOH), which will dissociate to HCHO + OH. Free H atoms will also effect this addition/elimination sequence, resulting in benzene + HCHO + OH.

Most of the reactions included in Scheme 1 are now relatively well characterized, from both experiment and theory. While benzoxyl radical decomposition has recently been studied theoretically, further work is required to better understand the dissociation products of the highly activated benzoxyl radical that forms in the benzyl + O reaction (as well as the potential products of ring addition). Also, little information on the potentially important benzylperoxy + benzyl reaction is available (our thermochemistry predicts

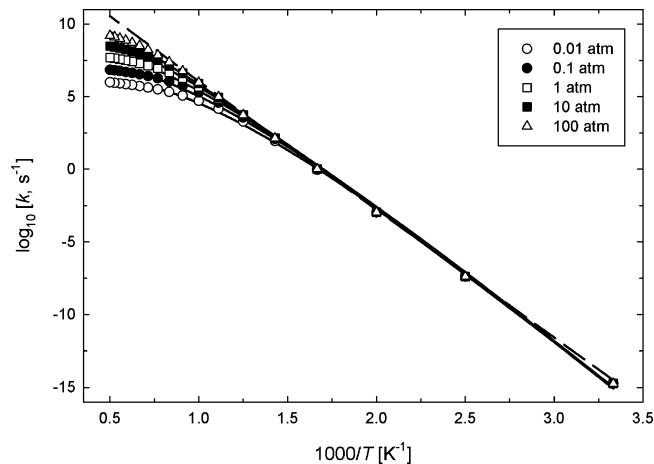


Figure 10. Rate constants for benzyl hydroperoxide decomposition to benzoxyl + OH. Solid lines represent three-parameter Arrhenius fits, dashed line represents high-pressure limit.

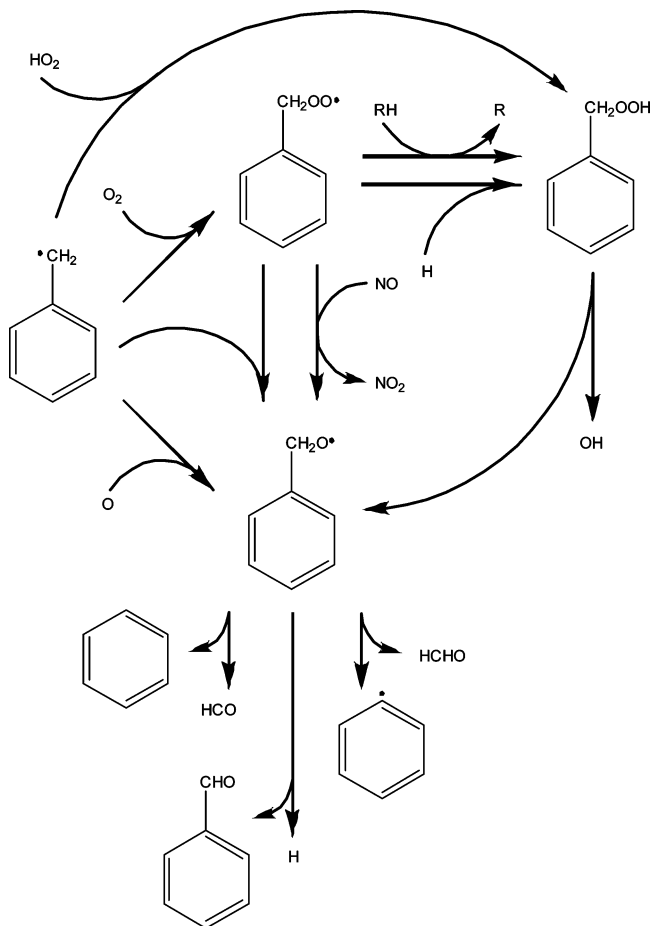
that this reaction will yield two benzoxyl radicals in a reaction that is 19.5 kcal mol⁻¹ exothermic).

All of the reaction pathways illustrated in Scheme 1 ultimately produce the benzoxyl radical, highlighting the key role that this intermediate plays in aromatic oxidation chemistry. The further products of benzoxyl decomposition are benzaldehyde + H, benzene + HCO, and phenyl + HCHO, where branching among these three product sets is dependent on temperature and on the energy at which benzoxyl is formed. Benzyl hydroperoxide is also seen to play an important role in benzyl radical oxidation, both as an intermediate in the benzyl + HO₂ and benzylperoxy + H reactions and as a stable product from hydrogen abstraction by benzylperoxy (where RH is a hydrocarbon or HO₂). In combustion systems, benzyl hydroperoxide will decompose to the benzoxyl + OH, but in the atmosphere, the further reactions of this species are less certain. Here, photolysis to benzoxyl + OH should be important, along with OH addition at the aromatic ring sites. Below, the potential role of benzyl hydroperoxide in the oxidation and ignition of toluene is explored in more detail.

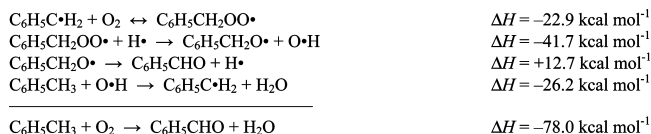
The major reactions in the benzyl + O₂ + H reaction sequence are listed below, along with reaction enthalpies. Hydrogen atom addition to benzylperoxy produces the benzoxyl radical + OH in a considerably exothermic process. The benzoxyl radical is unstable, and is unlikely to exist for any significant lifetime in a thermal environment. Benzoxyl predominantly decomposes to benzaldehyde + H, although benzene + HCO and phenyl + HCHO are also important product sets, particularly at higher temperatures.⁸ Irrespective, all three decomposition reactions are chain-propagating. When benzoxyl decomposes to benzaldehyde, the H atom initially consumed by benzylperoxy is regenerated. The overall reaction up to this point is benzyl + O₂ → benzaldehyde + OH ($\Delta H = -51.5$ kcal mol⁻¹). While this is a chain-propagating process and not directly the type of chain-branching reaction needed to initiate ignition, it does have the overall effect of converting the very unreactive benzyl radical into highly reactive OH, with a significant release of energy. Once OH is formed, it will readily abstract

Table 4. Apparent Rate Parameters for Decomposition of Benzyl Hydroperoxide to Benzoyl + OH, as a Function of Pressure

	A' (s^{-1})	n	E_a (kcal mol^{-1})
benzyl hydroperoxide \rightarrow benzoyl + OH (0.01 atm)	8.33×10^{28}	-4.39	45.32
benzyl hydroperoxide \rightarrow benzoyl + OH (0.1 atm)	1.56×10^{38}	-7.33	48.16
benzyl hydroperoxide \rightarrow benzoyl + OH (1 atm)	2.03×10^{47}	-10.27	50.71
benzyl hydroperoxide \rightarrow benzoyl + OH (10 atm)	1.39×10^{55}	-12.87	52.60
benzyl hydroperoxide \rightarrow benzoyl + OH (100 atm)	1.36×10^{61}	-14.95	53.65

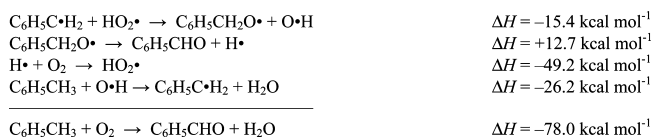
Scheme 1. Important Pathways in Benzyl Radical Oxidation

a H atom to form H_2O . For fuels like toluene (and other methylbenzenes), the predominant process will be to abstract a weak benzylic H atom (BDE of $86.7 \text{ kcal mol}^{-1}$, versus $118.8 \text{ kcal mol}^{-1}$ for HO-H). Including this reaction in our scheme, we arrive at an overall process in which toluene is oxidized by O_2 to benzaldehyde and water, along with a large production of energy. The exothermicity of this overall process aids ignition by increasing temperature, facilitating chain-branching decomposition reactions such as $\text{H}_2\text{O}_2 \rightarrow 2\text{OH}$.

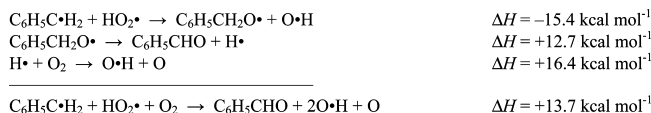


The similar benzyl + HO_2 reaction process is known to play a key role in methylbenzene autoignition. In a recent

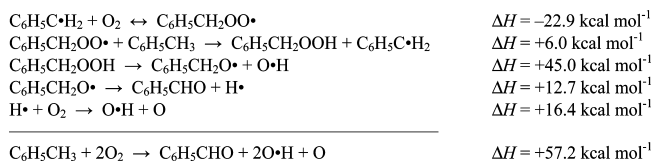
experimental and kinetic modeling study on xylene autoignition, ignition delays were found to be most sensitive to the methylbenzyl + HO_2 association reactions.²³ The important reactions that we foresee taking place following the benzyl + HO_2 reaction are shown below. Benzyl reacts with HO_2 to form benzoyl + OH in a mildly exothermic chain propagating reaction. Following decomposition of the benzoyl product, the free H atom can associate with O_2 to regenerate HO_2 (of course, other reactions are available), and if the reaction of toluene with OH is again included, we arrive at the same overall process as above.



At moderate to high temperatures the $\text{H} + \text{O}_2$ reaction is effectively chain branching, producing $\text{OH} + \text{O}$ in a mildly endothermic reaction. Under these conditions, the H atom formed in benzoyl decomposition will produce OH and O, as shown below. The O atom formed in this scheme can further react with benzyl to yield benzaldehyde + H (among other products), and the benzyl + $\text{O} \rightarrow$ benzaldehyde + O + OH chain reaction will be a key process in toluene autoignition. We expect that aromatic ignition behavior will be highly sensitive to branching in the benzoyl decomposition reaction between product sets such as benzaldehyde + H, phenyl + HCHO, and benzene + HCO.⁸



In addition to reaction with H, the benzylperoxy radical can abstract a hydrogen atom to form stable benzyl hydroperoxide. The following scheme indicates the likely reactions that would occur in toluene combustion. Chain-branching decomposition of benzyl hydroperoxide follows, which we show to be rapid at temperatures above around 900 K, with subsequent pyrolysis of the benzoyl radical to benzaldehyde + H. The overall process is now endothermic by $57.2 \text{ kcal mol}^{-1}$, but is highly chain branching with the formation of reactive OH radicals and $\text{O}(^3\text{P})$ atoms.



From the above reaction schemes we find that oxidation reactions proceeding via benzyl hydroperoxide aid in toluene autoignition, through exothermic and chain-branching processes. The benzyl radical can react with HO₂, or with O₂ and then H, in processes that ultimately result in the exothermic oxidation of toluene to benzaldehyde + H₂O. In order for these processes to take place, preliminary reactions producing benzyl, H, and HO₂ are required. Hydrogen abstraction from toluene by O₂ can also form HO₂ (+ benzyl), while toluene will react with most radicals to produce benzyl. At higher temperatures, toluene will pyrolyse to benzyl + H. The benzyl radical produced in any of the above processes will react with O₂ and then abstract a hydrogen atom to produce benzyl hydroperoxide, which decomposes in a chain-branching reaction at even low temperatures. Current kinetic models for the oxidation of toluene and other alkylated aromatics will be improved through inclusion of the reactions considered here.

Supporting Information Available: Cartesian coordinates and vibrational frequencies for benzylperoxy, benzyl hydroperoxide, and TS1–TS4; canonical rate constants for the benzylperoxy + H reaction as a function of transition state structure and temperature. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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