

# A Thermokinetic Theoretical Study of the Isomerization Processes in Toluene and *o*-Xylene Oxidation

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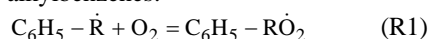
## Abstract

Determination of thermochemical data and kinetic parameters by means of quantum chemistry tools is a valuable solution to fill in the absence of experimental data. In this methodological study we have shown that the use of the elaborated CASPT2 method is needed to get a quantitative kinetic data for the 1,3s internal H-atom transfer of benzylperoxy radical. The rate constant computed at CASPT2/ANO-L-VDZP//B3LYP/ccpVDZ level of theory has been found in excellent agreement with the only one experimental rate constant available in the literature. Using the same level of theory we have also determined the rate constants for internal 1,3s and 1,6p H-atom transfers of *o*-xylylperoxy radical.

## Introduction

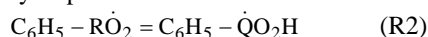
Aromatic compounds are currently used as solvent and are components of automotive and aeronautical fuels. Useful properties of aromatic compounds and their negative impact on environment and health have motivated many studies on their oxidation process. The main objective was to identify the formation and/or destruction pathways of aromatic compounds by means of detailed thermokinetic model validation. Detailed kinetic mechanisms of these models contain hundreds of elementary reactions and about hundred chemical species. The assignation of thermochemical data to species and kinetic rate constants to reactions is a complicated task due to the lack of information in the literature. This task is rendered more difficult because thermokinetic data must be known in large ranges of pressure and temperature to allow the use of thermokinetic models in conditions encountered in practical combustion systems. Determination of thermochemical data and kinetic parameters by means of quantum chemistry tools is a valuable solution to fill in the absence of experimental data. These new thermokinetic data will be included later in low-temperature oxidation thermokinetic models developed in our laboratory.

At low temperature, addition of molecular oxygen to aryl radicals occurs in the oxidation process of alkylbenzenes:

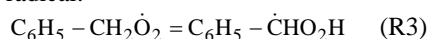


This reaction is an equilibrium which is very sensitive to the temperature. It shifts towards the

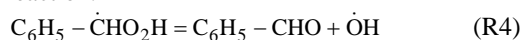
products when temperature overcomes the "ceiling temperature"<sup>1</sup>. The reaction (R1) is followed by an internal H-atom transfer producing an aryl hydroperoxide radical:



The internal transfer is easier when the transferred H atom is benzylic<sup>2</sup>. In the case of toluene, the only possible transfer is a 1,3s transfer involving one of the two secondary benzylic H atoms of benzylperoxy radical:



After formation by reaction (R3), the benzyl hydroperoxide radical decomposes to yield benzaldehyde and OH radical by the following reaction:



Benzaldehyde has been identified as a major oxidation product of pure toluene or alkane/toluene mixtures in studies at temperature below 800 K: in a static reactor between 723-788 K<sup>3</sup>, in a jet stirred reactor between 580-620 K<sup>4</sup> and in a rapid compression machine at 750 K<sup>5</sup>. The reaction sequence (R1)-(R3)-(R4) is often suggested to explain the benzaldehyde formation in the low-temperature oxidation mechanism of toluene.

In the reaction sequence (R1)-(R3)-(R4), the reaction (R3) is certainly the rate limiting step as it involves a strained four-center cyclic transition state. Thus a reliable value for the rate constant of this reaction is needed. In the literature, only one

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experimental determination of this rate constant is available<sup>6</sup>. It is a measurement based on an indirect method using addition of toluene to mixtures of H<sub>2</sub> and O<sub>2</sub>. The reported rate constant value is  $2.8 \times 10^3 \text{ s}^{-1}$  at 773 K under 0.67 bar total pressure. This experimental value will be used to validate our theoretical methodology for the estimation of the rate constant.

A very recent theoretical study has been performed by Murakami et al.<sup>7</sup> to determine the kinetics, the mechanism and the product branching ratios of the benzyl + O<sub>2</sub> reaction at the CBS-QB3 level of theory. The authors found that the reaction proceeded with an exothermic barrierless addition of molecular oxygen to the benzyl radical to form the benzylperoxy radical. The benzylperoxy radical can be dissociated (i) backwards with a 93.3 kJ mol<sup>-1</sup> energy barrier, (ii) into the C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>OOH radical with a 135.6 kJ mol<sup>-1</sup> energy barrier (iii) into the cyclic O<sub>2</sub> adduct with a 128.0 kJ mol<sup>-1</sup> energy barrier, and (iv) leading to the formation of benzaldehyde and OH radical with a 161.9 kJ mol<sup>-1</sup> energy barrier.

In this work, highly correlated quantum chemical calculations were performed in order to directly compute the barrier for the reaction (R3) without any energy adjustments. The energetics of the reactant and the TS was used together with Transition State Theory (TST) calculations to compute the rate constants in the temperature range 600–2000 K. To our knowledge, this is the first time that the temperature dependence of the rate constant for the benzylperoxy radical isomerization has been computed at a highly correlated level of theory. Using this methodology, we studied also the 1,3s and 1,6p H-atom transfers for the *o*-xylylperoxy radical.

Roubaud et al.<sup>8</sup> have measured in a rapid compression machine the oxidation products of *o*-xylene formed at a time after the first stage and before the second stage of the autoignition in the following conditions: 15.6 bar, 704 K, stoichiometric fuel/O<sub>2</sub>/inert mixture, dilution O<sub>2</sub>/inert = 0.37. The consumption of *o*-xylene was ~ 10% at this time. The amounts of product have been expressed in terms of carbon selectivities *i.e.* in number of carbon atoms in the species normalized to 100 carbon atoms of fuel consumed. The products exhibiting the highest selectivities are in decreasing order: 2-hydroxybenzaldehyde (~ 14%), *o*-xylene oxide (~ 13%), and 2-methylbenzaldehyde (*o*-tolualdehyde) (~ 9%). Toluene, isobenzofuran, 3-hydroxybenzaldehyde, *o*-phthalaldehyde, phthalide are among the minor aromatic oxidation products. The formation of the main oxidation products is explained by a low temperature oxidation scheme involving the formation of the *o*-xylylperoxy radical Ph(CH<sub>2</sub>OO°)(CH<sub>3</sub>) by addition of molecular oxygen to *o*-xylyl radical. Then, two internal H-atom transfer pathways of *o*-xylylperoxy

radical are considered: a 1,6p one yielding the radical Ph(CH<sub>2</sub>OOH)(CH<sub>2</sub>°) and a 1,3s one yielding the radical Ph(C°HOOH)(CH<sub>3</sub>). The radical Ph(CH<sub>2</sub>OOH)(CH<sub>2</sub>°) produces *o*-xylene oxide after the breaking of the weak O-O bond with removal of an OH radical and a cyclization. The radical Ph(C°HOOH)(CH<sub>3</sub>) forms *o*-tolualdehyde after breaking of the O-O bond with removal of an OH radical and the formation of a C=O bond. To explain the formation of 2-hydroxybenzaldehyde, the following reaction sequence is suggested. The radical Ph(CH<sub>2</sub>OOH)(CH<sub>2</sub>°) undergoes an O<sub>2</sub> addition followed by an internal H-atom transfer reaction to form the radical Ph(C°HOOH)(CH<sub>2</sub>OOH). This radical produces an oxohydroperoxide Ph(CHO)(CH<sub>2</sub>OOH) and an OH radical through the breaking of the weak O-O bond. Then, the oxohydroperoxide undergoes the breaking of the weak O-O bond to produce the radical Ph(CHO)(CH<sub>2</sub>O°) and an OH radical. This step is a branching pathway postulated in the low-temperature oxidation schemes of many fuels. Then, the radical Ph(CHO)(CH<sub>2</sub>O°) produces methanal and the *o*-formylphenyl radical °Ph-CHO by breaking of the C-C bond between the fragment CH<sub>2</sub>O° and the aromatic nucleus. Finally, this latter radical adds an OH radical to produce 2-hydroxybenzaldehyde.

The 1,6p internal H-atom transfer reaction of *o*-xylylperoxy radical is postulated to explain the formation of *o*-xylene oxide whereas the 1,3s internal H-atom transfer may be implicated in the formation of *o*-tolualdehyde. There could be a competition between the 1,6p and 1,3s transfer reactions. To our knowledge no experimental or calculated rate constant values are available for these aforementioned reactions. Thus a determination of the rate constants of these reactions is of high interest because it will allow us to incorporate them in a low temperature oxidation model of *o*-xylene.

## Computational methods

*Ab initio* and DFT calculations were performed using the GAUSSIAN03 and MOLCAS 6.0 software packages. Reactant and TS structures were fully optimized at HF-DFT (B3LYP), MPW1K, and MP2 level of theory using six different basis sets. Product geometries were fully optimized at MPW1K and MP2 level of theory with the same six basis sets. All TSs have been characterized by one imaginary frequency (first-order saddle points) on the Potential Energy Surface (PES). Special care was taken to determine Minimum Energy Pathways (MEPs), performing Intrinsic Reaction Coordinate analyses (IRC) using all levels of theory, in order to confirm that a specific TS connects the different local minima. Vibrational frequencies were determined within the harmonic approximation, at the same level of theory as for geometries. For the reactant and TS structures, single-

point energy calculations were carried out at different high levels of theory using in each case the optimized B3LYP, MPW1K, and MP2 geometrical parameters. Thus, electronic energies were obtained: (i) CCSD(T) level of theory with the 6-31G(d,p) basis set (ii) CASPT2 level of theory with the ANO-L-VDZP basis set.

Canonical TST was used to predict the temperature dependence of the rate constants. The calculation of the reaction rate constants using the TST formulation requires the proper computation of the partition functions of the reactant and the TSs. In this work, we adopt the simple and computationally inexpensive Wigner method in the calculation of all tunneling corrections. The rate constant calculations were performed over the temperature range of interest using the KISTHEP software<sup>9</sup>.

## Results and Discussion

### Energetics

Table 1 shows the computed vibrationally adiabatic barriers,  $E_0$ , for the benzylperoxy isomerization. The following relation defines these barriers:

$$E_0 = E_{TS} - E_R + ZPE_{TS} - ZPE_R$$

where  $E_{TS}$  and  $E_R$  are the computed energies of the TS and reactant, while  $ZPE_{TS}$  and  $ZPE_R$  are their corresponding zero-point energy corrections.

Table 1: Vibrationally Adiabatic Barriers  $E_0$  Calculated in  $\text{kJ mol}^{-1}$  at Different Levels of Theory

Level of Theory	Basis Set *					
	a	b	c	d	e	f
B3LYP//Basis Set <sup>†</sup>	159.7	160.1	159.9	162.1	162.3	155.6
CCSD(T)/6-31G(d,p)	178.7	178.6	178.6	177.7	177.9	178.7
//B3LYP//Basis Set <sup>†</sup>						
CASPT2/ANO-L-VDZP	145.0	145.1	145.2	143.3	141.6	137.1
//B3LYP//Basis Set <sup>†</sup>						
MPW1K//Basis Set <sup>†</sup>	174.1	174.7	174.4	175.6	176.2	170.0
CCSD(T)/6-31G(d,p)	178.4	178.9	179.0	178.0	178.6	177.7
//MPW1K//Basis Set <sup>†</sup>						
CASPT2/ANO-L-VDZP	143.1	139.3	139.2	139.7	139.5	138.4
//MPW1K//Basis Set <sup>†</sup>						
PMP2//Basis Set <sup>†</sup>	196.9	201.0	200.2	201.0	204.2	194.5
CCSD(T)/6-31G(d,p)	218.6	216.9	217.0	217.4	216.5	211.2
//PMP2//Basis Set <sup>†</sup>						
CASPT2/ANO-L-VDZP	182.9	180.5	180.7	180.2	179.8	172.3
//PMP2//Basis Set <sup>†</sup>						

\* Basis sets correspond to: a: 6-31G(d,p); b: 6-31+G(d,p); c: 6-31++G(d,p); d: 6-311G(d,p); e: 6-311+G(d,p); f: cc-pvdZ

The four-center isomerization appears to have a large electronic barrier. The calculated values with one method and six different basis sets are very consistent. If we compare the results obtained using the double  $\xi$  basis sets, 6-31G(d,p) and cc-pVDZ, it can be seen that the barriers decrease slightly. The vibrationally adiabatic barrier  $E_0$ 's calculated with the B3LYP density functional are systematically lower by about 14 to 40  $\text{kJ mol}^{-1}$  when compared to those obtained with the MPW1K density functional and the correlated *ab*

*initio* method PMP2. The barriers calculated at the CCSD(T)//B3LYP levels are very close to the ones computed at the CCSD(T)//MPW1K levels but are lower by about 38  $\text{kJ mol}^{-1}$  than those obtained at the CCSD(T)//PMP2 levels. Similar results are observed with the CASPT2 method although the barriers are lower compared to those calculated with the CCSD(T) method. We found also the UMP2 method was unsuitable, due to severe spin contamination for the TS, with expectation value of  $S^2$  between 1.21 and 1.25, instead of  $\langle S^2 \rangle = S(S+1) = 0.75$  while after spin projection, the  $\langle S^2 \rangle$  values are 1.10. The barrier calculated by Murakami et al.<sup>7</sup> at the CBS-QB3 level was 161.9  $\text{kJ mol}^{-1}$ . The vibrationally adiabatic barriers computed at the B3LYP levels are very close to the one reported by Murakami et al.<sup>7</sup> at the CBS-QB3 level. All the values calculated here seem apparently to diverge but it can be observed that for one given method there is little influence of the basis set size. For an accurate rate constant estimation, it is essential to choose the appropriate level of theory. In the literature, only one determination at 773 K of the rate constant for the benzylperoxy isomerization reaction is available<sup>6</sup>. Thus, the calculations of the rate constants with different methods are essential to allow us an assessment of the appropriate level of theory (see next subsection). It is worth noticing that the CASPT2 computed energy barriers from intramolecular abstraction are lower than that in alkylperoxy radical systems because of the weak benzyl-H bond energy resulting from resonance.

### Rate constants

The computed rate constants range from  $10^{-3}$  to  $10^3 \text{ s}^{-1}$ , showing the strong dependence of the rate constant on the level of theory. The MP2 method is unsuitable due to severe spin contamination in the TS. The calculated rate constant using CCSD(T) energies on the density functional geometries are at 773 K three orders of magnitude lower than the experimental value. We observe at 773 K a very good agreement between the experimental value of  $2.8 \times 10^3 \text{ s}^{-1}$  (obtained at 0.67 bar) and our high-pressure limit calculated values at the CASPT2//B3LYP and CASPT2//MPW1K levels which are ranging from  $6.68 \times 10^2$  to  $2.51 \times 10^3 \text{ s}^{-1}$ . By comparison to the experimental value, the most appropriate level of theory is the CASPT2/ANO-L-VDZP//B3LYP/cc-pVDZ. Murakami et al.<sup>7</sup> calculated the high-pressure limit rate constants at six different temperatures (300, 500, 700, 1000, 1200, and 1500 K). Using these values, one can derive from a linear regression the value at 773 K ( $k = 1.23 \times 10^1 \text{ s}^{-1}$ ) which is 200 times lower than the value calculated using the CASPT2 method. To conclude, we recommend the use of the CASPT2/ANO-L-VDZP//B3LYP/cc-pVDZ level of theory to compute quantitatively the temperature

dependence of the high-pressure limit rate constant of the four-center isomerization of the benzylperoxy radical.

#### Arrhenius parameters

The rate constants calculated at the CASPT2/ANO-L-VDZP//B3LYP/cc-pVDZ level of theory have been fitted to a three-parameter Arrhenius expression by the least-squares, giving the following relation (in units of  $s^{-1}$ ):

$$k(600\text{--}2000\text{ K}) = (1.29 \times 10^{10}) T^{0.79} \exp((-133.1 \text{ in kJ mol}^{-1})/RT)$$

This expression is in excellent agreement with the only one experimental data at 773 K (see Rate constants section above).

Using the same level of theory recommend above we have determined the two rate constants corresponding to the 1,3s and 1,6p H-atom transfers for *o*-xylylperoxy radical. The three-parameter Arrhenius expressions (in units of  $s^{-1}$ ) are given below:

$$k_{1,3s}(600\text{--}2000\text{ K}) = (3.33 \times 10^{10}) T^{0.79} \exp((-142.6 \text{ in kJ mol}^{-1})/RT)$$

$$k_{1,6p}(600\text{--}2000\text{ K}) = (5.10 \times 10^8) T^{0.85} \exp((-87.1 \text{ in kJ mol}^{-1})/RT)$$

We recommend the Arrhenius parameters computed here for use in the thermokinetic models involving aromatic compounds.

According to our calculations, the 1,6p internal H-atom transfer for *o*-xylylperoxy radical is largely favoured over the 1,3s transfer at low temperature. This later transfer becomes competitive over the 1,6p one above about 1000 K. Consequently, this channel can not explain the formation of 2-methylbenzaldehyde at low temperature as suggested in an earlier work.

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