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An extensive methodological theoretical study of the kinetics of the benzylperoxy radical isomerization

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ABSTRACT

Theoretical calculations are carried out on benzylperoxy radical four-center isomerization reaction. Geometry optimizations and vibrational frequency calculations are performed using three methods (B3LYP, MPW1K, and MP2) and seven basis sets (6-31G(d,p), 6-31+G(d,p), 6-31++G(d,p), 6-311G(d,p), cc-pVDZ, aug-cc-pVDZ, and cc-pVTZ). Single-point energy calculations are performed with the highly-correlated ab initio coupled cluster method in the space of single, double, and triple (perturbatively) electron excitations (CCSD(T)) using the 6-311G(d,p), 6-311+G(d,p), 6-311++G(d,p), 6-311+G(3df,2p), and cc-pVTZ basis sets, and with the CASPT2/ANO-L-VDZP level of theory. Canonical transition state theory with a Wigner tunneling correction is used to calculate the high-pressure limit rate constant. The rate constants at 773 K calculated with the CASPT2/ANO-L-VDZP//B3LYP/cc-pVDZ and CASPT2/ANO-L-VDZP//B3LYP/aug-cc-pVDZ levels of theory are in very good agreement with the literature value from Ellis et al. These levels of theory are then used to compute the temperature dependence of rate constant and leads to the following three-parameter Arrhenius expressions over the range 600–2000 K: k (s^{-1}) = 1.34 × 10^{10} $T^{0.79}$ exp(−133.1 kJ mol^{-1}/RT) and k (s^{-1}) = 1.85 × 10^{10} $T^{0.78}$ exp(−133.9 kJ mol^{-1}/RT) at the CASPT2/ANO-L-VDZP//B3LYP/cc-pVDZ and CASPT2/ANO-L-VDZP//B3LYP/aug-cc-pVDZ levels of theory, respectively. These relations can be used in oxidation thermokinetic models involving toluene and alkylbenzenes.

1. Introduction

The understanding of the elementary reactions that govern hydrocarbon low-temperature (less than 900 K) oxidation and autoignition has been developing over the course of last decades. Reviews of Pollard [1], Walker and Morley [2], and Robertson et al. [3] give thorough descriptions of the state of the knowledge about low-temperature hydrocarbon oxidation chemistry up to the mid-1990s. Rapid advances in computational chemistry have enabled the characterization of more and more complex reactions and the calculation of reliable rate constants for elementary reactions. These aspects are highlighted in the recent review of Zádor et al. [4], which concentrates on kinetics of peroxy $RO_2^{\cdot}$ and hydroperoxy $^{\cdot}$QOOH radical reactions. As stated in this review, the formation and reactions of $^{\cdot}$QOOH radicals are central to low-temperature autoignition chemistry. The isomerization of $RO_2^{\cdot}$ radicals to form $^{\cdot}$QOOH radicals proceeds through ring-shaped transition states. Because none of $^{\cdot}$QOOH radicals have ever been detected (due to their unstability), information about their kinetics of formation is derived either from indirect experimental determinations or theoretical calculations. At the present time, quantum chemistry and theoretical kinetics are accurate means of determining rate constants of $^{\cdot}$QOOH radical formation reactions.

Among peroxy radicals, the benzylperoxy radical is particular because its precursor, stabilized benzyl radical, reacts slowly with O_2 and thus the low-temperature autoignition tends to be inhibited. The benzylperoxy radical can isomerize through a four-membered ring transition state to the 1-hydroperoxybenzyl radical, whose fate is dissociation to OH + benzaldehyde. In a previous study [5], we have provided a detailed review of experimental and theoretical studies related to the kinetics of benzylperoxy radical reactions, which will not be recalled in this article. The rate constant at 773 K of the benzylperoxy four-center isomerization has been computed using 54 different levels of theory and compared to an indirect experimental value from Ellis et al. [6]. Geometry optimizations and vibrational frequency calculations have been performed using three methods (B3LYP, MPW1K, and MP2) and six basis sets (6-31G(d,p), 6-31+G(d,p), 6-31++G(d,p), 6-311G(d,p), 6-311+G(d,p), and cc-pVDZ). Single-point energy calculations have been performed with the coupled cluster method in the space of single, double, and triple (pertubatively) electron excitations CCSD(T) using the 6-31G(d,p) basis set, and with the CASPT2 level of theory with the ANOL-VDZP basis set. This methodological work has shown that standard theoretical methods such

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as B3LYP, MPW1K, and MP2 methods but even an elaborated method as CCSD(T) method, are not adequate to obtain a reliable rate constant for the reaction under study. The use of elaborated CASPT2 method has been proven essential to get a quantitative rate constant and the CASPT2/ANO-L-VDZP//B3LYP/cc-pVDZ level of theory has been identified as the most appropriate level of theory to calculate accurately the rate constant.

In the present article, the methodological character of the former study is reinforced by employing 69 new levels of theory. Six new geometry levels of theory based on Dunning style basis sets are employed: B3LYP/aug-cc-pVDZ, B3LYP/cc-pVTZ, MPW1K/aug-cc-pVDZ, MPW1K/cc-pVTZ, MP2/aug-cc-pVDZ, MP2/cc-pVTZ. Complementary CASPT2 single-point energy calculations are performed on these six new geometry levels of theory. CCSD(T) single-point energy calculations with four supplementary Pople style (6-311G(d,p), 6-311+G(d,p), 6-311++G(d,p), 6-311++G(3df,2p)) and the Dunning style cc-pVTZ basis sets more extended than those used in the previous study, are also carried out. The canonical transition state theory (TST) is used to calculate the high-pressure limit rate constants from the energetics of reactant and transition state (TS).

This article is organized as follows. Computational methods are described in Section 2 and results are presented and discussed in Section 3.

2. Computational methods

Ab initio and DFT calculations were performed using the Gaussian03 [7] and Molcas 6.0 [8] software packages. Reactant and TS structures were fully optimized with the hybrid density functional theories B3LYP [9,10] and MPW1K [11], and the second-order Møller–Plesset perturbation theory MP2 [12] using the following 6-31G(d,p), 6-31+G(d,p), 6-31++G(d,p), and 6-311G(d,p) Pople style basis sets [13] and cc-pVDZ, aug-cc-pVDZ, and cc-pVTZ [14,15] Dunning style basis sets. Product geometries were fully optimized using the MPW1K and MP2 methods associated with the same seven 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) [16] using all levels of theory, 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.

In this work, the energy differences between the TS and the reactant are determined using the CCSD(T) and CASPT2 highly correlated methods to carry out accurate rate constant calculations through TST at a later stage. The CCSD(T) method is a singles and doubles coupled cluster theory with a perturbative estimation for inclusion of triple excitations [17–20]. The frozen-core approximation has been applied in CCSD(T) calculations, which implies that the inner shells are excluded at estimating the correlation energy. The CASPT2 [21–24] method is carried out to incorporate both dynamic and nondynamic correlation effects on the relative energy ordering of the calculated stationary points. It is based on a second-order perturbation treatment in which the CASSCF wave function is taken as the reference function. In this study, CASPT2(3,3) single-point energy calculations were obtained with the ANO-L-VDZP basis set on the optimized geometries and excluding inner shells and corresponding virtual counterpart from the perturbation calculation. For the abstraction mechanism, the active space (3,3) that describes the C–H bond breaking and O–H bond formation includes the σ_{C-H} bonding molecular orbital (MO) with the associated σ^*_{C-H} antibonding MO and the single electron MO.

Single-point energy calculations for the reactant and the TS were carried out using the optimized B3LYP, MPW1K, and MP2 geometrical parameters. They were obtained employing (*i*) the CCSD(T) method with the 6-311G(d,p), 6-311+G(d,p), 6-311++G(d,p), 6-311++G(3df,2p), and cc-pVTZ basis sets and (*ii*) the CASPT2 method with the ANO-L-VDZP [25] basis set. Single-point energy calculations for the product were carried out using the optimized MPW1K and MP2 geometrical parameters. They were obtained using the CCSD(T) method with the 6-311G(d,p), 6-311+G(d,p), 6-311++G(d,p), 6-311++G(3df,2p), and cc-pVTZ basis sets.

The canonical TST [26–33] was used to calculate the high-pressure limit rate constants, $k(T)$, versus temperature, through:

$$k(T) = \Gamma(T) \times \frac{k_B T}{h} \times \frac{Q_{TS}(T)}{Q_{RE}(T)} \times \exp\left(-\frac{E_0}{k_B T}\right) \quad (1)$$

where $\Gamma(T)$ is the transmission coefficient used for the tunneling correction at the temperature T, k_B is Boltzmann's constant, h is Planck's constant, $Q_{TS}(T)$ and $Q_{RE}(T)$ are the total partition functions for the TS and the reactant at the temperature T, and E_0 is the vibrationally adiabatic barrier at 0 K.

E_0 is the difference between the energy of the TS and that of the reactant including zero-point vibrational energy. E_0 values were determined using:

$$E_0 = E_{TS} + ZPVE_{TS} - (E_{RE} + ZPVE_{RE}) \quad (2)$$

where E_{TS} and E_{RE} are the electronic energies of the TS and the reactant, while $ZPVE_{TS}$ and $ZPVE_{RE}$ are their corresponding zero-point vibrational energies.

The total partition function $Q_X(T)$ of a species X is calculated as the products of the translational $Q_X^{trans}(T)$, electronic $Q_X^{elec}(T)$, rotational $Q_X^{rot}(T)$, and vibrational $Q_X^{vib}(T)$ partition functions, as shown by:

$$Q_X(T) = Q_X^{trans}(T) Q_X^{elec}(T) Q_X^{rot}(T) Q_X^{vib}(T) \quad (3)$$

In this work, we adopt the simple and computationally inexpensive Wigner method [34] in the calculation of tunneling corrections to the rate constant. The expression of the corresponding transmission coefficient $\Gamma(T)$ is given by:

$$\Gamma(T) = 1 + \frac{1}{24}\left(\frac{h\nu^{\neq}}{k_B T}\right)^2 \quad (4)$$

where $\nu^{\neq}$ is the scaled imaginary frequency at the saddle point. This choice seems to be appropriate to the rate constants in the temperature range 600–2000 K because the values of $\Gamma(T)$ are small to moderate ($\leqslant 2$) [35–37]. More sophisticated and computationally demanding algorithms, such as the ones developed by Truhlar et al. [38–43] and Miller et al. [44,45], should be used if the transmission coefficients are much higher than the ones computed in this study. The rate constant calculations were performed over the temperature range of interest using the KISTHEP software [46].

3. Results and discussion

3.1. Geometric parameters and vibrational frequencies

Fig. 1 shows the structure and atom numbering of the reactant (benzylperoxy radical), the isomerization TS, and the product (1-hydroperoxybenzyl radical). Table 1 gathers selected bond lengths of this species calculated at different levels of theory. More detailed information regarding optimized Cartesian coordinates for these species is presented in Tables 1S–8S of the Supplementary material.

3.1.1. Geometric parameters for benzylperoxy radical

At all levels of theory, the global minimum for the benzylperoxy radical is found to be in a conformation in which the dihedral angles $C_3C_2C_1O_2$ and $C_2C_1O_2O_1$ are equal to about −90° and 180°,