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Rate constants of hydrogen abstraction by methyl radical from *n*-butanol and a comparison of CanTherm, MultiWell and Variflex

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Abstract

Rate constants of hydrogen abstraction by the $\dot{\text{C}}\text{H}_3$ radical from *n*-butanol have been calculated based on coupled-cluster in the complete basis set limit, CCSD(T)/CBS, electronic energies. Accurate rate constants have been calculated using MultiWell and Variflex for all possible abstraction channels employing conventional transition state theory and the rigid-rotor harmonic oscillator approximation for all but the torsional degrees of freedom. Geometries, frequencies, and hindrance potentials were obtained at the B3LYP/6-311G(2d,d,p) level. In addition, the same procedures have been used but at a lower energetic level, ROCBS-QB3, with three kinetic programs, namely, CanTherm, MultiWell and Variflex. Computed reaction rate constants show very good agreement among all three programs for the α , β , γ and alcoholic H-atom abstraction channels while larger discrepancies have been found for the δ abstraction channel. Variflex predicts the fastest rate constants for the δ -channel, and its ratio over the lowest rate constants, predicted by MultiWell, is 2.5 at 500 K and increases to 3.0 at 2000 K. Branching ratio analysis shows that α and γ channels are favoured while the contribution from the β , δ and alcoholic abstraction channels are minor. Both MultiWell and Variflex predict that the α -channel is favoured over the γ -channel, while CanTherm predicts the γ -channel as the most dominant.

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1. Introduction

n-Butanol has surfaced as a potential biofuel [1,2] mainly because it does not suffer from the drawbacks that the current most widely used bio-

fuel (ethanol) does. Compared to ethanol, *n*-butanol has a higher energy content, a lower vapour pressure, a much lower solubility in water and it is less corrosive [3]. Although it has a lower octane number than ethanol, being similar to that of gasoline, it is sufficient enough to allow its use as a fuel.

The favourable characteristics of *n*-butanol have led to an increasing number of studies investigating its use as a transportation fuel in

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both gasoline and diesel engines [4–11]. In addition, a number of studies focusing on *n*-butanol flame characteristics [12,13] as well as on the combustion chemistry of *n*-butanol [14–25] have been reported.

Hydrogen abstraction reactions by small radicals such as H, OH, HO₂ and CH₃, which are produced during the initiation and chain branching reactions, are important pathways in the high-temperature decomposition of many fuels, including *n*-butanol. Recently, we have studied the reaction mechanism and the rate constants of hydrogen abstraction reactions from *n*-butanol by OH and HO₂ radicals [26–29]. In addition, reaction flow analysis of available chemical kinetic models of *n*-butanol suggests that hydrogen atom abstraction by the CH₃ radical is a particularly important pathway during pyrolysis [30].

The energetics and kinetics of the reaction involving hydrogen abstraction by CH₃ radical from ethanol have been reported by Xu et al. [31]. The authors performed ab initio calculations using the G2M method and calculated the reaction rate constants using Polyrate [32]. Recently, we have studied all possible hydrogen abstraction channels by CH₃ radical from a range of *n*-butanol conformers at the ROCBS-QB3 level [33]. To the best of our knowledge, no direct experimental measurements of the rate constants of *n*BuOH + CH₃ are available.

This work focuses on computing the rate constants and product branching ratios for hydrogen abstraction by CH₃ radical from the different sites of *n*-butanol. There are two principal themes to this paper. The first is to compare the performance of three available kinetic programs, namely CanTherm [34], the THERMO module of the MultiWell suite (hereafter simply referred as MultiWell) [35] and Variflex [36] in calculating the one-step abstraction reaction rate constants with pronounced barrier heights. The second is to provide accurate and reliable reaction rates constants which could be used in future mechanisms of *n*-butanol combustion.

2. Computational methods

The different conformers of *n*-butanol [37] and their effect on the energetics of the hydrogen abstraction reaction by CH₃ radical [33] have been studied. Throughout this work the lower energy conformer, TGt, has been used.

In order to compare the three kinetic programs, the barrier heights and the reaction energies obtained from our previous study at the ROCBS-QB3 level [33] have been employed. Although the TGt conformer of *n*-butanol introduces an element of asymmetry, the calculations of Katsikadacos et al. [33] suggest that abstracting hydrogen atoms attached at the same carbon

position by CH₃ radical can be considered as identical. Thus, instead of calculating all 10 possible abstraction channels from *n*-butanol, only one hydrogen abstraction for the α, β, γ and δ channels have been considered, and particularly those representing the lowest barrier height. Frequencies obtained at the B3LYP/6-311G(2d,d,p) level have been scaled by 0.99 as recommended by Montgomery et al. [38] in our rate constant calculations.

In order to predict more accurate and reliable reaction rate constants, single point energy calculations at the stationary points have been carried out by the CCSD(T) method with the correlation-consistent polarised split-valence multiple-ζ basis sets [39], cc-pVTZ and the cc-pVQZ. Comparison of the kinetic applications at this level of theory has not been possible because the current version of CanTherm [34] only recognises calculations based on CBS-QB3 and G3 compound methods. The CCSD(T) total energies have been extrapolated to the complete basis set (CBS) limit according to the procedure of Halkier et al. [40]:

$$E_{\text{CBS}} = [E_X X^3 - E_{X-1} (X-1)^3] / [X^3 - (X-1)^3] \quad (1)$$

where $X = 4$ for the cc-pVQZ basis set respectively. The T1 diagnostics [41] for these channels are all lower than 0.015, and so a single-reference method is expected to give an adequate description of the wave function.

Rate constants for the title reactions were obtained from conventional transition state theory employing rigid-rotor harmonic-oscillator approximations for all but the torsional degrees of freedom [42]. The low-frequency torsional modes were treated as one dimensional hindered rotors (1D-HR) using the Pitzer–Gwinn-like approximation [43] applied to density of states calculations. The hindrance potentials were determined for every geometry around every possible dihedral angle by fitting Fourier series with several cosine and sine terms to the B3LYP/6-311G(d,p) energies along the relaxed internal rotation. Once the potential was obtained, the energy levels for the rotation were determined by solving a 1D Schrödinger equation:

$$-\frac{\hbar^2}{8\pi^2 I_R(\theta)} \frac{d^2 \Psi}{d\theta^2} + V(\theta) \Psi = E \Psi \quad (2)$$

where $I_R(\theta)$ is the reduced moment of inertia and $V(\theta)$ is the rotational hindrance potential for the internal rotation.

In both CanTherm [34] and Variflex [36] the reduced moment of inertia is calculated based on the structure of the most stable species, the axis of rotation, and the identity of all the atoms on each side of the rotated bond. The reduced moment of inertia is assumed to be constant, that is, *not* a function of the dihedral angle. In MultiWell [35] the reduced moment of inertia

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