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The elimination of water from a conformationally complex alcohol: A computational study of the gas phase dehydration of *n*-butanol

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ABSTRACT

Relative stabilities of the 14 conformers of *n*-butanol were calculated at the CCSD(T)/cc-pVTZ//MP2/6-311G(d,p) level. The three most stable structures found, TGt, TGg and TGg′ (*trans* (T or t) and *gauche* (G or g) with respect to the CC–CC, CC–CO and CC–OH dihedral angles, respectively) lie within 0.14 kcal/mol, $\Delta H(0\,K)$, with the TGt being favoured thermodynamically (the ZPVE corrections were found at the MP2 level). The rotational isomerizations to the other conformers were examined, in particular those involved in the elimination of water. The elimination of H_2O from *n*-butanol involving the formation of the corresponding carbene, 1-butene, methylcyclopropane and cyclobutane, 1,1-, 1,2-, 1,3- and 1,4-elimination, respectively, was systematically investigated. The 1,2-H_2O loss occurring from the TGg′ conformer and involving a four-center transition state has been found to be thermodynamically and kinetically the most favoured route. This elimination which leads to the 1-butene olefin isomer is endothermic by 8.25 kcal/mol, $\Delta H(0\,K)$, with an associated activation enthalpy at 0 K of 67.26 kcal/mol at the CCSD(T)/cc-pVTZ//MP2/6-311G(d,p) level (relative to the TGt conformer). The respective CBS-QB3 estimates are 7.84 and 67.88 kcal/mol.

1. Introduction

A combination of factors – the depletion of easily recoverable crude oil and the dawning realisation of the global changes wrought by anthropogenic emissions of greenhouse gases – is focussing attention on a shift from hydrocarbon fossil to biofuels. Since these new fuels will be sourced from biomass consisting of cellulose and starch, $(C_6H_{10}O_5)_n$, they will contain substantial amounts of oxygen which in turn will impact upon the formation of combustion by-products. Studies of the combustion chemistry of these next-generation biofuels is crucial therefore to a general understanding of the process and to the minimisation of the production of toxic intermediates such as aldehydes.

Bioethanol is at present the most widely produced biofuel and is used both as an additive to petrol/gasoline and as a fuel in its own right in specially-modified vehicles. Very recent work suggests that it may worsen local air quality and hence have a deleterious effect on human health [1]. It also suffers from a number of drawbacks as a liquid transport fuel such as low energy density, high vapour pressure and too high solubility in water, and, it compounds [2] the problem caused by leaking underground storage tanks contaminating groundwater with methyl *tert*-butyl ether [3] and spilt aromatics [4]. Higher alcohols and alkyl furans are thought not to suffer from these drawbacks and hence are the subject of the current studies to determine whether this is indeed the case or not. The search is thus on for oxygenates which can be readily and economically [5] produced from lignocellulosic material not destined for human consumption, perform well in engines and turbines and which will not unwittingly impact negatively on the environment; *n*-butanol is one such candidate [6].

Unimolecular elimination of H_2O is one possible fragmentation pathway of alkyl alcohols expected to be important in high-temperature environments, especially under combustion conditions [12,13]. Experimentally, the thermal decomposition of C2 to C4 alcohols has been investigated in the past 70 years over a wide temperature range [7–12,13]. In the present computational work we have been interested in persuing the detailed mechanism of the dehydration of *n*-butanol using ab initio second order perturbation theory (MP2) and coupled-cluster theory (CCSD(T)) and multi-level (CBS-QB3) methods. It is preceded by an in-depth study of the complex conformational isomerism of this alcohol using the above methods.

2. Computational methods

The structures were optimized using density functional theory (DFT) with B3LYP functional [14,15] and second-order Møller–Plesset perturbation theory (MP2) [16]. The 6-311G(d,p) basis set [17] was utilized. Harmonic vibrational frequency analysis was

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performed at both computational levels to confirm these structures are minima or first-order saddle points on the ground-state singlet potential energy surface of *n*-butanol and to provide zero-point vibrational energy (ZPVE) corrections. The ZPVE corrections were used without scaling (except where scaling was part of a multi-level method, see below). To verify that the reactant and product(s) are connected by a particular transition state, the intrinsic reaction coordinate (IRC) [18] was determined. Determining IRC was especially important to indicate a unique *n*-butanol conformer directly involved in a particular water elimination channel examined. The generated B3LYP and MP2 IRCs were consistent. Relative energies were improved via single-point calculations at the MP2 structures using the coupled-cluster singles, doubles and perturbative triples (CCSD(T)) [19] method and correlation-consistent polarized valence triple-zeta (cc-pVTZ) basis set [20].

The reaction energies and barrier heights were also evaluated using the CBS-QB3 method [21]. The B3LYP/6-311G(d,p) structures were utilized in the CBS-QB3 procedure. Such cost-effective multilevel schemes, based on a rigidly defined method sequence, can be potentially useful in a study of reaction mechanisms relevant to combustion, provided their performance has been benchmarked against the high level ab initio results. In order to compare the CCSD(T) energies with the CBS-QB3 thermochemical values, the electronic energy differences ΔE have been converted into 0 K enthalpy differences $\Delta H(0\,\mathrm{K})$ by adding the harmonic zero-point vibrational energy corrections (ΔZPVE). We also computed 298.15 K enthalpy differences, $\Delta H(298.15\,\mathrm{K})$, by adding thermal corrections determined with the harmonic oscillator and rigid rotor approximations and assuming an ideal gas at 1.0 atm. The calculations were carried out using Gaussian 03 [22].

3. Results and discussion

3.1. The n-butanol conformers

n-Butanol features complex conformational equilibria with multiple unique conformers involved [23–25]. To label these conformers we adopted the notation used elsewhere [23] and based on the rotational orientation of the CC–CC (denoted first), CC–CO (denoted second) and CC–OH (denoted third) dihedral angles along the C–C–C–C–O–H chain. In this notation, T or t correspond to *trans* orientation and G(G′) or g(g′) to clockwise(counterclockwise) *gauche* orientation. Here, the CC–CC and CC–CO dihedrals have an upper case notation, whereas the CC–OH dihedral has a lower case notation. Note that except for the TTt conformer of C_s symmetry, all other conformers of *n*-butanol of C_1 symmetry (see below) have equivalent mirror images. For instance, TGt and TG′t are such energetically equivalent structures. Throughout this work, we will use only a single designation for a unique *n*-butanol conformer.

Ohno et al. [23] investigated the conformational isomerism of *n*-butanol by analysing Raman and infrared (IR) spectra in the solid, liquid and glassy phases and in argon matrices. The observed IR bands due to the different conformers were assigned on the basis of ab initio RHF/6-31G calculations. These authors also performed a systematic computational study of the relative stabilities of the possible conformers of *n*-butanol in the gas phase and found the TGt structure to be the most stable. Wandschneider et al. [24] and Czarnecki et al. [25] measured IR spectra of *n*-butanol solutions, analysed the temperature dependence of the spectra and carried out B3LYP/6-31++G(d,p) and B3LYP/6-31G(d,p) calculations, respectively, for a limited number of *n*-butanol structures. Their computed energy differences between the four and two *n*-butanol structures examined in two cases were 1.7 kJ/mol (0.41 kcal/mol) and 2.0 kJ/mol (0.48 kcal/mol), respectively, with the TGt structure (labelled using the current notation) indicated to be energetically preferred [24,25].

Figs. 1 and 2 show the optimized structures of the 14 conformers of *n*-butanol found in this work. Both the number and types of the predicted unique structures are consistent with the results of Ohno et al. [23]. The seven conformers, TGt, TTt, TGg′, TTg, GGg, GTg and G′Gt (Fig. 1) are involved in the predicted H_2O elimination pathways (discussed in detail below). The relevant six rotational transition states enabling their interconversions are also displayed in Fig. 1. The remaining seven conformers, TGg, GTg′, GGg′, GG′g, GG′g′, GTt and GGt are included for completeness (Fig. 2).

For the C–C, C–O and O–H bonds and C–O–H bond angle, the B3LYP numbers are systematically larger than the corresponding MP2 values, however, just by 0.002–0.005 Å, 0.003–0.005 Å, 0.002–0.003 Å and 1.4–1.7°, respectively. In the case of the dihedral angles, these differences are more pronounced: those found by B3LYP lie (in the absolute sense) within 9.3° (CC–CC), 5.8° (CC–CO) and 5.5° (CC–OH) of the MP2 predictions, the worst agreement encountered for the three bent G-structures, GGt, GGg and GG′g.

The relative energies of the 14 conformers of *n*-butanol calculated at the levels of theory employed here are summarized in Table 1 and Fig. 3. The previously reported RHF/6-31G estimates [23] are also graphically displayed. Both Table 1 and Fig. 3 clearly show that energy differences between the conformers are small and that the most stable structure found is method dependent. At the CCSD(T) level, all the structures lie within a narrow range of 1.69 kcal/mol (ΔE), 1.86 kcal/mol ($\Delta H(0\,\mathrm{K})$) and 1.72 kcal/mol (($\Delta H(298.15\,\mathrm{K})$). Based on the CCSD(T) $\Delta H(0\,\mathrm{K})$ and $\Delta H(298.15\,\mathrm{K})$ results, the most stable structure is TGt, in agreement with the previous calculations [23]. The calculated enthalpy differences between TGt and TGg and TGg′ structures are, however, only 0.14 and 0.13 kcal/mol in $\Delta H(0\,\mathrm{K})$, and 0.04 and 0.10 kcal/mol in $\Delta H(298.15\,\mathrm{K})$, respectively. Due to the minuscule CCSD(T) electronic energy differences (ΔE) between the three most stable conformations, the ΔZPVE correction is significant because it reverses the ΔE based stability order (Table 1). In agreement with the CCSD(T) results, the CBS-QB3 predicted most stable rotamer is TGt. However, the CBS-QB3 enthalpy differences between the three lowest energy structures are somewhat larger than the CCSD(T) separations and indicate a different, $\Delta H(0\,\mathrm{K})$ based, relative stability order (Table 1).

3.2. The transition states for elimination of H_2O from n-butanol

Transition states for elimination of H_2O from *n*-butanol arise by elongating the unique C–O bond with a concomitant stretching of one of the C–H bonds. The abstraction of hydrogen can occur – at least formally – in consecutive positions C-1, C-2, C-3 and C-4 from the hydroxyl group, giving rise to 1,1-, 1,2-, 1,3- and 1,4-elimination, respectively. We have located transition states corresponding to the four H_2O elimination modes, denoted **TS1**, **TS2**, **TS3** and **TS4**, respectively (Fig. 4). The overall agreement between the MP2 and B3LYP transition state (TS) structures in Fig. 4 is moderate, with notable differences in some key bond distances as detailed below. However, as we discuss later on, these TS geometry differences have no significant effect on the computed elimination barriers by CCSD(T) and CBS-QB3 methods, respectively.

As seen from Fig. 4, in the **TS1** transition state, both the OH group and H atom are removed from C-1. This 1,1-elimination leads initially to the singlet carbene $CH_3–CH_2–CH_2–\ddot{C}–H$, as expected (see however below). The breaking C–O and C–H bonds of 2.05 (1.97) and 1.42 (1.51) Å and forming O–H bonds of 1.08 (1.03) Å at the B3LYP (MP2) level indicate the already formed H_2O product. The **TS2** represents a four-center transition state and involves abstraction of hydrogen from C-2, i.e., 1,2-elimination. Interestingly, the cleaving C–O and C–H bonds of lengths 1.89 (1.79) and 1.41 (1.48) Å, the forming O–H bond of 1.28