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Theoretical calculation of atmospheric reactions. The case of $CH_3–CH_xOH(CH_3)_{1-x}–CH_y(CH_3)_{3-y}$, ($x$ = 1,0; y = 2,1) + Cl

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ABSTRACT

In this work, the reactions of Cl with a series of secondary alcohols: 2-butanol, 2-methyl-2-butanol, 3-methyl-2-butanol, and 2,3-dimethyl-2-butanol have been studied through *ab initio* Möller–Plesset second order perturbation treatment (MP2) calculations with 6-311G** basis sets. Optimized geometries and vibrational frequencies have been obtained for transition states and molecular complexes appearing along the different reaction pathways. Furthermore, molecular energies have been calculated at Quadratic Configuration Interaction with Single, Double, and Triple Excitations (QCISD(T)) level in order to get an estimation of activation barriers. The theoretical rate constant was also calculated for the main reaction pathways using the Transition State Theory. The main aim of this work is to extend, from a theoretical point of view, the knowledge of this kind of reactions that play a significant role in atmospheric chemistry.

1. Introduction

Alcohols are directly emitted into the atmosphere from biogenic and anthropogenic sources. They are used as industrial solvents and fuel additives, and in rural and forested areas, vegetation has also been found to be a significant source of unsaturated and saturated alcohols [1,2]. However, they are also formed in the troposphere by photooxidation of non-methane hydrocarbons [3]. In particular, 2-butanol is present in coating formulations [4] and is emitted by solvent use and road traffic [5]. Other alcohols, such as 2-methyl-2-butanol, have been detected in ambient air of semi-rural and urban locations [6] and 3-methyl-2-butanol was found as a metabolite from microorganisms grown on humid building materials and synthetic media [7].

The oxidation of these volatile compounds in the troposphere is mainly initiated by reaction with OH radicals during the daytime and with NO_3 radicals at night. However, in recent years, the oxidation by chlorine atoms has gained great importance in the study of atmospheric reactions because they may exert some influence in the boundary layer, particularly in marine and coastal environments, and in the Arctic troposphere during springtime. Chlorine atoms may be key species in the atmospheric chemistry of marine environments where the ratio [Cl]/[OH] could be a factor of 1000 higher than usual [8]. The main source of tropospheric Cl atoms is believed to be the photolysis of chlorine-containing molecules generated by heterogeneous reactions of sea salt aerosols [9,10]. It has also been proposed that Cl atoms, produced in the photolysis of Cl_2 emitted from industrial processes, may enhance hydrocarbon oxidation rates and ozone production in urban environments [11,12]. Concerning to the oxidation mechanisms of alcohols, this oxidation produces aldehydes, ketones, and organic nitrates as major products [13]. Therefore, alcohols have a potential to contribute to the adverse effects that are caused by anthropogenic organic air pollutants, e.g. photochemical oxidant formation and haze.

In a previous paper, we reported relative and absolute rate coefficients for the Cl with 2-butanol, 2-methyl-2-butanol, 3-methyl-2-butanol, and 2,3-dimethyl-2-butanol reactions [14]. In that work, some products were also identified and the corresponding reaction mechanisms were proposed. Now, the purpose of this work is to analyse those reactions from a theoretical point of view, in order to get additional elements to confirm the previously proposed reaction mechanisms. Although there are some preceding theoretical works about primary alcohols (e.g. methanol, ethanol,...) with

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Cl reactions [15–17], this study is the first one dealing with secondary alcohols reactions.

As concerns primary alcohols, Jodkowski et al. [16] performed a twofold theoretical study at the MP2 level with 6-311G* and 6-311G** basis sets both for geometries and vibrational frequencies and at the G2 model for energies on the hydrogen abstraction reaction from methanol with chlorine and bromine atoms. The authors concluded that these reactions proceed *via* the formation of intermediate molecular complexes with a favored hydroxymethyl channel with, in the case of the chlorine atoms, a very low energy barrier which may explain the relatively high value of the rate constant.

Later, Rudic et al. [17] studied the reactions of hydrogen abstraction from methanol, ethanol and dimethyl ether (DME) by chlorine atoms. They carried out *ab initio* calculations at the MP2 level with 6-311G** basis sets as regards optimized geometrical structures and vibrational frequencies of molecular complexes and transition states on the reaction pathways while the energies were refined at the G2 level. They concluded that reactions of chlorine atoms with ethanol and DME show transition states with very low barriers and molecular complexes very similar to those reported previously for the methanol case.

As a consequence of a crossed molecular beam experiment on the abstraction of hydrogen from methanol by chlorine, a quantum diffusion Monte Carlo (DMC) study on this reaction has also been reported [18]. In this paper, an intrinsic reaction coordinate, IRC, calculation at MP2/6-311++G** identifies a direct reaction pathway at odds with previous statements according to which this reaction proceeds through intermediates. Also, an estimate of reaction barrier at DMC and MP2 level of theory, DMC heats of reaction, DMC, MP2 and DFT/B3LYP atomization energies and heats of formation were calculated.

Other previous work in this sense was carried out by our group about a set of reactions between primary alcohols, CH_3–$(CH_2)_n$–OH, n = 0–4 and chlorine [15]. Critical points of the potential energy surface were optimized at the MP2 (with all electron correlated for n = 0–2 and Frozen Core approximation for n > 2) level with 6-311G** basis sets. Activation energies and enthalpies at room temperature were calculated at the QCISD(T) level corrected with the ZPE and thermal corrections estimated at MP2/6-311G**.

2. Computational details

Ab initio calculations were carried out using Gaussian'03 [19] set of programs. Geometries of reagents, transition states (TSs) and molecular complexes (MCs) were optimized at the Möller–Plesset second order perturbation theory with all electrons correlated, MP2(Full), and the 6-311G** basis sets. An initial conformational analysis was carried out for the reagents in order to obtain the least energetic conformation. Afterwards, a second conformational analysis was also performed for each TS in order to confirm our initial choice for the most favored reaction pathway. All conformational analysis were also carried out at the MP2(Full)/6-311G** level and convergence problems were solved by use of Opt = CalcFC, SCF = Tight, and Int = Ultrafine options. The nature of the stationary points was assessed through the frequencies of the normal vibrations calculated through energy analytical second derivatives. First order saddle points, which are related to transition states, must show an imaginary value for the frequency associated to the eigenvector describing mainly the product formation step while real minima of the potential energy hypersurface, which are related to stable species must show all positive real values for vibrational frequencies.

For open-shell structures, spin contamination has been taken into account since, as known, if the value of the final total spin $\langle S^2 \rangle$ differs from $s(s+1)$, s being 1/2 times the number of unpaired electrons, by more than 10% it may affect the energetic and geometry of the system. This effect increases, in general, as a bond stretches what turns out to be interesting for transition states which contains elongated bonds [15]. In our systems, the spin expectation values $\langle S^2 \rangle$ before annihilation of contaminants differ from the theoretical value, 0.75, by no more than *ca.* 5%. Therefore, the spin contamination can be considered negligible. Single points calculations for reactants, molecular complexes, transition states and selected products have been computed at quadratic CI (single, doubles and triples), QCISD(T), level on geometries at the MP2 level with 6-311G** basis set.

Relevant zero-point energies and thermal corrections calculated with MP2 have been considered into the final values of QCISD(T) energies. Barrier energies, $\Delta E^{\ddagger}$, classical and zero point corrected, as well as activation enthalpies and energies at 298.15 K have also been calculated for the main reaction pathways. The calculated activation energies at 298.15 K, obtained through the expression $E_a = \Delta H^{\ddagger} + 2RT$ [15,20] were compared with the previously reported experimental activation energies [14]. Enthalpies at 298.15 K relative to the reactants were also calculated for molecular complexes, transition states and products of these reaction pathways. Finally, for each reaction pathway a theoretical rate constant was calculated using the Transition State Theory (TST). These constants were compared with the corresponding experimental rate constants reported in literature [14].

3. Results and discussion

This kind of reactions between saturated alcohols and tropospheric radicals such as OH, NO_3 or Cl proceed via hydrogen abstraction. This fact has been observed both in different experimental works [14,21–23] and theoretical studies [15–18]. In our previous work about primary alcohols, CH_3–$(CH_2)_n$–OH, n = 0–4 with Cl reactions, all possible pathways were studied [15]. Nevertheless, due to the larger size of these secondary alcohols and the loss of symmetry, the number of chemically different hydrogen atoms and possible transition states increases significantly. In this sense, only main reaction pathways such as hydrogen abstraction over >CH– and –CH_2– groups were studied. In several experimental and theoretical works, it has been observed that attacks to HO– and –CH_3 groups are minority reaction pathways [15–18,21–23].

3.1. 2-Butanol with Cl reaction

Two enantiomers are possible for this alcohol: *R*-2-butanol and *S*-2-butanol. Since they are chemically indistinguishable, only one of them was studied, *R*-2-butanol. Transition states calculated were noted as TS*n* where *n* indicates the position of the hydrogen atom that suffers the attack. Thus, we have kept the same numeration that in previous works [15,24] where the HO– group-attack is noted as TS0, the >C_αH– group-attack is noted as TS1, etc. In this reaction only TS2, TS3 *syn* and TS3 *anti* were calculated, which correspond at >CH– and –CH_2– groups exclusively. We have also distinguished between *syn* and *anti* depending on the Cl atom is on the same plane that HO– group or at the opposite one respectively. Likewise, molecular complexes calculated were noted as MC*n* where *n* indicates the position of the hydrogen atom that is attacked. Nevertheless, MC0 is a molecular complex previous to transition states wherein chlorine interacts with oxygen at large distance (>2.5 Å).

In Fig. 1, the rotational barrier for O–C_α–C_β–C_γ dihedral angle of TS2 at MP2(Full)/6-311G** level is plotted. The conformer 1 is the initial conformation obtained for TS2 coming from a previous conformational analysis for the reagent (2-butanol). Two more