Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Atmospheric Hydrocarbon Activation by the Hydroxyl Radical: A Simple yet Accurate Computational Protocol for Calculating Rate Coefficients

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Table 2 relates for all the abstraction sites of 2-methyl-2-butanol the corresponding value of the energy barriers for the selected rotamers and the resulting rate coefficients. Note that all the energy barriers ($\Delta E^{\ddagger}$) are expressed with respect to a common reference, the energy of rotamer 1. Therefore, the energy barriers given below contain also for rotamer 2, the energy difference between the 2 rotamers, ΔE = 1.34 kJ/mol. The Gibbs free energy difference (ΔG) between these two rotamers is slightly less than ΔE, ΔG = 1.19 kJ/mol. This ΔG value is used for the calculation of the Boltzmann factor that quantifies the difference of population between the 2 rotamers This factor, equal to 0.61 is already included in the value of k_{TST} reported in Table 2 for rotamer 2.

For rotamer 2, the symmetry of the molecule makes equivalent the 2a and 2a', 3a and 3a' hydrogens etc. Therefore, the rate coefficient for this rotamer is computed as $2(k_{tst2a}+ k_{tst3a} + k_{tst3b} + k_{tst3c} + k_{tst3d}) + k_{tst3e} + k_{tstOH}$. The overall rate for 2-methyl-2-butanol is the sum of the k_{TST} for the 2 conformers taken into account.

Table 2 Classical corrected barrier heights[a] ($\Delta E^{\ddagger}$ in kJ/mol) and computed rate coefficient (cm^3 $molecule^{-1}$ s^{-1}) including tunnelling for each non-equivalent hydrogen from 2- methyl 2- butanol for its two most energetically accessible rotamers at T=298 K.

Compounds	ΔG	$\Delta E^{\ddagger}$	k_{TST}		ΔG	$\Delta E^{\ddagger}$	k_{TST}
$(CH_3)_2C(OH)C_2H_5$							
Rotamer 1	0.00			Rotamer 2	1.19		
TS CH_{2a}		2.70	4.90×10^{-13}	TS $CH_{2a/2a'}$		-6.38	4.37×10^{-12}
TS CH_{2b}		-7.28	5.98×10^{-12}	TS $CH_{3a/3a'}$		5.75	5.41×10^{-14}
TS CH_{3a}		5.49	4.50×10^{-14}	TS $CH_{3b/3b'}$		6.67	2.87×10^{-14}
TS CH_{3b}		4.24	8.78×10^{-14}	TS $CH_{3c/3c'}$		13.12	6.55×10^{-15}
TS CH_{3c}		10.36	4.23×10^{-14}	TS $CH_{3d/3d'}$		9.99	1.58×10^{-14}
TS CH_{3d}		10.35	4.53×10^{-14}	TS CH_{3e}		12.87	2.62×10^{-14}
TS CH_{3e}		2.96	1.24×10^{-13}	TS OH		13.34	6.24×10^{-15}
TS CH_{3f}		17.71	1.65×10^{-15}				
TS CH_{3g}		9.59	6.53×10^{-14}				
TS CH_{3h}		-5.21	4.76×10^{-12}				
TS CH_{3i}		6.83	5.85×10^{-14}				
TS OH		12.38	8.97×10^{-15}				
			1.17×10^{-11}				8.99×10^{-12}

[a] $\Delta E^{\ddagger}$ contain the additive correction of 6.89 kJ/mol and are ZPE corrected

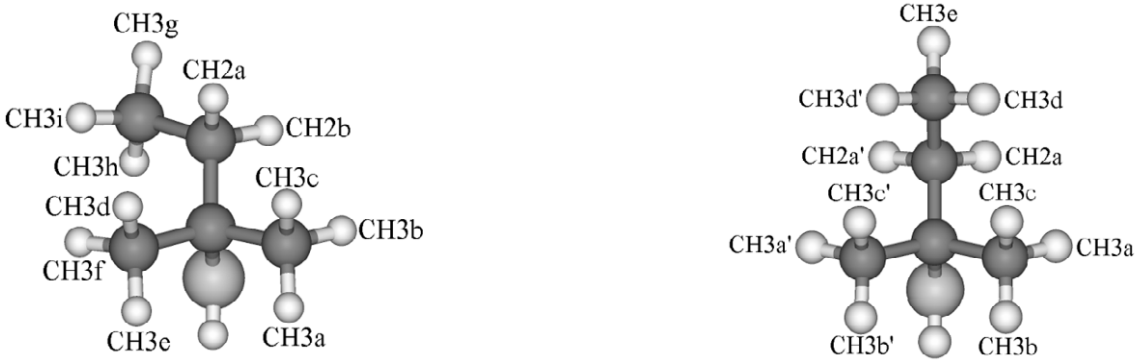

Figure 3 The two rotamers of 2-methyl-2-butanol (rotamer 1 on the left, rotamer 2 on the right) with indication of each abstraction site.

From the result of Table 2, one notes that the site specific rate coefficients span over 3 orders of magnitude, from ~10^{-12} to 10^{-15} cm^3 $molecule^{-1}$ s^{-1}. As expected, the lower the barrier is, the faster the rate. One notes also that the hydrogen of the OH group is a rather unfavourable abstraction site. Contrary to experiment where the challenging part is to obtain branching ratios, this information is readily extractable from our calculation procedure. Finally, this example highlights the importance of the isomeric pool in the calculation of accurate rate coefficient since in this case a low-lying isomer can have site-specific rates ($k_{CH2a/2a'}$) as fast as the fastest rate computed on the most stable isomer (k_{CH2b}) even though a difference of population exists between those two isomers.

Table 3 Value of the transmission coefficient computed with the one-dimensional Wigner factor computed for 2-methyl-2-butanol.

Rotamer 1	Transmission coefficient (κ)	Rotamer 2	Transmission coefficient (κ)
TS CH_{2a}	1.47	TS $CH_{2a/2a'}$	2.77
TS CH_{2b}	2.85	TS $CH_{3a/3a'}$	3.80
TS CH_{3a}	2.15	TS $CH_{3b/3b'}$	2.14
TS CH_{3b}	3.80	TS $CH_{3c/3c'}$	2.50
TS CH_{3c}	2.34	TS $CH_{3d/3d'}$	2.08
TS CH_{3d}	2.34	TS CH_{3e}	2.41
TS CH_{3e}	2.29	TS OH	5.78
TS CH_{3f}	3.07		
TS CH_{3g}	2.16		
TS CH_{3h}	3.47		
TS CH_{3i}	1.85		
TS OH	5.85		

In table 3, we report the magnitude of the Wigner factor for 2-methyl-2-butanol. One sees that the enhancement factor provided by tunnelling is rather large; the mean value of κ is 2.80 for rotamer 1 and 3.07 for rotamer 2. Therefore, accounting for tunnelling, even through a simple correction as the Wigner factor, is important for getting accurate rate coefficients.