Oxidative degradation of 2-butanol by the OH Radical from First-Principles Calculations

Ahmed M. El-Nahas,* Hadeer A. Shereef, Safinaz H. El-Demerdash, and Ahmed H. Mangood

Chemistry Department, Faculty of Science, Menoufia University, Shebin El-Kom, Egypt

ABSTRACT

Structures and energetics of the reactants, transition states, and products for bimolecular oxidation of 2-butanol by the OH radical have been investigated using ab initio composite methods (CBS-QB3 and G3B3). Five transition states have been located. The barrier heights and exothermicity of H-abstraction reactions follow the order $\alpha < \beta < \gamma < \beta m < O$. Abstraction of hydrogen atom from C_α and O sites is the most and least favored channels, respectively, both thermodynamically and kinetically. The rate constants and branching ratios for H-abstraction reactions were calculated using conventional transition state theory with Wigner correction in the temperature range 298 - 2000 K.

Key words: 2-Butanol, OH radical, CBS-QB3, G3B3, transition state theory, thermochemistry.

Corresponding Author: El-Nahas, A. M.

INTRODUCTION

Environmental concern of fossil fuel, depletion of its reserves, increase demand, and cost have paid attention of scientists to alternative fuels such those derived from biomass. Biofuels represent a promising alternative to petroleum-based fuels because of their renewability and better climate impact [1].

Most biofuels such as alcohols and esters are oxygenated compounds. Lower alcohols (methanol and ethanol) are hygroscopic and have low energy content but are still in use [1]. On the other hand, higher alcohols offer some advantages as gasoline substitutes because of their higher energy density and lower hygroscopicity [1]. The number of carbon atoms in butanol is similar to average molecular size found in gasoline. Therefore, butanols, either blended or on

their own, can be used in current engines without modification. Consequently, butanols have been recently suggested as a fossil fuel alternative [2-4]. Butanol has four structural isomers, 1-butanol, 2-butanol, isobutanol, and tert-butanol. A considerable effort has been devoted to produce biobutanol (1-, 2-, isobutanol) from biomass [5–11]. With increasing the interest in using biobutanol as a fuel, understanding of its combustion becomes essential [12]. Oxygenated fuels are known to release carbonyl compounds as pollutants and, therefore, understanding chemistry of their formation can assist in preventing hazardous emissions [12].

A number of experimental studies were reported for combustion of 1-, iso- and 2-butanol [12-23]. Theoretical investigations also contributed significantly in this field [24-31]. Compared to 1-butanol, oxidation reactions of 2-butanol with different oxidants are still limited. Study of 2-butanol combustion is very important for full understanding of its combustion mechanism [16]. This paper focuses on studying oxidation of 2-butanol by hydroxyl radical and calculating relevant thermodynamic and kinetic parameters. The paper is organized as follows: Section 2 presents computational details. Section 3 includes results and discussion. Section 4 summarizes the main conclusion.

COMPUTATIONAL DETAILS.

The electronic structures of the reactants, transition states, and products were optimized at CBS-QB3 level of theory [32-34]. In addition, G3B3 [35] composite method ws used to compute thermodynamic and kinetic parameters such as ΔE_0 and $\Delta E^{\#}$. All calculations were performed using the Gaussian09W program [36]. Vibrational modes were analyzed using ChemCraft program [37].

Rate constants for the bimolecular reaction of 2-butanol + OH → products have been calculated using Kisthelp package [38] using the transition state theory (TST) [39] .The second-order rate constant (k) in unit of cm^3 molecule^{-1} s^{-1} is given as:

$$k^{TST}_{(T)} = \sigma \frac{K_B T}{h} \left(\frac{RT}{P^\circ}\right)^{\Delta n} e^{-\Delta^\ddagger G^\circ (T)/K_B T}$$
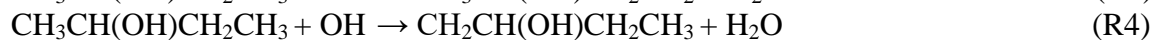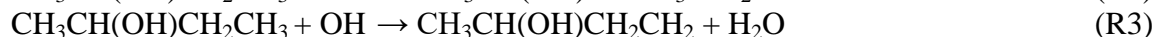
Where K_B is Boltzmann,s constant, T is the system's temperature in Kelvin, h is Planck,s constant, R is ideal gas constants, σ is reaction path degeneracy , $\Delta^\ddagger G^\circ$(T) is the standard Gibbs free energy of activation for reaction, P$^\circ$standard pressure of 1 atm, while Δn is 1 in case of bimolecular oxidation. Rate constant calculations were carried out using CBS-QB3 in the temperature between 298 and 2000 K. Wigner tunneling correction [40] is defined transmission coefficient χ (T) as:

$$\chi (T) = 1 + 1/24 [h\nu/k_B T]^2$$

where ν refers to the imaginary frequency in the transition state.

RESULT AND DISCUSSION

H-abstraction reactions from 2-butanol by the hydroxyl radical are defined as follows:

$CH_3CH(OH)CH_2CH_3 + OH \rightarrow CH_3C(OH)CH_2CH_3 + H_2O$ (R1)

$CH_3CH(OH)CH_2CH_3 + OH \rightarrow CH_3CH(OH)CHCH_3 + H_2O$ (R2)

$CH_3CH(OH)CH_2CH_3 + OH \rightarrow CH_3CH(OH)CH_2CH_2 + H_2O$ (R3)

$CH_3CH(OH)CH_2CH_3 + OH \rightarrow CH_2CH(OH)CH_2CH_3 + H_2O$ (R4)

$CH_3CH(OH)CH_2CH_3 + OH \rightarrow CH_3CH(O)CH_2CH_3 + H_2O$ (R5)

The contribution of each channel to the main oxidation process depends oى some factors such as bond strength, structure and energy of the transition state, stability of the products. Bond

dissociation energies (BDE_S) for individual bonds of 2-butanol at CBS-QB3 are collected in Table 1. The data reveal that the C_α-C_β bond is the weakest bond followed by C_α-$C_{\beta m}$ and then C_β-C_Υ. However, the O-H bond is the strongest one. The C_α-H bond is the weakest bond followed by C_β-H and the weakest is the $C_{\beta m}$-H bond. The BDEs are comparable with those obtained in previous work on 2-butanol and isobutanol [24,25].

Table 1. Bond dissociation energies (BDE_{298}, kcal/mol) of 2-butanol at the CBS-QB3 level.

Bonds	CBS-QB3
C_α-C_β	87.27
C_α-$C_{\beta m}$	88.20
C_β-C_Υ	91.75
C_α-H	94.83
C_β-H	100.96
C_Υ-H	102.08
$C_{\beta m}$-H	102.68
O-H	106.49

The optimized structures of reactants and transition states for the reaction of 2-butanol with the hydroxyl radical at CBS-QB3 are presented in Fig. 1.

Energy of reaction and energy barriers for bimolecular reactions of 2-butanol with the hydroxyl radical have been calculated at CBS-QB3, and G3B3 and are collected in Tables 2 and 3, respectively. As noticed from the data given in these Tables that all reactions are exothermic with the H-abstraction from C_α being the most exothermic one and the two theories agree within 0.5 kcal/mol for barrier heights and 2 kcal/mol for reaction energies. H-abstraction from C_α has the lowest energy barrier because it forms the most stable radical that is stabilized due to the presence of higher degree of hyperconjugation, five C-H bonds can interact with the radical center [24]. Moreover, some transition states can be stabilized by the presence of intramolecular hydrogen bond between the attacking hydroxyl radical and the alcoholic OH [25,31]. This leads to lower energy barriers compared to transition states without such interaction. It is evident that the order of reactivates of sites is given by $C_\alpha > C_\beta > C_\Upsilon > C_{\beta m} > O$ at CBS-QB3, and G3B3. Abstraction of hydrogen atom from C_α and O sites is the most and least favored channels, respectively, both thermodynamically and kinetically. These results are comparable to that obtained from our previous work on isobutanol [25].
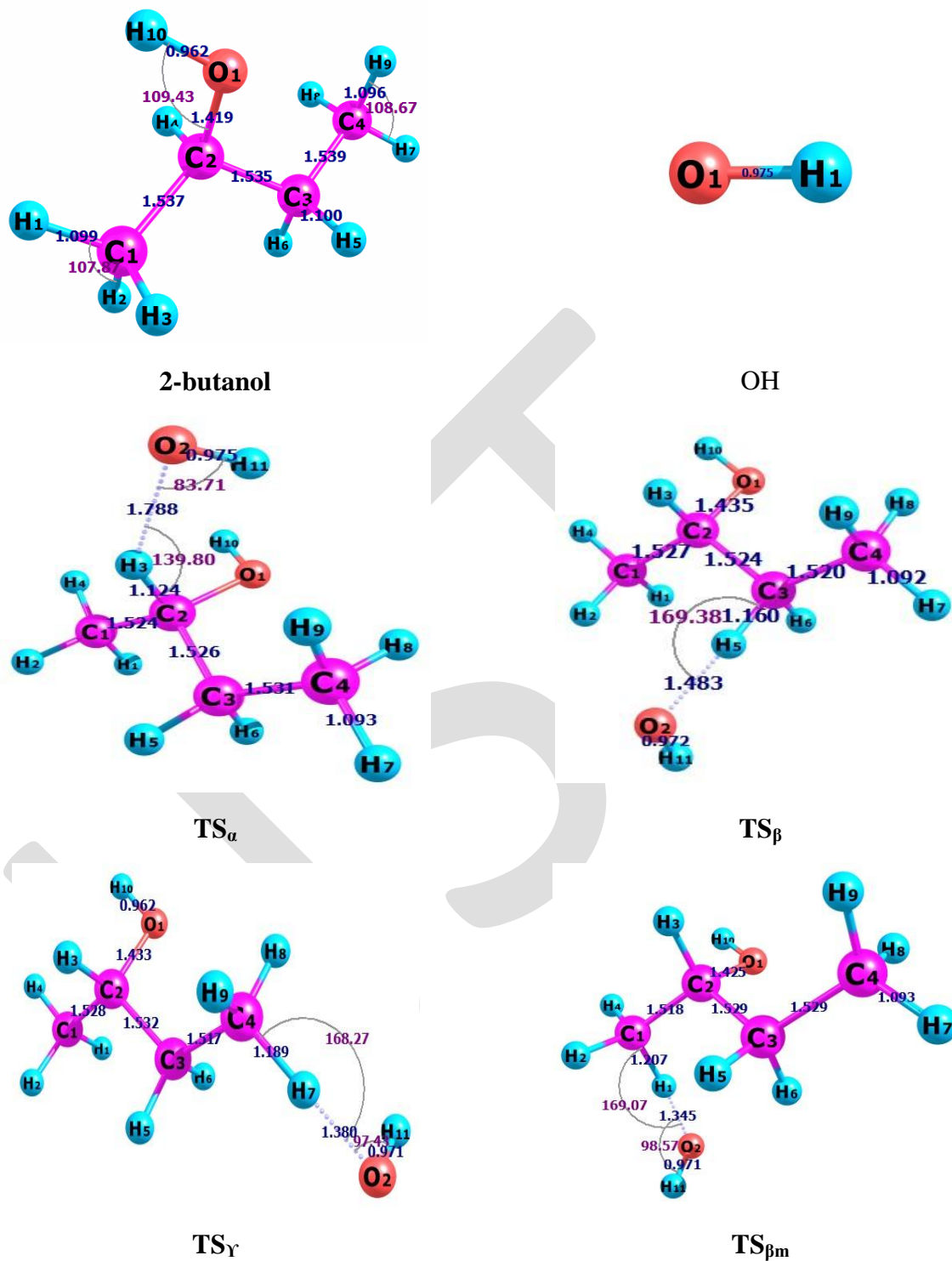
Fig 1. Optimized structures of 2-butanol, hydroxyl radical, and transition states at CBS-QB3 (bond lengths are given in Å and bond angles in degrees) .
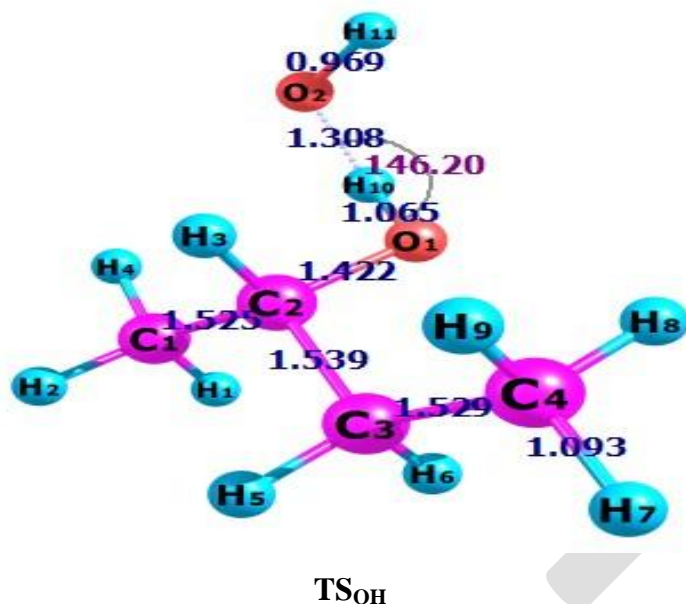
TS$_{OH}$

Fig 1. Continued.

Table 2. Reaction energy (ΔE_0, kcal/mol) for H-abstraction from 2-butanol by OH at different levels.

Site	CBS-QB3	G3B3
C_α	-25.03	-24.06
C_β	-19.02	-18.64
C_γ	-17.51	-17.48
$C_{\beta m}$	-16.86	-16.76
OH	-12.76	-10.45

Table 3. Energy barriers ($\Delta E_0^{\#}$, kcal/mol) for H-abstraction from 2-butanol by OH at different levels.

Site	CBS-QB3	G3B3
C_α	-1.56	-1.12
C_β	1.18	0.48
C_γ	1.77	1.56
$C_{\beta m}$	2.67	2.80
OH	2.88	3.37

Rate constants have been calculated using transition state theory with Wigner correction in the temperature range 298 - 2000 K. Plot of ln k for individual channel versus 1000/T is displayed in Fig. 2. Rate constant for each channel from 600 to 2000 K are collected in Table 4. The total rate constants and branching ratios for different reactions are illustrated in Fig. 3. The contribution from α-H-abstraction is 73.5% at 600 K and then decreases slowly to 20.3% at 2000 K; while Υ-H-abstraction contributes 13.5% at 600 K and then increase slowly to 42.6% at 2000 K. The hydrogen-abstraction from other sites is modest (starts at 1%) and increases slowly (up to 13%) with temperature. The relations are non-linear and, therefore, the three-parameter Arrhenius equation ($k = AT^n e^{-Ea/RT}$) should be used to describe kinetics of oxidation of 2-butanol with OH. The kinetic parameters are summarized in Table 5. The presence of negative activation energies for some channels implies the existence of pre-reactive intermediate at the entrance channels. The results are comparable to previous work that showed the C_α as the most accessible site for attack by the OH radical and hydroxyl hydrogen as the hardest one [16,25].

Table 4. Total and individual rate constant[a] (cm^3 mol^{-1} s^{-1}) for oxidation of 2-butanol with OH at 600-2000 K from CBS-QB3 calculations.

| T/K	k_α	k_β	k_γ	$k_{\beta m}$	k_{OH}	k_{total}
600	6.31E+11	7.42E+10	1.16E+11	2.11E+10	1.69E+10	8.59E+11
800	6.73E+11	1.52E+11	2.75E+11	5.87E+10	4.39E+10	1.20E+12
1000	7.90E+11	2.69E+11	5.38E+11	1.27E+11	8.98E+10	1.81E+12
1200	9.56E+11	4.32E+11	9.30E+11	2.37E+11	1.60E+10	2.71E+12
1400	1.16E+12	6.47E+11	1.48E+12	3.97E+11	2.58E+11	3.94E+12
1600	1.41E+12	9.20E+11	2.20E+12	6.17E+11	3.91E+11	5.54E+12
1800	1.70E+12	1.26E+12	3.12E+12	9.05E+11	5.61E+11	7.54E+12
2000	2.02E+12	1.66E+12	4.26E+12	1.27E+12	7.74E+11	9.98E+12

[a] Wigner correction is included

Table 5. Three-parameter Arrhenius coefficients for oxidation of 2-butanol by OH at CBS-QB3.

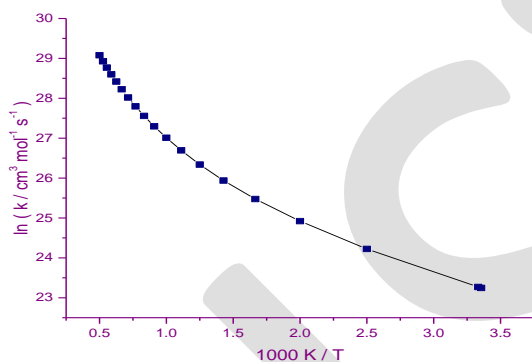| Parameter[a]\Channel	C_α	C_β	C_γ	$C_{\beta m}$	OH	Total
A	5.67E+03	1.21E+03	6.75E+02	1.16E+02	2.01E+02	1.99E+0.0
n	2.49	2.75	2.97	3.06	2.92	3.74
E	-3.12	-0.35	0.06	0.7	0.52	-3.43

[a]A is given in cm^3 mol^{-1} s^{-1} and E in kcal/mol
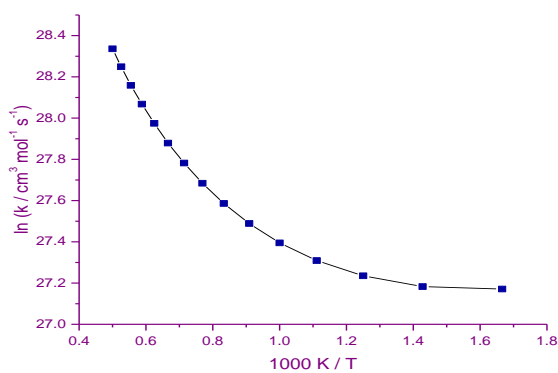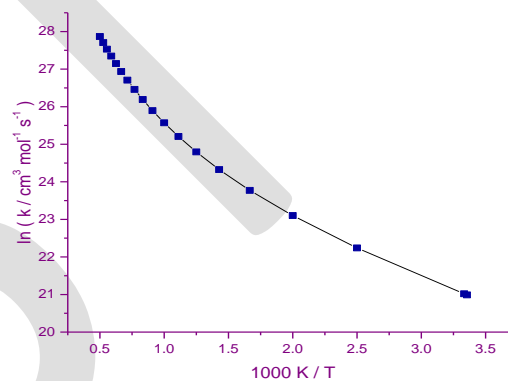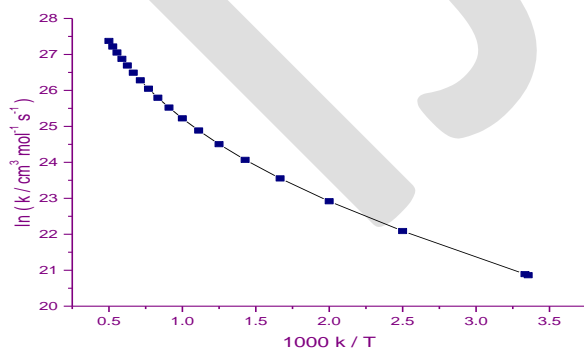
(a) α H-Abstraction
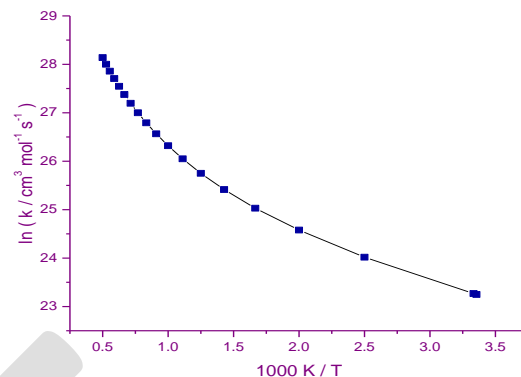
(b) β H-Abstraction

(c) ϒ H-Abstraction

(d) βm H-Abstraction

(e) alcoholic H-abstraction

Fig. 2. Rate constant (ln k, cm^3 mol^{-1} s^{-1}) against 1000 K/T for oxidation of 2-butanol with the hydroxyl radical at CBS-QB3.
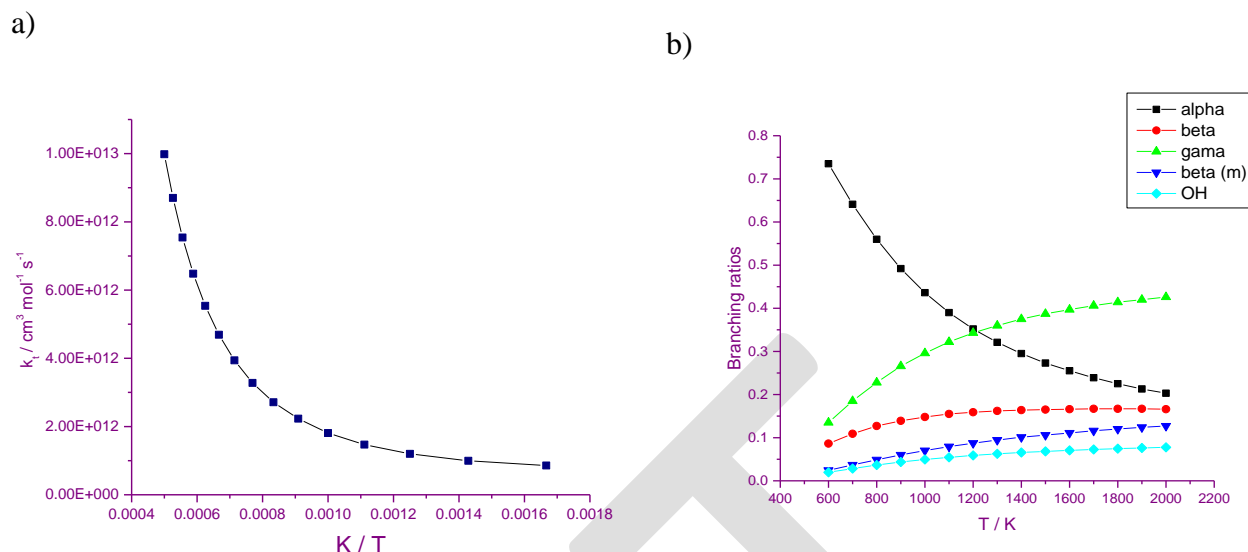
a)

b)

Fig. 3. (a) Total rate constants at CBS-QB3,   (b) Branching ratios at CBS-QB3.

CONCLUSION

In this work, thermochemistry and kinetics of bimolecular oxidation reactions of 2-butanol with the hydroxyl radical were calculated at CBS-QB3 and G3B3 levels of theory. The results obtained can be summarized as follows:

1. From the calculated bond dissociation energies (BDE$_S$) for different bonds of 2-butanol at CBS-QB3, the bond strength follows the order C_α-C_β < C_α-$C_{\beta m}$ < C_β-C_Υ. The O-H bond is the strongest one and the C-H bonds fall between the two extremes.

2. Thermochemistry (ΔE_0) and kinetics ($\Delta E_0^{\#}$) of H-abstraction reactions from 2-butanol by the OH radical were reported as $C_\alpha > C_\beta > C_\Upsilon > C_{\beta m} > O$ at CBS-QB3, and G3B3 with all pathways being exothermic.

3. The contribution from α-H-abstraction is 73.5% at 600 K and decreases slowly until it reaches 20.3% at 2000 K, while the ϒ-H-abstraction route contributes 13.5% at 600 K and increases slowly to 42.6% at 2000 K. The hydrogen-abstraction from other sites is modest (starts at 1%) and increases slowly (up to 13%) with temperature.

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